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Preparation and simultaneous sorption of CTMAB–HTCC bentonite towards phenol and Cd(II)

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ABSTRACT

An experimental study was performed to investigate the feasibility of using cetyltrimethyl ammonium bromide (CTMAB) and *N*-2-hydroxypropyl trimethyl ammonium chloride chitosan (HTCC) bentonite (CTMAB–HTCC bentonite) for simultaneous sorption of phenol and Cd(II). The preparation of CTMAB–HTCC bentonite was listed as follows: for bentonite (5 g), 1.0 g CTMAB and 0.2 g HTCC was adopted as the modifying reagents; the reaction was carried out for 2 h at 60°C. The role of competition between phenol and Cd(II) was studied. The sorption of Cd(II) onto CTMAB–HTCC bentonite decreased in the presence of phenol relative to the sorption obtained without phenol presence. This decrease resulted from the steric hindrance caused by phenol. The sorption of phenol onto CTMAB–HTCC bentonite in the presence of Cd(II) was less than the sorption observed when no Cd(II) was present. This decrease was attributed to the formation of complex between ∏-electron in phenol and Cd(II), which was unfavorable for the adsorption of phenol onto CTMAB–HTCC bentonite by partitioning mechanism. Although sorption was decreased in the presence of the other, CTMAB–HTCC bentonite tested had dual sorptive properties for both heavy metals and an organic contaminant.

Keywords: CTMAB; HTCC; Bentonite; Simultaneous sorption; Phenol; Cd(II)

1. Introduction

Industrial wastewater contains many contaminating organic and inorganic materials, such as aromatic compounds, heavy metals and dyes. Many organic compounds and heavy metals have been classified as hazardous pollutants because of their potential toxicity to human health. And these pollutions often coexist in wastewater. Therefore, more attention should be paid to the treatment of wastewater containing composite pollutions.

There are many methods for the removal of organic pollutants or heavy metals from aqueous solutions, such as adsorption, chemical precipitation, ion exchange, membrane processes, biological degradation and chemical oxidation. Adsorption is the most popular method in which activated carbon or ion exchange resins are usually applied. Activated carbons have the advantage of high adsorption capacity for organic compounds. However, because of its relatively high cost, there have been attempts to utilize low cost, naturally occurring adsorbents, to remove contaminants from wastewater [1,2].

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Recently, the usage of natural mineral adsorbents for wastewater treatment is increasing because of their abundance and low price. One type of clay minerals is bentonite. Simple ion-exchange reactions can significantly modify the surface properties of natural bentonite. When organic cations (cationic surfactants) of the form $(CH_3)_3NR^+$, where R is an alkyl hydrocarbon, occupy the exchange sites of bentonite clay, the surface properties transform from hydrophilic to hydrophobic. Recent studies have shown that the molecular structure of cationic surfactants used to modify clay affects the mechanism of nonionic organic contaminants (NOC) sorption [3–6]. Smith et al. [3] demonstrated that small organic cations create a relatively rigid, nonpolar surface amenable to NOC uptake by surface adsorption. In contrast, large organic cat-ions create an organic partition medium for NOC uptake through the conglomeration of their flexible alkyl chains. However, the uptake of heavy metal ions onto organobentonites often results from surface adsorption. At present, there are many papers in the literature concerning the adsorption of single organic contaminant or heavy metal on bentonite and organobentonites [7–13]. However, organobentonites obtained by modifying bentionite with single cationic surfactants such as CTMAB can adsorb organic contaminants effectively, but they become less effective absorbents for heavy metals due to more cationic surfactants on the surface [14,15]. Therefore, it is difficult for this kind of absorbent to realize the simulation adsorption of organic contaminants and heavy metals.

HTCC, as a cat-ion 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. It was often used for the adsorption of heavy metal from aqueous solution due to its special structure. There were many active groups such as –OH and $–NH_2$ in HTCC, and these groups were prone to chelation with many heavy metals. Besides, there was a distribution of positively charged groups $(CH_3)_3NR^+$) in HTCC, and thus HTCC would be considered to modify bentonite with a negatively charged surface. The use of biopolymers as adsorbers is an emerging technique for the treatment of industrial effluent containing toxic metals, and has been of great interest to researchers [16,17].

In the present study, organobentonite was prepared by modifying bentonite with CTMAB and HTCC. Effect of preparation conditions on the removal of phenol and Cd(II) were investigated in detail. Organobentonite prepared under optimal conditions was used to simultaneously remove phenol (as a representative NOC) and Cd(II) (as a representative heavy metal).

2. Materials and methods

2.1. Materials and apparatus

The natural bentonite composed primarily of Na^+-montmorillonite, is obtained from the chemical factory of Shentai, Xinyang, Henan, China. The bentonite sample was pulverized and passed through a 200-mesh sieve. Analytical grade cetyltrimethylammonium bromide (CTMAB) obtained from Bio Life Science & Technology Co. Ltd. (Shanghai, China) was used without any purification for the modification. HTCC, with a substitution degree of 86.9%, was prepared according to our pervious lecture [18]. XRD patterns of the samples were done using an X-ray diffraction with Cu anode, running at 40 kV and 40 mA. Diffraction measurements were conducted within the 2θ angle of 0–50, at the scanning rate of 4 min^{-1}.

2.2. Adsorbent preparation

The procedure for the adsorbent preparation was as follows. Bentonite (5 g) was soaked in 30 ml water. The resulting mixture was placed in a three-neck round bottom flask, and 1.0 g of CTMAB in 20 ml of distilled water was added to it. The contents were stirred thoroughly using a vigorous stirrer for 30 min, and then 0.2 g of HTCC in 30 ml distilled water was added. And the resulting suspension was stirred for 2 h at 60°C. The products were collected by centrifugation and washed with distilled water. Finally, the product was dried in an oven at 105°C for 2 h and then ground to obtain a particle size of 200 mesh. The final product was referred to as CTMAB–HTCC bentonite. XRD patterns of CTMAB–HTCC bentonite and raw bentonite shown CTMAB can intercalate in bentonite effectively, while HTCC was only loaded on the surface of bentonite. CTMAB-HTCC bentonite obtained had a bigger interlayer spacing (18.5 A), increased by 4.3 A relative to raw bentonite (14.5 A).

2.3. Adsorption experiments

Batch experiments were conducted to study the simultaneous sorption of phenol and Cd(II) onto CTMAB–HTCC bentonite. These experiments were carried out by shaking clay with 50 ml complex aqueous solutions of phenol and Cd(II) for 40 min in a water bath shaker at 200 rpm at room temperature, and then centrifuged 5000 r min^{-1} for 5 min. For the preparation of CTMAB–HTCC bentonite, these effects of the amounts of CTMAB and HTCC, reaction temperature and time on the removals of phenol and Cd(II) were measured. Here, the initial concentrations of phenol and Cd(II) were both fixed at 50 mg l^{-1}, and pH of the complex solution wasn't adjusted. For the simultaneous adsorption of phenol and Cd(II), the effects of adsorbent dosage, pH value of the complex aqueous solutions, adsorption time and temperature on the removals of phenol and Cd(II) were investigated. Besides, the interaction effect between phenol and Cd(II) were also measured. When performing the adsorption of Cd(II) in the presence of phenol, the concentration of phenol was fixed at 500 mg l^{-1}, while Cd(II) concentration changed from 50 to 500 mg l^{-1}. When performing the adsorption of phenol in the presence of Cd(II), the concentration of Cd(II) was fixed at 200 mg l^{-1}, while phenol concentration varied from 50 to 500 mg l^{-1}. Without special specifications, the initial concentrations of phenol and Cd(II) were both fixed at 50 mg l^{-1}. At the end of the predetermined time, the solutions were centrifuged and the supernatant solutions were analyzed for residual phenol and Cd(II) using a UV–visible spectrophotometer and Atomic Absorption Spectrometry (AAS), respectively. The amount of phenol and Cd(II) adsorbed was calculated by the difference between the initial and final solution concentrations. All experiments were at least duplicated.

3. Results and discussion

3.1. Determination of preparation conditions about CTMAB–HTCC bentonite

3.1.1. Effect of the amount of CTMAB on the removals of phenol and Cd(II)

CTMAB is one of the surface active reagents, which are often used to modify bentonite [19,20]. The interlayer distance of the resultant bentonite increases, and a hydrophobic environment exists near the surface of bentonite due to the conglomeration of the alkyl chains of CTMAB. The increase in interlayer distance and the conglomeration of the alkyl chains of CTMAB would be helpful to the removal of organic substances [21,22]. To investigate the effect of the amount of CTMAB on the removals of phenol and Cd(II), the amount of CTMAB changed from 0.2 to 1.5 g. The results were shown in Fig. 1. The adsorption of phenol onto the modified bentonite improved with increasing the amount of CTMAB up to 1.2 g, afterwards it increased slightly. For hydrophobic compound, phenol, it was expected that its removal increased with the increasing interlayer distance and formation of hydrophobic environment. Similar results for non-polar organic compounds (NOCs) were also seen at Sheng et al. [23,24]. They explained that partitioning of these NOCs caused both the interlayer volume of organoclays and the solvency of HDTMA phase to increase. However, the removal of Cd(II) onto CTMAB bentonite reduced slowly. This trend was attributed to the conglomeration of the alkyl chains of CTMAB, which hindered Cd(II) to approach adsorption sites to a great degree. Besides, it was found that raw bentonite unmodified with CTMAB shown a relatively high removal towards Cd(II), which mainly resulted from cat-ion-exchange between Cd(II) and bentonite. In addition. It was observed that more foam was formed and fewer products were obtained with the increasing amount of CTMAB. Considering the removals of phenol and Cd(II) together, 1.0 g CTMAB was chose for further experiments.

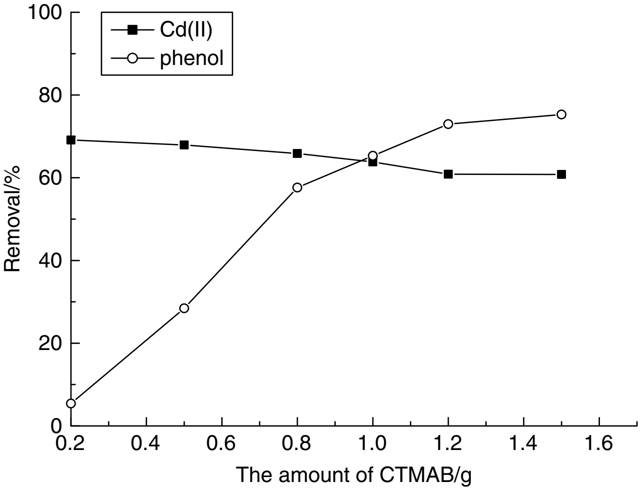

Fig. 1. Effect of the amount of CTMAB on the removals of phenol and Cd(II) Adsorption conditions: the complex solution tested was 50 mg l^{-1} phenol and 50 mg l^{-1} Cd(II); adsorption time was 40 min; adsorption temperature was room temperature; adsorbent dosage was 3 g; the pH value of solution was unadjusted.

3.1.2. Effect of the amount of HTCC on the removals of phenol and Cd(II)

From the results mentioned above, it was difficult for the bentonite modified with single CTMAB to improve the removal towards Cd(II), and thus bentonite would be modified together with CTMAB and HTCC. The amount of HTCC varied from 0 to 1.2 g, while the one of CTMAB kept constant at 1.0 g, the removals towards phenol and Cd(II) onto the bentonites prepared under different conditions were measured. These results (Fig. 2) shown that the removal of phenol decreased slightly, while the one of Cd(II) increased sharply, though a small dosage of HTCC was added. There are many active groups including –OH and $-NH_2$ in HTCC, so HTCC was prone to the chelation with Cd(II). When HTCC was used to modify bentonite, the bentonite obtained would allow a relatively high removal towards Cd(II) due to the significant chelation between HTCC and Cd(II). However, this removal didn't increase accordingly with a further increase in the amount of HTCC, which was ascribed to the low Cd(II) concentration tested.

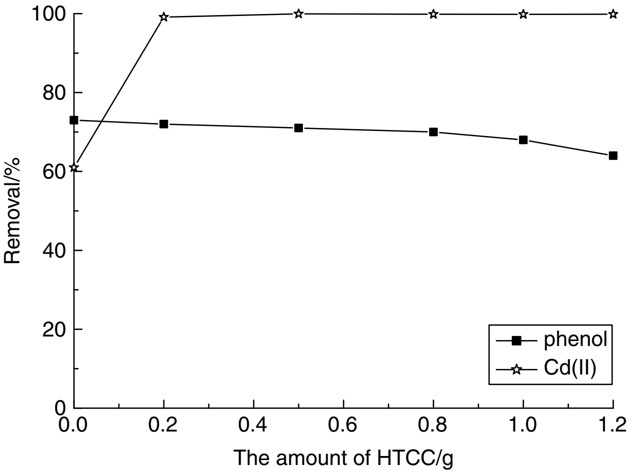

Fig. 2. Effect of the amount of HTCC on the removals of phenol and Cd(II) Adsorption conditions: the complex solution tested was 50 mg l^{-1} phenol and 50 mg l^{-1} Cd(II); adsorption time was 40 min; adsorption temperature was room temperature; adsorbent dosage was 3 g; the pH value of solution was unadjusted.

The explanation about the slightly decreasing removal towards phenol may be represented like this, the results from Huang et al. shown that HTCC was only loaded on the surface of bentonite, while CTMAB can interlacate in bentonite effectively, when HTCC and CTMAB were used to modify bentonite [25]. The adsorption of HTCC and CTMAB from water onto bentonite were governed mainly by electrostatic and hydrophobic interactions, respectively, but they interacted with bentonite, thus the competition adsorption onto bentionite existed between HTCC and CTMAB. HTCC loaded on bentonite had occupied a part of the finite adsorption sites on bentonite, so the bentonite modified with CTMAB and HTCC can't provide more sites for CTMAB with relative to the bentonite modified with single CTMAB, and hence the conglomeration of the alkyl chains of CTMAB reduced accordingly, leading to a decrease in the removal of phenol. The optimum amount of HTCC is 0.2 g.

3.1.3. Effects of reaction temperature and time on the removals of phenol and Cd(II)

The preparation of organobentonite was often carried out under a relatively high temperature [26–28]. To investigate the effect of reaction temperature on these removals, a serial of CTMAB–HTCC bentonites were prepared with 1.0 g CTMAB and 0.2 g HTCC under different temperature varying from 50°C to 90°C, and the removals towards phenol and Cd(II) were determined. The results (Fig. 3(a)) shown that the reaction temperature had a slight influence on the removal towards phenol, while it almost had no influence on the one towards Cd(II). Here, the reaction temperature of 60°C was chose.

For the effect of reaction time, these bentonites were prepared under 60°C and reaction time from 1 to 8 h. The removals towards phenol and Cd(II) were measured. As shown in Fig. 3(b), these removals towards phenol and Cd(II) had the similar trend to that of reaction temperature, when prolonging reaction time. These phenomena may be explained like this, as mentioned in Section 3.1.2, CTMAB and HTCC were adsorbed on bentointe by cation exchange or electrostatic interaction. The adsorption of CTMAB on bentonite was prone to be affected by external environment including reaction time and temperature relative to the one of HTCC on bentonite. Once the external environment changed, the adsorption

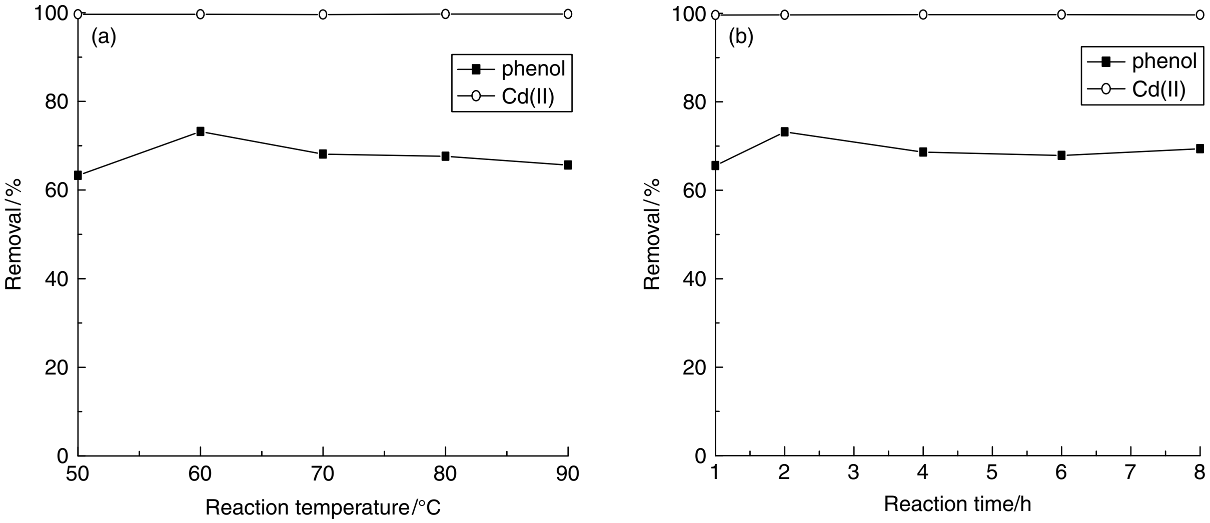

Fig. 3. Effect of the amount of reaction temperature and time on the removals of phenol and Cd(II) Adsorption conditions: the complex solution tested was 50 mg l^{-1} phenol and 50 mg l^{-1} Cd(II); adsorption time was 40 min; adsorption temperature was room temperature; adsorbent dosage was 3 g; the pH value of solution was unadjusted.

amount of CTMAB on bentonite changed accordingly, and thus the changing removals towards phenol were observed. Here, the reaction time of 2 h was adopted.

Through the investigation of the above factors, the optimum preparation conditions was presented as follows, for bentonite (5 g), 1.0 g CTMAB and 0.2 g HTCC were considered as the modifying reagents. The reaction was carried out for 2 h at 60°C. The CTMAB–HTCC bentonite prepared under optimal conditions was applied to conduct the following adsorption experiments.

3.2. Adsorption characteristics of CTMAB–HTCC bentonite

3.2.1. Effect of adsorbent dosage on the removals of phenol and Cd(II)

The influence of adsorbent dosage on the adsorption of phenol and Cd(II) was shown in Fig. 4. The removals of phenol increased with increasing dosage of the clay, and it was almost constant at higher dosages than 4.0 g. With increasing adsorbent dosage, more surface area was available for adsorption due to an increase in active sites on the adsorbent, and hence the removals increased reasonably. No change in adsorption was mainly attributed to the sites remaining saturated during the adsorption process. However, the high removal towards Cd(II) almost kept constant with the increasing adsorbent dosage, which resulted from the low Cd(II) concentration tested. Here, the adsorbent dosage of 4 g was chose for further experiments.

3.2.2. Effect of pH on the removals of phenol and Cd(II)

It is well known that the initial pH of an adsorption system was an important parameter for whether the adsorption of Cd(II) or phenol. The pH varying from 1 to 9 was investigated due to the precipitation of Cd(II) under alkaline condition. The results were shown in Fig. 5. The adsorbent had relatively high removals towards both phenol and Cd(II) in a wide range of pH (3–9), and thus it was considered that it was convenient for this adsorbent to conduct the simultaneous adsorption of phenol and Cd(II). On the whole, pH almost had no influence on the removal towards phenol. As we known, for phenol, the pKa value of phenol at 20°C is 10 or so. When the pH of the solution was low than the pKa of phenol, phenol existed in solution in the form of molecule under this experimental conditions. The constant removal towards phenol suggested that the adsorption of phenol onto CTMAB–HTCC bentonite was realized typically through a partitioning process. However, the adsorbent had a low removal towards Cd(II) when pH of complex solution was low than 3. At low pH values, a part of $-NH_2$ in HTCC was apt to the protonation at strong acidic medium, so more positively charged groups were introduced and, hence, these ions restricted the approach of Cd(II) due to repulsive force, leading to a low removal towards Cd(II). However, the possibility of a partial collapse of the bentonite framework took place due to highly acidic solution [29]. When increasing pH, the protonation of $-NH_2$ weakened, the electrostatic repulsion decreased due to the reduction of positive charge groups in HTCC. When the chelation between Cd(II) and –OH or $-NH_2$ in HTCC became progressively strong when increasing pH, the high removal towards Cd(II) occurred. The removals towards phenol and Cd(II) were 81.3% and 99.3%, respectively at pH 7 or so (i.e., not-adjusted), and thus this pH value was selected as the optimum pH for further studies.

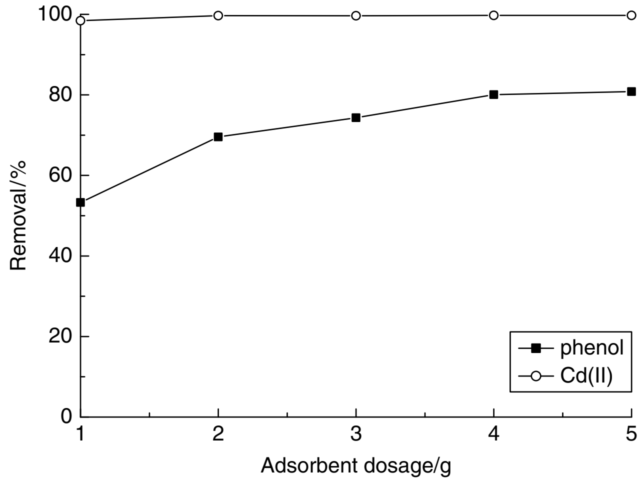

Fig. 4. Effect of adsorbent dosage on the removals of phenol and Cd(II) Adsorption conditions: the complex solution tested was 50 mg l^{-1} phenol and 50 mg l^{-1} Cd(II); adsorption time was 40 min; adsorption temperature was room temperature; the pH value of solution was unadjusted.

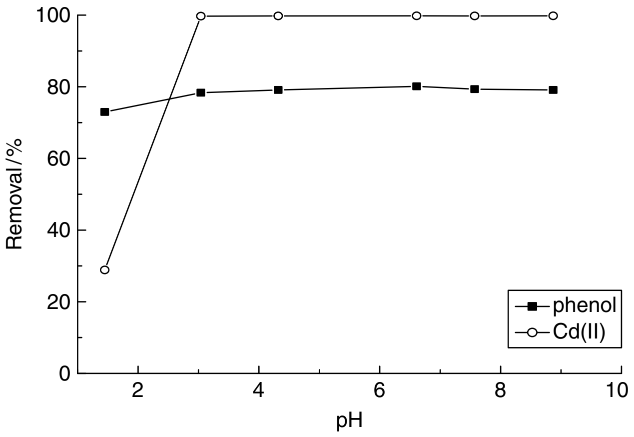

Fig. 5. Effect of pH the removals of phenol and Cd(II) Adsorption conditions: the complex solution tested was 50 mg l^{-1} phenol and 50 mg l^{-1} Cd(II); adsorption time was 40 min; adsorbent dosage was 4 g; adsorption temperature was room temperature.

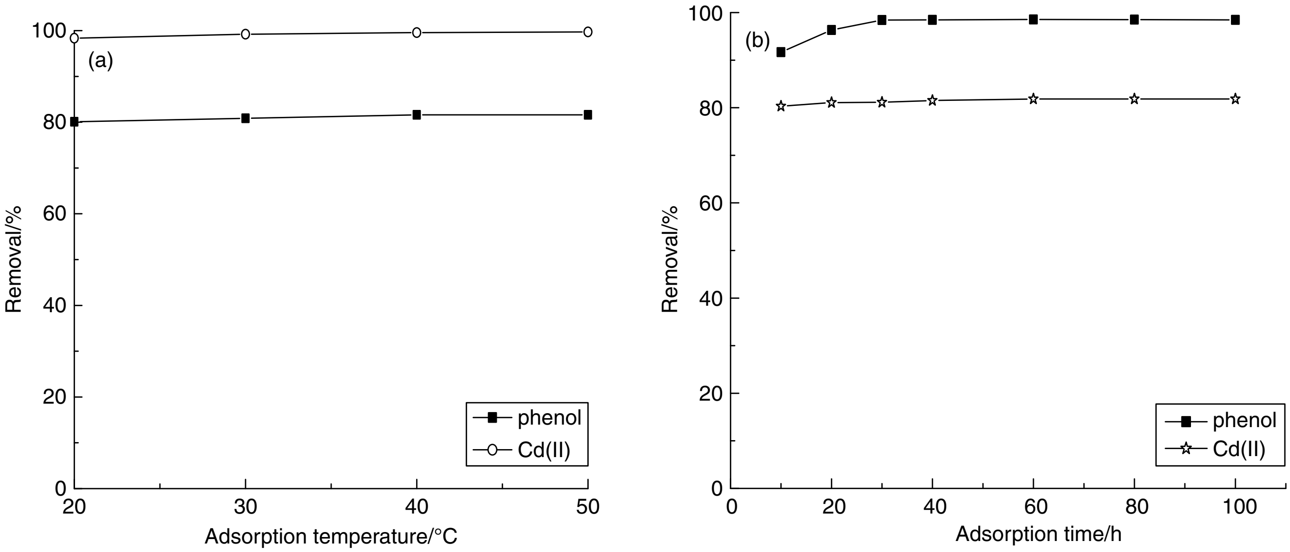

Fig. 6. Effect of adsorption temperature and time on the removals of phenol and Cd(II) Adsorption conditions: the adsorption condition in (a) are the complex solution tested was 50 mg l^{-1} phenol and 50 mg l^{-1} Cd(II); adsorbent dosage was 4 g; adsorption time was 40 min. The adsorption condition in (b) are the complex solution tested was 50 mg.l^{-1} phenol and 50 mg.l^{-1} Cd(II); adsorbent dosage was 4 g; adsorption temperature was room temperature.

3.2.3. *Effect of adsorption temperature and time on the removals of phenol and Cd(II)*

Here, the adsorption temperature from 20°C to 50°C was investigated. As shown in Fig. 6(a), the adsorption temperature had no influence on the removals of phenol and Cd(II). These results suggested that the adsorbent had constant properties, when performing the simultaneous adsorption of phenol and Cd(II). Therefore, the room temperature was adopted for further experiments.

To investigate the effect of adsorption time on the removals of phenol and Cd(II) under room temperature, the adsorption time changed from 10 to 100 min. The results (Fig. 6(b)) shown that the adsorptions attained equilibrium in a short time. These equilibrium times for phenol and Cd(II) were 40 and 30 min, respectively. Considering the removals of phenol and Cr(VI) together, 40 min of adsorption time was adopted.

3.2.4. *Adsorption of Cd(II) in the presence of phenol*

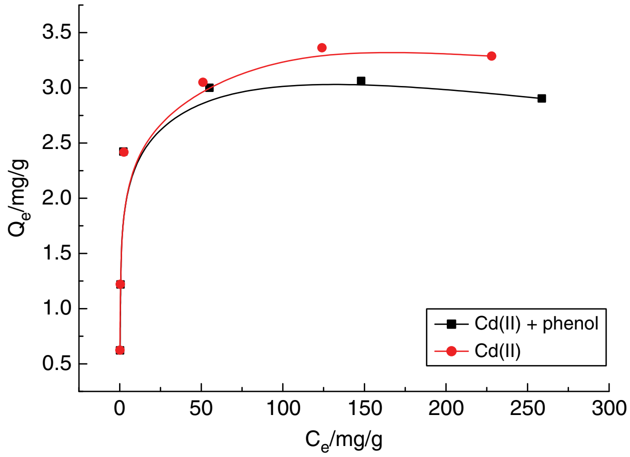

Fig. 7. Adsorption of Cd(II) in the presence of phenol Adsorption conditions: the complex solutions tested were 500 mg l^{-1} phenol and Cd(II) with a different concentration from 50 to 500 mg l^{-1} the single solution concentration of Cd(II) varied from 50 to 500 mg l^{-1} adsorbent dosage was 4 g; adsorption time was 40 min; adsorption temperature was room temperature; the pH value of solution was unadjusted.

Fig. 7 shown the sorptions of Cd(II) onto HTCC–CTMAB bentonite in the presence and absence of phenol. Sorption of Cd(II) was found to be non-linear, indicating that adsorption to the surface was the primary mechanism of Cd(II) uptake. Besides, the result indicated that the presence of phenol reduced Cd(II) sorption to HTCC–CTMAB bentonite relative to sorption data without phenol. In HTCC–CTMAB bentonite, the competition between Cd(II) and phenol was unexpected because Cd(II) and phenol were not sorbed at the same sites. Cd(II) was sorbed by the chelation action between Cd(II) and HTCC, while the adsorption of phenol was realized through a partitioning mechanism. Although Cd(II) and HTCC were not sorbed at the same sites, the presence of phenol could cause crowding at the surface and result in a steric hindrance which would decrease the amount of Cd(II) that could interact with HTCC. This similar result was also found by other researchers [30,31]. Oyanedel-Craver et al. [29] indicated that the metals (Cd, Pb and

Zn) and benzene were both adsorbed by surface adsorption in benzyltriethylammonium (BTEA)–bentonite. Although the metals and benzene are not sorbed at same sites, they are both interacting with the surface of the clay. The presence of benzene could cause crowding at the surface and result in a steric hindrance which could decrease the amount of metal that could interact with the surface.

3.2.5. Adsorption of phenol in the presence of Cd(II)

The results (Fig. 8) of sorption experiments in which both phenol and Cd(II) were sorbed onto HTCC–CTMAB bentonite were fit to a linear, suggesting that the majority of phenol removed by HTCC–CTMAB bentonite was through a partitioning mechanism. Besides, it was found that the sorption of phenol onto HTCC–CTMAB bentonite decreased in the presence of Cd(II), relative to the sorption of phenol as a single solute. Andini et al. [31] observed a decrease in the sorption of chlorobenzene in the presence of Cd and Pb in BDMOA-bentonite. In this case, the sorption of Pb and Cd on the silanol and aluminol groups in the clay surface may affect the sorption of the chlorobenzene molecules to the benzyl groups close to the clay surface, creating competition between the organic molecule and the heavy metals. However, Cd(II) and phenol were not sorbed at the same sites in our present study, the competition adsorption between Cd(II) and phenol was unexpected, but the presence of Cd(II) appeared to alter the phenol uptake slightly, causing a decrease in phenol sorption. When Cd(II) approached phenol in solution, a kind of complex ∏ electron between phenol and Cd(II) was formed. It was difficult for this complex to be adsorbed onto HTCC–CTMAB bentonite through a partitioning mechanism relative to single phenol, so a decrease in phenol adsorption occurred in the presence of Cd(II).

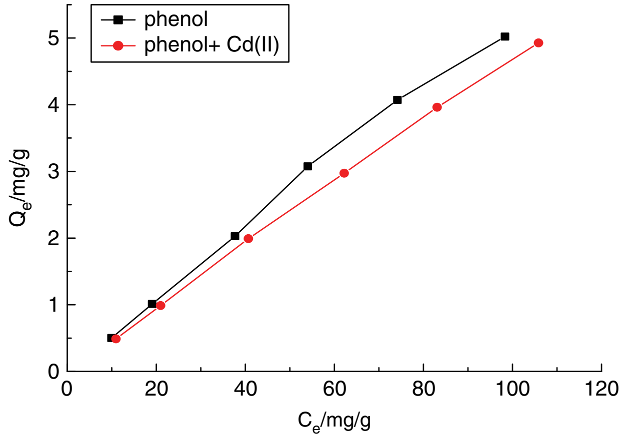

Fig. 8. Adsorption of phenol in the presence of Cd(II) adsorption conditions: the complex solutions tested were 200 mg l^{-1} Cd(II) and phenol with a different concentration from 50 to 500 mg l^{-1}; the single solution concentration of phenol varied from 50 to 500 mg l^{-1}; adsorbent dosage was 4 g; adsorption time was 40 min; adsorption temperature was room temperature; the pH value of solution was unadjusted.

4. Conclusions

An absorbent was prepared by modifying bentonite with CTMAB and HTCC. By the method of single-factor experiment, the preparation of CTMAB–HTCC bentonite was obtained. For bentonite (5 g), 1.0 g CTMAB and 0.2 g HTCC was adopted as the modifying reagents. The reaction was carried out for 2 h at 60°C. The simultaneous adsorption of phenol and Cd(II) onto HTCC–CTMAB bentonite was not affected by adsorption temperature and time, and was conducted in a wide range of pH. The sorption processes of Cd(II) and phenol onto HTCC–CTMAB bentonite occurred on different sites, but their simultaneous presence could result in decreased the sorption of both Cd(II) and phenol. The removals towards phenol and Cd(II) with a concentration of 500 mg l^{-1} phenol and 200 mg l^{-1} Cd(II) in a complex solution were 80.2% and 98.0%, respectively. Although sorption was decreased, HTCC–CTMAB bentonite studied had a potential for the stabilization of both organic and metallic aqueous contaminants.

Acknowledgements

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