ADSORPTION OF CHROMIUM, CADMIUM AND MANGANESE IONS USING NANOMAGNETIC ALUMINA COMPOSITES FROM AN AQUEOUS SOLUTION

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by

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LIST OF SYMBOLS

°C	Degree Celsius
o	Omega
γ	Gamma
α	Alpha
β	Beta
θ	Theta
η	Eta
δ	Delta

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
Al	Alumina
BET	Brunauer–Emmett–Teller
CoAl	Cobalt Alumina
CP	Chemical Precipitation
ESR	Electron Spin Resonance
FeAl	Iron Alumina
FTIR	Fourier Transform Infrared Spectroscopy
NiAl	Nickel Alumina
PM	Physical Mixing
SEM	Scanning Electron Microscope
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

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PENJERAPAN ION-ION KROMIUM, KADMIUM DAN MANGAN MENGGUNAKAN KOMPOSIT ALUMINA NANOMAGNETIK DARI LARUTAN AKUEUS

ABSTRAK

Pembuangan sisa kromium (Cr), kadmium (Cd) dan mangan (Mn) daripada industri boleh memberi kesan alam sekitar yang serius kepada kehidupan akuatik dan manusia kerana ketoksikan dan kesannya yang berbahaya. Oleh itu, penjerapan Cr, Cd dan Mn dari sistem akuatik sangat penting. Kajian ini bertujuan untuk menjerap ion-ion Cr, Cd, dan Mn dalam larutan berair menggunakan komposit nanomagnetik alumina (Al) menggunakan dua kaedah yang berbeza iaitu pencampuran fizikal (PM) dan pemendakan kimia (CP). Komposit-komposit nanomagnetik Al iaitu alumina yang dicampur nikel (NiAl), alumina yang dicampur kobalt (CoAl), dan alumina yang dicampur besi (FeAl) telah digunakan dalam proses penjerapan untuk membandingkan kecekapan mereka terhadap ion Cr, Cd, dan Mn. Penjerapan Cr, Cd dan Mn dilakukan dalam sistem kumpulan dengan pH awal (3-11), dos penjerap (0.01-0.06 g), kepekatan awal (10-100 mg L^{-1}) dan suhu (40-50°C) yang berbeza. Penjerap dicirikan menggunakan Pembelauan Sinar-X (XRD), Spektroskopi Inframerah Transformasi Fourier (FTIR), Mikroskop Elektron Pengimbasan (SEM), Brunauer–Emmett–Teller (BET), Spektroskopi Fotoelektron X-Ray (XPS), dan Resonansi Putaran Elektron (ESR). Keputusan menunjukkan bahawa komposit nanomagnetik Al yang dihasilkan dengan kaedah PM mempunyai kapasiti penjerapan yang lebih tinggi berbanding dengan kaedah CP. Kadar penjerapan tersebut terhadap ion-ion Cr, Cd dan Mn adalah dalam urutan berikut: FeAl> CoAl> NiAl> Al. FeAl dipilih sebagai penyerap terbaik. Hasil pencirian menunjukkan bahawa kadar penjerapan secara signifikan berkaitan dengan interaksi antara kerangka Al dengan komposit logamnya yang mendorong sifat kemagnetan terutamanya untuk FeAl. Analisis XRD, FTIR XPS dan ESR menjelaskan berlakunya penyingkiran Al dan penggantian isomorf setiap logam. FeAl mampu menjerap Cr, Cd dan Mn dengan kapasiti penjerapan masing-masing 500.0 mg g^{-1}, 285.7 mg g^{-1} dan 3.883 mg g^{-1} daripada larutan akueus pada pH 7 menggunakan 0.05 g penjerap, kepekatan awal 25 mg L^{-1} pada 30℃ (Cd, Mn) dan 40℃ (Cr). Model terbaik untuk menjelaskan penjerapan ion-ion Cr, Cd dan Mn adalah model Langmuir. Kinetik digambarkan oleh model psedo-urutan pertama, sementara kajian termodinamik menunjukkan bahawa penjerapan adalah eksotermik untuk Cr sementara Cd dan Mn adalah endotermik. Walau bagaimanapun, kesesuaian penjerapan adalah mengikut urutan Cr> Cd> Mn. Bagi semua logam berat, proses penjerapan menyokong sifat sistem yang tidak spontan.

ADSORPTION OF CHROMIUM, CADMIUM AND MANGANESE IONS USING NANOMAGNETIC ALUMINA COMPOSITES FROM AN AQUEOUS SOLUTION

ABSTRACT

The discharge of chromium (Cr), cadmium (Cd) and manganese (Mn) effluents from industries may cause serious environmental effect on aquatic life and human due to their toxicity and harmful nature. Hence, the removal of these heavy metals from an aquatic system is very crucial. This study aimed to remove Cr, Cd, and Mn ions from an aqueous solution using nanomagnetic alumina (Al) composites using two different methods, namely physical mixing (PM) and chemical precipitation (CP). Nanomagnetic Al composites which were nickel loaded alumina (NiAl), cobalt loaded alumina (CoAl) and iron-loaded alumina (FeAl) were applied in the adsorption process to compare their efficiencies towards Cr, Cd, and Mn ions. The adsorption of Cr, Cd and Mn ions were conducted in a batch system under varying initial pH (3-11), adsorbent dosage (0.01-0.06 g), initial concentration (10-100 mg L^{-1}) and temperature (40-50°C). The adsorbents were characterised using X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), Brunauer–Emmett–Teller (BET), X-Ray Photoelectron Spectroscopy (XPS) and Electron Spin Resonance (ESR). The results showed that the nanomagnetic Al composite produced through PM method has a higher adsorption capacity as compared to the CP method. The adsorptivity of those adsorbents toward Cr, Cd and Mn ions was in the following order: FeAl > CoAl > NiAl> Al. FeAl was chosen as the best adsorbent. The characterisation result revealed that adsorptivity was significantly related to the interaction between Al frameworks with the metal composites which increase the magnetism properties especially for FeAl. XRD, FTIR, XPS and ESR analysis explained the occurrence of dealumination of Al and isomorphous substitution of each metal. FeAl was able to remove Cr, Cd and Mn ions with the adsorption capacity of 500.0 mg g^{-1}, 285.7 mg g^{-1} and 3.883 mg g^{-1} respectively from an aqueous solution containing initial concentration of 25 mg L^{-1} at pH7 when using 0.05 g adsorbent, at 30°C (Cd, Mn) and 40°C (Cr). The best model for explaining the adsorption of Cr, Cd and Mn ions was the Langmuir model. The kinetics was best described by the pseudo-first-order model, while the thermodynamic study indicated that the adsorption was exothermic for Cr and both Cd and Mn were endothermic. However, the favourability of the adsorption was in the order of Cr>Cd>Mn. For all heavy metals ions, the adsorption process supports the non-spontaneous nature of the system.

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Water pollution control has become a global concern due to the prevailing heavy metals pollution from industrial effluent. Heavy metal discharged in natural water is not suitable for human consumption. Heavy metal pollution is affected by the process of natural weathering such as erosion, weathering of rock and leaching (Al-Badaii et al., 2016; Wei et al., 2018). In addition, water is also polluted due to anthropogenic activities such as agricultural, commercial and domestic (smelting, metals from corrosion of rocks and soils and automobile exhaust pipes (Akhtar et al., 2021; Astatkie et al., 2021). Since then, water quality has become a major concern.

Heavy metals, which have non-biodegradable properties are discharged into the environment directly or indirectly and accumulate in the food chain. Humans and aquatic life consume polluted water sources through inhalation, ingestion, or skin contact. They consequently give severe disorders such as kidney disease, nerve-related disorder, lung cancer etc. (Abbas et al., 2018; Adesiyan et al., 2018; Genchi et al., 2020). Removal of heavy metal from wastewater is an important environmental issue since the Environmental Protection Agency (EPA) regulates many metal contaminants.

Other researchers have developed several methods for treating wastewater, including membrane separation, coagulation and flocculation, filtration, adsorption, and chemical treatment (Demirbas et al., 2017; Qasem et al., 2021; Saleh, 2021). Among these technologies, adsorption has been recognized as an effective and economic method since it was simple, low cost, environmentally friendly and in some cases produces high-quality output (Bushra et al., 2021; Velusamy et al., 2021). On the contrary, other methods require high cost, complex methods, generate secondary wastes and consume more energy (Wagh & Nemade, 2015).

Adsorbents such as activated carbon, silica, zeolite, clay and graphene have been synthesized and applied for the treatment of pollutants (Burakov et al., 2018; Garshasbi et al., 2017). Agricultural wastes like wheat, husk, leaves, corn powder and fruit waste were also recently in demand as adsorbents. According to a recent study, nanomaterial composites have a large surface area with a higher capacity for adsorption due to their porosity and small diameter (Gusain et al., 2020). Al which draws potential as a good adsorbent for wastewater treatment, is one of the effective nanomaterial adsorbents due to its high porosity and large surface area (Ali et al., 2019). Besides, Al can remove 1000- or 10,000- times heavy metal ions than other alkaline metal ions (Salleh et al., 2017).

Despite the attention given to nanomaterials, the separation of the used adsorbents after treatment was difficult due to their smaller nano size. In order to overcome these problems, nanomagnetic metal oxide was introduced due to their high capacity and selectivity (Liu et al., 2016). Metal oxides that exhibit magnetism properties can be reused in the adsorption process which give benefit to the industrial property value by saving money for acquiring more raw products. For example, the magnetic boehmite sol-gel composites had improved the removal of heavy metals (Shapovalova et al., 2018). However, reports on these composite materials are still scarce. Therefore, the aim of this study is to synthesize the Fe, Co, and Ni loaded onto Al for the adsorption of Cr, Cd and Mn ions.

In this study, the physicochemical properties and adsorptivity performance of Fe, Co, and Ni metals loaded onto Al were studied using PM and CP methods. The characterisation of the potential adsorbents was conducted by utilizing various techniques of XRD, FTIR, SEM, BET, XPS and ESR. Based on these results, the structure of the composites and the mechanism for adsorption were proposed. Then, different parameters including contact time, pH, initial concentration, adsorbent dosage, and temperature were investigated. Additionally, kinetic, thermodynamic, and proposed mechanism studies were conducted to better understand the results.

1.2 Problem statement

Toxic and poisonous heavy metals discharged into the environment carry negative impacts on aquatic life and human health when they exceed EPA's allowable limit. As a result, the wastewater treatment system faces the challenging task of finding the appropriate methods and material to remove these toxic sources.

There are several methods for removing heavy metal ions in wastewater technology, including precipitation (Chen et al., 2018), electrolysis (Zhu et al., 2019), coagulation or flocculation (Shrestha et al., 2021), membrane filtration (Nazaripour et al., 2021), and ion exchange (Abdullah et al., 2019). However, these methods need to be reviewed and developed further because they might be ineffective, expensive, and environmentally unfriendly.

Al possesses a higher amount of hydroxyl groups which contributes to a higher adsorption capacity. Despite its excellent work, Al is difficult to be separated from the solution after the treatment. Thus, the use of magnetism is playing an important role in this study. Magnetism metals such as Fe, Co and Ni have been explored to form supporting composites on the Al matrix. Thus, the combination structure of materials is expected to improve the physical properties of metals Al composites and subsequently may increase the adsorption capacity towards metal ions.

1.3 Objectives of the research

1.3.1 General objective

To remove toxic heavy metal (Cr, Cd, Mn) ions from an aqueous solution using Al and nanomagnetic Al composites (FeAl, CoAl, NiAl).

1.3.2 Specific objectives

- To synthesize the nanomagnetic Al adsorbents by loading Fe (FeAl), Co (CoAl) and Ni (NiAl) metals using two different methods of PM and CP.

- To characterise the nanomagnetic Al (FeAl, CoAl, NiAl) adsorbents using XRD, FTIR, SEM, BET, XPS and ESR.

- To investigate the optimum conditions for the adsorption of Cr, Cd, Mn ions using the synthesized adsorbents, including contact time, pH, initial concentration, the dosage of adsorbent and temperature.

- To determine the adsorption isotherms, kinetics, thermodynamics and propose the mechanism of the adsorption.

1.4 Research significance

Toxic and poisonous heavy metals discharged into the environment must be disposed properly to prevent harm to aquatic life and human health. There are several methods for removing heavy metal ions in waste water technology. In view of this research, adsorption is the simplest method and is easy in the operation.

Furthermore, the studied adsorbents are environmentally friendly and cost-effective, leading to the reduction of industrial input. The modification of Al with various types of magnetism properties (Fe, Co, Ni) is a well worth adsorbent. Yet, they were not extensively explored to remove metal ions through adsorption.

Physical properties of the adsorbents such as higher surface area, the addition of OH^- quantity, the strong interaction of the composites and the magnetism effect give higher adsorption capacity to the composite Al. To sum up, the modification of the bare Al with the addition of magnetic composites would increase the adsorption capacity.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter reviews the origin of heavy metals (Cr, Cd and Mn), technology of wastewater remediation, adsorption, adsorbents, nanomaterials, Al composites and properties of magnetism.

2.2 Heavy metals

Heavy metals are dense or transition metals that belong to Period 4 and above, which is located in the periodic table of elements between Groups 3 and 16. Their molecular weights range from 63.5 to 200.6 and their specific density exceeds 5 g /cm^3 (Fiyadh et al., 2019). Heavy metals are typically metallic elements with a relatively high density that are toxic and poisonous (Ali et al., 2018).

In fact, heavy metals consist of 35 total elements like mercury (Hg), lead (Pb), Cr, Cd, arsenic (As), Mn and nickel (Ni). Other heavy metals such as copper (Cu), palladium (Pd), silver (Ag), zinc (Z n), iron (Fe), selenium (Se), molybdenum (Mo) and cobalt (Co) also are the primary sources of pollutants in industries that discharge wastewater. As proof, Pb can be found from the metallurgy process, batteries manufacturing, electroplating and the production of pigments and ammunition (Zou et al., 2019).

Environmental pollution is a severe problem that arises from the rapid development of industry, especially with the excessive discharge of heavy metals into water sources. Heavy metals have biological and medicinal uses. However, they have detrimental effects if they are above the limit of concentration. According to the US

EPA, heavy metals are carcinogenic contaminants that can damage organs (Xu et al., 2018).

Heavy metals, which subsists in trace amounts in the environment, are toxic and poisonous due to non-degradable and accumulative properties (Asiandu & Wahyudi, 2021). The accumulation of heavy metals in the food chain or direct intake poses a risk of toxicity to aquatic life, leading to adverse health effects and loss of biodiversity (Zou et al., 2019). For instance, improper control for discharging widely used palladium (Pd) in the industries leads to the aquatic life's death (Salleh et al., 2015).

Heavy metals from the environment then bio-accumulate in bones, kidneys, muscles, and the brain through inhalation, ingestion, or skin contact. The World Health Organization reported that heavy metals affect organs and tissues such as kidneys, liver and skin, which lead to lung irritation (pneumonia), gastric irritation, failure of respective organs, chronic asthma, liver damage and dermatitis (Ali et al., 2018; Briffa et al., 2020; Gopal et al., 2021).

These worldwide issues must be given the utmost attention in order to ensure the long-term sustainability of the planet. Hence, the wastewater system is vital for industries that discharge mostly toxic heavy metals in line with the stringent regulation of Environmental Protection Agency has imposed to protect human beings (Fakeeha et al., 2018). Table 2.1 displays the WHO (2011) and USEPA (2012) drinking water standards.

Table 2.1 Drinking groundwater standard and health effects of various toxic heavy metals (Boselli et al., 2021; Denil et al., 2017; Mohammadi et al., 2019)

Heavy metals	Drinking groundwater standard (μg L^{-1}) by:		Health Effects
	WHO (2011)	USEPA (2012)	
Lead	10	15	Anaemia, muscular weakness, arthritis, mental retardation or autism, birth defects, psychosis, dyslexia, insomnia, dizziness, allergies, headache, appetite & weight loss
Nickel	70	Not mentioned	Chronic bronchitis, various kind of cancer and respiratory problems, birth defects
Zinc	Not mentioned	5000	Nausea, vomiting, epigastric discomfort, lethargy, tiredness, and agitation
Copper	2000	1300	Long-term exposure causes nose, mouth, and eye irritation, headaches, kidney and liver damage, anaemia, and gastrointestinal problems
Chromium	50	100	Human carcinogenic, causing lung cancers and allergic dermatitis
Cadmium	03	05	Kidney and skeletal damage, decreased haemoglobin and haematocrit levels, stomach irritation, vomiting, and diarrhoea causes respiratory fibrosis, dyspnea, and weight loss
Manganese	50	50	Cancers of various types, respiratory issues, cardiac disorders, and birth abnormalities

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2.2.1 Chromium (Cr)

Cr is a silver-grey, brittle, and lustrous transition metal with an atomic number of 24, a molecular weight of 51.1, and a density of 7.19 g/cm^3. It does not tarnish in air and burns when heated (Briffa et al., 2020). Cr as pollutant is introduced into natural waters by a variety of industrial wastewaters coming out from the industries such as tanneries, paint manufacturing, mining, aircraft, leather tanning, textile production, metal manufacturing, steel production, electroplating, dyes, photographic material production, pesticide's application, wood preservation and pulp processing (Baby Shaikh et al., 2018; Shi et al., 2017). Although Cr has valence states ranging from -2 to +6, only Cr (VI) and Cr (III) are stable in nature (Briffa et al., 2020).

Cr (III) is an essential trace element for human and animal health due to its role in lipid and sugar metabolism. However, plants do not require it because they do not produce lipids or sugars (Das et al., 2021). In fact, due to the possibility of conversion to Cr (IV), the possible risk of Cr (III) cannot be ignored. Cr (III) ions in water can easily be adsorbed on solid things and found in sediments. Far too much Cr in the soil will have a substantial influence on organic matter nitrification and cause Cr accumulation in edible plants. As a result, Cr (III) may pose a risk to humans and animals (Shapovalova et al., 2018).

This dangerous toxic heavy metal is due to its carcinogenic and mutagenic effects on human health. Cr may cause chronic illness, including dermatitis, bronchitis, cancer, skin sensitization, system failure, liver damage and genetic defects (Kumar & Jena, 2017; Shapovalova et al., 2018). Due of its toxicity, the World Health Organization and US Environmental Protection Agency (EPA) have set the maximum limits of Cr in drinking water and discharge of Cr effluents to 0.05 mg L^{-1} (Vaiopoulou

& Gikas, 2020). Thus, eradicating Cr from contaminated water is critical for environmental protection.

2.2.2 Cadmium (Cd)

Cd is found naturally in the water, air, soil, food and even ores of the earth. Cd is one of the major pollutants that are highly toxic in drinking water that come from mostly industrial wastewater and incineration (Ali et al., 2019). The primary sources of Cd contamination include melting of non-ferrous metals, sintering of ores, electroplating industry, electroplating, paint pigmentations, smelting, fertilizers, refining, textile, dyes and pesticides manufacturing (Awual et al., 2018; Ihsanullah et al., 2015; Lei et al., 2019). Cd is also used in the production of batteries, anticorrosive agents and pigments production (Al Hamouz et al., 2017).

Cd which is soluble in water tends to move in the medium and its bio accumulation leads to prolonged exposure. It also has carcinogenic and teratogenic effects which affect the lungs, liver, bone, and human kidney, which will malfunction and damage protein metabolism if overdose. As proof, Cd that was primarily accumulated in the kidney (target organ) has a biological life around 10 to 35 years showing the level of Cd toxicity (Lei et al., 2019). Exposure to Cd ions, which tends to accumulate in different organs, could lead to flu-like symptoms, renal tubular failure, bone deterioration, and even more serious damage such fractured bones, cancer, hypertension, and renal dysfunction (Awual et al., 2018; Simonescu et al., 2020). Meanwhile, long-term exposure of humans or animals to even trace amounts of Cd could cause serious health problems, such as kidney failure, damage to reproductive organs and bones, and birth defects (Lei et al., 2019).

Japanese Itai-Itai disease (a bone disease with badly pain and fractures) is the case to point out regarding Cd poisoning which had an effect in Fuchu, Toyama prefecture in 1955 (Nishijo et al., 2017). According to the guidelines of the World Health Organization, the permissible limits of Cd in drinking water was set to a maximum concentration of 0.003 mg L^{-1} (Chen et al., 2015; Ihsanullah et al., 2015; Simonescu et al., 2020). The timely remediation of unforeseen accidents is essential for protecting human health; hence it is crucial to create a new approach to detect Cd ions quickly, sensitively, and selectively even in the presence of diverse matrices. Therefore, a feasible technique for removing Cd ions to minimise pollution and harm to humans and animals is required for environmental policymaking.

2.2.3 Manganese (Mn)

Mn is essential and the second most abundant in nature which is usually formed as carbonates, oxides, silicates, or other minerals. Mn is a naturally occurring element that can be found extensively in the environment and crucial micronutrient for the human body and organisms (Tran et al., 2018). Because the human body requires a specific amount of trace minerals as a cofactor for a range of enzymes in intracellular action, this metal is also known as trace minerals. It could be detected in ground water and certain water from reservoirs at the bottom of the anoxic zones.

Having a density of 7.43 g/cm^3, it is a dense, chemically active, and strong metal that is also easily oxidised. The ionic form of Mn is the bivalent cation, Mn^{2+}, which is soluble in water. The most stable form of Mn is in the (II) oxidation state, which has a faint pinkish colour. It has organoleptic qualities that make it a pollutant. When exposed to oxygen, the brownish-red colour and insoluble nature of Mn in water become apparent (Nadia et al., 2020).

Mn is one of the heavy metals which has been widely used in the steel production. Water purification facilities, mining operations, and factories have contributed to Mn pollution. Mn has a lot of benefits in the areas of ceramics, electrical coils, batteries glass, fireworks, fertilizer, stock food additive, organic synthesis catalysts and alloying composite (Nadia et al., 2020). According to the World Steel Association (2019), global steel demand increased in 2019 and is expected to climb by 1.0 percent by 2020, reaching 1,752 million tonnes. Mn contamination in water sources has become a severe problem as the global steel production has increased (Nadia et al., 2020).

By accumulating in the food chain, Mn can give detrimental effects beyond limited concentration. Even though Mn is an essential mineral, concerns have been raised that Mn consumption in drinking water may have a negative neurological impact on intellectual and cognitive development. Mn accumulation in specific brain areas has been linked to neurotoxicity and degenerative brain diseases (Yahya et al., 2020). In addition, Mn intake during pregnancy could be harmful, leading to issues like DNA damage, respiratory problems, and even manganese-induced parkinsonism (Tran et al., 2018). Damaged children performed worse on tests of physical dexterity, speed, short-term memory, and visual recognition as compared to children exposed to controlled levels of Mn (Tran et al., 2018).

Excess Mn also tarnished cooking utensils, clothing, toiletries, and polluted food supplies, discoloured laundry, and gave drinking water a metallic flavour (Tran et al., 2018). Mn in the water supply also encourages the production of oxide layers in damaged pipes. Thus, the water flow is disrupted, which lowers water quality and raises distribution costs (Nadia et al., 2020). Thus, the maximum Mn concentration in drinking water was permitted by the World Health Organization was 0.05 mg L^{-1} (Tran et al., 2018).

2.3 Technology of heavy metals remediation

The widespread production of heavy metals used in industry results in greater hazardous heavy metal concentrations in the wastewater system. As a result, wastewater treatment is required for industrial after-production to protect human and the environment from the harmful effects of heavy metals. In wastewater technology, there are several methods for removing heavy metal ions. Examples of these technologies include precipitation, ion exchanges, membrane filtration, flocculation, electrolysis methods, reverse osmosis, and adsorption, as well as biological methods and solvent extraction (Salleh et al., 2015; Shapovalova et al., 2018; Zou et al., 2019)**.**

Precipitation is the most used strategy in the industry for heavy metal removal up to parts per million (ppm/ mg L^{-1}) levels from inorganic effluent due to its simplicity and cost-effectiveness (Chen et al., 2018). The process is simple, but its effectiveness is hindered by its low pH and the addition of other salts (ions). In this conventional system, insoluble metal precipitation such as hydroxide, carbonate, and phosphate are produced by reacting the dissolved metal in the solution. Chemical agents are used in this process to transform metal ions into insoluble precipitates of hydroxide, sulphide, carbonate, and phosphate. The solid precipitate is then separated using filtration (Abdullah et al., 2019). Once the insoluble metal precipitate, the solid could be removed as sludge at a low concentration. Instead of using a natural product, the method requires the use of additional chemicals to assist in the removal process, incurring additional costs and generating a high-water sludge content (Chen et al., 2018).

Another effective technology for removing heavy metals from industrial wastewater is ion exchange using strong-acid cation-exchange resins. There are two types of resins, natural and synthetic; the latter have received more attention due to their usefulness in metal removal (Nazaripour et al., 2021). Special ion exchangers, such as synthetic resins, act as cations or anions in the solution by removing heavy metals. In this technique, solid ion exchange resin with a strong sulfonic acid group (-SO_3H) or carboxylic acid group (-COOH) is commonly utilized. Reversible ion exchange between solid and liquid phases could occur, with H^+ released from functional groups to facilitate metal complexation with the free functional group (Abdullah et al., 2019). Nevertheless, ion exchange is highly sensitive to the pH of the aqueous solution. This method is not specific for heavy metal removal due to electrostatic interaction. Ion-exchange technology is undesirable because it requires frequent regeneration and has high operating costs due to the presence of competing alkali and alkaline earth cations, which are typically present in contaminated water at higher concentrations (Nazaripour et al., 2021).

Due to its simplicity of treatment principles, ease of operation, and resilience in the face of large water volumes and high concentration wastewater, electrolysis is commonly employed for the fundamental removal of heavy metals from industrial wastewater (Abdullah et al., 2019). The pollutants in wastewater are kept at a reactive state using electrical charges. Heavy metal ions are removed from wastewater when they are separated from the high concentration solution and deposited on the cathode by an external direct current. At the same time, the anode material, which consists of reductive strong ions, is released. Cation exchange membranes were used to separate the anode and cathode chambers during treatment to avoid the anodic oxidation (destruction) of chelating ligands, enabling the recovery of chelating ligands for subsequent reuse and the simultaneous collection of metals via electrodeposition (Zhu et al., 2019). Nevertheless, electrolysis is still a costly method due to the consumption of electrical energy and soluble anode materials used to remove the complicated metal contamination. The formation of residual organic ligands results in secondary pollution, and the electrodes are quickly passivated, therefore this technique is not optimal for treating low-concentration complex heavy metal effluent (Zhu et al., 2019).

The processes of coagulation and flocculation are vital to the disposal of wastewater and the production of potable water. The application of a coagulant or chemical in wastewater causes a chemical reaction, resulting in coagulation (Shrestha et al., 2021). As they dissolve in water, colloidal particles clump together to create flocs. Metals and other suspended materials gravitate toward these tiny aggregates, also known as flocs. A positively charged coagulant is used to neutralise the particles' surface negative charge and facilitate aggregation. The positively charged aggregates react with the anionic flocculant, joining together to create a bigger group that may be isolated by filtration. Small flocs formed by slow mixing water may grow and settle within the solution (Shrestha et al., 2021). This is referred to as flocculation. Though it is a simple and non-metal selective heavy metal separation process, it generates a large amount of sludge and presents a separation problem by transferring the hazardous chemicals to the solid phase (Abdullah et al., 2019).

A membrane separation method is a technology that uses high pressure to force feed water through a semipermeable membrane to separate certain materials from a solution. This procedure can be classified as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis based on pore size (RO) (Nazaripour et al., 2021). Diffusion allows molecules or ions to flow across the membrane, and the rate of diffusion is affected by pressure, temperature, membrane permeability, and the concentration of molecules or ions in the solution. The membrane separation process is primarily governed by three fundamental principles: adsorption, sieving, and electrostatic phenomena (Nazaripour et al., 2021). The adsorption mechanism is based on the solute's hydrophobic interactions with the membrane. The separation of materials via the membrane is determined by the membrane pore size and the size of the solute. Varied membrane processes with various separation methods have been developed based on these ideas. Polymeric membranes are becoming more popular due to their appealing qualities such as flexibility, excellent mechanical integrity, and ease of production (Shrestha et al., 2021).

Unfortunately, it has always been a challenge to treat waste water systems as the concentration of Ca^{2+}, Mg^{2+} and other background substances are higher than a trace amount of toxic heavy metal by lowering the value according to the standard (Dong et al., 2010). These methods need to be reviewed and developed more as they are still less effective and sometimes secondary wastes are more toxic than the first sources of wastewater (Jaafar et al., 2012).

The adsorption process is vital in the treatment of waste water, where heavy metals are eliminated. Due of its resistance to toxicity, adsorption stands out as a particularly useful method. In addition to being relatively easy to operate, adsorption's simple design, adaptability, and capacity to severely reduce the heavy metal concentration also make it a desirable option (Shapovalova et al., 2018). Some advantages and disadvantages of treatment technology for the removal of heavy metal from wastewaters are tabulated in Table 2.2.

Table 2.2 Treatment technology for the removal of heavy metal from wastewaters and associated advantages and disadvantages

Technology	Advantages	Disadvantages	References
Precipitation	Simple, cheap, effective	Large sludge content, high maintenance cost	(Chen et al., 2018)
Ion exchange	Fast kinetic, convenient process, economic, high regenerations	Only suitable for low metal concentrations, highly sensitive to pH, and the presence of free acids may result in low binding affinity, high initial capital, and maintenance cost	(Abdullah et al., 2019)
Electrochemical treatment	Simple, no additional chemicals required, moderate metal selectivity, and high volume tolerate	High initial capital cost, H_2 production, and floc filtration method	(Zhu et al., 2019)
Flocculation-coagulation	Economic and simple	Incomplete; must be combined with precipitation process	(Shrestha et al., 2021)
Membrane filtration	Low solid waste generation, low chemical consumption, short space requirements, and potential metal selectiveness	High initial capital cost, high maintenance and operation costs, membrane fouling, and restricted flow rates	(Nazaripour et al., 2021)
Adsorption	Adsorbents of a wide variety, high capacity, low cost, and simple operation	After a difficult post-treatment process, certain adsorbents must be hybridised for optimal binding capability	(Razzak et al., 2022)

2.4 Adsorption

Adsorption is the process of accumulating a large number of atoms, molecules or ions on solid, liquid or gas surfaces, for example, liquid-solid, liquid-liquid, gas-solid or liquid-gas interaction (Palabıyık et al., 2019). Two components involved in adsorption are adsorbent, the substance that acts as a surface for adsorbing samples and adsorbate, the substances that have been adsorbed onto the adsorbent. The ability of the adsorption process is measured by the capability of adsorbents that can trap heavy metals onto themselves. In a way, adsorption suggests the solid (adsorbent) binds molecules of ions or substances by physical attraction, ion exchange and chemical binding (Liu et al., 2021).

There are two types of adsorptions which are physisorption (Van der Waals) and chemisorption (chemical molecular bond). Physisorption is the weak interaction between the surface of the solid with the adsorbed molecules while chemisorption is the strong chemical bond between the adsorbent and the adsorbate. According to Liu et al. (2021), adsorption of heavy metals (adsorbate) occurs on the surface of adsorbents by means of ionic exchange or chemisorption.

Adsorption plays an important role in the removal of heavy metals in waste water treatment. It comes out as a highly effective technique, compared to other techniques as adsorption is insensitive to toxic substances. Adsorption is also simple in design, flexible, ability to reduce the heavy metal concentration to the lowest level and ease in operation (Shapovalova et al., 2018).

Other conventional techniques for the removal of heavy metal incur high capital costs which were unreasonable for small scale industries (Ni et al., 2019**).** In addition, adsorption is relevant to be used in industrial wastewater treatment compared to other methods due to the ability to reverse the process known as desorption and plausibility of metal recovery (Eskandari et al., 2020).

2.5 Adsorbents

The adsorbent is a medium used in the adsorption process to adsorb heavy metals or other unwanted compounds. Adsorbents can be categorised into five categories: natural materials, natural materials processed to develop their structures and properties, manufactured materials, agricultural solid wastes/industrial by-products, and biosorbents (Crini et al., 2019). It was a challenging task for investigating suitable materials to remove these toxic heavy metals in the wastewater treatment system. Continuous improvement was developed in the search for effective adsorbents for optimizing the quality and reducing the cost of treating waste water.

Natural adsorbents such as sawdust, wood, perlite, kaolin, clay, and cellulosic materials were commonly used in waste water treatment due to their abundant in nature, cheap, and readily available (Jain & Yadav, 2017; Mustapha et al., 2019). However, chemical modification is required to increase the performance and capacity of the adsorbent (Asere et al., 2019). The porous structure, thermal durability, wide surface area, and low cost benefits made perlite as an excellent material for the creation of composite microspheres for coating (Parlayici, 2019).

To increase the performance of the naturally occurring adsorbents, materials must be treated to develop their structures and properties. These materials include activated carbons, activated Al, and silica gel. Shapovalova et al. (2018) reported that activated carbon is the most common adsorbent used in the treatment of waste water for the removal of pollutants and heavy metal ions. Activated carbon derived from carbonaceous raw material was proved to be effective in the heavy metal ions removal from aqueous solution. Nevertheless, the utilization of activated carbon is not feasible in the waste water treatment due to the high cost of commercial coal of activated carbon and many losses in the process regarding the regeneration of the material (Shapovalova et al., 2018). Carbon Nanotubes (CNT) is another adsorbent that proves to be efficient in removing heavy metals like Pb (II) and Cu (II) (Nyairo et al., 2018). It possesses a small, hollow-layered, and fibrous structure, large external surface area, well developed mesoporous.

Besides that, manufactured materials such as polymeric resins, zeolites, and aluminosilicates were explored as adsorbents. Zeolite, a crystalline aluminium, and silica mixture, has a range of micro and macroporous structure of tetrahedral. Due to being rich in cation and high surface area, zeolite is one of the potential adsorbents in the petrochemistry, refinement catalysis industry and gas purification (Shi et al., 2018). Physical, chemical, composites, alkaline, salt, and other methods can be used to modify zeolite. These adsorbents have the benefits of being high capacity and effective. However, the adsorbents are sensitive, non-selective, and unable to run in large amounts (Crini et al., 2019).

Due to their low cost and effectiveness, agricultural solid wastes, and industrial byproducts such as date pits, fly ash, and red mud are also promising materials. As proof, the emergence of diverse agricultural wastes such as wheat, husk, leaves, corn powder and fruit waste like banana peel (Crini et al., 2019). Coconut husk, a common agricultural waste in Malaysia, useful to solve waste management concerns because it is abundant, cheap, and has a high surface area due to being rich in fibres (Malik et al., 2017). Similarly, orange juice residue or orange-peel studies has demonstrated a relevant efficiency in removing heavy metal. As a low-cost adsorbent, orange peel contains lignin, cellulose components, hydroxyl and carbonyl groups in the structure that are suitable in removing heavy metal in wastewater remediation (Saleh et al., 2020). In addition, the reuse of waste fly ash resolves the air pollutant issue as it is regarded as an irritant (Marinina et al., 2021).

Biosorbents are materials obtained from biological sources like agricultural byproducts such as chitosan, fungus, or bacterial biomass. They act as an excellent adsorbent to collect elemental and toxic wastes from the environment, including industrial wastes, heavy metals, fertilizers, pesticides, and air pollutants (Singh et al., 2020). They are abundant, low-cost, and environmentally friendly alternative to traditional wastewater treatment processes. However, biosorbents have a small size and low density, as well as poor mechanical stability and flexibility, which causes issues with metal ion desorption, sorbent separation from the medium, and regeneration. As a result, the options for implementing continuous biosorbent processes for metal removal are decreased, and biosorption's practical application in industrial situations was limited (Velkova et al., 2018).

Simultaneously, emerging nano adsorbents have sparked interest in this field of waste water technology. As evidence, Al has demonstrated the potential for greater adsorption capability for eliminating a toxic heavy metal, resulting in less pollution and simplicity of preparation. On the other hand, inorganic transition materials have attraction as useful adsorbents namely AB_2O_3 general structure of mixed metal oxide, for example, nickel aluminate ($NiAl_2O_4$) (Salleh et al., 2015). Table 2.3 summarises the advantages and disadvantages of different adsorbents.

Table 2.3 Advantages and disadvantages of adsorbents

Type of adsorbents	Examples	Advantages	Disadvantages	References
Natural material	Sawdust, wood, perlite, clay, kaolin, cellulose	Readily available, cheap	Require chemical modification	(Asere et al., 2019)
Natural materials treated	Activated carbons, alumina, silica gel	High capacity, renewable	Costly, performance depends on material	(Shapovalova et al., 2018)
Manufactured materials	Polymeric resins, zeolites	Effective, high capacity	Non-selective, sensitive, incapable running in large amounts	(Crini et al., 2019; Shi et al., 2018)
Agricultural wastes/ industrial by-products	Coconut husk, orange peels residue, fly ash, red mud	Low-cost, effective	Low capacity, need modification, non-selective	(Crini et al., 2019)
Biosorbents	Chitosan, fungi, bacterial biomass	Low cost, abundant, renewable	Incomplete/ Slow process, poor chemical stability	(Singh et al., 2020; Velkova et al., 2018)

2.6 Nanomaterials and alumina (Al)

Adsorbents typically have diameters in the micron range to accommodate the adsorption process and improve surface area (Martins et al., 2020). However, the diffusion was limited within particles leading to the low absorption rate, especially for large macromolecules. Mesoporous materials, such as alumina, titania, silica, nickel, and others, typically have a consistent route to attract active metal. However, due to larger particles (greater than 10 nm reported), the catalytic stability performance cannot be obtained (Zhong et al., 2018). The nanomaterials' unique property of greater adsorption capacity is made possible by the size quantification effect and the short diffusion route (Di et al., 2020).

Alumina, Al_2O_3 (Al) is one of the most effective nanomaterial adsorbents, and ceramic-like alumina is commonly employed (Rathore & Mondal, (2017). Al crystal divided into many structures include δ, η, γ, θ, α, and many others. Among these, γ and α Al have received the most attention. Gamma Al (γ - Al_2O_3) is of relevance because it has a large surface area and is very stable over the temperature range of most catalytic processes. Catalyst supports can benefit from the inherent acid-base characteristics, attractive mechanical features, and changeable surface physicochemical properties of Al (Tabesh et al., 2018). Figure 2.1 displays the structure of Al.

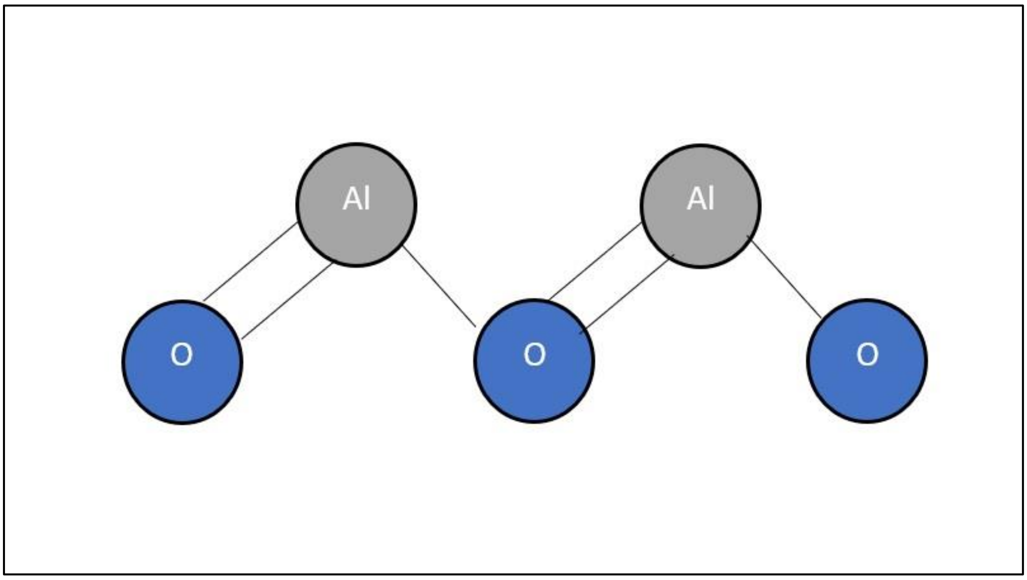

Figure 2.1 Structure of Al

Al is an adsorbent that can also support other materials composite with the ability to form active sites (Salleh et al., 2017). The benefit of the high surface area makes Al as popular support for metal ions. Modified Al was reported can remove various dyes, heavy metal, inorganic effluents, and many others in the industry. There is less work reported yet regarding the function of Al as ceramic support in composite materials. Nano-sized γ -Al_2O_3 particles synthesized by modified sol gel method using new precursors successfully adsorbed the Pb and Cd ions (Tabesh et al., 2018).

A comparison of Al-modified biomasses from agricultural residues for Ni and Cd removal was performed utilising three biomasses from agricultural residues (corn cob, orange peel, and oil palm bagasse) modified with Al nanoparticles. Increase in capacity adsorption confirmed the suitability of these Al-modified biomasses for the removal of heavy metal ions (Herrera-barros et al., 2021).

2.7 Al composites and magnetism

The demand for technologies for smaller materials leads to changes of these adsorbents in the nanoscale. In a more diminutive size, the stability of the adsorbents was reduced due to the agglomeration caused by the increase of the surface energy and the interactions between particles, including Van der Waals forces (Salleh et al., 2017). Despite their effectiveness in removing a heavy metal, the separation of the utilised adsorbents after treatment was challenging due to their smaller (nano) size, complex chemistry, and overlapping characteristics (Jiang et al., 2020).

To overcome these shortcomings, nanomagnetic metal oxide was utilized. Magnetic adsorbents can solve the major concern encountered by these nanoparticles due to their easy and rapid separation from water by an external magnetic field (Liu et al., 2016). Metal oxides (MOs) are emerging as potential adsorbents due to their large surface areas and favourable adsorption towards heavy metals, as well as their high adsorption capacity and selectivity (Gupta et al., 2021).

The adsorption of heavy metal using a modification of Al with MO has still not been extensively explored. It was anticipated that by enhancing their physical properties in the nano-scale industry, the studied combinations would be able to manufacture competent adsorbents with increased adsorption potential. While this may be true, simple, cheap, and less consuming time adsorbents are preferred. Notably, past research