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Kinetics and Isotherms Studies of the Adsorption of Hg(II) onto Iron Modified Montmorillonite/Polycaprolactone Nanofiber Membrane

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Abstract. Hg(II) ions from mining and urban runoffs can easily contaminate various water sources due to their high solubility in water. Due to its simplicity and viability, adsorption was utilized to treat Hg(II)-contaminated water. An adsorbent was fabricated by immobilizing Fe-modified montmorillonite particles in polycaprolactone through electrospinning. The SEM images of the fabricated membrane showed a nanofiber network with fiber diameter ranging from 96 nm to 569 nm and an average of 198 nm. The adsorption behavior of the fabricated membrane was investigated using kinetics and isotherm models. It was found that the adsorption of Hg(II) ions onto the membrane follows a pseudo-second order model and was best described by the Freundlich isotherm. The adsorption capacity was found to increase with increasing contact time and with increasing initial Hg(II) concentration, with the highest adsorption capacity of 14.25 mg/g. The sorption energy was calculated using the Dubinin-Kaganer-Radushkevich isotherm, which obtained a value of -2.68 kJmol^{-1} suggesting that the type of adsorption was physisorption.

1. Introduction

Dissolved mercury, Hg(II), is considered to be one of the most toxic heavy metals. The toxicity of mercury has been extensively studied and its concentrations in water sources are constantly monitored [1]. There are several methods to treat mercury laden waste water, however most are not preferred due to high costs, high energy consumption and difficulty of use [2] [3]. Among the available methods, adsorption is proven to be one of the most economical and efficient for removing heavy metals [4].

Adsorption is the adhesion of ions or molecules onto a solid surface. Several mathematical models have been proposed to describe the kinetics of adsorption. These models are used to describe the kinetic process of adsorption and the adsorption mechanism. These can generally be classified as adsorption reaction models (pseudo-first order rate equation, pseudo-second order rate equation, and Elovich equation) and adsorption diffusion models (liquid film diffusion model, and intra-particle diffusion model) [5]. Adsorption kinetics follows a three step mechanism: (i) film diffusion or the transfer of solute to the adsorbent surface (ii) intra-particle diffusion or the transfer of solute from the adsorbent surface to the intra-particle adsorption sites, and (iii) mass action or the retention of solute on the active site via adsorption complexation or precipitation [6]. The rate-limiting step, which can determine the overall adsorption rate of the system for the adsorption process, can be any of the three steps or a combination of two [7]. The linearized equations of the relevant adsorption reaction models and adsorption diffusion models are listed in table 1.

Table 1. Linearized equations of adsorption reaction and adsorption diffusion models.

Kinetic model	Linearized equation	
Lagergren pseudo-first order equation	$\log(q_e - q_t) = log q_e - \dfrac{k_1 t}{2.303}$	(1)
Pseudo-second order equation	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^2} + \dfrac{t}{q_e}$	(2)
Elovich equation	$q = \alpha \ln(a\alpha) + \alpha \ln(t)$	(3)
Liquid film diffusion	$\ln\left(1 - \dfrac{q_t}{q_e}\right) = -R^1 t$ $R^1 = \dfrac{3D_e^1}{r_o \Delta r_o k}$	(4)
Intra-particle diffusion	$q_t = k_{int} \cdot \sqrt{t}$	(5)

Similarly, there are several isotherms that can be used to describe adsorption. These isotherms are used to correlate the equilibrium adsorption data with the mathematical models describing kinetics. It describes the adsorbent-adsorbate interaction and is critical in optimizing the use of adsorbents [8]. The Langmuir and Freundlich isotherms are the two most commonly used isotherm model for adsorption. While the Dubinin-Kaganer-Radushkevich isotherm is commonly used to compute the sorption energy of the sorption process. The linearized forms of the relevant adsorption isotherms are shown in table 2.

Table 2. Linearized equations of isotherm models.

Isotherm model	Linearized equation	
Langmuir isotherm	$\dfrac{1}{q_e} = \dfrac{1}{K_a q_m} \dfrac{1}{C_e} + \dfrac{1}{q_m}$	(6)
Freundlich isotherm	$log q_e = K_F + \dfrac{1}{n} log C_e$	(7)
Dubinin-Kaganer-Radushkevich isotherm	$ln Q = ln Q_{max} - \beta \varepsilon^2$ $\varepsilon = RT ln \dfrac{1}{C_e}$	(8)

The objective of this study is to determine the kinetic model and adsorption isotherm that best describes the adsorption of Hg(II) onto the Fe-MMt/PCL nanofiber membrane. To achieve this, adsorption capacity was monitored as a function of contact time, and metal ion concentration.

2. Methodology

2.1. Fe-MMt clay preparation
The method used for the preparation of Fe-MMt clay was adapted from the study of [9] Nanofil 116 was dispersed distilled water while FeCl₃ solution was being added dropwise during dispersion. After which, additional amounts of distilled water and NaOH solution was added to the solution. The resulting solution was stirred at 500 rpm for 12 hours. It was then filtered, collecting only the residue which is the Fe-MMT clay. The residue collected was oven dried at 80 ℃ for 5 hours. The dried residue was ground and sieved, collecting only particles less than 45 μm and then ball milled for 2 hours at 100 rpm.

2.2. Fe-MMt/PCL nanofiber membrane fabrication
Fe-MMt clay and Cloisite 24A were dispersed in dichloromethane (DCM) solution. This mixture was sonicated for 30 minutes, and added with polycaprolactone (PCL) pellets. The new mixture was sonicated for 1 hour, and was shaken every 5 minutes for the last 30 minutes. This solution was electrospun at a voltage of 33 kV, spinning distance of 13 cm, and barrel collector speed of 450 rpm using an *Inovenso Nanospinner 24*. The process was done three times to fabricate a single sheet

composed of Fe-MMt/PCL nanofiber membrane. The fabricated membrane was cut into circular plates with a 58 mm diameter.

2.3. Adsorption experiments
Three different initial concentrations (10, 20, and 30 ppm) of Hg(II) ions at pH 3 were prepared. Adsorption experiments were conducted using a modified setup adapted from [10]. One liter of the Hg(II) solution was allowed to pass through the Fe-MMt membrane repeatedly for a total of 360 minutes. The changes in concentration were monitored by collecting 15 mL aliquots at 0, 15, 30, 45, 60, 120, 240, and 360 minute intervals during the adsorption duration.

2.4. Characterization
The fabricated membrane was viewed under a *Hitachi SU8230 Scanning Electron Microscope (SEM)* to examine its surface morphology. The fiber diameter was measured using ImageJ© software. EDS analysis was subsequently performed on the membrane surface to confirm the presence of Fe-MMt particles. Meanwhile, the concentration of the aliquot collected for each time interval of the adsorption experiment was determined using *X-Ray Fluorescence Spectroscopy (XOS HDXRF)*. The collected data was analyzed using OriginPro© to plot the linearized equations of the relevant kinetic models and isotherms.

3. Results and discussion

3.1 Morphology of Fe-MMt/PCL nanofiber membrane
Fe-MMt particles were immobilized in PCL through electrospinning. Figure 1 shows the resulting membrane made up of composite nanofibers.
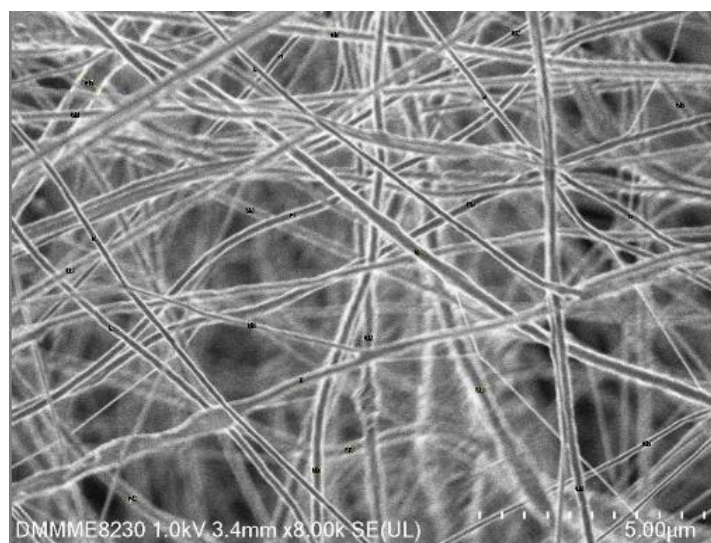

Figure 1. Morphology of Fe-MMt Membrane at 8000x.

The measured fiber diameter in figure 1 was found to be within the 96-569 nm range with an average fiber diameter of 198 nm. EDS analysis of exposed clay particles confirmed the presence Fe, Si, Mg, Al, and O. This suggests that the exposed clay paticles are indeed Fe-MMt.

3.2 Adsorption kinetics
The adsorption of Hg(II) ions onto Fe-MMt/PCL nanofiber membrane has been investigated as a function of time. Changes in the ion concentration were monitored at specific intervals from 0 to 360 minutes. Figure 2 shows the relationship between the adsorption capacity and contact time at three different initial concentrations of Hg(II): 10 ppm, 20 ppm, and 30 ppm.
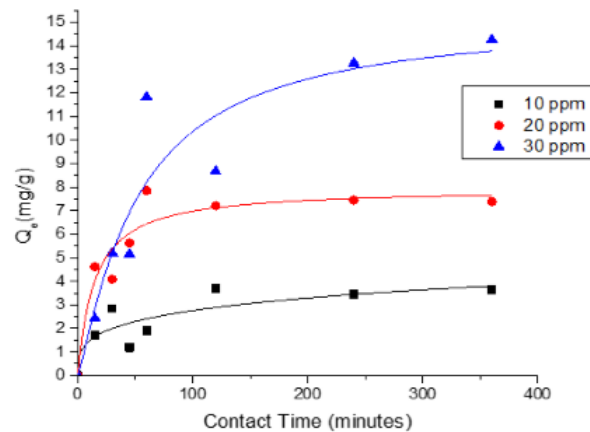
Figure 2. Adsorption Capacity Curve of Hg(II) ions.

Generally, it was observed that for all settings, the adsorption capacity increases with increasing contact time until no significant change in the adsorption capacity can be observed. A high initial removal was observed from the initial contact time up to 100 min. A slower removal followed until a plateau on the plot was observed, indicating equilibrium. This may be attributed to the high availability of adsorption sites at the start of adsorption. However, as adsorption progresses, the sites are gradually filled and ions have to intensely compete to be adsorbed [11]. The data collected from the adsorption as a function of time was used to determine the adsorption kinetic model and the rate limiting step of the Hg(II) adsorption. Figures 3-7 below show the linearized kinetic model plots for the adsorption of Hg(II) ions:
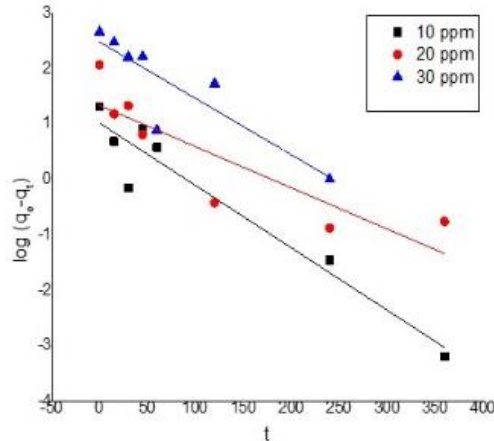

Figure 3. Linearized Lagergren pseudo-first order equation plot for Hg(II) adsorption.
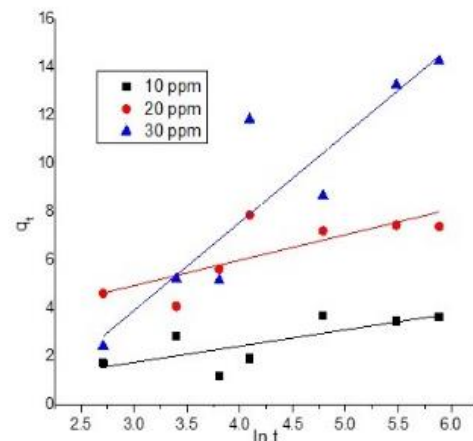

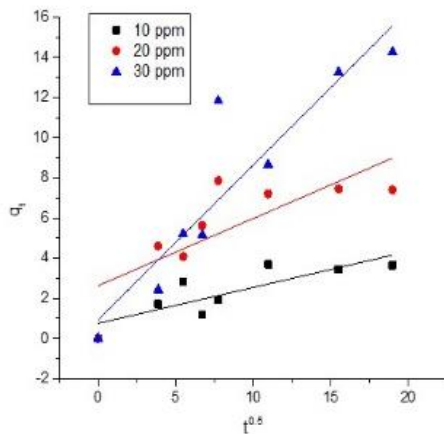Figure 4. Linearized Elovich equation plot for Hg(II) adsorption.

Figure 5. Linearized intra-particle diffusion model plot for Hg(II) adsorption.
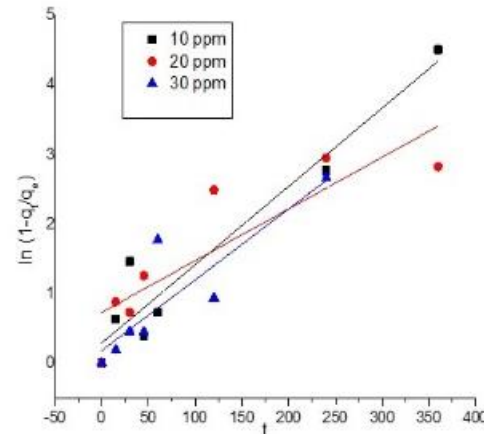

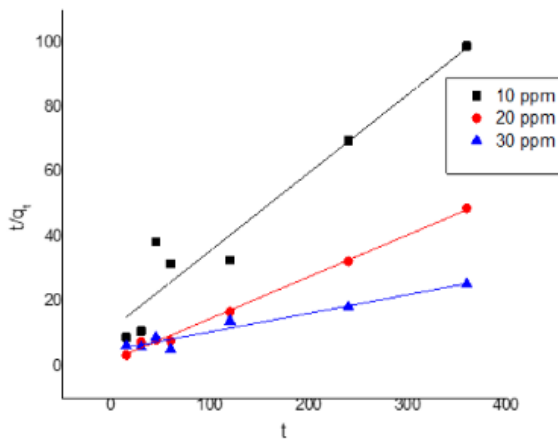Figure 6. Linearized liquid film diffusion model plot for Hg(II) adsorption.

Figure 7. Linearized pseudo-second order equation plot for Hg(II) adsorption.

Table 3. Summary of kinetic models correlation coefficients

Kinetic Model	R^2		
	10 ppm	20 ppm	30 ppm
Lagergren Pseudo-first order	0.929	0.764	0.772
Pseudo-second order	0.929	0.995	0.949
Elovich	0.558	0.621	0.827
Intra-particle diffusion	0.702	0.621	0.840
Liquid film diffusion	0.929	0.764	0.772

R^2 values for the pseudo-second order were generally higher than other kinetic models at different concentrations as shown in table 3; thus, adsorption of Hg(II) ions onto the Fe-MMt/PCL nanofiber membrane can be said to follow a pseudo-second order kinetics. Rate constant, k_2, was variable with no apparent trend at the different initial Hg(II) concentrations. In addition, table 4 below compares the calculated q_e to experimental q_e.

Table 4. Equilibrium adsorption capacity q_e

Hg(II) concentration, ppm	Calculated q_e, mg/g	Experimental q_e, mg/g	%deviation
10	4.15	3.69	11.1
20	7.73	7.86	1.68
30	17.42	14.25	18.2

The pseudo-second order model is usually used to describe adsorption where the surface-reaction kinetic step controls the overall adsorption rate. The reaction order for this model is two with respect to the number of adsorption sites which means that each adsorbed molecule is attached to two active sites of the adsorbent [7].

3.3 Adsorption isotherms
The adsorption of Hg(II) ions onto Fe-MMt/ PCL nanofiber membrane has been investigated as a function of initial concentration. It was observed in figure 8 that maximum adsorption capacity increases with increasing initial Hg(II) concentration.
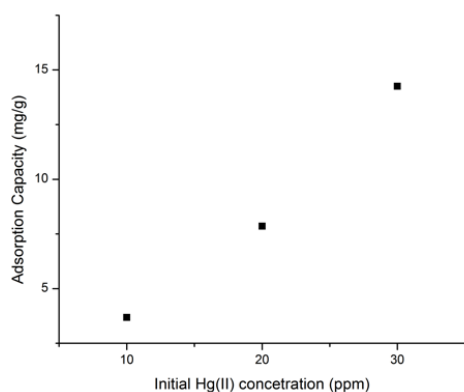

Figure 8. Adsorption capacity as a function of initial concentration.

Increasing the initial metal ion concentration increases the driving force to overcome the mass transfer resistance that hinders the movement of the metal ions from the bulk solution to the clay surface. This allows for more metal ions to come into contact with the adsorbent particles [12]. As a result, the adsorption capacity of the membrane increases as the initial metal ion concentration increases. This can be observed in figure 8, where the highest adsorption capacity of 14.254 mg/g was obtained for the adsorption of the 30 ppm Hg(II) solution.

The data obtained from the adsorption of Hg(II) as a function of initial concentration was analyzed in terms of the Langmuir, the Freundlich, and the Dubinin-Kaganer-Radushkevich isotherms as shown in figures 9, 10, and 11, respectively.
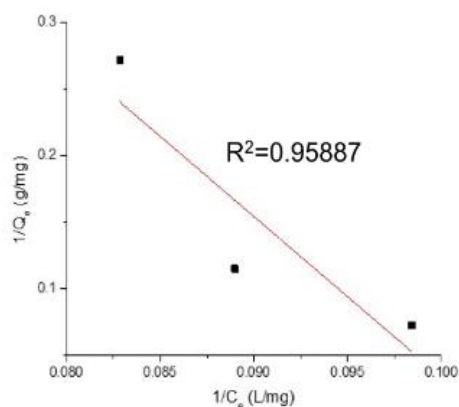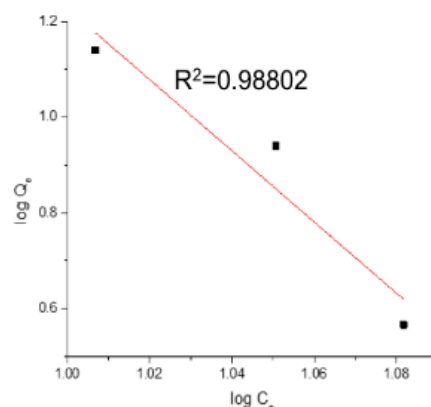

Figure 9. Langmuir isotherm.
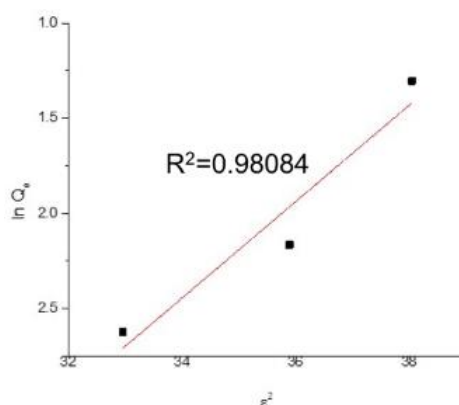

Figure 10. Freundlich isotherm.

Figure 11. Dubinin-Kaganer-Radushkevich isotherm.

Based on the values of the correlation coefficients (R^2) obtained, it was found that the Freundlich Isotherm best describes the adsorption behavior of Hg(II) on Fe-MMt/PCL. A previous study on Hg(II) adsorption onto montmorillonite also followed a Freundlich isotherm [13].

The multilayer adsorption described by the Freundlich isotherm is characterized by exponential distribution of heterogeneous sites [14]. The value of the Freundlich constant, K_F, is 0.0103 which suggests a low degree of heterogeneity. Another parameter, $1/n$, can classify the adsorption isotherm as either concave or convex depending on its value. A value of $(1/n) < 1$ denotes a convex isotherm where sorption energy is inversely proportional with surface concentration. Meanwhile, a value of $(1/n) > 1$ describes a concave isotherm where sorption energy is directly proportional with surface concentration [15]. The obtained value for $1/n$ is 2.3795 which is greater than unity thus, an increase in surface concentration increases the sorption energy.

The Dubinin-Kaganer-Radushkevich (DKR) isotherm was used to determine the value of the sorption energy E through equation 9, which can confirm the adsorption mechanism. When the value of E is in the range of -1 to -8 kJmol^{-1}, it is indicative of physisorption. When it is in the range of -8 to -16 kJmol^{-1} it is indicative of ion-exchange. While, when it is in the range of -20 to -40 kJmol^{-1} it is indicative of chemisorption [14]. The E value obtained for Hg(II) is -2.6803 kJmol^{-1}, well within -1 to -8 kJmol^{-1} which shows that the type of adsorption for Hg(II) ions is physisorption.

$$E = -\frac{1}{\sqrt{-2\beta}} \qquad (9)$$

4. Conclusion

Fe-MMt/PCL nanofiber membrane was successfully fabricated through electrospinning which produced a nanofiber network with fiber diameter ranging from 96 nm to 569 nm and an average fiber diameter of 198 nm. The adsorption experiments showed that the adsorption capacity of the nanofiber membrane increases with increasing contact time, and with increasing Hg(II) concentration. The highest adsorption capacity noted for the fabricated membrane was 14.25 mg/g. Furthermore, it was found that the kinetics of Hg(II) adsorption can be described by the pseudo-second order model and its adsorption behavior can be modeled using the Freundlich isotherm. Additionally, the sorption energy E, calculated using the Dubinin-Kaganer-Radushkevich isotherm, has a value of -2.68 kJmol^{-1}, which confirmed that the type of adsorption was physisorption.

Future studies can utilize the insights provided by this study on the adsorption behavior of the Hg(II) onto the Fe-MMt/PCL membrane to further improve its adsorption capacity. Furthermore, the Fe-MMt/PCL may be incorporated in a portable filtration set-up that can be deployed as rapid wastewater treatment set-up.

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