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Colloids and Surfaces A: Physicochem. Eng. Aspects 253 (2005) 137–144

COLLOIDS
AND
SURFACES A

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Enhancement of nitrophenol adsorption in the presence of anionic surfactant and the effect of the substituent position

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Received 23 February 2004; accepted 5 November 2004
Available online 15 December 2004

Abstract

Adsorption behavior of phenol, *ortho*-nitrophenol (ONP), *meta*-nitrophenol (MNP) and *para*-nitrophenol (PNP) on a kaolinite-type clay has been investigated by means of spectrophotometric method at 298 K. Adsorbability of the phenolic compounds in aqueous solution decreases in the following order; ONP > phenol > MNP ≅ PNP. Influence of an anionic surfactant, sodium dodecylsulfate (SDS), on adsorption behavior of phenol and nitro-substituted phenols onto kaolinite is studied by determining their adsorption isotherms. Experimental evidence has shown that phenol does not adsorb to the surface of kaolinite in the presence of SDS due to large repulsive, electrostatic barrier between negatively charged phenol and negatively charged adsorptive SDS micelles or hemimmicelles. The adsorption capacity of kaolinite for the aromatic nitro compounds in the SDS system is markedly increased compared with the adsorption onto bare kaolinite surface especially at high-concentration region. Adsorption results were interpreted by comparing isotherms of phenolic compounds and SDS. It is shown that bilayer structure of SDS forms even at low SDS concentrations. In this region, PNP molecules are adsorbed via adsolubilisation whereas penetration of ONP and PNP is difficult because of their structural properties and electrical interactions. However, adsolubilisation phenomenon dominates adsorption process of all nitrophenol compounds at higher concentrations. Data show that adsorption capacities of the adsorbates in the presence of SDS follow the order ONP > MNP > PNP. The differences in the adsorption capacities depending on position of nitro group on phenol ring are correlated with the capacity of SDS. The equilibrium isotherms of phenols have been analyzed using Freundlich and Langmuir equations.

Keywords: Adsorption; Adsolubilization; Kaolinite; Nitrophenol; SDS

1. Introduction

Phenol like pollutants occur in wastewater of a number of industries such as high-temperature coal conversion, petroleum refining, resins and plastics. Among the technologies for wastewater treatment, adsorption by solid phase is the most frequently used. Activated carbons [1–4], silica [5], glass powder [6], polymeric resins [7–9], fly ash [10] and variety of geologic materials including kaolinite [11], montmorillonite [12], and zeolites [12,13] have been proposed to remove the phenolic pollutants from wastewater. Generally, these materials are modified with different ways such as grafting of organic compounds, binding organic anions and cations.

Surfactants used in many human activities in domestic and industrial applications are also responsible for water contamination [14]. They may adsorb at solid/water interfaces to form aggregates of various geometries depending on substrate, the surfactant and its concentration [15]. In the low-concentration region, the adsorption of ionic surfactants onto oppositely charged mineral surfaces occurs primarily through attractive electrostatic forces [16]. It is generally accepted that at a defined surfactant concentration, the adsorbed ions begin to associate through the hydrophobic effect into surface aggregates. This surfactant concentration has been termed as hemimicelle concentration (HMC) and occurs at much lower concentration than corresponding bulk critical micelle concentration (CMC). The micelles and hemimicelles adsorbed at solid/liquid interface can be used to solubilize organic molecules in the same manner that was observed for micelles

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doi:10.1016/j.colsurfa.2004.11.004

in the solution phase [17,18]. The term of adsolubilisation is generally used to describe this phenomenon.

Benella et al. investigated adsolubilisation of phenol in aqueous solution of dodecyltrimethylammonium bromide on porous alumina silicates and non-porous silica surface [19]. They reported that uptake of phenol by the surfaces cationic surfactants adsorbed was markedly increased. Talbot et al. studied the incorporation of *para*-nitrophenol (PNP) into kaolinite/water interface by addition cetylpyridinium chloride (CPC) which is a cationic surfactant [15]. At low CPC concentration PNP adsorption decreases whereas it increases at concentration above CMC. These results suggest that CPC is adsorbed in micellar form on kaolinite surface only above CMC because of low cation exchange capacity of kaolinite. On the other hand, Hanna and Somasundaran [20] observed a 130% coverage of the kaolinite surface for the adsorption of an anionic surfactant, sodium dodecylbenzenesulfonate (SDBS), onto kaolinite. It has been reported that PNP is adsolubilized by the anionic surfactant, sodium dodecylsulfate (SDS), on bentonite [21]. This suggested that adsolubilisation can be applied to remove phenol and nitro-substituted phenols where anionic surfactants have been used.

In the present work, the adsolubilisation of phenol and its nitro-derivatives onto kaolinite/water interface has been studied by addition of SDS commonly used in the formulation of detergents. In order to compare adsolubilisation phenomenon with adsorption, experiments were also performed in the absence of surfactant.

2. Experimental

2.1. Materials

The kaolinite-type clay used in this study was obtained from Sogut-Inhisar region of Turkey. The anionic surfactant was provided by Sigma. Its CMC is 8.2×10^{-3} mol/L. Phenol and nitro-substituted phenols were supplied from Merck (Darmstadft).

2.2. Adsorbent specifications

X-ray diffraction method (XRD) was employed to study the structure of Sogut-Inhisar clay. XRD analysis indicated that the clay was essentially comprised of kaolinite. It contains minor impurities of mica and quartz. The clay had the following chemical composition by weight: Al_2O_3 22.0%, SiO_2 60.5%, Fe_2O_3 2.0%, CaO 0.6%, TiO_2 2.0%, MgO 0.3%, K_2O 1.85%, Na_2O 2.0%, loss of ignition 8.0%. The surface area measured with methylene blue adsorption method and cation exchange capacity determined by using ^{22}Na as index cation were 27.05 $m^2\,g^{-1}$ and 0.18 meq g^{-1}, respectively.

Potentiometric titration experiments were conducted for determining the value of pH at the point of zero charge (pH_{pzc}). Acidimetric and alkalimetric titrations were performed on a system containing suspended kaolinite particles in 0.1 M KCl as a supporting electrolyte. The system was first titrated with 0.1 M HCl up to approximately pH 3 and then with 0.1 M KOH up to about pH 10. Suspension was purged continuously with nitrogen gas. The value of pH_{pzc} of kaolinite was determined as 7.2 ± 0.2. It has been reported that the pH_{pzc} value of kaolinite mineral with different origin ranges from 3.9 to 7.5 dependent on the particular kaolinite crystal structure, titration method and supporting electrolyte [22]. Generally, this value has been found to be around 7 [23].

2.3. Adsorption experiments

2.3.1. Adsorption of phenol and nitrophenols in the presence of SDS

Amount of adsorbed solute was calculated by the following well-known relation:

$$q = (C_0 - C)\frac{V}{m} \tag{1}$$

where C_0 is the initial concentration, C is the final or equilibrium concentration (mol/L), V (L) is the volume of solution, and m (g) is the mass of adsorbent used.

In order to obtain relevant data for constructing adsorption isotherms of phenol and nitrophenols two types of adsorption experiments were performed as follows:

i- Initial concentrations were changed at constant ratio of V/m.
ii- Ratios of V/m were changed at constant initial concentration.

Firstly, the experiments were carried out at constant V/m ratio of 0.01 L/0.1 g (i.e., 0.1 L/g) and variable initial concentration in the range of 2.5×10^{-5} to 5.0×10^{-4} M in distilled water and in the presence of 5.0×10^{-4} M SDS. It was not attained to a plateau region on isotherm curves of *ortho*-nitrophenol (ONP), *meta*-nitrophenol (MNP) and PNP even in the most concentrated solution. On the other hand, both phenol and substituted phenols were hardly adsorbed on kaolinite/water interface at higher concentrations than 5.0×10^{-4} M because of solute–solute interaction in the solution. Therefore, further adsorption experiments were performed at constant solute concentration of 5.0×10^{-4} M by increasing solution volume up to 0.025 L.

In the experiments, the adsorbent was contacted with the solution for 1 h at 298 K in a thermostatic shaker/water bath. The mixture was then allowed to equilibrate for 48 h and liquid and solid phases were separated by centrifuging at 3500 rpm (825 G) for 20 min. Solution spectra were scanned in the range of 190–500 nm wavelengths using a Perkin Elmer 554 UV spectrophotometer. The final concentration of solutions was determined by measuring absorbance at the wavelengths of maximum absorption (λ_{max}). The values of λ_{max} of phenol, ONP, MNP and PNP in distilled water were 270, 350, 330 and 320 nm whereas they were 266, 344, 326 and 312 nm in SDS solutions, respectively.