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Structural and sorptive characteristics of the cetyltrimethylammonium and polyacrylamide modified bentonite

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ABSTRACT

In this work cetyltrimethylammonium bromide (CTMA) and cationic polyacrylamide (CPAM) were used to simultaneously modify bentonite, with the aim to synthesize novel organobentonites possessing high sorption capacity towards phenol, nitrobenzene and aniline. The XRD characterization results showed that the resulting organobentonites (C/P-Bt) had larger basal spacing than the corresponding CTMA modified bentonite (C-Bt) and CPAM modified bentonite (P-Bt). This indicated that the two modifying agents were simultaneously intercalated into the interlayers of C/P-Bt. FTIR characterization results showed that the $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ modes of CTMA on C/P-Bt shifted to low wavenumbers comparing with those on the corresponding C-Bt, which indicated CTMA had higher *trans/gauche* conformation ratio and packing density within the interlayers of C/P-Bt. C/P-Bt showed a synergistic sorption effect towards the tested sorbates, with a sorption efficiency better than that of C-Bt + P-Bt. In addition, the sorption capacity of C/P-Bt was shown to increase with the saturated CEC until the maximum, and then began to decrease as the saturated CEC further rose. The optimal saturated CEC was in the range 114–127%. Results of this work provided additional evidence that the packing density of organic cations could significantly influence the sorption capacity of organobentonites, and also showed a method for synthesizing novel organobentonites with high sorption efficiency towards organic pollutants.

1. Introduction

Bentonite is primarily composed of montmorillonite, a 2:1 type layered aluminosilicate clay mineral. Each layer of montmorillonite consists of one octahedral and two adjacent tetrahedral sheets, with the thickness of about 0.96 nm. Due to the isomorphous substitution within the layers (e.g., Al^{3+} replaced by Mg^{2+} in the octahedral sheet), the montmorillonite layers are negatively charged. Naturally, these charges are counter-balanced by inorganic cations (e.g., Na^+, Ca^{2+}) in the galleries between the layers. Under suitable conditions, these interlayer cations can be replaced by other cations, which can render the resulting materials novel properties [1–4]. For example, the organic cations exchanged bentonite, also known as organobentonites, show high affinity towards hydrophobic organic compounds (HOCs) and can be used for the control of HOCs pollution in various fields [5–10].

The most widely used organic cations for preparing organobentonites are the quaternary ammonium cations (QACs) [7–15]. If the small QACs (e.g., tetramethylammonium, TMA) are used, the resulting organobentonites can effectively uptake HOCs by an adsorption mechanism, and the hydrophobic siloxane surface is considered as the main adsorption sites [12,13,16,17]. With this respect, increasing the exposed siloxane surface can improve the sorption capacity of this type of organobentonites [12,17,18]. However, if the QACs with long alkyl chains (e.g., cetyltrimethylammonium, CTMA) are used, the resulting organobentonites are supposed to contain various sorption mechanisms for the uptake of HOCs, e.g., partition to the organic phase formed by the alkyl chain aggregates [11,16,18], solvation of the head of the organic cations [19,20], adsorption on the alkyl chain film over siloxane surface [7,21]. Because of the complexity of the sorption mechanism of this type of organobentonites, there is no clear idea as how to improve their sorption capacity.

Recently, we systematically investigated the influence of the loading amounts of organic cation and clay charge of bentonite on the structural characteristics and sorptive characteristics of the organobentonites [22–25]. Based on these results, we proposed that the arrangement model of the intercalated organic cations, especially their packing density, could significantly influence the sorption capacity of the organobentonites. In other words, the organobentonites would show better sorption capacity if the organic cations were packed within proper density range [22–25]. According to this hypothesis, the sorption capacity of

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the organobentonites can be improved by adjusting the packing density of the intercalated organic cations.

Traditionally, the methods for adjusting the packing density of the intercalated organic cations include changing the loading level of organic cations [7,18,21–23], choosing organic cations with different molecular structure [16,26,27], or using bentonites with different layer charges [22,28]. With these methods, it is possible to synthesize organobentonites with optimal sorption capacity. However, it is always expensive or inconvenient to adjust the packing density with above methods. For example, increasing loading level of organic cations will definitely increase the cost of the resulting organobentonites, while the organic cations with special structure may be extremely expensive. Thereby, novel methods are needed to adjust the packing density of the organic cations. Cationic polymers have also been used as modifying agents for synthesizing bentonites based sorbents. With their large charge/mass ratio, the cationic polymers can easily saturate the bentonite's CEC and change the interlayer environment of the bentonite. As a result, the resulting sorbents could effectively remove anionic dyes from water [29,30]. This enlightens us that cationic polymers might be used to adjust the packing density of the organic cations, and thus improve the sorption capacity of the resulting organobentonites.

In this work, CTMA and cationic polyacrylamide (CPAM) are employed to intercalate bentonite at their various ratios to obtain serials of novel organobentonites. Because of its high charge/weight ratio, CPAM is selected to saturate part of the bentonite's CEC, with the aim to adjust the packing density of CTMA and improve the sorption capacity of the resulting organobentonites. The structural characteristics of the novel organobentonites are characterized with XRD and FTIR, and the sorption capacities of the organobentonites towards three HOCs (phenol, nitrobenzene and aniline) are examined. The objectives of this work are to further verify our previous hypothesis and provide a novel method for improving the sorption capacity of organobentonites.

2. Materials and methods

2.1. Materials

Bentonite was obtained from Inner-Mongolia (China) with the cation exchange capacity (CEC) of 108 meq/100 g. XRD patterns showed that it was mainly composed of calcium montmorillonite (>95%). Cetyltrimethylammonium bromide, phenol, nitrobenzene and aniline were of analytical purity, and they were brought from Shanghai Chemical Co., China. CPAM was brought from Xianke Chemical Co., China. The purity of CPAM was above 98%, and its ionic degree and molecular weight were 14.6 mmol/g and 10 million.

2.2. Preparation of organobentonites

The organobentonites were synthesized according to the following process: 10 g of bentonite was first added to 100 mL of distilled water at 60 °C and stirred until they were thoroughly dispersed. Desired amounts of CTMA and CPAM were mixed in 100 mL distilled water at 60 °C. Then the modifying agents were added to the bentonite suspension under vigorous stirring. The mixed suspensions were stirred at 60 °C for 4 h and then aged at 60 °C for another 10 h. After that, the resulting products were washed with distilled water and dried at 70 °C. The added amounts of CTMA was equal to 60%, 80% or 100% of the bentonite's CEC, and the added amounts of CPAM was 2%, 4% or 6% of the bentonite's weight. The resulting organobentonites were denoted as *x*C/*y*P-Bt. Here *x* and *y* were used to represent the amounts of CTMA and CPAM, respectively. For example, 80C/4%P-Bt was used to denote the sample with CTMA equal to the bentonite's 80% CEC and with CPAM equal to 4% of the bentonite's weight. The symbol C/P-Bt was used to represent all of the CTMA and CPAM modified organobentonites. Moreover, we also used *x*C/P-Bt and C/*y*P-Bt to denote all the organobentonites with the same CTMA loading amounts and the same CPAM loading amounts, respectively.

Table 1
Saturated CEC and organic carbon content (f_{oc}) of the organobentonites.

Samples	Saturated CEC (%)	f_{oc} (%)	Samples	Saturated CEC (%)	f_{oc} (%)
2%P-Bt	27	0.99	80C/2%P-Bt	107	17.8
4%P-Bt	54	1.95	80C/4%P-Bt	134	18.2
6%P-Bt	81	2.87	80C/6%P-Bt	161	18.5
60C-Bt	60	13.2	100C-Bt	100	20.5
60C/2%P-Bt	87	13.8	100C/2%P-Bt	127	20.9
60C/4%P-Bt	114	14.5	100C/4%P-Bt	154	21.4
60C/6%P-Bt	141	15.1	100C/6%P-Bt	181	21.9
80C-Bt	80	16.9			

For comparison purpose, the CTMA and CPAM modified bentonite were also synthesized, and the resulting organobentonites were denoted as C-Bt and P-Bt, respectively.

2.3. Characterization methods

Basal spacing values of the synthesized organobentonites were detected on a Bruker D8 ADVANCE X-ray diffractometer operating at 40 kV and 40 mA with Cu Kα radiation. The 2θ range between 1° and 20° was recorded with a scanning speed of 2°/min. The basal spacing values were calculated according to the 2θ values of the peaks in the XRD patterns. FTIR spectra were recorded in the region 4000–400 cm^{-1} on a PerkinElmer 1725 FTIR spectrophotometer, operating at a resolution of 2.0 cm^{-1}. Organobentonites and KBr were mixed and milled to fine powder using a mortar and pestle. The powder was then made into a fragile pellet using a compression machine and placed inside the pellet cell for analysis. Sixty-four interferograms were collected for each sample. Organic carbon content (f_{oc}) was analyzed with a SHIMADZU TOC-V CPH organic-carbon analyzer. The natural bentonite had f_{oc} less than 0.04%.

2.4. Sorption of HOCs to the organobentonites

Sorption of phenol, nitrobenzene and aniline to the organobentonites was carried out with batch experiments. Desired amounts of organobentonites were added to the solutions with various sorbate concentrations, and then they were shaken at 150 rpm for 8 h under 25 °C to reach enough equilibrium. After centrifugation under 1500 × g, the concentration of the sorbates in supernate was detected with UV–vis spectrophotometer. The maximum wavelength used for the detection of phenol, nitrobenzene and aniline were 270, 268 and 230 nm, respectively. The control experiments showed that desorption of CTMA and CPAM from organobentonites was negligible, and the loss of the sorbates during the sorption process was less than 2%.

3. Results and discussion

3.1. Structural characteristics of the organobentonites

The determined f_{oc} values of the modified bentonties were presented in Table 1. It showed that with the addition of CPAM, the f_{oc} of C/P-Bt would increase comparing with those of C-Bt, and this was more evident for the samples with smaller CTMA loading amounts. The f_{oc} value in the filtration water was extremely small (less than 2 mg/L), this indicated that the added CPAM and CTMA were nearly completely adsorbed on bentonite. In this work we also calculated

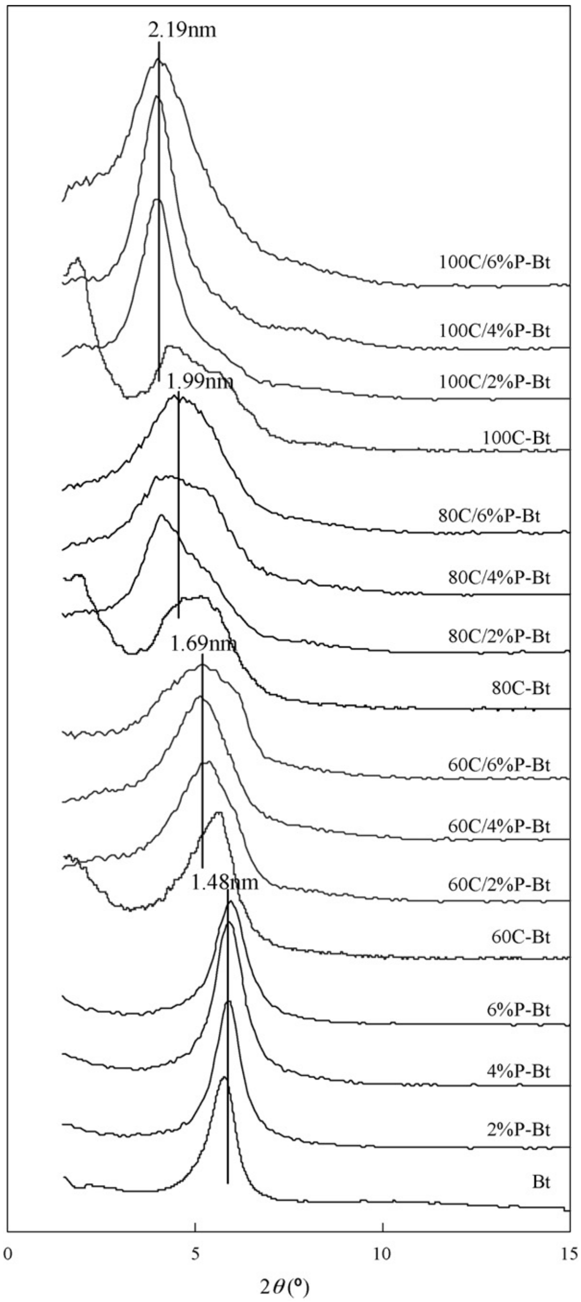

Fig. 1. XRD patterns of the organobentonites.

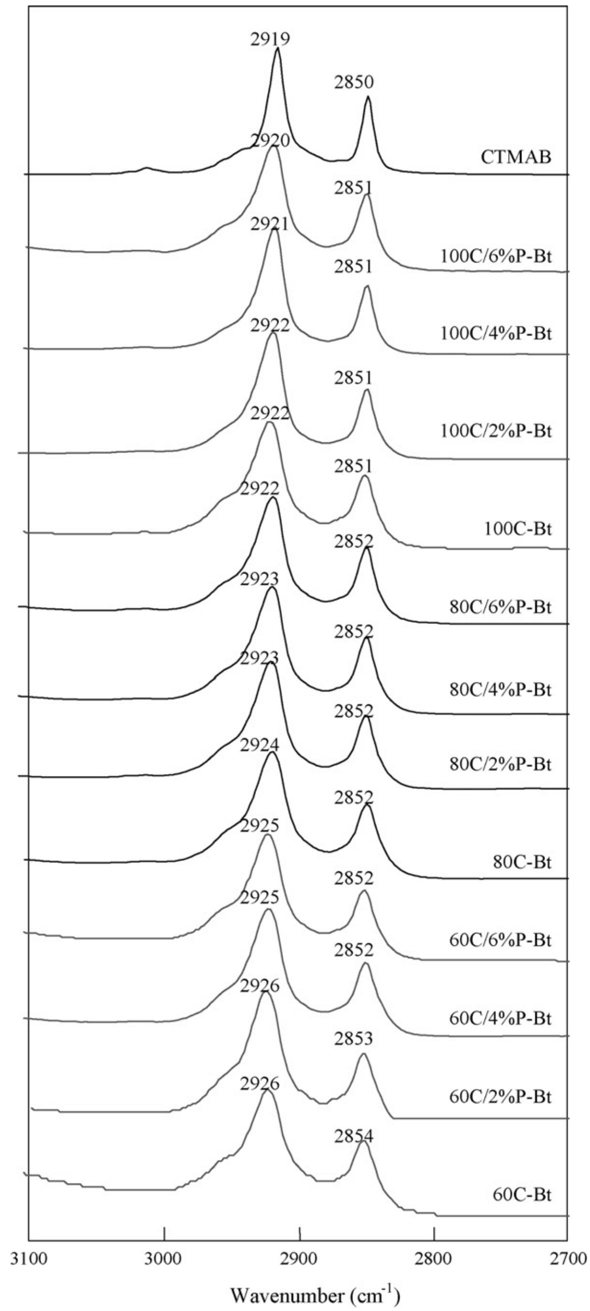

Fig. 2. FTIR patterns of the organobentonites in the range 3100–2700 cm^{-1}.

the saturated CEC of the bentonite by the intercalated CTMA and CPAM, and the results were shown in Table 1. Although the added amounts of CPAM were small, it could saturate a large part of the bentonite's CEC because of its large charge/mass ratio. The saturated CEC of 60C/P-Bt, 80C/P-Bt and 100C/P-Bt by CTMA and CPAM was in the range 60–141%, 80–161% and 100–181%, respectively.

Fig. 1 presented the XRD patterns of the original bentonite (Bt) and the modified bentonite. The basal spacing of Bt was 1.52 nm, while the three CPAM modified bentonites had slightly smaller basal spacing of 1.49 nm. This could be ascribed to the replacement of Ca^{2+} by CPAM, and the basal spacing of bentonite would decrease slightly. As for C-Bt, their basal spacing was shown to be proportional to the intercalated amounts of CTMA, in agreement with the previous reports [21,22,31]. With the addition of CPAM, the basal spacing of C/P-Bt was further increased comparing with the corresponding C-Bt. For example, the basal spacing values of 60C-Bt, 80C-Bt and 100C-Bt were 1.59, 1.73 and 2.06 nm, and they increased to 1.64, 2.15 and 2.23 nm respectively with the addition of 2% CPAM. This indicated that both CTMA and CPAM were intercalated into the interlayers of the bentonite. Further increase of CPAM loading amounts could not further increase the basal spacing of the C/P-Bt in most cases.

Previous reports showed that FTIR could be a useful method to probe the molecular environment of organic cations within the interlayer space of the bentonite. The CH_2 infrared absorption bands, particularly the CH_2 asymmetric stretch mode ($\nu_{as}(CH_2)$) and symmetric stretch mode ($\nu_s(CH_2)$), are very sensitive to the *gauche*/*trans* conformer ratio and packing density of the alkyl chains [27,31–34]. With this respect, the spectral region between 3100 and 2700 cm^{-1} for pure CTMA and the organobentonites were presented in Fig. 2. The pure CPAM and the P-Bt did not shown strong absorption in this spectral region, and thus their FTIR

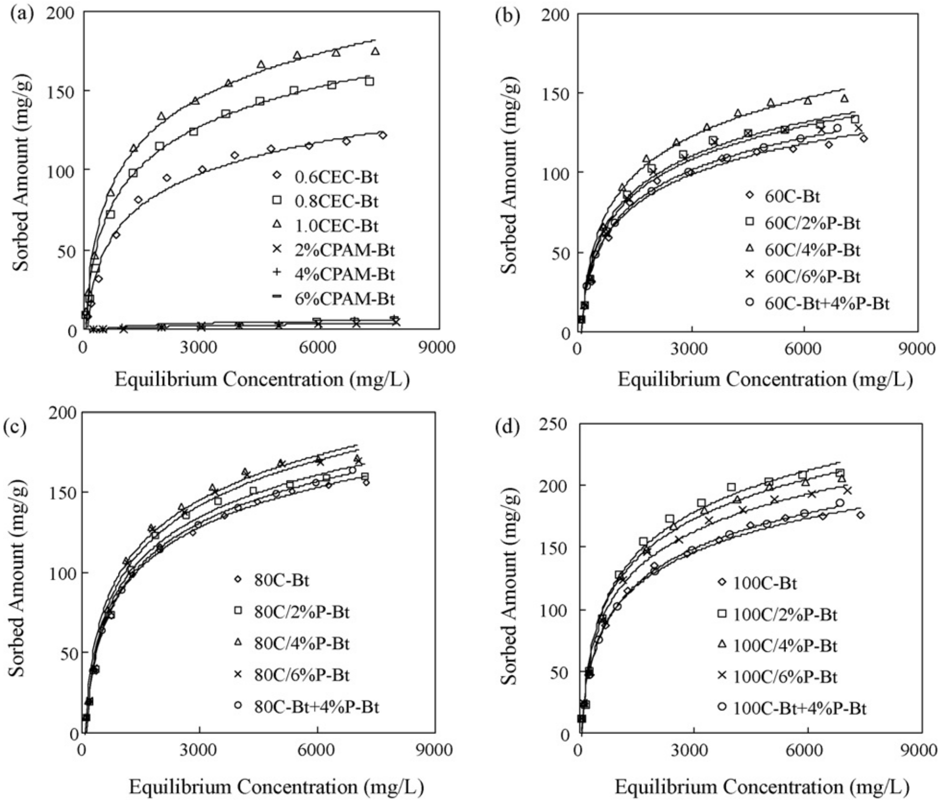

Fig. 3. Sorption isotherms of phenol to the organobentonites: (a) C-Bt and P-Bt, (b) 60C/P-Bt, (c) 80C/P-Bt, and (d) 100C/P-Bt.

spectra were not shown here. In agreement with the results of previous researches [32,33], with increasing CTMA loading amounts the $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ modes of the adsorbed CTMA was shown to evidently shift towards low wavenumber range. This indicated the decrease of *gauche*/*trans* conformer ratio and increase of packing density of the adsorbed CTMA [22,32,33]. With the addition of CPAM, the bands for $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ modes of the adsorbed CTMA was shown to evidently shift towards low frequency, and the shift was proportional to CPAM intercalation amounts. This indicated that the adsorbed CTMA had higher packing density as the added CPAM increased.

Above results showed that it was feasible to adjust the packing density of the adsorbed CTMA with the addition of CPAM. This could be ascribed to the high charge/mass ratio and large molecular size of CPAM. Because of the high charge/mass ratio, the adsorbed CPAM could take a great part of the charge sites in bentonite's interlayer. With this respect, the available charge sites for CTMA would reduce accordingly. On the other hand, because of the large molecular size of CPAM, each CPAM would cover a large siloxane surface area. This indicated that CTMA would arrange less freely within the interlayers of bentonite, and they would more likely aggregate with each other.

3.2. Sorption of the sorbates on the organobentonites

The sorption isotherms of phenol on the organobentonites were shown in Fig. 3. In Fig. 3(a), it showed that P-Bt had rather weak sorption capacity towards phenol. C-Bt had much better sorption capacity towards phenol, and the sorption capacity was shown to be proportional to the loading amounts of CTMA, in accordance with some previous reports [7,21,22,25]. The sorption isotherms of phenol on 60C/P-Bt, 80C/P-Bt and 100C/P-Bt were presented in Fig. 3(b)–(d), respectively. It was interesting that the sorption capacity of the C/P-Bt towards phenol was much better than that of the corresponding C-Bt, and the sorption capacity of C/P-Bt would reach maximum with the addition of suitable amount of CPAM. In particular, 60C/4%P-Bt, 80C/4%P-Bt and 100C/2%P-Bt showed the best sorption capacity among the samples of 60C/P-Bt, 80C/P-Bt and 100C/P-Bt, respectively.

In Fig. 3, we also compared the sorption capacity of C/P-Bt with the sorption capacity of C-Bt + P-Bt. 4%P-Bt was used as representative of P-Bt, and the isotherms of C-Bt + 4%P-Bt were plotted. It was shown that C/P-Bt had better sorption capacity than C-Bt + P-Bt. This indicated CTMA and CPAM had synergistic effect on C/P-Bt, and C/P-Bt was a novel organobentonites with better sorption capacity than the traditional C-Bt. The sorption of nitrobenzene and aniline on the organobentonites showed the similar phenomena as the sorption of phenol, and the sorption isotherms were presented in supplementary materials.

3.3. Correlation between sorption capacity and the saturated CEC

Since P-Bt had rather weak sorption capacity towards the sorbates, the excellent sorption capacity of C/P-Bt should be ascribed to the adsorbed CTMA. According to our previous hypothesis, the sorption capacity of organobentonites strongly depended on the packing density of the adsorbed cations [22–25]. To investigate how the packing density of CTMA influences the sorption capacity of C/P-Bt, we examined the correlation between the sorption coefficient (K_d, the ratio of the sorbate concentration on sorbent to that in solution) of the sorbates and the saturated CEC of C/P-Bt. As the results of some previous investigations [22,25,33] and also of this work showed that packing density of organic cations was proportional to the saturated CEC, we chose it as the indicator of the packing density of CTMA. The equilibrium concentrations of phenol, nitrobenzene and aniline were selected as 5000, 400 and 2000 mg/L to calculate the K_d. The calculated K_d against the saturated CEC and were shown in Fig. 4. According to Fig. 4(a), the K_d of phenol on the

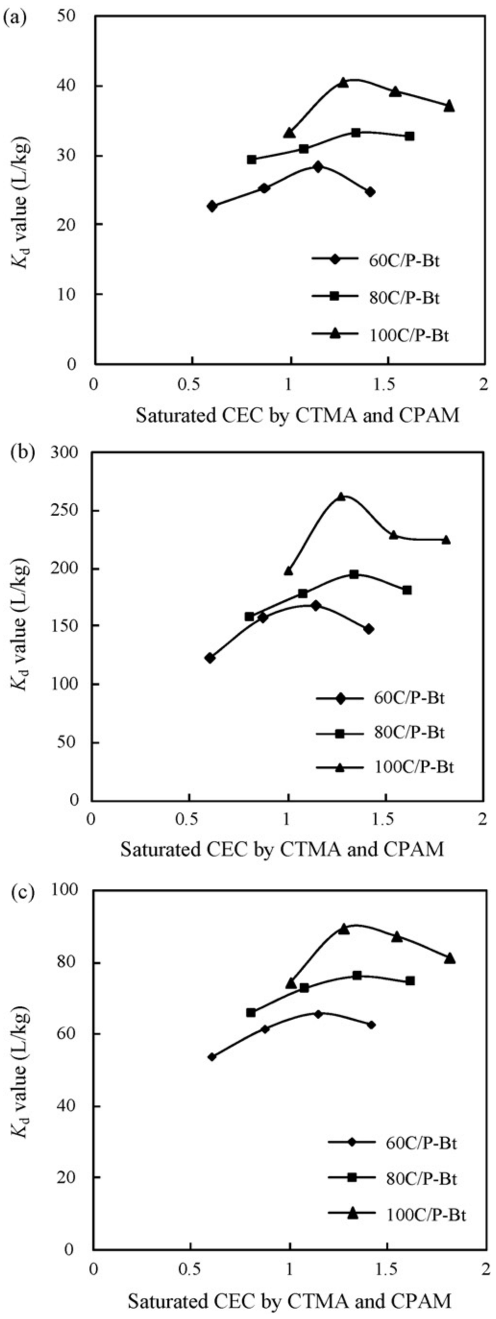

Fig. 4. Correlation between the K_d of the sorbates and the saturated CEC value of organobentonites by CTMA and CPAM. (a) Phenol (C_e = 5000 mg/L), (b) nitrobenzene (C_e = 400 mg/L), and (c) aniline (C_e = 2000 mg/L).

three serials of C/P-Bt was shown to first increase with the saturated CEC till the maximum and then begin to decrease. The interesting phenomenon was that the maximum K_d appeared at quite similar saturated CEC level for all the three serials of C/P-Bt (i.e., in the range 114–127%). Similar results were obtained for nitrobenzene (Fig. 4(b)) and aniline (Fig. 4(c)).

Several previous reports investigated the influence of organic cation loading level on the sorption capacities of organobentonites, and their results also showed that at the saturated CEC level a little above the bentonite's CEC (e.g., around 120%CEC), the resulting organobentonites would have the maximum K_d [7,21–23,25]. In our previous reports we ascribed this phenomenon to the packing density of the organic cation, and the organobentonites could have best sorption capacities if the packing density of organic cation fell within a suitable range [22,23,25]. Results of this work showed that we could obtain similar results using the cationic polymer CPAM. That was, we could adjust the packing density of CTMA within suitable range using CPAM, and synthesize novel organobentonites with optimal sorption capacity. More interestingly, the organobentonites, no matter prepared by CTMA alone or by CTMA together with CPAM, all had quite similar saturated CEC range at which the best sorption capacity could be obtained (e.g., a little above the bentonite's CEC). With this respect, result of this work further supported our hypothesis that packing density of organic cations could strongly influence the sorption capacity of organobentonites.

4. Conclusion

CPAM can be used to adjust the arrangement model of CTMA within the interlayers of bentonite. With the simultaneous intercalation of CPAM, the packing density and the *trans/gauche* conformation ratio of the intercalated CTMA was shown to increase evidently. The resulting organobentonites had larger basal spacings comparing with the CTMA intercalated bentonite. C/P-Bt showed a synergistic sorption effect towards phenol, nitrobenzene and aniline, and it had better sorption capacity towards these tested HOCs than C-Bt + P-Bt. In addition, the sorption capacity of C/P-Bt was closely related to the saturated CEC (or CTMA packing density). With increasing saturated CEC, sorption capacity of C/P-Bt first increased until the maximum, and then began to decrease. The optimal saturated CEC was in the range between 114% and 127%. This provided additional evidence for our previous hypothesis that the packing density of organic cations could significantly influence the sorption capacity of organobentonites.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.03.048.

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