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Preparation and simultaneous adsorption of an organobentonite towards phenol and Cr(VI)

Ruihua Huang[a,]*, Bo Wang[a], Bingchao Yang[c], Dongsheng Zheng[b], Zengqiang Zhang[a]

[a]*College of Science, Northwest A & F University, Yangling, Shaanxi 712100, China*
Tel. +86 029 87092226; email: huangrh20022002@aliyun.com
[b]*College of Resources and Environment, Northwest A & F University, Yangling, Shaanxi 712100, China*
[c]*Xi'an Institute of Geology and Mineral Resource, Xi'an, Shaanxi 710054, China*

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ABSTRACT

An adsorbent was prepared from bentonite modified by hexadecyltrimethylammonium bromide (HDTMAB) and N-2-hydroxypropyl trimethyl ammonium chloride chitosan (HTCC). This adsorbent was named as HDTMAB–HTCC bentonite. It would be used for the simultaneous adsorption of phenol and Cr(VI) from aqueous solution. By the method of single-factor experiment, the optimum preparation conditions of HDTMAB–HTCC bentonite were obtained. For bentonite (5 g), 1.0 g HDTMAB and 0.5 g HTCC were adopted as the modifying reagents. The reaction was carried out for 2 h at 80°C. The removals towards phenol and Cr(VI) enhanced with the increase in the amount of adsorbent dosage. The relatively high removals towards phenol and Cr(VI) occurred at a pH value of 1.5 or so. During the simultaneous adsorption process of phenol and Cr(VI), phenol was adsorbed by the partition from the organic phase formed by HDTMAB, while Cr(VI) was mostly adsorbed by the electrostatic interactions between HTCC and Cr(VI). No direct competition was observed due to different adsorption sites.

Keywords: Phenol; Cr(VI); HDTMAB–HTCC bentonite; Preparation; Simultaneous adsorption

1. Introduction

Phenol is widely distributed as an environmental pollutant due to its presence in the effluents of many industries, including oil refineries, petrochemical plants, ceramic plants, steel plants, and coal-conversion and phenolic resin industries. Due to its toxicity and adverse effect on humans and local biota, it is classified as a priority pollutant.

Many studies on removal of phenol and its derivatives from water by adsorption using organoclay have been reported [1,2]. Organobentonites are produced by the exchange of organic cations (typically having a quaternary ammonium and an aliphatic structure) for inorganic ions (e.g. H^+, Na^+, and Ca^{2+}) on the surface layers of bentonite [3]. As the bentonite is progressively intercalated by a surfactant, the surface properties of the clay change considerably, and so does the ability of the organobentonite to remove contaminants from water. Therefore, organobentonites are often better adsorbents for nonionic organics relative to natural bentonite and other clays [4,5]. Rawajfih and Nsour [6] and Senturka et al. [7] prepared an organobentonite by modifying bentonite with hexadecyltrimethylammonium bromide

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*Corresponding author.

(HDTMAB), and investigated the adsorption mechanism of single phenol on this organobentonite. The organic phase derived from adsorbed HDTMAB was the primary sorptive phase for phenol. Their results revealed that the bentonite modified with HDTMAB may remove phenol from aqueous solution effectively, with a max adsorption capacity of 105 and 333 mg/g, respectively.

However, in many countries (e.g. in China), municipal and industrial wastewaters are always mixed together, thus these wastewaters may contain a few organic contaminants including phenol and aniline, etc. and heavy metals such as Cr(VI), Pb(II), and Cd (II), etc. Various methods of wastewater treatment were examined and adsorption emerged as one of the important promising technique [8–10]. However, as an adsorbent, organobentonites obtained from a single surfactant became less effective for heavy metals with more cationic surfactants on the surface of bentonite [11,12]. Thus, it was necessary to prepare a new adsorbent to conduct the simultaneous adsorption of these pollutants from water. At present, there are only a few reports about the simultaneous adsorption of organic contaminants and heavy metals, and most researchers mainly focus on the simultaneous adsorption of cation metals ions such as Pb(II) and Cd(II), etc. and organic contaminants [13–16]. To our knowledge, there are no reports about the simultaneous adsorption of anion metals ions (Cr(VI)) and organic contaminants.

N-2-hydroxypropyl trimethyl ammonium chloride chitosan (HTCC) is one of the derivatives from chitosan. It is a cation polymer due to a distribution of quaternary ammonium groups in HTCC. HTCC is itself a good adsorbent and flocculent agent due to its unique properties, such as biocompatibility, biodegradation, biological activity, low toxicity, etc. 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 when it was applied in the adsorption of Cr(VI) as an adsorbent. Therefore, we consider if an adsorbent is prepared by HTCC loaded onto bentonite, the amount of HTCC would reduce, and the loss of HTCC would be avoided. Besides, the adsorption of Cr(VI) onto this adsorbent would be executed.

In this study, phenol and Cr(VI) were selected as the contaminants, and they coexist in aqueous solution. An adsorbent would attempt to be synthesized from bentonite modified with HDTMAB and HTCC. It was explored as a potential adsorbent to remove phenol and Cr(VI) simultaneously from the aqueous solution. The preparation of HDTMAB–HTCC bentonite was investigated. Simultaneous adsorption characteristics of the HDTMAB–HTCC bentonite obtained towards phenol and Cr(VI) were examined with batch experiments.

2. Materials and methods

2.1. Materials

HTCC(N-2-hydroxypropyl trimethyl ammonium chloride chitosan) with a substitution degree of 86.9% was prepared according to our pervious lecture [18]. Bentonite powder with a particle size of 200-mesh was acquired from the chemical factory of Shentai, Xinyang, Henan, China. Phenol and potassium dichromate were obtained from Aladdin (analytical grade) and used as obtained without further purification. A stock solution of 1,000 mg L^{-1} phenol was prepared by dissolving 1.00 g of phenol (Merck, Darmstadt, Germany) in 1 L of deionized water. The concentration of phenol was determined by a double-beam UV–vis spectrophotometer (Unicam UV-2) at 508 nm by the 4-aminoantipyrene method [19]. Stock chromiumsolution of 1,000 mg/L was prepared by dissolving 2.828 g of potassium dichromate in 1 L of deionized distilled water. All working solutions of varying concentrations were obtained by successive dilution. The total chromium concentration in the solution was determined by flame atomic adsorption spectrometry (HITACHI Z-2000). All other chemicals used in this work, were of analytical reagent grade, and were used without further purification.

2.2. Adsorbent preparation

The adsorbent was synthesized by slow addition of a certain amount of HDTMAB and HTCC complex solution to 5 g bentonite powder soaked in 30 mL water under vigorous stirring, and the resulting suspension was stirred for 2 h at 80℃. The composite obtained was then washed with deionized water. Washing was repeated until the supernatant solution was free of Br^- and Cl^- ions, as indicated by the $AgNO_3$ test. The clay was oven-dried at 105℃ until the water was completely evaporated. Large clumps of the organoclay were pulverized with a mortar and pestle. The organoclay was then stored in airtight containers until it was used in sorption experiments. The organoclay was referred to as HDTMAB–HTCC bentonite. The similar characteristics of HDTMAB–HTCC bentonite have been reported in our pervious study [20]. It was found that it was found that HDMTA was apt to intercalate in bentonite while HTCC cannot intercalate in bentonite effectively due to its big molecular structure, and hence was only loaded on the surface of bentonite.

2.3. *Adsorption experiments*

Batch experiments were conducted to study the simultaneous sorption of phenol and Cr(VI) onto HDTMAB–HTCC bentonite. These experiments were carried out by shaking clay with 50 mL complex aqueous solutions of phenol and Cr(VI) for 40 min in a water bath shaker at 200 rpm at room temperature, and then centrifuged at 5,000 rpm for 5 min. For the preparation of HDTMAB–HTCC bentonite, these effects of the amounts of HDTMAB and HTCC, reaction temperature and time on the removals of phenol and Cr(VI) were measured. Here, both the initial phenol and Cr(VI) concentrations were fixed at 50 mg/L, and pH of the complex solution was not adjusted. For the simultaneous adsorption of phenol and Cr(VI), the effect of adsorbent dosage and pH value of the complex aqueous solutions on the removals of phenol and Cr(VI) was investigated. Besides, the interaction effect between phenol and Cr(VI) was also determined. The reaction between phenol and Cr(VI) may be neglected because these adsorption experiments were conducted at room temperature. At the end of the predetermined time, the solutions were centrifuged and the supernatant solutions were analyzed for residual phenol and Cr(VI) using a UV–visible spectrophotometer and flame atomic adsorption spectrometry, respectively. The amount of phenol and Cr(VI) adsorbed was calculated by the difference between the initial and final solution concentrations. All experiments were at least duplicated, and the averages of the results were submitted for data analysis.

3. Results and discussion

3.1. *Determination of preparation conditions HDTMAB–HTCC bentonite*

3.1.1. *Effect of the amount of HDTMAB on the removals of phenol and Cr(VI)*

To investigate the effect of the amount of HDTMAB on the removals of phenol and Cr(VI), the amount of HDTMAB was varied from 0.2 to 1.6 g. The adsorbents prepared were named as HDTMAB–bentonite. It was found that more foam is formed, and fewer products are obtained with the increase in the amount of HDTMAB. The removals are presented in Fig. 1. It can be seen that the removal towards phenol enhances with increasing the amount of HDTMAB up to 1.0 g, afterwards it keeps constant. HDTMAB is one of cationic surfactants used to modify bentonite. HDTMAB is apt to intercalate in bentonite during the modifying process, resulting in the increasing interlayer distance. Meanwhile, a hydrophobic environment exists near the surface of bentonite. Therefore, it is expected that the removal towards phenol increases with the increasing interlayer distance and the formation of hydrophobic environment. However, the removal towards Cr(VI) is low than 20%, which is not plotted. This result suggests that HDTMAB–bentonite is not an effective adsorbent for Cr(VI) under this experimental condition. However, Sibel et al. and Krishna et al. observed a relatively high removal towards Cr(VI), when HDTMAB–bentonite was used for the adsorption of Cr(VI) [21,22]. The difference from this work can result from the different properties of the organoclay used, the adsorbates, and adsorption conditions. Here, 1.0 HDTMAB was chosen for further experiments.

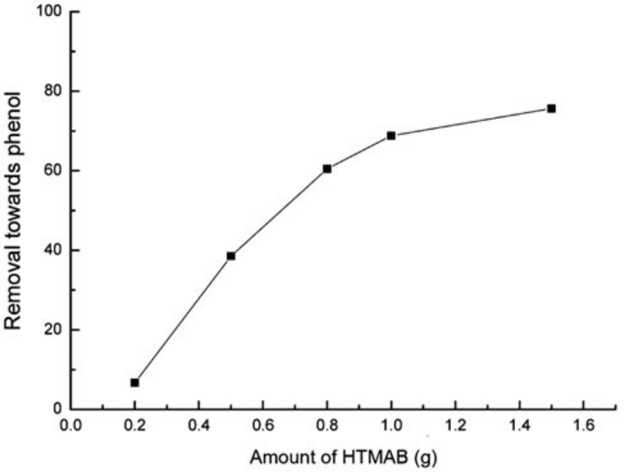

Fig. 1. Effect of the amount of HTMAB on the removal of phenol and Cr(VI).

3.1.2. *Effect of the amount of HTCC on the removals of phenol and Cr(VI)*

To improve the removal towards Cr(VI), bentonite was modified with HDTMAB and HTCC. The amount of HTCC changed from 0 to 1.5 g, and 1.0 g HDTMAB was kept. The results (Fig. 2) show that the removal towards phenol decreases, while the one towards Cr (VI) increases obviously when increasing the amount of HTCC. As mentioned previously, there is a distribution of quaternary ammonium groups in HTCC. When increasing the addition of HTCC, HTCC loaded on bentonite increases accordingly, so does the positively charge, and thus the removal towards Cr(VI)

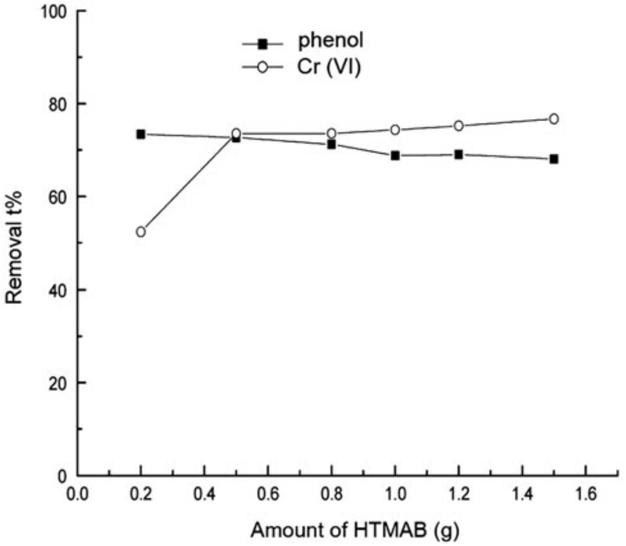

Fig. 2. Effect of the amount of HTCC on the removal of phenol and Cr(VI).

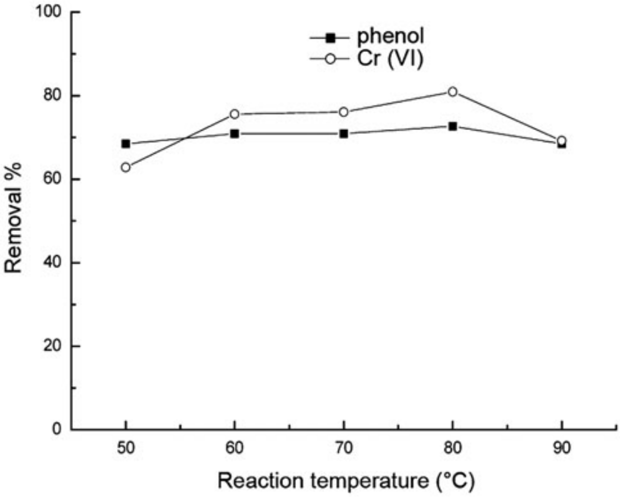

Fig. 3. Effect of reaction temperature on the removal of phenol and Cr(VI).

increases because of the substantial electrostatic interaction between HTCC and Cr(VI). However, the explanation about the decreasing removal towards phenol may be represented like this, when HDTMAB, and HTCC are applied in the modification of bentonite, HDTMAB and HTCC would compete for the finite adsorption sites of bentonite. HTCC loaded on bentonite has occupied a part of the finite adsorption sites on bentonite, so only finite HDTMAB can intercalate in bentonite, and hence the adsorption of phenol onto HDTMAB–HTCC bentonite decreases compared to the bentonite modified with single HDTMAB. Besides, the removal towards phenol reduces with the increase in the amount of HTCC loaded in bentonite. Considering the removals of phenol and Cr(VI) together, 0.5 g HTCC was adopted.

3.1.3. Effect of reaction temperature on the removals of phenol and Cr(VI)

For this effect, a serial of HDTMAB–HTCC bentonites was prepared with 1.0 g HDTMAB and 0.5 g HTCC under different temperature, and the removals towards phenol and Cr(VI) were investigated. The results (Fig. 3) show that the reaction temperature affects the removal towards Cr(VI), while it almost has no influence on the one towards phenol. Based on the results in Fig. 2, we found that HTCC played a pretty important role in the increase in the removal of Cr(VI). Therefore, it was thought that the reaction temperature mainly affected the contact between HTCC and bentonite. The molecular chain of HTCC becomes slack with the increase in reaction temperature. Therefore, HTCC is prone to approach bentonite due to its slack molecular chain, more HTCC would be loaded on bentonite, and hence an increase in the removal towards Cr(VI) is observed when increasing the reaction temperature. However, a further increase in reaction temperature can destroy the molecular structure of HTCC, so HDTMAB–HTCC bentonite prepared under a relatively high reaction temperature shown a decrease in the removal towards Cr(VI). Therefore, the reaction temperature of 80℃ was chosen.

3.1.4. Effect of reaction time on the removals of phenol and Cr(VI)

To investigate this effect, a serial of HDTMAB–HTCC bentonites was prepared with the reaction time ranging from 1 to 8 h, and the removals towards phenol and Cr(VI) were determined. The results (Fig. 4) show that the removal towards phenol enhances slightly, while the one towards Cr(VI) initially increases, and then decreases slightly when prolonging the reaction time. The maximum removal towards Cr(VI) occurs at 2 h. As mentioned in Section 3.1.3, HTCC plays a pretty important role in the removal of Cr(VI). More HTCCs approach bentonite with the increase in reaction time, HTCC loaded on bentonite increases accordingly, and thus HDTMAB–HTCC bentonites prepared show an increase in the removal towards Cr(VI). However, the loading process of HTCC on bentonite is also the adsorption process of HTCC onto bentonite, so the adsorption

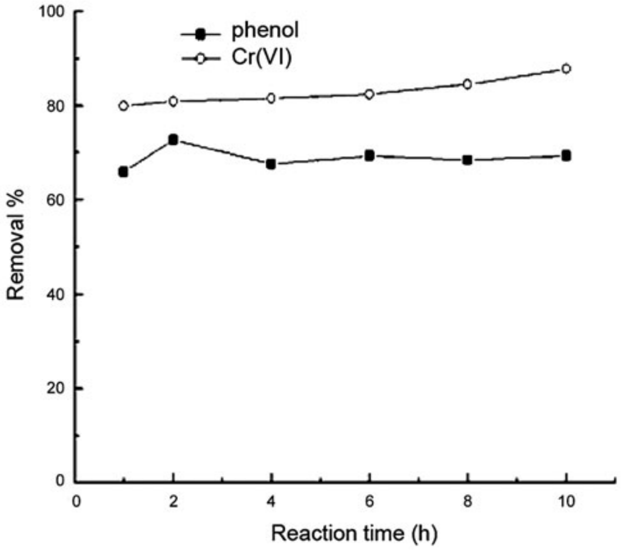

Fig. 4. Effect of reaction time on the removal of phenol and Cr(VI).

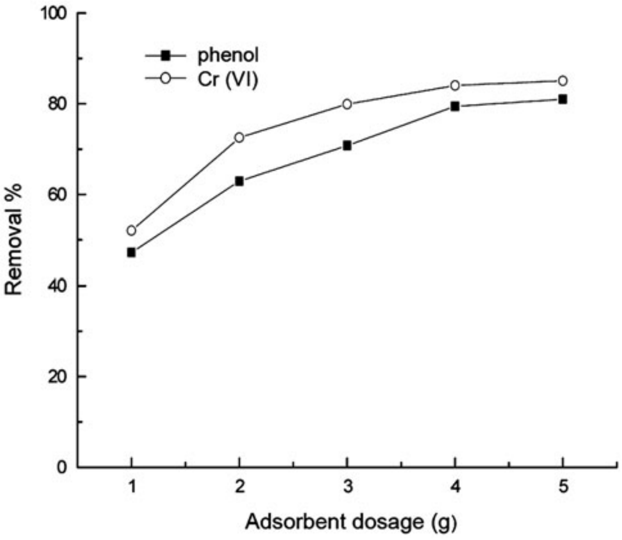

Fig. 5. Effect of the dosage of adsorbent on the removal of phenol and Cr(VI).

and desorption of HTCC would exist at the same time. When the desorption of HTCC predominates over the adsorption with a further increase in reaction time, the amount of HTCC loaded on bentonite decreases, and thus more adsorption sites are available for HDTMAB. Therefore, HDTMAB–HTCC bentonite shows a decrease in the removal towards Cr(VI) and an increase in the one towards phenol when prolonging the reaction time further. Considering the removal of phenol and Cr(VI) together, the reaction time of 2 h was chosen.

Through the investigation of the above factors, the optimum preparation conditions is presented as follows, for bentonite (5 g), 1.0 g HDTMAB, and 0.5 g HTCC are adopted as the modifying reagents, respectively. The reaction is carried out for 2 h at 80℃. The HDTMAB–HTCC bentonite prepared under optimal conditions would be applied to conduct the following adsorption experiments.

3.2. Adsorption Characteristics of HDTMAB–HTCC bentonite

3.2.1. Effect of the dosage of adsorbent on the removals of phenol and Cr(VI)

Experiments were conducted with HDTMAB–HTCC bentonites having different dosages varying from 1 to 5 g in order to determine the effect of adsorbent dosage on adsorption. The removals towards phenol and Cr(VI) increases with the increase in the dosage of the clay, and they are almost constant at larger dosages than 4.0 g as shown in Fig. 5. This is due to the fact that more active sites are available for adsorption when increasing adsorbent dosage, and hence the removals increased reasonably. However, no change in adsorption is mainly attributed to these sites remaining saturated during the adsorption process. Here, the adsorbent dosage of 4 g was chosen for further experiments.

3.2.2. Effect of pH on the removals of phenol and Cr(VI)

It is well-known that the initial pH of a system is an important parameter in the adsorption of Cr(VI) or phenol. In this study, the initial pH value varying from of 1–13 was investigated. The influence of the pH of the solution on the removals towards phenol and Cr(VI) is exhibited in Fig. 6. When changing the initial pH value from 1.5 to 10.6, the removal towards Cr(VI) decreases slowly, while the one towards phenol almost keeps constant. With a further increase in pH up to 13, they reduced sharply. For phenol, the pKa value of phenol at 20℃ is 10 or so. When the pH of the solution is low than the pKa of phenol, the phenol molecules exists in solution. The constant removal towards phenol suggests that the adsorption of phenol onto HDTMAB–HTCC bentonite is realized typically through a partitioning process. However, for Cr(VI), the major chromate ions coexisting in the solution are $HCrO_4^-$ and CrO_4^-, and 99.1% of the Cr(VI) species belong to $HCrO_4^-$ at pH lower than 4.0. Fig. 6 shows that the maximum adsorption of Cr(VI) ions is observed at pH 1.5 or so. Similar results were

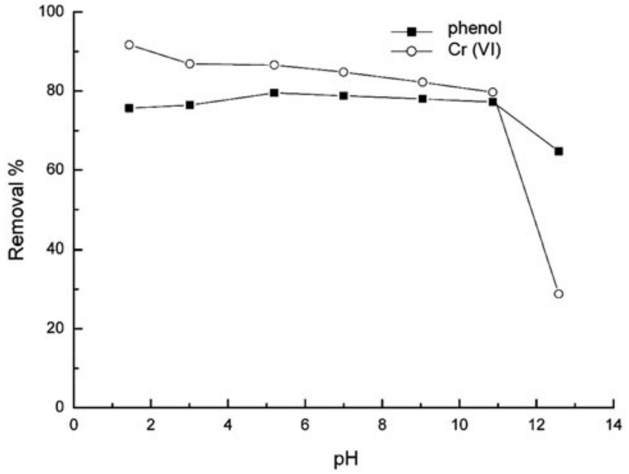

Fig. 6. Effect of pH on the removal of phenol and Cr(VI).

reported for adsorption of Cr(VI) species on poly (4-vinylpyridine) (P4VP)/bentonite composite [23]. 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. HTCC is one of the derivatives from chitosan, there are a part of unsubstituted –NH_2 groups in HTCC. In an acidic medium, the –NH_2 groups exists in the protonated ammonium (–NH_3^+). Besides, there is a distribution of positively charged quaternary ammonium groups in HTCC. These positive charged groups result in a stronger attraction for negatively charged Cr(VI) ions in the solution, and hence it would facilitated Cr(VI) ions to be adsorbed by HDTMAB–HTCC bentonite. With an increase in pH, less functional groups (–NH_2) are deprotonated. As the pH of the solution exceeds 11.0, the phenol molecules are ionized to the negative charged phenolate ions. Therefore, OH^- ions would compete with phenolate and Cr(VI) ions for the active surface sites, leading to a sharp decline in removals towards phenol and Cr(VI). Here, pH value of 1.5 was applied.

3.2.3. Adsorption of Cr(VI) in the presence of phenol

The removals of Cr(VI) by HDTMAB–HTCC bentonite in the presence and absence of phenol are shown in Fig. 7(a). Results indicate that Cr(VI) sorption is not affected by the initial concentration. Besides, no competitive effect is observed for Cr(VI) ions adsorption onto HDTMAB–HTCC bentonite in the presence of phenol. As mentioned in Section 3.2.2, the adsorption of phenol onto HDTMAB–HTCC bentonite is typically realized through a partitioning process, that is, the interaction between phenol and the organic phase created by the alkyl chains of the HDTMAB cations. However, Cr(VI) ions are mainly adsorbed onto HDTMAB–HTCC bentonite by the electrostatic interactions between HTCC and Cr(VI) ions. Therefore, Cr(VI) ions and phenol are not adsorbed at the same sites, and hence the adsorption of Cr(VI) ions is not affected by the addition of phenol onto HDTMAB–HTCC bentonite.

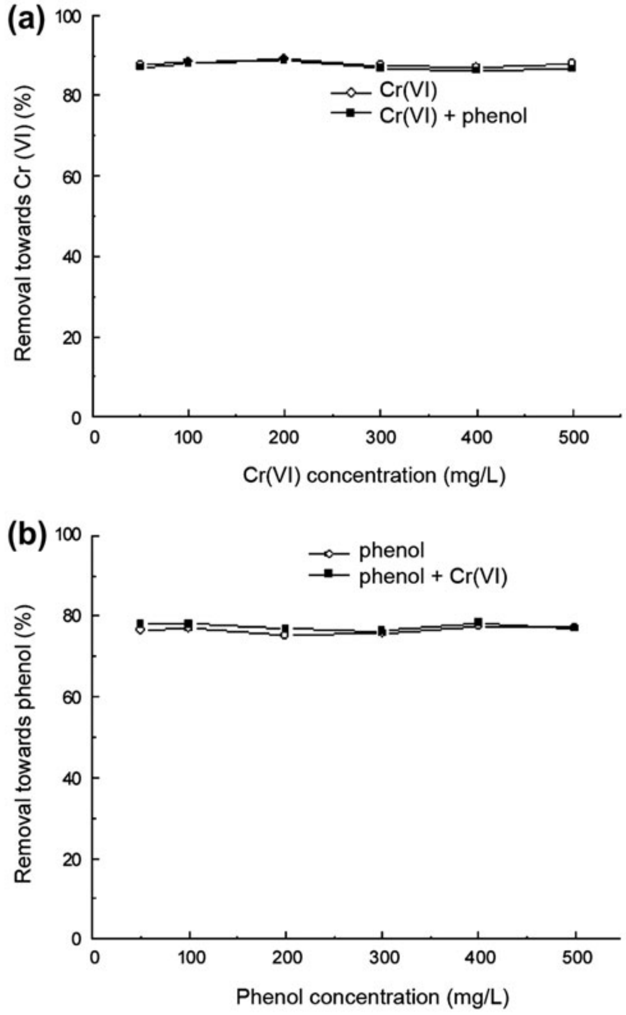

Fig. 7. The interactive effect between phenol and Cr(VI).

3.2.4. Adsorption of phenol in the presence of Cr(VI)

The removals of phenol by HDTMAB–HTCC bentonite in the presence and absence of Cr(VI) are shown in Fig. 7(b). The sorption of phenol is similar to that of Cr(VI) as shown in Fig. 7(a). Phenol sorption is not affected by the initial concentration. The adsorption of phenol onto HDTMAB–HTCC bentonite almost keeps invariable in the presence of Cr(VI), relative to the one of phenol as a single solute. The results indicate that there is no significant competition for adsorption between phenol and Cr(VI). The reason for this may come from the different sorption sites of phenol and Cr(VI) ions. While phenol is partitioned into the organic phase of interlayer space from HDTMAB, Cr(VI) ions are mostly adsorbed by the electrostatic interactions between HTCC and Cr(VI) ions. Cr(VI) ions and phenol are not adsorbed at the same sites.

By the investigation of Sections 3.2.3 and 3.2.4, a conclusion is obtained that no competition is observed between Cr(VI) and phenol, that is, the adsorption of Cr(VI) is not affected by phenol sorption, and vice versa in the concentration ranges used in this study. Similar results were also seen by Lee et al. [13]. When Lee et al. investigated the simultaneous sorption of lead and chlorobenzene by organobentonite, there was no obvious competition for sorption between chlorobenzene and lead. The reason for this came from the different sorption sites of chlorobenzene and lead. While chlorobenzene was partitioned into the organic phase of interlayer space, which was modified by HDTMAB, lead would be mostly adsorbed on cation exchange sites not occupied by HDTMAB and bound to the edge site of bentonite. In this study, it is just because of the different adsorption that no competition exists between Cr(VI) ions and phenol.

4. Conclusions

HDTMAB and HTCC are used to modify bentonite simultaneously. The composite obtained is named as HDTMAB–HTCC bentonite. It is applied in the simultaneous adsorption of phenol and Cr(VI) as an adsorbent. The preparation of HDTMAB–HTCC bentonite was investigated. The optimal conditions were listed: for bentonite (5 g), 1.0 g HDTMAB, and 0.5 g HTCC are adopted as the modifying reagents, respectively. The reaction is carried out for 2 h at 80˚C. Sorption experimental results show that the removals towards phenol and Cr(VI) ions increased with the increase in the amounts of HDTMAB and HTCC onto bentonite, respectively. Also, the reaction temperature and time affected the adsorption of Cr(VI) ions. No direct competition was noticed between Cr(VI) ions and phenol. During the simultaneous adsorption process of phenol and Cr(VI) ions, phenol was partitioned into the organic phase of interlayer space, while Cr(VI) was mostly adsorbed by the electrostatic interactions between HTCC and Cr(VI) ions.

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