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Kinetic Study for Adsorption of Heavy Metals on Zeolite

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Abstract: Heavy metals-polluted water has negative impact on the ecosystem. In Malaysia, minimum discharge limit for Cu^{2+} and Zn^{2+} are 1 mg/L and 2 mg/L, respectively. Zeolite is a highly porous adsorbent and its performance is affected by various factors, including contact time and pH. Thus, the objective of this study is to identify an ideal operating condition to treat Cu^{2+} and Zn^{2+} solutions up to the allowable discharge limit, by considering the pH and contact time factors. Six kinetic models were studied to identify the adsorption mechanism of the heavy metal removal process. Single solute batch adsorption experiment was conducted within pH 3-11 from 30 to 150 min. Results showed that hydration enthalpy (ΔH_{hyd}) governed the selectivity of heavy metals, where a maximum of 90.87% Zn^{2+} (ΔH_{hyd} = -1955 kJ/mol) and 82.15% Cu^{2+} (ΔH_{hyd} = -2010 kJ/mol) removals were found at pH ≥ 7. Without pH adjustment, selectivity towards Cu^{2+} was higher compared with Zn^{2+} due to the size of hydration radii, where Cu^{2+} is 0.11 Å smaller than Zn^{2+}. By considering both pH and contact time factors, this study shows that by adjusting the pH of Zn^{2+} solutions to a minimum pH value of 7, the contact time required to achieve maximum Zn^{2+} removal rate was 90%, which can be achieved within 60 min. Meanwhile, zeolite performed better in Cu^{2+} removal without any pH adjustment where a maximum of 94% was achieved at 120 min. Final concentration of 0.523 mg/L Cu^{2+} and 0.981 mg/L Zn^{2+} were obtained in this study. Kinetic study showed that Ritchie's equation predicted Cu^{2+} adsorption the best, while Zn^{2+} adsorption could be represented by Elovich model. This suggested that the adsorption on the activate site governed Cu^{2+} and Zn^{2+} removal process. Hence, future work should focus on modifying zeolite surface to improve the adsorptive performance.

Keywords: zeolite; heavy metal removal; pH; contact time

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0 Introduction

Nowadays, Cu, Zn, and Pb are highly demanded heavy metals in the market and it is projected that the supply would reach its maximum in 2030 to 2050[1]. This implies the rise of water pollution by these heavy metals from electronic industry, mining, paints industry, and glass industry in the near future. A recent report published by Kenai Watershed Forum found out that fertiliser, traffic intensification as well as general urbanization contribute to Zn and Cu pollution in Kenai River Watershed[2]. Furthermore, research done by Sankson et al.[3] reported that the combined sewer overflows discharge in Poland consist of 170 - 1890 μg/L Zn and 31 - 590 μg/L Cu. Moreover, Voghji River was highly polluted with heavy metal consisting of 1.28 - 82.5 μg/L Cu and 0.94-105.5 μg/L Zn due to mining activities[4].

Heavy metals cause deleterious effects to living organisms. Heavy metals could enter human body through different routes, such as inhalation of toxic gas and ingestion of contaminated drinking water and food. High exposure to heavy metal could lead to serious health effects and in extreme situation, it can lead to death. Cu^{2+} can cause stomach-ache, irritation in eyes, noses, mouths, and headache, while Zn^{2+} causes stomach cramps, nausea, and respiratory disorder[5]. Additionally, plants which are exposed to high level of Cu^{2+} will prohibit root elongation as well as root cell membrane[6]. Similarly, Zn^{2+} also causes growth inhibition in macroalgae, which is economically significant and a fast-growing commodity[7].

In Malaysia, the allowable discharge for Cu^{2+}

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according to standard A is 0.2 mg/L and 1 mg/L for standard B[8]. Meanwhile, the allowable discharge for Zn^{2+} is 2 mg/L for both standard A and B. To ensure good quality of life, it is compulsory to treat the wastewater to the allowable discharge limit. Chemical precipitation, coagulation-flocculation, ion exchange, and membrane filtration are the commonly used method to treat heavy metal polluted water. However, most of these methods have disadvantages including high energy consumption which results in high operating cost, low efficiency of heavy metal removal, and formation of toxic sludge where further treatment is required[9]. Lately, research has been conducted on genetically modified micro-organism to remove heavy metal such as Cd^{2+} and Pb^{2+}[10]. However, this is a newly introduced feature, which is not suitable for practical application for now.

Adsorption is a well-known separation method, and it is recognized by numerous scientists for wastewater applications in recent years[11]. It is because adsorption shows high efficiency in heavy metals removal at reasonable cost and minimizes the chemical and biological sludge produced[12]. Furthermore, regeneration of adsorbents can be performed in most of the adsorption process, which further reduces the maintenance cost. Isotherm and kinetics studies are commonly conducted in adsorption related research. This is because kinetic study is important to understand the adsorption mechanism and identify the rate of the controlling steps. Pseudo first order (PFO) and pseudo second orders (PSO) are commonly studied to investigate the adsorption mechanism. In PFO, low constant value, K_1, indicates slow adsorption process while high constant value, K_2, reveals an increase in adsorption rate[13]. Table 1 shows the list of adsorbents used for heavy metals adsorption. Generally, PSO presented the adsorption mechanism well with coefficient of determination, R^2, which is approximately 0.99.[13-16] q_e represents the absorbed amount at equilibrium.

Table 1 List of adsorbents used for heavy metals adsorption

Adsorbents	Performance	References
Albizia lebbeck pods	Fitted PSO with q_e = 0.7477 Cu^{2+} mg/g K_2 = 1.7887 (g/mg · min) q_e = 0.8332 Zn^{2+} mg/g K_2 = 1.4405 (g/mg · min) When 10×10^{-6} Cu^{2+} is used as feed, ~78% Cu^{2+} is removed. When 10×10^{-6} Zn^{2+} is used as feed, ~83% Zn^{2+} is removed.	[13]
Nanoscale zero valent iron impregnated cashew nut shell	Fitted PSO with q_e = 10.012 Cu^{2+} mg/g at 20×10^{-6} Cu^{2+} solution K_2 = 0.0216 (g/mg · min) When 20×10^{-6} Cu^{2+} is used as feed, 100% Cu^{2+} is removed.	[14]
Chitosan coated magnetic nanoparticles	Fitted PSO with q_e = 49.63 Cu^{2+} mg/g at 100×10^{-6} Cu^{2+} solution K_2 = 0.0024 (g/mg · min) When 100×10^{-6} Cu^{2+} is used as feed, ~100% Cu^{2+} is removed.	[15]
Poly(2-aminothiazole)	Fitted PSO with q_e = 120 Ag^{+} mg/g at 300×10^{-6} Ag^{+} solution K_2 = 0.002 (g/mg · min)	[16]

Zeolite is a popular adsorbent due to its inherent high porosity and excellent metal binding capacity. Numerous factors such as type of zeolite, pH, contact time, mass of adsorbent, and concentration of feed solution affect the performance of zeolite in heavy metal removal. Thus, the objective of this study is to identify an ideal operating condition to achieve maximum removal rate by considering the effect of pH and contact time on the performance of zeolite. Besides, kinetic study was also conducted to find out the adsorption mechanism.

1 Materials and Methods

1.1 Materials

Analytical grade zeolite crystalline alumiosilicates, which consist of silica and alumina, were supplied by ChemSoln. The zeolite was firstly sieved using

200 μm × 500 μm sieves and treated in the oven at 100 ℃ for 24 h before use. $CuCl_2$ and $ZnCl_2$ were used as received.

1.2 Methodology

0.5 g zeolite was exposed to 10×10^{-6} of Cu^{2+} and Zn^{2+} solutions at pH 3, 5, 7, 9, and 11. The pH of the solution was adjusted by adding either 0.1 N of NaOH or 0.1 N of HCl into the solutions. Sample was collected and filtered using syringe filter (Thermo Fisher, 0.22 micron) after 60 min to evaluate the adsorptive performance of zeolite. In order to find out the effect of contact time on heavy metal adsorption rate, sample was collected every 30 min within 150 min. The concentration of Cu^{2+} and Zn^{2+} before (C_i) and after (C_f) was measured using Atomic Absorption Spectrometer (Agilent Technologies, Model: 240 AA).

The percentage of removed Cu^{2+} and Zn^{2+} was calculated by using the following equation:

$$\text{Percentage of removal} = \frac{(C_i - C_f)}{C_i} \times 100\% \quad (1)$$

The kinetic of the adsorption process was determined by using PFO (Eq.(2)), PSO (Eq.(3)), Ritchie's equation (Eq.(4)), Boyd's external diffusion equation (Eq.(5)), Weber and Moris (W&M) (Eq.(6)), and Elovich (Eq.(7)). The equations are listed as below:

$$\log(q_e - q_t) = \log q_e - K_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_e and q_t are the amount of adsorbate (solute) adsorbed by the adsorbent (g/mg zeolite) at equilibrium and at time t. K_1 and K_2 are defined as the constant values for PFO and PSO models.

$$q_t = q_\infty - q_\infty(1 + (n-1) \propto t)^{\frac{1}{n-1}} \quad (4)$$

$$q_t = q_\infty(1 - e^{-Rt}) \quad (5)$$

$$q_t = k_{W\&M}\, t^{0.5} \quad (6)$$

$$q_t = \frac{1}{b}\ln(1 + abt) \quad (7)$$

The amount of adsorbate adsorbed on adsorbent at infinity time is labeled as q_∞, while n is known as the number of active sites on the adsorbent occupied by adsorbate in Ritchie's equation. R is the rate constants in Boyd's external diffusion equation while $k_{W\&M}$ is the intraparticle diffusion coefficient. For Elovich model, a is the initial adsorption rate constant while b is the desorption rate constant.

The following statistic parameters were used to evaluate the validity of the kinetic models.

$$R^2 = \frac{\sum (q_{mean} - q_{cal})^2}{\sum (q_{cal} - q_{mean})^2 + \sum (q_{cal} - q_{exp})^2} \quad (8)$$

$$\chi^2 = \frac{\sum (q_{exp} - q_{cal})^2}{q_{cal}^2} \quad (9)$$

$$\text{SSE} = \sum (q_{exp} - q_{cal})^2 \quad (10)$$

$$\text{MSE} = \frac{1}{N_{exp}} \sum (q_{exp} - q_{cal})^2 \quad (11)$$

R^2, Eq.(1), residual sum of square (SSE) and mean square error (MSE) are used.

2 Results and Discussion

2.1 Effect of pH

Fig.1 shows the adsorptive performance of zeolite in Cu^{2+} and Zn^{2+} under varied pH condition. Cu^{2+} removal increased from 30.16% to 82.15% when the pH of the solution increased from pH 3 to pH 7. However, the removal rate remained constant when the pH value increased from 7 to 11. This is because under acidic condition, the presence of free H^+ behaved as the competitor to both Zn^{2+} and Cu^{2+}. This reduces the number of active sites on the zeolite to adsorb Zn^{2+} and Cu^{2+}. This finding is similar to recent findings obtained by Refs. [17 - 18] where the presence of H^+ reduced the amount of Pb^{2+} adsorbed to both natural and Fe (III) modified zeolite alginate beads. Similar adsorptive trend was found in Zn^{2+} solution as shown in Fig.1, where the percentage of removal rate increased from 64.43% at pH 3 to 90.87% at pH 7 and the removal rate remained constant when the pH is further increased to pH 11.

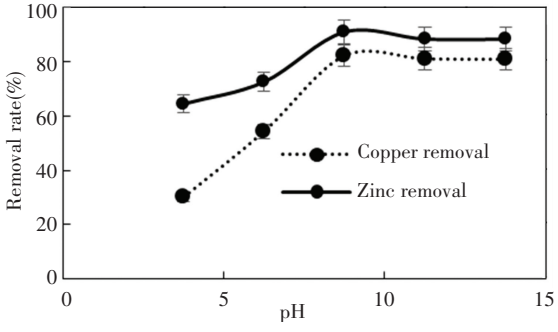

Fig.1 pH effect on the performance of zeolite

Comparatively, adsorptive performance of zeolite towards Zn^{2+} was higher compared with Cu^{2+}, where

the maximum removal rate was ~90% for Zn^{2+} and ~80% for Cu^{2+}. This is due to the effect of hydration enthalpy (ΔH_{hyd}), where $\Delta H_{hyd} = -1955$ kJ/mol for Zn^{2+} and $\Delta H_{hyd} = -2010$ kJ/mol for Cu^{2+}[19-20]. Hydration enthalpy describes the amount of energy required to detach water molecules from cations. In this case, Cu^{2+} needs to release higher amount of energy to detach from water compared with Zn^{2+}, thus its interaction with zeolites is lower compared with Zn^{2+}[21]. As a consequence, the percentage of removal for Cu^{2+} is lower compared with Zn^{2+} under the same pH condition.

2.2 Effect of Contact Time

Fig.2 shows the effect of contact time on Cu^{2+} and Zn^{2+} removal rate. Generally, the removal rate increased from t = 30 min to t = 120 min. Equilibrium point achieved at t = 120 min, where no further increment in terms of removal rate was found after t = 150 min. This is because the number of active sites of zeolites is higher at the beginning of the adsorption process. Rapid adsorption process occurred in the first 30 min, where approximately 60% removal was found for both Cu^{2+} and Zn^{2+}. At t = 60 min, the removal rate reduced, where additional 15% and 10% removal rate was recorded for Cu^{2+} and Zn^{2+}, respectively. This is due to the reduction in the number of active sites, which is available for adsorption. At the saturation point, no active sites are available for either Cu^{2+} or Zn^{2+}. Hence, the constant removal rate, which was 94% for Cu^{2+} and 90% for Zn^{2+}, was found after 120 min.

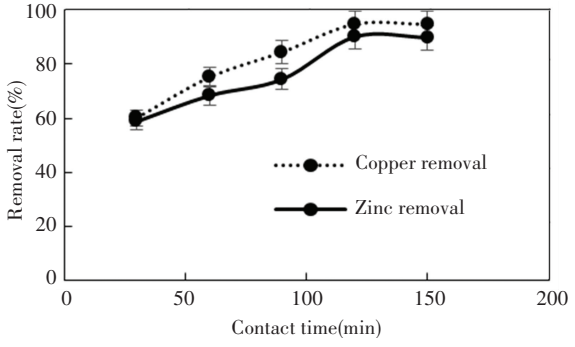

Fig. 2 Effect of contact time on the adsorptive performance of zeolite

q_e of zeolite calculated in this study was 0.36 mg Cu^{2+}mg/g zeolite and 0.376 mg Zn^{2+}mg/g zeolite when 10×10^{-6} Cu^{2+} and Zn^{2+} were used as the feed. Compared with adsorbents listed in Table 1, the adsorptive capacity of the zeolite is very much lower, although the reported removal rate was comparable which is within 90%-94%. Similar to a study done by Wang et al.[22], the adsorption capacity of SiO_2 encapsulated natural zeolite was 12.3 g/mg and 9.0 g/mg for Cu^{2+} and Zn^{2+}. The removal rate of Cu^{2+} and Zn^{2+} were 98% when 10×10^{-6} Cu^{2+} and Zn^{2+} were used as the feed. This suggested that the performance of the zeolite used in this study can be further enhanced by reducing the particle size of zeolite, Fe coating[17], and surfactant modification[23].

Compared with the findings observed in Fig.1, the adsorptive performance of zeolite was higher for Zn^{2+} (~90%) compared with Cu^{2+} (~80%). Without pH adjustment, the effect of hydration radii governs the adsorption process. Hydration radii show the size of ion after it interacts with water molecules. It equals to 4.3 Å and 4.19 Å for Zn^{2+} and Cu^{2+}, respectively[20]. Thus, Cu^{2+} with smaller size compared with Zn^{2+} reached the fine pores in zeolite and higher adsorption rate is achieved.

According to Tuzcu and Atalay[24], the pH of 10×10^{-6} Zn^{2+} solution is 6.3 while the pH for 10×10^{-6} Cu^{2+} is 6. The pH values reduced from 5.7 to 5.5 when the concentration of Cu^{2+} increased from 50×10^{-6} to 100×10^{-6}. Similarly, when the concentration of Zn^{2+} increased from 50×10^{-6} to 100×10^{-6}, the pH decreased from 6 to 5.9. It is reasonable to deduce that as the concentration of Zn^{2+} and Cu^{2+} reduced, the pH of the solution will go towards neutral. During the adsorption process, pH increased as the concentration of Zn^{2+} in solution reduced. This explains similar Zn^{2+} removal rate observed at t = 120 min and at pH 7, which is approximately 90%. Meanwhile, this also suggests that by adjusting the pH of Zn^{2+} solution to minimum pH7, the maximum Zn^{2+} removal rate 90% can be achieved within 60 min. Similar trend was also observed in Cu^{2+} solution, where zeolite adsorbed 82.15% of Cu^{2+} at pH≥7, and without pH adjustment, 75% of Cu^{2+} was removed at t = 60 min. However, this removal rate did not treat the water to the allowable discharge limit in Malaysia, which is 1 mg/L. Thus, the need to increase the contact time from 60 to 120 min was required to achieve 94% of Cu^{2+} removal, as shown in Fig.2. At this point, the allowable discharge limit was met, where the discharge concentration was 0.523 mg/L.

2.3 Kinetic Study

Kinetic study for adsorption process is important

as it provides valuable insights on the reaction pathways as well as the sorption reaction mechanism. It also describes the adsorbate uptake rate, which affects the residence time of adsorbate update at the solid-liquid interface. Fig.3 shows that the amount of adsorbed Cu^{2+} on activated carbon predicted by the 6 kinetic models is very close to the experimental data, except for W&M and Boyd's external diffusion equation. W&M model assumes diffusion of adsorbate is the slowest step while Boyd's external diffusion equation assumes internal diffusion is the rate determining step. Hence, both internal and external diffusion contributed less impact to the overall Cu^{2+} adsorption process, compared with adsorption reaction on the active site in this study.

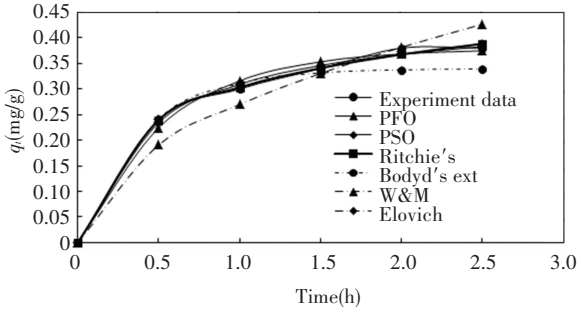

Fig.3 Predicted and experimental amount of Cu^{2+} adsorbed on adsorbent at different time interval

Table 2 presents the constant values of the respective kinetic models. Empirical models such as PFO and PSO are lack of physical meaning[25]. Elovich is commonly used to model chemisorption while Ritchie's equation assumes adsorption is dominated by the reaction at active sites. It is notable that Ritchie's equation and Elovich model predicted the experimental data well with R^2 value of 0.9977. Hence, this is difficult to justify which model fitted the data the best based on the R^2 value alone. Other statistical parameters such as SSE, MSE, and χ^2 are presented in Table 2 to verify the models, and it shows that Ritchie's equation is the best model with the lowest SSE, MSE and χ^2 values. This showed that adsorption at active sites is the rate of determining the steps in this study[25].

Similarly, Zn^{2+} adsorption data was also predicted by using 6 kinetic models, which covers the external diffusion, internal diffusion, and adsorption on active sites. The results in Fig.4 and Table 3 show that Elovich predicted Zn^{2+} adsorption the best with the highest R^2 value of 0.9913 and the lowest SSE (0.000783), χ^2 (0.002473), and MSE (0.000131) values compared with the other models. This indicates that the role of active sites in zeolite played an important role in determining the heavy metals removal rate. This adsorption process can be enhanced by modifying the surface of active site by considering the exchange of metal ion with the functional groups on the surface of adsorbent.

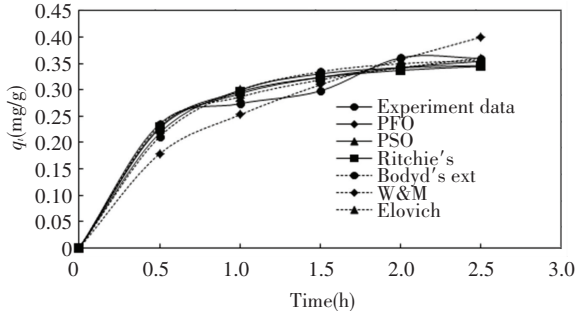

Fig.4 Predicted and experimental amount of Zn^{2+} adsorbed on adsorbent at different time interval

Table 2 Kinetic model constants and validity evaluation or Cu^{2+} adsorption

Kinetic models	Constants	R^2	SSE	χ^2	MSE
PFO	K_1 = 1.7905/h	0.9921	0.000834	0.002828	0.000139
PSO	K_2 = 4.6442 g/(mg · h)	0.9970	0.000304	0.000932	0.000051
Elovich	a = 2.1201 mg/(g · h) b = 10.3433 mg/g	0.9977	0.000238	0.000640	0.000040
Ritchie's equation	α = 0.5751/h n = 32.6348	0.9977	0.000234	0.000632	0.000039
Boyd's external diffusion equation	R = 2.4713/h	0.9606	0.003655	0.010840	0.000609
W & M	$k_{W\&M}$ = 0.2699g · mg/$\sqrt{h}$	0.9555	0.005599	0.021410	0.000933

Table 3 Kinetic model constants and validity evaluation for Zn^{2+} adsorption

Kinetic models	Constants	R^2	SSE	χ^2	MSE
PFO	K_1 = 1.9578/h	0.9749	0.002316	0.007847	0.000386
PSO	K_2 = 5.9565 g/(mg·h)	0.9862	0.001253	0.004091	0.000209
Elovich	a = 2.6320 mg/(g·h) b = 12.21666 mg/g	0.9913	0.000783	0.002473	0.000131
Ritchie's equation	α = 2.4688/h n = 1.3910	0.9806	0.001716	0.005436	0.000286
Boyd's external diffusion equation	R = 1.7624/h	0.9742	0.002496	0.009055	0.000416
W & M	$k_{W\&M}$ = 0.2527 g·mg/$\sqrt{h}$	0.9447	0.006166	0.028202	0.001028

3 Conclusions

Results obtained from this study show that zeolite exhibited promising adsorptive performance for Cu^{2+} and Zn^{2+} in both neutral and alkali conditions. 82.15% Cu^{2+} and 90.87% Zn^{2+} removal rate was found at pH 7. Under the same pH condition, selectivity towards Zn^{2+} is higher compared with Cu^{2+}, which may be due to the effect of hydration enthalpy. Without pH adjustment, selectivity towards Cu^{2+} is higher compared with Zn^{2+} due to smaller hydration radii of Cu^{2+}, which is 0.11 Å smaller than Zn^{2+}. Besides, rapid adsorption was found in the first 30 min of the experiment and saturation point was achieved at 120 min for both Zn^{2+} and Cu^{2+}. Kinetic study showed that adsorption reaction at the active site on zeolite dominated the heavy metal removal process. Hence, the performance of zeolite could be enhanced by modifying the surface properties such as surfactant coating, where the exchange of metal ion with the functional groups on the surface of zeolite is considered.

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