THE EVOLVING TREND OF ZEOLITE APPLICATIONS IN WATER, WASTEWATER, AND LEACHATE TREATMENT IN PAST 40 YEARS (1980-2020)

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THE EVOLVING TREND OF ZEOLITE APPLICATIONS IN WATER,

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YEARS (1980-2020)

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I hereby declare that all corrections and comments made by the supervisor(s)and   examiner have been taken into consideration and rectified accordingly.

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ABSTRAK

Zeolit merupakan media yang biasa digunakan dalam olahan air, air sisa dan larut lesap untuk menyingkirkan bahan pencemar melalui proses penjerapan dan pertukaran ion. Proses ini boleh berlaku secara serentak dalam sistem olahan, walau bagaimanapun masih kurang tumpuan diberikan oleh penyelidik untuk membezakan keduanya. Kajian ini dijalankan untuk mengkaji proses penjerapan dan pertukaran ion oleh zeolite sebagai dalam olahan air, air sisa dan larut lesapan. Faktor yang memberi kesan terhadap pretasi proses penjerapan dalam ujian kelompok iaitu pH, dos penjerap, masa dan kepekatan awal. Terdapat banyak penyelidik merumuskan bahawa isoterma Langmuir secara penjerapan lapisan mono adalah paling biasa terpakai untuk zeolit. Juga, terdapat banyak penyelidik telah membuktikan bahawa model susunan pseudo-kedua merupakan kinetic penjerapan yang sesuai untuk zeolit. Walau bagaimanapun, penjerapan sususan pseudo-kedua seperti model intra-partikel juga perlukan kajian lanjut. Dalam mekanisme pertukaran ion, pemilihan terhadap ion adalah berdasarkan pada kepadatan cas ion dan gubahan kimia dalam zeolit. Dalam kajian lajur, kadar aliran dan kedalaman dasar merupakan faktor yang memberi kesan terhadap kecekapanpenyingkiran bahan pencemar. Analisis bibliometrik terhadap trend aplikasi zeolit dalam olahan air, air sisa dan larut lesapan dalam 40 tahun yang lepas (1980-2020) juga telah dikaji. Dari pangkalan data Scopus, terdapat 3782 artikel yang telah diterbit berkaitan dengan menggunakan zeolit dalam olahan air, air sisa dan larut lesapan. China merupakan negara yang paling produktif menyelidiki aplikasi zeolit dalam olahan air, air sisa dan larut lesapan. Aplikasi zeolit dalam olahan air paling banyak dikaji sepanjang 40 tahun yang lepas manakala fokus kepada larut lesapan adalah yang terendah. Menggunakan perisian VOSviewer, penggunaan kata kunci "zeolite" adalah yang tertinggi dikuti oleh "adsorption" dan "clinoptilolite". Akhir sekali, rangkaian tindihan telah dijalankan untuk

menilai *trend* penyelidikan berdasarkan kata kunci penyelidik. Julat purata 5 tahun penerbitan teratas dalam pengulangan kata kunci oleh penyelidik berlaku pada tahun 2006-2014.

ABSTRACT

Zeolite is commonly used as an adsorbent to remove the pollutants in water, wastewater and leachate treatment through the adsorption and ion exchange mechanisms. However, not much work has been conducted to differentiate between the adsorption and ion exchange mechanisms, though they may occur concurrently. This study aims to review the adsorption and ion exchange mechanisms in water, wastewater and leachate treatment by using zeoliteas an adsorbent and/or ion-exchanger. The performance of the adsorption mechanism is affected by various parameters such as pH, adsorbent dose, contact time and initial concentration in the batch study. Many researchers found that Langmuir isotherm is the common adsorption isotherms found in zeolite, which is assumed to be monolayer adsorption. Many researchers also proved that the pseudo-second-order model is the common adsorption kinetics in zeolite to remove contaminants. However, the adsorption mechanism cannot be based on the simple fitting of the pseudo-second-order model, and further finding such as the intra-particles diffusion model need to be conducted. In the ion-exchange mechanism, the selectivity of ions is based on the charge density of the ions and the chemical composition of the zeolite. In the column study, flow rate and bed depth are the factors that would affect the removal efficiency of the pollutants in the experiment. The bibliometric analysis on the trends of zeolite application in water, wastewater and leachate treatment in the past 40 years (1980-2020) has also been conducted. From the Scopus database, 3782 papers had been published related to water, wastewater and leachate treatment. China is the most productive country among other countries on zeolite applications in water, wastewater and leachate treatment research. In the past 40 years, research on zeolite applications in water treatment has the highest number of publications compared to wastewater and leachate treatment. On the other hand, research on zeolite applications in leachate treatment is the

lowest. By using VOSviewer software, the highest occurrence author keyword is the "zeolite", followed by "adsorption" and "clinoptilolite". Lastly, an overlay network was carried out to discern the hottest research trend. The range of the average publication year of the top 5 occurrences author keywords in water, wastewater and leachate treatment research are from year 2006 – 2014.

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LIST OF SYMBOLS

SiO_2	Silicon Oxide
AlO_2	Aluminium Oxide
O	Oxygen
Si	Silicon
Al	Aluminium
Na^+	Sodium ions
K^+	Potassium ions
Ca^+	Calcium ions
Cd	Cadmium
Cr	Chromium
Cu	Copper
Pb	Lead
Zn	Zinc
R^2	Linear Coefficient
NaCl	Sodium Chloride
%	Percentage
C_e	Concentration of adsorbate at equilibrium
K_L	Langmuir constant related to adsorption capacity
q_e	Amount of adsorbate at equilibrium
q_m	Maximum adsorption capacity
K_F	Freundlich constant related to adsorption capacity
$1/n$	Adsorption intensity
R	Universal gas constant
b	Temkin constant

T	Temperature
β	Dubinin-Radushkevich constant
ε	Adsorption potential
A and B	Redlich-Peterson isotherm constant
P	Pressure in bar
C_o	Saturated adsorption concentration
a	Adsorption affinity
n	dimensionless parameter that qualitatively characterises the heterogeneity of the adsorbate-adsorbate system.
q_t	Adsorbate adsorbed onto the adsorbent at time
q_e	Equilibrium adsorption capacity
k_1	Rate constant per minutes
k_2	Pseudo-second-order rate constant
Pb^{2+}	Lead ions
Mn^{2+}	Manganese ions
NH_3-N	Ammoniacal Nitrogen
Kg	Kilogram
€	Euro sign

LIST OF ABBREVIATIONS

PBU	Primary Building Unit
SBU	Secondary Building Unit
CMC	Critical Micelle Concentration
GAC	Granular Activated Carbon
D-R	Dubinin-Radushkevich
COD	Chemical Oxygen Demand
SCG	Spent Coffee Grounds
USM	Universiti Sains Malaysia

CHAPTER 1

INTRODUCTION

1.1   Background

As rise in the world's population and the amount of industrial and municipal operations increased, the demand for water to be supplied to residents and the production of waste generated from these activities also increased. The world's population is estimated to increase by 2 billion people over the next 30 years, from 7.7 billion today to 9.7 billion in 2050, for a total of about 11 billion people about 2100 (World Population Prospects 2019 : Highlights, 2019). Water demand is estimated to grow by 1% per year after the 1980s, with similar rises expected to continue until 2050. The water demand increases from 20% to 30% above the existing demand for water due to increased industrial and domestic sectors (UN World Water Development Report 2019, 2019).

The world's waste is around 2.01 billion tonnes of waste, with a per capita average waste of 0.74 kg daily, but overall waste is projected to rise to 3.40 billion tonnes by 2050. The world's waste is around 2.01 billion tonnes of waste, with a per capita average waste of 0.74 kg daily, but the global waste is projected to rise to 3.40 billion tonnes by 2050 (Kaza et al., 2018). As demand for water and waste from industrial and municipal businesses is expanding year after year, treatments are required to increase water quality before discharge to water and human use.

Several heavy metals are found in wastewater and leachate, such as Zn, Cu, Pb and Fe, which trigger health hazards and environmental degradation (Briffa et al., 2020). These heavy metals are found in anthropogenic activities, landfilling and agricultural activities (Madhuppriya et al., 2020). Ammonium ion in the leachate and wastewater is another pollutant produced from landfill activities (Ye et al., 2015).

Adsorbents such as bentonite, zeolites, activated carbon, and nano-sorbents can eliminate heavy metals and ammonium ions from wastewater and leachate (Atkovska et al., 2018). Zeolite is an adsorbent widely used to extract heavy metals and ammonium ions due to its low expense, ecological and strong ion exchange capacity (Tasić et al., 2019).

In the method of heavy metal reduction, zeolite serves as an absorbent and ion exchanger. (Rashed and Palanisamy, 2018). On natural zeolite, the ion exchange and adsorption mechanisms occur concurrently with the hydrolysis step in an aqueous solution, with the adsorption process occurring first before the ion exchange process. A variety of variables affect the effectiveness in removing the heavy metals in zeolite during the treatment process, including the type and quantity of zeolite used, the surface area of zeolite, the initial concentration of pollutants, the pH content of the solution, temperature, and contact time (Margeta et al., 2013).

Zeolite was first identified by the Swedish mineralogist called Axel Fredrik Cronstedt in 1756 (Margeta and Farkaš, 2020). There are several types of zeolite, each with its chemical structure and other characteristics, such as Clinoptilolite, Heulandite and Natrolite (Moshoeshoe et al., 2017). Synthetic zeolites are a form of zeolite that can be made synthetically (Król, 2020). Those synthetic zeolites can be made in various ways, such as hydrothermal method, solvothermal method and Ionothermal method (Mgbemere et al., 2017).

Zeolite study was conducted in the form of research articles, journals, and reviews by various researchers. Tayler and Pauling have first discovered the chemical composition of natural zeolites in 1930. Following that, various authors focused on the discovery of several commercially available zeolites, as well as zeolite properties and zeolite modification. These experiments were also conducted to evaluate zeolite's ability

to successfully extract heavy metals in various areas, including wastewater treatment, water treatment, and leachate treatment (Margeta and Farkaš, 2020).

1.2 Problem Statement

Zeolites are commonly used to eliminate heavy metals and ammonium ions in wastewater, water and leachate treatment. It uses two methods to extract contaminants: adsorption and ion exchange. However, there is not much work done to analyse the difference between the adsorption and ion exchange process in the water, wastewater, and leachate treatment using the zeolite application. There are various zeolite applications in treating different types of contaminants in the water, wastewater and leachate. The performance and mechanism of each have not been widely analysed and reported.

Various research articles, journals, and review papers related to zeolite studies have been published in Scopus by different researchers. Since 1980, the number of research articles and review papers on zeolite studies in Scopus has increased. However, no analyses had done which the analysis of research trends in zeolite application in water, wastewater and leachate and the intensity of zeolite research and application started to increase from 1980. Therefore, studying the evolving trends of zeolite application in wastewater, water, and leachate treatment must also be conducted from 1980 to 2020.

1.3 Objective

The objectives of this study are as follows:

1. To conduct a review on zeolites as an adsorbent and as an ion exchanger in water, wastewater and leachate treatment and discuss the theory, mechanism and performance.

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2. To analyses the evolving trends of zeolites application in water, wastewater and leachate treatment over the past 40 years (1980 – 2020)

1.4   Scope of Study

The scope of the study involves:

1. To interpret the evolving trends of zeolites in water, wastewater and leachate treatment in the past 40 years.

2. Enable to differentiate between the theory and removal mechanism of the adsorption and ion exchange process that occurs in zeolites during water, wastewater and leachate treatment

1.5   Significance of the study

The review will provide information on the current gap in applying zeolite for water, wastewater and leachate treatment. This information helps identify these materials' future direction for environmental control, involving water, wastewater, and leachate treatment. The champion in the field will also be determined. Hence, possible research collaboration could be work on to establish a further treatment system.

1.6   Dissertation Overview

In this dissertation, adsorption and ion exchange mechanisms in zeolite for the water, wastewater and leachate treatment are discussed, and the evolving trends of zeolite applications in the past 40 years (1980-2020) is also analysed. In Chapter 1, the dissertation's overview is discussed, such as the problem statement and objective of the study are determined. The type of zeolite, structure and properties of zeolite, application of zeolite, zeolite performance, mechanisms of zeolite in the treatment process, and the

cost factor needs to be discussed in Chapter 2. Bibliometric analysis is also required to be discussed in this chapter to understand this analysis conducted by various authors.

Method of extracting the data from Scopus, the process of screening of data and the way to analyse the data have discussed in Chapter 3. In Chapter 4, the adsorption and ion exchange mechanisms in water, wastewater, and leachate treatment are reviewed. Different analysis categories have conducted, such as authorship analysis, journal analysis, country analysis and other analysis to analyse the evolving trends of zeolite applications in the past 40 years. The difference between the adsorption and ion exchange mechanisms and the top productive articles on zeolite applications is concluded in Chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1   Introduction

Natural zeolites are ecologically and commercially appropriate hydrated aluminosilicate structures with excellent ion exchange and adsorption properties. Their performance in different technological methods depend on their physical and chemical properties, strongly related to their geological deposits. Due to the abundance of negative charge on zeolite's surface resulting from the isomorphic substitution of silicon by aluminium in primary structural units, natural zeolites belong to the cationic exchanger group (Margeta et al., 2013).

2.2   Structure and Properties of Zeolites

The zeolites are made of the aluminosilicate framework's elementary configuration, consisting of the tetrahedral structure of the silicon cations and the aluminium cations, shrouded by four oxygen anions. Each oxygen ion in the Si-O and Al-O bond joins two cations and is shared by two tetrahedrons, resulting in a three-dimensional structure of the SiO_2 and AlO_2 tetrahedral building blocks. In the atoms' arrangement, each tetrahedron consists of four O atoms adjoining with the Si or Al cation, resulting in a three-dimensional silicate tetrahedron configuration (Moshoeshoe et al., 2017). SiO_4 and AlO_4 tetrahedrons are known as primary building units (PBUs) of zeolites, and when both of them are connected through oxygen ions, it forms secondary building units (SBUs) be created. Some silicon ions are substituted by aluminium ions, causing the structure to have a net negative charge. The counterions, which are generally alkaline or alkaline earth metals such as Na^+, K^+ and Ca^{2+}, will neutralise the negative charges (Margeta et al., 2013).
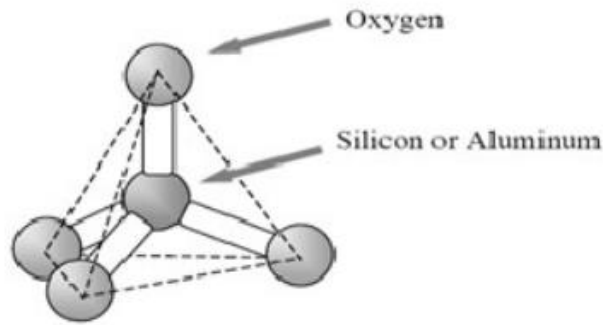
Figure 2.1: Schematic of Building Unit of Zeolite Structure (Mgbemere et al., 2017)
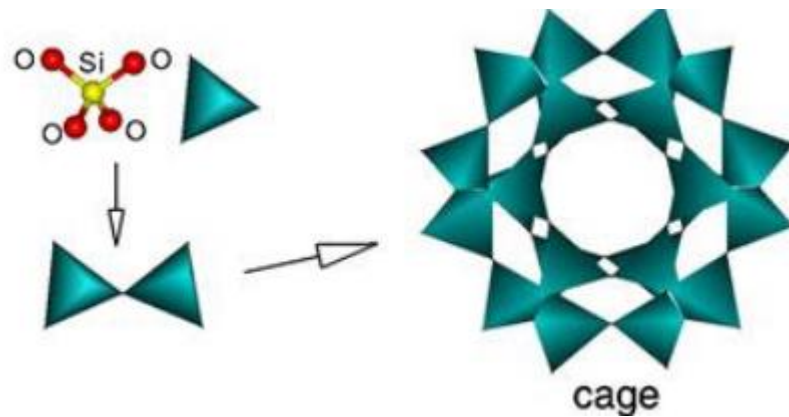
Figure 2.2: Combination of $(SiO_4)^{4-}$ PBUs to form SBUs, alignment of which results in a cage (Moshoeshoe et al., 2017)

The general chemical composition for zeolite is $M_{x/n}[Al_xSi_yO_{2(x+y)}]. pH_2O$, where M = Na, K, and/or Ca, Mg and n is the charge of the cation; y/x = 1-6, p/x = 1-4 (S. Wang and Peng, 2010). Different types of zeolite have various form of chemical formula. For example, clinoptilolite's general formula is $(K_2, Na_2, Ca)_3Al_6Si_{30}O_{72}.21H_2O$ (Tasić et al., 2019; Wang and Peng, 2010). However, numerous experiments have discovered that clinoptilolite has distinct chemical compositions. The removal performance of heavy metals in the treatment process would be influenced by clinoptilolite's chemical composition (Tasić et al., 2019).

One of the characteristics of zeolites' composition is their pore structure. Zeolites have pore structures that are defined by cavities or channels formed in the lattice of each zeolite, and the pore has a volume and diameter that are specific to each zeolite. The

cavities are joined together by pores, each of which has a unique diameter depending on the zeolite. The pore size and shape of a zeolite framework influence its adsorption properties and potential to function as a molecular sieve. The form of pore opening mechanism found in zeolites is known to influence their catalytic and adsorptive processes. The smaller the pore size, the lower the member rings, with 8 member rings having a smaller pore size than 12 member rings (Mgbemere et al., 2017). There is research on the role of zeolite pore structure on the adsorption of volatile organic compounds. In this analysis, they discovered that faujasite zeolites have a higher adsorption capacity than mordenite zeolites due to faujasite zeolites' large surface area and dependent on mesopore volume. In contrast, mordenite zeolites have a small surface area, dependent on the crystal structure (Kim and Ahn, 2012).

Zeolites have a variety of specific properties due to their unique structure, such as high degree of hydration, low density and large void volume when dewatered, the stability of crystal structure, cation exchange characteristics, regular molecular, ability to adsorb gases and catalytic properties (Ulmanu and Anger, 2012). Zeolites serve as ion exchangers, as adsorbents and as catalysis to eliminate heavy metals and ammonium ions (Mgbemere et al., 2017). However, some surrounding variables influence the efficiency of removing heavy metals, such as pH of the solution, contact time and initial metal concentration (Salam et al., 2011). Zeolite has undergone a process of alteration, such as physical modification and chemical modification, to enhance heavy metal removal efficiency (Shi et al., 2017).

2.3   Type of Zeolites

There are few types zeolite that can be obtained from nature or synthesized from raw materials. To have better performance in the treatment process, the zeolite is undergone the modification to increase the removal efficiency.

2.3.1   Natural Zeolite

Natural zeolites are present as cavity fillings in mafias of volcanic rocks, possibly due to fluid or vapour deposition (Zeolite, 2020). Natural zeolite formation occurs as the volcanic ash is transported by winds, settled down to establish dense ash beds. However, some of the ash dropped into the wetlands or sea, and the water infiltrated through the ash beds. Natural zeolite is formed from a chemical reaction between volcanic ash and saltwater (Rhodes, 2010).

Natural zeolites have a strong selectivity on heavy metal ions and ammonium ions. Heavy metal ions can be found in wastewater treatment and ammonium ions in municipal, industrial, and agricultural waste. Therefore, Zeolites used in environmental conservation and agriculture. On the other hand, natural zeolites have restricted industrial uses due to their crystal shape, narrow channel diameters that prevent large molecules from being adsorbed (Król, 2020).

Various researchers have discovered various types of natural zeolites. These zeolites are classified according to their chemical formula, as seen in Table 2.1:

Table 2.1: Structural Properties of natural zeolite (Margeta et al., 2013; Wang and Peng, 2010)

Zeolite	Chemical formula
Clinoptilolite	$(K_2, Na_2, Ca)_3Al_6Si_{30}O_{72}.21H_2O$
Mordenite	$(Na_2, Ca)_4Al_8Si_{40}O_{96}.28H_2O$
Chabazite	$(Ca, Na_2, K_2)_2Al_4Si_8O_{24}.12H_2O$
Phillipsite	$K_2 (Ca, Na_2)2Al_8Si_{10}O_{32}.12H_2O$
Scolecite	$Ca_4Al_8Si_{12}O_{40}.12H_2O$

Analcime	$Na_{16}Al_{16}Si_{32}O_{96}.16H_2O$
Laumontite	$Ca_4Al_8S_{16}O_{48}.16H_2O$
Erionite	$(Na_2, K_2, MgCa_{1.5})_4Al_8Si_{28}O_{72}.28H_2O$

2.3.2   Modified Zeolite

The detailed chemical/structure makeup of the adsorbent determines the adsorption properties of any zeolite. The adsorption mechanism is influenced by the Si/Al ratio, cation form, quantity, and location. The alteration methods are carried out to increase the removal performance of heavy metal ions in the zeolite (Wang and Peng, 2010).

Physical alteration is one method for modifying zeolite. Physical alteration is divided into two types: thermal modification and ultrasonic modification. Thermal modification is generated by muffle furnace heating or microwave heating, which may reduce zeolite's surface resistance and increase its exchange adsorption potential at high temperatures. This method's advantages are simple, heating time saving and high efficiency (Shi et al., 2017). Ultrasonic alteration utilises ultrasound to extract impurities from zeolite pores, improving adsorption effectiveness (Zieliński et al., 2016).

Another process for altering zeolite is chemical alteration. The chemical alteration may be categorised into many methods, including acid/base treatment, salt treatment, and surfactant treatment. In the acid/base treatment, the zeolite cations are substituted by hydrogen ions in acid-modified zeolite to improve porosity and unique surface area. Simultaneously, the silicon is dissolved in alkali modified zeolite to reduce the Si/Al ratio of the zeolite and create a uniform pore size (Shi et al., 2017). The advantages of acid/base treatment involve extracting impurities that clog pores, eventually eliminating cations to transform them to H-form, and dealuminate the

structure. However, it will reduce the cation exchange capacity (S. Wang and Peng, 2010).

Natural zeolites have no affinity for anions and poor adsorption for organics in an aqueous solution due to the structure's net negative charge (Wang and Peng, 2010). The zeolite surface must be modified with an inorganic salt solution to allow the zeolite to extract anions from water (Margeta et al., 2013). Therefore, the alteration of zeolite's surfactant may improve the anion removal rate. When the surfactant concentration is equivalent to or less than the critical micelle concentration (CMC), the zeolite surface's negative charge will adsorb surfactant cations by electrostatic force, allowing polluted cations in wastewater to replace with exchangeable zeolite cations. If the surfactant concentration in the solution transcend CMC, the surfactant's alkyl chains are drawn to each other through hydrophobic contact, resulting in the formation of bilayer molecules with positively charged head groups zeolite surface to adsorb anionic pollutants (Shi et al., 2017).

2.3.3   Synthetic Zeolite

Due to crystalline products' purity and particle sizes' uniformity, synthetic zeolites have been used widely more often than natural zeolites (Bogdanov et al., 2009). A few techniques are used in the laboratory to synthesise zeolites, such as the hydrothermal method, solvothermal method, and ionothermal method (Mgbemere et al., 2017). The synthesis reaction generally requires the use of special instruments, clean substrates, and energy. Consequently, the product's price could be considerably greater than the natural zeolite cost (Król, 2020).

The advantages of synthetic zeolite in the treatment process are as follows: high adsorption capacity for heavy metal ions (Kozera-Sucharda et al., 2020), larger pore size,

which enabling larger materials to be absorbed (Król, 2020), and greater thermal stability (Bogdanov et al., 2009). The nature of the reactants and their pre-treatments, process temperature, reaction time, and pH of the reaction mixture are all variables that will influence crystal purity and product yield (Bogdanov et al., 2009).

Various raw materials, such as kaolin, rice husk powder, and fly ash, may be used to synthesise zeolite (Mgbemere et al., 2017). The alkali fusion process, accompanied by the hydrothermal method, is used to create zeolite X from fly ash. The raw fly ash samples are first filtered via a BSS Tyler sieve. The fly ash samples are then processed with hydrochloric acid to improve their zeolite formation activity, which helped to dealuminate the fly ash and extract iron to a certain amount. The sodium hydroxide is then combined with fly ash in a pre-treatment ratio at temperatures ranging between 500 $^{\circ}$C to 600 $^{\circ}$C. After cooling to room temperature, the mixture is ground further and applied to water. Finally, the mixture is held at about 90 $^{\circ}$C for 6 hours without being disturbed, and then it is purified to eliminate excess sodium hydroxide. Zeolite X is obtained (Ojha et al., 2004).

Table 2.2 shows the synthetic zeolites that synthesised by various researchers from different raw materials.

Table 2.2: Type of synthetic zeolite synthesised from raw materials

Raw Material	Type of Zeolite Synthesised	Reference
Fly Ash	X-type Zeolite, Na-Zeolite	(Ojha et al., 2004) (Querol et al., 1997)
Kaolin	Zeolite Y, NaA Zeolite	(Somderam et al., 2019) (Bai et al., 2018)
Rice Husk Ask	Zeolite A, Zeolite L, Zeolite Beta	(Wajima et al., 2009) (Sundari et al., 2018) (Prasetyoko et al., 2006)
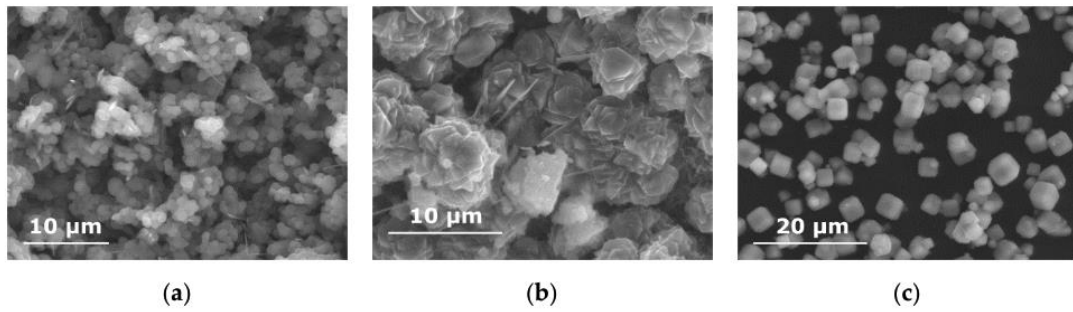
Figure 2.3: Microstructures of Zeolites obtained in hydrothermal conditions at low temperature (< 100 $^{\circ}$C): (a) Zeolite X; (b) Zeolite Na-P1; (c) Zeolite A (Król, 2020)

2.4   Application of Zeolites

Zeolites are widely used in the various fields such as water treatment, wastewater treatment and leachate treatment. Due to adsorption and ion exchange mechanism in zeolite, zeolite is applied on those fields to remove the contaminants or pollutants.

2.4.1   Water Treatment

Water is necessary for human consumption, but the water may be treated using zeolite to ensure its quality. Ammonia, humic acid, and heavy metal ions are some of the contaminants found in water and groundwater that harm human health when ingested and need to be removed (Wang and Peng, 2010).

Various studies have been carried out to extract pollutants from water using various zeolites under different conditions and shown in Table 2.3:

Table 2.3: Water treatment research conducted by various researchers

Type of Zeolite	Removal Pollutants	Parameters	Reference
Modified zeolite (modified by HNO$_3$ and NaOH)	Sb^{3+}, Mn^{2+}	Zeolite dosage, contact time, initial metal concentration, temperature, adsorption isotherm, adsorption kinetic	(Zhang et al., 2014)
K-Type Zeolite	Pb^{2+}	initial metal concentration,	(Kobayashi et al., 2020)

Type of Zeolite	Removal Pollutants	Parameters	Reference
		temperature, pH, contact time, adsorption capacity, adsorption isotherms	
Natural zeolite-alginate, Fe(III)-modified zeolite-alginate	Pb^{2+}	Adsorption isotherm, Initial metal concentration, pH	(Kragović et al., 2018)
Natural zeolite of the Yagodninsky deposits, Kamchatka region	Copper, nickel, cobalt, and iron	Adsorption isotherm	(Belova, 2019)
Zeolite 10A, Zeolite 13X, Natural Zeolite, Zeolite 3A	Zinc, cadmium	Initial metal concentration, Adsorption isotherm	(Kozera-Sucharda et al., 2020)

2.4.2   Wastewater Treatment

Since the number of pollutants in the water has risen due to increased industrial activity, the water must be treated before being discharged (Moshoeshoe et al., 2017). Heavy metals in wastewater will create severe environmental problems, so zeolite is used to extract them by the adsorption and ion exchange processes (Margeta et al., 2013).

There have been several studies done on the use of zeolite in wastewater treatment and shown in Table 2.4:

Table 2.4: Wastewater treatment research conducted by various researchers

Type of Zeolite	Removal Pollutants	Parameters	Reference
Natural zeolite	Copper, lead, cadmium	Adsorbent mass, Adsorption kinetics, Initial solution concentration, pH, adsorbent particle size, agitation speed	(Elboughdiri, 2020)
Al-Waste Based Zeolite	Ammonium ions	Contact time, pH, Adsorbent dose, Initial metal concentration, Adsorption kinetics, Adsorption isotherm	(Sánchez-Hernández et al., 2018)
Zeolite clinoptilolite	Copper, chromium, iron	pH, adsorption kinetics, adsorption isotherms,	(Zanin et al., 2017)

| Zeolite Y | Fatty acids, hydrocarbon compounds | pH, adsorption kinetics | (Navalon et al., 2009) |

2.4.3   Leachate Treatment

There are many ways for managing leachate, including aerobic biological treatment, anaerobic biological treatment, physiochemical treatment, coagulation, and specialised methods (Raghab et al., 2013). The application of zeolites in municipal wastewater treatment seeks to improve the performance of the pollutant removal process. Ammonium ions are one of the contaminants in leachate that must be eliminated (Moshoeshoe et al., 2017).

Various studies related to the leachate treatment by using the zeolite to remove the pollutants and shown in Table 2.5:

Table 2.5: leachate treatment conducted by various researchers

Type of Zeolite	Removal Pollutants	Parameters	Reference
Clinoptilolite	Ammonia	Adsorption isotherm, Adsorption kinetics, the concentration of ammonia, Contact time	(Liu and Lo, 2001)
Natural zeolite	Ammonium ions	Zeolite dosage, Contact time, pH, stirring speed	(Ye et al., 2015)
Clinoptilolite	Ammonia-nitrogen, Manganese, Cadmium	Oxygen content, Selective ions	(Kasmuri et al., 2018)
Clinoptilolite	Ammonium nitrogen, Dissolved oxygen demand, Colour	Particle size, Stirring rate, Zeolite dosage, pH, initial ammonium concentration, adsorption kinetics, adsorption kinetic	(Genethliou et al., 2021)
Heat-activated zeolite	Ammoniacal nitrogen, Colour, Chemical oxygen demand	Zeolite dosage, pH, adsorption isotherms	(Aziz et al., 2020)

2.5   Adsorption and Ion Exchange Mechanisms in Zeolite

Adsorption and ion exchange mechanisms are the mechanisms occur in the zeolite during the treatment process to remove the pollutants. Both mechanism is occur concurrently to remove the pollutant, where the the pollutant is adsorbed on the zeolite's surface and the heavy metals in the solution is exchanged with the cations in the zeolite.

2.5.1   Adsorption Mechanism

There is a relationship between adsorption and ion exchange, identical to both since the transition of mass from fluid to the solid phase is common in both processes. Ion exchange may be regarded as a adsorption mechanism, but ions are adsorbed species as opposed to adsorption, where electrically neutral species are adsorbed (Inglezakis and Poulopoulos, 2006). Zeolite consists of these two properties due to the reactive surface due to the existence of Al at the Si ion adsorption sites and the crystalline system of micropores. These properties enable zeolites to extract heavy metal ions from wastewater and leachate (Rashed and Palanisamy, 2018).
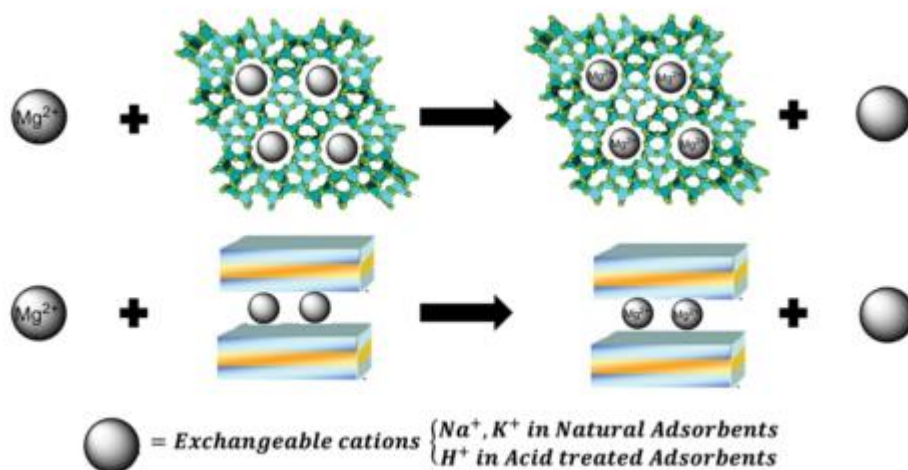
Figure 2.4: Mechanisms of adsorption of Mg (II) ions from aqueous solution on pristine and acid treated zeolite bentonite (Shahmirzadi et al., 2016)

2.5.1(a)   Adsorption Isotherm

The adsorption isotherm equation expresses the relationship between the quantity of solute adsorbed and the fluid phase's solute concentration (Salam et al., 2011). Adsorption isotherms are used to determine surface properties, including adsorbent affinity and adsorption capacity (Moshoeshoe et al., 2017). There are many forms of adsorption isotherms, namely Langmuir and Freundlich, commonly applied in the studies (Margeta et al., 2013).

Adsorption isotherms are categorised into Type I, Type II, Type III, Type IV, and Type V. Langmuir adsorption can be explained in Type I adsorption isotherm; the graph shown is monolayer adsorption. The type II adsorption isotherm differ significantly from the Langmuir model of adsorption, and monolayer formation occurs due to the intermediate flat region in the isotherm. At lower pressure, the Type III adsorption isotherm has an area similar to Type II. As a consequence, this describes the creation of a monolayer followed by a multilayer. The isotherm's intermediate flat area relates to monolayer forming. When the pressure below the saturation vapour pressure, the saturation level is achieved. The explanation of Type IV adsorption isotherm is almost similar to Type III adsorption isotherm. When the pressure below the saturation pressure of the gas, the saturation level is achieved. Lastly, Type V adsorption isotherm is identical to Type IV (Gawande et al., 2017). Figure 2.4 shows the graph of Type I to Type V isotherm.

(a)

(b)

(c)

(d)

(e)
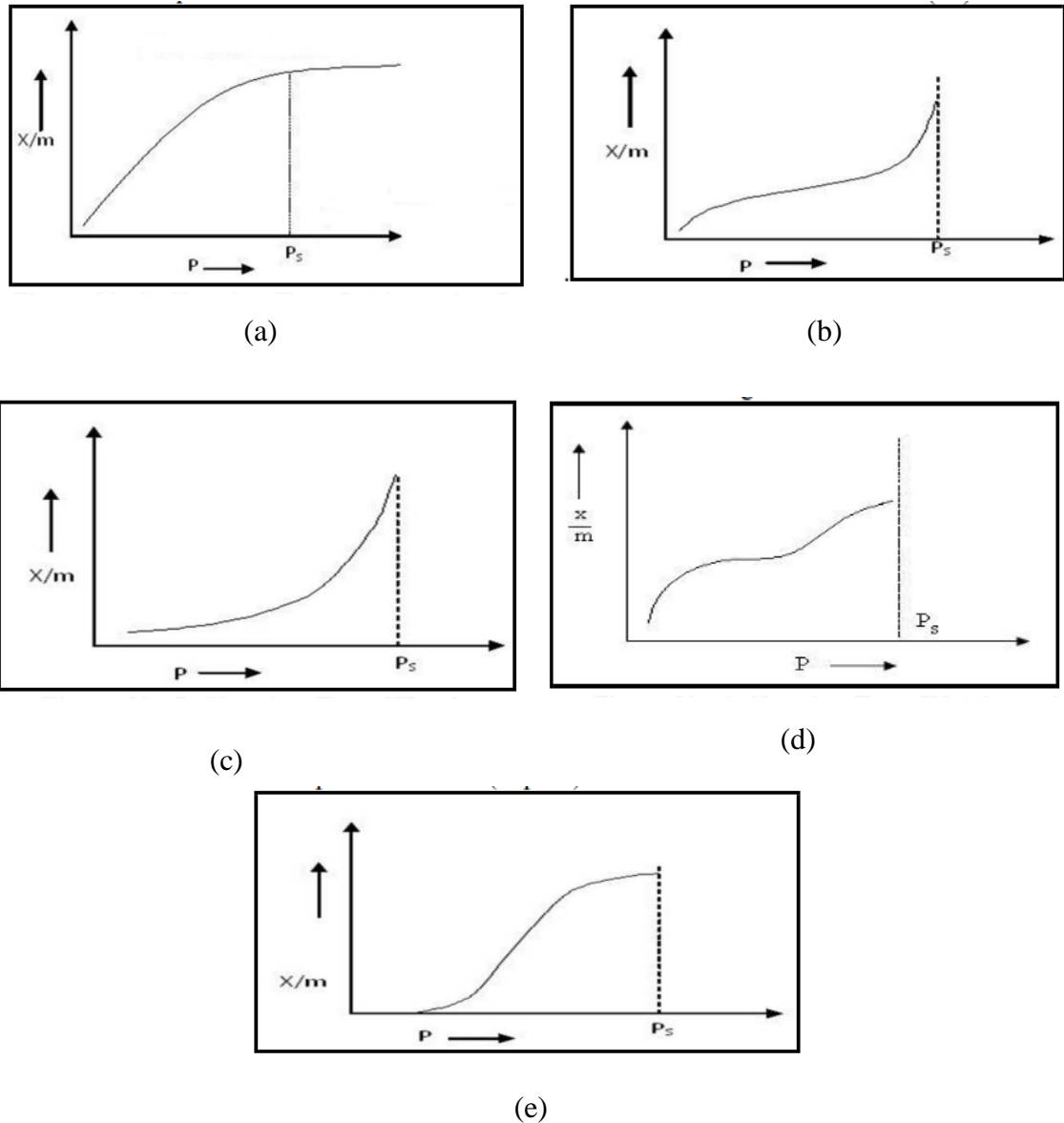
Figure 2.5: Graph of adsorption isotherm: (a) Type I, (b) Type II, (c) Type III, (d) Type Iv and (e) Type V (Gawande et al., 2017)

The Langmuir isotherm, which was created to explain gas-solid phase adsorption, is used to compare and measure different adsorbents' adsorptive capacity (Ayawei et al., 2017). At equilibrium, the rate of vapour desorption from the occupied sites is set equal to the rate of adsorption on the available site based on kinetic considerations (Chiou, 2003). The Langmuir equation can be expressed linearly as follows (Ayawei et al., 2017):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_e} + \frac{C_e}{q_m}$$ (2.1)

where C_e is the concentration of adsorbate at equilibrium (mg/g), K_L is Langmuir constant related to adsorption capacity (mg/g), q_e is the amount of adsorbate at equilibrium (mg/g), and q_m is the maximum adsorption capacity (mg/g).

The Freundlich isotherm applies to adsorption processes that take place on heterogonous surfaces. This isotherm generates a formulation that describes surface heterogeneity and the exponential distribution of active sites and their energies. The linear form of the Freundlich isotherm is shown below (Ayawei et al., 2017):

$$log\, q_e = log\, K_F + \frac{1}{n} log\, C_e \qquad (2.2)$$

where K_F is adsorption capacity (L/mg) and 1/n is adsorption intensity.

Temkin isotherm considers it is expected that rising surface coverage reduces the heat of adsorption of all molecules in the substrate linearly. By ignoring concentrations that are relatively low or extremely large, the model implies that the heat of adsorption of all molecules in the layer decreases linearly rather than logarithmically with extent. The equation of Temkin isotherm can be expressed as below (Dada et al., 2012):

$$q_e = \frac{RT}{b} ln\, K_T + \frac{RT}{b} ln\, C_e \qquad (2.3)$$

where R is the universal gas constant (8.314J/mol/K), b is the Temkin constant, and T is the temperature at 298K.

The Dubinin-Radushkevich isotherm is established to account for the impact of the permeable adsorbent arrangement. It was focused on the adsorption potential principle and assumed that adsorption was linked to micropore volume filling instead of layer-by-layer adsorption on pore walls. This isotherm is better than the Langmuir isotherm since it does not consider a homogeneous surface or constant adsorption potential. The equation of Dubinin-Radushkevich isotherm can be expressed as below (Hu and Zhang, 2019):

$$q_e = q_m \exp\left(-\beta\varepsilon^2\right) \tag{2.4}$$

where β is the Dubinin-Radushkevich constant and ε is the adsorption potential (kJ mol⁻¹).

The Redlich-Peterson isotherm combines the Langmuir and Freundlich isotherms. This isotherm has three parameters that combine the practical importance of Langmuir and Freundlich isotherms. The equation of Redlich-Peterson isotherms can be expressed as below (Guechi and Hamdaoui, 2016):

$$q_e = \frac{AC_e}{1 + BC_e^\beta} \tag{2.5}$$

where A (Lg⁻¹) and B (Lmg⁻¹)ᵝ are the Redlich-Peterson isotherm constant, and β is the exponent reflecting the heterogeneity of sorbent, which lie between 0 and 1.

The sips isotherm is generated from the restricting behaviour of the Langmuir and Freundlich isotherms. The model is relevant for localised adsorption with no adsorbate-adsorbate interference (Kumara et al., 2014). It decreases to the Freundlich isotherm at low adsorbate concentrations, whereas at large concentrations, it expects monolayer adsorption in the same way as the Langmuir isotherm does. The equation of Sips isotherm is expressed as below (Tzabar and Brake, 2016):

$$\frac{C}{C_o} = \frac{(ap)^{\frac{1}{n}}}{1 + (ap)^{\frac{1}{n}}} \tag{2.6}$$

where p is the pressure in bar, C_o is the saturated adsorption concentration, a is the adsorption affinity, and n is a dimensionless parameter that qualitatively characterises the heterogeneity of the adsorbate-adsorbate system.

Table 2.6 shows the type of adsorption isotherms commonly used by the authors when conducted their study to determine the adsorption mechanism occur during the experiment.

Table 2.6: Type of adsorption isotherm applied by various researches

Adsorbent	Removal Pollutant	Adsorption isotherm	Reference
Zeolite, Fly ash, Peanut husk charcoal	Zinc, copper	Freundlich isotherm, Langmuir isotherm	(Salam et al., 2011)
Heat-activated zeolite, raw zeolite	Nitrogen, Colour, COD	Freundlich isotherm, Langmuir isotherm	(Aziz et al., 2020)
Natural zeolite from Yagodninsky deposit	Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}	Langmuir isotherm, Freundlich isotherm	(Belova, 2019)
Clinoptilolite	Ammonium nitrogen, COD, and Colour	Langmuir isotherm, Freundlich isotherm, Temkin isotherm, Redlich-Peterson isotherm	(Genethliou et al., 2021)
K-Type Zeolite	Pb^{2+}	Langmuir isotherm, Freundlich isotherm	(Kobayashi et al., 2020)
Natural zeolite, Zeolite 3A, Zeolite 10A, Zeolite 13X	Zinc, cadmium	Langmuir isotherm, Freundlich isotherm, Dubinin-Radushkevich isotherm	(Kozera-Sucharda et al., 2020)
Clinoptilolite	Iron (III), Copper (II), Chromium (III)	Langmuir isotherm, Freundlich isotherm	(Zanin et al., 2017)
Al-waste Based Zeolite	Ammonium ion	Langmuir isotherm Freundlich isotherm Temkin isotherm Sips isotherm Toth isotherm Redlich-Peterson isotherm	(Sánchez-Hernández et al., 2018)
Modified zeolite (modified by HNO_3 and NaOH)	Sb^{3+}, Mn^{2+}	Freundlich isotherm Langmuir isotherm	(Zhang et al., 2014)

2.5.1(b)   Adsorption Kinetics

Adsorption kinetics is a curve that defines the rate at which a solute is retained or released from an aqueous surrounding to a solid-phase interface at a specified adsorbent dosage, temperature, flow rate, and pH (Kajjumba et al., 2018). Physical adsorption and chemical adsorption are two mechanisms that happen during adsorption. Physisorption take places by London-van der Waals forces of solid and adsorbate, while chemisorption is described by forming a strong bond between the solute and the adsorbent, which involves the transfer of ions (Chiou, 2003).

The pseudo-first-order model, also known as the Lagergren model, explains a solute's adsorption onto an adsorbent using a first-order mechanism (Kajjumba et al., 2018). This model is expressed by the equation below (Zhang et al., 2017):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2.7}$$

where q_t is adsorbate adsorbed onto the adsorbent at time t (mg/g), q_e is equilibrium adsorption capacity (mg/g), and k_1 is rate constant per minutes. After Equation (2.7) is integrated from t = 0 to t= t and q_t = 0 and q_t = q_t, it can be expressed as below (Yong Zhang et al., 2017):

$$ln(q_e - q_t) = \ln q_e - k_1 t \tag{2.8}$$

The Pseudo-second-order model indicates that the amount of solute adsorption is proportional to the vacant sites on the adsorbent. The pseudo-second-order model's reaction rate is determined by the quantity of solute on the adsorbent's surface. The driving force is proportional to the number of active sites on the adsorbent (Kajjumba et al., 2018). The equation of the pseudo-second-order model can be expressed as follow (Yong Zhang et al., 2017):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (2.9)$$

where k$_2$ is the pseudo-second-order rate constant. Equation (2.9) is integrated and formed a linearised integrated form of the equation as below (Yong Zhang et al., 2017):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2.10)$$

Table 2.7 shows the type of adsorption kinetics that commonly applied by researchers in their study to determine the way of adsorption mechanism that occurs in the experiment.

Table 2.7: Type of adsorption kinetic that applied in various researches

Adsorbent	Removal Pollutants	Adsorption Kinetics	References
Natural zeolite	Ammonia nitrogen, COD, Colour	Pseudo-first order, Pseudo-second order	(Genethliou et al., 2021)
K-Type zeolite	Pb^{2+}	Pseudo-first order, Pseudo-second order	(Kobayashi et al., 2020)
Clinoptilolite	Cu (II), Fe (III), Cr (III)	Pseudo-first order, Pseudo-second order	(Zanin et al., 2017)
Al-Waste Based Zeolite	Ammonium ions	Pseudo-first order, Pseudo-second order	(Sánchez-Hernández et al., 2018)
Modified zeolite (modified by HNO$_3$ and NaOH)	Sb^{3+}, Mn^{2+}	Pseudo-first order, Pseudo-second order	(Zhang et al., 2014)

2.5.1(c)   Batch Study vs Column Study

Batch studies provide essential information and parameters on adsorbate elimination, while column studies provide data on adsorption studies of various adsorbents used (Sazali et al., 2020). Batch studies are carried out in the experiment to determine the effect of several factors such as adsorbent dose, pH level, temperature, and contact time on the adsorption process (Gulipalli et al., 2011).

The impact of bed height and flow rate are determined in the column study (Upadhyay et al., 2017). The adsorption isotherms and adsorption kinetics study are also defined under the batch studies (Sazali et al., 2020).

Upadhyay et al. (2017) had conducted batch and column studies on the adsorption of copper and chromium. In the study, various parameters were considered for the batch study, such as pH, initial concentration, adsorbent dose, and contact time. The batch study is conducted to find out the optimum value of those parameters to remove the copper and chromium at the highest percentage. The maximum removal efficiency of copper at pH 7 and 40mg/L while the maximum removal efficiency of chromium at pH 3 and 10mg/L. In column study, flow rate and bed height are conducted. When the flow rate and bed height at the initial concentration of 10 mg/L are 2 L/hr and 2 respectively, the adsorption capacity of copper and chromium are 10.29 mg/g and 8.86mg/g, respectively. Both ions showed the highest percentage of removal.

Nguyen et al. (2015) had carried out batch and column studies on the adsorption of Cd, Cr, Cu, Pb and Zn by an iron-coated Australian zeolite. In the batch experiment, the type of adsorption isotherms and adsorption kinetics take place in the experiment are defined. Langmuir isotherm was used to determine linear regression between the individual metal and metals mixture. Natural zeolite and iron coated zeolite, in particular metal, showed higher R^2 in Langmuir isotherm than in a metal mixture. Therefore, the Langmuir isotherm was fitted to a single metal solution. In the adsorption kinetic, the pseudo-second-order model had higher R^2 than the pseudo-first-order model in natural zeolite and iron coated zeolite. In the column studies, a breakthrough curve had presented to show the adsorption of single and mixed heavy metals by zeolite and iron coated zeolite. The single metal solution has better adsorption capacity than the mixed metal solution, and iron coated zeolite has better adsorption than zeolite.