Removal of Copper and Lead from Aqueous Solution by Adsorption onto Cross-Linked Chitosan/Montmorillonite Nanocomposites in the Presence of Hydroxyl–Aluminum Oligomeric Cations: Equilibrium, Kinetic, and Thermodynamic Studies

LIAN DUAN1, NING HU1, TONGQING WANG1, HONG WANG1, LIXIA LING2, YUE SUN1, and XIANMEI XIE1

1School of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan, China
2Research Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan, China

Adsorption removal of Cu (II) and Pb (II) on cross-linked chitosan/Al13-pillared montmorillonite (CCPM) was examined in solutions. The chitosan dosage was drastically reduced in the new nanocomposite, which is made from the treated clay (Al13-pillared montmorillonite). Several important parameters that influenced the adsorption of Cu (II) and Pb (II) ions, such as cross-linked chitosan-to-clay ratio, pH, temperature, initial concentration, dosage, and contact time effect, were systematically investigated. Result showed that in the nanocomposite with cross-linked chitosan-to-clay ratio of 0.45:1, the maximum removal efficiencies of Cu (II) [pH 6.5, dosage 10 g/L, initial Cu (II) concentration 100 mg/L, contact time 2 h, 298 K] and Pb (II) [pH 6.0, dosage 5 g/L, initial Pb (II) concentration 100 mg/L, contact time 2 h, 298 K] were 96.0% and 99.5%, respectively. Kinetic and isotherm studies have indicated that the adsorption process of Cu (II) or Pb (II) nanocomposites was better fitted by the pseudo-second-order equation and the Freundlich equation, with chemical adsorptions as the rate-limiting step. The metal–ion affinity to the functional groups of CCPM followed the order Pb (II) > Cu (II). The thermodynamic parameters ΔH and ΔS values showed that the sorption process of Cu (II) or Pb (II) was spontaneous (ΔG < 0), was endothermic (ΔH > 0), and had decreased entropy (ΔS < 0). HNO3 (0.1 M) could be a good desorbent in the recovery of metal ions after adsorption and regeneration of the adsorbent.

Keywords: Adsorption; Chitosan; Epichlorohydrin; Heavy metals; Hydroxyl–aluminum oligomeric cations; Montmorillonite

Introduction

Heavy metal contamination in wastewater is mainly contributed by anthropogenic sources (Sari et al., 2008; Futalan et al., 2011). Common technologies for the removal of heavy metals include membrane separation, ion exchange, electrodeposition, and chemical precipitation. However, these methods have proven to be costly and inefficient, especially in removing trace amounts of heavy metals (Sari et al., 2008; Popuri et al., 2009). Adsorption technique is one of the most efficient and low-cost methods in cleaning heavy metal pollutants in the environment.

Montmorillonite (MMT) is a 2:1 type aluminosilicate that has a crystalline structure with an alumina octahedral between two tetrahedral layers of silica. Intercalation of the clays via exchange of cations located in their interlayer space with large organic or inorganic cations is an effective modification approach to obtain adsorbents. Hydroxyl–aluminum polycations are most intensively studied on inorganic-pillared MMT. These polycations are used to prepare Al13-pillared MMT and have been well defined because of their chemical composition and structure (Salerno and Mendioroz, 2002).

Chitosan, a polysaccharide composed mainly of poly-β-(1,4)-2-amino-D-glucose, is the deacetylated product of chitin (Wang et al., 2005). It contains reactive hydroxyl (–OH) groups and amino (–NH2) groups that have the potential to bind heavy metals. To avoid the softening and loss of chitosan in acid media, chemical modifications such as cross-linking step are required to reinforce the chemical stability of the biosorbents in acid solutions. Cross-linking reduces the adsorption capacity but enhances the resistance of chitosan against acid, alkali, and chemicals (WanNgah et al., 2005).

MMT is a promising support material because of its mechanical and chemical stabilities, low cost, and availability. Numerous studies have prepared chitosan/MMT...
composites and investigated the adsorption property of dyes or heavy metals (Futalan et al., 2011; Gecol et al., 2005; Wang and Wang, 2007). However, given that long-chain chitosan molecules would not easily intercalate into the clay, the chitosan/MMT nanocomposite in most studies was prepared by coating a thin layer of chitosan onto the MMT surface. This method leads to limited capacity of chitosan and invalids the function of MMT. Tan et al. (2008) introduced hydroxy–aluminum oligomeric cations into the preparation process. The presence of hydroxy–aluminum cation facilitates chitosan intercalation into the MMT and decreases the dosage of chitosan. X-ray diffraction (XRD) shows the intercalation of bilayers of chitosan (the d_{001} value of the clay with two layers of chitosan is about 2.02 nm) (Tan et al., 2008) into the interlayers of MMT and the formation of an intercalated nanostructure.

This study mainly aims to investigate the adsorptive features of the composite depending on the cross-linked chitosan-to-clay ratio, concentrations, initial pH, contact time, and adsorption temperature of Cu (II) and Pb (II). This study aims to determine the removal efficiency and the capacity of the cross-linked chitosan/Al_{13}-pillared montmorillonite (CCPM) in removing Cu (II) and Pb (II) from aqueous solution under static conditions. It also aims to determine the applicable isotherm model, illustrate the suitable kinetic mechanism, and determine the thermodynamic parameters.

**Experimental**

**Reagents**

Sodium montmorillonite (Na-MMT, 95%) was supplied by Zhejiang Sanding Technology Co., Ltd., Hangzhou, China. Chitosan (Aldrich, Shanghai, China) had an 80.0–95.0% degree of deacetylation and an average molecular weight of 9012-76-4. The reagents used in the determination of copper and lead are shown in the supplementary data.

All chemicals used in this study, including epichlorohydrin solution, formaldehyde solution, span-80, liquid paraffin, NaOH, HCl (36–38%), AlCl_3, 6H_2O, CH_3COOH, Cu(NO_3)_2·3H_2O, Pb(NO_3)_2, and Na_2CO_3, were of analytical reagent grade.

**Starting Materials of the Nanocomposite**

The cross-linked chitosan was prepared as previously reported (Yuan et al., 2004). Briefly, 3.0 g chitosan was dissolved in 100 mL of 5% (v/v) aqueous acetic acid solution, and then 100 mL liquid paraffin was poured into the mixed solution. The mixture was stirred for 10 min at room temperature and heated up to 50°C. Four drops of emulsifier (span-80) were added to the mixture and stirred for 1 min. The mixture was heated to 60°C, followed by the addition of 2 mL formaldehyde. The mixture was stirred for 1 h at the same temperature. 1 M NaOH solution was added to adjust the pH to 10.0. Then, 4 mL epichlorohydrin was added into the mixture, and the reacting solution was heated up to 70°C. 1 M NaOH solution was slowly added into the mixture to keep the pH at around 10. The mixture was stirred for 2 h at 70°C, cooled, filtered, and washed with distilled water. The filter cake was extracted with petroleum ether in a Soxhlet extractor to remove the organic solvent. The obtained product was treated with 1 M HCl for 9 h, washed with sodium carbonate solution and deionized water to neutral, and dried in vacuum.

The pillaring solution of hydroxy–aluminum oligomeric cations [aluminum Keggin ions [Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{2/3-}] was prepared by adding 0.4 M NaOH solution to 0.4 M AlCl_3 solution at a rate of 1 mL/min at 60°C under vigorous stirring until the OH⁻/Al³⁺ ratio reached 2.4.

**Preparation of Nanocomposite**

Na-MMT was first added to deionized water to form 5% clay suspension, which was stirred for 2 h at 60°C. The pillaring solution of hydroxy–aluminum oligomeric cations with a ratio of 10 mmol Al/g MMT was added to the clay suspension with stirring at 60°C for 4 h. Then, the cross-linked chitosan beads were added to the resulting clay suspensions. The ratios of glucosamine (MW = 161 g/mol) among the cross-linked chitosan to the cation exchange capacity (CEC) of MMT were approximately 0.20:1, 0.30:1, 0.45:1, 0.60:1, and 1.20:1. The mixture was continuously stirred for 4 h at 60°C. The resulting product was filtered, rinsed with deionized water, and dried at 60°C. The obtained sample is denoted as CCPM.

Al_{13}-pillared MMT was prepared as previously reported (Tan et al., 2008). Pillaring solutions were added to 5% Na-MMT solution with vigorous stirring at 60°C up to a ratio of 10 mmol Al/g MMT. The mixture was aged at 60°C for 48 h under continuous stirring, separated, and washed by centrifugation several times until no chloride was detectable by AgNO_3 test. The product was dried at 50°C. This material was designated Al_{13}-pillared montmorillonite (PM).

**Fourier Transform Infrared Spectroscopy Analysis**

See the supplementary data.

**XRD Analysis**

The resulting nanocomposites were characterized by XRD analysis. A thin layer of composites on the glass slides was examined on a Bruker D8/Advance Diffractometer using Cu Kα radiation (λ = 0.15404 nm) at 45 kV voltage and 30 mA current with a scan speed of 0.13°/s and a 2θ range of 3–35°.

**Adsorption**

Batch adsorption experiments were carried out on a temperature-controlled incubator shaker at 160 rpm. A known amount of CCPM was thoroughly mixed with 20 mL of Cu (II) and Pb (II) solutions, which were diluted from the stock solution. The pH of the reaction mixture was initially adjusted using 1 M HCl or 1 M NaOH. The flasks were shaken at a desired time, and the solid phase was separated by centrifugation. After suitable dilutions,
the supernatant was analyzed for Cu (II) and Pb (II) concentrations using an ultraviolet-visible spectrophotometer at 450 and 472 nm after complexation with diethyldithiocarbamate and dithizone, respectively (see the supplementary data). Adsorption was performed for different intervals (0.3–4 h), initial pH solutions (4.5–9), initial ion concentrations (20–500 mg/L, see the supplementary data), adsorption dosages (2.5–50 g/L), and so on.

The adsorption capacity was calculated according to the following equation:

\[ q = \frac{(c_0 - c_t)V}{m} \]  

(1)

The percent removal was calculated based on the following equation:

\[ R(\%) = \left( \frac{c_0 - c_t}{c_0} \right) \times 100 \]  

(2)

\( q \) is the amount of Cu (II) and Pb (II) adsorbed at time \( t \) or at equilibrium (mg/g), \( c_0 \) is the initial concentration of Cu (II) and Pb (II) solutions (mg/L), \( c_t \) is the liquid-phase Cu (II) and Pb (II) concentrations at time \( t \) or at equilibrium (mg/L), \( m \) is the mass of the adsorbent (g), and \( V \) is the volume of Cu (II) and Pb (II) solutions (L).

Desorption Studies

After the adsorption experiments with 100 mg/L Cu (II) and Pb (II) solutions, the spent adsorbent was collected and gently washed with deionized water to remove any unadsorbed metals. The adsorbent was agitated with 20 mL of 0.01 M Ethylene Diamine Tetraacetic Acid (EDTA) and 0.1 M HNO₃ solutions at 25°C. The amount of desorbed Cu (II) and Pb (II) was determined as previously described.

Results and Discussion

XRD Analysis

The clays were characterized by XRD to investigate the nanocomposite structure. Figure 1 shows the XRD patterns of Na-MMT and Al₁₃-PM and cross-linked CCPM. The XRD pattern of Na-MMT showed a reflection peak at about \( 2\theta = 7.02 \), corresponding to a basal spacing (\( d_{001} \)) of 1.26 nm. The XRD pattern of PM showed a reflection peak at \( 2\theta = 4.69 \). This peak corresponds to a basal spacing of 1.88 nm, which was attributed to the replacement of sodium ions with hydroxyl–aluminum cation. After the incorporation of chitosan and the pillaring solution within MMT, the (001) peak moved to a lower angle from \( 2\theta = 4.69 \) to \( 2\theta = 4.16 \)–4.34, corresponding to a \( d_{001} \) value of 2.12–2.03 nm. The increase in the interlayer distance for each nanocomposite can be calculated from its corresponding \( d_{001} \). Darder et al. (2003) reported that the \( d_{001} \) value reached 2.12 nm, which is comparable to the value of the aforementioned two nanocomposites. Moreover, the dosage of chitosan was sharply reduced in this new nanocomposite. When the ratio of cross-linked chitosan to clay increased to 0.30:1, 0.45:1, and 0.60:1, the \( d_{001} \) value remained approximately the same. The nanocomposite with the cross-linked chitosan-to-clay ratio of 0.45:1 was suitable in the Cu (II) or Pb (II) adsorption system (Figure s2).

Effect of pH on Cu (II) or Pb (II) Adsorption

Figure 2 illustrates the effect of pH during the removal of Pb (II) or Cu (II) ions from aqueous solutions using CCPM as the adsorbent. In the present study, the effect of pH on the adsorption of Pb (II) or Cu (II) on CCPM was investigated in the pH range of 4.5–9.0. Figure 2 shows that the adsorption behavior of Pb (II) or Cu (II) ions was sensitive to pH changes, especially at lower pH values. The low level of Pb...
(II) and Cu (II) at lower pH values could be attributed to the increased concentration of hydronium (H$_3$O$^+$) ions competing for Pb (II)- and Cu (II)-binding sites on CCPM. At high pH, precipitation usually occurred between metal ions and hydroxide ions (Bhattacharyya et al., 2006; Paulino et al., 2007). The amount on CCPM for Cu (II) reached a plateau after pH 6.5. For Pb (II), the decrease in adsorption efficiency at higher pH was attributed to the formation of soluble hydroxylated complexes of metal ions and their competition with the active sites (Erling Du et al., 2011; Maibam Dhanaraj Meitei et al., 2013). Finally, the optimum pH for the adsorption of Pb (II) ions was 6.0.

**Effect of CCPM Dosage on Cu (II) or Pb (II) Adsorption**

The effect of adsorbent dose on the removal efficiency and the adsorption capacity of Cu (II) or Pb (II) were investigated, as shown in Figure 3. The removal efficiency of Cu (II) and Pb (II) was observed to increase rapidly from 66.5% to 98.4% and from 80.4% to 99.5%, with an increase in the dosage of nanocomposite from 2.5 to 25 g/L and from 2.5 to 5 g/L, respectively. This trend suggests that more active sites are available with increase in the adsorbent dose. Furthermore, the figure shows that the removal efficiency of metal ions reached a plateau as the dosage increased. However, the adsorption capacity of the two metal ions decreased with the increase in the adsorbent dose because of the possible aggregation of the adsorbent. This result suggests that the economical adsorbent dose was 5 g/L for Pb (II) and 10 g/L for Cu (II).

**Effect of Initial Concentration on Cu (II) or Pb (II) Adsorption**

The influences of the initial Cu (II) or Pb (II) concentration on the adsorption capacity and removal efficiency of CCPM were investigated at various concentrations. Figure 4 shows that when the initial Cu (II) or Pb (II) concentration
increased from 20.0 to 500.0 mg/L, the adsorption capacity of CCPM increased from 1.99 to 42.9 mg/L for Cu (II) and from 4.00 to 88.8 mg/L for Pb (II). This result indicates that sufficient sites were available on the nanocomposite when the initial Cu (II) or Pb (II) concentration increased to 500.0 mg/L. Meanwhile, the removal efficiency of the two ions by CCPM remained at more than 80%.

**Effect of Contact Time and Temperature on Cu (II) or Pb (II) Adsorption**

The effect of contact time on the percentage of adsorption of Cu (II) or Pb (II) is shown in Figure 5. The same trend was observed for Cu (II) and Pb (II), where the extent of adsorption increased with time (Figure 5). At near equilibrium, the functional groups were abundantly available for binding, and the metal concentration present in the solution was high. At near equilibrium, the functional groups were almost occupied by metals. The adsorption surface was difficult to fill because of the repulsive forces between the metal ions bound on the CCPM and the metal ions still present in the solution. The 19.88 mg Pb (II) exhibited higher capacity to be adsorbed over 9.58 mg Cu (II). At near equilibrium, the extent of adsorption capacities of CCPM for Cu (II) and Pb (II) [Cu: Cu (II) 100 mg/L, Pb (II) 100 mg/L; adsorbent dosage: Cu (II) 10 g/L, Pb (II) 5 g/L; pH: Cu (II) 6.5, Pb (II) 6; contact time: 2 h].

*Fig. 5. Effect of contact time on removal efficiency and adsorption capacity of CCPM for Cu (II) and Pb (II) ions [Cu: Cu (II) 100 mg/L, Pb (II) 100 mg/L; adsorbent dosage: Cu (II) 10 g/L, Pb (II) 5 g/L; pH: Cu (II) 6.5, Pb (II) 6; temperature: 298 K].*

confirm this supposition, kinetic and thermodynamic experiments were carried out.

**Adsorption Kinetics**

To identify the type of adsorption mechanism, kinetic equations, namely, pseudo-first order, pseudo-second order, Elovich kinetic models, and intraparticle diffusion were used. The kinetic rate constants were also determined.

The pseudo-first-order equation takes the following linearized form:

\[
\ln(q_t - q_e) = \ln(q_e) - k_1 t/2.303
\]

where \(k_1\) (h \(^{-1}\)) is the pseudo-first-order kinetic constant and \(q_t\) (mg/g) is the adsorption capacity at time \(t\) (h) (Hameed et al., 2008).

The pseudo-second-order kinetic equation is given by

\[
t/q_t = 1/(k_2 q_e^2) + t/q_e
\]

where \(k_2\) (g/mg/h) is the kinetic constant (Hameed et al., 2008).

The Elovich kinetic equation proposed by Elovich in the 1930s states that the adsorption rate decreases exponentially with the increase in the adsorption capacity of the adsorbent surface (Chien and Clayton, 1980). This model is linearly expressed by the following mathematical equation:

\[
q_t = \ln(x_0 \beta_d) / \beta_d + \ln t / \beta_d
\]

where \(x_0\) [mg/(g \cdot h)] is the initial adsorption rate constant and \(\beta_d\) (g/mg) is the desorption rate constant.

The intraparticle diffusion model is given by the equation

\[
q_t = k_i t^{0.5} + C_i
\]

where \(k_i\) (mg/g/h\(^{0.5}\)) is the intraparticle diffusion rate constant and the intercept \(C_i\) obtained by extrapolation of the
linear portion of the plot of \( q_t \) versus \( t^{0.5} \) back to the axis, is proportional to the extent of the boundary layer thickness (Weber and Morris, 1963).

In Figure 7, the experimental data points of Cu (II) and Pb (II) fitted well with the nonlinear plots generated using the pseudo-second-order equation. Table I indicates the kinetic constants and the correlation coefficient \( R^2 \). The plots for the pseudo-first-order equation had low correlation coefficient value, suggesting that the value was not the rate-limiting step. The pseudo-second-order equation had the highest correlation coefficient \( (R^2 > 0.99) \), suggesting that chemisorption was the rate-controlling mechanism. This result further validates that the pseudo-second-order described the kinetic data. The constants also indicated that a covalent bond was formed through sharing of electrons between the metal ion and the adsorbent (Futalan et al., 2011; Chen et al., 2009). The adsorbed amounts obtained from the compatibility of the pseudo-second-order equation were given in \( q_e \) (calculated). The amounts from the experimental results at equilibrium \( q_e \) (found) are also compared in Table I. The experimental data were nearly consistent with the theoretical values for the pseudo-second-order equation.

The Elovich equation is empirical. Sparks (1987) pointed out that a heterogeneous diffusion process occurs when the experimental data fitted well with the Elovich equation. Figure 7 shows that the Pb (II) adsorption on CCPM at 303 K was much more aligned with the Elovich equation, and the initial adsorption rate \( \alpha \) \( (4.998 \times 10^{11} \text{mg/g h}) \) was very fast. Pb (II) adsorption on highly heterogeneous adsorbents was described and the chemisorptions were confirmed, but no definite mechanism was predicted (Ho et al., 2005).

According to Weber and Morris (1963), if the rate-limiting step is intraparticle diffusion, a plot of solute sorbed against the square root of the contact time should yield a straight line passing through the origin (Poots et al., 1976). However, the intraparticle diffusion plots of Cu (II) and Pb (II) showed dual linearity in the adsorption process, indicating that the two steps are operational (Figure 8). The first and sharper stage can be attributed to the diffusion of metal ions through the solution to the external surface of CCPM. The second stage describes the gradual adsorption and the equilibrium where intraparticle diffusion is rate limiting. The two stages in the plot suggest that the adsorption process occurred by surface adsorption and intraparticle diffusion. Figure 8 shows that the Cu (II) and Pb (II) adsorbed on CCPM exhibited similar behavior by fitting with the intraparticle diffusion model. For Cu (II), the slope of the first stage \( (k_{i1}) \) was much greater than that of the second stage \( (k_{i2}) \), indicating that the external surface adsorption was very fast and the intraparticle diffusion reached the equilibrium early. Compared with Cu (II), the two stages of Pb (II) adsorption were difficult to distinguish. However, the adsorption process was controlled by both surface adsorption and intraparticle diffusion because of the two different slopes of the two stages.

Table I. Kinetic parameters for pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion mechanism of Cu (II) and Pb (II) single-metal systems

| Metal | Pseudo-first order | Pseudo-second order | Elovich | Intraparticle diffusion |
|-------|--------------------|---------------------|---------|-------------------------|
|       | \( R^2 \) \( k_{i1} \) (h^{-1}) | \( q_e \) (mg/g) (calcd) | \( q_e \) (mg/g) (found) | \( R^2 \) | \( \beta_0 \) (g/mg) | \( k_{i1} \) mg/(g·h) | \( k_{i2} \) mg/(g·h^{1/2}) |
| Cu    | 0.991 | 3.880 | 5.275 | 9.520 | 0.999 | 0.513 | 10.166 | 9.520 | 0.940 | 583.169 | 0.733 | 4.447 | 1.340 |
| Pb    | 0.851 | 3.253 | 5.335 | 19.560 | 0.999 | 0.640 | 19.940 | 19.560 | 0.991 | 4.998 \( \times 10^{11} \) | 1.465 | 1.025 | 0.527 |
**Table II.** Thermodynamic constant parameters for Cu (II) and Pb (II) single systems

| Metal | Temperature (K) | \(\Delta G\) (kJ/mol) | \(\Delta H\) (kJ/mol) | \(\Delta S\) (J/mol·K) |
|-------|-----------------|----------------------|----------------------|-----------------------|
| Cu    | 303             | -1.762               | -28.143              | -87.066               |
|       | 313             | -0.891               |                      |                       |
|       | 323             | -0.021               |                      |                       |
| Pb    | 303             | -6.296               | -74.789              | -226.051              |
|       | 313             | -4.035               |                      |                       |
|       | 323             | -1.775               |                      |                       |

**Adsorption Thermodynamics**

The thermodynamic parameters, such as free Gibbs energy (\(\Delta G\)), enthalpy (\(\Delta H\)), and entropy (\(\Delta S\)), are shown in Table II. The constants were computed using the following equations:

\[
K_D = q_e/c_e \quad (7)
\]

\[
\Delta G = \Delta H - T\Delta S \quad (8)
\]

\[
\ln K_D = -\Delta H/(RT) + \Delta S/R \quad (9)
\]

where \(R\) is the universal gas constant (J/mol/K) and \(T\) is the solution temperature (K). At 303, 313, and 323 K, the values of \(\Delta G\) for Cu (II) and Pb (II) were negative, indicating that adsorption was spontaneous. The adsorption capacity of Pb (II) was higher than that of Cu (II) because the more negative the \(\Delta G\) value, the more spontaneous and the more favorable the adsorption. The negative \(\Delta H\) values for Cu (II) and Pb (II) suggest that the adsorption process was exothermic. Therefore, the increase in temperature resulted in a decrease in the metal adsorption capacity and removal efficiency (%), which agrees with the aforementioned temperature control experiment. The negative \(\Delta S\) values suggest that a decrease in randomness exists at the solid–solution interface of Cu (II) and Pb (II) on the CCPM surface.

**Adsorption Isotherm**

Several adsorption isothermal models have been developed to evaluate the equilibrium adsorption of CCPM from aqueous solutions, such as Langmuir, Freundlich, and Temkin equations (Figure 9).

Langmuir adsorption isotherm (Ozacar and Sngil, 2004; Chiang, 2001) was applied in equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites. This isotherm is represented in a nonlinear form as follows:

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (10)
\]

where \(C_e\) is the equilibrium concentration of metal (mg/L) and \(q_e\) is the amount of metal adsorbed (mg) per unit of adsorbent (g). \(q_m\) and \(K_L\) are the Langmuir constants related to adsorption capacity (mg/g) and energy of adsorption (L/g), respectively.

The adsorption data obtained were also fitted to the Freundlich adsorption isotherm (Kamari and WanNgah, 2009). These data can be applied for nonideal sorption on heterogeneous surfaces and multilayer sorption and expressed in a nonlinear form by the following equation:

\[
q_e = K_F C_e^{1/n} \quad (11)
\]

where \(K_F\) and \(1/n\) are the Freundlich adsorption isotherm constants depicting the extent of adsorption and the intensity of metal ions on the adsorbent, respectively.

Temkin isotherm (Zacar, 2003; Allen et al., 2003) has been used in numerous sorption processes. A linear form of the Temkin isotherm can be expressed as

\[
q_e = B \ln AC_e \quad ; \quad B = RT/z \quad (12)
\]

where \(B\) is the Temkin constant, \(z\) is the Temkin constant related to heat of adsorption (J/mol), \(R\) is the gas constant, 8.314 J/(mol·K), \(T\) is the absolute temperature (K), and \(A\) is the Temkin constant related to equilibrium binding energy (L/mg).

Table III shows the calculated Langmuir, Freundlich, and Temkin constants. Cu (II) and Pb (II) showed best fit with Freundlich isotherm. For the Freundlich constants, Pb (II) had higher \(K_F\) values over Cu (II). Moreover, Pb (II) had lower \(1/n\) values, indicating that Pb (II) had higher affinity to the functional groups of CCPM, resulting in a high \(K_F\). The Langmuir isotherm constants \(q_m\) and \(K_L\) followed the order of Pb (II) > Cu (II), which is similar to the fitting result of Freundlich isotherm. This finding indicates the higher affinity to bind to the functional groups, resulting in...
maximum monolayer adsorption capacity over Cu (II) (Futalan et al., 2011).

Moreover, studies have reported that if the equilibrium is described by Temkin empirical equation in adsorption systems, then the adsorption kinetics is expressed well by the Elovich model (Skodras et al., 2008; Banat et al., 2007). Pb (II) had better correlation coefficient value than Cu (II) for Temkin (Table III); therefore, the fitting result of Pb (II) should coincide more with the Elovich model. The Elovich model fitting of Pb (II) (0.991) confirmed this result, as shown in Table II.

**Desorption Studies**

Percentage desorption (Equation (14)) of Cu (II) and Pb (II) from the sorbent is shown in Table IV.

\[
\text{Desorption ratio} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100
\]

(13)

Table IV shows the percentage of Cu (II) and Pb (II) released after treatment with EDTA and HNO₃ desorbents. Both EDTA and HNO₃ were good desorbing agents, but HNO₃ was a little more efficient and less expensive than EDTA. Therefore, HNO₃ can be used as an excellent desorbent in washing treatment.

**Conclusion**

In this study, CCPM was prepared as a new adsorbent to remove Cu (II) or Pb (II) ions from aqueous solution. The prepared nanocomposites were characterized by XRD to assess the structure. Adsorption study showed that the new nanocomposite could be effectively used to remove Cu (II) or Pb (II) at cross-linked chitosan-to-clay ratio of 0.45:1. The results showed that the changes in the variables affected the adsorption process and changed the values of the amounts of ions adsorbed. To obtain the highest removal efficiency of Cu (II) ions in aqueous solution, pH 6.5, adsorbent dosage of 10 g/L, metal ion initial concentration of 100 mg/L, and contact time of 2 h at 298 K were the optimum conditions. The optimum conditions for Pb (II) were pH 6.0, dosage of 5 g/L, initial concentration of 100 mg/L, and contact time of 2 h at 298 K. The adsorption kinetics and isotherms showed that the adsorption process of the nanocomposites for Cu (II) and Pb (II) were both better fitted by the pseudo-second-order equation and the Freundlich equation, respectively. Thermodynamic results indicated that the adsorption was a spontaneous and exothermic process. Desorption experiment showed that 0.1 M HNO₃ is a satisfactory desorbent.

**Supplementary Information**

Supplemental data for this article can be accessed on the publisher’s website.

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