



A Series of Nanocomposites of Chitosan/Rectorite: Preparation, Characterization and Application for Adsorption of Cu(II), Pb(II) and Cd(II)

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In this study, a series of nanocomposites of rectorite/chitosan (REC/CS) was prepared *via* controlling different mass ratios of chitosan to rectorite using the water phase intercalation technique. The structure of the nanocomposites was characterized. The adsorption properties of the nanocomposite toward Cu(II), Pb(II) and Cd(II) were investigated. The results showed that when rectorite:chitosan (w/w) was 3:1, the adsorption capacities was best. Besides, the variable affected factors on adsorption capacities such as pH of the solution, adsorption time, initial metal concentration were also investigated. The results demonstrated that the maximum adsorption occurred at pH 6, the adsorption time is 0.5 h and the concentration of the metal solution was 20 mg/L. By analyzing the experimental data, intra-particle diffusion was found to take part in the adsorption process, the adsorption isotherm correlated with Langmuir adsorption model.

Key Words: Nanocomposite adsorbent, Heavy metal ions, Adsorption, Equilibrium isotherm.

INTRODUCTION

With the rapid increase in global industrial activities, more and more water resources are contaminated to some extent by heavy metal ions. This kind of contamination has arose great concern because of the toxic effects on human beings, other animals and plants in the environment¹. Owing to these adverse effects, a number of techniques such as filtration, reverse osmosis, chemical precipitation, ion exchange and electro-deposition have been used to remove the toxic metals from aquatic environment². However, these methods are not widely used due to their high cost and low feasibility for small-scale industries³. In contrast, the adsorption technique is one of the preferred methods in removal of heavy metals for its efficiency and low cost. Therefore, searching for cost effective materials for treatment of heavy metal ions from wastewater are of great significance.

Chitosan is a high molecular weight polysaccharide mainly composed of β -(1,4)-linked 2-deoxy-2-amino-D-glucopyranose units and partially of β -(1,4)-linked 2-deoxy-2-acetamido-D-glucopyranose. It has the properties of biocompatibility, biodegradability, non-antigenicity, *etc.* so chitosan has been used in many fields⁴. For example, due to its properties of high mechanical strength, hydrophilic character,

good adhesion and non-toxicity, chitosan is usually applied as food additive, supporting material for chromatography and chelating polymer for removal of heavy metals⁵⁻⁸. The cationic biopolymer chitosan can be intercalated in Ca²⁺-rectorite through cationic exchange and hydrogen bonding processes, the resulting nanocomposites show interesting structural and functional properties. Polymer/clay nanocomposites are of great interest because they combine the structure of physical and chemical properties of both inorganic and organic materials. Compared to the pure polymers, these nanocomposites demonstrate excellent properties, such as improved storage modulus⁹, decreased thermal expansion coefficients¹⁰, reduced gas permeability¹¹ and enhanced ionic conductivity².

Rectorite (REC) widely exists all over the world, especially in China. It is a kind of layered silicate. The structure and characteristics are much similar to those of montmorillonite. It is referred as an interstratified clay mineral made of regular 1:1 stacking of dioctahedral mica-like layer (non-expandible) and dioctahedral montmorillonite-like layer (expandible). Na⁺, K⁺ and Ca²⁺ contained in the interlayer region between 2:1 mica-like layers and 2:1 smectite-like layers, while the exchangeable hydrated cations reside in the latter. The structure of rectorite can also cleave easily between smectite-like interlayers, forming monolithic rectorite layers

of 2 nm thick. The interlayer cations can be exchanged easily by either organic or inorganic cations and therefore rectorite has a property of water swelling similar to that of montmorillonite, which makes it possible to prepare chitosan/rectorite nanocomposites by solution-mixing processing technique¹³. In this study an attempt has been made to intercalate chitosan into the interlayers of the silicate, meanwhile, exhibiting this technique to develop new organic-inorganic hybrid materials provided with properties that are inherent to both types of components is also the purpose¹⁴.

In the study, new clay/polymer nanocomposites were prepared and characterized. It has been investigated that nanocomposite have been used to remove Pb(II), Cu(II) and Cd(II) from wastewater. A series of experiments were performed in order to characterize heavy metals adsorption equilibrium of nanocomposite. Two different kinds of kinetic models (Lagergren-first-order and second-order equations) were chosen to figure out which of these mechanisms predominates in heavy metals adsorption by nanocomposites. The experimental data was also compared with Langmuir and Freundlich isotherms and found to be in agreement with them. This information will be meaningful for further application of the treatment system¹⁵.

EXPERIMENTAL

Chitosan (CS) was obtained from Golden-shell Biochemical Co. Ltd., China (Zhejiang, China). Its degree of deacetylation were determined as 92 % and its average molecular weight was 2.1×10^5 (determined by GPC method)¹⁶. Rectorite (REC) refined from the clay minerals was provided by Hubei Mingliu Inc. Co. (Wuhan, China). All of the used chemical reagents in experiment were analytical grade and solutions were prepared with ultrapure water. The stock solutions of Pb(II), Cd(II) and Cu(II) (1000 mg/L) were prepared from analytical grade $\text{Pb}(\text{NO}_3)_2$ ($\geq 99.99\%$), CuCl_2 ($\geq 99.99\%$), CdCl_2 ($\geq 99.99\%$) using ultrapure water and serially diluted to working solutions of varying initial concentrations for experimental purpose. 1 mol/L NaOH and HCl were used to adjust the pH of the solutions.

Preparation of chitosan-rectorite nanocomposites: The 2 % (w/v) solutions were prepared by dissolving an exact amount of chitosan in 1 % (v/v) acetic acid and stirring⁴ for about 4 h. The resulting solution was added slowly into the pretreated rectorite suspensions under stirring at 50 °C to obtain nanocomposites with initial rectorite/chitosan molar ratios of 1:1, 2:1, 3:1, 4:1, 5:1, the resulting mixture was agitated for 1 day, then precipitated with 1 mol/L NaOH and adjust the solution to be neutral. The formed composites which were washed with distilled water appear starchy. Then the starchy composites were fully soaked and put into oven, the nanocomposites were dried in oven at 50 °C, finally the dried nanocomposites appear in lumps and were ground into powder¹⁶.

Composites sorbent characterizations

Fourier transform infrared (FTIR): FTIR spectra of nanocomposites before and after adsorption of metal ions are recorded in the frequency range of 4000-400 cm^{-1} on a Bomen FTIR, MB-series using a Nicolet-5700, Thermo-Nicolet Fourier transform infrared spectrophotometer.

X-Ray diffraction: The X-ray diffraction analyses were performed using a diffractometer type D/max-rA (X-650, HITACHI, Japan) with Cu target and K_α radiation ($\lambda = 0.154$ nm) at 40 kV and 50 mA. The scanning rate was 1°/min and the scanning scope of 2θ was 0.7-10° at room temperature.

Scanning electron microscope: The morphologies of the rectorite, nanocomposite (REC/chitosan = 3:1) were examined using a Hitachi XA-650 scanning electron microscope (SEM; Hitachi, Osaka, Japan). Samples were cryo-fractured from liquid nitrogen and for morphological studies lms of samples were mounted on metal grids, using double-sided adhesive tape and coated with gold under vacuum.

Transmission electron microscopy studies: Ultrathin films for transmission electron microscopy were prepared by cutting from the epoxy block with the embedded nanocomposite sheet at room temperature using an LKB-8800 ultratome. The TEM micrographs were taken using a transmittance electron microscope [JEM-2010 FEF (UHR), JEOL, Japan] at an accelerating voltage of 200 kV.

Adsorption experiments: A volume of 200 mL heavy metal solution was put into a 250 mL bottle to start the experiments. The initial metal ion concentration used in the tests varies from 20 to 100 mg/L and then 0.3 g chitosan/rectorite nanocomposite was added to the solution. High pH can cause precipitation of some metals and low pH can cause few or no adsorption. So, in order to achieve high adsorption amount and free of precipitation effect, 1 M NaOH or 1 M HCl was used to adjust the suspension to $\text{pH } 6.0 \pm 0.2$. The solution was measured using a pH meter (Wuxi, China, METTLER TOLEDO-320). Samples were agitated with a speed of 200 rpm at 25 °C. At present time intervals of the experiments, the aqueous samples were taken and then filtered. Heavy metals concentration of the filtrates was analyzed using a Voltammetric Computrace (Metrohm 797, Switzerland). Adsorption of metal on glassware was found to be negligible and determined by running blank experiments. Experimental values of metal uptake capacities were the results of triplicate experiments reported as means. The amount adsorbed per unit mass of adsorbent at equilibrium Q_e (mg g^{-1}) was obtained using the eqn. 1

$$Q_e = \left(\frac{C_o - C_e}{m} \right) v \quad (1)$$

where C_o and C_e denote the initial and equilibrium metal ion concentrations (mg/L), respectively. 'v' was the volume of the solution in liters and 'm' was the mass of the adsorbent used (g).

Voltammetric determination of copper, cadmium, lead in water samples: Taking 1 mL liquid and 10 mL potassium chloride-sodium acetate buffer solution ($c(\text{KCl}) = 1.5$ mol/L, $c(\text{CH}_3\text{COONa}) = 0.5$ mol/L) to be measured, then using the standard addition method to record ion-dissolution curve and measure the amount of metal ions in aqueous solution. To obtain accurate results, the dissolution curve must be recorded in the same current range, but the difference between the peak value measured after adding the standard solution and that of ions should be as large as possible. Finally, calculate the ion concentration in liquid according to the peak value.

RESULTS AND DISCUSSION

Fourier transform infrared (FTIR) studies: The IR spectra of rectorite, chitosan, nanocomposite (rectorite/chitosan = 3:1) and the nanocomposite after adsorbing of Cu(II), Pb(II), Cd(II) ion for 0.5 h are shown in Fig. 1. Na-rectorite showed the basic characteristics peaks at 3640 cm^{-1} (water stretching vibrations), $1640\text{--}1630\text{ cm}^{-1}$ (there were the bands of flexing vibrations of free water at the edge of clay and in clay holes), 1020 cm^{-1} (Si-O stretching vibrations) and 486 cm^{-1} (Si-O-Al flexing vibration)¹⁷. Chitosan showed the basic characteristics peaks at 3430 cm^{-1} (O-H stretch), 2877 cm^{-1} (C-H stretch), 1154 cm^{-1} (bridge-O-stretching) and 1093 cm^{-1} (C-O stretching). Characteristic peaks of amine (N-H) vibration deformation appeared at 1595 cm^{-1} (N-H bending) for chitosan¹⁸. In the spectra of the nanocomposites (Fig. 1a), -NH deformation vibration peak appeared at 1566 cm^{-1} , -CO stretching vibration peak at 1420 cm^{-1} and the N-H bonded to O-H vibration band at 3448 cm^{-1} came from chitosan. Water stretching vibrations at 3646 cm^{-1} and Si-O stretching vibrations at 1020 cm^{-1} obtained from rectorite¹⁹. Characteristic peaks of chitosan and rectorites existed simultaneously. The appearance of all these peaks demonstrated that nanocomposites rectorite/chitosan (3:1) had been successfully prepared. And in the spectra of the nanocomposites after adsorbing of Cu(II), Pb(II), Cd(II) ion (Fig. 1b) for 0.5 h, characteristic peaks of amine (N-H) vibration deformation disappeared at 1595 cm^{-1} (N-H bending) for chitosan, indicating that the functional groups were not disturbed during the intercalation process and were available for interaction with the metal ions.

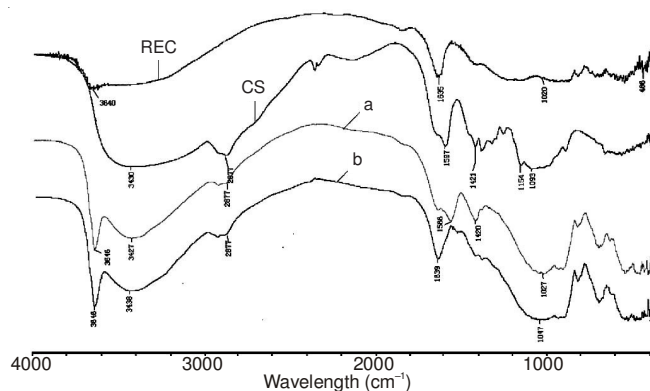


Fig. 1. (Fourier transform infrared) FT-IR spectra of rectorite, rectorite/chitosan = 3:1(c) and (d) after the adsorption of nanocomposites material on Cu(II), Pb(II) and Cd(II) ion

X-Ray diffraction studies: XRD patterns of rectorite and nanocomposites with different rectorite/chitosan ratios of 5:1; 4:1; 3:1; 2:1; 1:1 collected from $0.7\text{--}10^\circ$ (2θ) are shown in Fig. 2(a-f). It can be observed that unmodified rectorite exhibits $2\theta = 3.59^\circ$ and the Δd_L value (the interlayer distance) is 2.45 nm calculated by the Bragg's equation²⁰. In comparison with rectorite, the diffraction peaks of rectorite is shifted to the small-angle after being intercalated by chitosan, the results indicate that an intercalated nano-structure of rectorite/chitosan composites is formed. It can also be observed from the Fig. 2 that the layer spacing of the composite materials rectorite and the content of the chitosan are not proportional, when the ratio

of amount of rectorite and chitosan is 5:1, the layer spacing has little change compared to rectorite merely, but when the ratio is 3:1, the layer spacing achieves to the maximum value of 2.78 nm . Then with the increase of amount of chitosan, the layer spacing is no longer increased, but even tends to decrease, the possible reason is when the content of chitosan is inadequate, the driving force is not enough to carry out the intercalation into the rectorite. On the contrary, if the content of the chitosan is too much, chitosan molecular structure would be twisted together and wrapped rectorites, resulting in a larger structure, making it difficult to enter the narrow layer of rectorites, which make good effects can't be achieved. The interlayer distance and the 2θ value of adsorbents with different proportions are shown in Table-1.

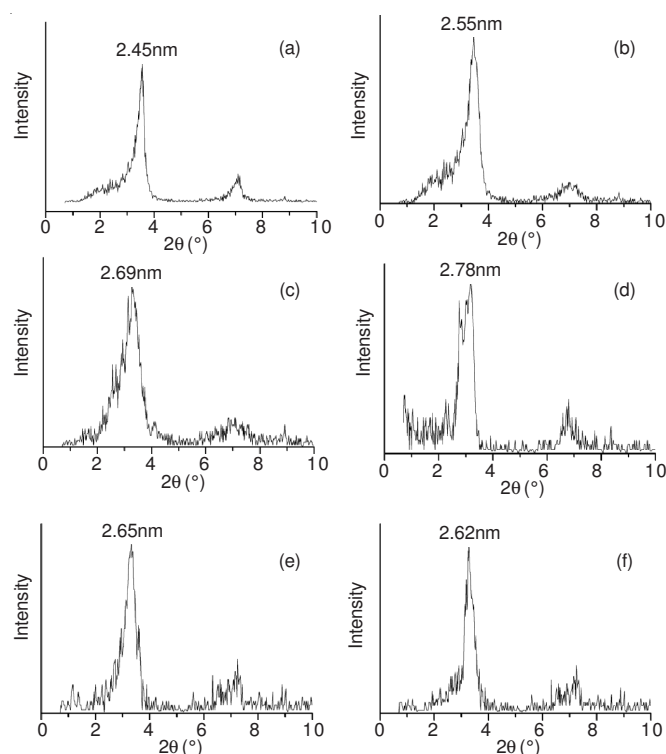


Fig. 2. X-Ray diffraction (XRD) patterns of (a) rectorite and XRD pattern of nanocomposites with different rectorite/chitosan ratios of (b) 5:1; (c) 4:1; (d) 3:1; (e) 2:1; (f) 1:1

Sample	2θ value ($^\circ$)	Interlayer distance (nm)
REC	3.59	2.45
REC:CS = 1:1	3.53	2.62
REC:CS = 2:1	3.52	2.65
REC:CS = 3:1	3.48	2.78
REC:CS = 4:1	3.51	2.69
REC:CS = 5:1	3.56	2.55

Scanning electron microscope: The SEM micrographs of rectorite, nanocomposite and the surface of the nanocomposite after adsorbing of Cu(II), Pb(II), Cd(II) ion for 0.5 h are shown in Fig. 3. The SEM of rectorite (Fig. 3a) suggests the surface is smooth, but it appears porous. The SEM of nanocomposite (rectorite/chitosan) (Fig. 3b), the chitosan molecule was partly inserted into the rectorite layer spacing,

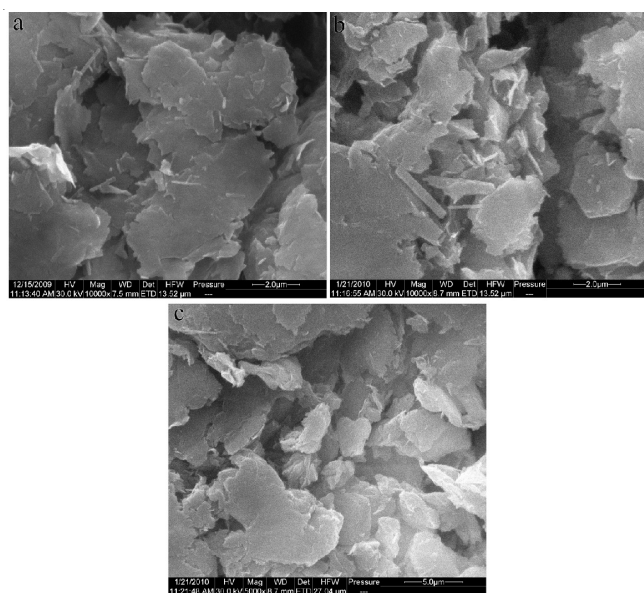


Fig. 3. Scanning electron microscopy (SEM) images of rectorite (a), nanocomposite (rectorite/chitosan = 3:1) (b) and (c) nanocomposite after adsorbing 0.5 h to Cu(II), Pb(II), Cd(II) ion

but the other part was largely carried on the surface of rectorite. Therefore, the surface of the nanocomposite is microporous and have many active groups, while it can be seen from the SEM of the micrographs (Fig. 3c), the surface is rude.

Transmission electron microscopy studies: The TEM micrographs of rectorite/chitosan nanocomposites (3:1) are shown in Fig. 4. It can be seen that the rectorites structure appears flaky and have many gaps between layers. The chitosan macromolecules distributed in these gaps. The composite is amplified by different times. The composites' particle appears a size with diameter of no more than a hundred nanometer, so it can be concluded that the prepared rectorite/chitosan composite was nanocomposite material. The result was consistent with water solution interaction technique, which directly embeds the polymer into the inorganic layer and remove the solution by using appropriate solvent to dissolve polymer and clay, then mixed and stirred to obtain nanocomposites²¹.

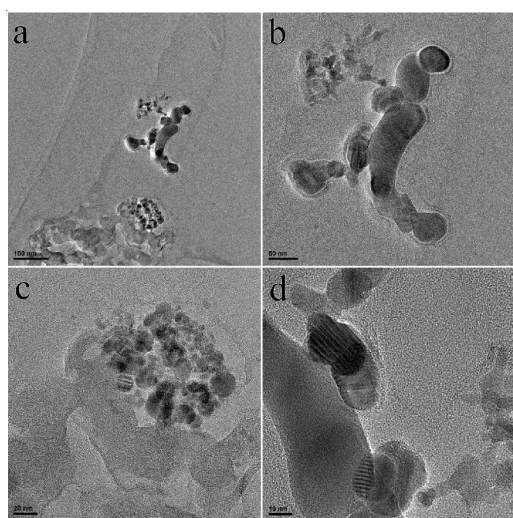


Fig. 4. Transmission electron microscopy (TEM) images of nanocomposites (rectorite/chitosan = 3:1) amplified by different times (a: 20 Kb; b: 40 Kb; c: 100K; d: 200 K)

Impact of different ratios on the adsorption: As the ratio of rectorite and chitosan is different, the resulting material structure also tends to be different, which was shown in XRD analysis. Similarly, the adsorption capacity on heavy metal ions is different when the ratio varies. The adsorption capacity on heavy metal ions of adsorbents with different proportions is shown in Table-2.

TABLE-2
ADSORPTION CAPACITY ON HEAVY METAL IONS OF
ADSORBENTS WITH DIFFERENT PROPORTIONS

Adsorbent	Adsorption capacities (mg/g)			
	Cu	Pb	Cd	
REC/CS (m/m)	1:1	10.06	11.574	9.814
	2:1	11.00	12.466	10.694
	3:1	12.04	13.16	11.80
	4:1	11.146	12.054	10.854
	5:1	10.186	11.374	9.746

It can be seen that the varied ratios of nanocomposite adsorbent result in the difference of adsorption capacity on heavy metal ions. When the ratio is 3:1 (rectorite/chitosan), the adsorption of Cu(II), Pb(II) and Cd(II) achieves its highest capacity of 12.04, 13.16 and 11.80 mg/g, respectively. The results consist with the XRD characterization. Unless otherwise specified, the adsorption experiment was performed in the optimum ratio of 3:1 (rectorite/chitosan).

Effect of pH values: One of the most important factors governing the uptake of metal ions is pH solution, which directly affect the metal adsorption sites on adsorbent surface and the chemical form of metal ions²². The hydrogen ions in solution can affect the capability of metal ions through protonation of active amino groups in chitosan. The effect of pH on rectorite/chitosan adsorption properties is determined by the presence and solubility of chitosan as well as the exchange amount between hydrogen ions and the metal ion in rectorites. When the solution turns alkaline, the precipitation of metal ions in the solution makes the concentration decrease, so the pH was studied in range 2 to 7. The effect of various pH on adsorption of Pb²⁺, Cu²⁺, Cd²⁺ by rectorite/chitosan is shown in Fig. 5. At pH 2-6 the adsorption capacities increases remarkably with increase in pH. The adsorption capacity is found to be low at lower pH value because of the dissolution of chitosan beads due to the protonation of the amino groups in the lower pH region. This reduces the number of binding sites available for the adsorption of metal ions. Moreover, the protonation of amino groups induced an electrostatic repulsion²³ of Pb²⁺, Cu²⁺, Cd²⁺. The maximum adsorption capacity of Pb²⁺, Cu²⁺, Cd²⁺ occurred at pH 6. This can be explained that the significantly increase of negative charge density on adsorption surface offers more metal adsorption sites. With the pH values in range from 6 to 7, the adsorption capacity of metal ions displayed a downward trend. It can be explained that metal hydroxide precipitates formed by OH⁻ combined with metal ions hindered the adsorption of rectorite/chitosan to Pb²⁺, Cu²⁺, Cd²⁺, leading to the decrease of adsorption capacity. Thus, pH 6 was selected as the optimum pH value of solution. The adsorption of Pb²⁺, Cu²⁺, Cd²⁺ from aqueous solution exhibits competitive for available adsorption surface site. Pb²⁺ has highest removal efficiency than Cu²⁺, Cd²⁺ at the same pH.

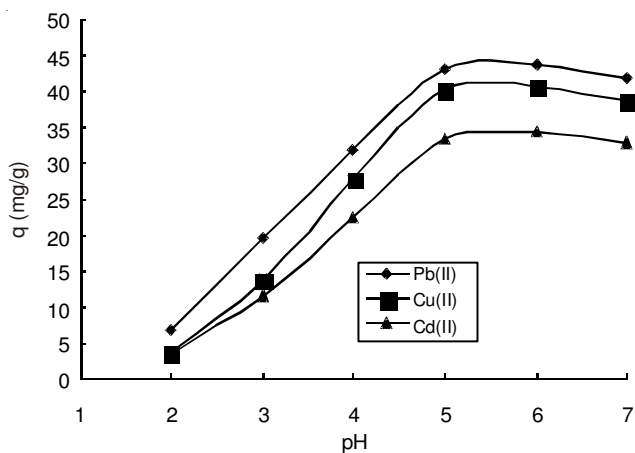


Fig. 5. Effect of pH on adsorption of Cu^{2+} , Pb^{2+} and Cd^{2+} by rectorite/chitosan (rectorite/chitosan = 3:1). (initial concentration: 100 mg/L rectorite/chitosan 1.5 g/L vibration time 30 min temperature at 25 °C)

Effects of adsorption time: Fig. 6 shows the time profiles of the adsorption of different heavy metals on nanocomposite. In the beginning period of the experiment, the adsorption of Cd(II), Cu(II) and Pb(II) showed a trend of rapid decreasing, then for ca. 0.5 h reaction time, the adsorption of Cu(II), Pb(II) and Cd(II) gradually achieved the equilibrium. The adsorption kinetics were described by pseudo-second order equation models and first-order rate equation models.

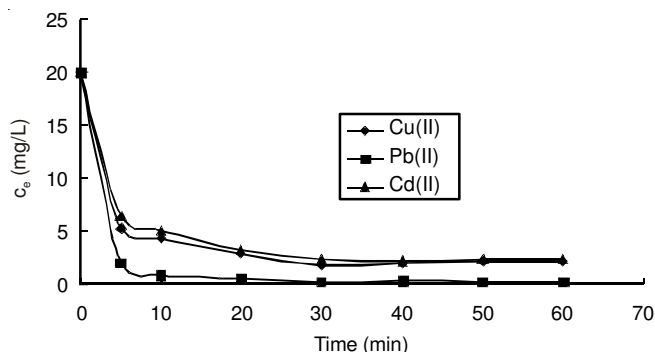


Fig. 6. Kinetic curves for the adsorption of Cu(II), Pb(II) and Cd(II) by nanocomposite (rectorite/chitosan = 3:1)

First-order kinetic: The linearized form of the first-order rate equation by Lagergren and Svenska²⁴ is given as eqn. 2

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303t} \right) \quad (2)$$

where q_t is the amount of adsorption time t (min) (mg/g); k_1 is the rate constant of the equation (min^{-1}); q_e is the amount of adsorption equilibrium (mg/g). In fact, it is required that calculated equilibrium adsorption capacity values q_e (theor.) should be in accordance with the experimental q_e (exp.) values²⁵. Experimental and theoretically calculated q_e values

and coefficients related to Lagergren's plots are shown in Table-3. Except R^2 of Cu(II) adsorption on composite sorbent is 0.9507, others are all lower than 0.95. But the calculated amount of adsorption equilibrium ($q_{e,c}$) is far from the actual amount of adsorption equilibrium (q_e). So, the Lagergren first-order equation is not suitable for heavy metals adsorption on nanocomposite²⁶.

Pseudo-second-order kinetic: Experimental results were also applied to the pseudo-second order kinetic model which is in the form of eqn. 3

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \quad (3)$$

where k_2 is the rate constant of the second-order equation ($\text{g mg}^{-1} \text{min}^{-1}$); q_t is the amount of adsorption time t (min); q_e is the amount of adsorption equilibrium (mg g^{-1}). The amount of adsorption equilibrium q_e , the rate constant of the equation (min^{-1}) k_2 , the calculated amount of adsorption equilibrium $q_{e,c}$ and the coefficient of determination R^2 are shown in Table-3. It is clear from these results that the rate law for a pseudo second-order kinetic model best described the experimental data with the correlation coefficients (R^2) of being over 0.9997. Successful fitting of the data with the second-order kinetic model suggests that the second-order equation is the better-fitting model than Lagergren-first-order equation because it has much higher R^2 .

Effect of initial metal concentration: To achieve a good adsorption capacity of the initial impact, the preparation of 20-100 mg/L solutions of different concentrations of 200 mL, composite adsorbent dosage of 1.5 g/L, the best pH value of 6.0 under the condition of Cd(II), Cu(II) and Pb(II) mL for adsorption experiments is indispensable. Fig. 7 showed that the adsorption capacities increase with the increase of the initial concentrations and reach a plateau which represent the maximum adsorption capacity of composite adsorbent. The increase in loading capacity of the nanocomposite with relation to the metal ions concentration can be explained with the high driving force for mass transfer. In fact, the more concentrated the solution is, the better the adsorption is.

The adsorption isotherm is based on the assumptions that every adsorption site is equivalent and that the ability of a particle to bind is independent of whether adjacent sites are occupied²⁵. The results of adsorption studies of tertiary mixture of Cu(II), Cd(II), Pb(II) at different concentrations ranging from 20 to 100 mg/L on a fixed amount of adsorbent are expressed by the following two widely used isotherms²⁶.

Langmuir adsorption isotherms: Langmuir isotherm models the monolayer coverage of the adsorption surface. This model assumes that adsorption takes place at certain homogeneous adsorption sites and as the distance from the surface of adsorbent increases, the intermolecular forces rapidly decrease.

TABLE-3
LAGERGREN-FIRST-ORDER, PSEUDO-SECOND-ORDER RATE PARAMETERS FOR
Cu(II), Pb(II) AND Cd(II) ADSORPTION BY NANOCOMPOSITE (REC/CS = 3:1)

Metal	First-order equation			Second-order rate parameters			
	K_1 ($\text{g mg}^{-1} \text{min}^{-1}$)	$q_{e, \text{calc}}$ (mg/g)	$q_{e, \text{exp}}$ (mg/g)	R^2	K_2	$q_{e, \text{calc}}$ (mg/g)	R^2
Cu^{2+}	0.0799	3.443	12.04	0.9507	1.521×10^{-2}	60.606	0.9997
Pb^{2+}	0.1076	1.689	13.16	0.9412	6.601×10^{-2}	65.789	1
Cd^{2+}	0.1407	7.62	11.8	0.9429	1.08×10^{-2}	60.241	0.9997

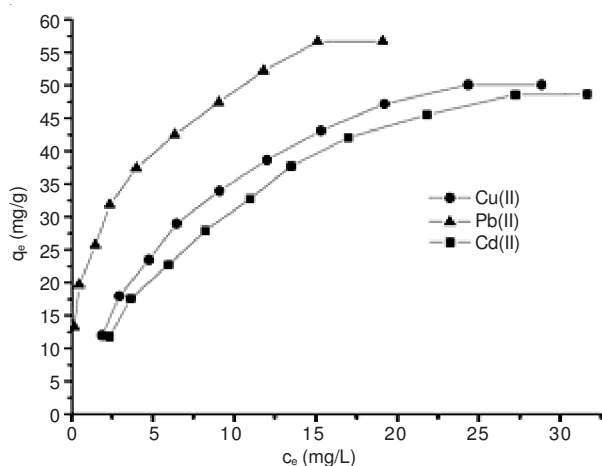


Fig. 7. Equilibrium adsorption isotherms on Cu(II), Cd(II) and Pb(II) adsorption by nanocomposites at different initial concentration (rectorite/chitosan = 3:1)

The Langmuir adsorption model further based on assumption that all adsorption sites are energetically identical and the adsorption occurs on the adsorbent which is structurally homogeneous. Linearized form of the Langmuir equation based on those assumptions is given as eqn. 4²³.

$$\frac{c_e}{q_e} = \frac{1}{Q^0 b} + \frac{c_e}{Q^0} \quad (4)$$

In above equation, q_e is the amount of metal ions adsorbed per unit mass of the adsorbent (mg g^{-1}), C_e is the equilibrium solution concentration (mg L^{-1}), Q^0 and b are the Langmuir equilibrium coefficients. The plots of c_e/q_e versus c_e give a straight line and the values of Q^0 and b can be calculated from the intercept and slope of the plots, respectively. For linear regression analysis, we use the Langmuir isotherm to deal with the adsorption isotherm results of Cu(II), Pb(II) and Cd(II). Langmuir constants and correlation coefficients (R^2) are given in Table-4. From the describing results, the adsorption of nanocomposite adsorbent on Cu(II), Pb(II) and Cd(II) fits Langmuir adsorption isotherm. After describing with Langmuir equation, the maximum adsorption capacity Q^0 is 41.32, 50.76 and 32.47 mg/g , respectively. The results were in agreement with Futalan *et al.*²⁷ and Apiratikul *et al.*²⁸. The experiments results of the Langmuir isotherm models provide further support that rectorite/chitosan nanocomposite has good selective adsorption of Pb(II).

Freundlich adsorption isotherm: The Freundlich adsorption isotherm²³ has been interpreted as sorption to heterogeneous surfaces or surface supporting sites of different affinities. Freundlich assumption is that stronger binding sites are first occupied and as such, binding strength decreases with increasing degree of site occupation²⁹. The Freundlich model is formulated as eqn. 5:

$$\log q_e = \log K_F + \frac{1}{n} \log c_e \quad (5)$$

where K_F and n were Freundlich constants, which affect the adsorption process, such as adsorption capacity and intensity of adsorption, respectively. The values of these constants, obtained by least square fitting of the data on $\log q_e$ and $\log C_e$. Experimental data obtained from the effect of initial concentrations to the adsorption of heavy metals on nanocomposites were also evaluated by applying this equation and the related constants are given in Table-4. The correlation coefficients showed that the Freundlich model fitted the results better than the Langmuir model. Especially, when a change in the mechanism of adsorption with concentration was considered, the Freundlich model fitted the data significantly better. The monolayer adsorption capacity (Q^0), as calculated from non-linear Langmuir isotherms, for Pb(II) was found to be relatively higher in comparison to Cu(II) and Cd(II)³⁰. Nanocomposites adsorbents' adsorption on heavy metal ions coincides with Langmuir and Freundlich model simultaneously. Therefore, both physical and chemical adsorption took place on the surface of adsorbents, the adsorption showed a complicated process of the combination of monolayer adsorption and multi-layer adsorption.

Comparison on the adsorption of different adsorbents on heavy metal ions: Preparing 200 mL mixed solution containing Cu(II), Pb(II) and Cd(II), respectively at a concentration of 20 mg/L into conical flasks, then add to 0.3 g of nanocomposites adsorbent, rectorite and chitosan. Measure the adsorption amount of different adsorbents on Cu(II), Pb(II) and Cd(II) at pH 6 and adsorption time is 0.5 h. The result is shown in Table-5. It can be seen that the adsorption amount of nanocomposites adsorbent on Cu(II), Pb(II) and Cd(II) is much greater than that of rectorite and chitosan, which can be explained as follows: First, nanocomposites adsorbent has the adsorption property of both rectorite and chitosan, so its adsorption capacity is larger than any of them separately. Second, the active group of chitosan molecule attached to the surface of rectorite can be chelated with Cu(II), Pb(II) and Cd(II) more effectively, which accelerates the process of adsorption equilibrium. Third, chitosan molecule is intercalated into the interlayers of rectorite, which increased the distance between layers of rectorite, therefore improving the structure of nanocomposites adsorbent.

Conclusion

A series nanocomposite adsorbent was prepared by varying the ratio of rectorite/chitosan. The analyses of SEM, TEM, FTIR, XRD indicated that the composite is nanocomposite, when the layer spacing is 2.78 nm, it has largest adsorption capacity on the three heavy metals. Characteristics of pH effect, equilibrium, kinetics which are used as nanocomposite

TABLE-4
FREUNDLICH AND LANGMUIR MODEL PARAMETERS FOR THE ADSORPTION OF Cu(II), Pb(II) AND Cd(II) BY NANOCOMPOSITE (REC/CS = 3:1)

Metal ion	Langmuir equations parameters			Freundlich equations parameters		
	b (L/mg)	Q^0 (mg/g)	R^2	K_F (mg/g)	n	R^2
Cu ²⁺	0.181	41.32	0.9926	9.399	2.3089	0.9946
Pb ²⁺	0.331	50.76	0.993	19.289	3.2175	0.9969
Cd ²⁺	0.092	32.47	0.9843	8.772	3.3456	0.9671

TABLE-5
COMPARISON OF DIFFERENT ABSORBENT IN
Cu(II), Pb(II) AND Cd(II) WASTEWATER TREATMENT

Adsorbent	Adsorption capacity (mg/g)		
	Cu ²⁺	Pb ²⁺	Cd ²⁺
Nanocomposites adsorbent (REC/CS = 3:1)	12.04	13.16	11.8
Chitosan	8.77	9.71	8.11
Rectorite	7.44	8.24	7.04

(rectorite/chitosan = 3:1) adsorbents for Cu(II), Cd(II) and Pb(II) were tested. The following conclusion can be made from this study: According to the comparison made with chitosan, rectorite, the adsorption capacity of nanocomposite adsorbent on Cu(II), Pb(II) and Cd(II) significantly increased. The adsorption data can be expressed better with both Freundlich and Langmuir type adsorption isotherms which show the adsorption capacities order is as Pb(II) > Cu(II) > Cd(II). In adsorption of heavy metal ions [Cu(II), Pb(II) and Cd(II)], chelating effect of the functional groups on nanocomposites is thought to take part in the adsorption process. The second-order equation appears to be better-fitting than Lagergren-first-order equation. The calculated amount of adsorption equilibrium ($q_{e,c}$) by second-order equation approaches to the actual amount of adsorption equilibrium (q_e). The second-order kinetic model best described the experimental data with the correlation coefficients (R^2), which shows that the adsorption of heavy metals on nanocomposite adsorbent might be a rate-limiting control.

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