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Journal of Colloid and Interface Science 281 (2005) 33–38

Journal of Colloid and Interface Science

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# Investigation of the factors affecting organic cation adsorption on some silicate minerals

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Received 20 May 2004; accepted 9 August 2004

Available online 21 September 2004

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## Abstract

In this study, the effects of some factors on the adsorption of a basic dye (methylene blue) on bentonite and sepiolite samples were studied. These factors are cation ($Na^+$ and $Ca^{2+}$) saturation of the samples and pH and ionic strength of the dye solution. The adsorption data were found to conform to the Langmuir equation within the concentration range studied and Langmuir constants were determined for each of the samples. The adsorption capacities of the samples were found to increase with cation saturation. Changes in the pH of the dye solution had no significant influence on the adsorption capacity and adsorption capacities were found to decrease with increasing ionic strength. The maximum sorption capacity of methylene blue exceeded the cation exchange capacity of bentonite and sepiolite.

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*Keywords:* Bentonite; Cation saturation; Ionic strength; Methylene blue adsorption; pH; Sepiolite

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## 1. Introduction

Clays are important in many different fields such as agriculture, oil drilling, and the building industry [1]. Owing to their interesting physicochemical properties (lamellar structure, high surface area, and high cation exchange capacity), clay minerals have great potential to fix pollutants such as heavy metals and organic compounds. In this respect the interaction between clay minerals and methylene blue (MB), a monovalent organic dye, has been extensively studied [2–8].

Organic cations may bind to clay by different modes. In the case of monovalent organic cations, the following kinds of clay–organic complexes can be found.

(1) A neutral complex may form by the binding of a cation to a monovalent negative site on the clay blocks. This reaction is mainly electrostatic, and should be considered for both organic and inorganic cations.
(2) A second organic cation may bind to a neutral clay–organic complex by noncoulombic interactions, forming a single positively charged complex with two organic cations and one charged site. This type of binding arises from hydrophobic interactions between large organic molecules and may lead at high loads to charge reversal [2]. The model does not consider the possibility of formation of such complexes in the adsorption of inorganic cations, and the assumption is that they occur only in organic molecules.
(3) In sepiolite, where neutral sites occur at the external surface, a monovalently charged complex may form by the binding of one organic cation and a neutral site. Such binding was found to be responsible for the very large number of monovalent organic cations adsorbed to sepiolite [9].

Bentonite and sepiolite form an important group of clay minerals that have the potential for catalytic and molecular sieve applications. Bentonite is hydrated aluminosilicate clay primarily composed of the smectite-class mineral montmorillonite [10]. It is a 2:1 type aluminosilicate;

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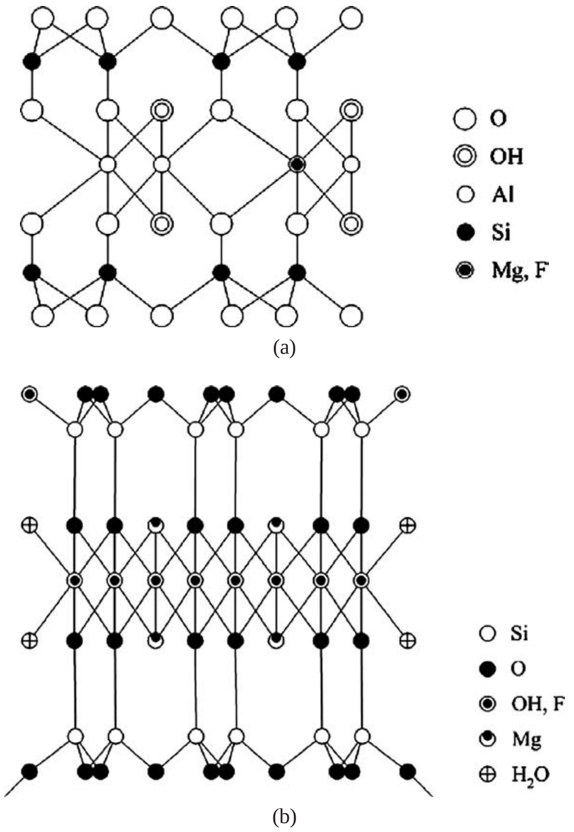
0021-9797/$ – see front matter © 2004 Published by Elsevier Inc.
doi:10.1016/j.jcis.2004.08.038



(a)

(b)

Fig. 1. The mineral structures for bentonite (a) and sepiolite (b).

that is, its crystalline structure presents an alumina octahedral layer between two tetrahedral layers of silica which, by isomorphous substitutions, require cations, denominated exchange cations, to compensate for the negative charges of their laminar edges. Bentonite has the capacity to exchange these cations with the ones present in aqueous solutions [11]. The bentonite mineral structure is shown in Fig. 1a. The ideal mineral formula for montmorillonite is [12] $(Na, Ca)_{0.33}(Al_{1.67}, Mg_{0.33})Si_4O_{10}(OH)_2 \cdot nH_2O$.

Sepiolite is a clay mineral with the formula of magnesium hydrosilicate, $Si_{12}O_{30}Mg_8(OH,F)_4(H_2O)_4 \cdot 8H_2O$ [13]. Sepiolite belongs to the phyllosilicate group of clay minerals. It has peculiar surface properties and important industrial interest due to its high sorbing capacity [14]. Its structure is quite different from that of smectites. It consists (Fig. 1b) in the alteration of blocks and tunnels that grow up in the fiber direction [13]. Each structure is built up of two tetrahedral silica sheets “in sandwich” with a central magnesia sheet in a way similar to that which occurs in other 2:1 silicates, although in sepiolite there is a discontinuity of the silica sheets that gives rise to those structural tunnels. This arrangement determines that silanol groups (SiOH) are present at the border of each block at the external surface of the silicate. These silanol groups, together with the water molecules coordinated to the Mg ions at the borders of the structural blocks, are the main active centers for adsorption [15]. These characteristics of sepiolite make it a powerful sorbent for neutral organic molecules and organic cations [14].

Sepiolite and bentonite have many industrial applications as an adsorbent. The high capacity values of these were also observed for heavy-metal-ion removal and wastewater treatment. The abundance and availability of these mineral reserves as a raw material sources and their relatively low cost guarantee their continued utilization in the future, and most of the world reserves are found in Turkey [16]. These properties of minerals are, however, of great commercial interest in other areas and have therefore been the subject of this study.

Several factors influence the adsorbability of ions on clays, including degree of loading on the adsorber, presence of ligands, complex formation, pH of the solution, and salt concentration. In this study, saturation, pH, and ionic strength effects were studied and the cation exchange capacities (CEC) and adsorption capacities of the samples were also compared.

## 2. Experimental

### 2.1. Materials

The silicate samples used as adsorbents were bentonite from the Uşak region and sepiolite from the Sivrihisar/Eskişehir region. The samples were named UB and SS, respectively, and were dried at 105 °C (24 h) and passed through a 200-mesh sieve.

The cation exchange capacities (CEC) of the samples were determined by $NH_4^+$ saturation using Kjeldhal distillation [17]. The values determined for bentonite and sepiolite were 32.35 meq/100 g and 6.62 meq/100 g, respectively.

In order to obtain samples saturated with sodium and calcium cations, 1 N sodium and calcium chloride solutions were used as described by Rich [18]. Samples were mechanically stirred for 48 h and then filtered through a white-band filter paper. They were rinsed with distilled water until they become chloride-ion-free, as shown by the silver nitrate test.

Table 1
Chemical analysis of the samples

| % | UB | SS |
|---|---|---|
| $SiO_2$ | 64.94 | 49.00 |
| $Al_2O_3$ | 16.93 | 0.41 |
| $Fe_2O_3$ | 1.95 | – |
| CaO | 0.72 | – |
| MgO | 0.65 | 24.30 |
| $P_2O_5$ | 0.27 | – |
| $K_2O$ | 1.60 | – |
| $Na_2O$ | 0.44 | 0.02 |
| $SO_3$ | 0.62 | 0.02 |
| Cl | 0.001 | – |
| $TiO_2$ | 0.62 | – |
| $SrO_2$ | 0.08 | – |
| $Mn_2O_3$ | 0.07 | – |
| Loss of ignition | 11.09 | 26.18 |

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