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Removal of chromium (VI) ions from aqueous solutions by N-2-hydroxypropyl trimethyl ammonium chloride chitosan–bentonite

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ABSTRACT

This study provided information on the preparation and the Cr (VI) adsorption potential of N-2-hydroxypropyl trimethyl ammonium chloride chitosan (HTCC)–bentonite nanocomposite as an absorbent. HTCC–bentonite was characterized by small angle x-ray diffraction, Fourier transforming infrared spectroscopy, scanning electron microscopy, and transmission electron microscopy. Batch adsorption experiment of chromium was performed to investigate the effects of pH, initial concentration, adsorbent dosage, contact time, etc. The maximum adsorption was observed at a pH value of 1. Adsorption of chromium on HTCC–bentonite was favored at lower temperature and established equilibrium in 30 min. The Cr (VI) adsorption followed Langmuir isotherm models, and the maximum adsorption capacity was obtained at 22.17 mg g^{-1}.

Keywords: Chromium; HTCC–bentonite; Adsorption; Isotherm model

1. Introduction

Hexavalent chromium Cr (VI) is highly toxic and classified as a human carcinogen [1,2]. In aqueous solution, Cr (VI) exists in the following forms: chromate CrO_4^{2-}, dichromate $Cr_2O_7^{2-}$, and hydrogen chromate $HCrO_4^-$. Its dominant species depend on the pH and the concentration of the solution [1]. Due to repulsive electrostatic interactions, Cr (VI) anionic species are poorly adsorbed by the negatively charged soil particles in the environment and hence, they can transfer freely into aqueous environment. Therefore, it is necessary to control Cr (VI) content in industrial effluents before their discharge into sewages or rivers in order to prevent the deleterious impact of Cr (VI) on the ecosystem and public health.

Conventional techniques for Cr (VI) removal from aqueous solution include ion exchange, chemical precipitation, evaporation, membrane filtration, reverse osmosis, electrodialysis, and adsorption [3–5]. In application of the method of adsorption, the most widely used adsorbent is activated carbon due to its relatively higher surface area. But the production of commercial activated carbon is still an expensive process. Therefore, it is necessary to search for a more cost-effective production process of activated carbon or other adsorbent materials used for wastewater treatment.

Clays are cost-effective for immobilizing toxic contaminants as they are low-cost, readily available and stable, and have high adsorptive and ion exchange properties. However, raw clays cannot effectively remove Cr (VI) from aqueous solution due to their negatively charged surface. Therefore, clay materials

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can often be modified using a variety of chemical/physical treatments to achieve the desired surface properties for best immobilization of contaminants. For example, when the surfaces of these clays are modified with organic molecules, the resulting products are called organoclays [6,7]. The organic modifiers used are generally cationic quaternary amine compounds which are commonly known as surfactants. Organoclays have extensively been studied for their unique sorption behavior towards various hydrophobic organic contaminants in the environment [8,9] and ionic contaminants such as heavy metals [10–14] and metalloids [15]. However, few studies have considered the modification of clay by cation polymer and the adsorption abilities of these clays were modified [16].

N-2-hydroxypropyl trimethyl ammonium chloride chitosan (HTCC), as a cation polymer, is itself a good absorbent and flocculent agent due to its unique properties, such as biocompatibility, biodegradation, biological activity, low toxicity, and so on. Viviane et al. found that HTCC was an effective adsorbent for the removal of Cr (VI) from aqueous solution [17]. However, HTCC is a relatively high-cost biopolymer and it is apt to loss based on the adsorption of Cr (VI) from aqueous solution, so it is expected that a novel adsorbent was prepared by HTCC loaded onto clay for the purpose of reducing the amount of HTCC and avoiding the loss of HTCC. Besides, after the bentonite modified with HTCC was applied in water treatment, the sequential treatment would become convenient.

This study attempts to characterize the organoclay synthesized from HTCC and bentonite and test its adsorption ability towards Cr (VI) from aqueous solution. Organic modification of the bentonite is established and characterized by X-ray diffraction (XRD), Fourier transforming infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Experimental parameters affecting adsorption process, such as pH, adsorbent dosage, contact time, and temperature, have been studied. The equilibrium adsorption data were evaluated by Langmuir and Freundlich isotherm models.

2. Materials and methods

2.1. Materials

All the reagents used were of analytical grade and without further purification. The 1,000 mg L^{-1} chromium standards were prepared from $K_2Cr_2O_7$. The stock solution was diluted appropriately when necessary. HTCC, with a substitution degree of 86.9%, was prepared according to our previous literature [18]. Its molecular structure is depicted in Fig. 1. Bentonite powder with a particle size of 200-mesh was acquired from the chemical factory of Shentai, Xinyang, Henan, China.

2.2. Instruments/apparatus

FT-IR spectra of the samples were taken by using an Avatar-360 IR spectrometer from Nicolet in the wave number range of 400–4,000 cm^{-1}. The TEM images of HTCC–bentonite were obtained by JEM-3010 (JEOL, Japan).The specific BET surface areas of bentonite and HTCC–bentonite were measured by N_2 adsorption. Measurements were performed by a surface measuring instrument (V-sorb 2800P, Beijing golden love music company). The small angle X-ray diffraction (SAXRD) was performed on type D/max-rA diffractometer (Rigaku Co., Japan) with Cu target. The scanning rate was 1°/min and the scanning scope of 2θ was 1–10°. The images of HTCC–bentonite before and after adsorption of Cr (VI) ions were examined by SEM (JEOLJSM-6380LV). The pH of the solution was measured with a laboratory-scale pH meter (LiDa instrument, Shanghai, China). A temperature controlled water bath flask shaker (Kanghua, Jiangsu, China) was used for shaking the solutions. The determination of the concentration of Cr (VI) in aqueous solution was done on a UV-visible spectrophotometer (model 754 N) made in Shanghai, China.

2.3. Preparation of HTCC–bentonite

HTCC–bentonite was prepared by the following procedures: bentonite (5 g) was soaked in 30 mL of water and taken in a three-necked round-bottom flask and HTCC (1.0 g) in 30 mL of distilled water was added to it. The contents were maintained at 80℃ for 2 h. The composite obtained was then washed with distilled water. Washing was repeated until the supernatant solution was free of Cl$^-$ ions, as indicated by the $AgNO_3$ test. The product was dried in an oven at 105℃ for 2 h and then ground to obtain particles of 200-mesh size. The composite was named as HTCC–bentonite.

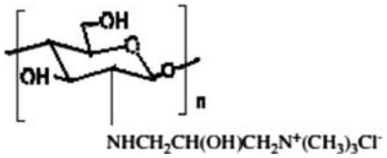

Fig. 1. The molecular structure of HTCC.

2.4. Batch adsorption procedure

The batch experiments are carried out in 250 mL borosil conical flasks. A specific amount of HTCC–bentonite (adsorbent) is added in 50 mL of aqueous Cr (VI) solution and then stirred for 40 min at 30°C and 200 rpm in a temperature controlled water bath flask shaker. Afterwards, the resultant solution is filtered using a filter paper. The effect of pH on the removal efficiency was carried out, followed by further search for the effect of initial concentration and adsorbent dosage on adsorption efficiency at the optimized pH value. Only one parameter was changed at a time, while others were maintained constant during the experiments. In the first set of experiment, the removal efficiency was studied at various pH values at 1.0 g HTCC–bentonite, 50 mL of chromium solution with a concentration of 57 mg L^{-1}. The second set of experiment was conducted with various initial Cr (VI) concentrations from 57 to 570 mg L^{-1} at constant adsorbent amount (1.0 g) and at optimized pH. In the third set of experiment, the dosage of HTCC–bentonite was varied (0.5–2.5 g), while other parameters such as initial Cr (VI) concentration (57 mg L^{-1}) and optimum solution pH were kept constant.

Additionally, the experiments were performed at varied temperature (between 20 and 50°C) and different contacting times (from 5 to 120 min), constant adsorbent amount (1 g), 114 mg L^{-1} chromium solution, and optimized pH. The time required for reaching the equilibrium condition was estimated by drawing samples at regular intervals of time till equilibrium was reached. The solutions were filtered and then subjected to quantitative analyses. The equilibrium concentrations of each solution were measured by spectrophotometer (Shimadzu UV-2101PC) at the λ_{max} value, which is 540 nm for Cr (VI). The amount of Cr (VI) adsorbed onto HTCC–bentonite surface was determined by the difference between the initial and remaining concentrations of Cr (VI) solution. Besides, the adsorption of Cr (VI) onto HTCC–bentonite was also evaluated at 273 K for the adsorption isotherms. In this study, the data presented were the averages of two measurements conducted with a standard deviation of 5%.

3. Results and discussion

3.1. Characterizations of HTCC–bentonite

3.1.1. FT-IR analysis of HTCC–bentonite

FT-IR spectra reveals the specific surface functional groups on bentonite and organobentonite surface qualitatively based on the characteristic absorbed energy for each bonds in certain groups [19]. The FT-IR spectra of bentonite and organobentonite are shown in Fig. 2. Fig. 2 reveals the presence of a symmetric and asymmetric stretching vibration at wavelength bands of 2,850 and 2,920 cm^{-1} or so. These bands are associated with the symmetric and asymmetric stretching vibrations of the methylene and methyl group CH_2, CH_3 of the aliphatic chain of HTCC. Also, a bending vibration of the methylene groups can be seen at wavelength bands of 1,475 cm^{-1} or so, verifying the introduction of $(CH_3)_3N^+R$. All these bands may be detected in HTCC–bentonite. Besides, it was found that because the characteristic peak of glucopyranoside at 1,060 cm^{-1} is overlapped with the stretching bands of Si–O–Si at 1,039 cm^{-1}, the band at 1,040 cm^{-1} or in HTCC–bentonite is wider than the one in raw bentonite. These observations show that bentonite has been modified by HTCC.

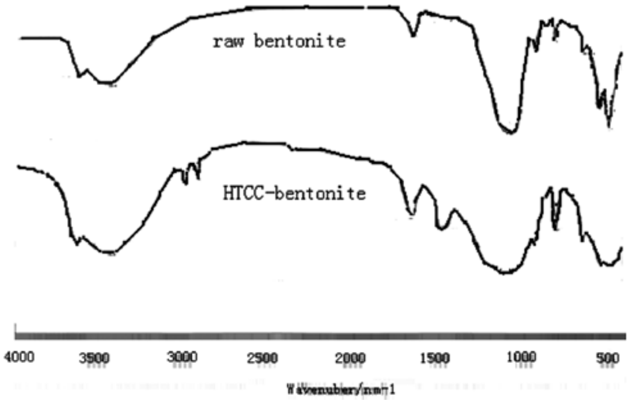

Fig. 2. The FTIR spectra of raw bentonite and HTCC-bentonite.

3.1.2. SAXRD diffraction analysis of HTCC–bentonite

To investigate the possible intercalation of HTCC in HTCC–bentonite, the SAXRD patterns of HTCC–bentonite and raw bentonite samples are recorded to measure the change of diffraction peak at d_{001} (Fig. 3). In the XRD powder patterns, the reflections of raw bentonite and HTCC–bentonite occurred at 1.92° and 1.70°, corresponding to basal spacings of 4.72 and 5.32 nm, respectively. It was found that the diffraction peak at d_{001} in HTCC–bentonite slightly shifted to a lower angle compared to raw bentonite, revealing that HTCC molecules partially intercalate into the interlayer spaces. Due to the influence of the interface constraint of polymer intercalation, the polymer cation cannot exchange the interlayer cations completely. The similar phenomena were obtained by other researchers [20–25], who studied the preparation and

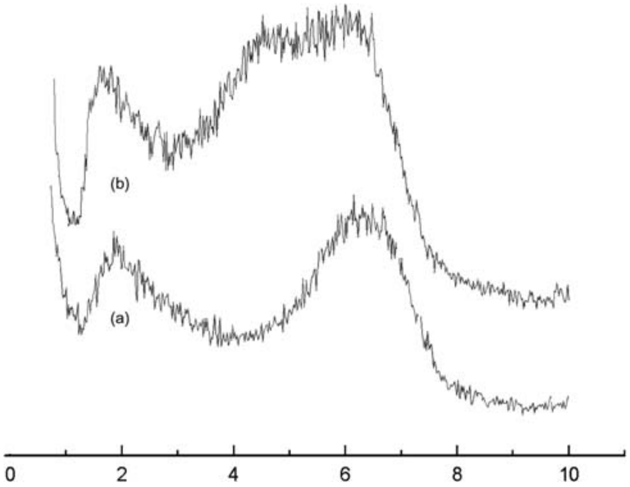

Fig. 3. SAXRD patterns of raw bentonite and HTCC-bentonite.

characteristics of rectorite/chitosan or its derivative nanocomposite. Their results shown chitosan or its derivatives can intercalate in bentonite effectively.

3.1.3. TEM analysis of HTCC–bentonite

To further obtain the dispersion of HTCC in bentonite, TEM images of HTCC–bentonite are presented in Fig. 4. The dark lines and the gray area represent bentonite and HTCC, respectively. The direct evidence of this nanometer-scale dispersion of HTCC in bentonite was found in the TEM images, as exhibited in Fig. 4(a). Therefore, HTCC–bentonite was nanocomposite. Besides, the layered structure of silicate particles was observed in Fig. 4(b), also, there was a distribution of many HTCC particles around the surface of bentonite, especially the outside surface. As mentioned in Section 3.1.2, HTCC molecules partially intercalate into the interlayer spaces. Therefore, other HTCC molecules were mainly loaded on the outside surface of bentonite.

3.1.4. Specific surface area of HTCC–bentonite

The specific surface areas of raw bentonite and HTCC–bentonite were obtained at 45.3 and 35.2 m^2/g, respectively, by BET method. The specific surface area of HTCC–bentonite reduces compared with raw bentonite. A decrease in specific surface areas may be attributed to the compact packing of the HTCC molecules in the interlayer space, resulting in pore blocking that inhibited the passage of nitrogen molecules.

3.1.5. SEM analysis of HTCC–bentonite

Samples of HTCC–bentonite before and after Cr (VI) adsorption were coated under a vacuum with a thin layer of gold and then examined by SEM. The SEM micrographs of HTCC–bentonite are shown in Fig. 5. It can be seen that bentonite particles were uniformly distributed in the matrix structure of HTCC and do not give an indication of aggregation in raw HTCC–bentonite (Fig. 5(a)). However, an obvious cluster around HTCC particles was observed in HTCC–bentonite after Cr(VI) adsorption, indicating Cr (VI) adsorption onto HTCC–bentonite.

3.2. Effect of adsorption conditions on Cr (VI) adsorption

3.2.1. Effect of pH on Cr (VI) adsorption

It is well known that the initial pH of a system is an important parameter in the adsorption of Cr (VI). In this study, the effect of initial pH on the adsorption of Cr (VI) using HTCC–bentonite as an adsorbent is studied in the initial pH range of 1–13. The relation between the initial pH of the solution and the removal efficiency of Cr (VI) is shown in Fig. 6. The maximum adsorption of Cr (VI) ions was observed at pH 1.0. A similar type of behavior was also reported for the adsorption of Cr (VI) species on poly(4-vinylpyridine)

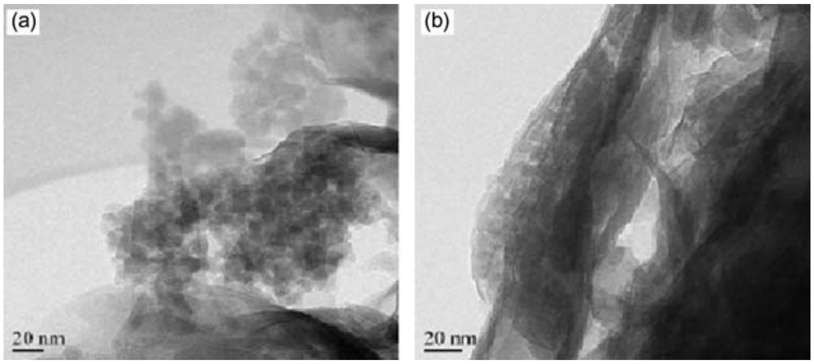

Fig. 4. TEM images of HTCC-bentonite.

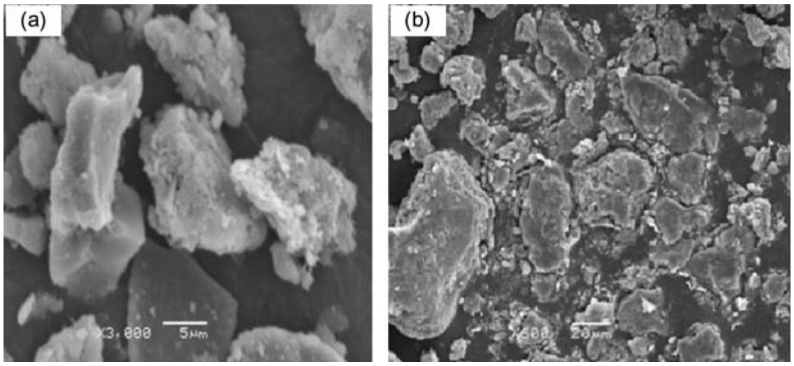

Fig. 5. SEM images of HTCC-bentonite before (a) and after (b) Cr (VI) adsorption.

(P4VP)/bentonite composite [26]. The pH effect on the removal capacity of polymer modified bentonites may be attributed to the combined effect of pH on the nature of bentonite surface, adsorbed Cr(VI) species, and the cationic or/and neutral character of polymer. For the polymer-modified bentonites, the maximum in Cr (VI) ions removal amounts was observed at lowest pH values. HTCC exhibits a part of unsubstituted –NH_2 groups. In an acidic medium, the –NH_2 groups exists in the protonated ammonium (–NH_3^+). The major chromate ions coexisting in the solution are $HCrO_4^-$ and CrO_4^{2-} and 99.1% of the Cr (VI) species belong to $HCrO_4^-$ at pH lower than 4.0. Therefore, the removal of Cr (VI) can be ascribed to the adsorption of $HCrO_4^-$ on HTCC–bentonite. At lower pH, the adsorption of Cr (VI) was realized by electrostatic interaction between HTCC and $HCrO_4^-$. With an increase in pH, less and less functional groups (–NH_2) was deprotonated and more OH^- ions competed with the coexistence of $HCrO_4^-$ and CrO_4^{2-} ions for the active surface sites. Consequently, it was difficult for them to form complexes and thus, the removal efficiency of Cr (VI) was decreased. Therefore, a pH value of 1.0 was applied for further experiments.

3.2.2. *Effect of initial Cr (VI) ion concentration on Cr (VI) adsorption*

Cr (VI) adsorption is significantly influenced by the initial concentration of Cr (VI) in aqueous solutions. The adsorption experiments are performed to study the effect of initial Cr (VI) concentration by varying it from 57 to 570 mg L^{-1} at an initial pH value of 1.0. Obtained results are presented in Fig. 7. The results show that with an increase in the Cr(VI) concentration from 57 to 570 mg L^{-1}, the removal efficiency decreases from 88.5 to 68.9% and the adsorption capacity increases from 2.52 to 17.9 mg g^{-1}. The decrease in the removal efficiency of Cr (VI) can be explained with the fact that all the adsorbents have

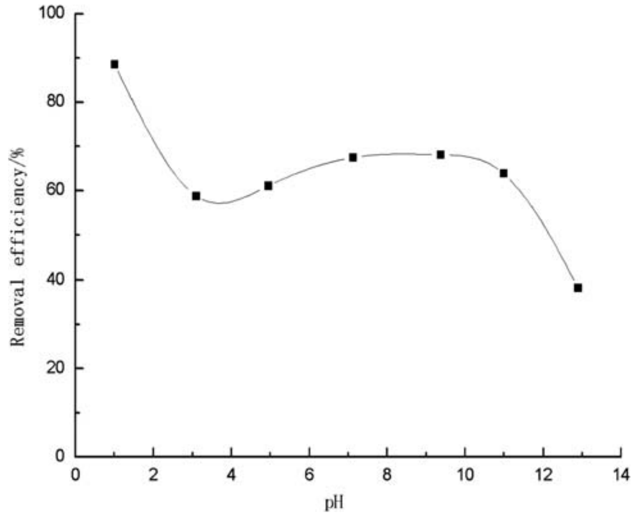

Fig. 6. Effect of pH on Cr (VI) adsorption.

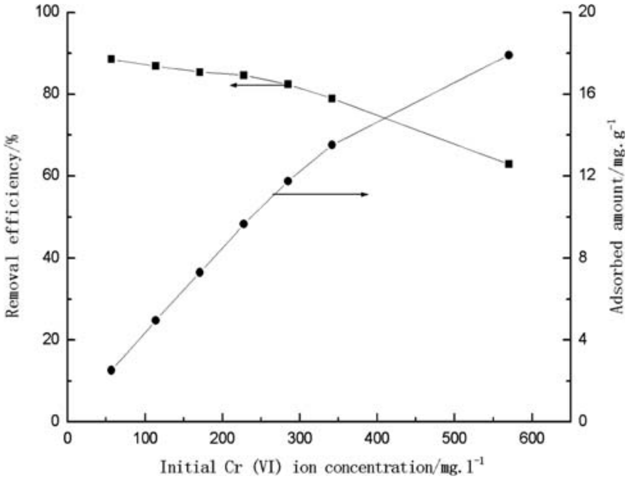

Fig. 7. Effect of initial concentration on Cr (VI) adsorption.

a limited number of active sites, which would saturate above a certain concentration. The increase in adsorption capacity with an increase in the Cr (VI) concentration may be due to the higher adsorption rate and the utilization of all the active sites available for the adsorption at higher concentration. For an initial Cr (VI) concentration of the 342 mg L^{-1}, the values of Cr (VI) removal and the amount absorbed were found to be 80.0% and 14.5 mg g^{-1}, respectively.

3.2.3. Effect of adsorbent dosage on Cr (VI) adsorption

The influence of HTCC–bentonite dosage varying from 0.5 to 2.5 g on the Cr(VI) adsorption is shown in Fig. 8. The removal efficiency of Cr (VI) increases from 77.5 to 88.5% as the amount changes from 0.5 to 1.0 g, afterward the removal efficiency decreases; while the amount absorbed decreases from 8.83 to 1.80 mg g^{-1} by increasing the adsorbent amount from 0.5 to 2.5 g. An increase in removal efficiency can be attributed to an increase in the number of active adsorption sites. However, the decreasing removal efficiency with a further increase in adsorbent dosage was unexpected. We cannot provide the reason about it. A decrease in adsorption capacity may be due to a reduction in both effective surface area and adsorbate/adsorbent ratio. Here, the adsorbent dosage of 1.0 g was chosen for the latter experiments.

3.2.4. Effect of contact time and temperature on Cr (VI) adsorption

The effect of contacting time on Cr (VI) adsorption on HTCC–bentonite is investigated at varied temperature from 20 to 50℃. Obtained results are shown in Fig. 9. It is evident that an increase in the contact time has a negligible effect on the removal efficiency. The nature of adsorbent and the available adsorption sites affect the rate of adsorption of Cr (VI). During the process of adsorption, the adsorbate needs to transfer from the solute to the solid including the diffusion through the fluid film around the adsorbent particle and the diffusion through the pores to the internal adsorption sites. In the initial stages of adsorption of Cr (VI), the concentration gradient between the film and the available pore sites was large and hence, the rate of adsorption of Cr (VI) was faster. The equilibrium time obtained was 30 min for the Cr (VI) adsorption on HTCC–bentonite. The removal efficiency of Cr (VI) changed slightly with a further increase in contact time. While increasing the temperature from 20 to 50° C, the removal efficiency decreased from 88.0 to 84.0% for initial 30 min of contact time. It implies that the adsorption of Cr (VI) was favored at lower temperature and it was controlled by an exothermic process.

3.3. Adsorption isotherm study

The equilibrium studies are useful to obtain the adsorption capacity of HTCC–bentonite for Cr (VI) removal. In this study, both Langmuir and Freundlich equilibrium models are analyzed to investigate the suitable adsorption isotherm.

3.3.1. Langmuir isotherm

To examine the relationship between adsorbent and adsorbate at equilibrium and to search for the maximum sorption capacity of adsorbent, sorption

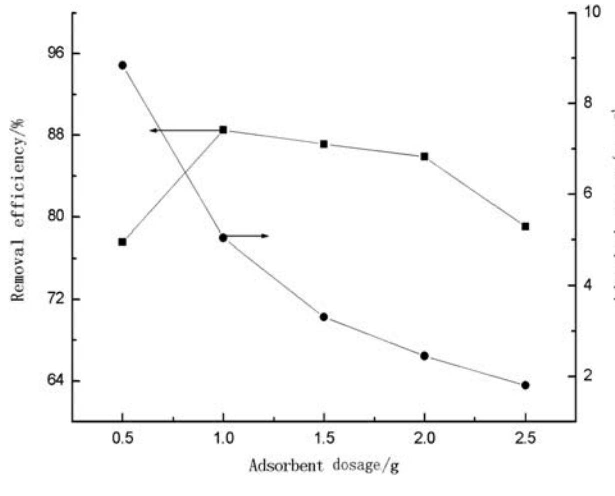

Fig. 8. Effect of adsorbent dosage on Cr (VI) adsorption.

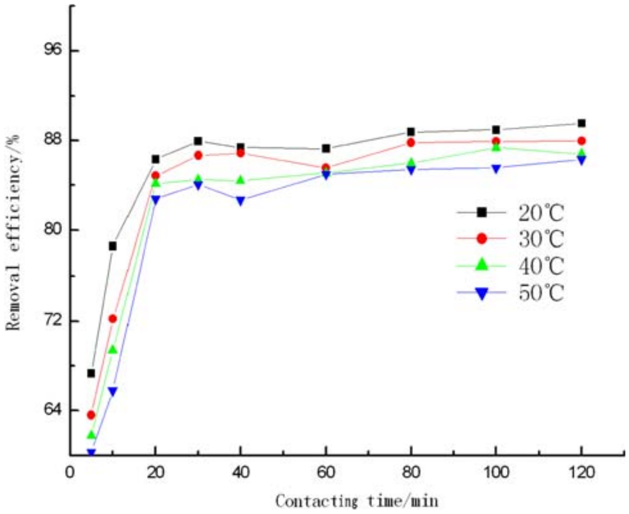

Fig. 9. Effect of contacting time and temperature on Cr (VI) adsorption.

isotherm models, such as Langmuir and Freundlich isotherms, are generally applied. The Langmuir isotherm equation is represented by Eq. (1):

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \left(\frac{1}{Q_m}\right)C_e \tag{1}$$

where, b is the adsorption equilibrium constant ($\mathrm{L\,mg^{-1}}$) that is related to the apparent energy of adsorption, Q_m is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent ($\mathrm{mg\,g^{-1}}$), and q_e is the amount adsorbed on unit mass of the adsorbent ($\mathrm{mg\,g^{-1}}$) when the equilibrium concentration is C_e ($\mathrm{mg\,L^{-1}}$).

A plot of (C_e/q_e) vs. C_e should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium. The slope and the intercept of this line then yield the values of constants Q_m and b, respectively. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L [27], also known as the separation factor, given by Eq. (2):

$$R_L = \frac{1}{1 + bC_0} \tag{2}$$

where C_0 is the initial concentration of Cr (VI) in $\mathrm{mg\,L^{-1}}$. The value of R_L is calculated from the above expression. The nature of adsorption process should be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

The isotherm data have been linearized using the Langmuir equation and is plotted between (C_e/q_e) vs. C_e which is shown in Fig. 10. The high value of coefficient of determination ($R^2 = 0.999$) obtained indicates a good agreement between the experimental values and isotherm parameters and reveals the monolayer adsorption of Cr (VI) onto the HTCC–bentonite surface. The monolayer adsorption capacity of HTCC–bentonite (Q_m) was obtained as $22.17\,\mathrm{mg\,g^{-1}}$. The Langmuir constant, b, which denotes adsorption energy, was found to be $0.0206\,\mathrm{L\,mg^{-1}}$. The dimensionless parameter, R_L, a measure of adsorption favorability, was in the range of 0.0785–0.4602 ($0 < R_L < 1$), which indicates the favorable adsorption process for Cr (VI) removal using HTCC–bentonite.

The maximum monolayer adsorption capacity, Q_m, has been widely used to compare the efficiency of an absorbent. Table 1 indicates that the HTCC–bentonite prepared in this work had a moderate adsorption capacity of 22.17 mg/g for Cr(VI) at 293 K, as compared to some data obtained from the other adsorbents based on clay.

3.3.2. Freundlich isotherm

The Freundlich adsorption isotherm can be expressed as follows:

$$\log q_e = \log k_f + \frac{1}{n}\log c_e \tag{3}$$

where k_f is the Freundlich constant, which indicates the relative adsorption capacity of the adsorbent related to the bonding energy, and n is the heterogeneity factor representing the deviation from linearity of

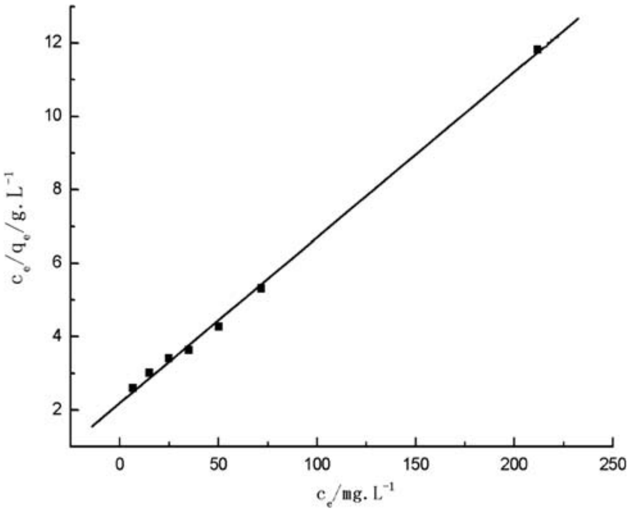

Fig. 10. Langmuir isotherm for the adsorption of Cr (VI) adsorption on HTCC-bentonite.

Table 1
Comparisons of the adsorbents based on bentonite

Adsorbent	Adsorption capacity	Reference
Mihalıççık clay (HDTMA-modified)	10.18 mg/g	[28]
Bentonite (QB) based organoclays synthesized from Arquad® 2HT-75 (Aq)	13.57 mg/g	[29]
Bentonitemodified with poly(4-vinylpyridine) (P4VP) (Bf0.3)	29.85 mg/g	[30]
Bentonite modified with cetylpyridinium bromide (CPBr)	0.72 mmol/g	[15]
Bentonite supported nZVI	16.67 mg/g	[31]
Palygorskite clay	58.5 mg/g	[32]
Bentonite modified with HTCC	22.17 mg/g	This study

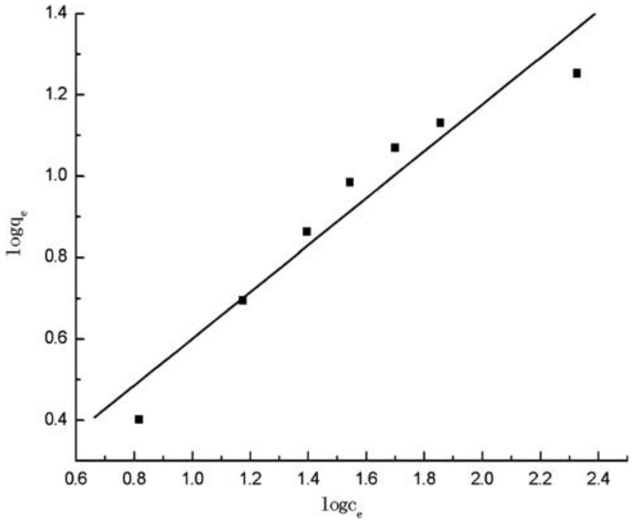

Fig. 11. Freundlish isotherm for the adsorption of Cr (VI) on HTCC-bentonite.

adsorption. The Freundlich coefficients can be determined from the plot of log q_e vs. log c_e (Fig. 11).

The values of k_f and n obtained are 1.0572 and 1.736, respectively. It is found the coefficient of determination for Freundlich isotherm model is obtained as 0.9668. The fit of the data for Cr (VI) onto HTCC–bentonite suggests that the Langmuir model gives slightly better fitting than the Freundlich model, as it is obvious from a comparison of these R^2 values. It suggests that the surface of HTCC–bentonite was made up of homogenous adsorption patches, not heterogeneous adsorption patches.

4. Conclusions

An adsorbent was prepared with HTCC and bentonite, which was named as HTCC–bentonite. It was nanocomposite. The results shown from SAXRD and TEM indicate that HTCC was not only loaded on the surface of bentonite, but also intercalated into the interlayer of bentonite. The adsorption of Cr (VI) ions onto HTCC–bentonite was investigated. The pH of the medium was the controlling parameter of this adsorption process. The maximum adsorption was observed at a pH value of 1. Adsorption of chromium on HTCC–bentonite was favored at lower temperature and established equilibrium in 30 min. The experimental data fit well with Langmuir isotherm model and the maximum adsorption capacity obtained was 22.17 mg g^{-1}. HTCC–bentonite can be used as an effective adsorbent for the removal of toxic Cr (VI) ions from aqueous solution.

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