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Adsorption behavior and mechanism of chlorophenols onto organoclays in aqueous solution

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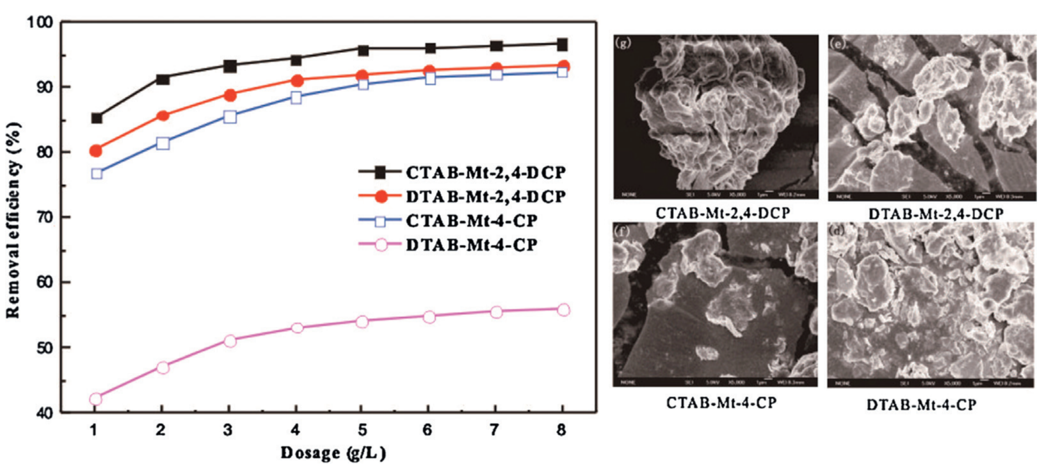
GRAPHICAL ABSTRACT



HIGHLIGHTS

- Different alkyl chain length surfactants were used to modify Na-montmorillonite.
- The organoclays were used as adsorbents for the removal of chlorophenols.
- The adsorption process is complex and involves multiple mechanisms.
- Adsorption involves partitioning, electrostatic and van der Waals forces.

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ABSTRACT

Organoclays were prepared by replacing exchangeable Na^+ ions in Na-montmorillonite (Na-Mt) with dodecyltrimethylammonium bromide (DTAB) and cetyltrimethylammonium bromide (CTAB). Organic modification is important in order to obtain good affinity between organoclays and organic pollutants. Hydrophobic DTAB-montmorillonite (DTAB-Mt) and CTAB-montmorillonite (CTAB-Mt) were studied as adsorbents for 4-chlorophenol and 2,4-dichlorophenol. The morphology, structure, and surface properties of Na-Mt and organoclays were characterized by scanning electron microscopy, X-ray diffraction, Fourier infrared spectroscopy, specific surface area, and zeta potential measurements.

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Adsorption was determined as a function of adsorbent dosage, pH, contact time, and temperature. It was found that pH and temperature had very important effects on the adsorption of chlorophenols. The Langmuir isotherm was the best choice to describe the adsorption behavior. The maximum adsorption capacities of CTAB-Mt for 4-chlorophenol and 2,4-dichlorophenol were 395.0 and 585.8 mg/g, respectively, whereas the maximum adsorption capacities of DTAB-Mt for 4-chlorophenol and 2,4-dichlorophenol were 331.1 and 458.2 mg/g, respectively. The kinetic data fitted the pseudo-second-order kinetic model. Thermodynamic parameters suggested that the adsorption process of chlorophenols onto organoclays was physisorption and exothermic. The adsorption mechanism is a complex process that involves a combination of partitioning, electrostatic attraction, and van der Waals forces.

1. Introduction

There have been many attempts to solve environmental problems originating from industrial wastes. Most industries produce toxic compounds, including phenols and phenolic compounds [1]. The high toxicity and hazardous nature of phenols can cause serious environmental and technical problems [1,2]. Phenols are important raw materials and are used in a wide range of applications. The petroleum and petrochemical, pharmaceutical, pesticide, plastic, coal conversion, phenol-producing, and pulp and paper industries are the main sources of phenolic wastewaters [1–3]. Because of their toxicity and potential harm to aquatic life, plants, and human beings even at low concentrations, phenols and phenolic compounds are listed as priority pollutants by the United States Environmental Protection Agency [3,4]. When phenols above a certain concentration are present in water, they cause health hazards, such as liver, lung, and kidney damage, skin and eye irritation, and systemic poisoning [4,5]. Therefore, their presence in the environment has become a great concern in recent years because of their extensive use and increased amount of discharge. Removal of phenols from wastewaters before they come in contact with natural bodies of water or are discharged into the environment is crucial to ensure the safety of water supplies.

Various treatment technologies, including adsorption, membrane separation, destructive oxidation, and biological treatment, are available to reduce phenol concentrations in wastewaters [6–9]. Adsorption is an effective, simple, and economical technique to remove phenols [6]. Many adsorbents have been investigated for the removal of phenols. However, phenols are highly hydrophobic and have poor biological activity. Most adsorbents have been found to have limited ability to remove phenols, and none can completely remove phenols from aqueous solution [10–12]. Therefore it is of great practical and academic interest to develop new adsorbents to remove phenols from aqueous solution [13].

Natural clay minerals have been used since the earliest days of civilization. Because of their low cost, abundance in most continents of the world, high adsorption properties, and potential for ion-exchange, clay minerals are strong candidates as adsorbents [14]. The most commonly used clay is montmorillonite (Mt) because of its high cation exchange capacity (CEC), swelling properties, high surface area, and strong adsorption ability [15]. Na-Mt is a typical 2:1 layered clay mineral, and is characterized by one Al octahedral sheet sandwiched between two Si tetrahedral sheets. It has a negative surface charge created by the isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer [14,15]. The montmorillonite surface is hydrophilic because inorganic cations, such as Na^+ and Ca^{2+}, become strongly hydrated in the presence of water. As a result, the adsorption ability of organic pollutants on natural Na-Mt is very low [14–16]. The adsorption properties of Na-Mt can be improved by modifying the clay mineral surface with a cationic surfactant [16]. The cationic surfactants, known as quaternary amine salts, are in the form $[(CH_3)_3NR]^+$ or $[(CH_3)_2NR_2]^+$, where R is an alkyl chain [15–18]. Replacement of inorganic exchangeable cations with cationic surfactants converts the hydrophilic silicate surface of clay minerals to a hydrophobic surface, and the obtained complex is an organoclay [16–18]. It is generally accepted that adsorption of hydrophilic long-chain quaternary ammonium cations onto clays occurs by an ion-exchange mechanism [18]. As a result of the modification of the clay, the surface properties change from highly hydrophilic to increasingly hydrophobic [19]. Such changes in the properties of the surfactants are important for the application of organoclays, and thus organoclays can be used as adsorbents for the removal of organic contaminants [15,20–22]. The improvement of the adsorption capacity of organoclays for organic compounds strongly depends on the charge density of the clay layers and molecular arrangements of surfactants within the organoclays. Understanding of the structure, surfactant arrangement, and surface properties of synthesized organoclays is essential for their adsorption applications [19–24]. To the best of our knowledge, only a few studies have attempted to describe the relationship between adsorption behavior, charge density, and the molecular arrangement of surfactants in the interlayer of organoclays.

In this work, 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP) were chosen as model pollutants. Dodecyltrimethylammonium bromide (DTAB) and cetyltrimethylammonium bromide (CTAB) were used as long alkyl chain cationic surfactants for the preparation of organoclays. This study is of great importance for understanding the structure, properties, and potential applications of organoclays, especially in water purification. We provide a detailed description of surfactant arrangement and the adsorption behavior of chlorophenols onto organo-Mt. The adsorption of 4-CP and 2,4-DCP was investigated under different environmental conditions, such as variation of pH, adsorbent dosage, contact time, and temperature. Adsorption isotherms and kinetics data were obtained and thermodynamic parameters were determined. The adsorption mechanism between organo-Mt and chlorophenols was also studied.

2. Materials and methods

2.1. Materials

Na-Mt was provided by the Xinjiang Technical Institute of Physics and Chemistry (CAS). The composition of Na-Mt was as follows (wt.%): Na_2O 7.233, MgO 4.133, Al_2O_3 19.986, SiO_2 56.851, P_2O_5 0.022, K_2O 0.442, CaO 0.698, MnO 0.053, TiO_2 0.368, and Fe_2O_3 7.936. Its CEC was 82.5 meq/100 g. The diameter of the Na-Mt particles was 1–2 μm, and the particles were used without further purification. The surfactants used for the preparation of organoclays were DTAB ($C_{15}H_{34}NBr$, >98%) and CTAB ($C_{19}H_{42}NBr$, >98%), which were obtained from Sigma–Aldrich. 4-CP and 2,4-DCP were