Adsorption of Cu(II) onto Fe(III)-Modified Montmorillonite – Kinetic, Isotherm, and Thermodynamic Studies

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Abstract. Trace metal ions, such as Cu(II), in wastewater could pose serious health threats when not treated. This study employed adsorption using an Fe(III)-modified montmorillonite (Fe-MMT), an abundant mineral in the Philippines, to remove Cu(II) ions in synthetic wastewater. Scanning electron micrographs of the synthesized clay showed its layered structure while elemental analysis confirmed the successful modification to Fe-MMT with high amounts of retained Fe in the clay. Batch adsorption was performed at varying adsorption time, initial Cu(II) concentration, and temperature, for which applicable models were then employed to understand the adsorption mechanism. Cu(II) adsorption showed a slow rate until the process reached equilibrium at 12 hrs corresponding to 85.86% removal. Adsorption of Cu(II) on Fe-MMT was found to agree with both the pseudo-first order and the liquid-film diffusion kinetic models. Isotherm modelling revealed that the process fitted well with the Langmuir model with theoretical adsorption capacity of Fe-MMT as 48.077 mg/g. On the other hand, Dubinin–Radushkevich isotherm suggests that the mechanism was via physisorption. From the thermodynamic modelling, it was obtained that the Cu(II) adsorption was an endothermic process which further translated to a $\Delta G^{\circ}_{298}$ of 5,696.89 J/mol.

1. Introduction

Untreated dissolved metals in water may cause a number of diseases and organ failures when ingested. Excessive copper, Cu(II), intake may alter structure and function of the liver and brain caused by a defect in copper excretion, now known as Wilson disease [1]. Locally, one of the most viable options for treatment of metal ions in wastewater is through adsorption, particularly using montmorillonite (MMT) clay. MMT has a structure that results to an overall slightly negatively charge, which makes it a potentially good adsorbent material [2]. However, modification is still necessary to improve the performance of MMT in removing said trace metals [3].

The adsorption process is defined as the transfer of a contaminant, known as the adsorbate, from the liquid phase to the solid material, known as the adsorbent, either by chemical and/or physical interactions [4]. The process is governed by three main steps: (1) transfer of the metal ion from the bulk liquid on to the surface of the adsorbent, also called the liquid film diffusion; (2) diffusion of the ions within the particle active site, also called intra-particle diffusion; and (3) retention of the metal ions through complexation, precipitation, or physical or chemical sorption [5]. Thus, it is also important to perform modelling to provide insights on the mechanisms involved in a specific adsorption system.
This study employs Fe(III)-modified montmorillonite (Fe-MMT) to remove Cu(II) ions in synthetic wastewater. Batch adsorption at varying time, initial ion concentration, and temperature will be utilized to fit kinetics, isotherm, and thermodynamic models that will aid in understanding the adsorption mechanism.

2. Methodology

2.1. Synthesis and characterization of Fe-MMT

The Fe-MMT was synthesized based on the methodology of Dela Cruz [6]. Ion exchange of Na-MMT (Southern Clay Products, Inc.) was performed using FeCl₃ and NaOH, which was stirred for 12 hours. The obtained particles were dried, ground, and sieved to particle sizes between 45 μm and 75 μm. The obtained Fe-MMT clay was characterized using a scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDX) (Hitachi S-3400).

2.2. Batch adsorption of Cu(II) ions

Synthetic wastewaters at 20ppm concentration were prepared from standard Cu(NO₃)₂, with pH maintained at 2.0 to 3.5. An orbital shaker was employed for all the batch experiments, using 50 mL of the aqueous solutions and 30 mg of the Fe-MMT. The clay was allowed to be in contact with the Cu(II) wastewater at varying time intervals until 24 hrs. For experiments involving varying initial concentrations, the Cu(II) were set at 30 ppm, 15 ppm, and 7.5 ppm. Finally, thermodynamic experiments were performed using a multi-stirrer at temperatures between 25°C and 60°C. All ion concentrations before and after adsorption were determined using an inductively coupled plasma-optical emission spectroscopy (ICP-OES, Prodigy7 Teledyne Leeman Labs).

3. Results and discussion

3.1. Morphology of Fe-MMT

SEM micrograph at 3,000x (figure 1) reveal the flaky nature and the wide range of particle size of the synthesized Fe-MMT. The smooth and relatively flat surfaces correspond to the basal plane of the clay. EDX characterization show the elements present in the clay such as silicon (16.96 wt%), iron (9.56 wt%), aluminum (5.03 wt%), magnesium (1.94 wt%), sodium, (0.56 wt%), calcium (0.29 wt%), and oxygen (55.41 wt%). The trace amount of Na suggests that there is an incomplete conversion of some Na-MMT particles to Fe-MMT.

![Figure 1. SEM micrograph of Fe-MMT at 3,000x.](image_url)
3.2. Adsorption kinetics

The two important parameters observed during adsorption are the %ion removal and the adsorption capacity at any given time \(q_t\), which may be calculated using equations (1) and (2), respectively. \(C_0\) and \(C_f\) are the initial and final concentrations while \(V\) is the solution volume and \(m\) is the adsorbent mass.

\[
\text{% ion removal} = \frac{C_o - C_f}{C_o} \times 100\%
\]

\[
q_t = \frac{(C_o - C_f)V}{m}
\]

Adsorption performance of Fe-MMT in removing Cu(II) ions from aqueous solutions is shown in figure 2. There was a steady linear increase in Cu(II) adsorption corresponding to 65.33% removal after 6 hrs. It was then followed by a slower adsorption up to the 12 hr. contact time with 85.86% Cu(II) removed, where it then plateaued and assumed to reach equilibrium. The highest calculated adsorption capacity of Fe-MMT was 34.446 mg/g.

![Figure 2. Percent removal of Cu(II) using Fe-MMT at varying time.](image)

Five kinetic models were utilized, namely Lagergren pseudo-first order, pseudo-second order, Elovich, liquid film, and intraparticle kinetic models. The first three models describe the reaction step of the adsorption while the last two differentiates the rate-determining step based on diffusion. Equations of the models are shown in table 1.

Plots of the reaction models are shown in figure 3 while diffusion models are shown in figure 4. Among three reaction models, the highest \(R^2\) value was obtained from the Lagergren pseudo-first order model for Cu(II) adsorption. From the model, the rate constant \(k_1 = 0.003 \text{ min}^{-1}\) and \(q_e = 35.552 \text{ mg/g}\) were calculated. It is worth noting that the calculated value is close to the experimental value of 34.446 mg/g. Based on the assumptions of the model, the sorption of Cu(II) on Fe-MMT only occurs at specific active sites, and that the Cu(II) ions are adsorbed as a single layer on the surface of the clay [7].
Table 1. Kinetic models and their corresponding equations$^1$.

| Model                  | Equation                                                                 |
|------------------------|---------------------------------------------------------------------------|
| Pseudo-first order     | $\ln(q_t - q_e) = \ln q_e - k_1t$                                         |
| Pseudo-second order    | $t = \frac{1}{k_2 q_e^{2}} + \frac{1}{q_e}$                              |
| Elovich                | $q_t = \beta \ln(\alpha \beta) + \beta \ln t$                          |
| Liquid film diffusion  | $\ln(1 - F) = -k_{sf}t$                                                  |
| Intraparticle diffusion| $q_t = k_i \cdot \sqrt{t}$                                              |

$^1$ Where $q_t$ is the adsorption capacity at any given time, $t$; $q_e$ is adsorption capacity at equilibrium; $F$ is fractional attainment of equilibrium which can be calculated by $q_t/q_e$; and all the other variables are constants relevant to each kinetic model.

![Figure 3. Experimental data with superimposed reaction kinetic models.](image3)

![Figure 4. Experimental data with superimposed diffusion kinetic models.](image4)
The diffusion kinetic plots shown in figure 4 were obtained setting the intercept at zero for which it is assumed that there were no adsorbent-adsorbate interactions yet. It can be observed that the Cu(II) adsorption is also governed by the liquid film diffusion model compared to the intraparticle diffusion model. It can thus be inferred that the adsorption process is also rate-determined by the diffusion of the Cu(II) from the bulk liquid to the surface of the Fe-MMT clay.

3.3. Adsorption isotherm modelling

Figure 5 shows the ion removed with respect to increasing ion concentration. A 98.02% removal was observed for Cu(II) at 8 ppm initial concentration, which plateaued at 16 ppm, before finally decreasing to 89.04% at 30 ppm Cu(II). Furthermore, calculations show that increasing the ion concentration also increases the adsorption capacity of the Fe-MMT. The highest adsorption capacity value was obtained at the highest Cu(II) concentration setting, corresponding to 44.945 mg/g.

![Figure 5](image.png)

**Figure 5.** Percent removal of Cu(II) and adsorption capacity of Fe-MMT at varying concentration.

| Adsorption isotherms models |  
|-----------------------------|
| **Langmuir**                | \[ \frac{c_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L}c_e; \quad R_L = \frac{1}{1 + K_L c_o} \] |
| **Freundlich**              | \[ \log q_e = \frac{1}{n} \log c_e + \log k_F \] |
| **Dubinin-Radushkevich**   | \[ \log q_e = \log q_s - \beta \varepsilon^2; \quad \varepsilon = RT \ln \left(1 + \frac{1}{c_e}\right); \quad E = \frac{1}{\sqrt{2\beta}} \] |

$^2$ Where $c_e$ is the equilibrium ion concentration in the liquid phase; $K_L/a_L$ corresponds to the monolayer adsorption capacity; $k_F$ is constant related to temperature.

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Three isotherm models were used in this paper, namely Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherms (see Table 2). It can be observed that from figure 6 that Cu(II) adsorption is better described by the Langmuir isotherm, which suggests that there is a monolayer preferential adsorption onto Fe-MMT. The theoretical monolayer adsorption capacity was calculated to be 48.077 mg/g. Further from the Langmuir model, a dimensionless parameter $R_L$ for each concentration may be calculated using. It is said that adsorption is not favored if $R_L > 1$, linear if $R_L = 1$, favored if $R_L$ is between 1 and zero, and irreversible if $R_L = 0$ [8]. The obtained $R_L$ values are in the range of 0.28 to 0.57 for the implemented settings, thus it may be said that the Cu(II) adsorption is favorable.

![Figure 6. Experimental data with superimposed Langmuir and Freundlich isotherms](image)

![Figure 7. D-R isotherm of Cu(II) adsorption.](image)

From the D-R isotherm (figure 7), the energy ($E$) value for Cu(II) adsorption was calculated to be 5,000 J/mol. Energy values below 8,000 J/mol is attributed to physisorption while $E$ greater than 8,000 J/mol describes chemisorption [9]. Noting that the calculated value falls below the lower limit, it may be concluded that Cu(II) ions adheres to the Fe-MMT surface via physical interactions.
3.4. Thermodynamic modelling

The adsorption of Cu(II) on Fe-MMT at varying temperature was also explored and shown in figure 8. It can be observed that Cu(II) is affected by the increase in temperature as removal and capacity also increases. This data may be used to calculate the thermodynamic parameters of the Cu(II) adsorption using equation (3). A plot of $\ln k_d$ versus $1/T$ is presented in figure 9 while a summary of the thermodynamic constants is shown in table 2. It can be deduced that the Cu(II) adsorption is an endothermic process with a calculated $\Delta H^\circ$ of 23,033.66 J/mol. Furthermore, the $\Delta S^\circ$ of the system was found to be 58.18 J/mol K with a corresponding $\Delta G^\circ$ at room temperature of 5,696.89 J/mol.

$$\ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

(3)

Figure 8. Effect of temperature on Cu(II) adsorption on Fe-MMT.
Figure 9. Equilibrium plot to obtain thermodynamic parameters of Cu(II) adsorption

Table 3. Thermodynamic parameters of the Cu(II) adsorption on Fe-MMT.

| Temp (K) | $\Delta H^\circ$ (J/mol) | $\Delta S^\circ$ (J/mol K) | $\Delta G^\circ$ (J/mol) |
|---------|-------------------------|---------------------------|------------------------|
| 298     | 23,033.66               | 58.18                     | 5,696.89               |
| 320     |                         |                           | 4,416.99               |
| 335     |                         |                           | 3,544.33               |

4. Conclusions
The study successfully utilized Fe-MMT for the adsorption treatment of Cu(II) in synthetic wastewater. The synthesized Fe-MMT showed a layered structure with elemental composition showing successful modification. During kinetic experiments but equilibrium was achieved after 12 hrs with the process being described by the Lagergren pseudo-first order and the liquid film diffusion models. On the other hand, a decrease in percent removal was observed with increasing initial ion concentration. Isotherm modelling showed that monolayer adsorption is apparent for Cu(II) while D-R isotherm showed that the adsorption of Cu(II) on Fe-MMT is via physisorption. Finally, thermodynamic parameters were successfully calculated.

The models and characteristic values obtained in this paper provide valuable insights when Fe-MMT is applied to actual wastewater. It is thus recommended to incorporate the modified clay in other adsorption set-ups that may be more practical for field applications.

References
[1] Uauy R, Maass A and Araya M 2008. Estimating risk from copper excess in human populations Am J Clin Nutr 88 867–71
[2] Krupskaya V, Zakusin S, Tyupina E, Dorzhieva O, Zhukhlistov A, Belousov P and Timofeeva M 2017. Experimental study of montmorillonite structure and transformation of its properties under treatment with inorganic acid solutions Minerals 7 49
[3] Uddin M K 2017. A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade Chem Eng J 308 438–62
[4] Kurniawan T A, Chan G Y S, Lo W H and Babel S 2006. “Physico-chemical treatment techniques for wastewater laden with heavy metals.” Chem. Eng J 118 83–98.
[5] Ijagbemi C O, Baek M H and Kim D S 2010. Adsorptive performance of un-calcined sodium exchanged and acid modified montmorillonite for Ni2+ removal: Equilibrium, kinetics, thermodynamics and regeneration studies.” *J Hazard Mater* **174** 746–55.

[6] Dela Cruz M L, Arano K, Dela Pena E M and Diaz L J 2013. “Nanoclay-supported zero-valent iron as an efficient adsorbent material for arsenic.” *Adv Mater Res* **686** 296–304.

[7] Largette L and Pasquier R 2016. “A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon.” *Chem Eng Res Des* **109** 495–504.

[8] Bessbousse H, Rhilalou T, Verchère J-F and Lebrun L 2008. “Sorption and filtration of Hg(II) ions from aqueous solutions with a membrane containing poly(ethyleneimine) as a complexing polymer.” *J Membr Sci* **997–1006**

[9] Demiral H and Güngör C 2016. “Adsorption of copper (II) from aqueous solutions on activated carbon prepared from grape bagasse.” *J Clean Prod* **124** 103–13.

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