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ALUM SLUDGE FOR ADSORPTIVE REMOVAL OF COPPER

AND ZINC FROM STORMWATER RUNOFF

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ABSTRACT

ADSORPTIVE REMOVAL OF COPPER AND ZINC FROM STORMWATER RUNOFF BY USING ALUM SLUDGE

By Mengke Wu

The investigation found that rainwater runoff, as a non-point source of pollution, carries various kinds of heavy metals that have threatened the diversity of aquatic life and human health. Therefore, in 2015, the UK Sustainable Drainage Systems promoting multi-functional, low-cost solutions to reduce and purify rainwater runoff.

Alum sludge (AS) is a byproduct from water purification plants, which is large output, low cost and easy to get. For most water purification plants currently the alum sludge is a waste product and the main fate is to direct AS to landfill, which wastes the residual value of AS. In order to reuse AS, the feasibility of recovering and the way to reuse air-dried AS to be an adsorbent was studied. The knowledge gap of this study is currently research on the recovery of AS were mainly focused on the adsorption of phosphorus and some high-concentration heavy metal wastewaters. The research on the use of AS to adsorb low-concentration runoff heavy metal pollution is still incomplete. This study systematically investigated the static and dynamic adsorption of Cu(II) and Zn(II) by AS. The results help us understand the adsorption mechanism of AS and provide suggestions for the recycling and reuse of AS. This study is a win-win strategy, which not only solve the AS disposal problem, but the use of low-cost AS also helped reduce the pollution load of heavy metals in runoff.

This thesis completed four tasks, including: 1) The composition and physicochemical properties of AS were studied by various characterization methods; 2) Batch experiments were carried out to determine the adsorption mechanism and capacity for Cu(II) and Zn(II); 3) By simulating the composition of stormwater runoff, the possible adsorption competition between multiple elements is studied; 4) The column experiment provides the completeness of AS adsorbent research from theoretical data to application performance.

AS was characterized by scanning electron microscopy, specific surface area measurement and Fourier transform infrared spectroscopy. The results show that AS is a porous material mainly composed of mesopores, with an average specific surface area of 75 m²/g for particle (1-2mm) and 58 m²/g for fine powder (< 0.15mm).

The results of batch experiments show that the adsorption of Cu(II) and Zn(II) conforms to the pseudo-second-order kinetic and the langmuir isotherm model, which indicates that the adsorption of Cu(II) and Zn(II) is a monolayer chemical adsorption. At pH = 6.5, the adsorption capacity for Cu(II) and Zn(II) was 22.9 mg/g and 8.7 mg/g, respectively.

The results of adsorption competition experiments show that the removal efficiency of AS for Cu(II) and Zn(II) in simulated stormwater runoff exceeded 95%, indicating that AS can be an effective adsorbent for Cu(II) and Zn(II) in stormwater runoff.

The results of the column experiment showed that when 160g AS is added, the adsorption saturation time for Cu(II) and Zn(II) is 600min and 240min, respectively. With the increase of AS dosage, the adsorption capacity of Cu(II) and Zn(II) increases. With the increase of flow rate, the adsorption capacity of Cu(II) and Zn(II) decreases.

In summary, this study explored the potential of AS for reduce Cu(II) and Zn(II) pollution levels in stormwater runoff, and also had a positive impact on waste utilization, economic conservation and environmental protection.

Keywords: alum sludge; heavy metals; adsorption; desorption; stormwater runoff treatment; filter media

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LIST OF ABBREVIATIONS

Aluminum (Al)

Alum Sludge (AS)

Barrett-Joyner-Halenda (BJH)

Bed-Depth/Service Time (BDST)

Best Management Practices (BMPs)

Brunauer-Emmet-Teller (BET)

Empty Bed Contact Time (EBCT)

Event Mean Concentration (EMC)

Fourier Transform Infrared Spectroscopy (FTIR)

Glass Beads (GB)

Hydraulic Conductivity (HY)

International Union of Pure and Applied Chemistry (IUPAC)

Low Impact Development (LID)

Low Impact Urban Design and Development (LIUDD)

Multi-Metals Solution (MMS)

Polyaluminium Chloride (PAC)

Root Mean Square Error (RMSE)

Scanning Electron Microscopy coupled Energy Dispersive Spectrometer (SEM-EDS)

Single Metal Solution (SMS)

Species Mean Acute Value (SMAV)

Stimulate Stormwater Runoff (SSR)

stormwater Priority Substances (SPS)

Stormwater Runoff (SWR)

Sustainable Drainage Systems (SUDS)

Thermo-Gravimetric Analysis (TGA)

U.S. Environmental Protection Agency (USEPA)

Water Framework Directive (WFD)

Water Sentitive Urban Design (WSUD)

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CHAPTER 1 INTRODUCTION

1.1 Background and Problem Statement

Rainwater has been recognized as an important part of the urban water cycle, forming the major source of replenishment of surface and groundwater (Yang, 2018). However, due to the rapid development of urbanization, the area of impervious surfaces has increased, and consequently rainwater cannot infiltrate quickly and instead form runoff on the ground (Qi, 2012). The formation of large amounts of runoff may lead to problems such as groundwater not being replenished (Yang, 2018). Moreover, runoff carries large amounts of pollutants such as oil, organic matter, inorganic matter, pathogens and suspended particles, which can pose a threat to surface and groundwater quality if not properly managed (Liu, 2020). Studies have found that in developed countries, point source pollution represented by industrial emissions is generally strictly controlled, while non-point source pollution mainly caused by stormwater runoff (SWR) has become the main factor threatening human health and the natural ecological environment (Pitt *et al.*, 1995). Therefore, non-point source pollution, and has become a major factor threatening the urban and natural ecological environment (Qi, 2012).

1.1.1 Stormwater Runoff Pollutants

Since 1960, people have begun to pay attention to surface water pollution caused by SWR and study the water quality characteristics, pollutant distribution, runoff models, risk assessment and pollution control measures of SWR (Wang, 2019). The Clean Water Act Amendments of 1987 from United States emphasized the importance of regulating non-point sources of stormwater pollution (Mahmud, 2024). Through the contribution ratio of different pollution sources (sewage, industrial pollution, SWR and agricultural wastewater) to the surface water pollution load, the SWR accounted for 9% (USEPA, 1990). In 1993, the U.S. Environmental Protection Agency (USEPA) defined stormwater runoff as the third-largest source of pollution in U.S. rivers and lakes (Zhou *et al.*, 2013). Surveys show that approximately 40% of rivers and 50% of lakes in the United States are polluted by runoff, Of the 404,000 miles of rivers, 7.4% are severely polluted by non-point sources, 21.5% are moderately polluted, and 11.8% are threatened by pollution (USEPA, 1995). Of the 20,000 hectares of lakes in China, 5.7% are severely polluted; among non-point sources, 22.7% are moderately polluted, and 23.9% are threatened by pollution (Zhang. 1988).

There are many forms of pollution in SWR, depending on the type of surface contacted by runoff. For example, when runoff flows over agricultural and human settlements, it is more likely to carry

1

relatively large amounts of pesticides, bacteria, and nutrients (Wei *et al.*, 2015). In parking lots and highway areas, SWR is more likely to contain oil and heavy metals (Rushton, 2001; Gan et al., 2008). Runoff from construction areas contains a large amount of suspended solids (Crobeddu *et al.*, 2008). Studies have shown that, among the 129 key pollutants in urban stormwater defined by the Water Framework Directive (Zgheib *et al.*, 2012), 50% were detected from SWR (Zhou *et al.*, 2012). Among various pollutants, toxic heavy metals, nutrients, pesticides, and sediments have been identified as common SWR pollutants (Table 1-1), and SWR is an important way for these pollutants to enter surface water and groundwater (Wang, 2019).

Pollutants	Concentration range (mg/L)
Total suspended solids	141-708
Total phosphorus	0.01-21.2
Ammonia	0.1-10.8
Zinc	0.056-0.93
Copper	0.022-7.03
Lead	0.0005-0.69
Chromium	0.01-0.22
Diethylhexylphthalate	0.0153-0.0609
Polycyclic aromatic hydrocarbons	0.000892-0.00136
Diuron	0.000394-0.000647
Polychlorinated biphenyls	<loq*-0.000727< td=""></loq*-0.000727<>

Table 1-1 Concentration range of some runoff pollutants (Göbel *et al.*, 2006; Bressy *et al.*, 2012; Li *et al.*, 2015;Terzopoulou and Voutsa, 2017; Wolowiec *et al.*, 2018; Pla *et al.* 2021)

These pollutants can cause many environmental problems (Table 1-2). The study shows that rainwater runoff is potentially harmful to the receiving water body and sediments, which may negatively affect biodiversity (Renata *et al.*, 2014). Pitt *et al.* (1995) studied the toxicity of storm runoff in 87 cities and showed that urban stormwater runoff contains various traditional and potentially toxic pollutants, which could degrade receiving waters and impair beneficial uses (Zgheib *et al.*, 2011). Renata *et al.* (2014) conducted *Daphnia similis* toxicity test, *Vibrio fischeri* toxicity test and *Ceriodaphnia dubia* chronic toxicity test on rainwater runoff is generally toxic and more toxic during the rainy season. The toxicity of rainwater runoff is not a simple accumulation of the toxicity of the pollutants present in the runoff. Investigations show that the complexity of rainwater toxicity evaluation is that the interaction of pollutants will enhance their toxicity in rainwater (Birch *et al.*, 2011). Based on the above observation, in order to reduce the toxicity of rainwater runoff, it is necessary to identify representative toxic pollutants and study feasible treatment methods to reduce their concentration.

Pollutants	Main sources	Environmental issue		
Polycyclic aromatic hydrocarbons	Transportation; Oil spills; Industrial emissions	Toxic; Pollution of sediments; Pollution water bodies		
Pesticides	Garden herbicide	Toxic; Polluting water		
Organic waste	Human activities; sewage silt; transportation	Oxygen consumption; Eutrophication		
Pathogenic microorganisms	Animal excrement	Health risk		
Nutrients	Fertilizers; Atmospheric deposition; Human activities	Eutrophication		
Heavy metals	Transportation; Atmospheric deposition; Urban surface leaching	Toxic		

Table 1-2 Major sources of runoff pollutants and potential environmental problems

In 2000, the European Union established the Water Framework Directive, which clearly specified 33 rainwater priority pollutants, however the stormwater priority substances (SPS) in the list were not tested in rainwater samples. Therefore, Zgheib et al. (2012) compiled a list of 88 SPS based on the Chemical Hazard Identification and Assessment Tool in 2008, including 65 organics, 8 metals and 15 volatile compounds, as well as conventional water quality parameters. Of these 88 stormwater priority substances, 45 were found in rainwater runoff including some metals, organotins, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, alkylphenols, pesticides, phthalates, chlorophenols and dichloromethane. Birch et al. (2011) investigated the types and concentrations of micro-pollutants in rainwater sewers in Copenhagen, Denmark; the results showed that all polycyclic aromatic hydrocarbons except naphthalene, Diethylhexylphthalate, copper and zinc exceeded the annual average environmental quality standards. Bressy et al. (2012) found that with the exception of polychlorinated biphenyls (mainly from the atmosphere), other micro-pollutants (polycyclic aromatic hydrocarbons, nanoparticles, octylphenol, Cu, Pb, Zn) from the atmosphere contribute less than 10%-38% of atmospheric dry deposition. Gasperi et al. (2014) and Zgheib et al. (2012) found that most of the heavy metals, polycyclic aromatic hydrocarbons, organotin and polychlorinated biphenyls are mainly combined with particles, while pesticides, alkylphenols, and zinc mainly appear in the runoff in a dissolved form. Since the toxicity of the rainwater runoff may affect the biodiversity of the receiving water body, it is necessary to explore appropriate methods to reduce the impact of rainwater runoff on the environment.

However, there are too many potential threats from SWR. For example, heavy metals such as Pb, Cu, Zn and Cr are commonly found in SWR, and these heavy metals are toxic and pose a threat to biodiversity and human health. Moreover, the relatively high concentration of nutrients in SWR is the

main cause of eutrophication of water bodies. Pollutants in the runoff have a certain potential for removal by adsorption. For this study, it is not possible to focus on all pollutants. Therefore, a representative selection of pollutants in SWR was undertaken (see below).

1.1.2 Management of Stormwater Runoff

Surface water and groundwater are threatened by runoff pollution and many developed countries have proposed measures to reduce the impact of runoff pollution. For example, Low Impact Development (LID) and Best Management Practices (BMPs) in the United States are technical systems that aim to control SWR volume and pollution through decentralized, small-scale source control (Pitt *et al.*, 2018). Water Sensitive Urban Design (WSUD) in Australia and Low Impact Urban Design and Development (LIUDD) in New Zealand advocate the increased use of permeable materials to achieve urban water cycle management with respect to natural water cycles and ecological processes (Wong, 2006; Ignatieva *et al.*, 2008). The UK has Sustainable Drainage Systems (SUDS), which use low-cost and low-impact methods to reduce urban runoff, purify rainwater and surface water (Wilson *et al.*, 2004).

For example, BMPs can be designed to treat runoff pollution at the location of discharge, or they can be designed to reduce runoff generation in an area to reduce the flush of surface pollutants (Yang, 2018). There are many SWR management solutions on the market such as Infiltration systems, Detention systems, Retention systems, Constructed wetlands, Vegetated systems, Filtration systems (biofilters), Bioretention basins and Permeable pavement (Clary et al., 2020; Fu et al., 2020). The design of these measures is based on two principles which are (i) to reduce the volume of SWR by rapid infiltration or interception, and (ii) to reduce the pollutant load of SWR by adsorption. According to USEPA summary of nutrient and metal concentrations in effluents from all BMPs, all measures are effective in reducing phosphorus concentrations. For example, The Water Research Foundation published BMP performance database in 2020, for some typical measures such as detention basin, retention pond, wetland basin the results show that they can effective remove total phosphorus for at least 8% by compared with BMP influent and effluent (Clary et al., 2020). Longterm retention systems, such as Retention systems and Constructed wetlands, are recommended as the best solution for reducing nitrogen (Clary et al., 2010; Clary et al., 2020). For heavy metals, all BMP types showed an effective reduction in effluent heavy metal concentrations, but the removal of dissolved heavy metals is poor (Clary et al., 2011; Clary et al., 2020).

In addition, the concept of source control has been introduced for the management of SWR pollutants, including scour control, stormwater facility maintenance and use of clean materials, etc. The aim is to reduce the risk of pollution sources in contact with rainwater and being washed into runoff (Pratt, 1995; Claire *et al.*, 2008). The Center for Watershed Protection from USEPA (2005) reports some

specific source control measures such as reducing fertilizer and pesticide use, driveway sweeping, pet waste pickup, septic system cleanouts. A successful example is that lead is a major threat to aquatic biodiversity and human health due to the large-scale use of leaded gasoline in the past. When this was recognized, there was no doubt that leaded gasoline was considered the main source of lead loads in runoff (Jacobsen *et al.*, 2010a). Currently, Lead concentrations in runoff have been significantly reduced by introducing unleaded gasoline into vehicles (Jacobsen *et al.*, 2010b).

1.1.3 Heavy Metal Problem in Stormwater Runoff

SWR has been regarded as the main non-point source pollution of surface water and groundwater (USEPA, 2009). Heavy metals come from natural and man-made sources. Natural sources mainly include volcanic activity, soil erosion, and biological activity, whereas man-made sources include rubbish, fuel burning, urban runoff, agricultural and industrial wastewater (Wolowiec et al., 2019). The main reason for the increase in heavy metal pollution from SWR is related to population growth in urban areas and the expansion of urban impervious areas (Pla et al., 2021). Moreover, studies have shown that vehicle exhaust, mineral burning, tire wear, asphalt, erosion of building materials, and industry can generate a large amount of heavy metals on urban impervious surfaces. The discharge of heavy metal pollutants is intensified by stormwater washing and causing the deterioration of surface water quality (Pla et al., 2021). For example, Li et al. (2015) investigated the event mean concentrations of iron, copper and zinc under different land use in Dongguan, Guangdong, China. The results showed that the industrial zone has the highest concentration of heavy metals in runoff, which are 4.27 mg/L (Fe), 3.50 g/L (Cu) and 0.31 g/L (Zn) respectively. Brown and Peake (2006) reported that concentrations of heavy metals in runoff from road debris in two rainwater catchment areas in Dunedin, New Zealand were 0.12-0.53mg/g for lead, 0.05-0.46 mg/g for copper, and 0.24-1.33 mg/g for zinc. The rainwater runoff of the three catchment areas in Paris mainly contains heavy metals such as lead, copper, zinc and cadmium, of which lead is 129 µg/L, cadmium 45 µg/L, copper 220 µg/L, and zinc 520 µg/L (Zgheib et al., 2012). Vlastos et al., (2019) assessed the toxicity of heavy metals in USWR in three cities in Greece. Various different heavy metals were detected such as Zn, Pb, Cr, Cd, Cu, As, Co, and Fe. The results showed that the concentration range of heavy metals was from 0.16 $\mu g/L$ (Co) to 86.6 $\mu g/L$ (Fe), and the pollution load of iron, copper, zinc and aluminum is relatively large.

Compared with other heavy metal pollution in SWR, Cu and Zn are pollutants that are ubiquitous in runoff, with relatively high relative concentrations and strong environmental toxicity. The World Health Organization (WHO) has defined the Cu permissible limit of 2 mg/L in drinking water (Kelli *et al.*, 2011; Wolowiec *et al.*, 2018). When Zn concentration above 5 mg/L (upper limit by Water Quality Criteria, 1972), it will affect the taste of drinking water (Ansari *et al.*, 2002; Woitke *et al.*,

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2003). However according to investigations, the concentration of Cu and Zn sometimes exceed this value, and their event mean concentration in SWR is 0.12 mg/l and 0.3 mg/l, which greatly exceed the environmental background value. This means that SWR has a deteriorating effect on the environment (Table 1-3), and their event mean concentration is several times higher than other heavy metals (Ellis et al., 2011; Ki et al., 2011; Rossi et al., 2013; Danuta et al., 2014). Cu in SWR mainly comes from brake pad wear, urban surface paint, wires for trams, fireworks, industries and Cu is often added to pig fodder as a supplement; these human activities leave a large amount of Cu in the air and urban surfaces as well as in agricultural areas. Through wet precipitation and erosion, rainwater scours part of the Cu into the surface water, which increases the cumulative content of Cu in the surface water. (Deng et al., 2016). Jiang (2019) reported that Cu is essential for animal metabolism, but excessive intake of Cu can cause changes in lung tissue fibrosis, renal failure, and central nervous system damage. Long time intake of high concentrations Cu may cause liver and kidney damage, vomiting, diarrhea and lung cancer (Yue et al., 2020). The maximum permissible limit of Cu published by the US Environmental Protection Agency is 1.3 mg/L (Yue et al., 2020) and toxicological studies of Cu have shown that humans are unlikely to tolerate long-term intake of Cu doses that are approximately 40 times higher than the human requirement, which is about 0.52 mg/kg body weight/day decided by Agency for Toxic Substances and Disease Registy (ATSDR) (ATSDR. 2024). Moreover, the damage of excessive Cu to plant roots cannot be ignored. The study by Huang et al., (2021) showed that the root rot was observed in plants when the plants are grown in 400µM Cu nutrient solution. Kopittke et al., (2009) conducted a 10-day plant growth observation to study the effect of Cu on the roots of Sabi grass. The results showed that Cu affected the growth of Sabi grass at a concentration of 1 μ M, and the relative fresh weight was reduced 50% by compared with normal growth Sabi grass (Kopittke et al., 2009). Zn in SWR comes from tires, anticorrosion layers on steel, exterior wall and roofing, mining activities and atmospheric deposition (Deng et al., 2016). Excessive intake of Zn can cause epilepsy, high blood pressure and coronary heart disease (Greenstein et al., 2004; Wolowiec et al., 2019; Vlastos et al., 2019). The maximum permissible limit of Zn is 5 mg/L (Deng et al., 2016) and the human daily maximum intake investigated by ATSDR is 0.3 mg/kg body weight/day (ATSDR. 2024). Research on the toxicity of heavy metals in runoff found that Cu in rainwater runoff poses the most serious threat to the biodiversity of receiving water bodies, as most data from sewers exceed the species mean acute value, the species mean acute value of Cu for the most sensitive species is 2.37ug/L (Danuta et al., 2014). Using the geoaccumulation index method to evaluate the pollution degree of Cu in river sediments in Dresden, Germany, the results are 1-1.9, indicating that Cu in the sediments is at a moderate pollution level (Zhang et al., 2017). The toxicity test on runoff samples found that each sample is toxic, and dissolved Zn may be the main cause of toxicity (Kayhanian et al., 2007). Therefore, it is necessary to take effective treatment measures to control Cu and Zn pollution in SWR.

Pollutants	Concentration $(\mu g/L)$	Anthropogenic Sources	Toxicity	TMPLW ^a (mg/L)	TMDIH ^b (mg/kg body weight/day)	Environmental Background Value (mg/L)
Cu(II)	22-7033	Mining operations, chemical, and pharmaceutical equipment, kitchenware, paper manufacturing	Menkes, Wilson, Alzheimer's, Parkinson's diseases, damages for eye and liver, vomiting, cramps, convulsions	1.3	0.52	sediment (mg/g) : 0.03; base flow (mg/g) : 0.00119
Zn(II)	56-6000	Mineral mining, automobile tire wear, anti- corrosion materials	Depression, lethargy, respiratory diarrhea, headaches	5	0.3	sediment (mg/g) : 0.95 base flow (mg/g) : < 0.05

Table 1-3 Basic overview of copper and zinc (Göbel et al., 2006; Wolowiec et al., 2018; Pla et al., 2021).

a) The maximum permissible limit in water.

b) The maximum daily intake in human body.

According to the survey of 1.1.3, among the various types of BMPs, except for the retention basin and retention pond which have shown a certain ability to remove dissolved heavy metals, other BMPs have not shown effective removal capabilities for dissolved heavy metals (Clary *et al.*, 2011; Clary *et al.*, 2020). Furthermore, Shaver *et al.* (2007) reported that a considerable amount of Cu, Zn and Cr were found in runoff in dissolved or colloidal form, and the dissolved heavy metals still pose a potential risk to the environment.

In summary, although most of time the concentration of Cu and Zn in rainwater runoff may not cause big problem currently. But it does not mean that we can ignore them. On the one hand, compare with other metals in runoff, Cu and Zn concentration is quiet high which should attract people's attention. On the other hand, sometimes the concentrations of Cu and Zn exceed the local environmental background value, which means that it brings a bad impact to local environment and in specific land use such as mining areas or industrial land, the Cu and Zn concertation may exceed the local surface water standard. Although there has been no incident of damage caused by excessive Cu and Zn, this is a risk that we should consider in advance. Therefore, it is necessary to consider finding an effective method to remove the dissolved Cu and Zn.

1.1.4 Control of Heavy Metal Pollution

In recent years, research on methods to remove heavy metals in stormwater runoff has made great advance. Commonly used methods include chemical precipitation, membrane filtration, ion exchange resin and adsorption (Wang, 2019). Studies on Cu and Zn treatment have found that most Zn is combined with colloids or organic matter, while Cu exists in the form of ions (Morquecho, 2005). The feasible solutions for the removal of dissolved metals are as follows:

1) Chemical precipitation

Chemical precipitation transforms heavy metal ions into low-solubility hydroxides for separation by adding chemical agents in water. Commonly used chemical precipitation methods include alkaline precipitation, metal chelation precipitation and sulfide precipitation (Jiang, 2019a, b). Xu *et al.* (2006) studied a new organic heavy metal chelating agent which can effectively remove Pb, Cd, Cu, and Hg in wastewater. At pH 3~6, the removal efficiency can reach more than 99.9%. The concentrations of four heavy metals in the treated wastewater are lower than 1, 0.1, 0.5 and 0.05 mg/L respectively. Chemical precipitation has the advantages of mature technology and easy operation. However, chemical precipitation is not suitable for the treatment of low concentrations of heavy metals, such as occurs in rainwater, and the precipitate can easily block the treatment facilities, which is not convenient for maintenance (Wang, 2019).

2) Membrane filtration

Membrane filtration uses the different osmotic pressures on both sides of the membrane and traps heavy metals on one side of the membrane to achieve removal from rainwater runoff (Hu, 2019). Sliesarenko *et al.* (2020) found that when the lead, cadmium, and chromium concentration in sewage is lower than 100mg/l, the polymer membrane with phosphonic acid and thiol group is an effective treatment, with an average removal efficiency of 8 mg heavy metal removal per gram of film; the removal capacity is as follows: Cd > Pb > Cr. Membrane filtration has the advantages of strong retention capacity and easy operation. However, the cost and energy demand of membrane filtration is high, and the filtration speed is slow, so it is not suitable for large-scale rainwater filtration applications (Jiang, 2019).

3) Ion exchange resin

Ion exchange is widely used to remove heavy metals in wastewater. Heavy metal ions are exchanged with the ions on the resin to fix them on the resin. Cation resins, anion resins and humic acid resins are frequently used exchange resins (Wang, 2019). Farha *et al.* (2009) used ion exchange resins to

adsorb Pb, Fe and Ce in wastewater, in which the adsorption capacity was Ce > Fe > Pb. Ion exchange has the advantages of simple operation, good treatment effect, and recyclable adsorbent. However, when dealing with large-scale low-heavy metal concentration wastewater, the cost is higher and it will cause re-pollution (Lv, 2020).

4) Adsorption

Adsorption is the use of surface functional groups of materials to adsorb heavy metals on the surface of the adsorbent. The adsorption method has the characteristics of simple operation, low cost, wide application range, and can treat various concentrations of heavy metals in wastewater. Currently it is a widely used method for pollutant removal (Lv, 2020). Commonly used media include activated carbon, natural material adsorbents and biological adsorbents. Rybicka *et al.* (1995) found that the removal of heavy metals by adsorption occurred with an efficiency of illite, beidellite and montmorillonite to adsorb Pb and Cu, and is as high as 80% and 70%, respectively. Zhang *et al.* (2010) explored the treatment of rainwater by high-efficiency biological filters, which could remove more than 90% of the pollution load.

The adsorbent has a large number of micro-pores, a large specific surface area and active groups, which is beneficial to the removal of heavy metals. However, the activated carbon adsorbent is expensive to make and is not convenient for large-scale use. The processing technology of natural materials is complicated, and the unmodified materials adsorption is not efficient. The adsorption rate of biosorbent is slow and the adsorption effect is unstable (Wang *et al.*, 2019a; Wang *et al.*, 2021).

In summary, according to the above review of heavy metal removal methods, considering the cost, adsorption efficiency and maintenance difficulty, adsorption seems to be an efficient process for further study.

1.1.5 Adsorption Materials

Adsorption is currently a mature and practical way to remove heavy metals from wastewater. There are many types of adsorbents, including activated carbon, cellulose nanotube adsorbents, biological adsorbents and various low-cost adsorbents such as biochar made from coconut shells and rice husks or steel slag (Lv, 2020).

1) Activated carbon adsorbent

Activated carbon is currently the most widely used adsorbent. Activated carbon can effectively remove heavy metal pollutants because of its internal pore structure. For instance, Kongsuwan *et al.* (2009) discussed the use of eucalyptus bark to prepare activated carbon to adsorb Cu and Pb. The maximum adsorption capacity of this material for Cu and Pb is 0.45 and 0.53 mmol/g, respectively. Muhammad *et al.* (2010) compared the removal efficiency of Cu and Pb by activated carbon prepared

from fibers and traditional coal, and the results showed that fiber activated carbon exhibits better metal binding capacity than coke. However, the cost of commercial activated carbon is high and the production is low, so the current research focuses on the use of low-cost alternative materials to prepare activated carbon.

2) Cellulose nanotube adsorbent

Cellulose nanotubes have a strong adsorption capacity for heavy metals. As a new kind of adsorbent, cellulose nanotubes have great potential for removing heavy metal ions such as lead, calcium, cadmium, copper, nickel, and zinc in water (Wang *et al.*, 2020b). Cellulose nanotubes remove heavy metals through various mechanism, such as complexation and electrostatic adsorption (Rao *et al.*, 2007). Hokkanen *et al.* (2013) studied the adsorption of heavy metals by acidified fiber nanotubes, which showed that the removal rates of Co, Ni, Cu, Zn and Cd by the modified cellulose nanotubes were 1.34, 0.74, 1.9, 1.61 and 2.06 mmol/g respectively. Although the cellulose nanotube adsorbent has a significant effect on the removal of heavy metals, the production process is complicated, the cost is high, and the maintenance is inconvenient.

3) Biosorbent

Biosorption is the use of biological method, such as microorganisms and plants, to adsorb pollutants from the environment through physical, chemical and microbial metabolic effects (Wei et al., 2016). It is a relatively new adsorption method because of its environmentally friendly characteristics and low cost, which can effectively remove heavy metal in wastewater. Biosorbents are widely used in large-scale water treatment such as constructed wetlands. They mainly remove heavy metal pollutants through the complexation of cells and heavy metals, ion exchange and inorganic micro-precipitation (Lv, 2020). Biosorption can selectively remove heavy metals at low concentrations, has high treatment efficiency and can effectively recover heavy metals. There are many sources of biosorbents such as shells, tree residues, microbes, fungi and algae (Aporatikul and Pavasant, 2008). There are also some low cost plant materials such as wood chips and the shells of various animals and plants. Ajjabi and Chouba (2009) used marine green Ceratium algae to adsorb Cu and Zn. Under the conditions of pH=5 and an adsorbent dose of 20 g/L, the adsorption capacity of marine green algae for Zn and Cu was 1.46 and 1.97 mmol/g. Azadirachta indica (NEEM) powder, as a biosorbent can remove lead in wastewater as high as 97.8% (Srinivasanl and Sadgir, 2018). However, the biosorption rate is relatively slow, and biological requirements for a living environment are strict, which is not a universally applicable adsorption method.

4) Low-cost adsorbent

There are various kinds of material used to remove heavy metals in wastewater, but it is difficult to define which material is the best, because adsorption materials have different performances under different conditions and backgrounds. By contrast, activated carbon is widely used in various

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environments due to its low manufacturing cost, good adsorption capacity and fast adsorption rate. It is worth noting that the use of agricultural, living and industrial waste to make adsorbents has received extensive attention from researchers in recent years due to its ubiquity, zero cost, certain adsorption capacity and environmental sustainability

There have been studies on the treatment of heavy metal from wastewater or SWR by natural zeolite, industrial waste, plant residues and agricultural waste. Bhattacharyya and Gupta. (2008) investigated the adsorption capacity of zeolite and montmorillonite for heavy metals. Kurniawan et al. (2006) compared the removal effects of various low-cost adsorbents for heavy metals in wastewater. Agoubordea et al. (2009) mixed sawdust and brine sediment with a solid-liquid ratio of 1:40 to adsorb Cu and Zn in wastewater, and the maximum adsorption capacity was 4.85mg/g and 4.69mg/g, respectively. Magnetic nanobiochar made from wheat straw was shown to be highly efficient in removing Hg from contaminated irrigation water, absorbing exceed 99% of Hg within 12 hours and a maximum adsorption capacity of 127.4 mg/g (Li et al., 2020). Vijayaraghavan et al. (2010) compared the adsorption of 11 heavy metals (Co, Ni, Zn, Cd, Cu, Pb and Mn) from simulated stormwater runoff by using seven adsorbents including a commercial ion exchange resin (Amberlite XAD17) and some low-cost adsorbents (sawdust, chitosan, peat, Sargassum, crab shell and sugarcane bagasse). The results showed that the removal efficiency of crab shell for all metals exceeded 90% (Vijayaraghavan et al., 2010). Similarly, the removal of Cu, Zn and Pb from SWR by natural quartz sand, sandy soil and three mineral-based adsorbent materials (combinations of various adsorbents such as zeolite, dolomite, activated carbon, clay and coconut fiber) was studied (Haile and Fuerhacker, 2018). It was found that except for natural quartz sand, the removal efficiency of Cu, Zn and Pb by other adsorbent materials exceeded 80% (Haile and Fuerhacker, 2018). Fuhrman et al. (2006) used activated bauxsolcoated sand, bauxsol-coated sand, iron oxide-coated sand, granulated activated carbon, granulated ferric hydroxide, natural zeolite, fly ash, alumina, bark, spinel (MgAl₂O₄) and sand as adsorbents to remove Cu, Zn, Ni, Cd, Cr and As in simulated stormwater runoff. The results show that the ability of these 11 adsorbents to remove heavy metals from stormwater runoff are as follow: alumina, bauxsolcoated sand, granulated ferric hydroxide, fly ash, granulated activated carbon, spinel, activated bauxsol-coated sand, iron oxide-coated sand, zeolite, bark and sand (Fuhrman et al., 2006). This result means that in the study of various adsorbents, porous adsorbent containing aluminum may have a good ability to adsorb heavy metals. Compared with various adsorbents, low-cost adsorbents have received extensive attention from researchers due to their low price and easy availability. Alum sludge, a low cost adsorbent from water purification plant is composed of a large amount of aluminum, so it has theoretical feasibility as an adsorbent for heavy metal pollution in SWR.

1.1.6 Alum Sludge

Alum sludge (AS) is a by-product of treatment processes in all water purification plants which use polyaluminium chloride (PAC) or alum as a coagulant. It agglomerates the organic matter into large particles which allows separation from the water via settlement. The agglomeration happens through the compression of the electric double layer, electric neutralization and adsorption bridging (Yang *et al.*, 2010). Furthermore, Figure 1-1 shows the species distribution of aluminium under different pH. The secondary hydrolysis of aluminium ions generates aluminium hydroxide (Al(OH)₃) particles, which have a precipitation net capture effect (Yang *et al.*, 2010). The particles capture suspended particles and colloids and form a dense precipitation (Yang *et al.*, 2010). AS mainly originates from the drainage of the sedimentation tank and the backwash of the sand filter.



Fig. 1-1 Al species distribution in distilled water at different pH

Generally, the amount of AS produced is 1-3% of the treated water (Zhao *et al.*, 2021). Due to the rapid growth of the world's population and urban expansion, the demand for clean water is increasing, following an increase in the production of AS. By estimate, approximately 67g of AS will be produced for every cubic meter of raw water treated depending on the raw water turbidity (Qiu *et al.*, 2015). A typical water purification plant (scale of 150,000 m³/d) can produce 10 tons of wet AS per day (Zhao *et al.*, 2021). AS is produced in most countries, but with large variations in the scale of AS production (Fig.1-2). In Fig.1-2, this is a list diagram which shows the total AS production of different countries in different years. This illustrates the magnitude of the alum production following dewatering processes. However yearly variations are likely to mean that comparisons between countries production should not be done using this data. For example, China produced about 22

million tons of AS in 2014 (Ren *et al.*, 2020), whereas about 2 million tons per year is produced in the USA (Soleimanifar *et al.*, 2019); the global average is around 10,000 tons of AS per day per treatment plant (Li *et al.*, 2018). The production of AS is increasing year by year, due to the growing need for drinking water (Wang *et al.*, 2019). Consequently, large amounts of AS are produced each year, requiring disposal (Ren *et al.*, 2020).



Fig. 1-2 Average annual production of AS by select countries (Babatunde *et al.*, 2009; Nimwinya *et al.*, 2016; Soleimanifar *et al.*, 2019; Ren *et al.*, 2020; Nagara *et al.*, 2022).

1.1.7 Properties of AS

Shen *et al.* (2019) reviewed data from 62 countries (25 in the Americas, 22 in Europe, 9 in Asia, 3 in Oceania, and 3 in Africa) and found that differences in raw water and treatment processes affect the physicochemical properties of AS. The metal content and main composition in AS varies greatly, with ranges in compositions shown in Table 1-4. In spite of these variations, x-ray fluorescence spectrometer analysis has shown that the main components in all AS are aluminum, iron, manganese, calcium, silicon and organic matter (Cui *et al.*, 2015). Due to the existence of organic matter, AS may contain various functional surface groups, such as hydroxyl groups, carboxyl groups and amino groups (Poormand *et al.*, 2017; Hu, 2019). Fourier transform infrared analysis results have shown that the structural peaks of hydroxyl groups are found in the wave band between 3500 cm⁻¹ and 3800 cm⁻¹ and 1000cm⁻¹ to 1500 cm⁻¹ (Siswoyo *et al.*, 2014; Elkhatib *et al.*, 2015). Moreover, wave band at 1080 cm⁻¹ was also found A – O stretching vibration (Qiu *et al.*, 2015), 1690 cm⁻¹ appear amino group characteristic peaks and 950-1100 cm⁻¹ shows phosphonate group characteristic peaks (Jiao *et al.*, 2016). The existence of these functional groups provides the theoretical possibility for AS to be used as an adsorbent.

AS composition	Parameter	Range (mg/kg dry solids)
	Al	36865-77500
	Fe	853-70000
	Ca	2873-22400
	Mn	522-10111
	Mg	647-3770
Metal composition	Zn	33.9-178
	Cu	13.6-109
	Ni	10-44.3
	Cd	0.5-20
	Со	1.1-20
	AS	0.76-16
Key composition	Al_2O_3	14.5-73.6
	Al(OH) ₃	26.4-49.9
	Fe ₂ O ₃	2.1-68.8
	FeOOH	31.2-38.2
	SiO_2	19.1-58.9
	MgO	0.18-1.9
	CaO	0.42-13.9
	K ₂ O	0.46-2.0
	Na ₂ O	0.14-4.1

Table 1-4 Metal composition and Key composition of AS (Wang *et al.*, 2016; Wang *et al.*, 2018; Siswoyo *et al.*,2019; Truong and Kim, 2021; Cheng *et al.*, 2018)

Generally, AS is amorphous (Kang *et al.*, 2019). Ippolito *et al.* (2011) analysed AS by XRD and found that the proportion of amorphous material was 85%, with the balance provided by crystalline material mainly composed of quartz (SiO₂), graphite (C) and calcite (CaCO₃), which accounted for 53%, 34% and 12%, respectively, of the remaining crystalline fraction of AS. AS may occasionally also contain feldspar, illite/montmorillonite, and kaolin (Cui *et al.*, 2015). Scanning electron microscopy (SEM) analysis has revealed that AS has a rough-surface, with non-uniform particles (Lian *et al.*, 2020).

The specific surface area is an important quality indicator of adsorbent materials. There is a large variation in the specific surface area of different AS media, as measured by Brunauer-Emmet-Teller (BET) analysis from 7 to 290 m²/g (Table 1-5). Caporale *et al.* (2013) found that the particle size of AS is an important factor affecting the specific surface area which increases significantly with decreasing particle size. The findings of Qiu *et al.* (2015) support the findings of Caporale *et al.* (2013), indicating that the specific surface area of AS is 138 m²/g for particle sizes of 1-2mm,

whereas when particle size decreased to below 0.15 mm the specific surface area increased dramatically to 250 m²/g. Qiu *et al.* (2015) also found that particle size has a little effect on micropore volume and total pore volume. Table 1-5 summarizes data for particle size and specific surface areas as reported in different papers. The table shows that the difference in specific surface area of AS does not shows the strong relationship with particle size. Therefore, the data in Tables 1-5 show that there are large differences in the specific surface area of AS from different water plants. For example, Zhou and Haynes (2011) tested the specific surface area of AS from the Seq-water Mount Crosby and North Pine water treatment plants in Brisbane by using a N₂-adsorption method. The result shows that the specific surface area of AS from Seq-water Mount Crosby was only 97 m²/g and hence significantly lower than the one comes from North Pine water treatment plants. This may due to the differences in raw water quality and treatment process control parameters, such as PAC concentration, PAC dosage, stirring strength.

Moreover, experimental methods also affect the results of the specific surface area. For example, the specific surface area of AS measured by N₂-BET is $135.55m^2/g$ but is $175.28m^2/g$ when measured in the same AS by the CO₂-BET method (Lv, 2020). Comparable results were obtained by Hovsepyan *et al.* (2009) who reported a specific surface area of $48m^2/g$ for AS using the N₂-BET method, but $120m^2/g$ when using the CO₂-BET method. The higher values using CO₂-BET indicate that N₂ cannot permeate all pores inside the AS, as N₂-BET is not suitable for pores <0.5 nm (Jonge, 1996). Hence experimental results may underestimate the specific surface area of the material (Jonge, 1996).

The results showed that the adsorption capacity of AS was attributed to its chemical adsorption of surface functional groups. For example, in order to explore the effective adsorption components in AS, Cheng *et al.* (2018) used ammonium chloride, sodium hydroxide and hydrochloric acid to continuously extract the adsorption-saturated AS ceramsites. The saturated AS was divided into physically adsorbed phosphorus (extracted with NH₄Cl solution), iron/aluminum adsorbed phosphorus (extracted with NaOH solution), and calcium/magnesium adsorbed phosphorus (extracted with HCl solution) (Cheng *et al.*, 2018). The results showed that the physical adsorption accounted for less than 0.1% of the total adsorption capacity, but the chemical adsorption from oxygen-containing functional groups bind with iron, aluminum, calcium and magnesium accounted for 80% of the total adsorption capacity of AS (Cheng *et al.*, 2018). Furthermore, a large number of AS adsorption kinetics experimental results show that chemical adsorption is the AS adsorption mechanism which refer to ion exchange and sharing, and these chemical adsorption capacities mainly come from the oxygen-containing functional groups on the AS surface (Castaldi *et al.*, 2015; Poormand *et al.*, 2017; Zeng *et al.*, 2020; Duan and Fedler. 2021).

Particle Size	Specific Surface Area	Total Pore Volume	Average Pore Size
	(m ² /g)	(cm ³ /g)	(nm)
< 125 µm	97.3 ^a	No data	No data
< 125 µm	290ª	No data	No data
< 125 µm	135.6 ^a	0.018	4.5
	175.3 ^b	0.018	
75 μm-150	7 ª	0.019	11.2
μm	,	0.017	11.2
< 150 µm	31.6 ^a	0.096	9.9
< 250 µm	36.7ª	0.062	6.8
1-2 mm	60.9 ^a	0.109	9.3
< 2 mm	48 ^a	N. 14.	No data
	120 ^b	ino data	

Table 1-5 Specific surface area and pore volume of AS (Hovsepyan *et al.*, 2009; Zhou and Haynes, 2011; Jeon*et al.*, 2018; Liu, 2018; Wang *et al.*, 2019; Lv, 2020; Duan and Fedler, 2021)

a) The specific surface area is measured using N_2 -BET method.

b) The specific surface area is measured using CO₂-BET method.

1.1.8 Toxicity of AS

According to chemical-based leaching experiments, the toxicity of AS is mainly derived from heavy metals (Shen et al., 2019). From the analysis of the sludge composition, AS contains a large amount of aluminum and iron ions (Qiu et al., 2015). The risk of heavy metal leaching from AS and its impact on the surrounding environment should be considered when it is used as an adsorbent. Many methods such as toxicity leaching test and ecotoxicology tests have been used to study the impact of AS on the environment and biology (Shen et al., 2019). For example, Babatunde and Zhao. (2010) investigated Al release from a pilot field-scale AS-based constructed wetland, used to remove phosphorus. During the one-year monitoring. Al was leached to a certain extent depending on the leaching pH. However, in the rainwater, the leaching amount is relatively low, always between 0.02-0.06 mg/L, much less than the maximum Al limit for drinking water specified by USEPA (0.2mg/L). Therefore, it was concluded that AS does not pose any imminent environmental and health risk. The results of using the Daphnia bioassay to evaluate the toxicity of AIS show that in 48h acute toxicity tests the survival rate of daphnids is 100% and in 14d chronic toxicity tests, no harmful effect on mortality was observed for AS (Rosana et al., 2005). Zhao et al. (2015) conducted laboratory and field scale experiments on the toxicity of AS leaching. The experiment showed that the leached Al concentration was 0.03~0.11 and 0.02~0.06 mg/L, respectively, which are lower than the drinking water standard. USEPA test results

suggest that AS is harmless (Yuan *et al.*, 2016). Additionally, the Water Research Center of the University of Dublin reviewed experiments on aluminum leaching from AS and carried out more than 42 weeks of monitoring of aluminum release from AS which is used in constructed wetlands (Babatunde *et al.*, 2010). The results show that the concentration of soluble Al leached from AS is less than 1mg/L, with most concentrations are between <0.01~<0.02 mg/l. The highest and lowest Al release occurred at pH 3 and pH 5, respectively (Babatunde *et al.*, 2010). The results also show that the amount of aluminum leaching is generally low, in the range of 0.02~0.06mg/L (Babatunde *et al.*, 2010). It suggests that the aluminum content in the leachate is within a reasonable range and is not enough to cause toxicity to aquatic organisms (Babatunde *et al.*, 2010). The study also found that the adsorption of phosphorus by AS further reduced the leaching of Al, which reduced Al release by approximately 54%-97% (Babatunde and Zhao, 2007). Therefore, the Water Research Center concluded that AS does not pose any imminent environmental and health risks (Babatunde and Zhao, 2007). The experiment of Maqbool *et al.* (2016) showed that Pb, Fe, Ni, Al and Cr in AS were all within an environmentally acceptable range, not enough to cause harm to the environment.

Therefore, based on the above reasons, it can conclude that AS has no acute or chronic toxicity to the environment, hence no further toxicity leaching experiments are required for this project.

1.1.9 Current Disposal of AS

As AS is normally a waste product from drinking water purification, it is currently disposed of after production. For example, the most common disposal methods for AS in China are: landfill, incineration, unknown and composting (Lv, 2020) (Fig. 1-4), where "unknown" includes unspecified amounts used in dried form to make permeable brick or adsorbents. Due to lowest economic cost landfill is currently the main disposal method. This means that the majority of AS is not reused, but causes intensive use of land resources and potentially wastes money (Lv, 2020). A survey found that in the Netherlands, the disposal cost is up to \$50 million per year to dispose of 0.1 million tons of AS (Zhao *et al.*, 2021). Similarly, the Australia Victorian Water Industry reported that they generate 0.15 million tons of AS per year and spend \$6.2 million to dispose to landfill or discharge it into sewers, while it is \$2.8 million per year in Ireland (Li *et al.*, 2018; Ren *et al.*, 2020). The re-use of AS waste therefore has the potential to save significant disposal costs as well as providing a raw material.



Fig. 1-3 Current disposal of AS in China (Lv, 2020)

1.1.10 Application of AS

There is considerable interest in the reuse of waste AS to avoid the costs of disposal. Dassanayake et al. (2015) reviewed the reuse of AS and pointed out that it can be recycled and reused in various applications such as agriculture and artificial wetlands. For example, in agriculture, AS can be used as soil ameliorant, which greatly improves the structure, porosity and nutrient level of the soil (Dassanayake et al., 2015). Due to the large amount of nutrients and organic matter contained in AS, the use of AS has not been found to have a negative impact on the soil environment and biological systems (Dassanayake et al., 2015). Moodley and Hughes (2005) reported that the use of grind 2 mm AS as a soil conditioner can effectively improve soil moisture content and porosity, which is good for plant growth. Wang et al. (2019) used AS as potting medium, by mixing AS, fly ash and bentonite in a ratio of 2:1:1 and making clay, they found that the clay had a hard texture and promoted plant growth. Environmental aspects AS has been studied as a coagulant, co-conditioner and artificial moisture matrix for wastewater treatment (Dassanayake et al., 2015). For example, it has been reported that the addition of AS as a coagulant to wastewater resulted in removal efficiencies of 71.5%, 76.4%, 95.4%, and 98.2% for total suspended solids, chemical oxygen demand, anionic surfactants, and turbidity, respectively (Jangkorn et al., 2011). In addition, the large amount of hydroxide in AS can enhance the sedimentation and dehydration rate (Babatunde and Zhao, 2007). Therefore, AS can also be used as a co-conditioner for sewage sludge conditioning and dehydration in sewage treatment plants (Babatunde and Zhao, 2007). In addition to agriculture, Babatunde and Zhao (2007) reviewed AS application and added its potential in construction area. For example, Huang et al. (2001) mixed AS with clay and fired it at 1050-1100°C successfully producing bricks that met the Chinese national standard without surface cracks and deformation. Wu et al. (2016) mixed AS and cement in a ratio of 5:5 to make bricks that can be used as building materials, and with an adsorption capacity of $\ge 80\%$ for phosphorus in runoff. The most important aspect is AS application in constructed wetlands. A large number of studies have pointed out that AS as a constructed wetlands matrix has the ability to remove various pollutants in the environment such as phosphorus, heavy metals, biochemical oxygen demand and ammonia nitrogen (Babatunde and Zhao. 2010; Zheng et al., 2016; Shen et al., 2018; Cheng et al., 2018; Li et al., 2018; Liu, 2018). Because AS is rich in aluminum and iron residues, these residues are strong adsorbents of phosphorus in wastewater (Jangkorn et al., 2011). Zhao et al. (2009) used AS as the main constructed wetlands matrix and achieved an average removal rate of 99.4% and 82.9% for phosphorus and biochemical oxygen demand respectively in animal farm wastewater. Similarly, Yang et al. (2011) and Wu et al. (2011) used laboratory-scale simulated AS-based multi-stage constructed wetlands and achieved an average removal efficiency of more than 95% for phosphorus and 88.4% for ammonia nitrogen.

In order to expand the research on the reuse of AS, consideration has been given in recent years to using AS as an adsorbent to treat heavy metal pollution (Siswoyo et al., 2014; Ma et al., 2020; Nagara et al., 2021). It has been experimentally verified that AS is an effective adsorbent to remove Cu, Pb, Hg, Co, Cd, Zn, V, Mo and Cr from water, and the adsorption capacity depends on the physicochemical properties of AS as well as the adsorption conditions (Ren, 2014; Silvetti et al., 2015; Soleimanifar et al., 2016; Hua et al., 2018; Lv, 2020). The different sources and preparation methods of AS imply that the physical properties of AS, such as specific surface area will vary between different regions. In addition, different adsorption conditions such as initial solution concentration, adsorption temperature, pH, AS dosage, adsorption time, solution ionic strength and adsorption competition also affect the adsorption capacity of AS for the same metal. For example, different regional sources of AS in Hokkaido, Japan, have different affinities for Cd, with maximum adsorption of 5.3 mg Cd/g for Miyamachi and 9.2 mg Cd/g for Nishino, and removal rates of 53% and 92%, respectively (Siswoyo et al., 2014). Under the same experimental conditions, the removal rate of Cd by AS from Nishino is as high as 92%, due to the relatively high specific surface area of Nishino AS (Siswoyo et al., 2014). A higher specific surface area provides more adsorption sites, which is beneficial for the adsorption of pollutants by AS. However, other studies have shown that while the specific surface area is an important factor in heavy metal adsorption by AS, other properties, such as the pore size, pore volume, elemental composition of AS and properties of functional groups on the AS surface also determine the adsorption capacity of AS (Zhou and Haynes, 2010; Zhou and Haynes, 2011).

As mentioned above, the solution pH is a key variable which affects metal adsorption. Under acidic conditions, protons and heavy metal ions in the solution compete for adsorption sites on the AS surface, whereas under alkaline conditions the metal ions and OH⁻ in the solution form hydroxide precipitates, which will cover the AS surface, potentially interfering with adsorption and reducing the adsorption capacity (Lv, 2020). Therefore, suitable pH conditions can exert a maximum adsorption capacity for AS. Ma *et al.* (2020) found that AS had a high affinity for Pb and Cu at pH 4-5, with maximum adsorption capacities of 138 mg Pb/g and 57 mg Cu/g, and removal rates of 86% and 57%, respectively (Ma *et al.*, 2020). Silvetti *et al.* (2015) investigated the adsorption of Cd and Zn by AS at pH 4.5, 5.5 and 7.0, identifying a maximum adsorption capacity for Cd and Zn at pH 4.5. Usually the water pH is between 4-7.8, wherein AS is reported to have a high affinity for Pb, Cu, Cd, Zn, Cr and Co(II) (Zhou and Haynes, 2011; Lin *et al.*, 2014; Silvetti *et al.*, 2015; Jiao *et al.*, 2016). Hence, AS can be an effective adsorbent for many heavy metals present in the natural environment.

1.1.11 Selective Adsorption of AS

The background ionic strength of the solution and competitive adsorption between heavy metals are also key factors affecting the adsorption capacity of AS (Hua et al., 2018). When the background solution contained 1mol/L of either Cl⁻, NO³⁻, SO_4^{2-} and PO_4^{3-} as interfering anions, the removal rate of Cr by AS decreased by 8.3%, 9.1%, 18.2% and 24.8%, respectively (Ren, 2014). This occurs because Cr exists as different anionic species in solution ($Cr_2O_7^{2-}$, $HCrO^{4-}$, and CrO_4^{2-}), such that competition from these can reduce the extent of Cr adsorption by electrostatic attraction (Uddin, 2017). Nagara (2022) investigated the effect of four cations (Na, K, Ca and Mg) and two anions (Cland NO³⁻) on the adsorption capacity of AS for Cd, Cr and Ni. That the background anions only had a significant effect on the removal of Cd, and the effects of the background cations on the removal of the three metals were in the following order: $Ca > Mg > K \sim Na$. Esfandiar *et al.* (2022) also showed that divalent cations inhibit metal removal more strongly than monovalent cations. Hence, metal adsorption by AS in multi-component solutions is a complex function of AS composition, AS properties and aqueous metal concentrations, which may result in competitive inhibition and synergistic relationships between metals for adsorption sites (Esfandiar et al., 2022). Preferential adsorption of heavy metals by AS is influenced by the hydrolysis energy, ionic radius, hydrolysis constant, hydration radius and electronegativity of heavy metals (Lv, 2020). In a multivariate system Qiu (2020) found that the adsorption of heavy metals by AS followed the order: Pb > Hg > Cd > Cr. Furthermore, in Pb, Cd and Ni mixtures, the metal removal capacity is in the order of: Pb > Cd > Ni; this trend is consistent with the order of ionic radii and hydrolysis energies of Pb, Cd and Ni (Abo-El-Enein et al., 2017).

1.1.12 Regeneration of AS

Studying the AS adsorption/desorption capacity is an important indicator to evaluate the application potential of AS as an adsorbent. Zhou *et al.* (2011) used 0.1M HNO₃ for eight consecutive adsorption/desorption cycles of AS and found very little loss of adsorption efficiency, which decreased from 75% to 60% for Pb and from 87% to 70% for Cr. This suggests that AS can be recycled as an efficient adsorbent for metals.

1.2 Scope of the study

This study will research the characterization and application of the industrial byproduct that is aluminium sludge for reuse as an innovative, low-cost filtration material to treat heavy metal pollutants in SWR, focusing mainly on heavy metal removal. The expected benefits of the study include: 1) reducing heavy metal pollution in SWR; 2) reusing AS to fully realise its value and reduce treatment costs; 3) extending the service life of the runoff filtration system by regularly replacing and regenerating AS. In this study, batch and column experiments were performed to quantify the ability of AS as a filtration medium to mitigate heavy metal pollution loads in SWR. The pollutants tested in this study are Cu and Zn. Because they are ubiquitous and abundant in SWR, they are of concern to the public and the ecological community. Other pollutants in SWR are beyond the scope of this study. The choice of adsorbent is AS from water purification plants. In fact, there are two types of waste from water purification plants. In addition to the aluminum-based sludge (AS) mentioned above, there is also iron-based sludge, which mainly depends on the flocculent material used by the water purification plant. In other words, if polyaluminium chloride is used as a flocculating additive in a sedimentation tank, the water purification plant by-product is AS, and if ferric chloride/ferrous sulfate is used as a flocculating additive in a sedimentation tank, the water purification plant waste is ironbased sludge. There are two main reasons why AS is chosen as the adsorption material instead of iron-based sludge: 1) AS is abundant and easier to obtain for this project; 2) Surveys show that compared with iron-based sludge, AS has more stable chemical properties in oxygen-limitation environment (Nagar et al., 2010). This is important to retain the adsorbent properties of AS under anaerobic conditions. As an adsorbent material, it usually works under oxygen-limitation conditions, so AS is a better choice for filtering SWR. On the contrary, under oxygen-limitation conditions, trivalent iron may be reduced to divalent iron and be mobilized, which can easily cause excessive iron concentration in the effluent (Kocar et al., 2006). For example, Nagar et al. (2010) used AS and ironbased sludge to adsorb arsenic and found that the leakage of iron dioxide occurred in the pH range of 7-9, which caused a decrease in the adsorption of arsenic, while AS maintained a removal capacity of about 100% for arsenic.
1.3 Aims and Objectives

The investigation found that most of the research on AS focused on its adsorption of phosphorus in SWR, while there were fewer studies on heavy metal adsorption and most of them focused on how to modify it to treat high-concentration heavy metal wastewater. The purpose of this study is to address the problem of heavy metal pollution at low concentrations (compared to wastewater) in SWR by using a low-cost, high-efficiency method. This study focused on the removal capacity of AS for Cu and Zn, which is important to evaluate feasibility of AS in treating runoff pollution. In addition, the study also included dynamic filtration experiments to simulate the performance of AS in filtering SWR and providing experience for future applications. The innovation of this project is to (i) systematically study the use of AS to treat low-concentration runoff heavy metal pollution, (ii) develop current understanding of Cu and Zn adsorption by AS from theoretical data to application, and (iii) explore its effectiveness and competitive adsorption phenomenon in adsorbing Cu and Zn in simulated runoff with complex pollution components. The specific objectives of this study are as follows:

1) Characterization of the physico-chemical properties of AS and evaluation of its feasibility as a heavy metal adsorbent;

2) Determination of the adsorption efficiency and adsorption mechanism of AS for selected metals by using batch experiments;

3) Determination of its effectiveness in adsorbing selected metals in a complex pollution background by using AS to adsorb simulated rainwater runoff;

4) Evaluation of the adsorption performance of AS under dynamic filtration system by simulating SWR.

1.4 Significance of the study

The significance of this study is that it provides a better understanding of AS as an adsorbent material to treat heavy metal pollution in wastewater and using AS to treat various pollutants in runoff. By studying the removal efficiency of Cu and Zn by AS, waste utilization and sustainable stormwater management strategies can be achieved. Moreover, research on reusing industrial waste to solve runoff pollution problems will support the environmental management of AS waste. On the one hand, AS is fully utilized and the cost of sludge disposal is reduced. On the other hand, a low-cost and low-environmental-impact method is adopted to reduce the runoff pollution load. In addition, the column experiment simulated the actual application of AS, providing valuable experience for its future application in SWR filtration. With the development of urbanization and climate change

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intensification, AS is an environmentally friendly and sustainable stormwater management solution that can be integrated into urban infrastructure.

1.5 Outline of the study

This study consists of six chapters.

Chapter 1: Introduction. It provides background information on SWR, identifies pollutant types and current status of pollutant loads, and briefly summarizes currently used stormwater management methods. Then, due to the large number of pollutants present in SWR, the characteristic pollutants that need to be focused on in this project were identified. The production, characteristics and application of AS and the research progress of using it to treat heavy metal pollution are introduced. Lastly, the research scope, purpose and significance of this study are introduced.

Chapter 2: AS characteristics and feasibility study. The feasibility of AS as a heavy metal adsorbent was fully studied through various characterization methods.

Chapter 3: Batch experiments. Batch adsorption quantified the adsorption capacity and efficiency of AS and studied the adsorption process of Cu and Zn by fitting the adsorption isotherm and adsorption kinetic model. Importantly, the adsorption mechanism of Cu and Zn was discussed by summarize the model fitting results, the effect of solution pH, and AS characterization in Chapter 2. Finally, the effects of different particle sizes as well as the regeneration and cyclic adsorption of AS were studied.

Chapter 4: Adsorption competition study. Chapter 3 explored the theoretical maximum adsorption capacity and adsorption process of Cu and Zn to demonstrate its potential as a heavy metal adsorbent. However, the actual components of SWR are more complex, and there may be competition for adsorption sites among each component. If AS is to be used to deal with runoff problems, it is inevitable to study the possible competition phenomenon in the adsorption process by using simulate runoff.

Chapter 5: Column experiment. A column experiment was used to examine the performance of AS in long-term dynamic adsorption of simulated rainwater. In this chapter, the effects of packing height and filtration rate on the dynamic adsorption capacity of AS were determined, and the risk of release of immobilized heavy metals was evaluated.

Chapter 6: Conclusion. This chapter summarizes the main conclusions of this paper and proposes future research directions.

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CHAPTER 2

ALUM SLUDGE COMPOSITION AND CHARACTERIZATION

2.1 Introduction

Low-cost and high-efficiency adsorbents are a research hotspot for water treatment materials, especially for the reuse of industrial waste by-products. This chapter introduces an underestimate adsorbent alum sludge (AS) which is a waste by-product from the water treatment plants. Using FTIR, SEM, TGA and other characterization methods to conduct a preliminary analysis of the surface structure, functional groups and components of AS, and evaluates its potential as an adsorbent for treating heavy metal pollution and possible adsorption mechanisms.

2.2 Methodology

AS adsorbent. Alum sludge were collected at Yorkshire Waterworks (South Yorkshire, UK). The surface water is the raw water of this water purification plant, aluminum salts as coagulant, and the AS is dehydrated by a plate press dehydrator and stored in the sludge cake yard. After collection, place the AS in a tray and air dry it at room temperature ($20^{\circ}C\pm5$) for 1 week, and then put them into sealed bags and stored at room temperature (Fig. 2-1).



Fig. 2-1 Raw alum sludge from the water treatment plant (After air drying)

Particle size distribution. For further study, manual grinding AS and passed through 2mm, 1mm and 0.15mm sieves in sequence to make two different particle size samples which are below 0.15mm and 1~2mm. Here, AS samples with a particle size less than 0.15 mm are defined as fine powder and the particle size range between 1mm and 2mm are defined as particle (Fig. 2-2). Using

MASTERSIZER 3000 (Malvern) to confirm that the particle size meets the requirements. About 5g dried AS was placed in the MASTERSIZER and the particle size distribution curve of the sample was obtained by laser diffraction.



(a)

(b)

Fig. 2-2 Fine powder (left) and particle (right) AS (a) Dried AS passed through 0.15mm sieve; (b) Dried AS passed through 2mm and 1mm sieves

Surface area and pore size analysis. The specific surface area and pore size of the samples under different particle size was obtained by using a 3Flex (Micromeritics) analyzer. The instrument uses N_2 adsorption-desorption isotherm under the temperature of 77K to measure the specific surface area, pore size and pore volume. About 0.5 g of the sample was weighed and degassed under vacuum at 343 K for 10 h, and then nitrogen was introduced into the degassed sample, the amount of nitrogen adsorbed by the sample at different relative pressures (P/P₀) was recorded by the 3Flex (Micromeritics) analyzer (details in Appendix).

Fourier Transform Infrared Spectroscopy (FTIR) analysis. In order to analyze the possible functional group characteristics on the sample surface, IRAffinity-1S (SHIMADZU) was used for scanning 50mg AS. The wavelength range is from 400-4000 cm⁻¹, and the scanning step length is 2cm⁻¹.

Scanning Electron Microscopy coupled Energy Dispersive Spectrometer (SEM-EDS) analysis.

The microstructure and elemental composition of the AS were obtained using JSM-6010LA (JEOL). According to Aimee (2023) report, the working principle of SEM is to emit electrons through an electron gun and accelerate them with an accelerating voltage to make the electrons more penetrating. Through the interaction between the electron beam and the sample surface, such as the formation of Secondary Electrons, Backscattered Electrons and x-rays, the features of the sample surface are converted into electrical signals (Aimee, 2023). Finally, the signal detector converts the electrical signal into an image (Aimee, 2023). EDS collects X-rays generated by the interaction between the electron beam and the sample in the SEM (Aimee, 2023). The type and roughly quantitative of the element in the AS are determined by analyzing the X-ray peaks at different energy positions (Aimee, 2023).

Take around 0.5g dried <0.15mm and 1-2mm AS and stick them on the specimen stubs with conductive glue, then spray gold on the samples to increase their conductivity. After being placed in the SEM and evacuated, the microscopic images of the samples were observed under 80,1000,3000 and 6000 magnifications and using an accelerating voltage of 20Kv which was set by the software. EDS map scanning was used to obtain quantitative information on the elemental composition of the AS surface.

Thermo-gravimetric analysis (TGA) test. To determine the water, organic matter, and ash contents of AS, thermogravimetric experiments were performed by using a TGA 4000 (PerkinElmer). Weigh 10 mg of AS (particle size <0.15mm) and place it in the instrument. Set the heating rate to 5°C/min under nitrogen background. The heating program was: Hold for 5 min at 30.00°C; Heat from 30.00°C to 950.00°C at 5 °C/min; Hold for 5 min at 950.00°C.

Metal release. It is well known that the release of metals from adsorbents is closely related to the pH of the solution. Since this project mainly considers using AS to treat rainwater runoff pollution, the heavy metal release experiment was carried out within a pH range close to the pH of rainwater. Weigh 10 portions of 0.1g AS (particle size <0.15mm) respectively and place them into a 100mL erlenmeyer flask. Add 20mL of distilled water into each beaker, which had already adjusted the pH to 6.5 by using 0.1M NaOH and HNO₃. Place the mixture into a shaker at 298K 130rpm/min and collect samples at a specific time interval (0, 1, 3, 5, 10, 30, 60, 90, 240, 480min) and then passed through a 0.45µm syringe filter and stored by adding 0.1mL 75% HNO₃ solution for Inductively Coupled Plasma Optical Emission Spectr (ICP-OES) analysis. Metals in the samples were determined using ICP-OES, including Al, Ag, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, V, U and Zn. The minimum metals detection limit was 1-10 µg/L.

2.3 Results and Discussion

2.3.1 Particle Size Distribution

Fig. 2-3 shows the particle size distribution of AS after sieving. It can be seen that the overall average particle size (d_{50}) of the two sizes is 0.06mm and 1.38mm respectively. The maximum size d90 of most particles is 0.122 mm and 2.4 mm respectively. These sizes of AS basically meets the two particle sizes required by further experiment, which are below 0.15mm and between 1 and 2mm.



(b)

Fig. 2-3 AS particle distribution of two different sizes (a) Particle size <0.15mm; (b) Particle size 1-2mm.

2.3.2 Specific Surface Area

Fig. 2-4 shows the adsorption-desorption isotherms for N_2 on the AS with particle size <0.15mm and 1-2 mm and pore size. By describing in the method, the AS isotherm is characterized by a linear increase in adsorption at low pressure, a significant increase in adsorption at medium pressure, and saturation at high pressure, accompanied by an obvious hysteresis loop. According to the IUPAC classification of nitrogen adsorption and desorption isotherms, this isotherm is a typical type IV (Carbó et al., 2013; Enein et al., 2017). At relatively high pressures, the amount of nitrogen desorbed is less than the adsorbed due to condensation in the pores or capillaries, which causes the adsorption and desorption isotherms to not overlap (Li et al., 2018). This non-overlapping region is defined as the hysteresis loop see by definition and characteristics of hysteresis loop (Fig. 2-4) in methodology (Sing et al., 1985; Carbó et al., 2013). By compared with Fig.2-4, the AS showed a hysteresis loop similar to that of the H3-type, which means that AS has a considerable number of flake or crack-like pores. However, the closure of the hysteresis loop indicates that in addition to the flake or crack-like pores, there are also some uniform mesoporous structures in AS. (Wang et al., 2016; Sing et al., 1985). In addition, the adsorption and desorption isotherms increased slowly in the low pressure stage $(P/P_0 < 0.4)$, which also proved that AS has a certain amount of mesopores (Ren, 2014). From the BJH pore size distribution plot (inset in Fig. 2-6), it can be seen that the average pore size of AS for both particle sizes is around 20nm. This is consistent with the conclusion of the adsorption-desorption isotherm, that AS is a porous material dominated by mesopores.



(a)



(b)

Fig. 2-4 The adsorption-desorption isotherms and BJH pore size distribution plot (a) Particle size <0.15mm; (b) Particle size 1-2mm

Table 2-1 lists the pore characteristics of fine powder and particle AS. It can be seen from Table 2-1 that the BET-specific surface area of fine powder AS is slightly larger than that of particle, which are 57.86 m^2/g and 57.88 m^2/g , respectively. This is also in line with common sense that the smaller the particle size, the larger the specific surface area. However, the specific surface area of fine powder has not increased significantly. This may be due to the grinding destroying the fragile silica walls in the AS microstructure, which destroyed the internal pores, resulting in a small increase in specific surface area (Cordeiro et al., 2011). It can be demonstrated by external surface area data that fine powder is 56.07 cm²/g and particle is 37.34 cm²/g which is much smaller than fine powder. This means that grinding leads to the clogging and destruction of internal pores, which greatly increases the proportion of external area. In general, due to the destroyed pore structure of fine powder which makes the internal surface area became small, and this may pose a negative impact on Van der Waals adsorption. It also can be seen from Table 2-1 that AS has a fairly rich internal structure, and the internal pores in the particle size AS account for 35% of the total specific surface area. The specific surface area of AS in this work is similar to the reported by Siswoyo *et al.* (2014) (50 m^2/g) and Wang *et al.* (2018) (50.1 m^2/g) but higher than that recorded by other common low cost adsorbents such as red mud (between the ranges of 20–30 m²/g) (Lima et al., 2017), fly ash (range from 3-5 m²/g) (Bada and Vermaak,

2008) and kaolinite (40.42 m²/g) (Kohno *et al.*, 2018). Moreover, with the decrease of particle size, the number of mesopores in AS decreased from 0.39 cm³/g to 0.25 cm³/g and the average pore size decreased from 23.8 nm to 19.1 nm. This may be because the mesoporous structure of AS was destroyed during grinding as mentioned above (Cordeiro *et al.*, 2011). In general, the relatively high specific surface area and porous characteristics make AS is a potential adsorbent to process environmental pollution.

Alum sludge	BET surface area	BJH Mesopore volume	External Surface area	BJH Average pore
	(m ² /g)	(cm3/g)	(cm^2/g)	size
				nm
Particle	57.86	0.39	37.34	27.86
Fine powder	57.88	0.25	56.07	19.1

Table 2-1 Specific surface area and pore characteristics of AS in this study

2.3.3 Scanning Electron Microscopy coupled Energy Dispersive Spectrometer

In order to understand the surface characteristics and internal composition of AS, the fine powder and particles were analyzed by scanning electron microscopy and energy dispersive spectrometer (SEM-EDS) (Fig. 2-5). It can be seen from Fig. 2-5 (a, b) that the surface of AS is relatively smooth and dense with a large number of crack-like pores which is good agreement with 2.3.2 result that AS has a considerable number of flake or crack-like pores. Although the surface of AS is relatively smooth under low magnification, it can be seen under high magnification that the surface of AS is loaded with abundant particles and accompanied by some pore structures. These particles and cracks can contribute to the specific surface area of AS, providing more sites for adsorption reactions which makes it suitable as an adsorbent for heavy metals removal.

The elemental composition of AS was characterized by EDS. Fig. 2-5 (c) and (d) show the surface element distribution results of fine powder and particle. It can be seen that AS mainly contains C and O elements, and their sum accounts for more than 70% of AS. The rest is mainly inorganic non-metallic Si (about 5%) and some metals such as Al (about 15%) and Fe (about 1%). C, O, and Si in AS is likely to mainly come from suspended particles in the raw water, while Al and Fe likely originates from flocculants and coagulants added during the water treatment process (Liu, 2018). By compared with other elements in AS, the higher Al content is likely to be what ensures that AS has stronger adsorption performance (Wang, 2019). The fact that no nitrogen was detected in the EDS results indicates that the AS surface may not contain amino functional groups. But it may also be related to factors such as the location selected in the SEM analysis (Mei, 2020).



(a)







(c)

46



Fig. 2-5 SEM images and EDS elemental composition of AS before adsorption Cu(II) and Zn(II) (a) fine powder SEM image; (b) particle SEM image; (c) fine powder EDS results and (d) particle EDS results

2.3.4 Thermo-gravimetric Analysis

Through thermo-gravimetric analysis (TGA) testing (Fig. 2-6), it can be seen that the relationship between the AS mass decay and heating temperature, thus roughly understand the ratio of bound water, organic matter and ash in AS (Kwon and Castaldi, 2008). It can be seen from Fig. 2-5, most of the mass loss of AS occurs between 100°C and 600°C, with a total weight loss of approximately 50%. The pyrolysis of AS can be divided into three stages:

1) The mass loss below 200°C is attributed to the evaporation of water in AS, which is about 17% (Qiu *et al.*, 2015);

2) The mass loss between 200°C and 600°C is generally due to the decomposition of organic matter and the dehydroxylation of polyaluminium hydroxide (i.e., $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$) (Tettamanti *et al.*, 2001; Choi *et al.*, 2019), 33% weight loss;

3) After 600°C, the quality of AS is basically stable, and the ash content accounts for 50%.

Since the mass of the final pyrolysis residue accounts for 50% of the total AS mass, it means that the mass loss of organic compounds from 200°C to 600°C should be small by compared with polyaluminium hydroxide. Therefore, the mass loss of AS in the second stage may be mostly

attributed to the dehydroxylation of Al(OH)₃ (Choi *et al.*, 2019). It means that AS may contain a large number of hydroxyl functional groups, which is beneficial to its adsorption of heavy metals. Furthermore, from the DTG curve which is the derivative of the TGA curve with temperature represents the rate of mass change, it can be seen that the peak around 100 °C is attributed to the rapid dehydration of AS. The water loss of hydroxide reaches its maximum at about 350°C, and then the pyrolysis rate tends to be flat, indicating that the organic part of AS decomposes mainly through volatilization after 350°C (Fungaro and Silva, 2014; Choi *et al.*, 2019). After 620°C, the mass decay of AS is not obvious, which may be attributed to the ash remaining after burning (Choi *et al.*, 2019). It is worth noting that an obvious mass decay peak of AS appears at about 830 °C (the mass loss is about 0.059 mg) which may be attributed to the decomposition of different carbonates formed during the carbonization of AS (Mohamed *et al.*, 2022).



Fig. 2-6 TGA plot of the fine powder AS

2.3.5 Fourier Transform Infrared Spectroscopy

Figure 2-7 shows the fourier transform infrared spectroscopy (FTIR) spectra of AS before adsorption of Cu(II) and Zn(II). The strong band of raw AS at 3361 cm⁻¹ represents the stretching vibration of hydroxyl group (-OH) (Siswoyo *et al.*, 2014; Siswoyo *et al.*, 2019; Jiang, 2019). The hydroxyl group here may come from the O-H bonded to Al, or it also may belong to the H-O-H bond in the coordinated water molecule (Elkhatib *et al.*, 2015; Li *et al.*, 2018). The absorption peak at 1638 cm⁻¹ may be attributed to the stretching vibration of C=O which is usually associated with the presence of carboxyl functional group (Ren, 2014; Siswoyo *et al.*, 2019; Liu *et al.*, 2021). The absorption peak at 1420 cm⁻¹ indicates the existence of oxygen-containing functional groups on the AS surface, representing the symmetrical stretching vibration of C-O or COO⁻ (Wang *et al.*, 2016; Jiang, 2019; Liu *et al.*, 2021), which indicates that there is organic matter in AS (Jiang, 2019). The strong

absorption peak at 1007 cm⁻¹ may be caused by the bending vibration of the hydroxyl groups on the metal oxide (Al-OH) (Elkhatib *et al.*, 2015). A small absorption peak at 912 cm⁻¹ may be related to the bending vibration of C-H (Siswoyo *et al.*, 2019). The absorption peak at 517cm⁻¹ comes from the stretching vibration of Al-O (Yang *et al.*, 2015; Kan *et al.*, 2017). And from the EDS mapping images (Fig. 3-11), it can be seen that the positions of Al and O on the AS surface are highly overlapped, further supporting the theory that the AS surface contains a large number of Al-O groups (Jeon *et al.*, 2018). The peak at 467cm⁻¹ corresponds to the bending vibration of Al-O-Al or Al-O-Si (Jiang, 2019; Siswoyo *et al.*, 2019; Jiang *et al.*, 2019). The FTIR scanning results show that there are a large number of hydroxyl groups, aluminium oxide groups and a certain amount of carboxyl groups on the surface of the AS. Moreover, these groups exist in the form of amorphous alumina and hydroxide, which is beneficial to the adsorption of Cu(II) and Zn(II) on AS (Qiu *et al.*, 2015). Because Siswoyo *et al.* (2014) studied the key components of AS adsorption cadmium by comparing the adsorption capacity of AS and iron-free AS and the results showed that the presence of oxygen-containing functional groups, such as Al₂O₃ and hydroxyl groups, are benefit to the adsorption of Cu(II) and Zn(II) by AS.



Fig. 2-7 FTIR plot of the AS

2.3.6 Metal Release

The toxic release of AS is the key to determining whether it can be used as an adsorbent to treat water pollution problems. From the EDS detection results in 2.3.3, it was found that the main components of AS are C, H, O, Al, Si, Fe, Mg, Ca and some organic compounds. Since heavy metals are generally toxic even at low concentrations, the main risk of AS comes from the possible release of heavy metals. Since most of the metals are below the detection limit, Fig. 2-8 lists the release curve of

relatively high concentration metals detected in AS within 480 minutes. From the results, the maximum release of Al, Fe, Mg, and Ca in the batch experiment within 480 minutes was 0.23 mg/L, 0.31 mg/L, 0.07 mg/L, and 11 mg/L respectively. This indicates that the metals present in AS are highly stable. Both the European Water Framework Directive (WFD) and the US Environmental Protection Agency (USEPA) have set out guidelines for safe emission concentrations of these metals in the environment. Mg and Ca mainly cause changes in water hardness and are generally not regulated as specific pollutants. Considering the USEPA recommended the maximum concentration of 500 mg/L for drinking water hardness, the leaching of AS is much lower than this standard (USEPA, 2024). To protect aquatic organisms from toxic effects, the WFD and USPEA recommend a limit of 1 mg/L of iron in surface water (USEPA, 2024; Johnson et al., 2007). The maximum leaching of iron in AS within 48 hours fully meets this requirement. However, Babatunde et al. (2011) designed a laboratory-scale constructed wetland using AS as the base and conducted Al leaching experiments for 42 weeks. The results showed that the leaching concentration of aluminum ranged from 0.058 to 1.106 mg/L, and the highest concentration leaching occurred mainly in the first three weeks (Babatunde et al., 2011). Babatunde et al. (2011) also found that except for the first three weeks, the effluent aluminum concentration ranged from 0.02 to 0.06 mg/L which was far below the standard. Therefore, they believed that AS as a water treatment material does pose a risk of aluminium release, but the aluminium release concentration in the effluent does not pose any imminent environmental or health risk (Babatunde et al., 2011). Furthermore, Mortula and Gagnon (2007) also observed similar conclusions. The Al leaching concentration increased first and then decreased, and the highest Al leaching concentration (<0.5 mg/L) was observed at pH = 3 (Mortula and Gagnon, 2007). It was also concluded that the leaching concentration of Al was within the reasonable range for surface water treatment and was not high enough to pose a threat to aquatic life (Mortula and Gagnon, 2007).



Fig. 2-8 Metals release from AS (Al, Mg, Fe are referring to right Y axis and Ca is refers to left Y axis)

2.4 Summary

This chapter mainly studies the physicochemical characteristics of AS through some characterization methods, such as specific surface area, composition, surface characteristics and functional group characteristics. The main conclusions are as follows:

1) AS is a porous material mainly composed of mesopores, with an average specific surface area of 75 m^2/g for particle and 58 m^2/g for fine powder;

2) The SEM-EDS analysis results showed that the AS surface was loaded with abundant particles accompanied by some pore structures. It is mainly composed of O, Si, Al, Fe and other elements, among which the contents of Al, Si and Fe are 15%, 5% and 1% respectively;

3) The results of TGA experiments indicated that organic matter and polyaluminium hydroxide in AS accounted for approximately 33% of the total weight, and ash accounted for 50%;

4) FTIR results showed that the AS contained abundant surface active groups such as hydroxyl, carboxyl and aluminium oxide groups;

5) Metal leaching experiments showed that AS may have the risk of aluminium release, but the leaching concentration was within the reasonable range for surface water treatment and the content was not enough to pose a threat to aquatic organisms;

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CHAPTER 3

BATCH EXPERIMENTS FOR DETERMINATION OF THE ADSORPTION CAPACITY OF ZINC AND CUPPER ONTO ALUM SLUDGE

3.1 Introduction

Low-cost and high-efficiency adsorbents are a research hotspot for water filtration materials, especially for the reuse of industrial and agriculture waste material (Li *et al.*, 2023; Sodkouieh *et al.*, 2023; Liu *et al.*, 2024; Manjunatha *et al.*, 2024; Pal *et al.*, 2024). In order to investigate the adsorption performance of alum sludge on copper and zinc remove in runoff, this chapter studied the influence of complex environmental conditions on the adsorption of copper and zinc by AS. In order to develop a baseline for the adsorption performance of alum sludge for the removal of copper and zinc, batch experiments were carried out. In these experiments different important parameters was varied such as different initial metal concentration, solution pH, contact time and particle size. The purpose of the experiments was also to determine the adsorption isotherms and reaction kinetics for adsorption of zinc and copper onto alum sludge and hence and provide a basis for the possible adsorption mechanism of AS on Cu(II) and Zn(II).

3.2 Methodology

3.2.1 Experiments Preparation

Batch adsorption condition setup. All batch experiments were performed in 100 mL Erlenmeyer flasks. Adding 0.1g AS into a number of 100mL Erlenmeyer flask containing 20 mL Cu (performed in 100 mL Erlenmeyer flasks. Using NaOH and HNO₃ to adjust the solution pH around 6.5 which is close to the stormwater runoff pH (NRC. 2008; Vlastos *et al.*, 2019). Once the AS (0.1g) is added to the single heavy metal solution, the mixture is immediately placed on a rotary shaker (LH Fermentation Incubator Shaker), at 298K 130rpm/min to ensure adequate contact between the adsorbent and the solution.

Chemical Reagents. Single metal pollutant solution was prepared by dissolving copper and zinc salt compounds respectively: Copper sulfate pentahydrate (CuSO₄·5H₂O) 99% produced by Fisher Scientific, Zinc nitrate hexahydrate (ZnNO₃·6H₂O) 98% produced by Fisher Scientific and the pH was adjusted to a designated level using 0.1 M NaOH (Fisher Scientific, NJ) and 0.1 M HNO₃ (Fisher Scientific, NJ) if needed. All solutions in the experiment were prepared by deionized water (Ω >18.2 M Ω -cm). All the chemical reagents used were analytical grade.

Alum Sludge adsorbent preparation. The air-dried AS were grinded and passed through 0.15mm, 1mm and 2mm sieve which make two different size AS (below 0.15mm and 1~ 2mm), and then put them into sealed bags and stored at room temperature for the further batch experiment.

Cu(II) and Zn(II) stock solution. An 0.015M stock solution of Cu(II) and Zn(II) was prepared by using an electronic balance to weigh 3.9348 ± 0.001 g CuSO₄·5H₂O and 4.5499 ± 0.001 g ZnNO₃·6H₂O and dissolve them in deionized water in a beaker. In order to allow the metal ions to dissolve quickly and preserve for a long time, 1mL sulfuric acid or nitric acid were added to CuSO₄·5H₂O and ZnNO₃·6H₂O, respectively. Then, transfer the solution into a 1000mL volumetric flask, dilute to the mark with deionized and store in a refrigerator.

Batch experiments. Batch experiments were conducted to study the adsorption performance and mechanisms of AS to single metal pollutant. In these batch adsorption experiments the effects of parameters such as contact time, initial metals concentration, initial metal solution pH and different particle size was investigated (Table 3-1). It is worth mentioning that when the initial solution concentration of Cu(II) and Zn(II) was fixed at 0.2 mg/L, which is consistent with the actual Cu(II) and Zn(II) concentration range in stormwater runoff, their concentrations in all samples after adsorption by AS are too low for ICP-OES detection. Therefore, when conducting adsorption competition experiments, we increased the heavy metal concentrations by 10 times which are 2 mg/L.

Description	Unit	Different pH	Different concentration	Different contact time
Adsorbent size (mm)	mm	< 0.15	< 0.15	< 0.15
Temperature (°C)	°C	298K	298K	298K
Dosage (g)	g	0.1	0.1	0.1
Initial solution concentration (mg/L)	mg/L	2	1,2,5,10,30,50,100,150	2/5
pH	-	2,3,4,5,6,7,8	6.5	6.5
Adsorption time (min)	min	120	120	1,2,3,4,5,10,15,30,60,90,120
Repeat experiment (time)	times	3	3	3

Table 3-1 Batch experiment setting

To evaluate AS adsorption kinetics, the effect of contact time was carried out by using two different initial concentrations. Using Cu (II) and Zn (II) stock solution to prepare 2mg/L and 5mg/L single metal solution. The pH of the solution was adjusted to 6.5 using 0.1 M NaOH or HNO₃ and adding 100 mg AS into solution with particle size < 0.15mm. The mixture was placed into the incubator (as described above) and shaken at 298K and 30rpm/min. As show in table 3-1 samples were collected at specific time interval from 1 to 120 minutes. Although shaken does speed up the adsorption rate, its purpose is to exclude the influence of external mass transfer resistance, concentration gradient and

internal diffusion (Karge and Weitkamp, 2008). Shaking may speed up the adsorption rate, but it will not completely distort the adsorption kinetics data. On the contrary, it can eliminate the influence of certain external factors and make the experimental data more stable. The adsorption kinetics experiment after shaken still has important scientific significance because it reduces the interference of external factors and makes the comparability between each samples (Karge and Weitkamp, 2008). The adsorption mode and ideal adsorption rate of the adsorbent can be analyzed from the kinetics. This is instructive for the understanding and application of adsorbents.

In order to test the maximum adsorption capacity of AS, the effect of different heavy metal initial concentration from1 to 200 mg/L was prepared by using stock solution and Adjust the solution pH to 6.5. Adding 100 mg AS with particle size < 0.15mm into 20mL Cu(II) or Zn(II) solution. After shaking for 24 hours, the heavy metal concentrations at equilibrium were measured to calculate the adsorption capacity of AS for Cu(II) or Zn(II). The maximum adsorption amount was determined by increasing the initial metal concentration. When the initial metal solution concentration continued to increase, the adsorption amount of AS did not change, which considered that it reached the maximum adsorption amount.

Metal solution pH is an important factor to describe adsorption mechanism. 2mg/L Cu(II) or Zn(II) solution were prepared by using stock solution and take 20mL into an Erlenmeyer flask. Using NaOH and HNO₃ to adjust the solution pH to: 2, 3, 4, 5, 6, 7 and 8, respectively. 100 mg AS with particle size <0.15 mm was then added to each flask. The mixture was placed into the shaker and shaken for 24 hours, and then the removal capacity of AS for Cu(II) or Zn(II) at different pH values was calculated.

In order to investigate the influence of adsorption capacity by different particle size of AS, experiments were carried out with the three different size fractions sieve (prepared as described about under section 2.2) prepared two different size: < 0.15mm and $1 \sim 2$ mm. The stock solution was diluted to 2 mg/L Cu(II) or Zn(II) and place 20 mL into a 50 mL conical flask, and the solution pH was adjusted to 6.5. 0.1 g of AS with particle size of < 0.15 mm and $1 \sim 2$ mm was weighed off per flask using an electronic balance with accuracy 0.1mg respectively. The AS was mixed with the solution and shaken, and then take samples for analysis at fixed time intervals. All batch experiments were conducted in 3 replicates.

Analytical method. All batch experiments samples were collected passed through a 0.45µm syringe filter and stored by adding 0.1ml 75% HNO₃ solution for metal concentration analysis. Metal concentration was measured by using Inductive Coupled Plasma Optical Emission Spectrometer (ICP-OES PerkinElmer, Optima 7300V) with the metal detection range from 0.01mg/L to 10,000 mg/L.

Solution pH was detected with a SciQuip Economic Benchtop pH/mV/Temperature meter, which was calibrated with calibration solutions of pH = 4, 7, and 10.

The prepared 10mL sample was placed in the injector, the liquid was converted into aerosol by the nebulizer and then the aerosol was sent into the plasma by argon gas. In the high temperature plasma, Cu (II) and Zn (II) elements are excited and ionized. By analyzing the light intensity of Cu (II) and Zn (II) at wavelengths of 324.754nm and 213.856nm respectively and comparing it with the standard curve, the instrument will automatically calculate the concentration of Cu (II) and Zn (II).

3.2.2 Adsorption Amount Calculation

The adsorption capacity (q, mg/g) is defined as the mass ratio, which is the ratio of the mass (mg) of the adsorbed heavy metal to the mass (g) of the adsorbent, which can be determined as shown in Eq 3-1.

$$q = \frac{(C_t - C_0)V}{m} \tag{3-1}$$

where $C_t (mg/L)$ is the concentration of heavy metals in the solution at time t, and $C_0 (mg/L)$ is the initial concentration of heavy metals in the solution. V (L) is the volume of solution; and m (g) is the mass of the adsorbent.

In some cases, removal percentage is used to describe AS adsorption capacity, which can be defended as Eq. 3-2.

%Removal =
$$\frac{C_0 - C_t}{C_0} * 100$$
 (3-2)

3.2.3 Adsorption Kinetics Models

Generally, adsorption kinetics include four steps: 1) molecular diffusion and convection diffusion of the adsorbate from the liquid phase to the surface of the adsorbent; 2) Diffusion of adsorbate from the solution through the liquid membrane to the surface of the adsorbent which the rate limitation comes from the transfer rate of adsorbed molecules through the liquid membrane; 3) Diffusion of adsorbate from the surface to the interior of the adsorbent. It mainly diffuses into the hole through the micropores on the adsorbent; 4) Physical/Chemical binding reactions of adsorbate at active sites in the adsorbent (Hovsepyan and Bonzongo, 2009; Hu and Han, 2019).

Adsorption kinetics studies the rate at which the adsorption reaction approaches equilibrium, and it defines the adsorption rate constant by using a specific contact time (Deng, 2018). Based on the sufficient stirring, the main rate limiting steps depending on the outside liquid film diffusion and the

inside pore diffusion of the particles (Hu and Han, 2019). In order to study the adsorption rate and the main rate-limiting stage of heavy metals by AS, the Pseudo-first-order, Pseudo-second-order, Elovich equation and Intra-particle diffusion models are commonly used to calculate the kinetic correlation coefficients (Elkhatib *et al.*, 2015; Kang *et al.*, 2019; Lian *et al.*, 2020).

Lagergren (1898) proposed to use a Pseudo-First-Order kinetic model to analyze the adsorption process. The Pseudo-First-Order kinetic model states that the number of unoccupied adsorption sites is proportional to the rate at which adsorbed molecules occupy the adsorption sites and its equation can be expressed as follows (Poormand *et al.*, 2017; Zeng *et al.*, 2020; Esfandiar *et al.*, 2022):

$$\frac{dq_t}{dt} = k_1 \quad (q_e - q_t) \tag{3-3}$$

The equation can be linearized:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{3-4}$$

Where, q_e (mg/g dry alum sludge) is the Cu(II) or Zn(II) adsorption at the equilibrium time. k_1 (1/min), is the adsorption rate constant of Pseudo-First-Order. q_t (mg/g dry AS) is the amount of Cu(II) or Zn(II) adsorbed at time t (min).

Ho and McKay (1999) proposed another adsorption kinetics, the Pseudo-Second-Order adsorption kinetics model, which includes all possible adsorption processes, such as external surface diffusion, surface adsorption, and powder internal diffusion. The Pseudo-Second-Order kinetic model indicates that the process of adsorbed molecules being adsorbed by the adsorbent is chemical adsorption and its equation are as follow (Zeng *et al.*, 2020; Esfandiar *et al.*, 2022):

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{3-5}$$

The equation can be linearized:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_{e2}}$$
(3-6)

Where, k_2 (g/(mg·min)) is the adsorption rate constant of Pseudo-Second-Order.

The Elovich model was proposed by Zeldowitsch (1934), which explained the adsorption process involves chemical reactions. This adsorption model is applicable to adsorbents with heterogeneous adsorption surfaces and describes the trend that the adsorption rate may decreases with the increase surface covered (Inyang *et al.*, 2016; Mukhopadhyay *et al.*, 2017). By fitting the Elovich model (Eq. 3-7), we can understand the kinetic behavior of the adsorption process, including the change pattern of the adsorption rate, etc (Lian *et al.*, 2020; Richard *et al.*, 2020).

$$q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t \tag{3-7}$$

Where, α (mg/(g·min)) is the adsorption rate constant of Elovich model and β (g/mg) is related to the adsorption energy or the extent of surface coverage (Lian et al., 2020).

Intraparticle diffusion models. Generally, there are three ways to control the adsorption rate: membrane diffusion control, intra-particle diffusion control, or a combination of both (Kang *et al.*, 2019; Hu and Han, 2019; Lian *et al.*, 2020). Pseudo-First-Order and Pseudo-Second-Order kinetic models cannot well explain the role of intra-particle diffusion in adsorption kinetics (Valderrama *et al.*, 2007; Hu and Han., 2019). Therefore, in order to confirm the rate limiting step in the adsorption process, introducing the Weber-Morris equation (Eq. 3-8) to fit the batch experiments results (Kang *et al.*, 2019):

$$q_t = K_i t^{0.5} + C \tag{3-8}$$

Where, K_i (mg/(g·min^{0.5})) is the intra-particle diffusion rate associated with the diffusion of the metals through the adsorbent and C represents the boundary layer diffusion effects such as external film resistance (Weber and Morris, 1963). C=0 indicates that the adsorption process is mainly intra-particle diffusion. The larger the C, the greater the influence of membrane diffusion and the thickness of the boundary layer is greater (Lian *et al.*, 2020).

3.2.4 Adsorption Isotherm Models

The adsorption isothermal equation describes the mathematical model of the difference between the adsorption amount and the influencing parameters when the system reaches equilibrium at a certain temperature, and characterizes the adsorption and desorption performance (Gregg, 1982). It reflects the distribution pattern of the adsorbate fixed on the adsorbent (Goldberg *et al.*, 2007). The maximum adsorption capacity of the material determined by adsorbing different initial concentrations of the adsorbate to reflect the strength and characteristics of the interaction between the adsorbate and the adsorbent (Ajouyed *et al.*, 2010). Studying the adsorption isotherm can help understand the rules of the adsorption process and evaluate the performance of the adsorbent, such as adsorption is favorable or not (Hu and Han., 2019). In order to investigate whether AS is an active and favorable adsorption of Cu (II) and Zn (II) and also to estimate its maximum adsorption capacity. The Langmuir, Freundlich and Temkin models were used to estimate the isotherm correlation coefficients.

Isotherm models. Based on the characterization results in chapter 2, AS has a flat surface with a small amount of particles and slits, and its specific surface area is much smaller than that of commercial adsorbents such as activated carbon. Therefore, it is speculated that AS may be mainly chemically adsorbed. Since AS is not a regular structure adsorbent material with exact chemical

adsorption expression, it also has some surface complexation and surface precipitation adsorption mechanism. So its adsorption of pollutants may exist in both mono-layer adsorption and multi-layer adsorption. Therefore, this experiment considered using the Langmuir, Freundlich and Temkin models to describe the adsorption mode of AS. Furthermore, quantitative adsorption performance parameters such as Langmuir's maximum adsorption capacity q_m, Freundlich's adsorption intensity 1/n, and Temkin's adsorption heat change factor b are used. The core value of adsorption isotherm model fitting lies in connecting experimental data with theoretical models and transforming macroscopic adsorption phenomena into expressions of microscopic mechanisms. Based on giving information we can also potentially transfer from one experimental setting to another or permit comparisons data with other adsorption media

The Langmuir adsorption isotherm model is the simplest isotherm model and assumes that there are several adsorption sites on the surface of the adsorbent but that adsorption happens as a monolayer process and that the molecules have equal attraction to all adsorption sites which does not affect each other (Langmuir, 1932; Vadi and Rahimi, 2014). When the adsorbent enters the reaction solution, the adsorption sites will quickly combine with ions in the solution until the sites are fully utilized and it is regarded as adsorption saturation (Langmuir, 1932; Tarlani *et al.*, 2016; Zeng *et al.*, 2020). Langmuir isotherm model is an ideal chemical adsorption model (Langmuir, 1932). It is considered that the adsorption material has a homogeneous adsorption surface, has the same adsorption site and same adsorption energy for the adsorbate, and the adsorption is monolayer adsorption (Langmuir, 1932). The solid surface is uniform and there is no interaction between the adsorbed molecules, and the adsorption equilibrium is dynamic equilibrium (Gregg, 1982).

Using the following equation (Eq. 3-9) to calculate the Langmuir isotherm model (Langmuir, 1932):

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L * q_m}$$
 (3-9)

And the equation could be transform into a linear form (Eq. 3-10):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L * q_m C_e}$$
(3-10)

where $C_e(mg/L)$ is the concentration of adsorbate in solution at equilibrium; $q_e(mg/g)$ is the adsorption capacity of the adsorbent at equilibrium; $q_m(mg/g)$ is the maximum adsorption capacity and $K_L(L/mg)$ is the constants of Langmuir related to the adsorption capacity and energy. From the equation, a plot of C_e/q_e versus C_e will be used to determine the values of q_m and K_L as the tangent and intercept of the curve.

The essential characteristics of the Langmuir isotherm can be expressed due to a dimensionless constant of the separation factor or equilibrium parameter, R_L, which is defined as (Siswoyo *et al.*, 2014):

$$R_L = \frac{1}{1 + K_L C_0} \tag{3-11}$$

where C_0 (mg/L) is the initial concentration of heavy metals in the solution. The R_L value indicates the shape of the isotherm which is related to the adsorption favorable (Siswoyo *et al.*, 2014):

- $R_L > 1$ unfavorable
- $R_L = 1$ linear
- $0 < R_L < 1$ favorable
- RL =0 irreversible

The Freundlich isotherm model mainly shows the relationship between the adsorption amount per unit mass of adsorbent and the solution concentration when the adsorption reaction reaches an equilibrium state, which explains the adsorption on a heterogeneous surface with uniform energy (Freundlich and Hatfield, 1926; Zeng *et al.*, 2020). It is believed that the adsorption material has a heterogeneous adsorption surface, the material has different adsorption sites and adsorption energy for the adsorbate, and it is a multi-layer adsorption (Gregg, 1982).

Freundlich isotherm equation is as follows (Eq. 3-12) (Freundlich and Hatfield, 1926):

$$q_e = K_f C_e^{\frac{1}{n}}$$
(3-12)

Where $C_e(mg/L)$ is the concentration of adsorbate in solution at equilibrium; $q_e(mg/g)$ is the adsorption capacity of the adsorbent at equilibrium; K_f $(mg^{1-n} \cdot L^n/g)$ and n are the Freundlich constants which are related to adsorption capacity and intensity, respectively. The Freundlich equation explains adsorption onto a heterogeneous surface with uniform energy. The linear form of the model is expressed as equation 3-13 (Siswoyo *et al.*, 2014., Hu and Han, 2019):

$$\text{Log}q_e = \log K_f + \frac{1}{n}\log C_e \tag{3-13}$$

Note that n value in the range of 1 to 10 can be regarded as an effective adsorbent. Moreover, the higher value of n than 1 indicates that adsorbate is uniformly adsorbed on the adsorbent surface. When the n value is higher than 3, it implies that the adsorbent has heterogeneous surface (Jeon *et al.*, 2018).

The Temkin isotherm was used to describe the interaction between adsorbent and adsorbate (Vadi and Rahimi, 2014). Temkin model assumes the adsorption energy will decrease due to the surface coverage which means that the adsorption energy is high in the initial step of adsorption process, and gradually decreases with the increase of surface coverage (Vadi and Rahimi, 2014; Deng, 2018; Lian *et al.*, 2020). The equation is as follows (Eq. 3-14)

$$q_e = B_T \ln(k_T C_e) \tag{3-14}$$

And the equation could be transform into a linear form (Eq. 3-15 and 3-16):

$$q_e = B_T \ln k_T + B_T \ln C_e \tag{3-15}$$

$$B_T = \frac{RT}{b} \tag{3-16}$$

Where, $C_e(mg/L)$ is the concentration of adsorbate in solution at equilibrium; $q_e(mg/g)$ is the adsorption capacity of the adsorbent at equilibrium; K_T (L/mg) is the Temkin isotherm equilibrium binding constant. B_T (kJ/mol) is related to adsorption heat.

The reasons for choosing these three adsorption isotherms for fitting are: These are mathematical descriptions of specific phenomena described under idealized settings. Secondly, these three models cover different mechanisms. For example, the Langmuir model describes a system with a single layer, uniform surface and no intermolecular forces. The significance is to quantitatively characterize the performance and adsorption strength of the adsorbent through the maximum adsorption capacity (q_m) and affinity constant (K_L). The Freundlich model is suitable for systems with heterogeneous surfaces, multilayer adsorption, or differences in energy distribution. The significance is that the parameters K_F (adsorption capacity) and 1/n (adsorption intensity) can be used to reflect the surface heterogeneity and the difficulty of adsorption. The Temkin model is applicable to systems where the heat of adsorption varies linearly with coverage. The significance is to introduce temperature parameters (T) and adsorption heat change factor (b) to reveal the thermodynamic characteristics of the adsorption process. In general, these fitting data support to the theory in the same way that the characterization does, we then put it all together and have our best estimate of what has actually happened.

3.2.5 Error Analysis

In order to analyze the error of experimental data and model data, compare the performance of different model data, the root mean square error (RMSE) (Eq. 17) was applied to determine the best fitting adsorption equation. The model with the RMSE closer to 0 is regarded as the better model (Duan *et al.*, 2011). In equation 3-17, E_j is the experimental value in the adsorption process, while M_j is the model value, and n is the total number of measurements.

RMSE =
$$\sqrt{\frac{\sum_{j=1}^{n} (M_j - E_j)^2}{n}}$$
 (3-17)

3.2.6 Regeneration and Cyclic Adsorption of AS

In order to study the reuse ability of AS, HCl was used as a desorbent agent to conduct desorption experiments on saturated AS (1-2 mm). The experiment was divided into three parts.

Effect of pH on the desorption of Cu(II) and Zn(II). 6 aliquots of 0.1g adsorption saturated AS (particle size 1-2mm) was weighed off using analytical scale and was added to 20 mL HCl solution with pH range 0.5, 1, 2, 3, 4, and 5. The samples were placed on a rotary shaker at 298K and shaken at 130rpm/min for 360min and then the liquid fraction was passed through a 0.45µm syringe filter and analyzed in ICP-OES using the method already described in section 3.2.1.

The effect of time on the desorption of Cu(II) and Zn(II) was determined by accurately weighing of 0.1g adsorption saturated AS (particle size 1-2mm) and adding it into 20mL HCl solution with pH = 2. The samples were placed on a rotary shaker at 298K and shaken at 130rpm/min. 39 such samples were prepared. Samples were taken at 1, 2, 3, 4, 5, 10, 15, 30, 60, 90, 120, 240, and 360 min, respectively, and passed through a 0.45 μ m syringe filter and analyzed in ICP-OES.

AS cycle adsorption performance. The AS which has desorbed above was dried in a 60°C oven, and weighing 0.1g dried AS added into 20mL 2mg/L Cu(II) and Zn(II) solution. The sample was placed on a rotary shaker at 298K and shaken at 130rpm/min for 2 hours. The sample was passed through a 0.45µm syringe filter and analyzed in ICP-OES. Repeat the above desorption and adsorption steps 5 times.

3.3 Results and Discussion

3.3.1 Observation

For the vibration adsorption experiment, no disintegration or re-disperse was observed in AS during the shaking process. This is because the free water in AS evaporates after air drying, and the particles are tightly bound by capillary force and van der Waals force to form a dense structure (Xu et al., 2020). Furthermore, the aluminum hydrochloride in AS may undergo polymerization during the air-drying process to form a more stable aluminum oxide structure (Al-O) (Pajak. 2023). According to the FTIR test results in Chapter 2, the obvious absorption peaks of AS at 1007cm⁻¹, 517cm⁻¹ and 467cm⁻¹ are related to the vibration of aluminum oxide functional groups. From the EDS mapping image (Figure 3-11), it can be seen that the positions of Al and O on the AS surface are highly overlapped, which further supports that the AS surface contains a certain number of Al-O groups. Due to the presence of aluminum oxide functional groups, the dense structure and stable chemical bonds prevent the dried AS from re-disperse again when shaken.

3.3.2 Kinetics studies

Effect of initial metal concentration. The concentration of Cu(II) in the mixed solution decreases with the increase of contact time and finally reaches an equilibrium state. For example, Figure 3-1 shows the adsorption curves of copper at initial concentrations of 2 mg/L and 5 mg/L. The adsorption

rate of Cu(II) by AS was very fast in the first 20 min. When the initial concentration of Cu(II) was 2 mg/L, the residual concentration dramatically went down to 0.22 - 0.23 mg/L in mixed solution, and the concentration rapidly went down to 0.19 - 0.20 mg/L when the initial concentration of Cu(II) was 5 mg/L. After 20 minutes, the adsorption rate of AS slowed down and reached equilibrium after about 60 minutes.



Fig. 3-1 Cu(II) concentration changes over time (pH =6.5; AS dose = 5g/L; T=25°C)

Of interest, it can be seen from Figures 3-2 that the initial concentration of Cu(II) seems to have a great influence on the adsorption process such as the higher the initial concentration, the greater the adsorption amount of AS. It was observed that the adsorption amount of AS for 5mg/L Cu(II) was about 0.98 mg/g which is better than 2mg/L Cu(II) initial concentration (about 0.32 mg/g). Moreover, their equilibrium Cu(II) concentration of 5mg/L solution after 60 minutes is 0.19 mg/L which is lower by compare with 0.21 mg/L for initial 2mg/L copper solution (Fig. 3-1). This may be because the higher the initial concentration, the higher the ratio of the initial molar concentration of Cu(II) to the AS available surface area, which increases the collision opportunity between Cu(II) and the AS surface and benefit for adsorption (Shalaby *et al.*, 2017). In addition, the increase in the concentration gradient of Cu(II) helps the adsorbent to overcome the mass transfer resistance between the aqueous phase and the solid phase, which also enhances the adsorption amount (Shalaby *et al.*, 2017). Furthermore, AS adsorbed faster in the first 20 minutes was because the AS uncovered surface area was large in the initial stage, which means that AS had a large number of active sites that could be utilized at the first 20 minutes, and the concentration of metals in the solution was higher than 60

minutes, which provided a higher driving force for Cu(II) to be rapidly enriched on the AS surface (Poormand *et al.*, 2017). As time goes by, the exposed surface of AS is covered and the active sites and metal ion concentrations are reduced, which cause the adsorption reaction tends to be gentle (Poormand *et al.*, 2017). In the late stage of adsorption, the metal ions in the solution diffuse to the inner surface of AS, and the adsorption mainly occurs on the inner surface area (Wang *et al.*, 2019). In other words, this trend reflects the adsorption process. First, the metal ions are rapidly adsorbed onto the AS surface through the membrane diffusion, and then a slow intraparticle diffusion process make the metal ions enter and fixed inside the AS through the pores. A similar phenomenon was observed for Zn(II) adsorption.







Fig. 3-2 Adsorption kinetics fitting of Cu(II) (a) Pseudo-first-order adsorption kinetics; (b) Pseudo-second-order adsorption kinetics; (c) Elovich equation fitting (pH=6.5; Shaking at 25°C for 120 minutes; AS particle size <0.15mm; AS dosage 5g/L; 2mg Cu(II) refers to the left Y axis, 5mg Cu(II) refers to the right Y axis).</p>

Cu(II)	Pseudo first-order			Pseudo second-order			Elovich equation		
Concentration	q _{e, 1} (mg/g)	K ₁ (1/min)	RMSE	q _{e, 2} (mg/g)	$\begin{array}{c} K_2 \\ (g/(mg\cdot min)) \end{array}$	RMSE	β (g/mg)	$\substack{\alpha \\ (mg/(g \cdot min))}$	RMSE
2 mg	0.319	2.29	0.0113	0.317	27.3	0.00481	49.435	9249	0.0229
5 mg	0.980	3.91	0.0069	0.985	33.7	0.00319	50.216	3.69×10^18	0.0224

 Table 3-2 Kinetic parameters for the adsorption of Cu(II)

Figure 3-2 shows the fitting results of the experimental kinetic data of Cu(II) using three different kinetic models and the parameters of different kinetic models are shown in Table 3-2. It can be seen from Fig. 3-2 that the modeling data of Pseudo-second-order kinetics are a good fit with the experiments data, which the RMSE for Pseudo-frist-order, Pseudo-second-order and Elovich are 0.0113, 0.0048 and 0.0229, respectively. This kinetic behavior is consistent with several previous studies on the adsorption of heavy metals by AS, which all observed that the adsorption of metals, such as Cd(II), Pb(II), Cr(III) and Cr(VI) by AS conforms to Pseudo-second-order kinetics (Soleimanifar et al., 2019; Zhou and Haynes, 2011; Du et al., 2020). In the literature review by Pajak (2023), the adsorption kinetics models of AS for different metals were summarized. The results showed that the adsorption experimental data of most metals or semi-metals (As(V), As(III), Se(VI), Mo(VI), V(V), Co(II), Cu(II), Cr(VI), Cr(III) and Zn(II)) were well fitted with pseudo-second-order kinetics, which means that chemical reaction is the rate-controlling step of AS adsorption of heavy metals. Comparison of the RMSE results also shows that the AS adsorption process of Cu(II) is more consistent with the pseudo-second-order adsorption kinetic model. For 2mg/L and 5 mg/L Cu(II), the RMSE are 0.00481 and 0.00319 respectively which means that the adsorption of Cu(II) is a process dominated by chemical adsorption, which may involve specific adsorption and surface precipitation. K is the rate constant of adsorption kinetics. When the initial concentration of Cu(II) increases from 2 mg/L to 5 mg/L, K increases from 27.3 g/(mg*min) to 33.7 g/(mg*min), indicating that as the initial concentration of Cu(II) increases, the adsorption rate tends to accelerate and the time for adsorption to reach equilibrium is shorter. This result is similar to the findings of Soleimanifar et al. (2019) that as the initial adsorbent dosage increased from 5 g/L to 50 g/L, the rate constants K of heavy metals Cu(II), Zn(II) and Pb(II) all increased significantly. This may be because that the above mentioned the increase in the concentration gradient of Cu(II) is beneficial for the adsorbent to overcome the mass transfer resistance between the aqueous phase and the solid phase, which enhances the adsorption capacity of AS.

The pseudo-second-order kinetics describes that the adsorption rate of Cu(II) by AS is controlled by chemical adsorption, but its model cannot recognize the role of intra-particle diffusion in the adsorption kinetics (Kang *et al.*, 2019). In order to further understand whether membrane diffusion and intra-particle diffusion are also rate-limiting steps, the intra-particle diffusion model was used to fit the experimental data and the results are shown in Figure 3-3. Table 3-2 lists the parameters of the

intra-particle diffusion adsorption model of Cu(II). It shows that the adsorption fitting results RMSE of 2mg/L and 5mg/L Cu(II) are both quite small, which is 0.005. This indicates that at least one stage of the adsorption process of AS on Cu(II) conforms to the intra-particle diffusion process. Refer to the Table.3-2 where it is clear to see that membrane diffusion C is not equal to 0, which means that the intra-particle diffusion is not the only limiting step of the adsorption rate. In most modeling, such as Pseudo-first-order and Pseudo-second-order kinetics, the diffusion process from the liquid boundary layer to the particle surface is usually neglected (Inglezakis *et al.*, 2020). However, the membrane diffusion plays a role in adsorption, although it is not obvious but should be considered. As shown in Figure 3-3, the adsorption rapid rise in the first 10 minutes is likely due to membrane diffusion; the slow rise in the second stage from 10 to 40 minutes is due to the participation of intra-particle diffusion; the equilibrium stage after 40 minutes is due to the low adsorbate concentration in the solution, which slows down the intra-particle diffusion rate (Ren, 2014).

As shown in Table 3.3, that the membrane diffusion C value increases with the increase of the initial Cu(II) concentration, which indicates that at higher adsorption concentrations, the influence of boundary layer diffusion (external mass transfer barrier) on the Cu(II) adsorption process may be greater (Lin and Zhan, 2012). However, for low initial Cu(II) concentration, the value of membrane diffusion C is 0.297 mg/g for 2mg/L initial Cu(II) concentration and 0.968 mg/g for 5mg/L initial Cu(II) concentration from this experiment, by compare with other research this adsorption capacity is quite low. For instance, Lian et al. (2020) used heated modified AS to adsorb Mo(V) and its the membrane diffusion C range was from 5 mg/g to 30 mg/g when the starting concentration of the metal were from 10mg/L to 150mg/L. In addition, the membrane diffusion C for Cr(VI) adsorption by AS modified with Fe(OH)₂O₃-chitosan was 18 mg/g for 50 mg/L Cr(VI) and 35 mg/g for 100 mg/L Cr(VI) (Jiang and Liu, 2019). The reason for the rapid adsorption rate of Cu(II) by AS within the first 10 min as shown in Fig. 3-3 is because the membrane diffusion C is proportional to the thickness of the boundary layer, although the membrane diffusion C is very small, which means that the boundary layer has little effect on the diffusion of the liquid phase around AS to the particle surface, resulting in a very fast membrane diffusion rate (Lin and Zhan, 2015; Jiang and Liu, 2019). But it can still be observed in the experiment, so membrane diffusion is also one of the rate-limiting steps of Cu(II) which cannot be ignored. In addition, the adsorption rate constant of AS was relatively low at 0.002 mg/(g·min^{0.5}) (Table 3-3) also confirms that it involves a slow adsorption process likely to involve intra-particle diffusion (Truong and Kim, 2021).

In summary, since the adsorption data for AS has a good fit with either pseudo-second-order and intra-particle diffusion models, the adsorption rate may be the result of the combined effects of chemical adsorption, membrane diffusion, and intra-pore diffusion.



Fig. 3-3 The Intra-particle diffusion plot for Cu(II) (2mg Cu(II) refers to the left Y axis, 5mg Cu(II) refers to the right Y axis)

		Intra-particle diffusion	
Cu(II) Concentration	$K_i * 10^{-2}$ (mg/(g·min ^{0.5}))	C (mg/g)	RMSE
2 mg	0.246	0.297	0.00477
5 mg	0.223	0.968	0.00486

Table 3-3 Intra-particle diffusion parameters for the adsorption of Cu(II)

Kinetic fitting of zinc adsorption. The change of the adsorption amount of Zn(II) is shown in Fig. 3-4, including two stages: rapid adsorption and stable adsorption, which is similar to the adsorption of Cu(II) by AS. Base on the initial concentrations of 2 mg/L and 5 mg/L, the equilibrium concentrations of Zn(II) were 0.037 mg/L and 0.023 mg/L respectively, and the adsorption was keep balanced after the contact time reached 60min.



Fig. 3-4 Zn(II) concentration changes over time (pH =6.5; AS dose = 5g/L; T=25°C)

The adsorption kinetics fitting results are shown in Fig. 3-5 and the fitting parameters are shown in Table. 3-4. According to the results, the RMSE value of the Pseudo-second-order kinetic model for Zn(II) at different concentrations is smaller than that of the pseudo-first-order kinetic model and the Elovich equation. The q_e obtained by the pseudo-second-order kinetic model is 0.343 mg/g and 0.84 mg/g, which are also close to the experimental values of 0.341 mg/g and 0.827 mg/g. This indicates that similar to Cu (II), chemical effects are also involved in the adsorption process of Zn(II). It is worth noting that the Elovich equation fitting curve is also consistent with the experimental data and the RMSE is also small. But the q_e obtained by the Elovich equation is 0.006 mg/g and 0.015 mg/g respectively, which are much smaller than the measured values. Therefore, it is considered that the Elovich equation cannot explain the adsorption process of Zn(II).





Fig. 3-5 Adsorption kinetics fitting of Zn(II) (a) Pseudo-first-order adsorption kinetics; (b) Pseudo-second-order adsorption kinetics; (c) Elovich equation fitting (pH=6.5; Shaking at 25°C for 120 minutes; AS particle size <0.15mm; AS dosage 5g/L; 2mg Zn(II) refers to the left Y axis, 5mg Zn(II) refers to the right Y axis).</p>

7n (II)	Pseudo first-order		Ps	Pseudo second-order			Elovich equation		
Concentration	q _{e, 1} (mg/g)	K ₁ (1/min)	RMSE	q _{e, 2} (mg/g)	K2 (g/(mg·min))	RMSE	β (g/mg)	α (mg/(g·min))	RMSE
2 mg	0.340	2.64	0.0075	0.343	24.19	0.00490	164.04	1×10^20	0.00641
5 mg	0.836	2.76	0.0316	0.840	9.49	0.00694	66.598	1×10^20	0.00825

Table 3-4 Kinetic parameters for the adsorption of Zn(II)

In order to determine whether the adsorption of Zn(II) by AS also involves an intra-particle diffusion step. Figure 3-6 shows the fitting results of intra-particle diffusion of Zn(II) and the fitting parameters are shown in Table 3-5. Refer to Table 3-5 where this is clear that the intra-particle diffusion has a good fitting result for Zn(II) and membrane diffusion $C\neq 0$ which indicates that the intra-particle diffusion is not the only rate-controlling step. Similar to Cu(II), although the membrane diffusion C value is very small, the effect of boundary layer diffusion on the adsorption rate cannot be ignored.

Therefore, the adsorption process of AS on Zn(II) is the same as that of Cu(II), which is the result of the combined effect of chemical adsorption, membrane diffusion and intra-pore diffusion.



Fig. 3-6 The Intra-particle diffusion plot for Zn(II) (2mg Zn(II) refers to the left Y axis, 5mg Zn(II) refers to the right Y axis)

		Intra-particle diffusion	
Zn (II) Concentration	K _i *10 ⁻² (mg/(g·min ^{0.5}))	C (mg/g)	RMSE
2 mg	0.056	0.329	0.00721
5 mg	0.212	0.788	0.01681

Table 3-5 Intra-particle diffusion parameters for the adsorption of Zn(II)

3.3.3 Isotherm studies

Isotherm fitting of copper adsorption. The adsorption isotherm reflects the relationship between the concentration of the adsorbate and the adsorption capacity of the adsorbent under a constant temperature condition (Lou *et al.*, 2015). Three different adsorption isotherms were fitted based on the equilibrium data at different initial concentrations and the fitting results are shown in Table 3-6.

It can be seen from Fig. 3-7 that as the initial concentration of Cu(II) increases, the adsorption amount of AS increases, reaching the maximum adsorption amount at around 20 mg/L. The adsorption isotherm of Cu(II) is characterized by a steep initial slope which represent a rapid increase in adsorption capacity stage. And then gradually becomes stable, finally reaches a saturated adsorption capacity. The shape of this isotherm shows similarities to the Langmuir model. By compared with data in Table 3-5, the RMSE of Freundlich, Langmuir and Temkin are 1.51, 0.66 and 0.99, respectively. This fit indicates that the Langmuir isotherm model gives a description of a lot of the adsorption of Cu(II) to AS. This therefore supports that monolayer adsorption is potentially a good assumption to apply to the AS adoption system. This theory is furthermore supported by the

characterization of the AS which showed that the internal pore volume may not be very significant and the FTIR analysis demonstrating chemical adsorption sites to potentially form part of the adsorption mechanism. This shows that the adsorption of AS on Cu(II) is consistent with the uniform adsorption of the monolayer (Vadi and Rahimi, 2014). However, from the correlation of the curves, the adsorption of Cu(II) on AS also conforms to the Freundlich model, which means that the adsorption of Cu(II) includes not only monolayer adsorption dominated by chemical bonds, but also multilayer adsorption dominated by Van der Waals forces. The theoretical maximum monolayer adsorption capacity of AS for Cu(II) is 22.9 mg/g at 298 K. The R_L value in Eq. 11 is usually used to predict the favorableness of the adsorption process, when the R_L value is from 0 to 1 the adsorption is favorable (Siswoyo *et al.*, 2014). The R_L values obtained through calculation were all < 1 (Table 3-5). So the AS is favorable for the adsorption of Cu(II). At the same initial concentration, R_L values are Cu(II) >Zn(II), illustrating that Cu(II) is more stable when combined with AS and is more easily adsorbed (Wang and Bian, 2017; Du *et al.*, 2020).

Setting initial	Testing Cu(II) initial	Testing Zn(II) initial	RL		
concentration (mg/L)	concentration (mg/L)	(mg/L)	Cu(II)	Zn(II)	
5	4.513	4.752	0.092	0.146	
10	9.850	9.637	0.045	0.078	
30	28.157	27.474	0.016	0.029	
50	49.969	45.168	0.009	0.018	
100	90.356	93.400	0.004	0.009	
150	142.684	138.433	0.003	0.004	

Table 3-6 Calculated R_L values for Cu(II) and Zn(II)



(b)



Fig. 3-7 Adsorption isotherm fitting of Cu(II) (a) Freundlich isotherm; (b) Langmuir isotherm; (c) Temkin isotherm (pH=6.5; Shaking at 25°C for 120 minutes; AS particle size <0.15mm; AS dosage 5g/L).

_	Freundilich Isotherm			Langmuir Isotherm			Temkin Isotherm		
Heavy metals	$\underset{(mg^{1-n}\cdot L^n/g)}{K_F}$	n	RMSE	q _m (mg/g)	K _L (L/mg)	RMSE	BT (KJ/mol)	K _T (L/mg)	RMSE
Cu (II)	9.81	3.60	1.51	22.88	2.18	0.66	3.00	77.32	0.99
Zn (II)	4.57	6.44	0.90	8.74	1.23	0.77	0.97	300.64	0.80

Table 3-7 Isotherm parameters for the adsorption Cu(II) and Zn(II)

It is worth noting that Table 3-7 shows the RMSE of Freundlich and Temkin seems to be slightly larger than the fitting result of Langmuir. However, it can be observed from Fig. 3-7 that the fitting curves of Freundlich and Temkin are also highly correlated with the results of experimental data, indicating that in addition to the monolayer adsorption of AS, there is also non-uniform multilayer adsorption. But monolayer adsorption is dominant (Li *et al.*, 2018; Lv *et al.*, 2020). Moreover, n in Freundlich Isotherm is above 1 also proves that the adsorption process is favorable. The experimental data are consistent with the Temkin model suggesting that the adsorption energy of AS for Cu(II) decreases with increasing surface coverage, which also explains the finding in section 3.3.1 that the adsorption rate gradually slows down with increasing surface coverage (Lian *et al.*, 2020). According to the Temkin fitting results, the adsorption energy of AS on Cu(II) is 3 KJ/mol suggesting that the adsorption process is endothermic and there is a strong interaction between AS and Cu(II) (Aghagoli *et al.*, 2017).

Isotherm fitting of zinc adsorption. Figure 3-8 reflects that the adsorption amount of Zn(II) increases with the increase of initial concentration. Table 3-5 shows that the fitting correlation of Langmuir isotherm is slightly better than that of Freundlich and Temkin, but the RMSE results of these three models are very close which are 0.77, 0.90 and 0.80 respectively. This indicates that the adsorption of Zn(II) by AS is similar to that of Cu(II). Its adsorption process involves both monolayer adsorption and multilayer adsorption and the maximum adsorption capacity of monolayer adsorption is 8.74 mg/g.

Interestingly, compared with the Temkin fitting data (Table. 3-6), the AS adsorption energy (B_T) for Zn(II) is 0.97 KJ/mol which is much smaller than that for Cu(II). This result is also consistent with the R_L values Zn(II) < Cu(II) mentioned above, indicating that the binding energy between AS and Zn (II) is worse than that between AS and Cu(II).



(a)



Fig. 3-8 Adsorption isotherm fitting of Zn(II) (a) Freundlich isotherm; (b) Langmuir isotherm; (c) Temkin isotherm (pH=6.5; Shaking at 25°C for 120 minutes; AS particle size <0.15mm; AS dosage 5g/L).

Figure 3-9 shows the relationship between the adsorption capacity and removal rate of Cu (II) and Zn (II) under different initial concentrations of AS. As shown in the figure, with the adsorption amount of AS gradually increases, the removal rate tends to be stable at first and then decrease rapidly. This

shows that although increasing the initial concentration is beneficial to promoting the adsorption capacity of AS, the increased adsorption amount was not enough to offset the increase metal ion concentration in the solution (Jiang and Liu, 2019). Therefore, if the heavy metal concentration is found to be quite high, a high AS dosage is required to ensure the removal efficiency.



Fig. 3-9 Relationship between AS removal rate and adsorption capacity (Bar chart (Cu(II) and Zn(II) adsorption capacity) refer to the left Y axis, Line chart (Cu(II) and Zn(II) removal rate) refer to the right Y axis)

Table 3-8 lists the adsorption capacity of some low cost adsorbents for Cu(II) and Zn(II). It can be seen that the adsorption capacity of AS for Cu(II) and Zn(II) is better than that of some common low cost adsorbents such as red mud and wheat straw. The adsorption capacity of AS for Cu(II) is similar to that of steel slag, and for Zn(II) is similar to that of coal fly ash, which indicates that AS is suitable for use as an adsorbent for Cu(II) and Zn(II) in storm-water runoff (Du *et al.*, 2020).

In conclusion, the results of adsorption isotherms show that AS has a strong adsorption capacity for Cu(II) and Zn(II) and its capacity is much higher than that of some common low cost adsorbents. In addition, AS is very easy to obtain and is produced in large quantities every year (Ren *et al.*, 2020). It makes AS a potential to be an adsorbent which can be widely used in constructed wetlands (Babatunde *et al.*, 2009), filtration systems (Wang and Bian, 2017) or bio-retention ponds (Zhang *et al.*, 2020) to mitigate Cu(II) and Zn(II) pollution problems in surface and groundwater.

	Adsorption cap	pacity				
Adsorbents	(mg/g)		pН	(°C)	References	
	Cu(II)	Zn(II)		(0)		
Steel slag	16.21	-	5.5	18	Feng et al., (2004)	
Coal fly ash	-	6.5–13.3	6.5	30	Banerjee et al., (2006)	
Wheat straw	7.05	-	5	25	Wu et al., (2009)	
Red mud	5.35	-	5.5	30	Nadaroglu et al., (2010)	
Coal fly ash	48.8	-	7.11	25	Wu et al., (2018)	
Alum sludge	22.88	8.74	6.5	25±8	This work	

Table 3-8 Compared with other common low-cost adsorption materials

3.3.4 Different pH studies

The solubility and ionization degree of metals in water vary under different pH conditions, which may affect the adsorption capacity. Therefore, this section investigates the performance of AS in removing Cu(II) and Zn(II) under different pH values (Duan and Fedler, 2021). As shown in Figure 3-10, when the solution pH increases from 2 to 8, the adsorption of Cu(II) and Zn(II) by AS shows a slightly increasing and then decreasing significantly. When pH < 4, the removal of Cu(II) and Zn(II) by AS increases slightly with increasing pH. The adsorption reaches its maximum in the pH range of 5-6 and decreases when pH>6 mainly because the increase of OH⁻ in water forms precipitation with two metal ions (Duan and Fedler, 2021). Stormwater runoff is generally weakly acidic (about 6). When pH = 6, the adsorption capacity of AS is 0.34 mg Cu(II) /g AS, with a removal rate of 98%; 0.36 mg Zn(II) /g AS, with a removal rate of 99.5%. Previous studies reported similar pH effects for the adsorption of heavy metals by AS. For example, Wang (2019) using AS mixed with clay in a ratio of 1:2 and then calcined to make beads. The removal rate of the beads for Cu(II), Zn(II) and Pb(II) increased first and then decreased with the increase of pH, and the maximum adsorption rate was at pH = 5 (Cu(II) = 94.3%; Zn(II) = 85%) (Wang, 2019). Furthermore, Du et al. (2020) found that the adsorption of Cu(II) and Zn(II) by clay-modified AS showed the same trend at different pH values, and the maximum adsorption occurs at pH = 5. The removal rate of both metal ions by AS decreased with increasing pH, which is due to the phenomenon of proton competition for AS adsorption sites during the adsorption process (Zhou and Haynes, 2011). It is worth noting that in most research reports, the adsorption of AS increases rapidly in the pH range of 4-6 (Hovsepyan and Bonzongo, 2009; Siswoyo et al., 2014; Du et al. 2020). In this study, because a lower initial concentration of heavy metals was used in this experiment. Since the concentration of heavy metals in rainwater runoff is generally low, which means that AS has enough adsorption sites to provide to cations.



Fig. 3-10 Effect of different pH values on AS adsorption capacity (a) Cu(II) (b) Zn(II) (Initial metal concentration 2mg/L; Shaking at 25°C for 120 minutes; AS particle size <0.15mm; AS dosage 5g/L)

Zeta potential is often used to study the surface charge of an adsorbent, which is related to its adsorption capacity. Recent research data have revealed the relationship between AS surface charge and solution pH. The investigation found that the unmodified AS zero point of charge is distributed in

the range of 5.6-6.1 (Zhou and Haynes. 2011; Hua et al., 2015; Yang et al., 2015). For example, Hua et al. (2015) reported that the AS zero point of charge was 5.6, which is the same as Zhou and Haynes' (2011) result. Yang et al. (2015) used modified AS to adsorb ammonia in wastewater and found that the unmodified AS zero point of charge was 6.1. After using sulfuric acid, sodium hydroxide and ultrasonic modification, the zero-point charge of AS shifted significantly to the left, which indicates that the surface chemical properties of the AS have changed (Yang et al., 2015). The investigation found that when the pH is around 6.5, the zeta potential of AS is about -10mv (Yang et al., 2015). In addition, When the pH is about 7.5, the zeta potential of AS is about -20mv (Wang et al., 2016; Chen et al., 2017). Based on the above, it can be inferred that at pH = 6.5, the surface of AS may be a negative charge which is compatible with the adsorption of metal cations.

3.3.5 SEM-EDS for AS after Adsorption Cu(II) and Zn(II)

Fig. 3-11 is the SEM-EDS results after AS adsorbed Cu(II) and Zn(II). By compare with Chapter 2 - Section 2.3.3 - Fig.2-7, it can be seen from the figure that loading Cu(II) and Zn(II) has no effect on the surface morphology. However, from the results of EDS element characterization, the contents of Cu(II) and Zn(II) increased from 0.01% before adsorption to 0.22% and 0.39%, respectively. The significant increase of Cu(II) and Zn(II) is mainly attributed to the fixation of Cu(II) and Zn(II) ions from water.







(c)

Fig. 3-11 SEM images and EDS elemental composition of AS after adsorption Cu(II) and Zn(II) (a) Fine powder SEM-EDS results; (b) Particle SEM-EDS results and (c) Mapping scanning plot

3.3.6 Adsorption Mechanisms

Identifying the types of functional groups on the AS surface by FTIR is underpinning the study of the possible mechanism of its adsorption of Cu(II) and Zn(II) (Fig. 3-12). By comparing the raw sludge (Chapter 2- Section 2.3.5-Fig. 2-9) with the curve after adsorption of Cu(II) and Zn(II), it can be found that the absorption peaks at wave numbers 3361 cm⁻¹ and 1007 cm⁻¹ are significantly weakened. This indicates that hydroxyl groups are involved in the adsorption of heavy metals, and hydroxyl substitution reactions occur on the surface of AS (Du *et al.*, 2020). Two new bands appeared at 1217 cm⁻¹ and 1736 cm⁻¹, which may be caused by the aggregated ZnxOy species (Lian *et al.*, 2020). In addition, strong bonds usually vibrate faster than weaker bonds, so after AS adsorbs Cu(II) and Zn(II), the absorption peak at 1420 cm⁻¹ shifts to a lower wave number of 1375 cm⁻¹ (Elkhatib *et al.*, 2015). This indicates that Cu(II) and Zn(II) are firmly bound to the oxygen-containing functional groups, and

that metals can form strong covalent bonds with the oxygen-containing functional groups on the AS surface (Jiao *et al.*, 2017). The weakening of the absorption peaks at wavenumbers 517 cm⁻¹ and 467 cm⁻¹ also indicates the occurrence of surface complexation reaction (Lian *et al.*, 2020). AS can fix heavy metals on its surface by sharing lone pair electrons with heavy metals through Al-O (Lian *et al.*, 2020). In general, the adsorption mechanism of AS for Cu(II) and Zn(II) involves hydroxyl substitution, surface complexation and so on.



Fig. 3-12 FTIR plot of the AS before and after adsorb Cu(II) and Zn(II)

Moveover from 3.3.3, we can see that the absorption of Cu(II) and Zn(II) by AS is affected by protons concentration. Because the functional groups on the surface of AS such as hydroxyl (R-OH) and amino (R-NH₂) will undergo protonation and deprotonation at different pH, making the surface of AS positively and negatively charged (Abo-El-Enein *et al.*, 2017). This means that the charge density on the surface of the adsorbent plays an important role in promoting or blocking the electrostatic adsorption of Cu(II) and Zn(II) by AS (Abo-El-Enein *et al.*, 2017).

Figure 3-13 shows the Cu(II) and Zn(II) species at different pH (Powell *et al.*, 2013; Liu *et al.*, 2015; Yang *et al.*, 2015 and Quiroz, 2021). When pH \leq 4, the solution is strongly acidic, and Cu(II) and Zn(II) exist in the form of Cu²⁺ and Zn²⁺. At this point, a large number of H⁺ ions in the solution protonate the AS surface, making it positively charged (as show in equation 18) (Lian *et al.*, 2020). Positively charged AS will generate electrostatic repulsion with metal cations, which hinders the adsorption of Cu(II) and Zn(II) on the AS surface (Lian *et al.*, 2020). The lower the pH value, the more obvious the protonation effect and the worse the adsorption capacity (Jiang *et al.*, 2019).

$$\mathbf{R} - \mathbf{OH} + \mathbf{H}^{+} \Leftrightarrow \mathbf{R} - \mathbf{OH}_{2}^{+} \tag{18}$$

When $4 < pH \le 6$, the degree of AS surface protonation decreases (Eq. 19, 20) and the heavy metals in the solution mainly exist in the positively charged forms of Cu²⁺, Cu(OH)⁺ and Zn²⁺. The slight increase in the adsorption amount in this pH range that has been shown in 3.3.3 indicates that the electrostatic repulsion is weakened. At this pH range, the O from the functional group -OH on the AS surface has an available lone pair of electrons, and the metal cation can be adsorbed onto the AS by forming a covalent bond through sharing of electron pairs between the metal ion and the oxygen atom (Eq. 21, 22) (Deng, 2018).

$$\mathbf{R} - \mathbf{OH}_2^+ + \mathbf{OH}^- \Leftrightarrow \mathbf{R} - \mathbf{OH} + \mathbf{H}_2\mathbf{O} \tag{19}$$

$$\mathbf{R} - \mathbf{OH} + \mathbf{OH}^{-} \Leftrightarrow \mathbf{R} - \mathbf{O}^{-} + \mathbf{H}_{2}\mathbf{O}$$
(20)

$$\mathbf{R} - \mathbf{O}^{-} + \mathbf{M}\mathbf{e}^{2+} \Leftrightarrow \mathbf{R} - \mathbf{O}\mathbf{M}\mathbf{e}^{+}$$
(21)

 $R - O^{-} + Me(OH)^{+} \Leftrightarrow R - OMe(OH)$ (22)

$$Me^{2+}+2OH- \Leftrightarrow Me(OH)_2\downarrow$$
 (23)

Where, $R - OH_{2^+}$, R - OH and $R - O^-$ represent the morphology of hydroxyl functional groups on the AS surface in the protonated, neutral and ionized states, respectively; Me^{2+} , $Me(OH)^+$ and $Me(OH)_2$ represent the valence states of Cu(II) and Zn(II) during the adsorption process.

When $6 < pH \le 8$, the proportion of Cu^{2+} continued decrease, the proportion of $Cu(OH)^+$ increased and a large amount of $Cu(OH)_2$ precipitate was produced (Eq. 23) (Fig. 3-13). The proportion of Zn^{2+} decreases, the proportion of $Zn(OH)^+$ increases, and $Zn(OH)_2$ precipitation begins to occur when 7< $pH \le 8$. The decrease adsorption capacity of AS in this part is mainly due to the precipitation reaction between metal ions and OH⁻ (Jiang and Liu, 2019). Therefore, without considering the effect of precipitation, the weak acidity of stormwater runoff (pH = 6-7) is benefit for adsorption Cu(II) and Zn(II) by AS.



Fig. 3-13 Cu(II) and Zn(II) species distribution in distilled water at different pH

In addition, Fig. 3-14 shows that during the adsorption of Cu(II) and Zn(II) by AS, the pH of the solution first decreased and then stabilized over time, which means that during the adsorption process

the H^+ concentration increases resulting in a decrease in the pH of the solution. It shows that AS can not only bind to hydroxyl groups via electrostatic attraction, but also replace H^+ by ligand exchange (Eq. 24, 25) (Jiang and Liu, 2019).

$$2R - OH + Me^{2+} \Leftrightarrow (R - O)_2Me + 2H^+$$
(24)



$$R - OH + Me(OH)^{+} \Leftrightarrow R - OMeOH + H^{+}$$
(25)

Fig. 3-14 Changes of solution pH during AS adsorption of Cu(II) and Zn(II)

Interestingly, when using simulated stormwater runoff (2mg/L Cu and Zn, 1mg/L PO₄³⁻, 25mg/L NH₄⁺-N, 6mg/L NO₃⁻ -N, 584mg/L NaCl and 252mg/L NaHCO₃) as the base. There is no Cu(OH)₂ precipitation was found by adjusting the solution pH around 7. By compared with Figure 3-11, it should have Cu(OH)₂ at around pH=6.8. However, the removal efficiency of AS for Cu(II) has an increase trend when the pH increased (Fig. 3-10). The visual MINTEQ was used to study the species of Cu(II) and Zn(II) in water under different pH. It was found that Zn(II) maintains almost the same species distribution characteristics as Zn(II) in distilled water solution. But Cu(II) keep dissolved in the pH = 7 and Cu(OH)₂ appears around pH = 8 (Fig 3-15). This means that precipitation may occur on the AS surface, through surface complexation followed by the formation of hydroxides that precipitate on the adsorbent surface, when pH around 7 to 8. (Eq. 26, 37) (Deng, 2018). Surface precipitation has been shown to be an important pathway for the adsorption of cations on metal oxides, and this reaction tends to occur at high pH (Csobán and Joó, 1999; Deng, 2018).

$$2R - OH + Me^{2+} = (R - OH)_2 Me^+$$
(26)

$$R - OH + Me(OH)^{+} = R - OHMeOH$$
(27)



Fig. 3-15 Metal species distribution calculated by MINTEQ base on the stimulate stormwater runoff (a) Cu(II) and (b) Zn(II) (Simulating stormwater runoff prescription 2mg/L Cu and Zn, 1mg/L PO₄³⁻, 25mg/L NH₄⁺-N, 6mg/L NO₃⁻ -N, 584mg/L NaCl and 252mg/L NaHCO₃)

Farley *et al.* (1985) proposed a model to explain that cations form new hydroxide surfaces on the adsorbent after surface complexation, and that surface complexation is a major adsorption mechanism when the cation concentration in the solution is low. Solid hydroxide precipitation occurs only when the cation concentration increases and the complexation sites on the adsorbent surface are saturated (Deng. 2018). Therefore, surface complexation reactions may also exist during the adsorption of Cu(II) and Zn(II) by AS (Zhou and Haynes, 2010).

In summary, the adsorption of Cu(II) and Zn(II) by AS not only includes the process of intra-particle diffusion, but also involves the electrostatic attraction between metals and oxygen functional groups on the surface of AS, hydroxyl substitution, and surface complexation reaction.

3.3.7 Different Particle Size

Generally, fine powder has a higher specific surface area which means that it has a faster adsorption rate and higher adsorption capacity (Shen et al., 2018). Therefore, two kinds of AS with different particle sizes (<0.15 mm and 1-2 mm) were prepared in this experiment. The study found that the particle size of AS has a significant effect on the adsorption of Cu(II) and Zn(II), especially the adsorption rate (Fig. 3-16). When the AS particle size <0.15 mm, its adsorption capacity for Cu(II) and Zn(II) are 0.388 mg/g and 0.343 mg/g respectively. When the AS particle size ranges from 1 to 2 mm, its adsorption amount for Cu(II) and Zn(II) were 0.331 mg/g and 0.388 mg/g respectively. It is worth noting that with the increase of particle size, the adsorption equilibrium time for Cu(II) and Zn(II) is significantly extended. When the particle size is below 0.15 mm, the adsorption rate of Cu(II) and Zn(II) is very fast, normally reaching equilibrium within 60 min. However, for AS in the range from 1 to 2 mm, it will take much longer time, average 200 minutes, to reach adsorption equilibrium. Lv et al. (2017) reported similar results, they prepared three different particle sizes of AS (<0.15mm, 1-2mm, 2-5mm) to study their adsorption effects on Pb(II), Hg(II) and Cr(VI). The results show that the smaller the particle size, the larger the specific surface area, the more adsorption sites, and the more benefit for adsorption heavy metals (Lv et al., 2017). Furthermore, the adsorption of As(III) and As(V) by alum sludge also showed similar results (Caporale et al., 2013). As the particle size decreases, the adsorption of As(III) and As(V) increases from 459.1 to 537.1 mmol/kg and 600.0 to 667.1 mmol/kg, respectively (Caporale et al., 2013). Therefore, it is reasonable to believe that particle size has a significant effect on the adsorption of heavy metals by AS, which could provide data guidance for subsequent filter column experiments.


Fig. 3-16 Effect of different particle sizes on AS adsorption capacity (a) Cu(II), (b) Zn(II) (AS dosage 5g/L; Initial metal solution concentration 2mg/L; Shaking at 25°C for 500-600 minutes; pH=6.5; 1-2mm refers to the left Y axis and <0.15mm refers to the right Y axis)

Since this research is considering the use of AS for the heavy metal pollution in runoff, the batch experiments did not reach the maximum adsorption capacity of both particle sizes due to the low initial concentration. This can be explained by the Langmuir adsorption isotherm equation.

$$\Theta = \frac{KC}{1+KC} \tag{3-18}$$

Where, θ represents the fraction of all available adsorption sites that are occupied; K is the adsorption constant and C is the concentration of the reactant. At low concentrations, the denominator is close to 1 and the fraction adsorbed varies linearly with concentration which is the first-order region (Alan. 2017). In this region it can be seen that higher concentrations increase the tendency of adsorption (Alan. 2017). However, as the concentration increases, the number of available adsorption sites on AS decreases, which makes further adsorption increasingly difficult. Due to this experiment refers to the heavy metal concentration in stormwater runoff, the adsorbate concentration C is low which makes θ is close to 0. It indicates that AS did not reach the maximum saturated adsorption sites. This was also confirmed by the adsorption isotherm study that the removal amount of heavy metals by AS increased with the increase of initial concentration under the same AS dosage (Fig. 3-7).

In addition, From the specific surface area data in 2.3.2, we can see that the specific surface areas of particles and fine powder are both 58 m²/g, but the surface area of particles is 37 cm²/g, and the fine powder is 56 cm^2/g . This indicates that the reduction in particle size leads to the collapse of the internal pore structure, as the specific surface area remains unchanged even when the particle size is reduced significantly; the loss of internal pore structure is offset by the increase in external surface area. It can be seen from Figure 3-16 that the time it takes for the larger particles to reach adsorption equilibrium is longer than that for fine powder. This is because the fine powder has a high surface area which results in heavy metals adsorbing quickly to the surface. In other words, the larger particles contain a certain amount of internal pores which makes the adsorption characteristics of fast at first (for surface adsorption) and then slow (for internal pore adsorption). Moreover, from the adsorption amount, the adsorption of Cu(II) by fine powder is generally slightly higher than that by particle. This indicates that Cu(II) is mainly fixed on the functional groups on the surface of the adsorbent, which is confirm to kinetics studies that the adsorption mechanism of AS for heavy metals is mainly chemical adsorption. But this does not mean that there is no physical adsorption in the particles. It was demonstrated in Chapter 4 that the functional groups on the AS surface have a greater affinity for Cu(II), due to the rapid surface fixation, maybe the physical adsorption of Cu(II) is not obvious. The adsorption of Zn(II) by particles is slightly higher than that by fine powder, which shows that in addition to surface adsorption, part of Zn(II) can be fixed by diffusion into the internal pores. Based on a survey of the atomic radius of both metals, Zn(II) is smaller than that of Cu(II). Therefore, Zn(II) can more easily enter the internal pores of AS than Cu(II).

3.3.8 Desorption

Investigating whether Cu(II) and Zn(II) can be effectively adsorbed and desorbed is an important indicator to evaluate the performance of AS (Ren, 2014). It can evaluate the ability of AS to be recycled. Fig. 3-17 shows the desorption of fixed Cu(II) and Zn(II) under different pH.



Fig. 3-17 Effect of different pH for Cu(II) and Zn(II) desorption (Desorption time 360min; AS particle size 1-2mm)

It can be seen from the above figure that the desorption rate of Cu(II) and Zn(II) decreases with the increase of pH. When the solution pH = 1, the maximum desorption rate of Cu(II) and Zn(II) are 94% and 99% respectively. No more desorption is observed when the pH is further reduced. This may be because at low pH, the H⁺ concentration in the solution is high, and a large amount of H⁺ can replace Cu(II) and Zn(II) which were fixed by AS before. When the pH is greater than 2, the H⁺ concentration in the solution decreases significantly. At this point, the adsorption rate of Cu(II) and Zn(II) and Zn(II) is greater than the desorption rate, which leads to a significant reduction in the desorption efficiency (Liu, 2014). Moreover, when pH \leq 2, the desorption rate of Cu(II) and Zn(II) exceeded 70%.

According to the investigation, the decomposition mechanism of the fixed heavy metals is due to the addition of a large amount of acid to the water, which increases the proton concentration in the solution and causes a protonation reaction on the surface of AS (Eq. 28) (Chiang et al., 2012; Gao et

al., 2020; Zeng et al., 2020). The proton replaces the metal that adsorbed on the hydroxyl functional groups.

$$(\mathbf{R}-\mathbf{O})_2\mathbf{M}\mathbf{e} + 2\mathbf{H}^+ \Leftrightarrow 2\mathbf{R} - \mathbf{O}\mathbf{H} + \mathbf{M}\mathbf{e}^{2+}$$
(28)

According to the investigation, Ren. (2014) used 0-2 mol/L hydrochloric acid (HCl) to desorb the modified AS that fixed Cr(VI). The results showed that the amount of Cr(VI) desorbed increased with the increase of HCl concentration and reached the maximum when the HCl concentration was 1.5 mol/L (Ren. 2014). Wang. (2019) used HCl to adjust the solution pH from 1 to 6 to decompose AS adsorbed with Cu(II), Zn(II), Pb(II) and Cd(II). The results showed that when the pH was greater than 3, the concentration of desorbed heavy metals decreased significantly. Therefore, she suggested selecting HCl solution with a pH=2 as the adsorbent for Cu(II), Zn(II), Pb(II) and Cd(II), which is similar to the results of this work. Furthermore, Zhou and Haynes. (2011) found that using 0.01 M nitric acid solution which pH = 2 could release about 50% of the Pb(II) and Cd(II). When pH=1, the desorption amount increases by 80% (Zhou and Haynes. 2011). By considering the economic cost and literature report, pH=2 was selected as the optimal condition for desorb Cu(II) and Zn(II) in this experiment.

In order to quantify the optimal desorption time, Fig.3-18 shows the desorption rate at different time intervals.



Fig. 3-18 The influence of time on the desorption rate of Cu(II) and Zn(II) (pH=2)

It can be seen from Fig.3-18 that when the solution pH = 2, the desorption of Cu(II) and Zn(II) increases with time. The desorption rate increased rapidly in the first 50 min, and then the desorption

rate slowed down and reached the maximum at 240 min. Therefore, 240 min was selected as the optimal desorption time for Cu(II) and Zn(II). The research found that the adsorption and desorption of Cu(II) and Zn(II) would fluctuate and eventually reach a dynamic equilibrium (Chen, 2015 and Wang, 2019). It also can be seen from Fig.3-15 and Fig.3-16 that Zn(II) is easier to desorb than Cu(II). Combined with section 3.3.2 result, AS has a greater adsorption capacity for Cu(II), which shows that the more easily adsorbed metal, the more difficult it is to desorb. This reflects that the binding force between AS and Cu(II) is stronger than Zn(II).

3.3.9 Regeneration

The adsorbent can be recycled is the key to evaluating whether it can be used in actual engineering. AS was conducted to five adsorption-desorption cycles, and the results are shown in Fig. 3-19.



Fig. 3-19 The cyclic adsorption of AS

It can be seen from Fig.3-19 that with the increase of cycle times, the adsorption capacity of Cu(II) and Zn(II) gradually decreases. The adsorption capacity after 4 cycles can only reach half of the initial capacity, and after the 5 cycles, AS completely loses its adsorption capacity for Zn(II). This is because continuous adsorption and desorption will cause a damage and mass loss to the surface of AS (Ren, 2014). On the other hand, due to economic considerations, we selected desorption pH=2 which does not reach the pH that can completely desorb the Cu(II) and Zn(II). Therefore, a part of Cu(II) and

Zn(II) is remained on AS because of incomplete desorption, which makes the adsorption sites on the AS surface occupied by metals which not desorbed before. So the adsorption sites and rate are reduced. However, experiments have shown that the removal rate of Cu(II) and Zn(II) after three adsorption-desorption cycles is still over 65%. This indicates that AS is an effective and reusable adsorption material, but the number of repetitions is limited. According to the investigation of Ren (2014), in the study of cyclic adsorption of Cr(VI) by thermally modified AS, the removal rate of Cr(VI) decreased from 70.4% to 50.8% after 4 cycles and after the third cycle removal rate decreased significantly (Ren. 2014). Gao et al., (2020) also found that the phosphorus removal efficiency of AS decreased from 95% to 80% after three cycles. Zeng et al., (2020) also recommends that the gregeneration time of AS for adsorb As (V) should not exceed 4 times. After the 4th regeneration, the removal rate of As (V) drops to 60%. Studies have shown that the regeneration changes with cycles may be due to the fact that the heavy metal ions adsorbed on the AS surface in the last experiment cannot completely desorbed, inevitably some metals will remain on the AS surface, resulting in a decrease in the adsorption sites and a decrease in the adsorption rate (Wang. 2019). Moreover, in terms of mechanism, when desorbed by using HCl solution, some aluminum metal oxide/hydroxide groups will undergo dissolution and corrosion, regenerating aluminum metal ion form (Al³⁺) (Ren. 2014). This reduces the number of oxygen-containing functional groups on the AS surface, which affects the adsorption capacity of AS (Ren. 2014). In general, for this study, it is recommended to reuse it three times. The order of magnitude in recovery in these studies is consistent with what was found experimentally in the present work.

3.4 Summary

This chapter studies the adsorption characteristics of AS for single heavy metals Cu(II) and Zn(II), mainly investigating the effects of solution pH, contact time, initial metal concentration and particle size, discusses the adsorption mechanism. The main conclusions are as follows:

1) The adsorption rates of Cu(II) and Zn(II) both decreased from fast to slow, and were more consistent with the pseudo-second-order adsorption kinetic model. The fitting results of the intraparticle diffusion model showed that in addition to chemical adsorption, AS also involved the effects of film diffusion and intra-pore diffusion for adsorb Cu(II) and Zn(II).

2) With the increase of initial metal concentration, the AS adsorption amount of Cu(II) and Zn(II) showed a trend of first increasing and then stabilizing. The adsorption isotherm fitting results show that in addition to monolayer adsorption, AS also has non-uniform multilayer adsorption, but the monolayer adsorption is dominant.

3) Solution pH has a significant effect on the adsorption of Cu(II) and Zn(II) by AS. Without considering chemical precipitation, the optimal pH range is 5-6 and stormwater runoff is generally weakly acidic, which is benefit for the adsorption of Cu(II) and Zn(II).

4) The adsorption process of AS for Cu(II) and Zn(II) not only includes the Intra-particle diffusion, but also involves the electrostatic attraction between the metal and the oxygen-containing functional groups, hydroxyl substitution and surface complexation reaction

5) Particle size has an effect on the rate of AS adsorption of heavy metals. Compared with 2 mm AS, 0.15 mm AS has a shorter adsorption equilibrium time for Cu(II) and Zn(II).

6) When HCl is used as the desorbent agent, the desorption rate of Cu(II) and Zn(II) decreases with the increase of solution pH, and the desorption effect of Cu(II) and Zn(II) is best when pH ≤ 2 . When the solution pH = 2, the desorption of Cu(II) and Zn(II) increases with time and became stable after 240 min. Therefore, the desorption condition for AS was selected as solution pH = 2 and desorption time is 240 min.

7) AS has good reuse performance. After three times of adsorption and desorption cycle, the removal rate Cu(II) and Zn(II) is still over 65%. However, the number of repetitions is limited. In this study, it is recommended to reuse it three times.

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CHAPTER 4

EFFECTS OF COMPETITION ON ADSORPTION OF COEXISTING IONS IN RAINWATER RUNOFF - BATCH STUDIES

4.1 Introduction

The chapter 3 demonstrated that AS has the potential to be used as a Cu(II) and Zn(II) adsorbent, but for application in sustainable urban drainage systems (SUDS) the complexity and variability of stormwater runoff needs to be taken into consideration. The consequence is that there may be adsorption competition between multiple elements and hence affect the adsorption capacity of AS for removal of Cu(II) and Zn(II). For example, there may be competition for adsorption sites between Cu(II) and Zn(II). In addition to Cu(II) and Zn(II), stormwater runoff usually contains many chemicals such as calcium, magnesium, phosphorus and nitrogen, these elements are likely to compete with Cu(II) and Zn(II) for adsorption sites. The coexistence of multiple elements will increase the difficulty of AS adsorbing Cu(II) and Zn(II).

This chapter examines the adsorption competition phenomenon between Cu(II) and Zn(II) in detail through batch experiments. Furthermore, by simulating the pollutants commonly found in stormwater runoff as adsorption targets for AS to conduct batch competition experiments. The adsorption competition under different conditions, such as different coexisting ions, different background ions and different ionic strengths, was studied by the results from batch competition experiments. The feasibility of AS as an adsorbent for treating actual stormwater runoff was evaluated based on the results.

4.2 Methodology

4.2.1 Simulate Runoff Recipe

In order to prepare a recipe for artificial storm water runoff (SSR), pollutant types and ranges of concentrations for simulated stormwater runoff (SSR) were reviewed based on several reports in Table 4-1). These reports formed the basis for the selected pollutants and concentrations (Table 4-1).

Pollutants	Concentration range (mg/L)	Ref.
		Soleimanifar et al., 2019;
Cu(II)	0.01- 0.48	Pitt et al., 2004;
		Pitt et al., 2018;
		CIWEM. 2024;
Zn(II)	0.08-0.56	Pitt et al., 2018;
		Soleimanifar et al., 2019;
		Pitt et al., 2004;
Total Phosphate	0 09-0 29	Kayhanian et al., 2007;
		Gan et al., 2007;
		Gobel et al., 2007;
$\mathbf{NH}_{4}^{+}\text{-}\mathbf{N}$	0.1-3.39	Kayhanian et al., 2007;
		Pitt et al., 2018;
		Gobel et al., 2007;
NO ₃ ⁻ -N	0.28-11.8	Gan et al., 2007;
		Pitt et al., 2004;

 Table 4-1 Survey on pollutant concentration range in stormwater runoff from highway, roof, grassed areas and car park

In order to truly reflect the concentration ratio of each pollutant in the stormwater runoff, we stimulated all elements in the SSR as show in Table 4-2, NaCl (10mM) was used as background electrolyte for ionic strength and NaHCO₃ (3mM) is buffer solution to minimize pH changes. Use 0.1M HCl and NaOH to adjust the solution pH around 6.5.

Elements	Concentration (mg/L)	Source
Cu	2	CuSO4·5H2O
Zn	2	ZnNO ₃ ·6H ₂ O
Phosphate	1	NaH ₂ PO ₄
NH4 ⁺ -N	25	NH4Cl
NO ₃ ⁻ -N	6	NaNO ₃
Ionic strength	584	NaCl
Buffer solution (pH around 6.5)	252	NaHCO ₃

 Table 4-2 Stimulate stormwater runoff recipe

In particular, only one metal concentration was used here in order to simulate stormwater runoff. According to Chapter 1, the concentration of heavy metals in stormwater runoff is generally low and rarely exceeds 2 mg/L. This chapter examines whether adsorption competition occurs between Cu(II) and Zn(II) at the most unfavorable concentrations under the stormwater runoff background, so different Cu(II) and Zn(II) ratios are not considered in this chapter.

All solutions in the experiment were prepared by deionized water (Ω >18.2 M Ω -cm) and all chemical reagents were used analytical grade from Fisher Scientific.

4.2.2 The Influence of Different Environmental Parameters

Studies have shown that when adsorbents remove multiple heavy metals, there is competition for adsorption sites among the various heavy metals, but most competition experiments are focused on wastewater with high heavy metal concentrations (10mg/L-500mg/L) (Nematollah *et al.*, 2016; Wang *et al.*, 2017; Jiao *et al.*, 2016; Hua *et al.*, 2018). In order to verify whether AS also has obvious adsorption competition in the removal of low-concentration Cu(II) and Zn(II) pollution in stormwater runoff, three different adsorption conditions were simulated which are different runoff compositions, different ionic strengths and different background ions:

- **Different coexisting ions.** In order to study whether there is adsorption competition between different components such as heavy metals and between heavy metals and nutrients. Three different solution matrices were set up for batch adsorption experiments: single metal solution (SMS), multi-metals solution (MMS) which is Cu(II) and Zn(II) mixed solution and simulated stormwater runoff (SSR). This setting method is used to compare the adsorption competition phenomenon between Cu(II) and Zn(II), and explore the adsorption competition phenomenon between metals and the chemicals in Table 4-2.
- **Different ionic strengths.** In order to study the effect of different ionic strength for AS adsorb Cu(II) and Zn(II). 1mM, 10 mM, 100 mM and 500 Mm NaCl were prepared as background electrolytes, and the concentrations of other components in SSR unchanged.
- **Different background ion species.** To study the effect of different background ion species for AS adsorb Cu(II) and Zn(II). 10mM CaCl₂ and NaNO₃ were prepared as background electrolytes, and the concentrations of other components in SSR unchanged.

All the batch competition experiments were repeated three times and conducted under the optimal adsorption conditions which are described in Chapter 3: The initial Cu(II) and Zn(II) concentrations was 2 mg/L, adsorption time was 30 min, pH was 6.5, AS dosage was 0.1 g, the AS particle size was below 0.15 mm, the adsorption solution volume was 20 mL, adsorption temperature was 298 K and shaking intensity was 130 rpm/min. The collected samples were passed through a 0.45 μ m syringe filter and analyzed for Cu(II) and Zn(II) concentrations by using ICP-OES (Refer to the section 3.2.1 in chapter 3).

4.2.3 Engineering Thermodynamics Calculation

Activity (a) is a correction for actual concentration and is used to describe the "effective concentration" of a component in a non-ideal mixture (Trinh et al., 2014). The formula is:

$$a = \gamma * x \tag{4-1}$$

where, a is the activity, γ is the activity coefficient used to correct for non-idealities and x is the molar fraction of the metal solution.

Adsorption binding energy refers to the energy released when a molecule is adsorbed to the AS surface and is usually associated with an adsorption isotherm such as the Langmuir or Freundlich model (Yasir and Ibrahim. 2023). Here we can see from Chapter 3 that Langmuir is more suitable to describe the adsorption behavior of AS on Cu(II) and Zn(II). So Langmuir parameters are used for further calculation.

Chemical potential (μ) represents the change in molar free energy of a component in a system at constant temperature and pressure (Trinh et al., 2014). For non-ideal mixtures, activity needs to be introduced to correct for non-ideality (Trinh et al., 2014; Bangar et al., 2021). The formula is:

$$\mu = \mu^0 + RT \ln a \tag{4-2}$$

Where, μ is the chemical potential (J/mol); μ^0 is the standard chemical potential (J/mol); R and T (K) are constant and temperature respectively; a is the activity.

4.3 Results and Discussion

4.3.1 Different Coexisting Ions

The adsorption competition for the Cu(II) and Zn(II) coexist system under low concentration conditions is shown in Fig. 4-1. It can be seen that in the adsorption of the binary system, there is a certain adsorption competition between Cu(II) and Zn(II). The saturated adsorption capacity of Cu(II) decreased from 0.40 mg/g to 0.397 mg/g, and Zn(II) decreased from 0.394 mg/g to 0.381 mg/g, which indicates that the adsorption competition between Cu(II) and Zn(II) and Zn(II) at low concentrations is not obvious now. This may be because 0.1g AS has enough adsorption sites for Cu(II) and Zn(II) at 2mg/L concentrations. Similarly, when AS was used to adsorb Hg(II) and Cr(*III*), the competition for adsorption sites was not obvious at 2mg/L, but as the concentration of competing substances increases, the removal efficiency of Hg(II) decreases (Wu *et al.*, 2011). Uddin. (2017) reviewed heavy metal adsorption by clay minerals over the past 10 years also showed that as the concentration of heavy metals increases, the mutual adsorption competition intensifies (Uddin, 2017).



Fig. 4-1 Adsorption competition in coexist systems (a) Cu(II); (b) Zn(II)

Furthermore, it also can be seen from Figure 4-1 that AS maximum adsorption amount for Cu(II) is around 0.4mg/g and for Zn(II) is about 0.39mg/g, and the isotherm studies in chapter also shows that AS has a stronger adsorption capacity for Cu(II). This infers that AS maybe has a greater affinity for Cu(II) by compared with Zn(II). Studies have shown that the priority adsorption order among heavy metals is related to their hydrolysis constant, ionic radius, hydration radius, electronegativity and so

on (Lv and Qiu, 2020; Wang et al., 2019; Esfandiar et al., 2022). For heavy metals of the same valence, the radius of their hydrated ions determines the adsorption capacity (Wang et al., 2015; Liu et al., 2007). Table 4-3 lists the basic physical and chemical properties of Cu(II) and Zn(II) (Parr and Pearson, 1983; Jiang and Liu, 2019; Wang, 2012). The metal ions with smaller hydrated ion radius are more likely to conduct replacement reactions with cations in AS, and the hydrated ion radius of Cu(II) (0.419 nm) < Zn(II) (0.430nm) (Jiang and Liu, 2019). Therefore, AS has a stronger adsorption capacity for Cu(II). In addition, from the adsorption mechanism conclusions of Chapter 3, it can be seen that electrostatic attraction is an important method for AS to adsorb Cu(II) and Zn(II). According to the principles of electrostatics, the greater the ratio between charge and radius of a metal ion, the stronger its bond energy (Wang et al., 2015; Wang, 2012). Due to Cu(II) and Zn(II) have the same charge, the smaller the ion radius, the easier it is to be preferentially adsorbed (Esfandiar et al., 2022). The ionic radii of Cu(II) and Zn(II) are 73 pm and 74 pm respectively which means that the charge-toradius ratio of Cu(II) is larger. Therefore, Cu(II) is more easily adsorbed and less affected by Zn(II). Furthermore, some studies show that the electronegativity of heavy metal elements determines their adsorption priority, which is the greater the electronegativity of the metal, the stronger the bond energy between the metal and the oxygen-containing functional group on the surface of AS, and the easier it is to be preferentially adsorbed (Du et al., 2020; Hu et al., 2011). Since the electronegativity of Cu(II) is 1.9 which is greater than that of Zn(II) (1.65), AS has a greater selectivity for Cu(II) than for Zn(II). Secondly, the smaller the hydrolysis constant pK_1 of metal ion, the stronger its ability to form hydroxylated ions through hydrolysis (Lv and Qiu, 2020; Abo-El-Enein et al., 2017). Compared with heavy metals, the average charge of hydroxylated ions is reduced, resulting in a decrease in secondary hydration capacity, so the energy required to be fixed on the adsorbent is reduced, which it is easier to be adsorbed by the adsorbent (Liu *et al.*, 2021). The hydrolysis constant pk_1 of Cu(II) (7.34) is smaller than that of Zn(II) (8.96), so AS has a higher affinity for Cu(II). Therefore, the research results show that AS has selective adsorption for Cu(II) and Zn(II). Whether it is the maximum adsorption capacity or the priority adsorption order, Cu(II) is greater than Zn(II), which is also consistent the physical and chemical properties of Cu(II) and Zn(II).

Heavy	Ionic radius	Hydrated ion radius	Electropogativity	Hydrolysis constant	charge-diameter
Metals	(pm)	(nm)	Electronegativity	pK_1	ratio
Cu(II)	73	0.419	1.90	7.34	2.74
Zn(II)	74	0.430	1.65	8.96	2.10

Table 4-3 physical and chemical properties of Cu(II) and Zn(II)

In particular, the activity (a), activity-corrected chemical potential (μ), and adsorption binding energy (ΔG_{ads}) of AS for Cu(II) and Zn(II) were calculated based on the relevant engineering thermodynamic equations. The results show that in terms of activity, Cu(II) is 1.98×10^{-5} and Zn(II) is 1.92×10^{-5} . They

are similar but Cu(II) is slightly higher. Check the chemical potential that Cu(II) is 38.18 kJ/mol which is high energy and Zn(II) is -173.91 kJ/mol (low energy). This shows that in the binary system, AS prefers to adsorb Cu(II), by compared with Zn(II). Because the chemical potential of Cu(II) is positive, it indicates that its adsorption from solution to the AS surface is a spontaneous process (energy reduction). However, the chemical potential of Zn(II) is negative, indicating that it is already in a lower energy state in the solution and the driving force for adsorption is weak. Moreover, the adsorption binding energy of Cu(II) is -2.50 kJ/mol and Zn(II) is -1.07 kJ/mol, indicating that the driving force of Cu(II) is stronger. This is also confirmed by the Langmuir model coefficients, where the K_L of Cu(II) is 2.18 L/mg and Zn(II) is 1.23 L/mg, indicating that Cu(II) has a higher adsorption efficiency and is more easily adsorbed by AS at low concentrations. Therefore, in summary, compared with Zn(II), AS has a greater affinity for Cu(II) at low concentrations.

In order to study whether there is adsorption competition between heavy metals and other potential pollutants in storm runoff, adsorption experiments were conducted by using stimulate stormwater runoff and test the Cu(II) and Zn(II) adsorption capacity. The result is shown in Figure 4-2.



Fig. 4-2 Adsorption capacity of AS for Cu(II) and Zn(II) under different matrices

It can be seen from Fig. 4-2 that the different matrices have a certain impact on the adsorption of Cu(II) and Zn(II), especially for Cu(II). For example, comparing SMS and SSR, the adsorption capacity of AS for Cu(II) decreased by 0.02 mg/g, and the adsorption capacity for Zn(II) decreased by 0.01 mg/g. Normality tests were performed on the data of Cu(II) and Zn(II) under different matrices. The Shapiro-Wilk test significance of all Zn(II) data was p > 0.05, which was consistent with normal

distribution. So ANOVA test was performed on the Zn(II) adsorption data. According to the results of statistical analysis (Table 4-4), the ability of AS to adsorb Cu(II) in the three matrices showed a decreasing trend. The significance p less than 0.05 indicate that the adsorption capacity under these three conditions is significantly different. The adsorption difference of Zn(II) by AS is much less significant than that by Cu, but its significance p<0.05 indicates that the adsorption of Zn by different matrices is also significantly affected, although the adsorption difference in Figure 4-2 is not large. The reason for this difference may be that the presence of nutrients affects the adsorption capacity of Cu(II) and Zn(II). The research shows that the binding strength between AS and phosphorus is very high, making it is a very effective phosphorus adsorbent (Shen *et al.*, 2018; Babatunde *et al.*, 2010; Truong and Kim, 2021). It is speculated here that this may be because H₂PO₄⁻ is more likely to bind to the AS surface through electrostatic attraction, which may occupy the adsorption sites of Cu(II) and Zn(II). Similarly, Zeng *et al* (2020) found that the presence of H₂PO₄⁻ strongly affected the adsorption of Arsenic by AS. However, in general, the AS still had sufficient capacity to remove more than 95% of Cu(II) and Zn(II) due to the relatively low pollutant concentration levels in the real stormwater runoff.

Metals S		Sample number (n)	Adsorption capacity(average ± standard deviation)	Nonpara	Nonparametric tests		ANOVA	
	Solutions [*]			Н	Significance	F	Significance	
	SMS	3						
Cu	MMS	3	0.332±0.01	7.26	0.027	-	-	
	SSR	3						
	SMS	3	0.337 ± 0.0347					
Zn	MMS	3	0.332±0.005	-	-	7.1	0.026	
	SSR	3	0.331±0.0005					

Table 4-4 One-way ANOVA test for Cu(II) and Zn(II)

*: SMS refer to single metal solution, MMS refer to multi-metals solution and SSR refer to stimulate stormwater runoff

4.3.2 Different Ionic Strengths

Studies have shown that the ionic strength of the solution may affect the adsorption of heavy metals at the solid-liquid interface (Nagara *et al.*, 2022). Therefore, the effect of ionic strength in SSR on the adsorption of Cu(II) and Zn(II) was studied by changing the concentration of NaCl from 1mM to 500mM. The results are shown in the Fig. 4-3.



Fig. 4-3 Adsorption capacity for Cu(II) and Zn(II) under different ionic strength

When the solution ionic strength increases from 1 mM to 500 mM, the removal rate of Cu(II) and Zn(II) tends to decrease. For Cu(II), the adsorption capacity began to decrease significantly (from 0.45 mg/g to 0.37 mg/g) when the SSR ionic strength was greater than 10 mM, a decrease was observed for Zn(II) after 100 mM, from 0.37 mg/g to 0.32 mg/g. This may be because when the SSR ionic strength increases, a large number of positively charged Na⁺ in the solution may occupy the adsorption sites on AS and hinder the adsorption of Cu(II) and Zn(II). Similarly, Jiang et al. (2019) also observed a similar trend in the adsorption of Cu(II) and Pb(II) using Fe-Mn oxides modified AS. Kan et al. (2017) found the opposite trend when using ultrasound-modified AS to adsorb Cr(VI), which is that the higher the ionic strength, the higher the removal rate of Cr(VI). This was attributed to Cr(VI) existing in the form of anions in the solution, and the increase in Na⁺ concentration can compensate for the surface charge generated when Cr(VI) is adsorbed (Hu et al., 2014), which support the opposite effect that the presence of Na⁺ has an inhibitory effect on the same cations Cu(II) and Zn(II) adsorption. Generally, the background electrolyte of the solution is in the same flat with the outer compound, so the outer compound is much easier to be affected by the changes of ionic strength (Goldberg et al., 2007). So it can be seen that the reduction in the adsorption capacity of Cu(II) and Zn(II) indicates that the adsorption mechanism of AS may involve surface complexation. This is also consistent with the discussion on the AS adsorption mechanism in Chapter 3. However, even if the ionic strength of SSR is increased to 500 mM, the removal efficiency of Cu(II) and Zn(II) still

exceeds 95%, indicating that AS is an effective adsorption material for treating complex environmental stormwater runoff.

4.3.3 Different Background Ion Species

By using 10mM CaCl₂ and NaNO₃ to replace NaCl in SSR, we studied the effects of two common cations (Na⁺ and Ca²⁺) and two anions (Cl⁻ and NO₃⁻) as background electrolytes on the removal of Cu(II) and Zn(II) by AS. The results are shown in Figure 4-4.



Fig. 4-4 Adsorption capacity for Cu(II) and Zn(II) under different background electrolyte

The histograms of NaCl and NaNO₃ were compared to examine the effect of background anions Cl⁻ and NO₃⁻ on the Cu(II) and Zn(II) adsorption. It was found that different background anions had little effect on the adsorption for both Cu(II) and Zn(II). It is worth noting that by comparing CaCl₂ and NaCl, it was found that the presence of Ca²⁺ had a significant effect on the adsorption of Cu(II) and Zn(II) with its adsorption capacity dropping sharply from 0.4 mg/g to 0.009 mg/g for Cu(II), and from 0.33 mg/g to 0.02 mg/g for Zn(II). A similar trend was also reported for the adsorption of Th(IV) on Na-rectorite (Xu *et al.*, 2007). This phenomenon may be because the valence state of Ca(II) is the same as that of Cu(II) and Zn(II), their existence form in the solution is similar, and the concentration of Ca(II) added in SSR is much greater than that of Cu(II) and Zn(II), which cause a significant inhibition effect. Furthermore, Yang *et al.* (2009) found that compared with monovalent cations, divalent cations are more easily adsorbed on the adsorbent by electrostatic attraction, and their inhibitory effect on heavy metal removal is more obvious. Therefore, divalent Ca is more easily adsorbed on AS than monovalent Na, which shows a more obvious inhibitory effect than adding NaCl. Compared with Na⁺, Ca²⁺ can occupy two adsorption sites, so its inhibitory effect on Cu(II) and Zn(II) is more obvious. However, in general, the concentration of Ca²⁺ in actual stormwater runoff is low (around 0.2 mM) (Göbel *et al.*, 2007), which would not have a significant inhibitory effect on AS adsorption.

4.4 Summary

This chapter studies the adsorption effect of Cu(II) and Zn(II) in SSR. The effects of different SSR types, different ionic strengths and different background ions on adsorption Cu(II) and Zn(II) are mainly investigated. The conclusions are as follows:

1) There is an adsorption competition between Cu(II) and Zn(II), and Cu(II) is greater than Zn(II) in both the maximum adsorption capacity of AS and the priority adsorption order. The selective adsorption of AS indicates that the adsorption is related to the hydrolysis constant, ionic radius, hydration radius and electronegativity of heavy metals.

2) The addition of SSR and observed a not significant slight decrease in the removal of heavy metals, but the removal efficiency of Cu(II) and Zn(II) in SSR still exceeded 95%, indicating that AS can handle variable stormwater runoff.

3) When the solution ionic strength increases from 1 mM to 500 mM, the adsorption capacity of Cu(II) decreases from 0.45 mg/g to 0.37 mg/g, and the adsorption capacity for Zn(II) decreases from 0.37 mg/g to 0.32 mg/g.

4) Compared with Na⁺, Cl⁻ and NO₃⁻, Ca²⁺ has a very obvious inhibition on the adsorption capacity of AS. Its adsorption capacity for Cu(II) dropped sharply from 0.4 mg/g to 0.009 mg/g, and its adsorption capacity for Zn(II) dropped from 0.33 mg/g to 0.02 mg/g. This is related to the high concentration of Ca²⁺ in SSR and the stronger electrostatic attraction of divalent cations. However, according to the investigation of actual stormwater runoff, the inhibitory effect of Ca²⁺ concentration level for AS adsorption is not very obvious.

5) In conclusion, according to the investigation of adsorption competition, the variable stormwater runoff does not have much effect on the adsorption of Cu(II) and Zn(II) by AS which can be used as

an effective adsorbent for treating stormwater runoff for the subsequent dynamic adsorption experiments.

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CHAPTER 5 DYNAMIC ADSORPTION EXPERIMENTS

5.1 Introduction

Studying the actual application performance of AS is key to exploring the reuse value of AS. In the previous chapters, the physical and chemical properties, adsorption mechanism and theoretical adsorption capacity of AS were studied through batch experiments. Furthermore, the simulated runoff was used in batch experiments to study the possible adsorption competition between pollutants commonly present in runoff.

Batch studies estimate maximum sorption capacity under optimum conditions and deduce any limits on sorption processes. Columns link sorption potential to flow under operational conditions which more closely represent deployment. In order to achieve the column study, this chapter investigated the dynamic removal of metals by AS, considering effects such as different packing heights and flow rates, using Cu(II) and Zn(II) in stimulated runoff. Several common breakthrough curve models such as Thomas (Thomas, 1944), Yoon-Nelson (Yoon and Nelson, 1984), Bohart-Adams (Bohart and Adams, 1920) and Bed-depth/service time (Hutchins, 1973) model were used to fit the experimental data and calculate the relevant parameters. The prospect of applying AS for the dynamic adsorption of simulated runoff was analyzed using several model parameters. Finally, the risk of re-release of adsorbed Cu(II) and Zn(II) from AS under dynamic flow conditions was evaluated.

5.2 Methodology

5.2.1 Column Design

The column experiment was carried out at room temperature $(25 \pm 8 \text{ °C})$ and two sets of polyvinyl chloride (PVC) columns with a height of 15cm and inner diameter of 7.5cm were set up (Fig. 5-1). There are water inlets and outlets at the top and bottom of the column. Before the experiment, the inner wall of the column was polished with coarse sandpaper to reduce the potential for sidewall flow and leakage which may occur during the experiment. There was no evidence of this effect from the results.



Fig. 5-1 Column setup with alum sludge loaded (arrows represent the direction of flow)

The packing from bottom to top consists of a support layer, transition layer and packing layer. The packing methods are shown in Table 5-1. According to the results of adsorption isotherms in Chapter 3, the theoretical adsorption capacities of AS for Cu(II) and Zn(II) are 22.88 mg/g and 8.74 mg/g, respectively. Because the AS adsorption capacity for Zn(II) is smaller than that of Cu(II), Zn(II) may be more easily to saturation and penetrate earlier in the dynamic experiment. Therefore, considering the effectiveness of dynamic filtration, the adsorption capacity of Zn(II) should be selected as a design reference. Based on the theoretical adsorption capacity, in order to completely adsorb 50 L simulated runoff solution with a Zn(II) initial concentration of 2 mg/L should have an inner diameter 8.2 cm and length 16.4 cm column. However, due to the long production time of making column, the actual column size was designed before the conclusions of Chapter 3 were available (Table 5-1). The support layer supports the overall filter bed and is filled with large gravel of 2 cm nominal diameter. In order to prevent the filter media leaking or getting stuck in large gravel, 0.5 cm glass beads (GB) were used to fill 1cm as a transition layer. Through filtration experiments, it was found that fine powder AS (< 0.15mm) is relatively impermeable. Balkaya (2015) showed that the hydraulic conductivity (HY) of AS (< 0.06mm) is about 10^{-8} cm/s and considered AS has impervious nature. Therefore, in order to improve the water permeability, AS with a particle size of 1-2 mm was selected

as the filler media in the column. When filling the column, the media was distributed and compacted every 1cm, repeated insteps until he designed depth was reached.

Column parameter	Theoretical column	Actual column
Length (cm)	16.4	15
Inside diameter (cm)	8.2	7.5
Cross sectional area of column (cm ²)	52.78	44.16
Support layer thickness (cm)	1	1
Transition layer thickness (cm)	1	1
Alum sludge size (mm)	1-2	1-2

 Table 5-1 Filter column design parameters

5.2.2 Dynamic Adsorption Experiment

Different packing height. Fig. 5-2 shows the change of HY at different overall packing heights and different mixing ratios of AS and GB. It can be seen that the average HY is the largest when the overall packing height is 3.8cm, and basically the same as values for packing heights of 7.6cm and 11.4cm. The depth of 3.8 cm is not convenient for controlling the filtration rate because its HY is too high. Therefore, this column experiment was filled to 7.6cm. The HY data shows that a packing height of 7.6cm will not clog the column. It saves AS compared to the 11.4cm packing height. Moreover, based on the 7.6cm packing height, as the AS proportion increases from 0% to 100%, the HY fluctuates in value. In the experiments with different filling heights (chapter 5.3.2), an AS packing height of 7.6cm, 3.8cm and 1.8cm was selected. These correspond to 100% AS, 50% AS+50% GB and 20% AS+80% GB. This is because this packing method includes the maximum HY (50% AS+50% GB) and average HY (20% AS+80% GB) in the overall 7.6 cm packing height. In order to maintain the consistency of HY in the column, 1.5 mm GB + 1-2 mm AS were used to fill the column to a total depth of 7.6 cm.

The relationship between Darcy flow resistance (Eq. 5-1) and AS dosage was used to design the AS loading in the filter column.

$$R_{Darcy} = \frac{L}{K*A}$$
(5-1)

Where, L is the filter media packing height (cm); A is the cross-sectional area of the column (cm²) and K is the permeability coefficient of the medium (cm/s). In its original form, Darcy's law describes the relationship between flow rate and pressure gradient (Noreen *et al.*, 2023). By introducing the fixed permeability k, the viscosity of water can be included in the formula. Therefore, the modified Darcy formula is:

$$\mathbf{K} = \frac{k * \rho g}{\mu} \tag{5-2}$$

$$R_{Darcy} = \frac{\mu * L}{k * \rho g * A} \tag{5-3}$$

Where k is the fixed permeability (m²), which depends on the pore structure of the AS; μ is the dynamic viscosity of water (Pa·s); ρ is the density of water (kg/m³) and g is the gravity acceleration (9.81 m/s²). The relationship between Darcy flow resistance and AS volume are showed below.



Fig. 5-2 Variation in Darcy flow resistance (s/cm³) of columns packed with different heights and mixing ratios of AS and GB

For dynamic adsorption, the packing height and flow rate of the column have a significant impact on the adsorption process (Xia and Wang, 2014). The dynamic adsorption effect of AS was studied by changing the operating conditions of the filter column. According to the results above (Fig. 5-2), the total height of the filter bed was fixed at 7.6 cm, and the effect of different AS packing height was achieved by changing the ratio of AS and GB. As show in Table 5-2, the AS packing heights were set to 7.6 cm, 3.8 cm, and 1.8 cm, respectively, and the corresponding dry AS quality were 160 g, 85 g, and 29 g. The stimulated runoff was continuously fed into the top of the column at a flow rate of 5.2 ml/min, which reflects the contact time of 60min. According to the kinetic data in the batch experiments, the contact time of 60min ensures the removal efficiency of AS for Cu(II) and Zn(II) is above 90%, and also meets the minimum permeability of the basin of 0.5 cm/h (Soleimanifar *et al.*, 2019).

Parameters	Packing h Alum sludge	eight (cm) Glass beads	Bed volume rates (BV/min)	Metal concentration (mg/L)
Packing height (cm)	7.6	0	0.07	
	3.8	3.8	0.02	2
	1.8	6.8	0.01	
Flow rate (mL/min)			0.02	
	7.6	0	0.03	2
			0.07	

 Table 5-2 Dynamic adsorption design

Different flow rates. Since the application scenarios of filter systems and the intensity of each rainfall event are different, studying the pollutant removal efficiency under different flow rates is key to guiding the application of AS in filtration system. When the column was filled with 7.6cm of the AS media, a peristaltic pump (Cole-Parmer) was used to maintain the flow rate at 0.02 BV/min, 0.03 BV/min and 0.07 BV/min, corresponding to empty bed contact time (EBCT) of 60 min, 30 min and 15 min, respectively. The EBCT is the time required for water to completely pass through a filter column, regardless of the porosity of the filter media and the equation is shown in Eq. 5-4 (Du *et al.*, 2018). Fig. 5-3 shows the calibration of the peristaltic pump with the tube diameter to confirm that the designed maximum and minimum flow rates can meet the filtration rate requirements. It can be seen that when using L/S 16 tube, the flow rate of the pump at the minimum and maximum speed is from 5.2 mL/min to 481.4 mL/min, which meets the design flow rate (5.2-22.4 mL/min).

$$EBCT = \frac{V_c}{Q}$$
(5-4)

where, V_c (mL) and Q (mL/min) represent the volume of the filter media and the flow rate of the liquid, respectively.


Fig. 5-3 Peristaltic pump flow rate calibration

Water inlet and outlet of the column. The simulated stormwater runoff (SSR) in Chapter 4 was used as the inlet water quality for the dynamic adsorption experiment (Table 5-3). At the beginning of the experiment, DI water was gradually introduced from the top to cover the entire column and the column gently tapped to eliminate bubbles, and then simulated runoff was introduced to carry out the dynamic adsorption experiment. Since no suspended solids or complexes are added to the simulated rainwater runoff, the filtration did not change the outlet flow and head loss due to blockage. Effluent samples were collected, filtered through a $0.45 \,\mu m$ syringe filter, and analyzed for Cu(II) and Zn(II) concentrations by ICP-OES.

Elements	Concentration (mg/L)	Source
Cu	2	$CuSO_4 \cdot 5H_2O$
Zn	2	ZnNO ₃ ·6H ₂ O
Phosphate	1	NaH ₂ PO ₄
NH4 ⁺ -N	25	NH ₄ Cl
NO ₃ ⁻ -N	6	NaNO ₃
Ionic strength	584	NaCl
Buffer solution	252	NaHCO ₃

Table 5-3 Simulated stormwater runoff (SSR) recipe

The removal rate (% Removal) of AS is calculated by the following formula:

%Removal =
$$\frac{(C_0 - C_t)}{C_0} * 100$$
 (5-5)

5.2.3 Breakthrough Curve and Dynamic Adsorption Model

The breakthrough curve reflects the dynamic adsorption behavior of Cu(II) and Zn(II) on AS, which is expressed as the ratio of the inlet and the outlet Cu(II) or Zn(II) concentration (C_t/C_0) changing with time. The breakthrough time is defined as the time when the effluent metal concentration reach 10% of the influent metal concentration and the exhaustion point is defined as the time when the effluent metal concentration is greater than 95% of the influent metal concentration (Ren, 2014).

The column experiment cannot fully reflect the results of the field study due to the scale of the experiment (Wang, 2017). In this study different models - Thomas (Thomas, 1944), Yoon-Nelson (Yoon and Nelson, 1984), Bohart-Adams (Bohart and Adams, 1920) and Bed-depth/service time (BDST) (Hutchins, 1973) - were used to evaluate the dynamic adsorption data of Cu(II) and Zn(II) and predict the application prospects of AS in a filtration system. The application of the different models is described below.

Thomas model. This model is currently the most widely used to describe the process of dynamic adsorption (Tiwari *et al.*, 2007; Chu, 2010; Hasan *et al.*, 2010; Zach *et al.*, 2011; Chen *et al.*, 2012; Du *et al.*, 2016; Guo *et al.*, 2017; Mosai *et al.*, 2021). It is derived from the Langmuir isotherm and second-order reversible reaction kinetic theory (Ismael *et al.*, 2010). The Thomas model considers that all adsorption is feasible, as it assumes that the adsorption process follows the Langmuir adsorption isotherm and the model also assumes that the adsorption rate is controlled by both mass transfer and surface reaction (Ji *et al.*, 2024). It is applicable to some adsorption processes that do not contain external and internal diffusion limitations (Nguyen *et al.*, 2017). Thomas's equation is as follows (Eq. 5-6):

$$\frac{c_t}{c_0} = \frac{1}{1 + \exp(\frac{k_T q_0 m}{v} - k_T C_0 t)}$$
(5-6)

where, C_t (mg/L) and C_0 (mg/L) represent the effluent and influent Cu(II) and Zn(II) concentrations at time t (min), respectively; k_T is the Thomas rate constant (L/mg·min); q_0 is the equilibrium adsorption amount of the adsorbent (mg/g); m represents the mass of the adsorbent in the column (g); t is the duration of the entire adsorption process (min); v is the volumetric flow rate of the column (mL/min).

Bohart-Adams model. This is typically used to analyze the kinetics of the initial stage of dynamic adsorption (Saleh *et al.*, 2012; Gu *et al.*, 2013; Mohammad *et al.*, 2014; Omitola *et al.*, 2022;). The model is based on surface reaction rates and assumes that the adsorption rate is proportional to the number of available sites on the adsorbent (Berna, 2022; Hutchins, 1973). The equation is as follows (Eq. 5-7):

$$\frac{C_t}{C_0} = \exp(K_{AB}C_0 t - K_{AB}N_0 \frac{Z}{F})$$
(5-7)

where, C_t (mg/L) and C_0 (mg/L) represent the effluent and influent Cu(II) and Zn(II) concentrations at time t (min), respectively; K_{AB} (L/mg·min) is the Bohart-Adams rate constant which represents the rate of the adsorption process in the column; Z (cm) and F (mL/min) are the depth of the packing height and the column filtration rate, respectively; N_0 (mg/L) is the saturated adsorption capacity per unit volume of the adsorbent in the column, which is the maximum mass of Cu(II) and Zn(II) fixed by the AS; T (min) is the service time.

Yoon-Nelson model. This model describes the breakthrough of the adsorbate fixed on the adsorbent (Nkem *et al.*, 2011; Olivares *et al.*, 2013; Ai *et al.*, 2014;). It assumes that there is a proportional relationship between the adsorption probability of the adsorbate and the probability that each adsorbate may be adsorbed (Yoon and Nelson, 1984). The Yoon-Nelson model is a simple theoretical model that can effectively describe the dynamic adsorption of the adsorbate (Berna, 2022). The equation is as follows:

$$\ln \frac{c_t}{c_0 - c_t} = k_{\rm YN} t - \tau k_{\rm YN}$$
(5-8)

where, C_t (mg/L) and C_0 (mg/L) represent the effluent and influent Cu(II) and Zn(II) concentrations of column at time t (min), respectively; k_{YN} (1/min) represents the Yoon-Nelson rate constant and τ (min) is the time required to penetrate 50% of the adsorbent.

Bed-depth/service time (BDST) model. This is a simple model that predicts packing depth and the time until filter media exhausted (defined as column service time) are based on inlet water concentration and adsorption conditions (Kumar *et al.*, 2006; Rangabhashiyam *et al.*, 2016; Zheng *et al.*, 2018). It is often used to help design and optimize filter system operating parameters (Chen *et al.*, 2011; Sweta *et al.*, 2017). The BDST model assumes that the adsorption rate is controlled by the surface reaction between the adsorbate and the unused adsorbent, and ignores the mass transfer resistance (Hutchins, 1973; Qaiser *et al.*, 2009; Ghosh *et al.*, 2014). There is mass transfer resistance in the adsorption process, containing external resistance (membrane resistance) and internal resistance (Hovsepyan and Bonzongo, 2009). In the adsorption process from liquid to solid, the fluid film exits resistance to the mass transfer of adsorbate molecules, and the adsorbate molecules must pass through this fluid film to reach the outer surface of the adsorbent (Inglezakis *et al.*, 2020). The resistance of the fluid film depends on the concentration gradient, flow rate and size of the adsorbent (Inglezakis *et al.*, 2020). Moreover, When the adsorbate molecules overcome the fluid film and reach the surface of the adsorbent to reach the adsorption site (Wernke *et al.*, 2018). Therefore, the structure of the pores of the adsorbent will generate internal resistance to the

adsorbate molecules (Wernke *et al.*, 2018). In other words, the adsorption rate is limited by intraparticle diffusion (Hovsepyan and Bonzongo, 2009). In most adsorption modeling studies, mass transfer resistance is usually neglected (Inglezakis *et al.*, 2020). Based on the neglect of mass transfer resistance, BDST model assumes a linear relationship between packing depth and column service time (Du *et al.*, 2018). Therefore, if adsorption data for various packing depth are known, the model can be used to predict adsorption performance for any packing height (Sun *et al.*, 2014). The BDST equation is shown below (Eq. 5-9):

$$t = \frac{N_0}{C_0 U_0} Z - \frac{1}{k_a C_0} \ln(\frac{C_0}{C_t} - 1)$$
(5-9)

where, C_t (mg/L) and C_0 (mg/L) represent the effluent and influent Cu (II) and Zn (II) concentrations of column at time t (min), respectively; U_0 (cm/min) is the flow rate of the filter column; K_a (L/mg min) is the rate constant of the BDST model; t (min) is the time to reach the breakthrough point; Z (cm) is the depth of the column and N_0 is the saturated adsorption capacity of the adsorbent (mg/L).

The performance of different models was reviewed to compare the error between the experimental data and model data. The root of the mean square error (RMSE) was applied to determine the best fitting model (Eq. 5-10).

RMSE =
$$\sqrt{\frac{\sum_{j=1}^{n} (M_j - E_j)^2}{n}}$$
 (5-10)

where, E_j is the experimental value in the adsorption process, while M_j is the model value, and n is the total number of measurements.

5.2.4 Dynamic Release of Heavy Metals Accumulated in AS

When the metal adsorption capacity of AS is saturated, heavy metals fixed by AS may have a risk of being released again (Wang, 2019). The pH value of tap water was adjusted to pH around 6.5 using HCl and NaOH, to simulate the runoff in the late rainfall event and research the effects of different flush conditions on the release of heavy metals accumulated in the AS.

In order to study the effect of flush time, tap water was injected into the column at a rate of 0.07 BV/min and water samples were collected from the outlet at the bottom of the column every 10 minutes. Furthermore, in order to study the influence of flush intensity, the filtration rates of the filter column were set to 0.02 BV/min, 0.03 BV/min and 0.07 BV/min, respectively, and water samples were collected from the outlet at the bottom of the filter column every 10 minutes. All collected samples were filtered through a 0.45μ m syringe filter, and the concentrations of Cu(II), Zn(II) and Al(III) were analyzed by ICP-OES. The average concentration of the effluent is calculated by using the event mean concentration (EMC) (Eq. 5-11):

$$EMC = \frac{M}{V} = \frac{\int_0^T C_t Q_t dt}{\int_0^T Q_t dt}$$
(5-11)

where, M (g) and V (L) are the total amount of heavy metals adsorbed by AS and the total volume of simulated runoff filtered by AS, respectively; C_t (mg/L) is the effluent heavy metal concentration at time t; Q_t (L/min) is the total filtration volume and T (min) represents the total filtration time.

5.3 Results and Discussion

5.3.1 Dynamic Adsorption of Cu(II) and Zn(II) by AS

Testing the dynamic adsorption capacity of AS is key to verifying whether it has application potential. Figure 5-4 shows the dynamic adsorption curve of Cu(II) and Zn(II).



Fig. 5-4 Dynamic breakthrough curves for Cu(II) and Zn(II) (Packing height 7.6cm; Flow rate 0.02 BV/min; Media ratio 100%AS)

In the experiment of dynamic simultaneous removal of Cu(II) and Zn(II), the breakthrough time of Cu(II) and Zn(II) was 180 min and 150 min, respectively. It is worth noting that after the column infiltration, the effluent concentration of Zn(II) increased faster than that of Cu(II) and Zn(II) reached saturation after 240 min. It indicates that there may be adsorption competition within the column and the filter column has a higher selectivity for Cu(II) (Wang, 2017). The exhaustion time of Cu(II) and Zn(II) in the column was 570 min and 240 min, respectively. The exhaustion time of Zn(II) in the column was earlier than that of Cu(II). It is consistent with the results of the batch experiment that the adsorption amount of Cu(II) by AS was greater than that of Zn(II).

It should be noted that in the experiment we found that the breakthrough curve of Cu (II) increased in a stepped feature. This may be due to the heterogeneity of the adsorption surface, which means that Cu (II) adsorption on different AS surfaces may produce multi-level breakthrough curves (Yan et al., 2023). In other words, the surface of AS contains a variety of adsorption sites, high-affinity sites such as aluminum oxide functional groups, which conformed in section 2.3.5, preferentially adsorb Cu (II) and are quickly saturated. Low-affinity sites such as internal pores or weak binding sites begin to adsorb after the high-affinity sites are saturated, and the adsorption rate slows down, causing the curve to rise again. This leads to the emergence of multi-level breakthrough curves. This suggests that AS may have regions with different adsorption characteristics that the distribution of adsorption sites is uneven. One side may be rich in hydroxyl groups that can quickly adsorb Cu (II) through surface complexation. However, some surfaces that come into direct contact with water may not have a large number of hydroxyl groups, Cu (II) needs to overcome the layer diffusion resistance to enter the pores, so the adsorption rate is slow. For example, Tang et al., (2019) used the Density Functional Theory (DFT) model to calculate the adsorption behavior of calcium-based adsorbents for adsorb oxidized mercury and predicted that the reactivity of O2- and Ca2+ on different surfaces of calciumbased adsorbents is closely related to their coordination numbers and mercury has four different adsorption modes with different affinities on calcium-based surfaces. Similarly, Zeng et al. (2020) also found this trend. When using granular AS to adsorb 0.15 mg/L As(V), the effluent concentration of As(V) also showed a stepped feature upward after filtering 1200 bed volumes (Zeng et al., 2020). Babatunde et al. (2009) used unmodified AS and Cheng et al. (2018) used modified AS in the column experiments for the range of 2-10 mg/L phosphorus adsorption, and their effluent concentrations and removal rates also showed a stepped feature. In addition, the formation of the plateau may also be related to multilayer adsorption, which is when the monolayer adsorption reaches saturation, multilayer adsorption of Cu (II) may form at some sites on the AS surface. For example, Ying et al., (2020) used magnetic adsorbents to remove selenium from wastewater and found that when the adsorbent surface reached monolayer adsorption saturation, the adsorption of selenium mainly entered the mesopores through mass transfer and formed multilayer adsorption on the adsorbent surface which also found a plateau phenomenon in the breakthrough curve. The appearance of the plateau prolongs the adsorption saturation time of Cu (II). As can be seen from Fig. 5-4, the formation of the plateau increases the exhaustion time of Cu (II) by about 200 minutes. Adsorption competition between simulated stormwater runoff may also be the reason for the step-like increase in adsorption. For example, Rangsivek and Jekel. (2007) found that the breakthrough curve of Cu (II) showed a step-like upward trend when studying the effect of natural organic matter on the removal efficiency of Cu (II) and Zn(II) in roof runoff. He believed that this was mainly caused by the competition between natural organic matter and Cu (II) (Rangsivek and Jekel. 2007). Xiong et al., (2021) also found similar results when using modified biochar to adsorb Cu(II), Zn(II), Pb(II) and Cd(II) in runoff. The competition between different heavy metals and the competition between organic matter and Cu (II) led to the

fluctuation of column Cu (II) effluent concentration (Xiong *et al.*, 2021). Finally, the uncertainty due to the low concentration of Cu (II) in runoff may be one of the possible reasons for the outflow fluctuation. Similarly, Ernst *et al.*, (2015) also found a plateau phenomenon when using different media to adsorb Cu (II) ($36 \mu g/L$) in simulated highway runoff. The breakthrough curve of the simulated roadway stormwater runoff column experiment with 100 $\mu g/L$ Cu (II) also found a fluctuating upward trend (Haile and Fuerhacker. 2018)

In summary, the stepped feature rise in the breakthrough curve of Cu(II) is due to the unavoidable experimental error caused by the long service time of the column need to multiple refill the low-concentration heavy metals solution in the inlet tank. However, the overall trend of the Cu(II) breakthrough curve is similar to that of Zn(II) and can be used for further analysis.

NaCl is a tracer in which the Cl⁻ is usually not adsorbed. Adding it after the column is saturated can reflect the flow characteristics of the fluid within the packed media. It can be seen from Fig. 5-4 that the breakthrough time of NaCl is very short, about 5 minutes. Compared with Cu(II) and Zn(II), their breakthrough times are all after 150 min. It demonstrates that the column has a certain adsorption capacity for Cu(II) and Zn(II), which makes Cu(II) and Zn(II) have a longer breakthrough time. In addition, when the flow rate was 0.02 BV/min, the dynamic adsorption breakthrough and exhaustion times of the column for Cu(II) were 180 min and 570 min, respectively. This indicates that when the column packing 160g AS, it will break through when the output reaches 936mL and be exhausted at 2964 mL. Similarly, for Zn(II), the column reached a breakthrough point at 780 mL. It was exhausted at 1248 mL, and no further adsorption of Cu(II) and Zn(II) was observed after reaching the exhaustion point. This shows that when treating 2mg/L Cu(II) and Zn(II) solutions, the maximum capacity of AS for Cu(II) is 18.5mL/g, and for Zn(II) is 7.8mL/g, which can be used as a reference for the application of on-site runoff filtration systems.

The shape of the breakthrough curve is related to the filtration rate, initial solution concentration and packing height of the filter colum (Saadi et al., 2015a; Saadi et al., 2015b). In order to deeper understanding of the mass transfer process of Cu(II) and Zn(II) in the column, a one-dimensional model was used to analyze the axial dispersion coefficient (Saadi et al., 2015a; Saadi et al., 2015b). According to the principle of mass transfer, the element accumulation can be expressed as the accumulation of the internal volume fluid and the accumulation of the pore fluid (Yang *et al.*, 1996; Rai and Ish. 2007), and its expression is:

$$-D_{z}\frac{\partial^{2} c}{\partial z^{2}} + \frac{\partial(\mu c)}{\partial z} + \frac{\partial c}{\partial t} + \frac{1-\varepsilon}{\varepsilon} \left(\varepsilon_{p} \frac{\partial c_{p}}{\partial t} + \rho_{p} \frac{\partial q}{\partial t} \right) = 0$$
(5-12)

Where, D_z is the axial dispersion coefficient (m²/s); μ is the fluid velocity (m/s); ϵ is the intraparticle void fraction of bed; ϵ_p is the porosity of the adsorbent; C and C_p are the adsorbate concentration in

the bulk fluid (mol/L) and adsorbate concentration in the pore (mol/L), respectively. t is the flow time (s), and z is the axial step size after dividing the column length into n grids.

The mass transfer rate can be expressed by Ni, and the equation is as follows (Saadi et al., 2015b):

$$N_i = \rho_p \frac{\partial q}{\partial t} = K_i (q_e - q) \tag{5-13}$$

Where, ρ_p is adsorbent particle density (mg/L); K_i is lumped mass transfer coefficient; q is amount of Cu(II) and Zn(II) adsorbed per unit weight of AS (mg/g) and qe is equilibrium adsorption capacity of adsorbent (mg/g).

In order to calculate the overall mass transfer coefficient, the internal and external mass transfers need to be added together (Saadi et al., 2015b):

$$\frac{1}{K_{overall}} = \frac{R_p}{3k_f} + \frac{R_p^2}{15D_p^e \varepsilon_p}$$
(5-14)

Where, $K_{overall}$ is the total mass transfer coefficient (1/s); R_p is the particle radius of the adsorbent (m); k_f is the external mass transfer coefficient (m/s) and D_p^e is the effective pore diffusivity coefficient (m²/s). Since the diameter of the adsorbate molecules is much smaller than the adsorbent pore size, Knudsen diffusion is neglected (Ghorai and Pant. 2004). Therefore, the effective pore diffusivity coefficient (D_p^e) can be calculated using the following formula (Saadi et al., 2015b):

$$D_p^e = \frac{D_m}{\tau_p} \tag{5-15}$$

Where, D_m is the molecular diffusion coefficient (m²/s) and τ_p is tortuosity factor. Since the pore path of the adsorbent is not straight, the tortuosity factor (τ_p) needs to be calculated according to the following formula (Wakao and Funazkri. 1978):

$$\tau_p = \frac{1}{\varepsilon_p} \tag{5-16}$$

Since in Eq5-13, k_f is unknown, it can be estimated using the empirical formula proposed by Ghorai and Pant. (2004) that using activated alumina to adsorb synthetic fluoride:

$$Sh = \frac{k_f d_p}{D_m} = 1.85 \left(\frac{1-\varepsilon}{\varepsilon}\right)^{0.33} (R_e^{0.33} * S_c^{0.33})$$
(5-17)

Where, R_e and S_c are Reynolds number and Schmidt number respectively. This relation is valid for R_e < 40, which this project calculates Re=1.58 to meet the formula requirements.

According to Eq5-14, the molecular diffusion coefficient (D_m) is unknown and can be estimated by the Stokes-Einstein equation (Mason. 2000):

$$D_m = \frac{kT}{6\pi\eta r} \tag{5-18}$$

Where, k is the Boltzmann constant $(1.38 \times 10^{-23} \text{ J/K})$; T is the temperature (298 K); η is the viscosity of water (0.001 Pa·s) and r is the hydrated ion radius of the heavy metal (m). Due to the low fluid velocity, it is assumed that axial diffusion is the main diffusion process in the filter column (Ghorai and Pant. 2004), and the empirical formula is:

$$\frac{D_z}{D_m} = \gamma_1 + \gamma_2 \frac{dpu}{D_m} \tag{5-19}$$

Among them, $\gamma 1=20/\epsilon$ and $\gamma 2=0.5$. This result is selected based on the best empirical coefficients proposed by Saadi *et al.*, (2015).

By calculating the above equations, the axial diffusion coefficient and mass transfer coefficient of AS for Cu(II) and Zn(II) can be obtained. It can be seen from the formula above that the size of the filter media will change the fluid state in a filtration system. For example, the Re=1.58 calculated here represents laminar flow in the filter column, and the diameter of the filter media also affects its mass transfer and diffusion coefficients. Therefore, when selecting the filter media diameter, the efficiency of mass transfer and diffusion as well as the permeability of the filter media should be considered. It was estimated that the axial diffusion coefficients of Cu(II) and Zn(II) were 4.70×10^{-8} m²/s and 4.57×10^{-8} m²/s, respectively, and the total mass transfer coefficients were 1.41×10^{-2} 1/s and 1.36×10^{-2} 1/s, respectively. Among them, the diffusion coefficient reflects the diffusion ability of the substance in the flow direction (Saadi et al., 2015a). The larger the value, the faster the substance diffuses in the axial direction (Saadi et al., 2015a). The axial diffusion coefficient of Cu(II) is greater than that of Zn(II), indicating that under the same conditions, the axial diffusion rate of Cu(II) ions in the filter column will be faster than that of Zn(II) ions. This may be related to the different physical properties of these ions that discussed in Chapter 4. From the mass transfer coefficient, the total mass transfer coefficient of Cu(II) is slightly higher than that of Zn(II), which means that the overall mass transfer efficiency of Cu(II) is higher than that of Zn(II) during the adsorption process. This also reflects that the adsorption capacity of the filter column for Cu(II) is greater than Zn(II).

5.3.2 Different Packing Height

The AS packing height will directly affect the breakthrough time of the column (Wang, 2019). Fig. 5-5 shows the effect of different packing heights on the adsorption of Cu(II) and Zn(II) by AS. As the packing height decreased from 7.6cm to 1.8cm, the breakthrough times decreased from 180 min to 20 min for Cu(II) and from 140 min to 25 min for Zn(II). The exhaustion time decreased form 570 min to 70 min for Cu(II) and from 240 min to 55 min for Zn(II). As the packing height decreases, the breakthrough curve becomes steeper. This is mainly because at the same infiltration rate, the reduction in the amount of packed media means that the contact time between heavy metals and AS is shorter, so Cu(II) and Zn(II) have less chance to diffuse into the AS (Gupta and Badu, 2009). In addition, the reduction in packing height leads to a decrease in the adsorption sites (ie. capacity) available for Cu(II) and Zn(II), thus accelerating the AS exhaustion time (Berna, 2022).



(b)

Fig. 5-5 Breakthrough curves for columns with different packing heights (a) Cu(II) (b) Zn(II) (Flow rate 0.02 BV/min; Cu(II) and Zn(II) inlet concentration 2mg/L; Packing method: 100%AS (7.6cm), 50%AS+50%GB (3.8cm), 20%AS+80%GB (1.8cm))

It is also indicated that the total volume of Cu(II) and Zn(II) treated by AS increases with an increase of packing depth. It can be seen from Fig. 5-6 that when the packing depth increases from 1.8 cm to 7.6 cm, the exhaustion volume increases significantly from 364 mL to 2964 mL for Cu(II) and 286 mL to 1248 mL for Zn(II). This can be regarded as a simple and direct signal for replacing the AS after exhaustion. For example, a binary micro-pollution filtration system with Cu(II) and Zn(II) as the main pollutants is proposed as an example. When the infiltration rate is fixed, the dosage of AS in the filtration system can be used as a parameter to predict the saturation time and the maximum Zn(II) processing capacity can be considered as an indicator to replace or regenerate the AS.



(b)

Fig. 5-6 Maximum water treatment capacity of AS with different packing heights (a) Cu(II) (b) Zn(II) (Flow rate 0.02 BV/min; Cu(II) and Zn(II) inlet concentration 2mg/L; Packing method: 100%AS (7.6cm), 50%AS+50%GB (3.8cm), 20%AS+80%GB (1.8cm))

In summary, column packing height has a positive effect on the removal performance and exhaustion time for Cu(II) and Zn(II) attenuation. However, many studies have shown that excessive packing heights will increase the fluid permeability which is not conducive to adsorption (Balkaya, 2015; Ahmed *et al.*, 2022; Yang *et al.*, 2023;). Therefore, the key to engineering application is to select the appropriate packing height based on the raw water quality and the dynamic filtering characteristics of AS. For example, when we use 1-2 mm particle AS to filter stormwater runoff, in filtration systems of different sizes, it is recommended that the ratio of the design depth of the filtration system and the AS packing depth should be around 2:1. On the one hand, this ratio ensures that the runoff can infiltrate smoothly while allowing sufficient contact time between solids and liquids. On the other hand, it will not increase the fluid permeability or cause material waste if overfilling.

5.3.3 Different Flow Rate

Fig. 5-7 shows the changes in the breakthrough curves of Cu(II) and Zn(II) at different infiltration rates. Similar to the packing height, different infiltration rates directly affect the contact time between heavy metals and AS. It is obvious that as the infiltration rate (dosing rate) increases, the time it takes for the adsorbent to reach saturation is significantly reduced. When the infiltration rate increases from 0.02 BV/min to 0.07 BV/min, it means that the residence time of Cu(II) and Zn(II) in the column is reduced from 60min to 15min and the corresponding breakthrough and exhaustion time are reduced. For example, when the flow rates were 0.02 BV/min, 0.03 BV /min and 0.07 BV/min, the breakthrough time of Cu(II) was 180 min, 25 min and 15 min, and the exhaustion time was 570 min, 250 min and 50 min, respectively. The breakthrough time of Zn(II) was 140 min, 15 min and 5 min, and the exhaustion time was 240 min, 70 min and 30 min, respectively. This is because the flow rate affects diffusion and mass transfer efficiency, the contact time between the simulated runoff and the AS is insufficient, the utilization rate of the AS per unit weight is low which may cause the adsorption effect decreases (Soleimanifar, 2018; Yang et al., 2023;). Han et al. (2009) believed that when the flow rate increases, the membrane mass transfer resistance on the adsorbate surface decreases and the solution transmission distance is shortened, so the time for Cu(II) and Zn(II) stay and adsorb on the AS surface is reduced. This leads to a shortened saturated time of AS, thus affecting the dynamic adsorption performance of AS.



Fig. 5-7 Column breakthrough curves with different flow rates (a) Cu(II) (b) Zn(II) (Packing height 7.6cm; Cu(II) and Zn(II) inlet concentration 2mg/L; Media ratio 100%AS)

From the total volume of simulated runoff treated (Fig. 5-8), although the infiltration rate increased, the total filtration volume of the column was exhausted and tended to decrease. For example, as the infiltration rate increases, the total treatment volumes for Cu(II) are 2964 mL, 2800 mL and 1120 mL, respectively, and for Zn(II) are 1248 mL, 784 mL and 672 mL, respectively. This also can be used as

a reference for engineering applications. When the AS dosage is determined, the filtration rate can be used as a parameter to predict the saturation time of the AS and the maximum Zn(II) adsorption capacity can be considered as an indicator for filtration system replacement or regeneration.



(b)

Fig. 5-8 Maximum water treatment capacity of AS with different flow rates (a) Cu(II) (b) Zn(II) (Packing height 7.6cm; Cu(II) and Zn(II) inlet concentration 2mg/L; Media ratio 100%AS)

In summary, the slower the infiltration rate, the better the filtration performance of the column, but also larger dispersion. According to the results of the kinetic study in Chapter 3, the optimal contact time is about 200 minutes. When the contact time of the column exceeds 200 minutes, the AS adsorption performance will not be increased, and also an infiltration rate which is too slow may lead

to a decrease in treatment efficiency. For example, Long *et al.* (2012) used modified peanut shells to dynamically adsorb cadmium from water and found that the flow rate was too low. Although the contact time of cadmium with the adsorbent was longer, the breakthrough time was too long, which they consider was not suitable for practical application (Long *et al.*, 2012). The investigation showed that Elkhatib *et al.* (2015) used AS from an Egyptian water purification plant to adsorb As(V) and found that the adsorption rate of AS on arsenic exceeded 80% at 200 min. Moreover, AS from a water purification plant in Italy reported an adsorption equilibrium time of approximately 200 min for Pb(II) and Cu(II) (Castaldi *et al.*, 2014), and an AS from China also reported an adsorption equilibrium time of 120 min for Pb(II) and 240 min for Cu(II) (Duan and Fedler, 2021). Similarly, Zhou and Haynes. (2011) tested the adsorption kinetics of Cr(III) and Cr(VI) by AS from a water purification plant in Australia and the results showed that the adsorption equilibrium time for Cr(III) and Cr(VI) was approximately 120 min. Therefore, 200 minutes is a relatively reasonable contact time which could be used as a reference for designing field filtration system.

5.3.4 Breakthrough Curve Fitting for Cu(II)

Thomas model. The Thomas model was used to analyses the data for the different packing height and infiltration rate on the dynamic adsorption in section 5.3.2 and section 5.3.3 (Fig. 5-9) to study the breakthrough of Cu(II) on AS. The Thomas adsorption rate constant (K_T) and the saturated adsorption capacity (q_0) were calculated according to Eq. 5-2, and the results listed in Table 5-4. Table 5-4 also lists the error (RMSE) between the adsorption data and the fitted data, and the regression coefficient (R^2).



(a)



(b)

Fig. 5-9 Application of Thomas model for dynamic adsorption Cu(II) (a) Different packing height (100% AS (7.6cm), 50% AS+50% GB (3.8cm), 20% AS+80% GB (1.8cm)); (b) Different flow rate (Media ratio 100% AS)

It can be seen from Fig. 5-9 that the Thomas model curve does not fully match the experimental data because of the experimental error caused by long-term operation and replacement of water inlet. However, the data have a certain correlated with model, and could be obtained some guidance from the simulation results. According to the analysis of regression coefficient and RMSE in Table 5-4, it is also shown that the Thomas model can describe the adsorption of Cu(II). The R² values are between 0.86-0.96 and the RMSE results are less <0.1, except when the filtration rate is 0.07 BV/min. This is because when the filtration rate is 0.07 BV/min, the exhaustion time of the AS is too fast, resulting in too little sample volume that can be analyzed, which may cause a large error.

It can be seen from Table 5-4 that the Thomas adsorption rate constant k_T is closely related to the flow rate and the packing height. K_T decreases with the increase of the packing height. This is because as the packing height increases, there is greater residence time for the liquid which effect on the decreased adsorption rate (Chen et al., 2011; Yang et al., 2023). It is worth noting that the adsorption capacity q_0 shows an opposite trend with K_T . q_0 shows an increasing trend with the increasing packing height. This is because when the AS dosage increases, the number of adsorption site increases, because more AS was added to the column. Therefore, although the adsorption rate is reduced, the number of adsorption sites in the column is increased and sufficient length for heavy metals to contact with AS, which compensates for the reduction in adsorption rate, and increases the adsorption capacity (Du et al., 2017). Furthermore, when the packing height is 7.6 cm, the theoretical saturated adsorption capacity of the Thomas model is 22.64 mg/g, which is close to the isotherm fitting results in chapter 3 and inferred that the number of adsorption sites for Cu(II) is about 2.14×10^{20} /g. This also proves that the Thomas model can describe the adsorption of Cu(II) well. Similar results have been reported in other column studies (Wang et al., 2016; Berna, 2022). In general, a higher packing height is beneficial for the dynamic adsorption of Cu(II), but excessive increase in packing height will lead to increased flow resistance and construction costs, which is not conducive to the engineering application of AS.

In addition, it can be seen from the Table. 5-4 that the Thomas adsorption rate constant K_T increases with increasing flow rate. This phenomenon is related to the flow resistance and mass transfer driver in the adsorption system (Du *et al.*, 2017). In other words, the movement of adsorbate to the adsorbent surface is affected by flow resistance and mass transfer rates. Flow rate has a great influence on flow resistance. According to the knowledge of fluid mechanics, flow resistance increases exponentially with increasing flow rate (Arfaie *et al.*, 2018). The mass transfer rate is the rate of solute to adsorbent during the adsorption process (Díaz-Blancas *et al.*, 2020). This mass transfer process requires overcoming the flow resistance and is related to the flow rate and adsorption efficiency (Chaumat *et al.*, 2005). The increase in flow rate allows the solute to be transported to the adsorbent surface at a higher rate, thereby reducing membrane resistance and increasing mass transfer rate, so the increase in mass transfer overcome the flow resistance, resulting in an increase in the rate constant (Du *et al.*, 2017). However, it was found that the adsorption capacity q_0 decreased with increasing flow rate. Due to the higher flow rate, the membrane resistance on the AS surface is reduced and the HY is also reduced. This means that Cu(II) does not have enough time to be adsorbed to the AS surface through intra-particle diffusion, resulting in a decrease in the AS adsorption capacity. On the contrary, when the flow rate is too slow, the flow resistance and head loss will increase and be accompanied by undesirable backflow phenomenon which may also affects the removal efficiency of Cu(II) (Xia and Wang, 2014). Therefore, choosing a reasonable HY (60 min in this experiment) is key to maximize the adsorption capacity of AS.

Packing height (cm)	Bed volume rate (BV/min)	$\begin{array}{c} k_{T} \ x \ 10^{-2} \\ (L/mg \cdot min) \end{array}$	q ₀ (mg/g)	RMSE	R ²
1.8		5.68	12.62	0.03837	0.9646
3.8	0.02	1.34	12.89	0.09780	0.8822
7.6		0.67	22.64	0.09982	0.8633
	0.02	0.67	22.64	0.09982	0.8633
7.6	0.03	0.94	10.63	0.07632	0.8542
	0.07	6.93	6.48	0.12183	0.8887

Table 5-4 Thomas model parameters for Cu(II) removal by AS under different operating conditions

Bohart-Adams model. The Bohart-Adams model analyzes the efficiency of the column in the initial stage (Nguyen *et al.*, 2017). Therefore, the Bohart-Adams model was used to fit the data from the beginning to the breakthrough period ($C_t / C_0 = 0.2$) under different operating conditions of the column. The fitting results are shown in Figure 5-10 and the model parameter are shown in Table 5-5.



Fig. 5-10 Application of Bohart-Adams model for dynamic adsorption Cu(II) (a) Different packing height (100%AS (7.6cm), 50%AS+50%GB (3.8cm), 20%AS+80%GB (1.8cm)); (b) Different flow rate (Media ratio 100%AS)

Since the breakthrough time of Cu(II) is too short when the infiltration rate is 0.07 BV/min, the amount of sample that can be analyzed is too small and only part of the fitting data is listed here. It

can be seen from Fig. 5-10 that the trend of the Bohart-Adams rate constant K_{AB} is the same as the Thomas rate constant K_T and the saturated adsorption capacity N_0 per unit volume of AS is approximately 311 mg/L. This saturation capacity decreases with increasing flow rate because insufficient contact affects the adsorption efficiency of AS. According to Table 5-5, the range of R^2 shows a poor correlation, so the Bohart-Adams model cannot be used to describe the dynamic adsorption process of Cu(II) in this project. Similarly, Han *et al.* (2009) found that Bohart-Adams is a simple model for evaluating dynamic adsorption performance, but its scope of application is limited. It can be seen that the fitting data at the packing height of 7.6 cm is slightly better than that at the heights of 1.8 cm and 3.8 cm. This indicates that the Bohart-Adams model may be more suitable for describing the dynamic adsorption when the packing height is relatively higher (7.6cm in this project).

Packing height (cm)	Bed volume rate (BV/min)	K _{AB} x 10 ⁻² (L/mg·min)	N ₀ (mg/L)	RMSE	R ²
1.8		2.39	384	0.02626	0.5760
3.8	0.02	2.00	242	0.05427	0.5610
7.6		1.79	311	0.03551	0.7080
76	0.02	1.79	311	0.03551	0.7080
7.0	0.07	5.30	103	0.02824	0.9375

Table 5-5 Bohart-Adams model parameters for Cu(II) removal by AS under different operating conditions

Yoon Nelson model. Based on the experimental data, the Yoon Nelson model was used for nonlinear regression analysis (Figure 5-11) and the Yoon Nelson model parameters K_{TN} and τ were obtained (Table 5-6).



(a)



(b)

Fig. 5-11 Application of Yoon Nelson model for dynamic adsorption Cu(II) (a) Different packing height (100% AS (7.6cm), 50% AS+50% GB (3.8cm), 20% AS+80% GB (1.8cm)); (b) Different flow rate (Media ratio 100% AS)

It can be seen from Fig. 5-11 that the Yoon Nelson model can describe the dynamic adsorption of these metals under different operating conditions well, with an R² >0.85 (Table 5.6). It also indicates that the model is consistent with the experimental results. In addition, the model predicted the time required to achieve 50% breakthrough (τ_{cal}), close to the experimental data (τ_{exp}), indicating that the dynamic adsorption data of Cu (II) fitted was described well by the Yoon Nelson model. In dynamic adsorption, the higher the τ value, the better the adsorption performance (Omotola *et al.*, 2022).

The Yoon-Nelson rate constant K_{YN} decreases with increasing packing height but increases with increasing flow rate. This shows a different trend from τ , because higher K_{YN} indicates that adsorption reaches saturation faster, which means that the breakthrough time is shortened. Similar findings were reported by Du *et al.* (2018). According to the model fitting results comparing the filtration rate and packing height, a packing height of 7.6 cm and a filtration rate of 0.02 BV/min were considered to be the best operating conditions, which are also consistent with the fitting results of the Thomas model.

Packing height (cm)	Bed volume rate (BV/min)	k _{YN} x 10 ⁻² (L/mg⋅min)	τ _{cal} (min)	τ _{exp} (min)	RMSE	R ²
1.8		11.35	35	35	0.03837	0.9646
3.8	0.02	2.67	105	95	0.09780	0.8822
7.6		1.68	368	380	0.09832	0.8678
	0.02	1.68	368	380	0.09832	0.8678
7.6	0.03	1.84	88	70	0.09294	0.8542
	0.07	13.86	27	20	0.12183	0.8887

Table 5-6 Yoon Nelson model parameters for Cu(II) removal by AS under different operating conditions

BDST Model. The BDST model is designed to predict the service time of AS based on packing height (Chen *et al.*, 2011). The model also plays an important role in practical applications, as it can be used to predict the performance of filter media at any packing height (Sun *et al.*, 2014). Therefore, the BDST model is specially fitted to the experimental data of different packing heights. The fitting results are shown in Figure 5-12 and Table 5-7.



Fig. 5-12. Application of BDST model for dynamic adsorption Cu(II) under different breakthrough point (AS packing height 7.6cm; Flow rate 0.02 BV/min)

The BDST model assumes that there is a linear relationship between the packing height and the service time of the column based on the different breakthrough values. Therefore, Fig. 5-12 fits the experimental data when the breakthrough values C_t / C_0 are set to 0.1, 0.2 and 0.3 respectively. The values of R² all exceed 0.88, which shows that the BDST model can fit the experimental data well. K_a represents the rate at which Cu(II) transfers to the AS surface. The higher the value, the faster the adsorption rate (Erkurt *et al.*, 2018). It can be seen from Table 5-7 that the adsorption rate of AS slightly decreases at different column heights. This may be because the increase in dosage leads to an increase in flow resistance, which affects the mass transfer (Du *et al.*, 2018). This result is consistent with the conclusion of the Thomas model above. Generally, it is preferable to use a large amount of adsorbent to reduce the frequency of filter bed replacement. But based on the results in Table 5-7, too high a packing height may lead to a decrease in the adsorption rate which affects the treatment efficiency of AS. Therefore, calculating the appropriate packing height based on K_a value can optimize the filter media performance.

It can be seen from Table 5-7 that as C_t / C_0 increases, the adsorption capacity N_0 increases. This is because when the breakthrough value is low, some adsorption sites on the AS surface are not occupied by Cu(II) in time, and AS has an unsaturated state, so the adsorption capacity N_0 must be low (Sun *et al.*, 2014). Moreover, N_0 reflects the adsorption capacity of AS for Cu(II) under dynamic conditions. It was found that when 10% is defined as the breakthrough point, the adsorption capacity of Cu(II) is 292 mg/L, which is similar to the result of the Bohart-Adams model (311 mg/L). This shows that the results of the two models are consistent when the packing height is 7.6 cm. On the one hand, it proves that the Bohart-Adams model is suitable to interpret the column solute breakthrough data with relatively high packing heights. Conversely, it is also proved that the BDST model can be used to predict the adsorption of AS for Cu(II) under other operating conditions, such as different concentrations.

Packing height (cm)	C_t/C_0	K _a x 10 ⁻² (L/mg⋅min)	N ₀ (mg/L)	R ²
1.8		2.29		
3.8	0.2	1.85	292	0.9893
7.6		1.73		
	0.1	2.6	230	0.8848
7.6	0.2	1.73	292	0.9893
	0.3	0.23	325	0.9981

Table 5-7 BDST model parameters for Cu(II) removal by AS under different packing height

5.3.5 Breakthrough Curve Fitting for Zn(II)

Thomas model. Similarly, the dynamic adsorption data for Zn(II) were analysed using the Thomas model based on the data from column experiment. The results are shown in Figure 5-13 and Table 5-8.



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(b)

Fig. 5-13 Application of Thomas model for dynamic adsorption Zn(II) (a) Different packing height (100%AS (7.6cm), 50%AS+50%GB (3.8cm), 20%AS+80%GB (1.8cm)); (b) Different flow rate (Media ratio 100%AS)

The fitting of Zn(II) adsorption by AS using the Thomas model has a similar pattern to that of AS adsorption of Cu(II). The rate K_T of Zn(II) decreases with the increase of packing height and increases with the increase of flow rate. It is worth noting that the maximum adsorption capacity (q₀) of Zn(II) does not change with the height of AS. This is because the adsorption rate of Zn(II) is from 8.63 to 1.85 L/mg·min, which is much faster than the adsorption of Cu(II) (5.68-0.67 L/mg·min). This may lead to the flow resistance will not affect the mass transfer of Zn(II). This also shows that the packing height of 7.6 cm is too high for Zn(II), which does not reach the optimal operating condition of the column. However, since the treatment aim of the column experiment is simulated runoff containing a binary composition of Cu(II) and Zn(II), it is necessary to choose Cu(II) as a reference for setting the column operating conditions.

The dynamic average adsorption capacity of Zn(II) is 11.49 mg/g, which is close to the isotherms results from the batch experiment, indicating that the Thomas model can also describe the adsorption of Zn(II) well and inferred that the number of adsorption sites for Zn(II) is about 1.84×10^{20} /g. Moreover, similar to Cu(II), the adsorption capacity of Zn(II) decreased significantly with the increase of flow rate. This is because there is not enough time for Zn(II) to be adsorbed to the AS surface through intra-particle diffusion with the increase of flow rate, resulting in a decrease in the adsorption capacity of AS.

Packing height (cm)	Bed volume rate (BV/min)	$\begin{array}{c} k_{T} \ x \ 10^{-2} \\ (L/mg \cdot min) \end{array}$	q ₀ (mg/g)	RMSE	R ²
1.8		8.63	11.74	0.04487	0.9897
3.8	0.02	3.48	12.74	0.02995	0.9706
7.6		1.85	10.00	0.06610	0.9162
	0.02	1.85	10.00	0.06610	0.9162
7.6	0.03	3.36	3.42	0.09157	0.9178
	0.07	5.87	2.41	0.03489	0.8992

Table 5-8 Thomas model parameters for Zn(II) removal by AS under different operating conditions

Bohart-Adams model. Based on the data for dynamic adsorption of Zn(II), the Bohart-Adams model was used to analyze the experimental data from the beginning of the experiment to $C_t / C_0 = 0.2$. The fitting results are shown in Figure 5-14 and Table 5-9.



Fig. 5-14 Application of Bohart-Adams model for dynamic adsorption Zn(II) in different AS packing height (100% AS (7.6cm), 50% AS+50% GB (3.8cm))

When the infiltration rate is 0.03 BV/min, 0.07 BV/min and the packing height is 1.8cm, the breakthrough time of Zn(II) is too fast, such that the amount of sample that can be collected is too small to analyse. Therefore, only fitting data for some packing heights are listed here. From the results of the model fitting process (Table 5-9), it can be seen that the Bohart-Adams model has a high correlation with the experimental data for Zn(II) (R^2 >0.8), but according to the RMSE results, when the packing height is 3.8cm, there is a very large error. This also proves that the scope of application

of the Bohart-Adams model is limited. From the results of this study, the Bohart-Adams model is not suitable for describing the adsorption of Zn(II), because the number of samples that can be analyzed is too small.

Packing height (cm)	Bed volume rate (BV/min)	K _{AB} x 10 ⁻² (L/mg·min)	N ₀ (mg/L)	RMSE	\mathbb{R}^2
3.8	0.02	2.73	338	0.83221	0.8082
7.6	0.02	1.19	335	0.03973	0.8201

Table 5-9 Bohart-Adams model parameters for Zn(II) removal by AS under different operating conditions

Yoon Nelson model. The Yoon Nelson model was used to perform nonlinear regression analysis on the Zn(II) data (Figure 5-15). The model parameters K_{TN} and τ obtained are shown in Table 5-10.



(a)



Fig. 5-15 Application of Yoon Nelson model for dynamic adsorption Zn(II) (a) Different packing height (100% AS (7.6cm), 50% AS+50% GB (3.8cm), 20% AS+80% GB (1.8cm)); (b) Different flow rate (Media ratio 100% AS)

It can be seen from the RMSE (<0.1) and R^2 (>0.89) that the adsorption of Zn(II) conforms to the Yoon Nelson model. The Yoon Nelson rate constant K_{YN} decreases with increasing packing height but increases with increasing flow rate, which is the same as reported in Bakar *et al.* (2016) and Fan *et al.* (2019). The 50% breakthrough time τ of Zn(II) is much smaller than that of Cu(II), which indicates that the adsorption capacity of Zn(II) is much smaller than that of Cu(II). This result is also consistent with the Thomas model parameter q₀, which is 22.64 mg/g for Cu(II) and 10 mg/g for Zn(II).

Packing height (cm)	Bed volume rate (BV/min)	k _{YN} x 10 ⁻² (L/mg⋅min)	$ au_{cal}$ (min)	$ au_{exp}$ (min)	RMSE	R ²
1.8		17.26	33	35	0.04492	0.9897
3.8	0.02	6.95	104	105	0.02867	0.9706
7.6		3.70	178	170	0.06610	0.9162
	0.02	3.70	178	170	0.06610	0.9162
7.6	0.03	8.39	23	20	0.09157	0.9178
	0.07	14.68	8	10	0.07911	0.8992

Table 5-10 Yoon Nelson model parameters for Zn(II) removal by AS under different operating conditions

The Zn (II) data is also fitted with the BDST model, and the fitting results are as follows.



Fig. 5-16 Application of BDST model for dynamic adsorption Zn(II) under different breakthrough point (AS packing height 7.6cm; Flow rate 0.02 BV/min)

The BDST model showed a high correlation with the Zn(II) data ($R^2>0.97$). The adsorption rate K_a of AS for Zn(II) is much greater than that of Cu(II), which indicates that the adsorption rate of Zn(II) is faster but the adsorption capacity is less than that of Cu(II). It can also be seen from N₀ that the adsorption capacity Cu(II) is 292 mg/L, while Zn(II) is much smaller than Cu(II), only 201 mg/L, and it conforms to the trend of breakthrough curve (Figure 5-14) which is that the breakthrough and exhaustion time of Zn(II) is earlier than that of Cu(II).

Packing height (cm)	$C_t \ / \ C_0$	K _a (L/mg·min)	N ₀ (mg/L)	\mathbb{R}^2
1.8		0.13		
3.8	0.2	0.19	201	0.9770
7.6		0.14		
	0.1	0.1	202	0.9896
7.6	0.2	0.14	201	0.9770
	0.3	0.08	228	0.9824

Table 5-11 BDST model parameters for Zn(II) removal by AS under different packing height

5.3.6 Model and AS Application

The reason why AS adsorb Cu(II) and Zn(II) fit Thomas model, Yoon-Nelson model and BDST model is that different models simulate different conditions. For example, Yoon-Nelson simulates the 50% breakthrough time of the column through the adsorption and desorption behavior of Cu(II) on AS, which is a simple dynamic model that does not provide information about the adsorption capacity and adsorption efficiency and is only used to predict the midpoint of the adsorption process. The Thomas model studies the maximum adsorption capacity and adsorption efficiency of the column and is often used to describe the entire adsorption process. Therefore, although Thomas and Yoon-Nelson have different assumptions and focus on different dynamic adsorption parameters, there is no conflict between those. Similarly, BDST predicts the relationship between packing depth and breakthrough time, which is normally used to predict filtration running time. In summary, different models reflect different conditions, and these results can guide the application of AS under different conditions. For example, if the scale of the filtration system is already known, the fitting results of BDST model can be used to predict the running time of different packing depths AS, and based on the actual running time requirements to predict packing depth. When a specific packing depth is decided, the Thomas model can simulate the entire adsorption process to estimate the maximum adsorption capacity and adsorption rate. For Yoon-Nelson model, when the research data of the material is insufficient, Yoon-Nelson model can be used to roughly estimate the 50% breakthrough time and adsorption rate of the adsorption material to determine whether the material meets the engineering design requirements. Therefore, for different engineering design requirements, these models can provide relevant prediction data as a guide for selecting AS and filling height.

Studies have shown that AS is a promising pollution control material, but filtration experiments have shown that find powder AS (<0.15 mm) is impermeable, so the permeability of AS needs to be considered in actual engineering applications. Granular AS can be screened by extrusion/grinding (Huang and Wang, 2013) and applied in most stormwater Best Management Practices (BMPs). There have been successful cases of using AS in small subsurface constructed wetlands, and it has been found that AS have the effect of enhancing phosphorus removal in constructed wetlands (Hu, 2019). Soleimanifar (2018) used AS as the matrix of the bioretention basin and found that it had a certain adsorption capacity on phosphorus and various heavy metals such as Cu(II), Zn(II), Pb(II) in runoff, and no pollutant breakthrough occurred in the bioretention basin during the one-year operation. Furthermore, Wang *et al.* (2017) considered the use AS in combination with steel slag in a permeable reactive barrier and showed high removal rates of Cu(II) and Pb(II) in laboratory-scale simulations. In terms of cost, since AS is a waste product from water purification plants, it has no cost from itself. The operation is similar to that of normal commercial adsorbents, and the costs mainly come from transportation, grinding, removal when the AS saturation and regeneration.

5.3.7 Dynamic Re-release of Accumulated Heavy Metals

This section explores the effect of flushing intensity on the release of heavy metals accumulated in AS. The results are shown in Fig. 5-15.



Fig. 5-17 Dynamic release of accumulated metals in AS based on different flushing intensities

It can be seen from Fig. 5-17 that Cu(II), Zn(II) and Al(III) decrease with the decrease of flushing intensity, and the release concentration of heavy metals at a flow rate of 0.07 BV/min is significantly higher than that at 0.03 BV /min and 0.02 BV/min. However, in general, the released load of heavy metals was very low, averaging 0.012 mg/L for Cu(II), 0.017 mg/L for Zn(II) and 0.003 mg/L for Al(III). According to calculations, the total amount of Cu(II) and Zn(II) desorbed in 30 min accounted for 0.4% and 1.5% of the total adsorption, respectively, which indicates that the Cu(II) and Zn(II) fixed by AS are not easy to release. Furthermore, the effect of flushing duration time on the re-release of heavy metals was investigated. The results are shown in Fig. 5-16.



Fig. 5-18 Dynamic release of accumulated metals in AS based on different flushing duration time

It can be seen from Fig. 5-18 that with the increase of flushing time, the release of Zn(II) was dramatically decreased from 0.05 mg/L to 0.02 mg/L, whereas Cu(II) shows a slight decrease. This may indicate that Zn(II) is more easily desorbed than Cu(II) at the beginning of flushing. After 40 minutes of flushing, the concentrations of Cu(II) and Zn(II) were similar. This may be because the heavy metals released into the solution reached a dynamic equilibrium state between the aqueous and adsorbed concentrations (Wang, 2019). The concentration of Al(III) fluctuates within the range of $0.005\pm0.005 \text{ mg/L}$. This is because no additional Al(III) was added in the column experiment. The Al(III) here is released completely from the AS components, so its concentration will only fluctuate within a range.

5.4 Summary

This chapter presents column studies which assess the dynamic adsorption of AS on Cu (II) and Zn (II), mainly examining the effects of different packing heights and infiltration rates. Furthermore, the risk of Cu(II) and Zn(II) release after AS saturation was evaluated. The conclusions are as follows:

1) In the column experiment, with 160 g AS, 2 mg/L Cu(II) and Zn(II) stimulated runoff, the adsorption of Zn(II) reached equilibrium after 240 min and the removal rate did not increase with further reaction, but it took 600 min for Cu to reach saturation.

2) With the increase of dosage, the adsorption capacity for Cu(II) and Zn(II) increases. When the packing depth increases from 1.8 cm to 7.6 cm, the stimulated runoff processing volume of the column increases significantly from 364 mL to 2964 mL for Cu(II) and 286 ml to 1248 ml for Zn(II). In contrast to the observations on column packing height, the adsorption capacity for Cu(II) and Zn(II) decreased with increasing flow rate. When the flow rate increased from 0.02 BV/min to 0.07 BV/min, the exhaustion time of Cu(II) decreased sharply from 570 min to 50 min, and the exhaustion time for Zn(II) decreased from 240 min to 30 min.

3) When comparing the models, the Thomas, Yoon-Nelson and BDST models are more suitable for describing the dynamic adsorption of Cu(II) and Zn(II) than the Bohart-Adams model. It was proved that the adsorption rate, adsorption capacity and 50% breakthrough time of Cu(II) and Zn(II) were all affected by flow rate and AS packing height. Simply increasing the AS dosage could prolong the breakthrough time, but could not fully utilize the adsorption capacity of AS.

4) The flushing time and flushing intensity had an effect on the release of heavy metals that had accumulated in the AS. However, the overall concentrations of Cu(II), Zn(II) and Al(III) released from the AS media were very low, with an average of 0.012 mg/L for Cu(II), 0.017 mg/L for Zn(II) and 0.003 mg/L for Al(III).

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CHAPTER 6 CONCLUSIONS AND FUTURE RESEARCH

6.1 Conclusions

This paper systematically studies the properties of AS and its adsorption performance for Cu(II) and Zn(II). AS is obtained from water purification plants, air-dried and ground into particles, which are used as low-cost adsorbents for Cu(II) and Zn(II). Batch experiments were performed to obtain the AS adsorption capacity and optimal adsorption conditions under different conditions, such as initial metal solution concentration, pH, contact time and AS particle size. Kinetic and isotherm studies were performed, and the theoretical maximum adsorption capacity and adsorption rate of AS were calculated. Then, the adsorption competition phenomenon between different components in the runoff was studied by using SSR as solution. Finally, a dynamic adsorption study of AS was performed to estimate the effect of different packing heights and filtration rates on AS exhaustion. We also conducted research on metal leakage, regeneration and cyclic adsorption after AS saturation to provide more data for the application of AS.

The results of characterization experiments (Chapter 2) show that AS is a porous material mainly composed of mesopores, with an average specific surface area of 75 m²/g for particle (size 1-2mm) and 58 m²/g for fine powder (Size<0.15mm). The surface of AS is loaded with abundant particles accompanied by some amorphous pore structures. AS is mainly composed of O, Si, Al, Fe and other elements, among which the contents of Al, Si and Fe are 15%, 5% and 1% respectively, and its surface contains abundant active groups such as hydroxyl, carboxyl and aluminum oxide groups.

The results of batch adsorption experiments (Chapter 3) showed that the adsorption to AS conformed to the Langmuir isotherm model which means that the adsorption of Cu(II) and Zn(II) by AS occurs on a relatively uniform surface and is a monolayer adsorption. The maximum adsorption capacities for Cu(II) and Zn(II) were 22.88 mg/g and 8.74 mg/g, respectively, at pH = 6.5. The pseudo-second-order model better explains the adsorption process of Cu(II) and Zn(II), indicating that the adsorption rate is controlled by chemical adsorption. Solution pH has a great influence on the adsorption of Cu(II) and Zn(II). Without considering chemical precipitation, the optimal pH range is 5-6, but the pH in the experiments is in the range of 6.5-7 because the research target is stormwater runoff. The adsorption mechanism of Cu(II) and Zn(II) includes not only the intra-particle diffusion process, but also the electrostatic attraction between metal and oxygen-containing functional groups on the surface of AS, hydroxyl substitution and surface complexation reaction. The particle size has a significant effect on the rate of AS fix Cu(II) and Zn(II), but has little effect on the adsorption capacity. The adsorption equilibrium time of fine powder AS is 60 minutes, and about 200 minutes of particle AS. When HCl is used as the desorbent, the desorption rate of Cu(II) and Zn(II) decreases with the

increase of solution pH, and the desorption effect of Cu(II) and Zn(II) is best when $pH \le 2$. When the desorbent pH = 2, the desorption of Cu(II) and Zn(II) increases with time, and the optimal desorption time is 240 min. AS has good cyclic adsorption performance, after three times of adsorption and desorption, the removal rate of Cu(II) and Zn(II) is still over 65%.

The results of the adsorption competition experiment (Chapter 4) show that there is an adsorption competition between Cu(II) and Zn(II), and Cu(II) is greater than Zn(II) in both the maximum adsorption capacity of AS and the priority adsorption order. The selective adsorption of AS is related to the hydrolysis constant, ionic radius, hydration radius and electronegativity of the heavy metals. The addition of SSR reduced the adsorption capacity of AS for Cu(II) by 0.02 mg/g and for Zn(II) by 0.006 mg/g, indicating that the presence of nutrients inhibits the adsorption of Cu(II) and Zn(II), but the removal efficiency of Cu(II) and Zn(II) in SSR still exceeded 95%. When the solution ionic strength increases from 1 mM to 500 mM, the adsorption capacity of Cu(II) decreases from 0.45 mg/g to 0.37 mg/g, and the adsorption capacity for Zn(II) decreases from 0.37 mg/g to 0.32 mg/g. This indicates that high concentrations of Na ions may occupy adsorption sites on AS and hinder the adsorption of Cu(II) and Zn(II), but this inhibition is not obvious. The inhibition of the AS adsorption capacity by Ca ions was very obvious, and its adsorption capacity for Cu(II) dropped sharply from 0.4 mg/g to 0.009 mg/g, and for Zn(II) also dropped from 0.33 mg/g to 0.02 mg/g.

The results of column experiments (Chapter 5) show that in the dynamic removal of Cu(II) and Zn(II), the breakthrough time of Zn(II) is faster than Cu(II). When 160g AS 2mg/L heavy metal solution was added, after 240min the adsorption of Zn(II) reached saturation, but it took 600min for Cu(II). The adsorption capacity of AS for Cu(II) and Zn(II) increases with the increase of AS dosage and decreases with the increase of filtration rate. By compared with the Bohart-Adams model, the Thomas, Yoon-Nelson and BDST models are more suitable for describing the dynamic adsorption process of Cu(II) and Zn(II). It was proved that the adsorption rate, adsorption capacity and 50% breakthrough time of Cu(II) and Zn(II) were all affected by flow rate and AS packing height. Simply increasing the AS dosage could prolong the breakthrough time, but could not fully utilize the adsorption capacity of AS. The flushing time and flushing intensity had a certain effect on the release of heavy metals that had accumulated in AS, but the overall concentrations of Cu(II), Zn(II) and Al(III) were low, with an average of 0.012 mg/L for Cu(II), 0.017 mg/L for Zn(II) and 0.003 mg/L for Al(III). This shows that AS is a safe and reliable filtering material.

6.2 Future Works

This study systematically investigated the use of AS as a filter material for Cu(II) and Zn(II) in SSR. Although encouraging data have been obtained, this study does not solve all problems. Some aspects that deserve investigate in the future: 1) Simulate more adsorption conditions. Long term column experiments were conducted in the laboratory to simulate the adsorption performance of AS under actual application conditions. However, many factors that affect adsorption cannot be completed in a laboratory environment. For example, temperature is the main factor affecting adsorption capacity, but all our column experiments are carried out at room temperature. A field study is needed to investigate the effect of temperature changes throughout the year on AS adsorption capacity. Moreover, microorganisms effect, runoff may contain large amounts of bacteria and algae in addition to chemical pollutants. Studies have shown that bacteria and algae may promote the adsorption of pollutants by adsorbents (Wei *et al.*, 2016; Fan, 2017). The presence of microorganisms was not simulated mainly because the laboratory environment cannot fully stimulate the microbial composition in real SSR. Therefore, more field study is needed to supplement this part and field research can also test the adsorption performance of AS in more complex pollutant coexistence in the real SSR.

2) Apply AS to remove other pollutants in runoff. There are various kinds of pollutants in real SSR. AS has been successfully used to fix phosphorus and some heavy metals in runoff (Babatunde *et al.*, 2010; Xu *et al.*, 2019). In this study the number of target pollutants were limited to have enough capacity to go into detail with the relevant adsorption mechanisms, but the potential impact of AS on other pollutants is still of interest in the storm water runoff. For example, studies have shown that porous adsorbents such as zeolites are effective in removing E. coli from runoff (Sidhu *et al.*, 2012; Du, 2017; Shan, 2018). Therefore, the detection of AS fixation of bacteria in runoff is a supplement to the application of AS.

3) The influence of rainfall characteristics. Different rainfall events have different characteristics such as duration of rainfall, duration of previous dry weather and rainfall intensity. Although the pollutant concentration range of a single rainfall event is relatively narrow, the runoff velocity will approach to a normal distribution trend due to the first flushing effect. However, our single column experiment used the peristaltic pump to continuously supply SSR at a fixed flow rate. Future work is needed to supplement the column experiments with normal distribution filtration rate.

4) Life cycle assessment of AS. Although regeneration and cyclic adsorption studies were conducted in this paper, these were based on the results of batch experiments. It is recommended that a full life cycle assessment (LCA) of AS should be conducted in future studies. Because LCA can evaluate the balance between reducing runoff pollution load and economic, climate change and environmental costs when AS is used as a sorbent to handle stormwater runoff problems. Based on the LCA results we can determine whether AS is environmentally and economically sustainable.

REFERENCE-CHAPTER 6

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Appendix

1. According to 3Flex manual book (2017), when nitrogen was introduced, the equipment will monitor the amount of nitrogen injected, and record the ratio of the gas pressure P in the sample chamber to the saturated vapor pressure P₀ of the gas under standard conditions through the pressure sensor. The amount of adsorbed nitrogen is calculated by the ideal gas state equation (PV=nRT) (3Flex manual book, 2017). The specific surface area of the samples was calculated by using the Brunauer-Emmett-Teller (BET) method. When the relative pressure (P/P₀) is recorded, the instrument's built-in software puts the data into the BET equation as follows (3Flex manual book, 2017):

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \times \frac{P}{P_0}$$
(1)

Where, P/P_0 is the relative pressure; V is the volume of gas adsorbed by the sample at the relative pressure which is measured by the instrument (cm³/g); C is the BET constant; V_m is the volume of gas adsorbed per monolayer (cm³/g). The instrument calculates V_m and C through linear fitting results and put them into the specific surface area equation (Eq. 2):

$$S = \frac{V_m N A}{M}$$
(2)

Where, S is the specific surface area (m^2/g) ; N is Avogadro's number $(6.023*10^{23})$; A is cross sectional area of N₂ gas $(16.2A^{02})$ and M is molecular mass of nitrogen.

The pore size was calculated using the Barrett-Joyner-Halenda (BJH) method (ranged from 1.7 to 300 nm). The BJH method is based on the Kelvin equation (Eq.3) to calculate the pore size of materials (3Flex manual book, 2017):

$$\ln\left(\frac{P}{P_0}\right) = -\frac{2\gamma V_m}{rRT} \tag{3}$$

Where, P/P_0 is the relative pressure; γ is the tension of the gas-liquid interface (usually 8.85 mN/m for nitrogen); Vm is the volume of the gas adsorbed per monolayer (cm³/g); r is the radius of the pore (nm); R is the gas constant and T is the temperature 77K.

Types of adsorption and desorption isotherms. The International Union of Pure and Applied Chemistry (IUPAC) provides six types of isotherms (Fig. S1) (Muttakin *et al.*, 2018).

• Type I Isotherm: The characteristic of the curve is that it rises rapidly and then stabilizes. Typically, microporous materials (pore size < 2 nm), such as activated carbon and zeolites, will have this isotherm characteristic;

- Type II Isotherm: The characteristic of the curve is that it rises gently and then gradually tends to be flat with no obvious hysteresis loop. Usually relates to non-porous materials or materials with only a small amount of micropores and mesopores such as glass.
- Type III Isotherm: The characteristic of the curve is that it rises slowly at first and then rapidly with no apparent hysteresis loop. Usually occurs on materials with weak adsorption capacity.
- Type IV Isotherm: The characteristic of the curve is that it rises slowly at first and shows a clear hysteresis loop at higher pressures. This characteristic commonly found in mesoporous materials such as silicon and alumina.
- Type V Isotherm: The characteristic of the curve is that it rises slowly at first, and as the pressure increases the adsorption amount gradually increases, usually with a hysteresis loop. This characteristic commonly found in mesoporous materials with weak adsorption capacity
- Type VI Isotherm: The curve shows a clear step-like upward trend, which is usually associated with highly structured materials such as crystalline materials.



Fig. S1 Adsorption-desorption isotherm type from IUPAC (Muttakin et al., 2018)

After the sample was degassed, the sample chamber was filled with nitrogen. As the relative pressure (P/P_0) increases, the gas begins to condense on the surface and in the pores of AS, eventually reaches saturation (Sotomayor *et al.*, 2018). When the pressure is reduced, the gas evaporates from the pores (Sotomayor *et al.*, 2018). The condensation of gas during adsorption and evaporation during desorption are not symmetrical, which forms different pressure paths and produces a hysteresis loop

(Sotomayor *et al.*, 2018). The shape of the pore has a great influence on the type of hysteresis loop. According to the IUPAC classification, hysteresis loops are mainly divided into five categories (Fig. S2).

H1 type hysteresis loop: The gap between the adsorption and desorption isotherms is large, the shape is relatively symmetrical, the adsorption and desorption paths are roughly parallel and a relatively steep and narrow hysteresis loop is presented. This hysteresis loop is usually associated with uniformly distributed macropores or cylindrical pores, and is common in uniform mesoporous materials.

H2 type hysteresis loop: The adsorption isotherm is relatively flat, but the desorption isotherm drops sharply. Its shape is asymmetric, and the desorption process lags significantly behind the adsorption process. This kind of hysteresis loops are usually associated with pores of irregular shape or complex structure such as activated carbon or heterogeneous mesoporous materials. This hysteresis loop is divided into two types: H2 (a) and H2 (b), which is mainly related to the blockage of the pores. H2 (a) type hysteresis loops are common in some ordered three-dimensional mesoporous materials and H2 (b) type hysteresis loops are common in mesoporous silicon materials.

H3 type hysteresis loop: The adsorption isotherm and desorption isotherm are separated at higher pressures and the adsorption and desorption curves are not closed, forming an open hysteresis loop. H3-type hysteresis loops are usually associated with cracks or layered like pores such as clay and graphite.

H4 type hysteresis loop: The gap between the adsorption and desorption isotherms occurs in the lower relative pressure range, by compared with H3 type hysteresis loop. H4-type hysteresis loops are usually associated with micropores and cracks like pores, especially materials with mixed microporous and mesoporous structures such as zeolites.

H5 type hysteresis loop: This hysteresis loop is relatively rare and is found in mesoporous materials with partially blocked pores. This kind of material have both open and blocked mesoporous structures.

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Fig. S2 Hysteresis loop type from IUPAC (Sotomayor et al., 2018)