ADSORPTION ISOTHERMS AND KINETIC STUDIES ON THE REMOVAL OF LEAD (II) IONS BY RUBBER SEED COAT

NUR FATINI BINTI NOR HISYAM

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by

NUR FATINI BINTI NOR HISYAM

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LIST OF SYMBOLS

Symbol	Description	Unit
T	Absolute temperature	K
q_t	Adsorption capacity at time	mg/g
q_e	Capacity of biosorption at equilibrium	mg/g
R^2	Coefficient of correlation	-
C_e	Concentration at equilibrium	L/mg
n	Constant	-
β	Dubinin-Radushkevich constant	-
K_F	Freundlich constant	mg/g
R	Gas constant	J/mol.K
K_H	Halsey isotherm constants	-
α	Initial adsorption rate	mg/g.min
K_L	Langmuir constant	L/mg
C	Layer thickness of the boundary	-
q_{max}	Maximum capacity of biosorption	mg/g
E	Mean adsorption energy	J/mol
E	Mean adsorption energy	J/mol
ϵ	Polanyi potential	-
k_1	Pseudo-first-order rate constant	1/min
k_2	Pseudo-second-order rate constant	g/mg min
Kp	Rate constant	mg/g.min$^{0.5}$
b	Temkin constant related to heat of adsorption	J/mol
K_T	Temkin isotherm constant	L/g
t	Time	min

LIST OF ABBREVIATIONS

Symbol	**Description**
DOE	Department of Environmental
D-R	Dubinin-Radushkevich isotherm model
HCl	Hydrochloric acid
HNO_3	Nitric acid
NaOH	Sodium hydroxide
$Pb(NO_3)_2$	Lead nitrate
RSC	Rubber seed coats
SDGs	Sustainable Development Goals
SSE	Sum-of-squared error

MODEL GARIS SESUHU PENJERAPAN DAN KAJIAN KINETIK KEATAS PENYINGKIRAN ION PLUMBUM OLEH KULIT BIJI GETAH

ABSTRAK

Kulit biji getah yang telah melalui pra-rawatan bersama larutan asid dan alkali digunakan untuk mengkaji penyingkiran ion plumbum melalui proses penjerapan. Kulit biji getah yang telah dirawat bersama larutan alkali menunjukkan peratusan penyingkiran ion plumbum paling tinggi berbanding kulit biji getah yang lain. Data diperoleh melalui eksperimen telah digunakan untuk mengenalpasti model garis sesuhu yang paling sesuai untuk menggambarkan proses penjerapan dengan lebih mendalam iaitu model Langmuir, Freundlich, Temkin, Dubinin-Radushkevich dan model Halsey. Secara asasnya, melalui model garis sesuhu yang telah dikaji, kulit biji getah yang telah dirawat bersama larutan alkali menunjukkan ciri-ciri penjerapan seperti mempunyai ekalapisan diatas permukaan bahan biopenjerap, proses penjerapan dimana interaksi secara tidaklangsung antara biopenjerap dengan bahan terjerap dan ia menunjukkan proses penjerapan secara fizikal. Selepas itu, data eskperimen digunakan untuk mengenalpasti kesesuaian dengan model kinetik iaitu pseudo-tertib-pertama, pseudo-tertib-kedua, resapan intrazarah dan Elovich model. Kulit biji getah menunjukkan padanan terbaik bagi model pseudo-tertib-kedua. Ia menunjukkan penjerapan permukaan adalah langkah mengawal kadar bagi penjerapan ion plumbum pada kulit biji getah dan berdasarkan model Elovich, pengerapan kimia mungkin adalah langkah penentuan kadar pada kepekatan yang lebih tinggi.

ADSORPTION ISOTHERMS AND KINETIC STUDIES ON REMOVAL OF LEAD (II) IONS BY RUBBER SEED COAT

ABSTRACT

Rubber seed coats (RSC) were treated with acid and base to investigate the removal of lead (II) ions by adsorption process. Among all biosorbents that were investigated, base treated rubber seed coats showed the highest removal percentage of lead (II) ions. The experimental data were fitted to Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Halsey isotherm models to further describe the biosorption process. Generally, from adsorption isotherm models, base treated RSC have the characteristics such as having monolayer coverage of adsorbate on biosorbent surface, adsorption process of indirect interaction between adsorbent with adsorbate and it exhibits physical adsorption process. Next, experimental data were fitted to pseudo-first-order, pseudo-second-order, intraparticle diffusion and Elovich model. RSC showed best fit in pseudo-second-order kinetic model. RSC showed that surface adsorption may be contributing to the rate controlling step in the biosorption of lead (II) ions on RSC and based on Elovich kinetic model, chemisorption may be the rate determining step at higher concentration of lead (II) ions.

CHAPTER 1

INTRODUCTION

1.1 Background

Lead is a type of metal with unique properties due to its high malleability, a ductile material and resists corrosion which leads to its widely usage for automobiles, paint, ceramics and plastics industries. Lead is non-biodegradable in environment hence it can potentially cause harm and adverse effects to human health even with low concentration of lead. The effects of lead to human health are of critical as it will cause disruption to the central nervous, hematopoietic, hepatic and renal system leading to health disorders. Since water can be easily contaminated with lead from various sources, it must be treated before releasing to the environment because once the lead contaminants enter human bodies, it will ruin the organs inside the body and it is very troublesome and difficult to completely remove the traces of lead from the body (Flora, Gupta, & Tiwari, 2012).

In Malaysia, majority of lead contamination comes from wastewater released from industries and port activities like Port Klang, Selangor (Sany et al., 2013). Heavy metals pathways involve processes such as adsorption due to strong affinities possessed by lead, and biological uptake. Metals will accumulate at the bottom of the sediments and will form into liquid phase from solid due to physical and chemical factors such as the pH and temperature. These factors will eventually change the bioavailability, mobility and degree of toxicity exhibited by metals. This occurrence will pollute the water. From the study done by Sany et al. (2013), they have observed that the concentration of lead was very high at Port Klang. The sources of lead were coming from heavy industries such as the palm oil, cement and food industries. Development of industries at that area was increasing because of rapid increase in human population and agricultural activities which aggravation of heavy metal pollution of water sources at Port Klang. Not only at Port Klang, Juru River in Pulau Pinang has been contaminated with lead concentrations up to 117 μg/g but the contamination has not affected the fishes like it did to some of the bivalves and seaweeds in the affected area (Shazili, Yunus, Ahmad, Abdullah, & Rashid, 2006). Industrial effluents released must be monitored regularly so that the heavy metals, lead specifically should be within the range that has been stated in related legislations such as Environmental Quality (Sewage and Industrial Effluents) Regulations of 1979 and the Environmental Quality (Scheduled Wastes) Act of 1989 (Shazili et al., 2006). Lead has been in the center of attention to be removed from water due to its high toxicity in environment. In addition, the study of technology to reduce pollutants in environment is important to contribute to the Goal 6 of Sustainable Development Goals (SDGs) that mentions improvement of water quality from pollution and reducing hazardous chemicals or materials released (Jarvis, 2020).

There are many ways to remove lead such as precipitation, electroplating, chemical coagulation, ion-exchange and membrane separation but these methods require very high operational cost, therefore adsorption method to remove lead from water is a very interesting and favorable method due to its low cost adsorbents and environmentally friendly (Zahra, 2012a). Generally, adsorption process is a process where molecules of adsorbate will accumulate on the surface of the adsorbent to form a molecular film where one of the most popular adsorbent used is activated carbon in the form of powder or pellets which is high porosity, amorphous structure with graphite lattice (Da’na, 2017). Other than that, biomass from agricultural activities such as banana peel is also very advantageous. Agricultural wastes are abundant and easily accessible so wastes can be reduced by utilizing it for metal removal from water.

Biomass can provide active sites for the heavy metals even though it is not alive. Biosorption of heavy metals on adsorbents are selective based on the type of biosorbents used, the pretreatment of the biosorbent and the chemico-physical process surrounding. These parameters can be manipulated to ensure the sorption uptake of a specific metal. Biosorption uptake studies are done by examining the equilibrium sorption studies and kinetic studies to find out the rate controlling factor during the biosorption process. The process modelling such as Langmuir adsorption isotherm model is useful for estimating the efficiency or performance of the biosorption process when it is done under different process conditions such as pH and temperatures (Volesky, 2001).

Rubber seed coat, also known as *Hevea brasiliensis* is a potential agricultural waste that can be used as biosorbent for adsorbing specifically lead (II) ions from water (Abilasha & Lisy, 2016). Malaysia is among the world's rubber producer by 20 % rubber production with annual production of 1.2 million metric tons (Harun, Afzal, & Azizan, 2010; Muthusamy et al., 2014). From Table 1.1, rubber seed availability in Malaysia is considered high and abundant. Hence, waste from rubber production such as the rubber seed shell can be used as manure or disposed until it rots (Muthusamy et al., 2014). This waste can be properly utilized as biomass for many other purposes such as biosorption processes. Thus, in this study, adsorption isotherms and kinetic studies by rubber seed coat will be studied as a biosorbent for removal of lead (II) ions by biosorption process based on data from previous study by Sanusi, F. (2009).

Table 1.1 Rubber seed availability and planting area of countries in southeast asia (Ng, Lim, Bt Mohamad Izhar, Lam, & Yusup, 2014).

Country	Rubber planting area ('000 ha)	Rubber seed availability (t/year)
Indonesia	3,445	861,250
Thailand	2,895	723,800
Malaysia	1,029	257,250
China	1,002	250,500
India	712	178,000
Vietnam	715	178,750
Phillipines	130	32,500
Cambodia	143	35,750

1.2 Problem Statement

Traces of heavy metal in wastewater is a very critical concern and it is a priority pollutant. One of the heavy metals, lead, is toxic and it can cause anemia, kidney failure, disrupt brain tissue and death. Lead traces in wastewater comes from various sources like metal plating, mining processes, alloy manufacturing and so on (Hemati, 2015). Hence, it is important to treat wastewater effluent so that lead (II) ions present in wastewater is within permissible limit. Based on allowable standard discharge of metal by Department of Environmental (DOE), Malaysian standard A prescribed that effluent discharge limit of lead into any inland water within catchment is 0.10 mg/L and standard B to any other inland water or Malaysian waters is 0.50 mg/L (Khaled & Mustafa, 2015; Sabeen et al., 2018). Technologies used for removal of lead (II) ions such as precipitation, ion exchange, electro-winning have been utilized for heavy metal removal but these require high operating cost so, interest has been focused more on adsorption technology due to its lower cost, flexibility and effectiveness to achieve high quality of purified product (Ince & Kaplan İnce, 2017). Adsorbents used for adsorption plays an important role to adsorb lead (II) ions on the adsorbent such as activated carbon. Since lower cost is highly preferred for adsorption, biosorption is a very potential technology where it uses a biomass as biosorbent to adsorb heavy metals such as lead. There are many biosorbents that have been studied such as banana peel (Mohd Salim, Khan Chowdhury, Rayathulhan, Yunus, & Sarkar, 2016), chestnut shell (Ince & Kaplan İnce, 2017) and tea waste (Alavi, Zilouei, & Asadinezhad, 2014). In this study, rubber seed coat was explored as a biosorbent for removal of lead from wastewater. Rubber seed coat (RSC) has the ability to adsorb lead (II) ions from wastewater efficiently, however it is important to understand the mechanism of adsorption through the isotherms and kinetics of the biosorption. Chemically modified RSC should yield higher removal of lead (II) ions from the isotherm models and kinetic studies since the surface area of rubber seed coat is increased by acid and alkali treatment for enhanced adsorption of lead (II) ions to occur.

1.3 Objectives of the study

The aim of this study is to understand the mechanism of adsorption of rubber seed coat as biosorbent on the removal of lead (II) ions based on data from previous study done by Sanusi, F. (2009). It can be achieved by the following objectives:

i) To study the modelling of various adsorption isotherms which are Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Halsey isotherms and compare them to find the best suited isotherms for biosorption of rubber seed coat.

ii) To investigate the mechanism and rate-controlling steps of biosorption of lead (II) ions on rubber seed coat by modelling of pseudo-first-order, pseudo-second-order, intraparticle diffusion and Elovich models.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption Process

Adsorption process is known as a common process for wastewater treatment where pollutants such as heavy metals in solution will adhere to adsorbent so that the risk of environmental pollution is under control (Guo & Wang, 2019). To remove heavy metals from aqueous solutions, many physicochemical alternatives processes have been applied such as metal extraction, ion-exchange process, metal precipitation in form of insoluble salts and membrane process to separate unwanted heavy metals from a solution. However, these alternative processes mentioned have their own drawbacks such as expensive operational cost, low selectivity of heavy metals, low removal of metal ions and what is worse is that the generation of additional wastes during the separation process. Due to these limitations, adsorption has been an interesting method that is used to remove heavy metals.

The challenges of development of the adsorption technology are the choice of adsorbent needed to carry out the treatment of heavy metal. Adsorbents must be chosen based on the adsorption and regeneration characteristics of the adsorbents because it will affect the cost needed for the process. An adsorbent should be able to regenerate to reduce the cost of purchasing the adsorbent because adsorbents can be very expensive (Sadeek, Negm, Hefni, Abdel Wahab, & Wahab, 2015).

Furthermore, kinetic parameters based on the adsorbent used is crucial to determine the adsorption rate, time dependent of metal ions in solution and to figure out the mechanisms of adsorption process where these parameters are important to be able to design an adsorption system (Guo & Wang, 2019). Common kinetic modelling that has been used for the study of adsorption are pseudo-first-order and pseudo-second-order kinetics (Lima, Adebayo, & Machado, 2015)..

Other than the kinetic studies of adsorption, adsorption isotherm is also essential where at a condition of constant temperature known as isotherm, it relates the amount of adsorbate or heavy metal ions by the adsorbent and the concentration of heavy metal ions that remain in an aqueous solution during equilibrium. Adsorption isotherm models such as Langmuir and Freundlich isotherms are able to give out information on surface properties, adsorption mechanism and the relationship between adsorbent and adsorbate (Lima et al., 2015).

2.1.1 Activated carbon as a common adsorbent

Activated carbon is a very common adsorbent type that has been used conventionally for various type of pollutants from domestic or industrial wastewater (Sheth, Dharaskar, Khalid, & Sonawane, 2021). It can remove unwanted odor, color, taste, organic and inorganic substances from an aqueous solution (Bansal & Goyal, 2005). Interesting characteristics that the activated carbon has are high porosity structure due to the amorphous material and high surface area. Activated carbon can be produced by combusting, partial combusting or thermal decomposition of a highly carbonaceous materials such as pyrolysis process (Bansal & Goyal, 2005). Activated carbon can be obtained from various biomass such as Persian mesquite grain, Lapsi seed stone, doum palm shell and rice husk (Gaya, Otene, & Abdullah, 2015; Lemraski & Sharafinia, 2016; Shrestha, Pradhananga, Varga, & Varga, 2013; Thajeel, 2013). Two-staged process carbonization is done on the materials to produce activated carbon and followed by activation process. Where it is essential to increase carbon content and increase porosity structure of the activated carbon before it is used for adsorption (Shrestha et al., 2013).

Various preparation method of activated carbon from various sources were studied. From a study done by Gaya et al. (2015), Persian mesquite grain was used to prepare activated carbon by pyrolysis in a stainless-steel reactor at a rate of 7 ℃/min for 2 hours at operating temperature of 600 ℃. Another study by Lemraski and Sharafinia (2016), Lapsi seed particles that have been crushed into 100 μm was treated with sulphuric acid and mixture of sulphuric acid and nitric acid where each set were labeled as Carbon-1 and Carbon-2 respectively. Doum palm shells studied by Shrestha et al. (2013) were grounded to granular mesh size ranging from 1 to 2 mm where the doum palm shells were then impregnated with chemical activating agents solid KOH, NaOH and $ZnCl_2$. Activated carbon used in another study by Thajeel (2013) sourced from rice husk was prepared by only physical method in electrical furnace for 2 hours at 500 ℃ at rate of 30 ℃/min almost similar to a study by Gaya et al. (2015) without chemical agents.

Furthermore, improvement on activated carbon has been studied where activated carbon particles are encapsulated or also known as immobilizing the activated carbon by polymeric supports such as chitosan. Chitosan is derived from chitin through deacetylation and depolymerization. Chitosan contains hydroxyl, amino groups and protonated NH_3^+ which are favorable for treating aqueous solution. It is commonly used in form of hydrogel beads due to its crystalline structure to reduce adsorption in amorphous region of the crystalline structure. It is usually modified by using a crosslinking agent such as glutaraldehyde and epichlorohydrin because chitosan alone is unstable due to amine protonation (Quesada et al., 2020). Despite it having many advantages, the limitations of activated carbon are high production cost, lower regeneration and additional separation requirement needed (Sheth et al., 2021).

2.1.2 Utilization of biosorbents

To overcome the limitations by the activated carbon due to the high production cost, lower regeneration and additional separation requirement needed, biosorbents are the potential adsorbents that can be used for pollutants removal as well (Sheth et al., 2021). Biosorbents undergo physio-chemical process to adsorb and remove pollutant in aqueous solution such as heavy metals by exchanging ions, chelation and metal ions coordination. The cost of biosorbents are efficient, lower cost and environmentally friendly biosorption process (Fathollahi, Khasteganan, Coupe, & Newman, 2021). Materials for biosorbents are composed of agricultural waste, plant-based and algae which are sustainable and abundant to be used for biosorption to water contaminants (Almomani & Bohsale, 2020).

Algae can be used as biosorbents for removal of different contaminants from wastewater. The study of algae strains such as *Spirulina platensis* and *Chlorella vulgaris* were presented by Almomani and Bohsale (2020). In the mentioned research, the algae strains were treated with an acid which is sulphuric acid to restructure the functional groups present on algae surface to increase electronegativity of the biosorbents and enhance the toxic metals removal of aluminium, nickel and copper ions from wastewater. The algae strains were cultivated for 21 days in an incubator (Almomani & Bohsale, 2020). In another study where biosorbent used is marine dead algae with scientific name of *Sargassum filipendula* was not treated with any chemicals. *Sargassum filipendula* was prepared by washing the algae with deionized water to remove any impurities or cations present on the surface that may interrupt biosorption process of metal ions from wastewater (Verma, Kumar, & Kumar, 2016). *Sargassum filipendula* was studied on its capability to remove lead (II) ions which was not studied by Almomani and Bohsale (2020) which used algae strains to remove aluminium, nickel and copper ions. Optimum operating condition for microalgae known as *Aphanothse sp.* was studied by Keryanti and Mulyono (2020) where the microalgae was cultivated for 14 days in a photobioreactor with BG-11 medium (Keryanti & Mulyono, 2020).

Different bacterial biomasses are commonly used as biosorbents as well. The use of bacterial strains with scientific name of *Methylobacterium hispanicum* (EM2) strain is a pellicle-like biofilm that produces the EM2 strain, which is isolated from mine tailing soil was used to study its ability to treat contaminants with lead (II) ions. The isolated bacterial strains were cultured in a medium containing tryptone, glucose and yeast in absence or presence of agar. This bacterial strain is interesting due to its unique characteristic where it is highly tolerant and resistant to lead (II) ions which means, the cell growth of the bacterial strains are not affected under high concentration of lead (II) ions in an aqueous solution (Jeong, Kim, Yang, & Choi, 2019). Other than that, novel bacterium *Bacillus subtilis* was also investigated by incubating it in an agar consisting of beef extract, peptone and sodium chloride for a day at 37 ℃. It is then purified from growth medium and cultured in trypticase soy broth agar at 28 ℃ for up to 50 hours. The cultured *Bacillus subtilis* were killed by drying for a day at 70 ℃. *Bacillus subtilis* were utilized to not only remove lead (II) ions but also to remove Sb (III) ions as well through co-biosorption process (Cai et al., 2018). In another study of lead (II) removal by using *Alcaligenes sp.* BAPb.1 from aqueous solution where the bacterium strains were inoculated in sterile Luria-Bertani liquid medium and then cultivated at 30 ℃. The dead biomass was used and investigated showed high resistance to various metal ions such as lead (II) ions, copper (II) ions, zinc (II) ions, nickel (II) ions and chromium (VI) ions (Jin et al., 2017).

Next, agricultural wastes are also used as biosorbents for heavy metal removals. In a study done by Mohd Salim et al. (2016), banana peel powder as biosorbent was prepared by pretreatment of biosorbent by a strong base, sodium hydroxide (NaOH). By adding the strong base, the structure of the banana peel can be altered to improve the active sites available for adsorption of lead (II) ions on the surface of biosorbent with removal of 95 % of lead (II) ions from the solution (Mohd Salim et al., 2016). However, when banana peel is modified by treating it with different chemical solutions which are sodium hydroxide (NaOH), hydrochloric acid (HCl) and phosphoric acid (H3PO4), the study showed that treatment with sodium hydroxide has the best adsorption capacity for modified banana peel (Massocatto et al., 2013). In another study that used durian husk activated carbon was prepared by mixing durian husk powder with potassium hydroxide (KOH) (Ngabura, Hussain, Ghani, Jami, & Tan, 2019). Another study done to use low cost adsorbent from agricultural waste with presence of external magnetic field to separate the adsorbent easily from solution (Safinejad, Chamjangali, Goudarzi, & Bagherian, 2017). Shells of walnut were milled into powder form to be activated. Co-precipitation method was done to produce the magnetic adsorbent to remove lead. The magnetic adsorbent from walnut shell is efficient due to the fast process within 4 minutes because there is no internal diffusion resistance (Safinejad et al., 2017).

2.2 Adsorbent Characterization

Agricultural wastes are lignocellulosic materials that composed of cellulose, hemicellulose and lignin. These compositions may vary for every biomass material for instance, rice straw contains 25 to 35 % of cellulose but cotton waste contains higher amount ranging from 80 to 95 % of cellulose. These compositions are important for heavy metal ions adsorption process where it influences the number of active sites available for adsorption to take place (Abdolali et al., 2014). Many studies improved and modified the adsorbent to increase its surface area by acid treatment or alkali treatment (Massocatto et al., 2013; Mohd Salim et al., 2016). Harripersadth et al. (2020) reported that functional groups of hydroxyl, carbonyl and aromatic rings are responsible for binding of metal ions of lead and cadmium by using bagasse, which is an agricultural waste (Harripersadth, Musonge, Makarfi Isa, Morales, & Sayago, 2020). The purpose of the FTIR experiment is to identify the functional groups on the biosorbent surface and their interactions with metal ions. It is determined based on the peaks corresponding to functional groups of biosorbent before and after biosorption of lead ions. It is also shown based on the change in vibrational frequency of functional groups of a biosorbent of lead (II) ions (Verma et al., 2016).

Not only that, electrostatic interactions were also identified between metal ions and functional groups present on *Acacia Gummifera* which are hydroxyl and carboxyl groups (Jamoussi, Chakroun, Jablaoui, & Rhazi, 2020). The presence of functional groups on biosorbent surface will influence the nature of the biosorbent where it could be negatively charged or positively charged depending on the type of functional groups involved. For example, presence of functional groups such as alkanes, hydroxyl, carboxyl and amine, will cause microbial surface to be negatively charged (Hussain, Khazaal, & Hatif, 2020).

2.3 Factors affecting adsorption performance.

An adsorbent should have high adsorption ability, safe and able to regenerate to reduce the cost with no additional waste generation. Factors affecting the performance of adsorption are important parameters that can be altered in a study such as pH, temperature, adsorbent dose and contact time.

2.3.1 Effect of pH

In nature, the pH value of wastewater effluents is not always neutral, and the pH value may vary depending on external conditions of the environment itself hence pH value must be studied to have a better view on understanding on the adsorption performance. Different value of pH may cause heavy metal ions to exist in different oxidation states. In many cases that have been reported in other literatures, heavy metal ions will cause precipitation with hydroxide in certain range of pH values (Sheth et al., 2021). In a study of walnut shell powder as biosorbent, Safinejad et al. (2017) reported that lead (II) ions will hydrolyze in aqueous solution beyond pH value of 6 and precipitates into form of $Pb(OH)_2$.

Precipitation also occurs when concentration of lead (II) ions is high even though the pH value is lower than 6. This phenomenon can be explained due to high competition between lead (II) ions and H^+ protons to be adsorbed on the surface of adsorbent in low pH solutions (Safinejad et al., 2017). Under acidic conditions, hydroxide groups present on adsorbent surface will be protonated which can lower the ability of adsorption of lead (II) ions which is positively charged. The optimum pH value for walnut shell powder was reported to be at pH of 5.0 (Safinejad et al., 2017). Massocatto et al. (2013) found out that when banana peels were treated with acid solution, it can avoid sudden pH changes in aqueous sample where the optimum pH is 5.0 (Massocatto et al., 2013). Therefore, optimum pH value may vary for different biosorbent type to achieve a good removal of heavy metal ions from aqueous solution as summarized in Table 2.1.

Table 2.1 Optimum pH values for different adsorbent types.

Adsorbent type	Adsorbate	Pretreatment involved	Optimum pH value	Reference
Walnut shell powder	Pb	Alkali treatment (NaOH)	5.0	(Safinejad et al., 2017)
Banana peels	Pb	Chemical treatment (NaOH, HCl, H_3PO_4)	5.0	(Massocatto et al., 2013)
Durian husk activated carbon	Pb	-	7.0	(Ngabura et al., 2019)
Banana peel powder	Pb, Cu	Alkali treatment (NaOH)	7.0	(Mohd Salim et al., 2016)
Peanut seahells	Pb	-	5.5	(Taşar, Kaya, & Özer, 2014)

Point of zero charge known as pH_{zpc} is a pH value where the net surface charge is zero which it depends on the amounts of functional groups and its affinity to H^+ and OH^- ions. Positive surface charge occurs below pH_{zpc} where adsorbent tend to attract negatively charged ions under influence of electrostatic force. On the contrary, negative surface charge will happen at higher pH_{zpc} to attract positively charged ions under the influence of electrostatic force (Sheth et al., 2021). In conclusion, due to pH value that is higher than $pH_{zpc,}$ adsorbent will become negatively charged to attract heavy metal ions that are positively charged.

2.3.2 Effect of temperature

Temperature has a significant impact to aid a chemical reaction by increasing solubility and stability of metal ions and ligands. Temperature has a huge impact on adsorbent nature to improve the reaction and increase the quality of adsorption process. In most cases, temperature effects were insignificant compared to other parameters such as pH of aqueous solution and dose of adsorbent (Beni & Esmaeili, 2020; Gomez-

Gonzalez et al., 2016). Taşar et al. (2014) reported that the equilibrium uptake of lead (II) ions under high temperature which is 40 ℃ will cause lower surface activity. The optimum temperature reported in the mentioned study was 20 ℃ when using peanut shell as biosorbent. The behavior showed that it is an exothermic nature due to lower removal efficiency at higher temperature (Taşar et al., 2014). Generally, uptake of lead (II) ions will increase when increasing temperature due to increase in mobility of lead (II) ions from bulk solution to the surface of the biosorbent (Zahra, 2012b). On the contrary, Verma et al. (2016) stated that for the case of *Sargassum filipendula* algae as biosorbent, reaction of lead (II) ions is endothermic in nature. Layer surrounding the biosorbent will become thinner when temperature increases to 35 ℃ which will reduce resistance of external layer. Micropores are wider and deeper to provide more surface area and increase active sites availability of the biosorbent (Verma et al., 2016). Other bacteria typed biosorbent, *Bacillus subtilis*, showed endothermic nature of Pb (II) and Sb (III) ions as well at optimum temperature of 35 ℃ (Cai et al., 2018).

Safinejad et al. (2017) found out that the increase of temperature did not give significant impact on removal efficiency of lead (II) ions by magnetic walnut shell powder assisted by ultrasonic. However, when the initial concentrations of lead (II) ions are higher which is at 25 mg/L, the removal efficiency of lead (II) ions are also high (Safinejad et al., 2017). For agricultural biomass as biosorbents, acid pretreatment should be used in lower concentration to avoid breaking of cellulose structure and reduce toxicity level. However, alkali pretreatments are more efficient compared to acid pretreatments under similar conditions by solving cell wall matrix because alkali pretreatment can provide better diffusion through wall by the increase density of functional groups present on biosorbent and thermodynamically stable (Abdolali et al., 2014). In conclusion, most biosorbent require low temperature to adsorb heavy metal ions such as lead (II) ions. Hence, optimum temperature is important to be considered to achieve low energy consumption to reduce operating cost without sacrificing the removal efficiency of metal ions.

2.3.3 Effect of adsorbent dosage

Adsorbent dosage is related to adsorbent capacity which is the amount of adsorbent is needed to adsorb metal ions with respect to the functional groups. Theoretically, adsorption of heavy metal ions will increase when adsorbent dosage is increased because of more active sites are available to adsorb metal ions on the surface until it reaches saturation. Up until some point, further increase of adsorbent dosage will not cause any changes to the removal efficiency of heavy metal ions anymore. For scale-ups of adsorption process in industry, optimum adsorbent dosage is very important depending on functional groups present on adsorbent surface and availability of active sites on adsorbent surface (Sheth et al., 2021).

For bacterial typed biosorbent, heavy metal ions such as Ni (II), Pb (II), Mn (II), Cr (III) and Zn (II) removal increased as the biosorbent dosage is increase but only until not more than 5 g/L before the biosorbent capacity decreased beyond the optimum dosage (Fathollahi et al., 2021). Besides, under high biosorbent dosage, from algae strains, agglomeration of algae strains is the cause of lower active sites availability for biosorption (Almomani & Bohsale, 2020). From a study of lead removal by walnut shell powder as biosorbent, the optimum biosorbent dosage required for maximum removal efficiency was 2.0 g/L. Safinejad et al. (2017) reported that by increasing adsorbent dosage will not only cause increase in metal removal but also reduced adsorption capacity (Safinejad et al., 2017).

2.3.4 Effect of contact time

Effect of contact time for biosorption to take place is important for the study of adsorption kinetics because it influences the amount of lead (II) ions being adsorbed on adsorbent (Massocatto et al., 2013). Massocatto et al. (2013) reported that the modified banana peels reached equilibrium in 300 minutes, while Mohd Salim et al. (2016) reported that untreated and treated banana peel powder has contact time of 120 minutes and 150 minutes respectively. Furthermore, longer contact time will enhance the efficiency of biosorption at the maximum value of adsorption capacity until it reaches constant which is at equilibrium time for the biosorption (Taşar et al., 2014).When contact time increases, availability of active sites for adsorption to take place decreases. Metal ions are unable to fill up the remaining active sites due to the presence of repulsive forces between metal ions on adsorbent surface and in aqueous phase (Mohd Salim et al., 2016).

2.4 Adsorption isotherm models

Experimental data is required to study the performance of an adsorbent through modelling of adsorption isotherm. These models are crucial for estimation and comparison for adsorption performance to understand the mechanism pathways of the adsorption process, adsorbent capacities so that an effective design of adsorption system can be further improved. In this section, linear analysis of different isotherm models, which is an alternative mathematical approach, will be compared to study the behavior of the adsorption process. Linear analysis is common due to easy parameters prediction, even though linear analysis has its own limitation which is deviation between predictions and experimental data (Chen, 2015).

2.4.1 Langmuir isotherm

From a study done by Harripersadth et al. (2020), adsorption of lead and cadmium ions by eggshells and sugarcane bagasse best fitted Langmuir isotherm under conditions of ph 5.5, with maximum capacity of 277.78 mg/g and 13.62 mg/g for lead and cadmium removal respectively. This showed that data for adsorption of lead and cadmium are well described by langmuir isotherm model where no further adsorption can occur on an occupied site and higher value of Langmuir constant indicates higher affinity of the binding site and the interaction between metal ions and adsorbent (Harripersadth et al., 2020).

Table 2.2 Langmuir isotherm modelling parameters for lead.

Adsorbent type	Operating conditions	Maximum adsorption capacity (mg/g)	Langmuir constant (L/mg)	R^2	Reference
Egg shells	pH 5.5, room temperature	277.78	0.952	1.38	(Harripersadth et al., 2020)
Sugarcane Bagasse		31.45	0.9967	196.08	
Acacia Gummifera	pH 6.5, 303 K	18.3	0.12	0.989	(Jamoussi et al., 2020)
Persian mesquite grain activated carbon	pH 5.0	270.27	0.05918	0.9958	(Lemraski & Sharafinia, 2016)
Lapsi seed stone activated carbon	pH 5.0, 26 °C	423.7	0.339	0.998	(Shrestha et al., 2013)
Doum palm shell activated carbon	pH 6.0, 30 °C	500	4.01×10^{-5}	1.00	(Gaya et al., 2015)
Magnetic walnut shell	pH 5.0, 25 °C	28.57	0.1408	0.9786	(Safinejad et al., 2017)

2.4.2 Freundlich isotherm

Thajeel (2013) reported in a study where rice husk was used as biosorbent for removal of lead (II) ions from aqueous solution. In the study, Freundlich isotherm model fitted the best compared to other models due to the high value of correlation coefficient, R^2 for lead (II) ions. It can be concluded that the adsorption in the study showed multilayer adsorption on rice husk activated carbon. Gaya, Otene and Abdullah (2015) concluded that the adsorption of lead on doum palm shell activated could fit both Langmuir and Freundlich isotherm models with value of R^2 close to 1.0 for both models.

Table 2.3 Freundlich isotherm modelling parameters for lead.

Adsorbent type	Operating conditions	Maximum adsorption capacity (mg/g)	Freundlich constant (L/mg)	$1/n$	R^2	Reference
Magnetic Activated Carbon (from rape straw powder)	pH 5, 25 ℃	253.2	80.5	0.181	0.949	(Zhang, Wang, Zhang, Liu, & Xing, 2021)
Doum palm shell activated carbon	pH 6.0, 30 ℃	500	0.02	1.00	1.00	(Gaya et al., 2015)
Rice husk activated carbon	pH 3.0, 25 ℃	162.667	-	1.7419	0.966	(Thajeel, 2013)

2.4.3 Temkin isotherm

Temkin isotherm model describes the synergy between biosorbent and biosorbate through its linear form (Oguz, 2020). Assumption made for this model is the function of surface coverage from the adsorption free energy. Gibbs equation is used for the evaluation of adsorption energy where the energy retention of adsorbate molecules is homogenous on adsorbent surface. This model can be applied not only for gaseous adsorbates on adsorbent, but also for determination of adsorption energy in liquid phases (Jamoussi et al., 2020). From the study done by Jamoussi et al. (2020), they reported that *Acacia Gummifera* biomass adsorption is an exothermic process due to positive value of adsorption energy from Temkin model even though in that study, Langmuir and Freundlich models fitted the data better. They also concluded from Temkin model of *Acacia Gummifera* biomass showed that physical interactions are involved in the biosorption process (Jamoussi et al., 2020). Temkin isotherm constants for adsorption of lead (II) ions by various biosorbents type are summarized in Table 2.4 where A_T and b_T represent Temkin isotherm equilibrium binding constant and Temkin isotherm constant related to adsorption energy.

Table 2.4 Temkin isotherm constants for adsorption of lead (II) ions by various biosorbents.

Adsorbent type	Operating conditions	A_T (L/mg)	b_T (kJ/mol)	R^2	Reference
Acacia Gummifera	pH 6.5, 40 °C	16.73	15.90	0.972	(Jamoussi et al., 2020)
Abies bornmulleriana cone	pH 5.0, 20 °C	0.00775	2.32E-3	0.98	(Oguz, 2020)
Hazelnut shell	pH 4.0, 25 °C	0.001147	2.534E-3	0.989	(Kaya, Arslan, & Yildiz Uzun, 2020)
Walnut shell	pH 4.0, 25 °C	0.001885	12.30E-3	0.971	(Kaya et al., 2020)
Persian mesquite grain	pH 5.0, 20 °C	0.27	0.189	0.904	(Lemraski & Sharafinia, 2016)

2.4.4 Dubinin-Radushkevich isotherm

D-R isotherm is a semi-empirical model to describe adsorption mechanism through determination of Gaussian energy distribution on heterogenous surface. This model is applicable for medium metal ions concentration ranges due to its unideal asymptotic behavior and unable to predict Henry's law under low pressure. This model assumes Van der Waal's forces are involved and micropore volume filling involved (Ayawei, Ebelegi, & Wankasi, 2017a; Jamoussi et al., 2020). This model differs than the other isotherm model due to its independent on pH effect and adsorption of functional groups on adsorbent surface. This model is also particularly helpful to determine whether it involves physical or chemical adsorption from the free energy parameter (Jamoussi et al., 2020). Wajda et al. (2017) reported that Dubinin-Radushkevich isotherm model fitted the data well in their research where they confirmed the biosorption mechanism involves chemical sorption due to the value of free sorption energy that they have obtained (Wajda, Duda-Chodak, Tarko, & Kamiński, 2017). Free sorption energy ranges between value of 8 to 16 kJ/mol and 0 to -20 kJ/mol indicate ion-exchange mechanism and electrostatic interaction, respectively (Jamoussi et al., 2020). Ion-exchange mechanism is a chemisorption process while electrostatic interaction is a physisorption process (Ali, Al Mesfer, Khan, Danish, & Alghamdi, 2019). Table 2.5 summarizes D-R parameters from various studies where K_{ad} is D-R isotherm constant related to adsorption energy ($mol^2.J^{-2}$) and E is mean free energy per molecule of adsorbate (kJ/mol).

Table 2.5 Dubinin-Radushkevich isotherm parameters for different biosorbents.

Adsorbent type	Operating conditions	E (kJ/mol)	R^2	Reference
Acacia Gummifera	pH 6.5, 40 °C	1.38	0.956	(Jamoussi et al., 2020)
Abies bornmulleriana cone	pH 5.0, 20 °C	14.43	0.99	(Oguz, 2020)
Arthrospira platensis	pH 4.5, 25 °C	<8.00	0.9124	(Wajda et al., 2017)
Juniperus procera	pH 4.6, 25 °C	2.42	0.851	(Ali et al., 2019)

2.4.5 Halsey isotherm

Halsey isotherm is not as common as Langmuir and Freundlich isotherm but it is still used in some studies to determine the multilayer adsorption at a far distance from the surface (Ayawei et al., 2017a). Khaskheli et al. (2017) used linearized Halsey isotherm model in their study and it showed high value of correlation coefficient, R^2

which indicates that the data fitted the isotherm model well. It is an evidence of heteroporous, which are microporous and microporous nature of the sorbent used to adsorb lead (II) ions (Khaskheli et al., 2017). Halsey isotherm model was also well fitted in another study by Almalike, Al-Asadi and Abdullah (2020) that approves the multilayer adsorption and non-homogenous nature (Almalike, Al-Asadi, & Abdullah, 2020). Halsey isotherm model is applied in many studies by various researchers and it is summarized in Table 2.6.

Table 2.6 Halsey isotherm model for adsorption of lead (II) ions from various adsorbents.

Adsorbent type	pH	n_H	K_H	R^2	Reference
Okra leaves	6.0	0.44	3011	0.94	(Khaskheli et al., 2017)
Soils	-	1.044	1.244959	0.9992	(Almalike et al., 2020)
Hybrid adsorbent	-	1.030	5.659	0.998	(Liu & Wang, 2013)
Coconut shell carbon	-	-1.6753	0.3082	0.9972	(Song et al., 2013)
Otostegia persica	5.5	1.92	38.46	0.695	(Alavi et al., 2014)

2.5 Adsorption kinetic models

Pseudo first order, pseudo second order, intraparticle diffusion and Elovich models are discussed in this section where all the model parameters are summarized in Table 2.7.

2.5.1 Pseudo first order model

Pseudo first order model is also recognized as Lagergren model where the rate of constant in linear expression of this model is inversely proportional to the initial concentration of the solute due to longer time needed for higher initial solute concentration. This model varies according to Henry regime adsorption and when adsorbent dosage is increased. Zhou, Zhu and Fei (2018) found out that the adsorption of oxytetracycline by the reed residues followed the pseudo first order kinetic model. Linearized pseudo first order is fitted well based on the high value of regression coefficient, R^2 and similarity between the calculated and experimental values of adsorption capacity at equilibrium. They have concluded that the adsorption mechanism of reed residues is based on mono controlling of solution concentration (Zhou, Zhu, & Fei, 2018).

2.5.2 Pseudo second order model

Many studies have shown that the adsorption of lead (II) ions followed the linearized pseudo second order model to determine the rate-controlling steps in adsorption process by various biosorbents such as rapeseed, peanut shells and durian husk activated carbon (Morosanu, Teodosiu, Paduraru, Ibanescu, & Tofan, 2017; Ngabura et al., 2019; Taşar et al., 2014). Pseudo second order model proves that the adsorption of lead (II) ions onto the adsorbent is based on chemical reaction that involves exchange of ions between lead (II) ions and adsorbent (Morosanu et al., 2017). The good fit for pseudo second order model is evaluated based on the high value of correlation coefficient, R^2 and low discrepancy between q_e from calculated value and q_e from experimental value. In some cases, temperature plays a significant role in determining the rate of biosorption such as peanut shell which it is faster under high temperatures (Taşar et al., 2014).

2.5.3 Intraparticle model

Intraparticle model is useful to determine the contribution of diffusion of adsorbate within the biosorbent (Alavi et al., 2014). A plot of q_t against $t^{0.5}$ is used to observe. If a line passes through the origin in the constructed plot then it can be concluded that intraparticle diffusion is the rate-controlling step for the adsorption process (Morosanu et al., 2017). In a study done by Morosanu et al. (2017), the plot did not pass through the origin and it was not a straight line. This means that the are other mechanisms other than diffusion that are involved at the solid-liquid interface. From the plot in the study, it showed three phases of curves. First phase is the fast lead (II) ions uptake on external surface of biosorbent. Second phase involves metal ions entering the pores of biosorbent where diffusion rate will decrease, and it becomes the rate-controlling step (Morosanu et al., 2017). The third phase is the slow intraparticle diffusion of lead (II) ions into the micropores. In short, it involves bulk diffusion into solid-liquid interface, intraparticle diffusion of metal ions into internal solid surface from the pores of adsorbent and lastly adsorption of metal ions on the active sites of the biosorbent (Alavi et al., 2014).

2.5.4 Elovich model

This model is particularly useful for understanding chemisorption nature of an adsorbent. Mass and surface diffusion, activation and deactivation energy of a system can be evaluated from linearized Elovich model for gaseous or liquid systems. This model is based on assumptions that solute adsorption rate will be reduced exponentially when the amount of adsorbed solute becomes higher (William Kajjumba, Emik, Öngen, Kurtulus Özcan, & Aydın, 2019). From the linearized model, plot of q_t vs t can be used for determining the adsorption nature on heterogenous adsorbent surface regardless it is chemisorption or otherwise (William Kajjumba et al., 2019). Adsorption of Nickel and Cadmium ions by okra leaves followed Elovich model which proved its chemisorption nature for the absorption process (Khaskheli et al., 2017).