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Cooperative coadsorption of 4-nitrophenol and basic yellow 28 dye onto an iron organo–inorgano pillared montmorillonite clay

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ABSTRACT

Sorption properties of an iron surfactant-modified pillared montmorillonite (Fe-SMPM) toward two organic pollutants, basic yellow 28 dye (BY28) and 4-nitrophenol (4-NP), were studied at different pH values in both single component and binary pollutant systems. The pseudo-first-order model fits well with the kinetic data obtained in single component studies and sorption capacities of both BY28 and 4-NP increased with the pH value. A sorption synergetic mechanism was observed in binary systems; 4-nitrophenol adsorption was enhanced by the presence of BY28 in the mixture and increased with dye concentrations. Isotherms were described using the Freundlich model in single component systems and the Sheindorf–Rebhun–Sheintuch (SRS) model, an extended Freundlich model, in binary mixtures systems. Hydrophobic interactions between the surfactant-modified pillared clay and the pollutants were suggested to explain the sorption mechanisms.

1. Introduction

Industrial processes generate wastewaters containing organic pollutants with negative impacts for humans and ecosystems. Among these pollutants, the compounds difficult to remove by means of conventional wastewater treatment technologies are of special concern such as 4-nitrophenol (4-NP). It is a toxic compound even at low concentration (4-NP is considered to be a hazardous waste by the US Environmental Protection Agency) and its presence in natural waters can lead further to the formation of halogenated derivatives during the chlorine disinfection process. In another way, many industries use dyes in order to color their products. They consequently generate a high amount of colored wastewaters and many of these dyes reduce light penetration, have a derogatory effect on photosynthesis, and are also potentially toxic/carcinogenic, leading to a serious hazard to aquatic leaving organisms.

Among the various treatment options (coagulation and flocculation, membrane filtration, biological treatments, adsorption, advanced oxidation processes), adsorption has been regarded as a promising technology [1–8] and several authors have investigated adsorption in multicomponent systems [9–11]. Activated carbon (powder or granular form) is one the more popular and widely used adsorbent due to its large surface area, microporous structure, and high adsorption capacity, but the high cost (including regeneration and reuse) restricted its widespread use. Therefore, extensive investigations are being carried out to identify alternative sorbents [12]. In recent years, pillared clays have been proposed as a new class of microporous materials due to easy availability and catalytic properties in different reactions [13]. These solids are obtained by introducing large polyoxycations into their interlayer regions. The separation between the layers can be kept stable and depends on the polyoxycation used. The polymeric compounds most frequently used as pillaring agents are species of Al, Ti, Cr, and Fe [14,15]. However, the organic–inorganic modification of clay minerals offers the potential to be adsorbents in the removal of both organic and inorganic pollutants from wastes, due to their structural diversity [16]. In this way, numerous studies have been directed toward the use of mixed pillared clay for the removal of metal ions, organic pollutants, and dyes from waters and wastewaters [14–17].

The first part of this paper deals with the sorption of basic yellow 28 (BY28), a basic dye currently used in Algeria, and 4-nitrophenol (4-NP) onto an iron organo-inorgano pillared clay (Fe-SMPM) in single systems. The second part concerns the cooperative/competitive coadsorption mechanisms of these pollutants in mixtures at different pH values and BY28/4-NP molar ratios.

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2. Materials and methods

2.1. Sorbent

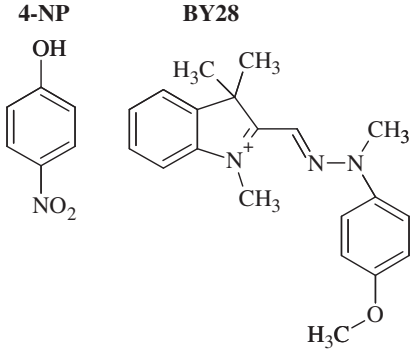
The starting material was a bentonite extracted from the Roussel site in Maghnia (Western Algeria); its characteristics were done in a previous work [18]. This clay underwent a purification stage according to the procedure given by Bouras et al. [14,15]. The homoionization was performed by dispersing purified bentonite in molar NaCl in order to replace all exchangeable cations with Na^+ and washing up with distilled water, followed by a centrifugation and dialysis to eliminate all other solid phases and excess chloride anions. The montmorillonite fraction (<2 μm) was recovered by decantation and was named Na-montm.

The iron pillaring solution (PCBF) was prepared following a neutralization of Fe $(NO_3)_3{\cdot}9H_2O$ by NaOH up to a molar ratio OH/Fe = 2. PCBF solutions which give Fe-polyhydroxy species were left at room temperature for 10 days according to procedures provided elsewhere [18] and the final iron concentration was 0.2 M. Na-montm suspension (0.5% (w/w)) was iron-intercalated by adding dropwise the iron pillaring solution (PCBF) to homoionic montmorillonite suspension. After filtration and washing several times with distilled water, the solid named $Fe_x(OH)_y$-montm was dried at 40 °C for at least 72 h, ground, and sheltered from light. In order to increase its hydrophobicity by coadsorption with a surfactant, a suspension of $Fe_x(OH)_y$-montm was treated with cetyltrimethylammonium bromide (CTAB) (0.5% (w/w)) at room temperature. The resulting solid, named Fe-SMPM, was separated by vacuum filtration, washed several times with distilled water, dried at 40 °C for at least 72 h, and was finally ground and sheltered from light before use.

2.2. Adsorption experiments

2.2.1. Adsorption kinetics

Basic yellow 28 (CAS 54060-92-3; PM = 433 g mol^{-1}) and 4-nitrophenol (CAS 100-02-7; PM = 139 g mol^{-1}) (Fig. 1) were purchased from Dystar and Merck, respectively, and were used both in single and binary systems. Stock solutions of BY28 and 4-NP (1 g L^{-1}) were prepared by dissolving the appropriate amount of each solute in distilled water at room temperature, shaken for several hours (4 h), and then filtered through Sartorius membrane (0.45 μm) before use. Solutions used in this study were chosen to be representative of the amount rejected in industrial wastewaters (Boufarik, Algeria) and were prepared by dilution in distilled water. The maximum wavelengths (Fig. 1) were recording using a Shimadzu 1700 UV/visible spectrophotometer.



	4-NP	BY 28
λ_{max}	317 nm (acidic medium) 397 nm (basic medium)	437 nm

Fig. 1. Molecular structures.

Kinetic studies in single systems were conducted in brown flasks at room temperature by shaking 0.1 g of sorbent (Fe-SMPM) with 100 mL of solution containing BY28 (34.6 μmol L^{-1}) or 4-NP (80 μmol L^{-1}) at 200 rpm on a mechanical shaker (Bendienungsanleitung Labtec). The samples were withdrawn from the shaker at intervals from 5 to 1440 min and filtered through a 0.45-μm membrane and the concentrations of BY28 and 4-NP were determined by UV–visible spectrophotometry. The same procedure was used in binary mixtures.

2.2.2. Adsorption isotherms in single systems

Isotherm studies were conducted at pH 5, 7, and 9 in brown flasks by shaking different amounts of Fe-SMPM (varying from 5 to 100 mg) with 100 mL of solution containing BY28 (34.6 μmol L^{-1}) or 4-NP (80 μmol L^{-1}) at 200 rpm on a mechanical shaker for 24 h. The residual concentrations of BY28 and/or 4-NP were determined by UV absorbance at appropriate wavelengths.

The data were analyzed by using the Freundlich model

$$Q_e = K_F C_e^n \tag{1}$$

where Q_e (μmol g^{-1}) and C_e (μmol L^{-1}) are the amount of solute and equilibrium concentration, respectively, K_F (μmol$^{(1-1/n))}$ $L^{1/n}$ g^{-1}) is the Freundlich constant, and n is relative to the sorption intensity or surface heterogeneity [19]. Nonlinear regression analyses were performed using ORIGIN 7.5 software running on Windows XP platform [20].

2.2.3. Adsorption isotherms in mixture systems

The same procedure as described in part 2.2.2 was used for the mixture systems. Experiments were performed at different (BY28/4-NP) molar ratios (0.11, 0.32, 0.96, and 2.88) to study the influence of BY28 onto the adsorption of 4-NP and different (4-NP/BY28) molar ratios (9.4, 3.1, 1.04, and 0.35) to study the influence of 4-NP onto the adsorption of BY28 (therefore the ratios between BY28/4-NP were kept constant). A correction was applied for the spectrophotometric determination of residual concentrations in mixture systems by using the equations [21]

$$C_{BY_{28}} = \frac{k_{4\text{-NP2}} d_{\lambda 1} - k_{4\text{-NP1}} d_{\lambda 2}}{k_{BY1} k_{4\text{-NP2}} - k_{BY2} k_{4\text{-NP1}}}, \tag{2}$$

$$C_{4\text{-NP}} = \frac{k_{BY1} d_{\lambda 2} - k_{BY2} d_{\lambda 1}}{k_{BY1} k_{4\text{-NP2}} - k_{BY2} k_{4\text{-NP1}}}, \tag{3}$$

where C_{BY28}, $C_{4\text{-NP}}$, $k_{4\text{-NP1}}$, $k_{4\text{-NP2}}$, k_{BY1}, $d_{\lambda 1}$, and $d_{\lambda 2}$ are respectively the concentration of basic yellow 28 and 4-NP, the calibration constants for the dye and 4-NP at their characteristic adsorption wavelength (i.e., λ_1 and λ_2), and the optical densities at the two wavelengths λ_1 and λ_2.

When several components are present, interferences and competition phenomena for sorption sites occur and lead to more complex mathematical formulations of equilibrium. Various researchers have developed models in binary systems such as the Sheindorf–Rebhun–Sheintuch (SRS) model, an extended Freundlich model [22].

$$Q_{e.BY} = K_{BY} C_{e.BY} (C_{e.BY} + a_{12} C_{e.NP})^{n_{BY}-1}, \tag{4}$$

$$Q_{e.NP} = K_{NP} C_{e.NP} (C_{e.NP} + a_{21} C_{e.BY})^{n_{NP}-1}, \tag{5}$$

where a_{12} and a_{21} are respectively the competition coefficients (interaction parameters) of BY28 versus 4-NP and 4-NP versus BY28; K_{BY}, K_{NP}, n_{BY}, and n_{NP} are Freundlich equation constants in the single solute systems.

This equation was derived under the assumption that: (1) each component in a single system obeys the Freundlich model and (2) for each component in a multicomponent system, the adsorption