Simultaneous sorption of crystal violet and 2-naphthol to bentonite with different CECs

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ABSTRACT

This work was to examine the feasibility and efficiency to use bentonite for simultaneous removal of cationic dyes and hydrophobic organic carbons (HOCs) from water. The sorption capacities of crystal violet (CV) on two bentonites and one activated carbon were compared. Simultaneous sorption of CV and 2-naphthol on the two bentonites were tested, and the removal efficiencies of 2-naphthol by the simultaneous sorption method and by CV modified bentonite was also compared. The experimental results in this study showed that the bentonite is more effective in sorption of CV than the activated carbon. With the sorption of CV, bentonite surfaces were altered from hydrophilicity to hydrophobicity, and thus 2-naphthol could be simultaneously removed. The aromatic effect between CV and 2-naphthol was supposed to be the primary driving force for the sorption of 2-naphthol. The simultaneous sorption method was shown to be more effective in the sorption of 2-naphthol than the CV modified bentonite. Results of this work could provide novel information for the treatment of wastewater containing both cationic dyes and HOCs.

1. Introduction

Wastewater from dyestuff manufacture and application industries contains large amounts of organic chemicals, and they are main sources of water pollution. The organic chemicals and their degradation products are always carcinogens and toxic to mammals, thus it is urgent to remove these organic chemicals from the wastewater [1–5]. Since dyes are not easily broken down by the biological and chemical methods, sorption has been proved to be a practical method for the treatment of the dye wastewater, and many sorbents have been developed and used for the removal of dyes from the dye wastewater [6–10]. Among these sorbents, bentonite is proved to be a promising sorbent for the removal of cationic dyes from wastewater, due to high efficiency, low cost and commercial availability [5,11–14].

Bentonite is primarily composed of montmorillonite, 2:1 type of layered aluminosilicate clay mineral. Due to the isomorphous substitution within the layers (e.g. Al^{3+} replaced by Mg^{2+} or Fe^{2+}, Si^{4+} replaced by Al^{3+} in the tetrahedral sheet), the clay layer is negatively charged, which is counter-balanced by cations (e.g., Na^+, Ca^{2+}) in the galleries between layers. These interlayer cations can be replaced by other cations (e.g., organic cations), rendering bentonite efficient sorbent for cationic dyes [13–16].

Beside dyes, the dye wastewater may also contain other organic chemicals such as the aromatic compounds that are used as precursor for synthesizing dyes. However, few researches have reported the sorption efficiency of bentonite towards the system containing both dyes and other coexisting organic chemicals. This may be due to that the interlayer of original bentonite is naturally hydrophilic and show weak affinity towards hydrophobic organic compounds (HOCs). On the other hand, several studies showed that after the replacement of original interlayer inorganic cation with cationic dyes, the surface of bentonite could be changed from hydrophilicity to hydrophobicity. As a result, the resulting bentonite showed high affinity towards HOCs and could be used to remove HOCs from water [17–19]. This enlightened us that bentonite can also remove HOCs from water while they adsorb cationic dyes from water, i.e., bentonite could simultaneously remove both cationic dyes and HOCs from water.

The objective of this work was to examine the feasibility and efficiency of bentonite to simultaneously remove cationic dyes and HOCs from water. Crystal violet (CV) and 2-naphthol were selected as representatives of cationic dyes and HOCs, respectively, and the sorption capacities of two bentonites with different cationic exchange capacities (CEC) towards CV and 2-naphthol were examined. The removal efficiency of 2-naphthol by the simultaneous

sorption method was also compared with that by the CV modified bentonite. Results of this work might provide novel information for using bentonite in the treatment of dye wastewater containing both cationic dyes and HOCs.

2. Materials and methods

2.1. Materials

The used bentonites were obtained from Hebei Province (China) and Inner-Mongolia Autonomous Region (China), and they were denoted as HB-Bt and NM-Bt, respectively. Both of them were primary calcium bentonite. XRD patterns showed that they were composed of mainly montmorillonite (>95%). CEC values of HB-Bt and NM-Bt were 76 and 106 meq/100 g, respectively. Activated carbon was provided by Shanghai Chemical Co., China, with a specific surface area of 750 m^2/g. CV and 2-naphthol were of analytical grade, and they were obtained from Shanghai Chemical Co., China. Molecular structure of CV and 2-naphthol were shown in Fig. 1. All of the reagents were used as received.

2.2. Sorption of CV to bentonites and activated carbon

Sorption of CV to the two bentonites and the activated carbon were carried out with batch experiments. 0.2 g bentonite or activated carbon was combined with 20 ml CV solution with designed concentration in 25 ml glass centrifuge tubes. The tubes were sealed with Teflon-lined caps, and then were shaken at 150 rpm for 6 h under 25 °C (Preliminary experiments showed that the sorption equilibrium could be reached within 4 h on both bentonite and activated carbon). After centrifugation, the concentrations of CV in supernate were detected using a UV–vis spectrophotometer at the wavelength of 590 nm [5], and then the adsorbed amounts were calculated according to the difference between the initial and the equilibrium concentrations.

2.3. Simultaneous sorption of CV and 2-naphthol to bentonites

Simultaneous sorption of CV and 2-naphthol to the two bentonites were carried out with batch experiments, and the sorption processes were similar to those described in Section 2.2. After centrifugation, the concentrations of 2-naphthol in supernate were detected at the wavelength of 224 nm [20]. Since 2-naphthol had no absorption at the wavelength of 590 nm, it had no influence on the detection of CV. However, CV was shown to have absorption at the wavelength of 224 nm; thus it is necessary to control the equilibrium concentrations of CV at extremely low level. Towards this purpose, the initial concentrations of CV were controlled below 3700 mg/L. With this respect, the equilibrium concentrations of CV were smaller than 2 mg/L, and the controlling experiment showed that CV had no evident influence in the detection of 2-naphthol at a such low concentration level.
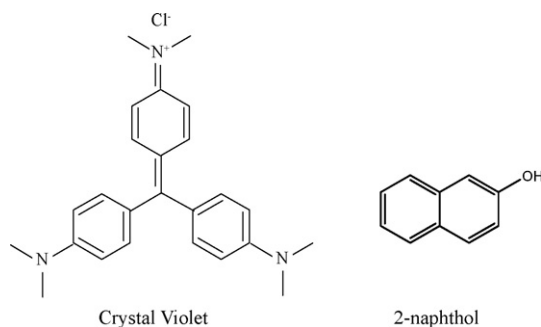
Sorption of 2-naphthol on the bentonite pretreated with CV (or CV modified bentonite) was also tested to make a comparison. 0.2 g bentonite was mixed with 10 mL CV solution of designed concentrations in 25 mL centrifuge tube. The tubes were shaken for 6 h to make sure that CV was adsorbed on bentonite. Then another 10 mL 2-naphthol solution with designed concentration was added into the tube. The tube was shaken for another 6 h to reach 2-naphthol solution equilibrium. The sorbed amounts of 2-naphthol were calculated as described above.

3. Results and discussion

3.1. Sorption of CV to bentonites and activated carbon

Sorption capacities of CV to HB-Bt and NM-Bt were examined. The sorption isotherms and removal efficiencies were presented in Fig. 2(a) and (b), respectively. It can be seen that the bentonites had extremely large sorption capacities toward CV, and the maximum sorption amounts reached 800 mg/g (or 1.98 mmol/g) for NM-Bt and 500 mg/g (or 1.25 mmol/g) for HB-Bt, respectively. This reflects that bentonite with larger CEC value would have bigger sorption capacity. The adsorbed amounts of CV were about 187% and 169% of NM-Bt's and HB-Bt's CEC. This suggests that parts of CV were adsorbed as molecular form. Rytwo et al. [21] and Eren and Afsin [9] also found that the binding amounts of CV could be much larger than the bentonite's CEC, and they attributed this to

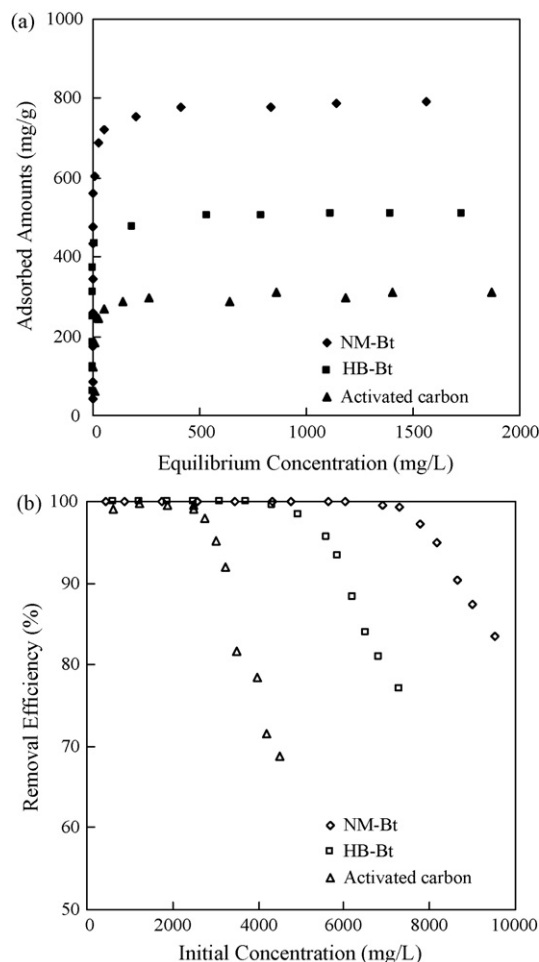Fig. 1. Molecular structure of CV and 2-naphthol.

Fig. 2. CV sorption isotherms (a) and removal efficiencies (b) by bentonite and activated carbon.

the hydrophobic interactions of the large organic cation. Fig. 2(b) showed that bentonite had strong affinity towards CV, and the removal efficiencies were remained above 99% even when the initial concentration reached 4000 mg/L for HB-BT and 7000 mg/L for NM-Bt.

For comparison purpose, sorption of CV to a commercial activated carbon was also examined. It showed that both of the tested bentonites had much bigger sorption capacities than the activated carbon. The maximum sorption capacity of the activated carbon was about 300 mg/g, which was just about 60% and 38% of the maximum sorption capacities of HB-Bt and NM-Bt, respectively. Besides the strong affinity of bentonite towards CV, expansion of bentonite interlayers can also be helpful for the sorption of CV, because most of the interlayer surfaces can be reached by CV molecules. While for the activated carbon, it can not expand during the sorption process, and thus some of the inner surfaces are unavailable for the sorption of CV. In addition, the cost of bentonite was much lower than that of activated carbon. This further made bentonite promising sorbent for removing CV from water.

3.2. Simultaneous sorption of CV and 2-naphthol

Simultaneous sorption capacities of CV and 2-naphthol on the two bentonites were tested with two different experiments. In the first experiment, the concentration of 2-naphthol was fixed (100 mg/L), and the concentration of CV was varied in a range (from 430 mg/L to 3700 mg/L) to satisfy various CEC. In this concentration range, most of the added CV was adsorbed, and the remaining CV concentration was below 2 mg/L. As shown in Fig. 3, sorption capacities of 2-naphthol on both HB-Bt and NM-Bt were shown to increase with CV concentration (i.e., the loaded CV amounts), and this tendency was extremely evident in the low CV concentration range.

Another interesting phenomenon was that HB-Bt and NM-Bt had quite similar sorption capacity towards 2-naphthol under this experimental condition. As we know, if bentonite was modified by small organic cations (e.g., TMA$^+$), siloxane surface was often considered as the most important sorption sites for HOCs due to its hydrophobic nature [22–24]. With the respect to CV modified bentonite, the aromatic effect between CV and 2-naphthol could also contribute to the strong sorption of 2-naphthol, similar to the sorption of HOCs containing aromatic group [17,22,25,26]. According to previous reports, at the same organic cation loading level the bentonite with lower charge density will always have more
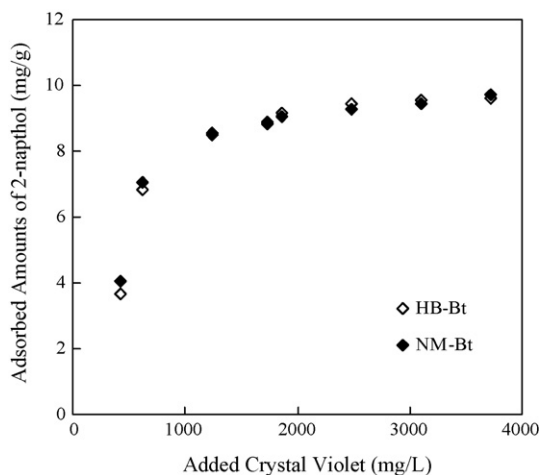

Fig. 3. Sorption amounts of 2-naphthol to bentonite in the presence of various amounts of CV (*Note*: the initial concentration of 2-naphthol was 100 mg/L).
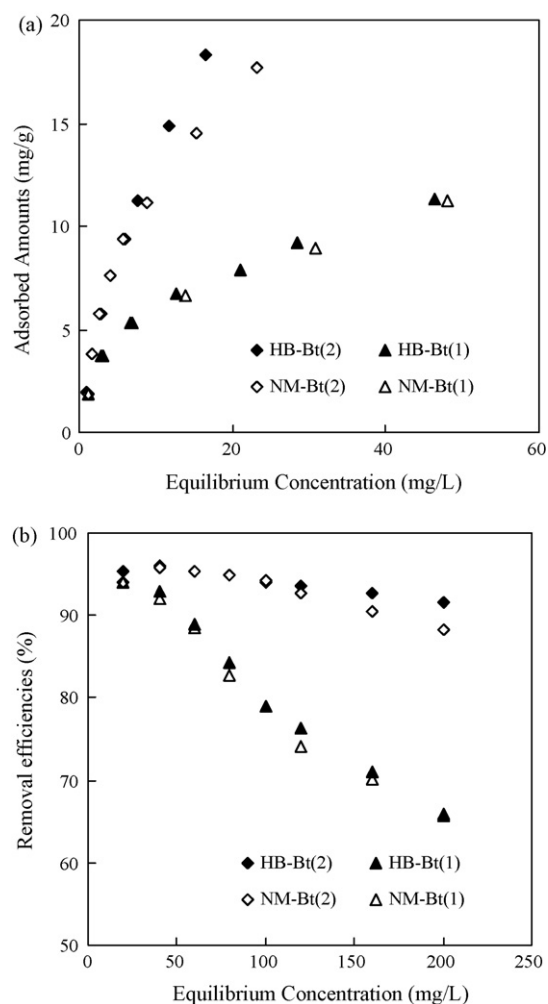

Fig. 4. 2-naphthol sorption isotherms (a) and removal efficiencies (b) by bentonite in the presence of various amounts of CV. (*Note*: (1) and (2) mean that the initial CV concentrations were 1239 mg/L and 3097 mg/L, respectively).

exposed siloxane surface [22,23,27]. Since the two bentonite had similar sorption capacity but quite different charge density, the siloxane surface seemed not be the predominant sorption sites for 2-naphthol. Further work should be done to clarify the relative contribution of siloxane surface and CV to the sorption of HOCs on CV modified bentonite.

In the second experiment, the initial CV concentrations were fixed at 1239 mg/L and 3097 mg/L, corresponding to 40% and 100% of HB-Bt's CEC, and the concentrations of 2-naphthol were varied from 20 mg/L to 200 mg/L. As shown in Fig. 4(a), the sorption capacities of 2-naphthol on HB-Bt and NM-Bt were quite similar in the tested concentration range for the 1239 mg/L CV system. For the 3097 mg/L CV system, however, the two bentonites had similar sorption capacity towards 2-naphthol in the low concentration range (<100 mg/L), and HB-Bt had bigger sorption capacities in the high concentration range (>120 mg/L). The cause for this phenomenon is not clear, and further investigation should be done.

Fig. 4(b) showed that the removal efficiencies of 2-naphthol by the bentonites decreased as the initial concentration increased. For the 3097 mg/L CV system, the removal efficiencies of 2-naphthol were all above 90% in the tested concentration range, and the maximum removal efficiency reached 96%. This indicated that bentonite could be used as efficient sorbents for the simultaneous removal of both CV and 2-naphthol.
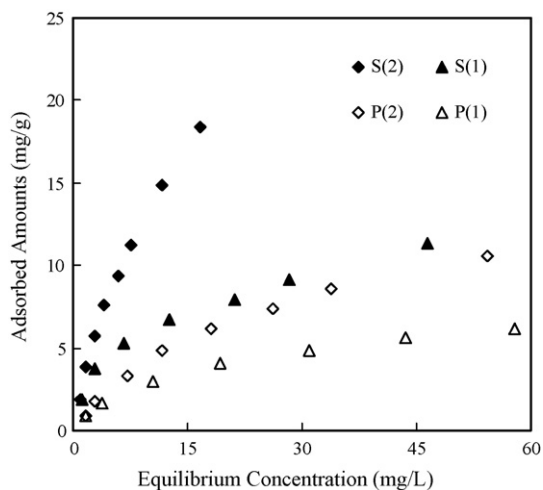
Fig. 5. Influence of CV sorption processes on the sorption capacities of HB–Bt towards 2-naphthol. (*Note*: S denoted that CV and 2-naphthol were simultaneously sorbed by HB–Bt. P denoted that HB–Bt was pretreated with CV, and then 2-naphthol was sorbed successively. (1) and (2) mean that the initial CV concentrations were 1239 mg/L and 3097 mg/L, respectively).

3.3. Comparison of sorption capacities with the CV modified bentonite

Several previous reports showed that the CV modified bentonite could be effective sorbents for HOCs [17–19]. In this work, the sorption efficiencies of HB-Bt to 2-naphthol by the simultaneous sorption method and by the CV modified bentonite were compared. As shown in Fig. 5, the simultaneous sorption method had bigger sorption capacity than the CV modified bentonite did. This phenomenon was rather unexpected. Ma and Zhu [28] also used the simultaneous sorption method (or one-step sorption process) for the removal of CTMA$^+$ and HOCs from water, and they found that the sorption capacity by this method was similar to that by using the CTMA$^+$ modified bentonite.

According to the molecular structure difference between CV and CTMA$^+$, we proposed the following explanation for the different sorption results. CTMA$^+$ has long alkyl chains, which are flexible and interact with each other by hydrophobic interactions. Thereby, the alkyl chains are packed loosely, and HOCs molecules can penetrate into the alkyl chain domains freely [29,30]. That is to say, it will not consume much free energy to change the arrangement models of the previously sorbed CTMA$^+$ during the sorption of HOCs molecules. Thereby, HOCs had similar sorption capacities for the two sorption methods. The molecular structure of CV is rigid, and the interaction force between each other is relatively strong [31], so the adsorbed CV cations will pack rigidly, and more free energy is needed for HOCs molecules to change the arrangement model of the previously sorbed CV in the sorption process. Thereby, the simultaneous sorption method will be much effective in sorption of HOCs comparing with the sorption method using CV modified bentonite.

4. Conclusions

Bentonite could more effectively remove CV from water than the activated carbon did, and the sorbed amounts of CV could be much larger than bentonite's CEC. The adsorbed CV would change the bentonite surfaces from hydrophilicity to hydrophobicity, and thus bentonite could also effectively sorb 2-naphthol during the sorption of CV. Siloxane surfaces seemed not to be the predominant sorption sites for 2-naphthol, and the aromatic effect between CV and 2-naphthol was supposed to be the primary driving force for the sorption of 2-naphthol. The simultaneous sorption method

was more effective in the sorption of 2-naphthol than the method using CV modified bentonites. Results of this work indicated that bentonite could be effective sorbent for the simultaneous removal of cationic dyes and HOCs from water.

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