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Mechanism and performance for adsorption of 2-chlorophenol onto zeolite with surfactant by one-step process from aqueous phase

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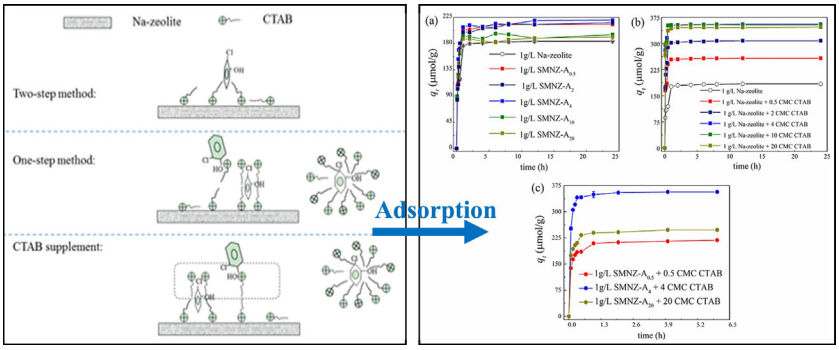
HIGHLIGHTS

- Zeolite and surfactant in a one-step process had high adsorption capacity for 2-CP.
- Different roles of surfactant in one- and two-step adsorption processes were explained.
- 2-CP adsorption mechanisms of the one- and two-step processes were proposed.
- Surfactant supplement was crucial for enhancing adsorbent reusability.

GRAPHICAL ABSTRACT



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ABSTRACT

To decrease the power, material, and time consumption in wastewater treatment, a one-step process was performed to remove 2-chlorophenol (2-CP) from aqueous phase using zeolite and cetyltrimethylammonium bromide (CTAB). Compared with the traditional two-step process, the one-step process used in this study achieved almost eight times higher 2-CP adsorption capacity within a shorter time and maintained high removal efficiencies (around 65%) in reuse tests, thus becoming an efficient and economically acceptable alternative process. For the one-step process, the kinetic data fitted well with a nonlinear pseudo-second-order model, and the isotherm data fitted well with the Dubinin-Astakhov (DA) model. The uptake of 2-CP was highly dependent on pH, increasing in the pH range of 3–6. The enhanced 2-CP removal in a one-step adsorption process can be explained by the larger amount of surfactant loading (≥0.056 mmol/g), as determined from the total organic carbon (TOC) and zeta potential. Due to the formation of a loose CTAB bilayer, the hydrophobic partition and the interaction with the positively charged "head" of CTAB bilayers were decisive for the enhancement of pollutant adsorption. Therefore, organic pollutants could be removed from water alongside the synthesis of hydrophobic zeolite in a one-step process, which is a promising technology for the in-situ treatment of organic wastewater.

1. Introduction

Chlorophenols are used extensively as fungicides, herbicides, algicides, insecticides, ovicides, pharmaceuticals, dyes, preservatives, and intermediates (Manne and Gaub, 1995; Nezamzadeh-Ejhieh and

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Ghanbari-Mobarakeh, 2015). Most chlorophenolic compounds are persistent toxic substances, which threaten human health through direct contact and bio-accumulation (Haggerty and Bowman, 1994; Liu et al., 2014; Spurlock and Biggar, 1994). Contamination by chlorophenolic compounds in air, soils, and natural waters has generated widespread concern (Baker and Ghanem, 2009; Nezamzadeh-Ejhieh and Khorsandi, 2014). Therefore, the development of effective techniques to remove chlorophenols in water treatment is imperative.

Zeolites are promising adsorbents for organic pollutants because of their relatively high specific surface area, mechanical strength, local availability, and low price (Haggerty and Bowman, 1994; Li and Bowman, 1998). Due to the net negative charge on the framework and hydrophilicity on their surfaces, raw natural zeolites usually have little or no affinity for negatively charged organics in aqueous solution (Quina et al., 1995). To increase the adsorption affinity, zeolites should be modified by cationic surfactant and the formed surfactant layer adsorbs organic matters (Hasheminejad and Nezamzadeh-Ejhieh, 2015; Nezamzadeh-Ejhieh and Mirzaeyan, 2013; Nezamzadeh-Ejhieh and Tavakoli-Ghinani, 2014; Sharafzadeh and Nezamzadeh-Ejhieh, 2015; Abraham, 1993; Quina et al., 1995). In the traditional two-step process, the zeolites are first treated by surfactant loadings with several washes, centrifuging, and drying, and the surfactant-coated zeolites are then used to remove pollutants from wastewater by adsorption (Li et al., 2011; Sprynskyy et al., 2009). However, the relatively high cost of the process, time-consuming operation, and complexity of the technique in the two-step process restricts its application and limits sustainability. Therefore, a one-step process has been established, which simultaneously modifies adsorbents by surfactants and removes pollutants from wastewater by dispersing them in the solution at the same time (Ma and Zhu, 2007). Bentonite with a cationic surfactant in a one-step process has been used to achieve efficient removal of organic compounds, such as polycyclic aromatic hydrocarbons, phenols, and dyes (Khenifi et al., 2009; Ma and Zhu, 2007; Wu and Zhu, 2012; Zhu and Ma, 2008). Its outstanding adsorption capability is due to the large number of hydrophobic sites created by the adsorbed surfactant in the interlayer and on the surface of the negatively charged bentonite (Wu and Zhu, 2012; Zhu and Ma, 2008). Furthermore, good dispersion properties and rapid bentonite sedimentation are also observed in the one-step process (Khenifi et al., 2009). Thus, many studies have focused on the optimum conditions for treating organic wastewater by organophilic bentonite in a one-step process (Ma and Zhu, 2007; Zhu and Ma, 2008).

However, the different conformations and roles of surfactants between one- and two-step processes have not been discussed. Moreover, the interactions among the surfactant, pollutant, and adsorbent in the one-step process are largely unknown. Understanding the adsorption mechanism and behavior of surfactants in the one-step process is important for predicting contaminant adsorption and its environmental implications. For zeolites, there is no available literature on its adsorption of organic chemicals in the presence of a surfactant in a one-step process. In addition, to apply zeolite in a one-step adsorption process for chlorophenol removal, the experimental parameters need to be studied systematically. The optimal ratio of zeolite and surfactant, influence of operating parameters (i.e., adsorption time, organic pollutant concentration, temperature, and pH), and reusability of the adsorbent with and without the addition of surfactant must be determined to successfully remove contaminants and reduce the costs, which are largely unknown to date.

In this study, a cationic surfactant, cetyltrimethylammonium bromide (CTAB), was used to modify a zeolite and then to remove 2-chlorophenol (2-CP) from an aqueous system by one- and two-step processes, respectively. The aims of this study were to determine: (1) how and to what extent surfactant can enhance the adsorption of 2-CP onto zeolite in one- and two-step processes, and the conformations of the surfactant in the two processes, (2) adsorption isotherms, kinetics, and mechanisms in the one-step process, (3) the main factors influencing 2-CP removal, and (4) the reusability of the adsorbent.

2. Materials and methods

2.1. Chemicals and materials

CTAB with a purity of >99.0%, was purchased from China Medicine (Group) Shanghai Reagent Co. (Shanghai, China) and 2-CP was purchased from Aladdin Reagent Co., Ltd (Shanghai, China). The characteristics of CTAB and 2-CP are listed in Table S1. Zeolite from the gismondine group, with a pore size of 3.1 Å × 4.5 Å [100] and 2.8 Å × 4.8 Å [101] (Xie et al., 2012), was purchased from Aladdin Reagent Co., Ltd., and its selected properties are presented in Table S2. All other reagents were of analytical grade.

2.2. Preparation and characterization of adsorbents

Zeolite samples (10 g) were treated with 1 mol/L NaCl solution to reach a final homoionic state, thus improving their performance in ion exchange applications. This was followed by several washings with distilled water; the samples were then centrifuged to remove the excess NaCl, with a silver nitrate solution used as the indicator. The products were then dried in an oven at 333 K and stored for further experiments. At this stage, they were referred to as Na-zeolite.

To prepare the CTAB-modified Na-zeolite (SMNZ), 1 g Na-zeolite was mixed with 1 L CTAB. The CTAB concentration ranged from 0 to 20 times the critical micelle concentration (CMC, 0.09 mmol/L). The mixtures were shaken at room temperature in a mechanical shaker for 24 h. The adsorbents for the traditional two-step process were labeled as SMNZ-A, and were prepared by washing with distilled water three times. The mixture was separated by centrifugation and dried in an oven at 333 K. The adsorbents used for simulating the state of CTAB in a one-step process were labeled as SMNZ-B, separated by filtering without washing, and then freeze-dried for 24 h. The different labels used are listed in Table 1 and refer to the CTAB dose used for coating, as well as the different washing and heating processes.

The concentrations of CTAB solution ranged from 0.0165 to 0.66 g/L with a fixed amount (1.0 g/L) of Na-zeolite powder, and the conical flasks were shaken in a thermostatic shaker for 6 h at 298 K and 120 rpm. The samples were then separated by centrifugation, and the residual CTAB concentrations were measured using a Vario total organic carbon (TOC) system (Elementar Analysensysteme GmbH, Hanau, Germany). The amount of CTAB adsorbed was obtained by the following equation:

$$q_{CTAB} = \frac{\frac{(C_{T0} - C_{Te})}{12 \times 19}}{m} V \quad (1)$$

where q_{CTAB} is the equilibrium adsorption quantity of CTAB adsorbed per unit mass of Na-zeolite (mmol/g); C_{T0} and C_{Te} are the initial TOC concentration of CTAB (mg/L) and the equilibrium TOC concentration of CTAB (mg/L), respectively; V is the volume of the CTAB solution (L); m is the weight of the Na-zeolite (g); 12 is the molecular mass of carbon; and 19 is the number of carbon atoms in CTAB.

Table 1
Labeling of adsorbents.

Adsorbent	Label		m_{CTAB} (g/L)	CMC_{CTAB} multiples
Na-zeolite	Na-zeolite		0	0
	Washing three times and heating at 333 K	Without washing and freeze-drying		
SMNZ	SMNZ–$A_{0.5}$	SMNZ–$B_{0.5}$	0.0165	0.5
	SMNZ–A_2	SMNZ–B_2	0.066	2
	SMNZ–A_4	SMNZ–B_4	0.132	4
	SMNZ–A_{10}	SMNZ–B_{10}	0.33	10
	SMNZ–A_{20}	SMNZ–B_{20}	0.66	20

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