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# Application of Iron Sand Magnetic Material (MM) and Silica Coated Iron Sand Magnetic Material (MM-SiO<sub>2</sub>) as Cd<sup>2+</sup> Adsorber in Aqueous System

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**Abstract.** The adsorption of Cd<sup>2+</sup> using iron sand magnetic material (MM) and silica-coated magnet material (MM-SiO<sub>2</sub>) was carried out using the batch method to determine the effect of pH, contact time, and concentration. The optimum adsorption of Cd<sup>2+</sup> metal ions by MM and MM-SiO<sub>2</sub> occurred at pH 6 and pH 5, respectively. The adsorption occurs quickly until the contact time of 60 minutes with the adsorption capacity of 3.53 mg/g and 7.24 mg/g, respectively. Adsorption of Cd<sup>2+</sup> metal ion by MM tended to follow the first-order pseudo reaction kinetics with the k<sub>1</sub> is 3.9x10<sup>-2</sup> g.mg<sup>-1</sup>.min<sup>-1</sup> while MM-SiO<sub>2</sub> follow the second-order pseudo reaction kinetics with k<sub>2</sub> is 12.2x10<sup>-3</sup> g.mg<sup>-1</sup>.min<sup>-1</sup>. The maximum adsorption of Cd<sup>2+</sup> metal ion by MM and MM-SiO<sub>2</sub> occurred at a concentration of 200 mg/L with an adsorption capacity of 14.08 mg/g and 22.063 mg/g respectively and followed the Langmuir and Temkin adsorption isotherms, respectively.

## INTRODUCTION

The heavy metal cadmium is a polluting metal found in the paint industry, casting of zinc, in the refining of tin and copper [1]. Exposure to cadmium shall increase high blood pressure, kidney and respiratory system disorders, and death at very high levels of contaminants [2]. The threshold limit value for cadmium in water is ~5 ppb [3]. Several techniques have been applied to reduce heavy metal contents in water samples, including coagulation and adsorption. The adsorption method is considered very easy to apply and does not produce toxic gases. The adsorption process on heavy metals occurs due to heavy metal ions being attached to functional groups of the adsorbent surface such as -COOH, -OH, -SH, and -NH groups [4].

Iron sand's magnetic material (Fe<sub>3</sub>O<sub>4</sub>) is often used as an adsorbent. The advantage of Fe<sub>3</sub>O<sub>4</sub> is its magnetic properties, it is straightforward to separate using an external magnet [5]. However, iron sand's magnetic material

properties are very easily oxidized in air to produce maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ). Therefore, an inert and biocompatible material such as silica is needed to coat magnetic materials. Silica has been widely used as an adsorbent to adsorb heavy metals. The silica surface contains active groups of silanol ( $\equiv\text{Si-OH}$ ) and siloxanes ( $\equiv\text{Si-O-Si}\equiv$ ), thus, it allows silica to be modified with the Fe-OH group present in an iron sand magnetic material [6-7].

This research carried out the coating of magnetic material with silica using the sol-gel method, then performed the adsorption test using a  $\text{Cd}^{2+}$  ion solution under parameters variation of pH, time, and concentration, as well as the determination of the adsorption capacity and adsorption order. Coating magnetic materials using silica can increase the adsorption capacity since it may expand the surface area and the active site of the adsorbent.

## METHODS

The chemicals used in this study were a solution of sodium silicate, hydrochloric acid, sodium hydroxide, and a standard solution of cadmium (1000 mg/L). All chemicals are pro analysis (p.a). The buffer solution is made from a mixture of potassium chloride, potassium hydrogen phthalate, and hydrochloric acid. Magnetic material (MM) was picked up from iron sand of Bugel Beach, Yogyakarta, Indonesia.

The iron sand was washed with purified water and dried for 18 hours at  $95^\circ\text{C}$ . The MM from the iron sand was then separated using a regular magnet. The obtained MM was ground with a mortar and sieved (200 mesh). MM smaller than 200 mesh was washed with purified water, then dried for 18 hours at  $95^\circ\text{C}$ . MM was refluxed with 4 M of sodium hydroxide solution for 2 hours at  $75^\circ\text{C}$ , then washed with purified water until neutral pH was reached and final-dried in an oven at  $95^\circ\text{C}$  (18 hours). Synthesis of silica-coated iron sand magnetic materials was done by using 1 gram of MM activated with 1 mL of 1 M hydrochloric acid, then 2 mL of sodium silicate (13%) solution followed by the addition of  $\pm 2$  mL of 1 M hydrochloric acid to form sol-gel. The materials were sonicated by using an ultrasonicator and aging for 18 hours, then dried at  $75^\circ\text{C}$  for 5 hours to produce the so-called silica-coated magnetic material (MM-SiO<sub>2</sub>) [8]. Adsorption of  $\text{Cd}^{2+}$  metal ion on MM and MM-SiO<sub>2</sub> as an adsorbent was done with a variation of pH, concentration, and contact time. The adsorption process was conducted by batch method. The non-adsorbed  $\text{Cd}^{2+}$  was analyzed by using an atomic absorption spectrophotometer (AAS). The adsorption capacity ( $Q_e$ ) and adsorption efficiency (EA) of  $\text{Cd}^{2+}$  metal ions at equilibrium conditions were determined using equations (1) and (2).

$$Q_e = \frac{C_o - C_i}{m} V \quad (1)$$

$$EA (\%) = \frac{C_o - C_i}{C_o} \times 100 \quad (2)$$

with  $Q_e$  (mg/g) stands for the capacity of adsorption,  $C_o$  (mg/L) belongs to initial concentration of  $\text{Cd}^{2+}$ ,  $C_i$  (mg/L) is concentration of  $\text{Cd}^{2+}$  after adsorption,  $V$  is volume of solution (liter), and  $m$  is adsorbent mass (milligram).

## RESULTS AND DISCUSSION

### Synthesis of MM and MM-SiO<sub>2</sub> Adsorbents

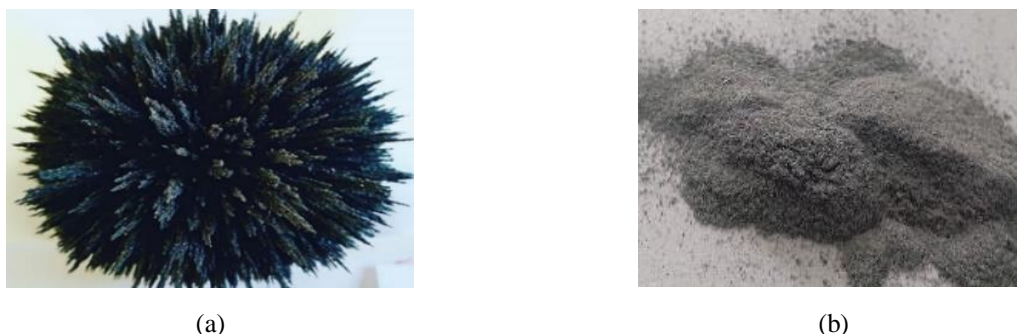
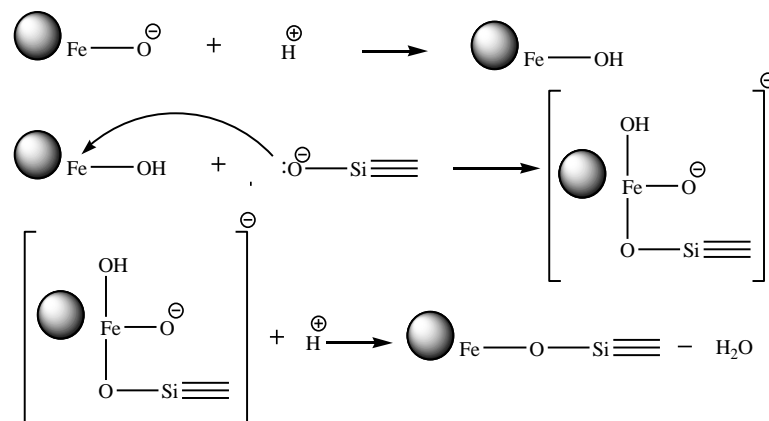


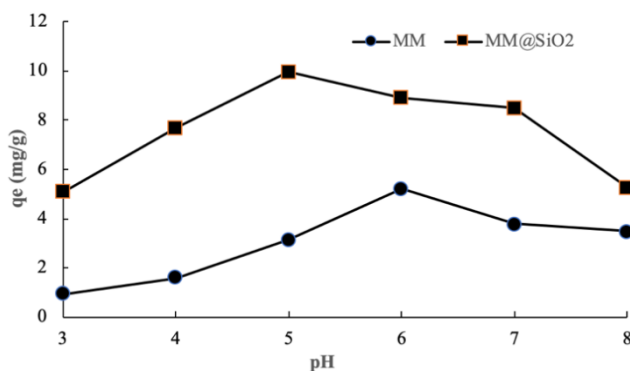
FIGURE 1. The appearance of (a) MM and (b) MM-SiO<sub>2</sub>



**FIGURE 2.** The sol-gel mechanism of Fe-O-Si formation on the surface of magnetite material [9]

### Cd<sup>2+</sup> Adsorption Under Controlled pH

Figure 3 shows the effect of pH on the ability of MM and MM-SiO<sub>2</sub> adsorbents to adsorb Cd<sup>2+</sup> from the solution system. The adsorption capacity ( $Q_e$ ) of the MM adsorbent increased from 0.92 mg/g (pH 3) to 5.21 mg/g (pH 6) and decreased to 3.48 at pH 8. However, the adsorption capacity ( $Q_e$ ) of the MM-SiO<sub>2</sub> was found 5.08 mg/g, 9.94 mg/g, and 5.96 mg/g at pH 3, 5, and 8, respectively. The high adsorption capacity of MM-SiO<sub>2</sub> adsorbent compared to MM suggests that the addition of Si-OH group of silica in MM is able to rise the ability of the adsorbent to adsorb Cd<sup>2+</sup> ion. At pH 8, both adsorbents experienced a decrease in the ability to adsorb Cd<sup>2+</sup> which was probably due to the formation of complex compounds between Cd<sup>2+</sup> and OH<sup>-</sup> ions. At acidic pH (pH 1 to 4), the formation of silanol groups (Si-OH) increased due to the large number of H<sup>+</sup> ions in solution [10]. The increase in H<sup>+</sup> ions will suppress the release of hydrogen atoms from the silanol group, which results in a reduction in the number of adsorbed Cd<sup>2+</sup> metal ions. Figure 3 recommends that adsorption was performed at pH 6 for MM and pH 5 for MM-SiO<sub>2</sub> in this study.



**Figure 3.** Adsorption of Cd<sup>2+</sup> on MM and MM-SiO<sub>2</sub> adsorbent under controlled pH. Experimental setting: 10 mg adsorbent per 10 mL of 25 mg/L Cd solution, 2 hours of contact time at room temperature

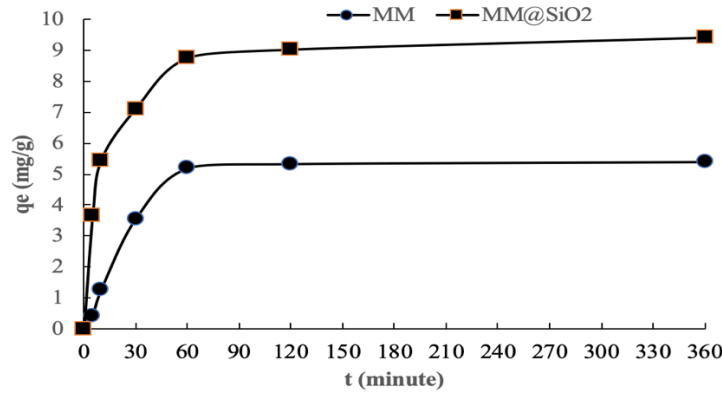
### Adsorption Kinetics

A contact time of 0-360 minutes was applied to examine the adsorption kinetics of Cd<sup>2+</sup> on both MM and MM-SiO<sub>2</sub> adsorbents. Cd<sup>2+</sup> ions were absorbed more rapidly at the start of contact, before reaching equilibrium at 60 min (Fig. 4). Figure 5 shows the pseudo-first order and pseudo-second order adsorption kinetics when applied to the case of Cd<sup>2+</sup> adsorption onto MM and MM-SiO<sub>2</sub> adsorbents.

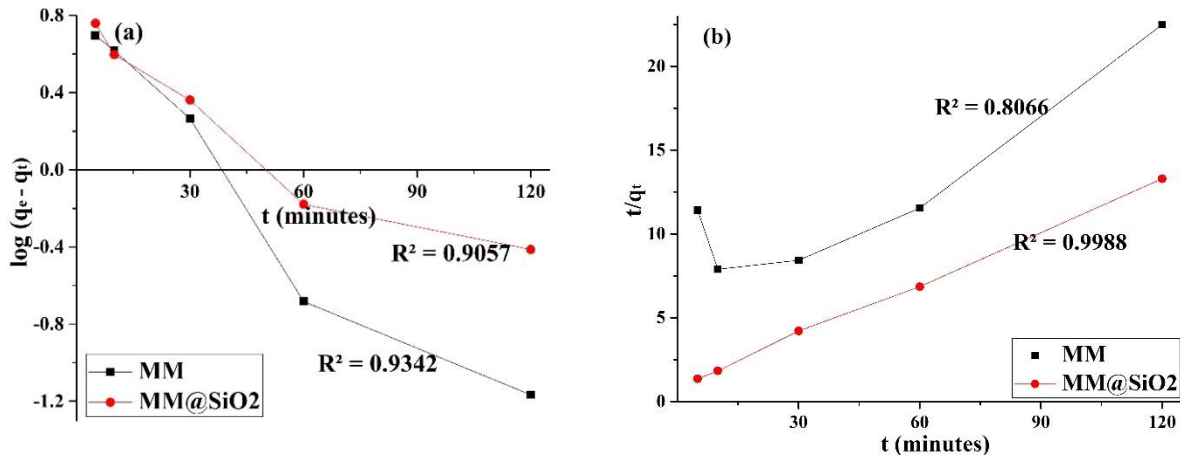
$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2,303} t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where  $k$  stands for the adsorption rate constant ( $\text{g}\cdot\text{min}^{-1}/\text{mg}$ );  $k_1$  for pseudo-first order and  $k_2$  for pseudo-second order,  $q_t$  is the amount of  $\text{Cd}(\text{II})$  being adsorbed ( $\text{mg}/\text{g}$ ), and  $q_e$  is the capacity of adsorption at equilibrium ( $\text{mg}/\text{g}$ ). The values of  $k_1$  and  $k_2$  can be quantified based on the plot of the relationship between  $\log (q_e - q_t)$  versus  $t$  and  $t/q_t$  versus  $t$  of the equations 3 and 4, respectively. The plot results are tabulated in Table 1.



**Figure 4.** Effect of contact time on  $\text{Cd}^{2+}$  adsorption onto MM and MM-SiO<sub>2</sub> adsorbents. Experimental setting: 10 mg adsorbent per 10 mL of 25 mg/L Cd solution, 0-360 minutes of contact time at room temperature



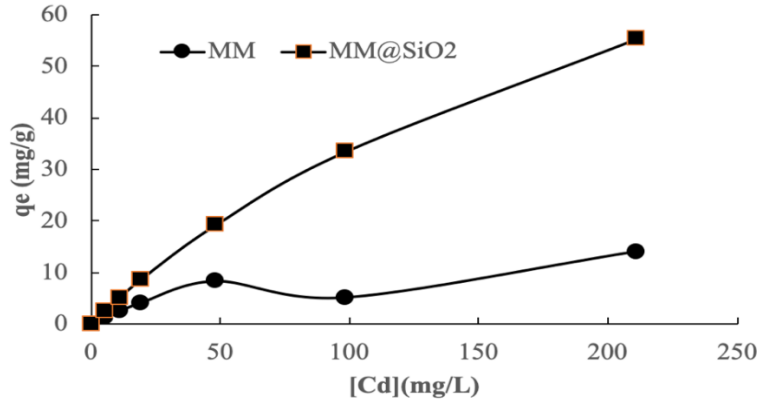
**Figure 5.** Kinetic parameters curve of (a) Pseudo-first order and (b) Pseudo-second order

**TABLE 1.** Values of  $k_1$  and  $k_2$  for  $\text{Cd}^{2+}$  adsorption on MM and MM-SiO<sub>2</sub> adsorbents

Adsorbent	Pseudo-First-Order			Pseudo-Second-Order		
	$q_e$ (mg/g)	$k_1$ ( $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ )	$R^2$	$q_e$ (mg/g)	$k_2$ ( $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ )	$R^2$
MM	5.13	$3.90 \times 10^{-2}$	0.934	8.89	$1.70 \times 10^{-3}$	0.807
MM-SiO <sub>2</sub>	4,81	$2.35 \times 10^{-2}$	0.906	9.69	$12.20 \times 10^{-3}$	0.999

## Adsorption Isotherm

The model of adsorption interaction, capacity of adsorption, and level of accumulation of  $\text{Cd}^{2+}$  ions on the adsorbent can be approached using isotherm studies [11]. Investigation result of  $\text{Cd}^{2+}$  adsorption isotherms (concentration = 5-200 mg/L) on MM and MM-SiO<sub>2</sub> adsorbents is shown in Figure 6. The capacity of adsorption of  $\text{Cd}^{2+}$  ion onto MM and MM-SiO<sub>2</sub> adsorbents is 4.213 mg/g and 7.237 mg/g, respectively at the initial concentration (5 mg/L) of  $\text{Cd}^{2+}$  solution. The capacity of adsorption raised to 14.084 mg/g and 22.063 mg/g, respectively when reaching the maximum concentration (200 mg/L) of  $\text{Cd}^{2+}$  due to the silica coating effect.



**FIGURE 6.** Effect of  $\text{Cd}^{2+}$  initial concentration on adsorption onto MM and MM-SiO<sub>2</sub>. Experimental setting: 10 mg adsorbent per 10 mL of 5-200 mg/L Cd solution, 2 hours of contact time at room temperature

The Langmuir adsorption isotherm is used to provide information that an adsorption process occurs chemically by forming a chemical bond between the active groups of the adsorbent and the adsorbate. Langmuir isothermal adsorption assumes that the maximum adsorption capacity occurs at an adsorbent's active sites in a uniform (homogeneous) surface layer. Freundlich isotherms model assumes adsorption is carried out physically. This model provides the postulate that adsorption occurs in more than one surface layer (multilayer) [11], because the adsorption process occurs on a heterogeneous surface, and each site has different energy and adsorption capabilities.

The adsorption isotherm model which can explain the adsorption process that occurs between physical and chemical processes is the Temkin adsorption isotherm. This model can provide information in the adsorption process where chemical bonds are formed on the surface of the heterogeneous [12]. The isotherm adsorption equations of Langmuir and Freundlich are formulated at equations (5) and (6), respectively, while that of the Temkin model follows equations (7) and (8).

$$\text{Langmuir: } \frac{1}{q_e} = \frac{1}{K_L q_{\max}} \frac{1}{C_e} + \frac{1}{q_{\max}} \quad (5)$$

$$\text{Freundlich: } \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

$$\text{Temkin: } q_e = B \ln A + B \ln C_e \quad (7)$$

$$q_e = \frac{R T}{b T} \ln C_e + \frac{R T}{b T} \ln K_T \quad (8)$$

where  $C_e$  belongs to the metal ion concentration when it reaches equilibrium (mg/L),  $q_{\max}$  (mg/g) is the capacity maximum of adsorption, and  $K_L$  (L/mg) is the Langmuir constant which corresponds to the adsorption energy,  $K_L$  is obtained from the slope and intercept determination of the linear plot  $C_e/q_e$  versus  $C_e$ .  $K_F$  (L/mg) is the Freundlich constant,  $n$  is the heterogeneity factor (the intensity of the adsorbent's interaction with the adsorbate).  $K_F$  is derived

from the slope and intercept of a linear plot of  $\ln q_e$  versus  $\ln C_e$ .  $K_T$  is the bond equilibrium constant ( $L \cdot mol^{-1}$ ) associated with the maximum bond energy,  $B = RT/b_T$ , where  $R$  is the general gas constant ( $8.314 JK^{-1} \cdot mol^{-1}$ ),  $T$  is the temperature in Kelvin,  $b_T$  is the adsorption heat value.  $A$  is the bond equilibrium constant, and  $B$  is related to the calorific value of the adsorption.  $A$  and  $B$  can be generated the intercept, and the slope from the  $q_e$  versus  $\ln C_e$  linearity plot, the result of the straight-line slope is the same as  $RT/b_T$  and the intercept  $(RT \ln K_T)/b_T$ .

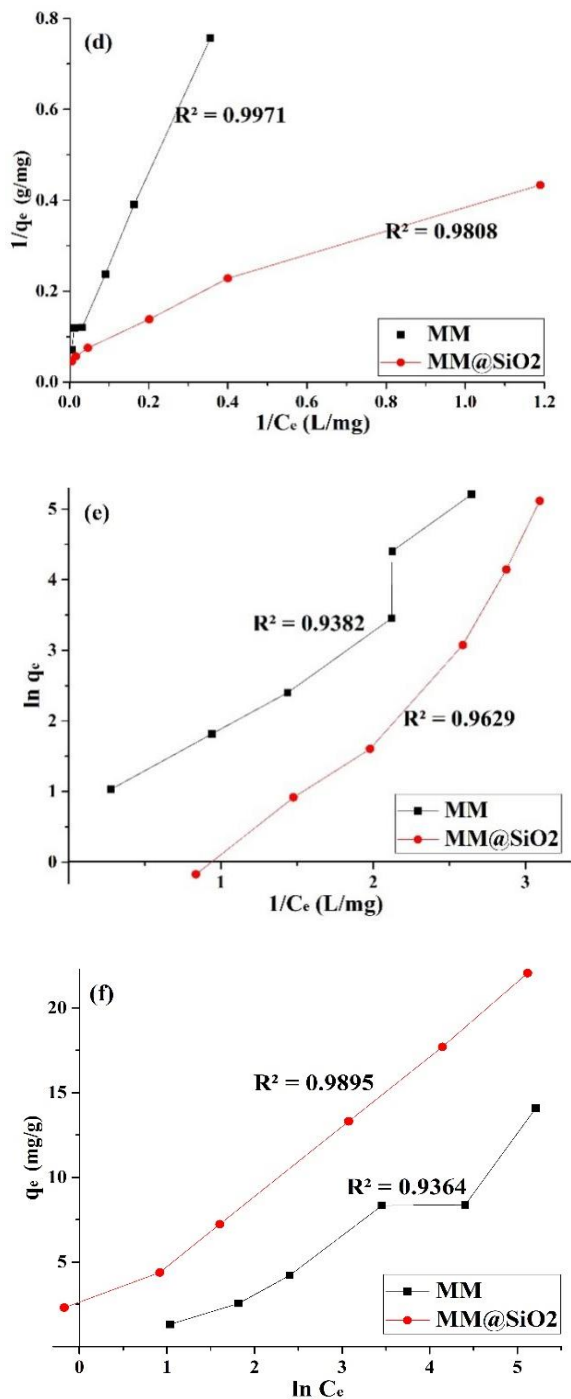


FIGURE 6. Adsorption isotherm curve of (a) Langmuir, (b) Freundlich, and (c) Temkin

The Langmuir adsorption isotherm parameters in Table 2 shows that  $K_L$  and  $q_{max}$  of the adsorption  $Cd^{2+}$  on MM and MM-SiO<sub>2</sub> are  $3.6 \times 10^{-3}$  L/mg, 14.14 mg/g, and  $1.9 \times 10^{-1}$ , 15.95 mg/g, respectively, with the  $R^2$  of 0.997 and 0.981, respectively. Moreover, the Freundlich isotherm adsorption parameter such as  $K_F$ ,  $n$ , and  $R^2$  for  $Cd^{2+}$  adsorption on MM and MM-SiO<sub>2</sub> adsorbent are 9.63 L/mg; 1.87; 0.938 and  $30.07 \times 10^{-1}$ ; 2.35; 0.962, respectively. The MM-SiO<sub>2</sub> adsorbent more closely follows the Temkin isotherm equation with  $R^2$  is 0.989, this provides information that the adsorption process takes place chemically on a heterogeneous surface of the adsorbent. The Temkin constant ( $K_T$ ) for adsorption by the MM-SiO<sub>2</sub> adsorbent was obtained at  $15.62 \times 10^{-1}$  L.mg<sup>-1</sup> with an average adsorbent-adsorbate ( $b_T$ ) interaction energy of 650.5 J/mol. The addition of silica to the magnetic material of iron sand makes the magnetic material's surface undergo a modification of non-uniform functional groups, thus allowing chemical bonds to occur on a heterogeneous surface [13].

**TABLE 2.** Adsorption isotherm parameters of  $Cd^{2+}$  adsorption on MM and MM-SiO<sub>2</sub> adsorbents.

Adsorbent	Adsorption Isotherm								
	Langmuir			Freundlich			Temkin		
	$K_L$ (L/mg)	$q_{max}$ (mg/g)	$R^2$	$K_F$ (L/mg)	$n$	$R^2$	$K_T$ (L/mg)	$b_T$ (J/mol)	$R^2$
MM	$3.6 \times 10^{-3}$	14.14	0.997	$9.63 \times 10^{-1}$	1.87	0.938	$4.49 \times 10^{-1}$	872.6	0.936
MM-SiO <sub>2</sub>	$1.9 \times 10^{-1}$	15.95	0.981	$30.07 \times 10^{-1}$	2.35	0.962	$15.62 \times 10^{-1}$	650.5	0.989

## CONCLUSION

The adsorption of  $Cd^{2+}$  onto MM and MM-SiO<sub>2</sub> adsorbents is strongly pH-dependent, quite fast at the beginning, and reaches equilibrium within 60 minutes. Adsorption of  $Cd^{2+}$  metal ion by MM tended to follow the first-order pseudo reaction kinetics with the  $k_1$  is  $3.9 \times 10^{-2}$  g.mg<sup>-1</sup>.min<sup>-1</sup> while MM-SiO<sub>2</sub> follow the second-order pseudo reaction kinetics with  $k_2$  is  $12.2 \times 10^{-3}$  g.mg<sup>-1</sup>.min<sup>-1</sup>. Coating of MM using silica can increase the adsorption capacity of MM-SiO<sub>2</sub> due to the silanol and siloxane functional group. The Langmuir, Freundlich, and Temkin isothermal adsorption can be applied for determining the adsorption isotherm models.

## ACKNOWLEDGMENTS

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