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A novel adsorbent: Fe^{2+}-modified vermiculite was prepared in a two-step reaction. Adsorption experiments were carried out as a function of pH, contact time, and concentration of Cr(VI). It was found that Fe^{2+}-modified vermiculite was particularly effective for the removal of Cr(VI) at pH 1.0. The adsorption of Cr(VI) reached equilibrium within 60 min, and the pseudo-second-order kinetic model best described the adsorption kinetics. The adsorption data follow the Langmuir model more than the Freundlich model. At pH 1.0, the maximum Cr(VI) sorption capacity (Q_{max}) was $87.72\,mg \cdot g^{-1}$. Desorption of Cr(VI) from Fe^{2+}-modified vermiculite using NaOH treatment exhibited a higher desorption efficiency by more than 80%. The sorption mechanisms including electrostatic interaction and reduction were involved in the Cr (VI) removal. The results showed that Fe^{2+}-modified vermiculite can be used as a new adsorbent for Cr(VI) removal which has a higher adsorption capacity and a faster adsorption rate.

Keywords adsorption; Cr (VI) anion; Fe^{2+}-modified vermiculite; mechanism

INTRODUCTION

Chromium is a potential carcinogen and is highly toxic to humans, animals, and plants. Cr(III) is much less toxic than Cr(VI), which has limited hydroxide solubility making it relatively immobile and less available for biological uptake. Cr(VI) is one of the extremely toxic heavy metals found in various industrial waters and can cause health problems such as liver damage, pulmonary congestions, vomiting, and severe diarrhea (1). Due to the severe toxicity of Cr(VI), the EU Directive, WHO, and the United States EPA have set the maximum contaminant concentration of Cr(VI) in domestic water supplies as 0.05 mg/l (2). Consequently, the removal of Cr(VI) from industrial wastewater has become a research topic of great interest in recent times.

The conventional methods for the removal of Cr(VI), such as chemical precipitation, ion exchange, membrane separation, evaporation and so on, have certain limitations and are often not economical (3). Recently, more and more emphasis is being made on the development of cheaper and environmentally friendly Cr (VI) adsorbents such as activated carbon (4), microbial biomass (5–7), biosorbents (2,8), sol-gel adsorbent (9), clays and related minerals (10–14). Vermiculite is a kind of natural 2:1 type layered clay mineral, which is relatively cheap and easily available. It has the characteristics of permanent negative charge, large surface area, and profound reactive surface sites and has high ability for cation sorption, e.g., a large cation exchange capacity (CEC). Such unique properties enable vermiculite to be a promising ion exchanger for metal ions. The use of vermiculite in wastewater treatment has been studied in recent years and experimental results have shown it to be a suitable adsorbent for the removal of heavy metals like Pb(II), Cd(II), Cu(II), etc. from wastewaters (15–20).

However, natural vermiculite has a low adsorption capacity to Cr (VI) due to the lower anion-exchange capacity. In this present study, Fe^{2+}-modified vermiculite was first prepared fot the removal of Cr (VI) as a function of pH, time, and initial Cr (VI) concentration. The kinetics of the adsorption was studied. The sorption characteristics were modeled using the Langmuir and Freundlich isotherms. The competition adsorption, the desorption and regeneration, and the application to electroplating industry wastewater were also studied. A particular objective of this study was to evaluate the mechanisms of Cr (VI) adsorption on Fe^{2+}-modified vermiculite by FTIR and XPS.

EXPERIMENTAL PROCEDURE

Adsorbent

Vermiculite used in this work was supplied by the Xinjiang Yuli Xinlong Vermiculite Company, China. Vermiculite was initially rinsed with deionzed water several times, and dried in an oven at 80°C. The X-ray diffraction pattern for Mg-saturated vermiculite shows strong peaks at

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1.45 and 1.28 nm, the former corresponding to vermiculite and the latter to a mica-type mineral, indicating that the sample was a mixture of clay minerals. The peak heights under the (001) basal reflections of the identified clay minerals were used for the quantitative analysis (21), and the vermiculite component was 62%. Authors such as Vali and Hesse also observed these peaks in ethyleneglycolated vermiculite, (22), interpreting the peak at 1.43 nm as vermiculite and the peak at 1.2 nm as a biotite–vermiculite mixed layer mineral with 50–70% biotite component. The chemical composition of the vermiculite was performed by X-ray fluorescence (XRF, ARL 9800 XP, Switzerland), the result is SiO_2, 37.01%; Al_2O_3, 10.63%; MgO, 22.82%; K_2O, 4.81%; CaO, 2.00%; Na_2O, 1.34%; TiO_2, 1.39%; Fe_2O_3, FeO, 6.45%; Cr_2O_3, 0.34%; MnO, 0.05%; BaO, 0.23%; loss on ignition, 12.92 wt%. The cation exchange capacity (CEC) was determined by the method of ammonium acetate (23), resulting in a value of 73.30 mmol/100 g.

The natural vermiculite was chemically modified with $FeSO_4$ (analytical grade). The synthetic procedure was as follows. Step 1: the natural vermiculites were exchanged five times at 95°C with 10 ml 3 mol l^{-1} NaCl solution per gram of solid, under continuous stirring. Then the treated solids were washed with deionized water and dried at 80°C. Step 2: the samples collected at step 1 were exchanged two times with 10 ml 40 wt.% $FeSO_4$ solution per gram of solid under continuous stirring, followed by washing and drying at 80°C.

Adsorption Methods

A stock Cr (VI) in solution (1000 mg l^{-1}) was prepared from analytical grade $K_2Cr_2O_7$ to prepare solutions of varying initial concentrations. The other chemicals were analytical grade. All batch reactors were placed on a shaker at 200 rpm under controlled temperature of 25°C. The pH value was adjusted by 0.1 mol l^{-1} HNO_3 and 0.1 mol l^{-1} NaOH solution.

Batch pH experiments were studied by using 25 ml of 20 mg l^{-1} solution of Cr (VI) adjusted to initial pH of 1.0 to 9.0 and agitated with 0.1000 g (± 0.0001) of natural vermiculite or modified vermiculite for 60 minutes. The suspensions were then filtered for analyzing the equilibrium concentration of Cr (VI) by UV-Vis spectrophotometer (Perkin-Elmer Lambda 35). The total Cr concentration in solution was measured by AAS (Varian, SpectrAA-220FS). The Cr (III) concentration was calculated from the difference between the total Cr and Cr (VI) concentration.

Batch kinetic experiments were studied by agitating 25 ml of 200 mg l^{-1} solution of Cr (VI) with 0.1000 g (± 0.0001) of Fe^{2+}-modified vermiculite at pH 1.0. The contact time was in the range from 1 to 300 min.

Batch adsorption isotherms were studied by agitating 25 ml of different initial concentration of Cr (VI) in the range from 20 to 500 mg l^{-1} with 0.1000 g (± 0.0001) of the Fe^{2+}-modified vermiculite at pH 1.0 for 60 minutes.

Adsorption of Cr (VI) on the walls of glass flasks, plastic bottles, which was found negligible, was determined by running blank experiments. The experiments were performed in duplicate and the mean values were considered. In order to ascertain the reproducibility of the results, the group experiments were repeated a number of times and the results were found to vary within ±5%.

Competitive Adsorption

The competitive adsorption was carried out by agitating 25 ml 50 mg l^{-1} Cr (VI) mixed with various concentrations of orthophosphate ($H_2PO_4^-$) prepared from KH_2PO_4, sulfate (SO_4^{2-}) prepared from K_2SO_4 and chloroactic (Cl^-) from KCl, agitated with 0.1000 g (± 0.0001) of Fe^{2+}-modified vermiculite at pH 1.0 for 60 minutes.

Desorption and Regeneration Study

After adsorption experiments, Fe^{2+}-modified vermiculite adsorbed Cr(VI) was separated from the solution by filtration and washed gently with distilled water to remove any unadsorbed Cr(VI). Then the spent adsorbent was mixed with 100 ml of 0.01 mol l^{-1} NaOH, and agitated for 60 minutes. Then, the adsorbent was washed with distilled water and dried at 80°C. Regeneration experiments were carried out with different initial concentration of Cr(VI) from 20 to 500 mg l^{-1} and an initial pH value of 1.0.

XPS and FTIR Analysis

High-resolution XPS spectra were taken with a pass energy of 25 eV using Mg KR X-rays (Perkin-Elmer PHI model 04–51 X-ray source). All binding energies were referenced to the neutral C 1 s peak at 284.6 eV to compensate for surface charging effects. A software package, XPS peak 4.1, was used to fit the XPS spectra peaks, and the full width at half-maximum (FWHM) was maintained at 1.4 for all components in a particular spectrum. FTIR (670 NEXUS, Nicolet USA) spectrophotometer was taken using the reflection mode in the wavenumber range of 400–4000 cm^{-1}.

Preparation of $FeCl_2$ modified vermiculite absorbed Cr for XPS and FTIR analyses involved using 2.0 g $FeCl_2$ modified vermiculite reacted with 50 ml 0.1 mol l^{-1} $K_2Cr_2O_7$ for 24 h. The pH of the reaction mixture was initially adjusted to 1.0. After 24 h, the particles were rinsed with deionized water several times, and dried in an oven at 80°C, then stored for XPS and FTIR analysis.

RESULTS AND DISCUSSION

FTIR

Figure 1 shows the FTIR spectra of the natural vermiculite, Fe^{2+}-modified vermiculite and Fe^{2+}-modified

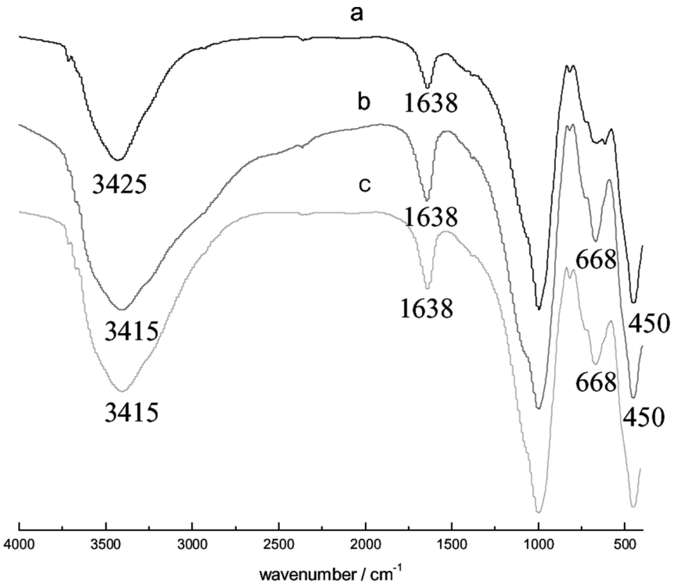


FIG. 1. FTIR spectra of the vermiculite. (a) natural vermiculite; (b) Fe^{2+}-modified vermiculite; (c) Fe^{2+}-modified vermiculite adsorbed Cr(VI).

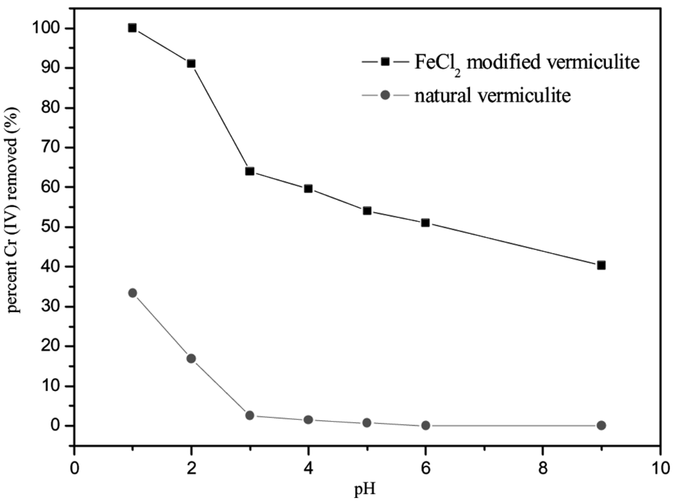


FIG. 2. Effect of pH on Cr (VI) removal by natural vermiculite and Fe^{2+} modified vermiculite (vermiculite dosage 4.0 g l^{-1}, Cr (VI) 20 mg l^{-1}, contact time 60 min).

vermiculite absorbed Cr (VI). The broad and strong peak at near 3400 cm^{-1} can be assigned to H_2O stretching vibration. The strong peaks at near 1000 cm^{-1} and 450 cm^{-1} can be assigned to Si-O-Si stretching vibration and bending vibration. After the vermiculite was modified by the Fe^{2+}, a new band at near 650 cm^{-1} attributed to Fe-O vibration is observed (Fig. 1b, 1c), indicating that Fe(II) successfully reacted with the hydroxyl groups on the vermiculite surface. To further verify the chemical reactions taking placed in the Fe^{2+}-modified vermiculite absorbed Cr (VI), please see Fig. 9. (XPS Cr 2p and Fe 2p spectra on the sorbent surface).

pH Dependency of Cr (VI) Sorption

An important parameter affecting metal ions sorption is pH. It not only influences the properties of the sorbent surface, but also affects the metal speciation in solution. Figure 2 shows the removal of Cr (VI) on the Fe^{2+}-modified vermiculite and the natural vermiculite as a function of the initial solution pH. For the two vermiculites, an increase in pH both produced a decrease in Cr (VI) removal. The maximum removal of more than 99.5% for Cr (VI) occurred at pH 1.0 for the Fe^{2+}-modified vermiculite at 20 mg l^{-1} Cr (VI) concentration, whereas the maximum removal of Cr (VI) was only 33.4% at pH 1.0 for natural vermiculite.

Total chromium in the equilibrium solution (25 ml) after adsorption (at 20 mg l^{-1} Cr (VI) concentration and pH 1.0) on the Fe^{2+}-modified vermiculite was found to be 246.5 ug, whereas Cr (VI) was 0.25 ug, indicating that 246.25 ug of Cr (VI) gets converted to Cr (III) during the removal and remains in the equilibrium solution along with the remaining Cr (VI). And the total chromium adsorption onto the adsorbent was 253.5 ug. This behavior can be explained by the changes in the speciation of Cr(VI) in the solution. At pH 1, $HCrO_4^-$ anion is the predominant species in the initial Cr(VI) of 20 mg $\cdot$ l^{-1}, and $HCrO_4^-$ anions are more easily reduced to Cr (III) by Fe^{2+}. A similar finding has been reported by Krishnani et al. (24) for the adsorption of chromium on lignocellulosic substrates where also the adsorption was greater at low pH and was found to decrease with increasing pH. At low pH, ligin reportedly reduced hexavalent chromium into Cr (III), which was subsequently adsorbed on the biosorbent.

Adsorption Kinetics

The removal of Cr(VI) by Fe^{2+}-modified vermiculite as a function of time from 1 min to 300 min at initial Cr(VI) concentration of 200 mg l^{-1} is displayed in Fig. 3. Results showed that the rate of Cr(VI) removal by Fe^{2+}-modified vermiculite was quite rapid. More than 70% of the Cr(VI) was removed in the first 1 min. The equilibrium was reached in about 60 min, and there were no further increases in the Cr(VI) removal up to 60 min. This is in agreement with the work of the other investigators (25) who proposed that the Cr(VI) removal by montmorillonite-supported magnetite nanoparticles was much faster and the equilibrium was reached in about 1 h.

The dynamics of the adsorption process in terms of the order and the rate constant can be evaluated using the kinetic adsorption data. The process of Cr(VI) removal from an aqueous phase by any adsorbent can be explained by using kinetic models and examining the rate-controlling mechanism of the adsorption process such as chemical

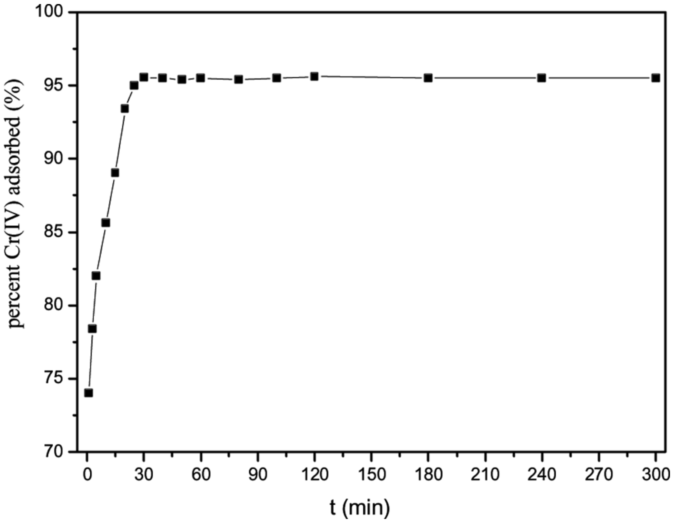


FIG. 3. Effect of contact time on the Cr (VI) removal by Fe^{2+}-modified vermiculite (vermiculite dosage 4.0 g l^{-1}, Cr (VI) 200.0 mg l^{-1}, initial pH 1.0).

reaction, diffusion control, and mass transfer. The kinetic parameters are useful in predicting the adsorption rate which can be used as important information in designing and modeling of the adsorption operation (26). In order to understand the kinetics of removal of Cr(VI) using Fe^{2+}-modified vermiculite as an adsorbent, pseudo-first-order, pseudo-second-order, and Elovich kinetic models are tested with the experimental data.

The pseudo-first-order kinetic model known as the Lagergren equation (27):

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}t \tag{1}$$

where Q_t and Q_e are the amounts of Cr(VI) adsorbed at time t and equilibrium (mg g^{-1}), respectively, and k_1 is the rate constant of pseudo-first-order adsorption process (min^{-1}).

The pseudo-second-order kinetic model (28):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{2}$$

where k_2 is the equilibrium rate constant of pseudo-second-order sorption (g mg^{-1} min^{-1}).

The sorption data may also be analyzed using the Elovich equation, which has the linear form (29):

$$Q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{3}$$

where α is the initial sorption rate constant (mg g^{-1} min^{-1}), β is related to the extent of surface coverage and activation energy for chemisorption (g mg^{-1}).

The kinetics constants for the removal of Cr(VI) on vermiculite are tabulated in Table 1. It can be seen that the pseudo-second-order kinetic model fits the experimental data better than the other kinetic models, and the correlation coefficients obtained for the pseudo-second-order kinetic model are greater than 0.999 for the Fe^{2+}-modified vermiculite. This result indicates that the sorption system is a pseudo-second-order reaction, implying that the rate-limiting step may be a chemical sorption involving valency forces through sharing or exchanging of electrons between the sorbent and the sorbate (30). Table 2 presents the comparison of pseudo-second rate constant (k_2) of Fe^{2+}-modified vermiculite with that of other adsorbents (25,31–34) for the removal of Cr(VI) from aqueous solutions, which show that Fe^{2+}-modified vermiculite is a good adsorbent for the removal of Cr(VI) from wastewater.

Adsorption Isotherms

The experimental results demonstrated the effect of initial concentration of Cr (VI) on the Cr (VI) removal by Fe^{2+}-modified vermiculite. From Fig. 4, it can be seen that with the increase in the initial concentration of Cr (VI) from 20–500 mg l^{-1}, the removal of Cr (VI) in 25 ml of solution increases from 4.998 to 85.00 mg g^{-1}.

Adsorption data were fitted to the Langmuir and Freundlich isotherms. The Langmuir adsorption model is valid for monolayer sorption due to a surface of a finite number of identical sites and is expressed in the linear form as:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} b} + \frac{C_e}{Q_{\max}} \tag{4}$$

where $Q_{\max}$ (mg g^{-1})is the maximum adsorbed material in mg per 1 g of the adsorbent and b (l mg^{-1}) relates the heat of adsorption.

TABLE 1
The kinetics constants for the removal of Cr(VI) by Fe^{2+}-modified vermiculite

Pseudo-first-order equation		Pseudo-second-order equation			Elovich equation		
k_1 (min^{-1})	R^2	Q_e (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2	α (mg $g^{-1}min^{-1}$)	β (g min^{-1})	R^2
0.1272	0.8243	47.73	0.1152	0.9997	4.475×10^8	0.4983	0.8239

TABLE 2
Comparison of pseudo-second rate constant (k_2) of various sorbents for Cr(VI)

Adsorbent	R_2	k_2	References
Fe^{2+}-modified vermiculite	0.9997	0.1152	this work
microMag	0.997	0.08	25
MagMt-H	0.999	0.07	25
activated tamarind seeds	0.998	0.049	34
aluminum magnesium mixed hydroxide	0.9992	0.02	31
Oxidized multiwalled carbon nanotubes	0.9769	0.01	32
Ocimum americanum L. seed pods	0.9909	0.008	33

The essential feature of the Langmuir adsorption can be expressed by means of R_L, a dimensionless constant referred to as the separation factor or equilibrium parameter for predicting whether an adsorption system is favorable or unfavorable. R_L is calculated using the following equation:

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

where C_0 is the initial Cr(VI) concentration (mg l^{-1}). If the R_L values lie between 0 and 1, the adsorption is favorable.

The Freundlich adsorption isotherm describes the heterogeneous surface energies by multiplayer adsorption and is expressed in linear form as:

$$\log Q_e = \frac{1}{n}\log C_e + \log K \tag{6}$$

where K and $1/n$ are the Freundlich constants related to the adsorption capacity and the adsorption efficiency, respectively.

In the present study, the adsorption data obtained from the initial Cr (VI) concentration from 20 to 500 mg l^{-1} at pH 1.0 show that the adsorptions follow both the Langmuir model ($R^2 = 0.9981$) and Freundlich model ($R^2 = 0.9507$), see Fig. 5, Fig. 6, and Table 3. Yet, the correlation coefficient of the Langmuir curve is distinctly higher than that of the Freundlich curve. The results are in agreement with those previously reported by other authors for adsorption test on this type of solid (25,31,32). This observation implies that monolayer sorption, as well

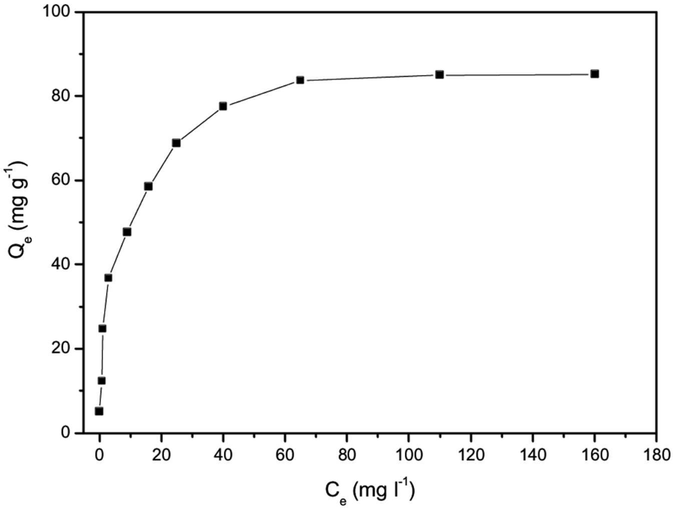


FIG. 4. Adsorption isotherm of Cr (VI) onto Fe^{2+}-modified vermiculite (vermiculite dosage 4.0 g l^{-1}, initial pH 1.0, contact time 60 min).

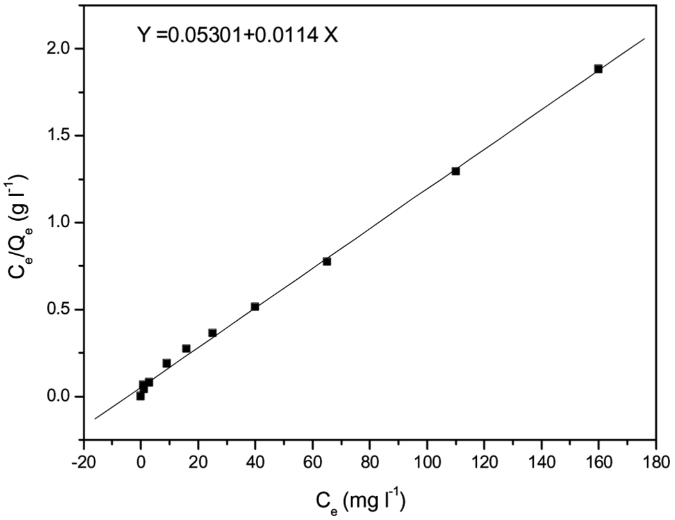


FIG. 5. Langmiur isotherm of Cr (VI) onto Fe^{2+}-modified vermiculite (vermiculite dosage 4.0 g l^{-1}, initial pH 1.0, contact time 60 min).

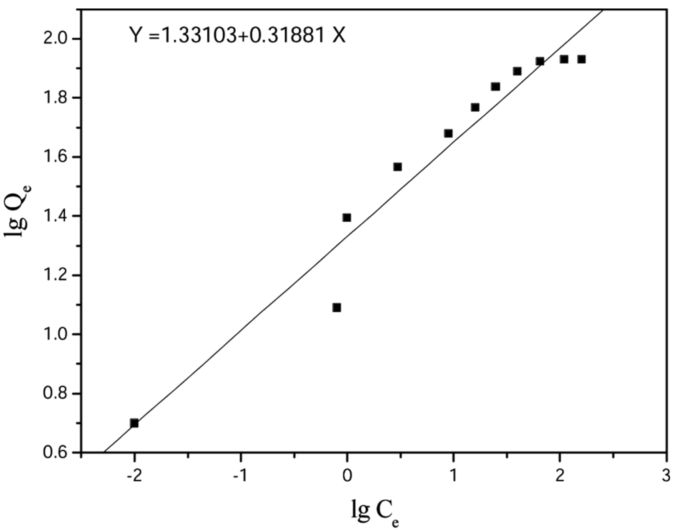


FIG. 6. Freundlich isotherm of Cr (VI) onto Fe^{2+}-modified vermiculite (vermiculite dosage 4.0 g l^{-1}, initial pH 1.0, contact time 60 min).

TABLE 3
Langmuir and Freundlich isotherm parameters for adsorption of Cr(VI) on Fe^{2+}-modified vermiculite

Langmuir constants			Freundlich constants		
R^2	Q_{max} (mg g^{-1})	b (l mg^{-1})	R^2	K	1/n
0.9981	87.72	0.2151	0.9507	21.43	0.3188

as heterogeneous surface conditions, may coexist under the applied experimental conditions. Hence, the overall sorption of Cr (VI) on the Fe^{2+}-modified vermiculite is complex, involving more than one mechanism, such as ion exchange, surface complexation, and electrostatic attraction, which will be elucidated in the section titled Sorption Mechanisms. On the basis of the Langmuir isotherm, the maximum chromium sorption capacity (Q_{max}) was 87.72 mg g^{-1}, indicating that the adsorbent had a high capacity to remove Cr(VI) ions. At initial Cr (VI) concentration from 20 to 500 mg l^{-1}, R_L was calculated from 0.1886 to 0.0092, which indicate that the adsorption is favorable. Table 4 presents the comparison of adsorption capacity of Fe^{2+}-modified vermiculite with that of other adsorbents (4,9,10,25,31,32,36,38) for the removal of Cr(VI) from aqueous solutions, which show that Fe^{2+}-modified vermiculite is a good adsorbent for the removal of Cr(VI) from wastewater.

TABLE 4
Comparison of maximum sorption capacities of various sorbents for Cr(VI)

Adsorbent	pH	Q_{max} (mg g^{-1})	References
Aluminum magnesium mixed hydroxide	4.0	105.3	31
Fe^{2+}-modified vermiculite	1.0	87.72	this work
Cross-linked chitosan	5.0	78	36
Iron complexed protein waste	4.0	50.5	38
Commercial activated carbon	2.0	48.5	4
Layered double hydroxide	6.0	28.0	9
Montmorillonite-supported magnetite nanoparticles	2.5	13.88	25
Kaolinite	4.6	11.6	10
Acid-activated kanlinite	4.6	13.9	10
ZrO-kaolinite	4.6	10.9	10
TBA-kaolinite	4.6	10.6	10
Oxidized multiwalled carbon nanotubes	2.0	4.26	32

Competitive Adsorption

The results of batch testing with competing anions are shown in Table 5. In all cases, regardless of any competing anions present in solution, Fe^{2+}-modified vermiculite was still able to reduce the concentration of hexavalent chromium in solution by over 80%. This may be due to the reduction of Cr(VI) to Cr(III) by Fe^{2+} on the sorbent surface, while the other anions like $H_2PO_4^-$, SO_4^{2-}, and Cl^- can not be reduced by Fe^{2+}. Similar results have been obtained by Ochola and Moo-young (13) for the adsorption of Cr (VI) by reclaimed limestone residual RLR (modified steel slag), who reported that in the coexist of Cl^-, SO_4^{2-}, and $H_2PO_4^-$, more than 90% Cr (VI) can be removed by RLR.

Regeneration Studies

The saturated adsorbent which contains Cr(VI) is not safe for the disposal due to the stringent environmental constraints. It is important and appropriate to propose a method for the regeneration and reuse of the adsorbent so as to reduce the load on the environment in terms of the disposal of the polluted adsorbent. In the present study, Fe^{2+}-modified vermiculite absorbed Cr(VI) was desorbed and regenerated, then was used for the removal of Cr(VI) at different initial Cr(VI) concentration ranging between 20 and 500 mg l^{-1} as used for fresh Fe^{2+}-modified vermiculite. Figure 7 shows the comparison of the percentage

TABLE 5
Competition batch test results for the Fe^{2+}-modified vermiculite

Competing anions	Final Cr(VI) concentration (mg l^{-1})	Reduction (%)
50 mg l^{-1} Cr (VI)	22.80	84.4
50 mg l^{-1} Cr (VI) + 50 mg l^{-1} Cl^-	22.95	84.1
50 mg l^{-1} Cr (VI) + 50 mg l^{-1} SO_4^{2-}	22.55	84.9
50 mg l^{-1} Cr (VI) + 50 mg l^{-1} $H_2PO_4^-$	24.15	81.7
50 mg l^{-1} Cr (VI) + 50 mg l^{-1} Cl^- + 50 mg l^{-1} SO_4^{2-} + 50 mg l^{-1} $H_2PO_4^-$	23.80	82.4

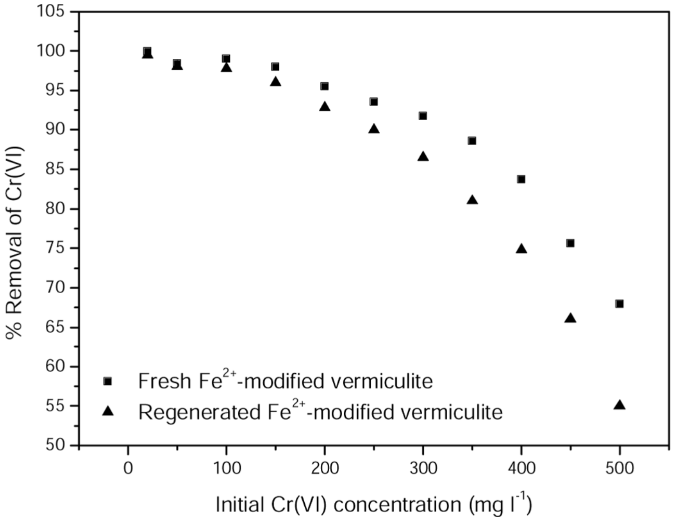


FIG. 7. Comparison of the percentage removal of Cr(VI) using fresh and regenerated Fe^{2+}-modified vermiculite. (dosage 4.0 g l^{-1}, initial pH 1.0, contact time 60 min).

removal of Cr(VI) using fresh and regenerated Fe^{2+}-modified vermiculite. The percentage removal of Cr(VI) is found to decrease from 99.5% to 55.0%, respectively, as compared to the corresponding values for the fresh adsorbent ranging from 99.95% to 67.98%. These results using regenerated Fe^{2+}-modified vermiculite exhibit higher desorption efficiency by more than 80% of the fresh Fe^{2+}-modified vermiculite for the removal of Cr(VI).

Sorption Mechanisms

The most commonly reported mechanisms for sorption of metal ions include ion exchange, electrostatic interaction, chelation, precipitation, and compelxation. For anions, electrostatic interaction plays an important role in allowing the approach of the ions to the sorbent surfaces.

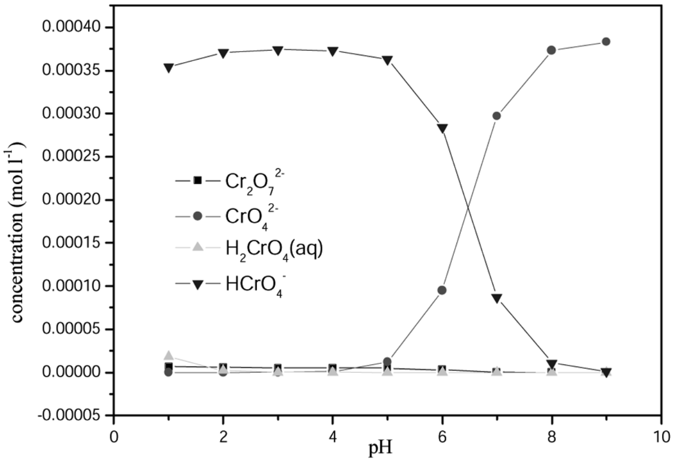


FIG. 8. Visual MINTEQ calculated distribution of Cr(VI) species (Cr(VI) 20 mg · l^{-1}, pH 1–9, T = 25°C).

To understand the sorption mechanisms of Cr (VI) anions on the Fe^{2+}-modified vermiculite, it is necessary to consider the Cr (VI) speciation at different solution pH. The speciation of Cr (VI) is determined by both pH and chromium concentration. In our study, the abundances of Cr (VI) species in the initial solution of

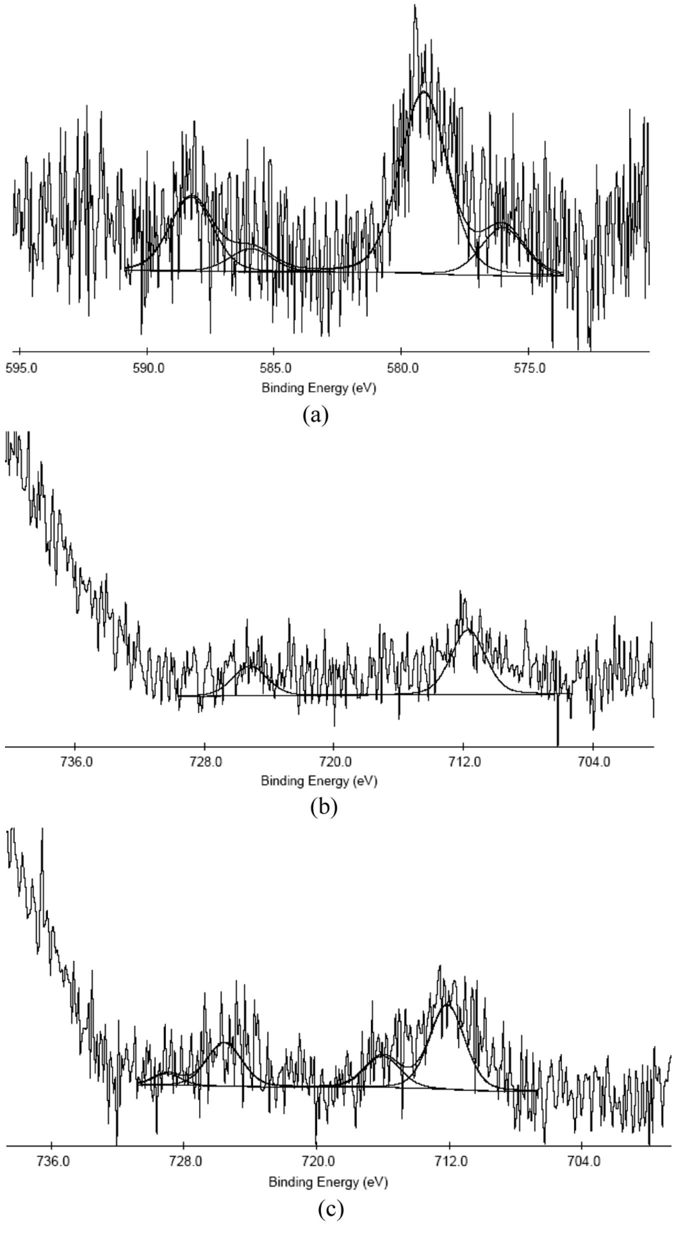


FIG. 9. XPS Cr 2p and Fe 2p spectra on the sorbent surface. a. Cr 2p spectra on the Fe-modified vermiculite surface after sorption of Cr (VI); b. Fe 2p spectra on the Fe-modified vermiculite; c. Fe 2p spectra on the Fe-modified vermiculite after sorption of Cr (VI). The peaks at ~579 and ~588 eV binding energies represent Cr (VI) and peaks at ~577 and ~587 eV binding energies represent Cr (III). The peaks at ~712 and ~725 eV binding energies represent Fe (II) and at ~717 and ~732 eV binding energies represent Fe (III).

$20\,mg \cdot l^{-1}$ Cr(VI) at pH 1–9 were calculated by the software of Visual MINTEQ, see Fig. 8. $HCrO_4^-$ anion is the predominant species at pH below 5; CrO_4^{2-}, and $HCrO_4^-$ are major species in the pH range of 5–8; CrO_4^{2-} is the predominant species at pH above 8. At $pH = 1.0$, $HCrO_4^-$ is major species. For the Fe^{2+}-modified vermiculite, the Fe^{2+} would be protonated and adsorb anionic hexavalent chromium $CrO_4^{2-}, HCrO_4^-, Cr_2O_7^{2-}$ via electrostatic attraction as follows:

$$F_e^{2+} + HCrO_4^- \rightarrow F_e^{2+} \cdots\cdots HCrO_4^-$$

$$F_e^{2+} + CrO_4^{2-} \rightarrow F_e^{2+} \cdots\cdots CrO_4^{2-}$$

$$F_e^{2+} + Cr_2O_7^{2-} \rightarrow F_e^{2+} \cdots\cdots Cr_2O_7^{2-}$$

The Cr (VI) anion demonstrates a very high positive redox potential. It can be reacted with Fe (II)at the different pHs as follows:

$$C_r(VI) + 3F_e(II) \rightarrow C_r(III) + 3F_e(III)$$

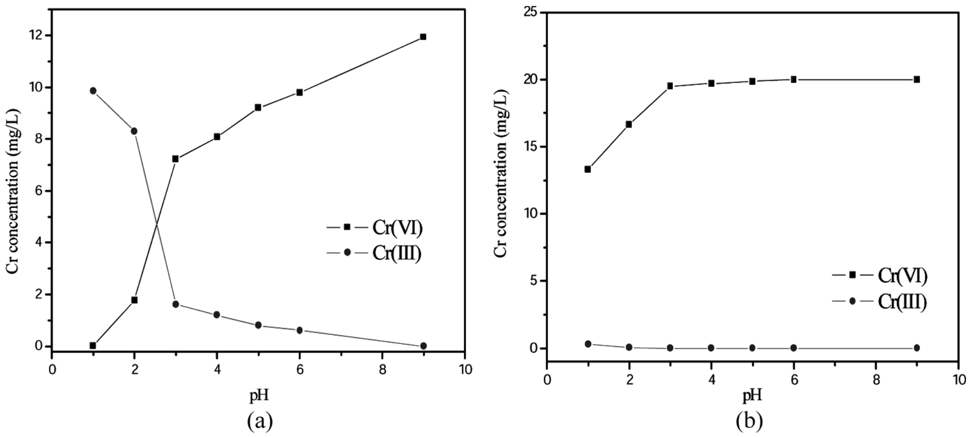
The reduced Cr (III) ions were then adsorbed on the vermiculite surface. Figure 9a shows the Cr 2p spectra on the Fe^{2+}-modified vermiculite surface after the sorption of Cr (VI). The binding energies at ~579 eV ($2p_{3/2}$) and ~588 eV ($2p_{1/2}$) can be assigned to Cr (VI), ~577 eV ($2p_{3/2}$) and ~587 eV ($2p_{1/2}$) can be assigned to Cr (III). It is evident that both Cr (VI) and Cr (III) are present on the surface, indicating that Cr (VI) anions were partly reduced to Cr (III) ions during the removal process. The Fe 2p spectra for the Fe^{2+}-modified vermiculite and Cr (VI) loaded Fe^{2+}-modified vermiculite are shown in Figure 9b and 9c. The binding energies at ~712 eV ($2p_{3/2}$) and ~725 eV ($2p_{1/2}$) can be assigned to Fe (II), ~717 eV ($2p_{3/2}$) and ~732 eV ($2p_{1/2}$) can be assigned to Fe (III), thus one can readily see that oxidation of Fe (II) to Fe (III) occurred during the reaction with Cr (VI).

At the same time, the reduced Cr (III) ions may exist in solution. Figure 10 shows the distribution of Cr (VI) and Cr (III) species in solution after removal by the Fe^{2+}-modified vermiculite and natural vermiculite at different pHs. For the Fe^{2+}-modified vermiculite, the residual Cr (VI) concentration in solution is lowest at pH 1.0 and increases with increasing pH up to 9.0, while the Cr (III) concentration decreases with an increase in pH over the same pH range, indicating that Cr (VI) anions are more easily reduced to Cr (III) in acidic solution. However, for the natural vermiculite, the residual Cr (VI) concentration is higher than that for the Fe^{2+}-modified vermiculite, and the Cr (III) concentration is almost zero with the variation of pH 1.0–9.0.

It can be concluded that the sorption of Cr (VI) anions on the Fe^{2+}-modified vermiculite is a complex process and several mechanisms are involved in the sorption process. Cr (VI) anions were first adsorbed on the sorbent surface by electrostatic attraction and then reduced to Cr (III) species on the Fe^{2+}-modified vermiculite surface. Similar results have been obtained by Yuan et al. (39) for the removal of Cr (VI) by the diatomite-supported magnetite nanoparticles, who reported that the Cr(VI) uptake onto these synthesized magnetite nanoparticles was a physicochemical process, including an electrostatic attraction followed by a redox process in which Cr(VI) was reduced into Cr(III).

Application to Electroplating Industry Wastewater

In addition, the Fe^{2+}-modified vermiculite was applied for Cr (VI) removal from a local wastewater stream originating from the electroplating industry. The main characteristics of wastewater employed are shown in Table 6. The Cr (VI) removal of real wastewater was studied by the



(a) (b)

FIG. 10. Distribution of Cr (VI) and Cr (III) in solution after removal by the Fe-modified vermiculite (a) and natural vermiculite (b) at different solution pHs. (vermiculite dosage $4.0\,g\,l^{-1}$, Cr (VI) $20\,mg\,l^{-1}$, contact time 60 min).

TABLE 6
The main characteristics of wastewater stream from electroplating industry

Wastewater characteristics	Values
Particles in suspension	$10\,mg\,l^{-1}$
pH	5.0
Cr (VI)	$90\,mg\,l^{-1}$
Cr (III)	$2.5\,mg\,l^{-1}$
Zn (II)	$1.57\,mg\,l^{-1}$
Cl^-	$37.6\,mg\,l^{-1}$
SO_4^{2-}	$169\,mg\,l^{-1}$

dosage of adsorbent $20\,g\,l^{-1}$, shaking at 200 rpm, 25°C for 60 min at pH 1.0. In this case, the removal efficiency of Cr (VI) was more than 90%, indicating that Fe^{2+}-modified vermiculite can be a promising low-cost adsorbent applied for industrial effluent treatment.

CONCLUSIONS

A novel adsorbent named Fe^{2+}-modified vermiculite prepared in a two-step reaction was used for the removal of Cr (VI) ions. The presence of Fe^{2+} on the vermiculite surface was verified by FTIR and XPS analysis. Batch experiments showed that the solution pH strongly influenced the adsorptive capacity of the adsorbent. An increase in pH produced a decrease in Cr (VI) removal. The maximum removal of more than 99.5% for Cr (VI) occurred at pH 1.0 of $20\,mg\,l^{-1}$ Cr (VI) for the $4.0\,g\,l^{-1}$ Fe^{2+}-modified vermiculite. Kinetic studies confirmed that the rapid adsorption equilibrium was reached within 60 min. Data were better fitted to the pseudo-second-order kinetic equation ($R^2 = 0.9997$) and the rate constant (k_2) was $0.1152\,g \cdot mg^{-1} \cdot min^{-1}$ at $200\,mg\,l^{-1}$ Cr(VI) concentration. Though the equilibrium data were successfully modeled by both Langmuir and Freundlich models, data were better fitted to Langmuir model ($R^2 = 0.9981$). The maximum chromium sorption capacity (Q_{max}) was $87.72\,mg\,g^{-1}$, indicating that the adsorbent had a high capacity to remove Cr (VI) ions. The Fe^{2+}-modified vermiculite exhibited a high selectivity toward Cr (VI) regardless of any competing anions present (Cl^-, SO_4^{2-}, and $H_2PO_4^-$) in solution. The saturated adsorption is regenerated by NaOH treatment. The adsorption efficiency of the regenerated Fe^{2+}-modified vermiculite is found to be more than 80% of fresh Fe^{2+}-modified vermiculite for the removal of Cr(VI). XPS results showed that Cr (III) existed on the Fe^{2+}-modified vermiculite surface at pH 1.0, suggesting that some Cr (VI) anions were partly reduced to Cr (III). Sorption of Cr (VI) anions on the Fe^{2+}-modified vermiculite is a complex process. Cr (VI) anions were first adsorbed on the sorbent surface by electrostatic attraction and then reduced to Cr (III) species on the Fe^{2+}-modified vermiculite surface. Furthermore, the Fe^{2+}-modified vermiculite was applied for Cr (VI) removal from a local wastewater stream originating from the electroplating industry, indicating that it can be a promising low-cost adsorbent applied for industrial effluent treatment.

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NOMENCLATURE

$\alpha =$	initial sorption rate constant ($mg\ g^{-1}\ min^{-1}$),
$\beta =$	extent of surface coverage and activation energy for chemisorption ($g\ mg^{-1}$).
$b =$	Langmuir coefficient for adsorbate-adsorbent equilibrium, mg^{-1}
$C_0 =$	initial concentration of Cr (VI), $mg\ l^{-1}$
$C_e =$	equilibrium concentration of Cr (VI) in the solution, $mg\ l^{-1}$
$C_t =$	concentration of Cr (VI) in the solution at time t, $mg\ l^{-1}$
$K_1 =$	pseudo-firstorder rate kinetic constant, min^{-1}
$k_2 =$	pseudo-second-order rate kinetic constant, $g\ mg^{-1}\ min^{-1}$
$K =$	Freundlich constant
$n =$	Freundlich constant
$Q_e =$	amount of Cr (VI) adsorbed at equilibrium, $mg\ g^{-1}$
$Q_t =$	amount of Cr (VI) adsorbed at time t, $mg\ g^{-1}$
$Q_{max} =$	adsorption capacity, $mg\ g^{-1}$
$R_L =$	separation factor or equilibrium parameter
$R^2 =$	correlation coefficient

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