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Correlation between eletrokinetic mobility and ionic dyes adsorption of Moroccan stevensite

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A B S T R A C T

This study aims at establishing a correlation between the electrical charge of Moroccan stevensite particles and ionic dyes adsorption. The electrophoretic mobility, (U_e), of the stevensite particles in water, was measured at pH 2.5–12 by microelectrophoresis. At pH between 2.5 and 8, U_e remained constant ($U_e = -1.6\,10^{-8}$ m^2/(V s)), as resulting from the permanent charge of the clay mineral planar surfaces. At pH>8, the magnitude of electrophoretic mobility increased ($U_e = -2.7\,10^{-8}$ m^2/(V s)) due to the deprotonation of silanol groups on the surfaces. The anionic Orange G adsorption at the clay mineral–water interface was negligible whereas the methylene blue cations were strongly adsorbed due to the electrostatic attraction.

Keywords:
Stevensite
Dyes
Electrophoretic mobility
Adsorption

1. Introduction

The use of dyes is widespread in many industrial activities such as textiles preparation, pulp mills, leather, printing, food, and plastic production. Many of dyestuffs are harmful to humans and toxic to microorganisms. Therefore, treatment of dye wastewaters, before their discharge into receiving natural media, is needed and has received great interest over the past decades. Adsorption on solids has been proven as an economical and efficient technique. Activated carbon is widely used due to its high adsorption capacity for organic compounds. Nevertheless, due to its high cost and the difficulty of regeneration, there is a need for cheaper alternative adsorbents. Clay minerals, especially the smectite family, have received considerable attention owing to their physicochemical properties (Bergaya et al., 2006). The surface charges of smectites depend on the ionic strength and the pH of the aqueous medium, and the variation of these two parameters will in turn affect the adsorption of organic dyes (Sondi et al., 1996; Thomas et al., 1999; Czimerova et al., 2004; Ma et al., 2004; Echeverria et al., 2005; Tsuchida et al., 2005; Gürses et al., 2006; Hajjaji et al., 2006; Kosmulski, and Dahlsten, 2006; Weng and Pan, 2007).

The present paper deals with the study of the electrophoretic mobility as a function of pH of trioctahedral Mg-rich stevensite from Jbel Rhassoul clay (Morocco), and the adsorption of cationic methylene blue (MB) and anionic Orange G (OG), two model pollutants frequently used, for instance in photocatalysis tests (Sarantopoulos et al., 2009).

2. Experimental

2.1. Materials

Homoionic sodium stevensite (labelled Na-stevensite), having particle sizes <2 μm, was isolated and characterized from Moroccan Rhassoul clay according to procedure described elsewhere (Rhouta et al., 2008). Methylene blue (MB) and Orange G (OG) were purchased from Aldrich.

2.2. BET surface area measurements

Nitrogen adsorption isotherms at 77°K were determined by using an ASAP 2020 V 3.01 H Adsorption Analyser from Micromeritics. Prior to the N_2 adsorption–desorption measurements, the Na-stevensite sample weighing 0.162 g, was out gassed at T = 150 °C during 24 h. The specific surface area was determined by the well-known Brunauer–Emmett–Teller (BET) method (Rouquerol et al., 1998; Gregg and Sing, 1982).

2.3. Titration of stevensite surface charge and PCD measurements

The Na-stevensite surface charge was evaluated by titration of the clay mineral particles with aqueous MB solution at the original pH, *i.e.* without adding any amounts of hydrochloric acid or sodium

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hydroxide. The procedure and the device (Particle Charge Detector, PCD, Müteck instrument), used for such titration were similar as described elsewhere (Jada et al., 2006). The measuring cell is composed of a cylindrical poly (tetrafluoroethylene) (PTFE) container with a PTFE piston inside. The titratable aqueous clay mineral dispersion (10 ml) was filled into the gap (0, 5 mm) between the container wall and the piston, and various amounts of the MB aqueous solution were added. The resulting streaming induced potential (SIP) was measured between two gold electrodes located at the top and the bottom of the gap.

2.4. Microelectrophoresis

For the microelectrophoresis measurements, the dispersions were shaken for a few minutes and the final pH was either original or adjusted at 2.5–12, by adding small amounts of hydrochloric acid or sodium hydroxide solutions. The electrophoretic mobility was measured at ambient temperature using the Zetaphoremeter II model Z3000 (Jada and Ait Chaou, 2003). These measurements were performed in the absence of electrolytes, since the present study did not deal with the salt effect on electrophoretic mobility of the clay mineral particles, but rather with the pH effect. The Zetaphoremeter used in the present work allows the measurement of electrical conductivity of the aqueous dispersions, and the calculation of the electrical double layer (EDL) thickness. The pH effect on the electrophoretic mobility of the clay mineral particles was studied by adjusting the dispersion to the desired pH value. The initial pH was 7.5 ± 0.1.

2.5. Adsorption experiments

Adsorption experiments were carried out in a batch reactor by mixing 25 mg of Na-stevensite in 25 ml of distilled water, and by stirring the dispersion for 2 h. To this dispersion 0.5 ml of MB or OG solutions (10^{-3} M) were added so that the final concentration of the dyes was fixed to 10^{-5} M. For studying the pH effect on the dye adsorption, the procedure was similar to that described above in microelectrophoresis measurements. All adsorption experiments were performed at 25 °C. To determine the non-adsorbed amount of dye, aliquots were taken from the mixture at regular time intervals and centrifuged at 12,500 rpm for 5 min. The dye concentration in the supernatant was obtained from linear calibration curves representing the absorbance of the 664 nm and 480 nm bands versus MB and OG concentrations (UV–Vis–NIR Perking Elmer spectrophotometer).

3. Results and discussion

3.1. Nitrogen adsorption–desorption isotherms

The adsorption–desorption isotherm of nitrogen on Na-stevensite (Fig. 1) was of type IV, with a hysteresis loop of type H4, indicating the presence of both micro- and mesopores. The BET equation was applied for the relative pressure range $0.02 \leq p/p_0 \leq 0.33$. The specific surface area of the stevensite was 150 m^2/g.

3.2. Specific surface area and surface charge of Na-stevensite by titration with MB

The surface area of Na-stevensite was also determined from the titration curve of stevensite with MB (Fig. 2). The point of zero charge, PZC, was found at 0.0089 mmol MB added. This corresponded to a specific surface area of 279 m^2/g taking into account the surface area of one methylene blue cation ($a_{MB} = 130$ Å^2). As expected, this area was considerably larger than the specific BET surface area due to the intercalation of the MB cations into the stevensite.

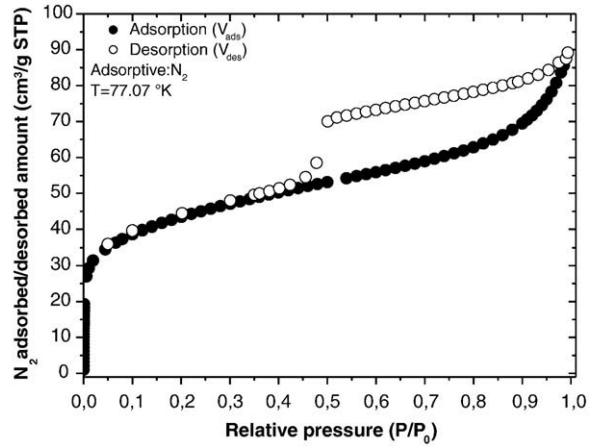

Fig. 1. Adsorption–desorption isotherms of N_2 on Na-stevensite.

3.3. Electrophoretic mobility

Without adding to the stevensite dispersions hydrochloric acid or sodium hydroxide solution, the electrophoretic mobility was $U_e = -1.6\,10^{-8}\ m^2\,V^{-1}\,s^{-1}$. The electrophoretic mobility, U_e, of clay minerals is determined by the relative proportions of planar and edges surfaces that are exposed to the aqueous solution (Thomas et al., 1999). Mermut and Lagaly (2001) reported that the edge charge of smectite particles is generally between 10 and 30% and on average it is ≈20% of the total CEC. The edge charges represent only around 5% of the total charge for the Na-stevensite (Rhouta et al., 2008).

The variation of U_e with pH is plotted as shown in Fig. 3. Na-stevensite particles remained negatively charged in the pH range between 2.5 and 12. From pH = 2.5 up to pH = 7.5 (zone 1), the negative values of U_e were constant ($-1.6\,10^{-8}\ m^2\,V^{-1}\,s^{-1}$). Between pH = 7.5 and pH = 10.5 (zone 2), the magnitude of U_e increased from $-1.6\,10^{-8}\ m^2\,V^{-1}\,s^{-1}$ to $-2.7\,10^{-8}\ m^2\,V^{-1}\,s^{-1}$, U_e remained constant at pH 10.5–12 (zone 3). These results were different from those reported recently by Gürses et al. (2006) concerning a mixture of Turkish smectites (montmorillonite and nontronite). In that case, the variation of U_e as a function of pH exhibited two IEP. Nevertheless, our results were consistent with those reported in literature for montmorillonite (Sondi et al., 1996; Thomas et al., 1999), showing that the silicate charges remained negative at all pH values. The U_e values at pH 2.5–7.5 indicated the predominance of the permanent charges. The increase of the magnitude of the mobility at higher pH is due to the deprotonation

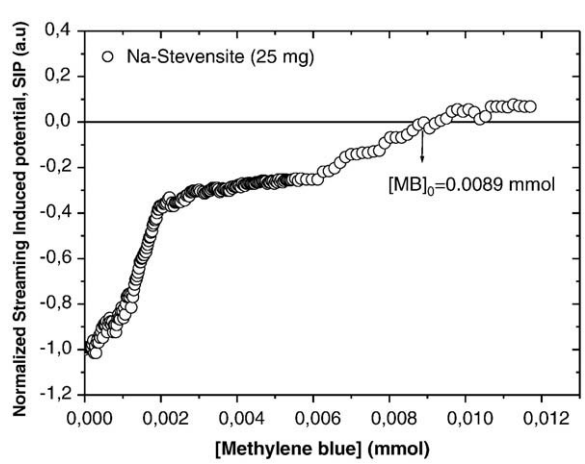

Fig. 2. Variation of the streaming induced potential with methylene blue, MB, concentration for Na-stevensite particles in aqueous dispersions.

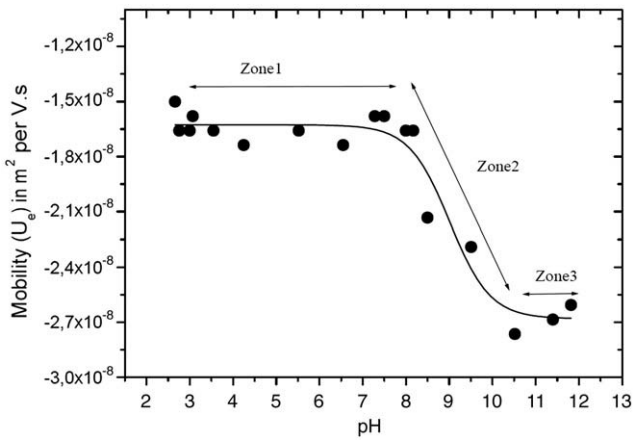

Fig. 3. Variation of electrophoretic mobility of stevensite particles with pH of the aqueous dispersion.

of the silanol groups at the edges of the stevensite particles, because aluminol surface groups are absent (Leroy and Revil, 2004). Beyond pH = 10.5 the mobility U_e levelling out at $-2.7\,10^{-8}\,m^2\,V^{-1}\,s^{-1}$ indicated the total ionization of all edge silanol groups of the clay mineral particle.

3.4. Adsorption of MB and OG dyes

The absorption spectra of Orange G remained unchanged at all contact times indicating that OG was not adsorbed by stevensite due to repulsive forces between the negatively charged stevensite layers and the anionic dye. In contrast, the absorption spectra of MB, (Fig. 4), revealed that almost all initial MB amounts were retained by the stevensite particles due to the electrostatic interactions between the positive MB species and the negatively charged sites of the stevensite layers (Rhouta et al., 2008). This high MB uptake was in good agreement with the electrophoretic mobility data (Fig. 5). At pH 2–9, the maximum amount of MB adsorbed was about 220 mg/g. At pH > 9, the amount of MB adsorbed increased to 240 mg/g at pH = 11, due to deprotonation of the silanol groups on the edge sites of the clay mineral particles as evidenced by the microelectrophoresis data.

4. Conclusions

A strong correlation was established between the adsorption of ionic dyes onto stevensite from Jbel Rhassoul clay and the nature of surface charge. At pH 2–12, stevensite particles are formed of negatively charged layers responsible via Coulombic attractions of the strong

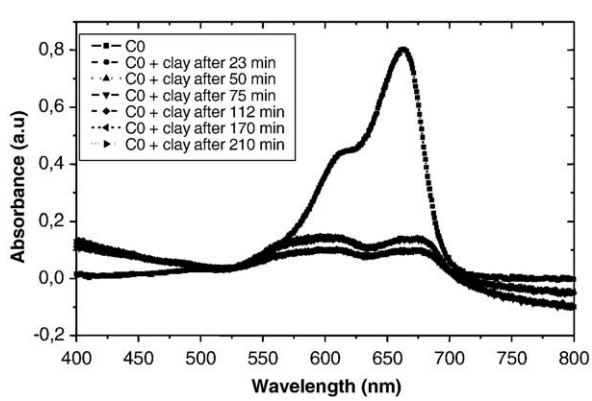

Fig. 4. UV absorption spectra of methylene blue in the supernatant at various contact times.

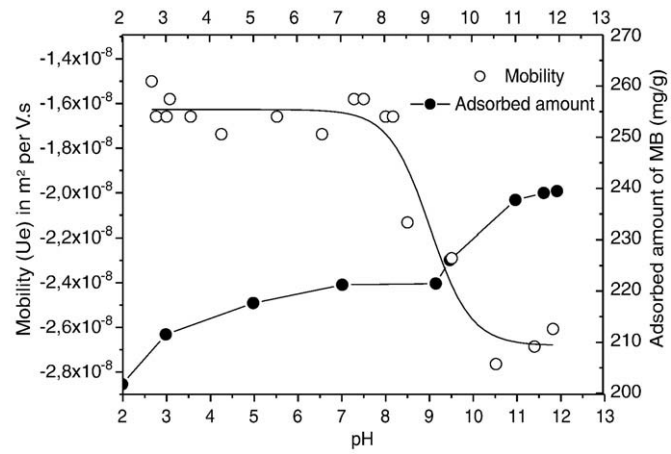

Fig. 5. Na-Stevensite electrophoretic mobility of the stevensite particles and amounts of MB adsorbed.

retention of cationic methylene blue dye by contrast to the anionic Orange dye. Consequently, the highest MB adsorption (240 mg/g) was reached at pH = 12. The adsorption of the anionic dye Orange G was negligible.

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