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Investigation of a basic dye adsorption from aqueous solution onto raw and pre-treated bentonite surfaces

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Abstract

The effects of temperature, pH and ionic strength on the adsorption of crystal violet (CV^+) by raw, Ni-saturated (Ni-), Co-saturated (Co-) and Zn-saturated (Zn-) bentonite samples were investigated. The amounts of CV^+ adsorbed in equilibrium at 298.15 K were 0.27, 0.37, 0.49 and 0.54 mmol g^{-1} bentonite, which correspond to 108%, 148%, 196% and 216% of the cation exchange capacity (CEC) of the raw, Ni-, Zn- and Co-saturated bentonite samples, respectively. The adsorption of the dye on these samples is pH-independent within the range (2.5–8.5), and it increases with ionic strength from 0 to 0.6 mol l^{-1}. Thermodynamic and Langmuir parameters showed that cation-saturated bentonite samples have relatively stronger ability than the raw bentonite towards the crystal violet (CV^+) cation.

Keywords: Metal-saturated bentonite; Adsorption thermodynamics; Charge reversal; Crystal violet; Ionic strength

1. Introduction

Cationic dyes, commonly known as basic dyes, are widely used in acrylic, nylon, silk, and wool dyeing. This group of dyes include a broad spectrum of different chemical structures, primarily based on the substituted aromatic groups. Due to the complex chemical structure of these dyes, they are resistant to breakdown by chemical, physical and biological treatments. Furthermore, any degradation by physical, chemical or biological treatments may produce small amount of toxic and carcinogenic products. Adsorption is known to be a promising technique, which has great importance due to the ease of operation and comparable low cost of application in the decoloration process. Although activated carbons have been most widely used for the adsorption of dyes, clay materials have been increasingly gaining attention because they are cheaper than activated carbons and their sheet-like structures also provide highly specific surface area [1–3].

Adsorption of cationic dyes by clay minerals has been widely studied to understand the co-adsorption behavior towards pesticides [4,5], color removal of industrial effluents [6,7], ion type inorganic antibacterial material properties [8,9], ecologically important intermediates [10], and determination of the surface properties of clays [11–15]. Margulies and co-workers [16] showed that when negatively charged clay particles are introduced into an ionic solution, migration of the ions occurs, and either neutral or charged complexes may arise from the binding of monovalent organic cations to monovalent sites through several mechanisms. Furthermore, a second organic cation bound to a neutral complex by hydrophobic interactions leads to a charge reversal of the particle.

In this work, the effects of pH, ionic strength of medium and adsorption temperature on the interaction of crystal violet with the raw, Ni-saturated (Ni-), Co-saturated (Co-) and Zn-saturated (Zn-) bentonite samples were investigated in order to elucidate the role of bentonite surface in the sorption process of basic dye (CV^+). Thermodynamic parameters which were obtained from adsorption equilibrium experiments using the van't Hoff equation contribute to the driving force for adsorption reactions.

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2. Experimental

2.1. Materials

The bentonite sample (from Unye, Turkey) was ground and washed in deionized water several times at a 1:10 clay/water ratio. The mixture was stirred for 3 h and then kept standing overnight. After the clear liquid was decanted off the top, the solid was exposed to slow evaporation to dryness, and then ground and sieved through a 78–120 μm size.

2.1.1. Preparation of cation-saturated bentonites

The sample of raw bentonite was rehydrated with deionized water at a ratio of 10 g raw bentonite:100 ml water and 10 g metal chloride of corresponding salts was added to homoionic form. The resulting mixtures were stirred for 24 h and centrifuged at 3000 rpm until attaining chloride-ion-free form, as shown by the silver nitrate test.

The cation exchange capacities (CEC) of the samples were determined by the adsorption of Cu(II) ethylene diamine complex [17]. The values determined for raw bentonite was 0.25 mmol g^{-1}.

2.2. Chemical analysis

The chemical compositions of the raw and acid activated bentonites are given in Table 1. The mineralogical composition of the raw bentonite sample was determined from X-ray diffractograms (Fig. 1). X-ray analyses of the samples were made using the three principal lines [18]. The following mineral phases were identified: montmorillonite, quartz (α), calcite, dolomite, magnesite and mica.

2.3. Thermal analysis

Air dried clay samples were dispersed in 50 ml water. The suspensions were kept in the dark and after 24 h the organoclay was separated by centrifugation. Samples were washed with distilled water to remove excess dye. Thermal studies were carried out on Rigaku TG 8110 analyzer equipped with TAS 100 (range: 20–1000 °C) under flow of air at a heating rate of 10 °C min^{-1}. Calcinated α-alumina was taken as the reference.

2.4. Adsorption studies

Adsorption of CV^+ (analytical grade, chloride salt, obtained from Reidel-de Haen) was carried out in a batch process at various pH, temperature and salt concentration values of the medium. A 50 mg sample was mixed with a 50 ml CV^+ solution of known concentration in the polyethylene bottle. The pH values were adjusted by adding a few drops of dilute NaOH or HCl, and were measured by a Jenway 3040 model pH-meter, and were calibrated to pH = 4.0 and 9.0 buffer solutions. The pH increased slightly (0.1–0.3) at the end of the adsorption process. With salt added, the change in pH was between 0.2 and 0.4.

Table 1
Chemical composition of raw bentoite

Sample	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)
Raw bentonite	62.70	20.10	2.16	2.29	3.64	0.27	2.53

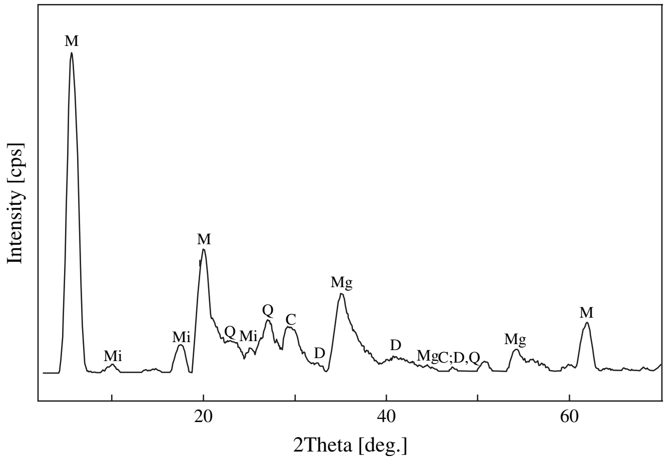
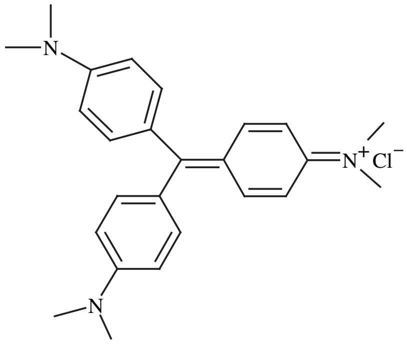


Fig. 1. The XRD patterns of the raw bentonite (M: montmorillonite, Mi: mica, Q: quartz, C: calcite, Mg: magnesite, and D: dolomite).

The adsorption process of CV^+ cations on each of the tested samples was completed in 24 h. Rytwo and co-workers [19] reported that the adsorption equilibrium of CV^+ on Na^+- and Ca^{2+}-exchanged montmorillonite was reached within 24 h and 72 h, respectively. Different equilibirium time results were given in the literature; e.g., the adsorption process of methylene blue cations on the montmorillonite samples tested by Ma and co-workers [20] and Rytwo and co-workers [19] reached the equilibrium positions in 4 h and 24 h, respectively. Different equilibirium times arise from different clay content.

The supernatant was centrifuged for 10 min at 5000 rpm at the end of the adsorption period and then it was diluted between the ratios of 1:10 and 1:125 with deionized water for obeying Lambert–Beer's laws and avoiding from dye aggregation. The amount of the dye adsorbed was determined from the difference between initial and equilibrium concentration values by measuring the absorbance at 590 nm by a Unicam UV2-100 spectrophotometer.

The structure of the dye studied is shown below:



Crystal Violet