Adsorption of methylene blue and orange II onto unmodified and surfactant-modified zeolite

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Abstract

Adsorption of cationic methylene blue and anionic orange II onto unmodified and surfactant-modified zeolites was studied using a batch equilibration method. The effects of equilibrium time, solution pH, and adsorption temperature were examined. The results suggested that 2% sodium dodecyl benzenesulfonate (SDBS)- and 3% sodium dodecyl sulfate (SDS)-modified zeolites had higher adsorption capacities for methylene blue than the unmodified zeolite, while 2% cetylpyridinium bromide hexadecyl (CPB)- and 2% hexadecylammonium bromide (HDTMA)-modified zeolites were the best adsorbers for orange II. The adsorption conditions were optimized, and the mechanisms of adsorption are briefly discussed.

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1. Introduction

The discharge of dye effluents to the environment, especially to water system, is becoming a major concern due to their toxicity. The origins of these dyes are usually from industries such as textiles, dyestuff manufacturing, dyeing, and printing. These dyes can consume the dissolved oxygen required by aquatic life and some of them have direct toxicity to microbial populations and can consume the dissolved oxygen required by aquatic life and even can be toxic and/or carcinogenic to mammals. The problems associated with dye pollution could be reduced or minimized by physical, chemical, and biological processes, for example, by microbial degradation, chemical oxidation, coagulation, or filtration and membrane separation [1,2]. But these processes have their disadvantages and limitations, such as high cost, generation of secondary pollutants, and poor removal efficiency. Thus adsorption has been found to be the most effective economic alternative with high potential for the removal and recovery of dyes from wastewater [1,2]. Activated carbon is one of the most widely used adsorbents for this purpose [3–5]. However, activated carbon suffers from high cost of production and regeneration [5,6]. Alternatively, relatively cheap natural adsorbents or their modified products are a choice. Clay minerals, as low-cost natural materials, are natural scavenger of pollutants from water through ion exchange and adsorption [7–10]. Natural zeolite, as an abundant resource that is available globally, has already found many applications because of its high cation-exchange capacity and surface area, etc. Structurally, it is mainly composed of aluminosilicates with a three-dimensional framework structure bearing AlO4 and SiO4 tetrahedra that are linked to each other by sharing all of their oxygens to form interconnected cages and channels containing mobile water molecules and alkalis and/or alkaline earths [11,12]. Zeolite is a good adsorbent for heavy metal ions from wastewater [13–15] and for organic dyes [5,16–18]. However, there has been little study of dye removal by organic-surfactant-modified zeolites [19]. Generally, methylene blue (MB) is present as a cationic dye, and orange II (OII) as an anionic dye in wastewater. The objective of this study was to investigate the adsorption of MB and OII onto unmodified and surfactant-modified zeolites using a batch equilibration method. This study helps to understand the adsorption properties and potential applications of unmodified and modified zeolites for dye removal from aqueous environments.

2. Materials and methods

2.1. Chemicals and reagents

Zeolite (40–80 mesh, ZSM-5) was purchased from Shanghai Reagents Co. and used as received. MB (3,7-bis(dimethylamino)-phenazathionium chloride, C16H12ClN2S·3H2O, molecular weight 373.9) and OII (4-(2-hydroxy-1-naphthylazo)benzenesulfonic acid sodium, C18H12N2NaO4S, molecular weight 350.32) were obtained from Shanghai Reagents Co. Both dyes had a purity of >98%. The structures of MB and OII are illustrated in Fig. 1. Stock solutions of MB and OII were prepared by dissolving the appropriate amounts in distilled water. All working solutions were prepared by diluting the stock solutions with distilled water. Organic surfactants used were sodium dodecyl benzenesulfonate (SDBS), sodium dodecyl sulfate (SDS), cetylpyridinium bromide hexadecyl (CPB), and...
hexadecylammonium bromide (HDTMA). All these chemicals are of analytical reagent grade (Sinopharm Chemical Reagent Co., Ltd.).

2.2. Analyses of MB and OII

The concentrations of MB and OII in all samples used during the adsorption experiments were analyzed with a Model 721 spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd.) at 665 nm for MB and 485 nm for OII, respectively.

2.3. Zeolite modifications

Zeolite was washed with distilled water to remove inorganic impurities. Samples of 100 ml of SDBS, SDS, CPB, and HDTMA solutions were prepared in 12 conical flasks, and 5 g of zeolite was added to each flask. The mixtures were shaken at 200 rpm in a 25°C water bath for 24 h. Then the modified zeolites were recovered by centrifuging and washing several times with distilled water to remove extra surfactants, dried in an oven at 120°C, and then stored in a desiccator for later use. In this study, since OII has negative sulfonate groups, which will be repelled by negatively charged zeolite surfaces [17], CPB and HDTMA were used to modify zeolite for OII removal, as these surfactants are cationic ones; while similarly SDBS- and SDS-modified zeolites were used for MB adsorption, since these surfactants are anionic chemicals and MB is a positively charged basic dye. Our previous study (unpublished) suggested that 2% SDBS- and 3% SDS-modified zeolites had good sorption capacities for MB, and 2% CPB- and 2% HDTMA-modified zeolites were the best adsorbents for OII, so in this study, these four modified zeolites (unless otherwise noted) were chosen and investigated in detail.

2.4. A batch adsorption experiment

Certain amounts of adsorbents (M) were placed in tubes containing organic dye solutions (V₀) of known mass concentration (ρ₀) and pH. The solutions were shaken for a certain period of time (t) on an end-over-end rotary shaker. The adsorbent was separated using a centrifuge. The supernatant volume was described as (V). The dye concentrations (ρ) in the supernatant were determined spectrophotometrically. The dye adsorption rate on zeolites and zeolite-based materials η (%) and the adsorbed amounts of MB and OII, Q (mg/g), were calculated as follows:

\[ \eta \% = \left( \frac{\rho V_0 - \rho V}{\rho V_0} \right) \times 100\% \]  
\[ Q \ (mg/g) = \frac{(\rho V_0 - \rho V)}{M}. \]

3. Results and discussion

3.1. Influence of equilibrium time on MB and OII adsorption

In order to optimize the equilibrium time, a series of experiments were performed at 25 ml of 25 mg/L MB or OII solutions with unmodified zeolite. The initial pH for each dye solution was set at 6.43 and 1.00 for MB and OII, respectively. The suspensions were shaken at 25°C for certain time intervals, and then the dye concentrations in the supernatants were analyzed to calculate the adsorbed MB and OII on the zeolites. In another group of experiments, 0.1 g of 2% SDBS- and 3% SDS-modified zeolites were added to 25 ml of 50 mg/L MB solutions; and 0.4 g of 2% CPB- and 2% HDTMA-modified zeolites were added to 25 ml of 50 mg/L OII solutions; the initial pH of the two dye solutions was set at 6.43 and 1.00, respectively. The suspensions were shaken at 25 and 35°C, respectively, for certain times. These experiments were performed against time (10, 20, 30, 40, 50, 60, 70, 80, and 90 min) and the effect of equilibrium time on the adsorption of MB and OII onto the unmodified and modified zeolites is presented in Fig. 2. The results suggest that the adsorption of MB onto the unmodified and SDBS- and SDS-modified zeolites increased gradually over the first 30 min and then remained unchanged with further increasing equilibrium time. However, the adsorption of OII onto unmodified zeolite was almost instantaneous and an apparent equilibrium was reached within the first 10 min, which is faster than with other
3.2. Adsorption isotherms of MB and OII

The adsorption of MB and OII was performed by shaking 0.1 g of zeolite in 25 ml of MB or 0.25 g of zeolite for the adsorption of OII at 25 °C for 1 h; the pH of MB and OII was set at 6.43 and 1.00, respectively, and the initial concentrations of MB and OII were increased from 5 to 55 mg/L. The data show from the isotherms that the adsorption of MB and OII increased with an increase in their initial concentration. The adsorption curve was linear over the initial concentration ranges of 5–35 mg/L MB and OII for unmodified zeolites, and 10–60 mg/L MB and 10–50 mg/L OII for modified zeolites, suggesting that partition is a main mechanism for the adsorption of MB and OII.

The maximum adsorbed MB and OII amounts on unmodified zeolite were 8.67 and 0.63 mg/g, respectively. This big difference may arise from the structure of zeolite, which has open and large internal surface area usually at 400–800 m²/g. The structural cations on zeolite may exchange with cations from solutions and thus improve the adsorption capacity for cationic MB, while for anionic dyes, OII in this case, the adsorption is only through porous zeolite without any ion-exchange effect.

Another series of experiments were carried out with 0.1 g 2% SDBS- and 3% SDS-modified zeolites in MB solution with different concentrations at 25 °C or with 0.4 g 2% CPB- and 2% HDTMA-modified zeolites in OII solutions at 35 °C. The pH of MB and OII was 6.43 and 1.00, respectively. It was demonstrated that the amount of MB adsorbed reached its maximum when initial MB concentration was 60 mg/L, where 2% SDBS- and 3% SDS-modified zeolite can absorb 15.68 and 14.87 mg/g MB, respectively; and in the case of OII, the adsorption amounts were 3.62 and 3.38 mg/g when initial OII concentration was 50 mg/L. Compared with the performance of untreated zeolites, surfactant-modified ones have higher adsorption capacities. In addition, there was no negative adsorption of dyes on untreated zeolites, as demonstrated in some other studies [17].

3.3. Influence of pH on MB and OII adsorption

Adsorption tests as a function of pH were carried out and the results are shown in Figs. 3a and 3b. In the experiments 25 ml of 25 mg/L MB or OII and 0.1 g and 0.25 g of unmodified and modified zeolites were respectively used and the initial pH varied from 4 to 10 for MB and 1 to 7 for OII. As shown in the figures, the adsorbed MB increased with increasing initial solution pH and reached its maximum (about 6.1 mg/g) on unmodified zeolite at pH 6–9. This is comparable to other investigations [4,6,21–24]. It is probably because at lower pH the presence of H⁺ ions will compete with cationic MB for adsorption sites. When pH is increased, the zeolite surface is more negatively charged, resulting in an increase of adsorption, since electrostatic repulsion between MB and surface is decreased. For OII, the adsorption amount decreased as the pH was increased. When pH was kept at <2 the maximum adsorbed OII was found to be about 0.6 mg/g. This may be because at high pH, OH⁻ groups on the surface of the adsorbent will repel the anionic dye molecules.

For modified zeolites, 0.1 g of 2% SDBS- and 3% SDS-modified zeolites were added respectively to 25 ml of 25 mg/L MB, while 0.4 g of 2% CPB- and 2% HDTMA-modified zeolites were added to 25 mg/L OII solutions, respectively. The initial pH of MB and OII solutions was adjusted to 6.43 and 1.00, respectively, and the dye concentration was determined after shaking at 25 and 35 °C, respectively, for certain time intervals. Figs. 3a and 3b also show the dye adsorption on the modified zeolites and it seems that the equilibrium pH has less effect on adsorption onto modified zeolites than that of unmodified ones. The adsorbed amounts of MB on SDBS- and SDS-modified zeolites reached their maximum values when pH was between 6 and 9; and for OII, the maximum adsorption was reached when pH was adjusted to be less than 2. In all cases, the adsorption of dyes increased greatly on surfactant-modified zeolites over that on unmodified ones.

3.4. Influence of temperature on MB and OII adsorption

Figs. 4a and 4b show the effect of equilibrium temperature on the adsorption of MB and OII onto unmodified zeolite. As seen from the figure, temperature had little effect on MB adsorption on
zeolite, while for orange II, this effect became relatively noticeable and the optimum temperature was found to be 25 °C, as shown in Fig. 4b. For modified zeolite (see Fig. 4a), MB adsorption on SDBS-modified zeolite almost kept constant with increased temperature, but there was a small variation of adsorbed MB with increasing temperature for SDS-modified zeolite, and in both cases, the opti-
mum temperature can be kept at 25 °C. Temperature had similar effects on OII adsorption on the CPB- and HDTMA-modified zeolites, where the adsorption capacity increased with increasing temperature, indicating that the adsorption is an endothermic process; this may be due to the enhanced rate of external and intraparticle diffusion of the adsorbate [20], and it will reach their peak values at 35 °C with about 3 mg/g adsorbed.

3.5. Influence of adsorbent amount used on MB and OII adsorption

In order to obtain the optimum zeolite amount required for adsorption at pH 6.43, a series of experiments were undertaken with different amounts of adsorbents in 25 ml of 25 mg/L MB solutions. The MB and OII concentrations were tested after 1 h of shaking at 25 and 35 °C, respectively. The zeolite amounts added against adsorbed MB/OII (mg/g) and adsorption rate (%) are shown from Figs. 5a–5f. Examination of these figures revealed that adsorbed MB and OII decreased with increasing adsorbents, while the adsorption rate (%) increased when amount of adsorbents increased. As shown in Figs. 5a–5c, the adsorption rates of MB on 0.08 g of unmodified zeolite and 2% SDBS- and 3% SDS-modified zeolites can reach 98.22, 99.44, and 98.47%, respectively; and the maximum MB adsorption on unmodified zeolite was about 35 mg/g, which is comparable to other studies [25]. For OII (Figs. 5d–5f), the adsorption rates of orange II on 0.5 g untreated and 0.4 g 2% CPB- and 0.5 g 2% HDTMA-modified zeolites were 11.48, 96.30, and 97.36%, respectively; i.e., the removal rates of OII on modified zeolites were much higher than that on unmodified zeolite.

4. Conclusions

Unmodified zeolite is not a suitable adsorbent for OII, although it may adsorb more MB than OII due to its negative surface charges. The adsorption capacities for MB can be improved when zeolites are modified with SDBS or SDS. SDBS-modified zeolite has an advantage, because of its relatively cheaper price and similar adsorption capacity compare with SDBS-modified zeolites. For unmodified and 2% SDBS-modified zeolites, the optimum conditions for MB adsorption are at 25 °C, pH 6.85, and 1 h equilibrium time with adsorption capacities of 8.67 and 15.68 mg/g, respectively. For OII adsorption on unmodified zeolite, the best condition is at 25 °C and pH 1 for 20 min equilibrium time with adsorption capacity of 0.63 mg/g. Similarly, there are no big differences between CPB- and HDTMA-modified zeolites on OII adsorption, so HDTMA as a cheaper surfactant is chosen and its optimum condition for OII adsorption is at 35 °C, pH 1 for 1 h of equilibrium time; the removal capacity was 3.38 mg/g. This study has shown the potential of modified zeolites for the removal of these organic dyes from wastewater streams due to their relatively low price and abundance in nature.

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