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Electrokinetic and ionic dyes adsorption studies of Moroccan stevensite Jbel Rhassoul clay

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This study aims at establishing correlation between the nature of electrical charge of morocan stevensite Jbel Rhassoul clay particles and ionic dyes adsorption phenomenon. The electrical charges of the clay mineral particles were assessed by measuring zeta potential (ζ) using micro electrophoresis technique. Measurements were carried out onto aqueous clay dispersions by varying the pH in the range 2.5 – 12 with additions of HCl or NaOH. On the whole, the electrical charges of stevensite particles remain negative in the whole pH range. Nevertheless, depending on the pH values, two behaviours were observed. For pH ranging from 2 to around 8, the negative electrical charge remains constant (ζ = - 20 mV) and corresponds to permanent charges of basal surfaces formed of –O-Si-O- groups insensitive to pH variation. Beyond pH = 8, the electrical charge increases (ζ = - 35 mV) as a result of deprotonation of silanol edge groups. Ionic dyes adsorption experiments show that anionic orange G adsorption is negligible whereas that of cationic methylene blue is greater due to columbic interactions. In accordance with eletrokinetic measurements, the methylene blue adsorption capacity onto stevensite particles significantly increases beyond pH $\approx$ 8 due to the increase of the whole electrical charge of stevensite particles evolved by silanol edge sites deprotonation.

Keywords: Stevensite, Organic dyes, Adsorption, Zeta potential, Surface charges

1. Introduction

The use of dyes is widespread in many industrial activities. Many of dyestuffs are harmful to human and toxic to microorganisms. So, treatment of dyes wastewaters, prior to their discharge into receiving natural media, is needed and has received great interest over the past decades. Activated carbon is unanimously known to be the most widely used adsorbent due to its high capacity for the uptake of organic compounds. Nevertheless, due to its high cost and the difficulty of regeneration, there is a need for cheaper alternative adsorbents. Clay minerals, especially smectites family, have received considerable attention owing to their physicochemical properties.

Indeed, in addition to their high surface area, smectites are characterized by 2:1 lamellar structure built-up by two tetrahedral silica sheets and a central octahedral sheet of alumina or magnesia [1]. On the other hand, they are characterized by permanent structural negative electrical charges on silicate crystal surfaces, generated by isomorphic substitution within the layers that are compensated by alkali or alkaline earth exchangeable cations in the interlayer space. Also, they are characterized by induced edge electrical charge due to protonation or deprotonation of unsaturated silanol hydroxyls upon pH variation [2]. The surface charges of smectites depend on several physicochemical parameters such as ionic strength, pH,…which in turn affect the adsorption capacity of organic dyes [3, 4].

This paper deals with the study of the charges surfaces as a function of pH of trioctahedral Mg-rich stevensite smectite from Jbel rhassoul clay (Morocco) and on the influence of the surface charges magnitude on the adsorption capacity of these natural clays for cationic Methylene bleue (MB) and anionic Orange G (OG) dyes.

2. Experimental

The homoionic sodium saturated setvensite (labeled Na-stevensite), considered in this study, was isolated from morocan Rhassoul clay. It corresponds to Mg-rich trioctahedral smectite with a CEC of ~60 mEq/100 g and specific surface area around 150 m^2/g. The structural formula is: $(Na_{0.25}K_{0.20})$ $(Mg_{5.04}Al_{0.37}Fe_{0.20}{}_{0.21})_{5.61}$ $(Si_{7.67}Al_{0.24})_8O_{20}(OH)_4$ [5]. Na-stevensite has been considered in micro electrophoresis measurements as well as in adsorption experiments.

The zeta potential of Na-stevensite particles, which somewhat represents the surface charge of clay particles, was measured at ambient temperature using Zetaphoremeter II model Z3000. The clay aqueous dispersions were prepared by introducing a given amount of the clay (0.1 wt %) in aqueous solutions. The resulted dispersion was agitated for few minutes and the final pH

value of the system was either natural or varied in the range 2.5–12, by adding to the dispersions small amounts of hydrochloric acid (HCl) or sodium hydroxide (NaOH) aqueous solutions. Adsorption experiments were carried out in batch reactor by considering 25 mg - sample of Na-stevensite dispersed in 25 ml distilled water and stirred for 2h. To this dispersion was added 0.5 ml of MB or OG solutions (10^{-3} M) so that the final concentrations of the dyes was fixed to 10^{-5} M. To study the pH effect, it was adjusted to the desired value, starting from the natural value (7.5 ± 0,1), by addition of given amounts of HCl or NaOH to the clay aqueous dispersion. All adsorption experiments were performed at 26 °C. To determine the dye unretained amount, samples were taken from mixture at regular contact time intervals and centrifuged at 12500 rpm for 5 mn. The dye concentration in the supernatant was determined from an experimental curve representing the absorbance of the 664 nm and 380 nm bands (measured by means of a UV-Vis-NIR Perking Elmer spectrophotometer) versus MB and OG concentrations, respectively.

3. Results and discussion

3.1 Microelectrophoresis

At natural pH, *i.e.* without adding to the clay aqueous dispersions any amounts of hydrochloric acid (HCl) or sodium hydroxide (NaOH), the zeta potential measured for stevensite aqueous dispersion is around –20 mV. As expected, this value indicates that stevensite layers are negatively charged. On the other hand, the ξ-potential of clay minerals is determined by the relative proportions of planar and edges faces that are exposed to the aqueous solution. Knowing that the edge charges represent only 5 % of the total charge for the clay mineral [6], we deduce that these negative surface charges are predominated by planar permanent structural charges. According to the structural formula, these charges result from isomorphic substitutions of Si^{4+} for Al^{3+} in tetrahedral layers and of Al^{3+} for Mg^{2+} in octahedral layers that are compensated by Na^+ and K^+ exchangeable cations in the interlayer space.

Starting from the clay natural pH, increasing amounts of HCl or NaOH were added to stevensite aqueous dispersion. Fig. 1 shows the variation of the zeta potential versus the pH of the aqueous phase in the range 2.5-12.
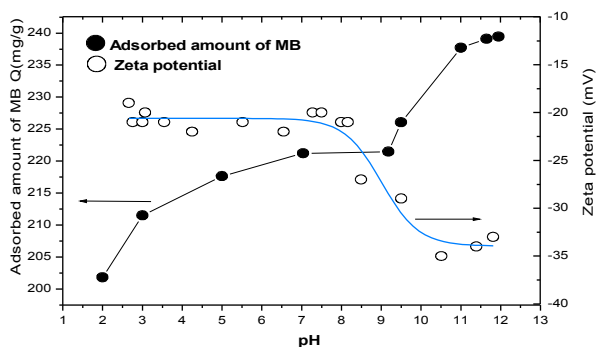
In agreement with the negative value of zeta potential previously reported at natural pH, Na-stevensite particles remain negatively charged in the whole pH range considered in this study. Hence, no Isoelectric Point (IEP), *i.e.* the pH at which ξ = 0, was found for Na-stevensite in the whole pH range investigated. Fig. 1 shows three distinguished zones corresponding to different electrical charging mechanisms of stevensite particles. Up to pH 7.5 (zone I), the negative values of the zeta potential are constant (-20 mV). Beyond this pH value till pH 10.5 (zone II), a very noticeable decrease of zeta potential from -20 mV to -35 mV was observed. Thereafter, the negative values of zeta potential become again constant for pH ranging from 10.5 to 12 (zone III). Fig. 1 indicates that the ξ-potential is insensitive to the pH of the stevensite aqueous dispersion for pH ranging from 2 to 7.5. This denotes the predominance of the permanent structural negative electrical charge within this pH range. Indeed, as reported by Leroy et al [2], the basal {001} plane of smectites carries only siloxane >Si-O-Si< (where > stands for clay framework) surface sites inert towards H^+ and OH^- ions.

As far as the basic reagent is added (pH ranging from 7,5 to 10,5), we observe an increase of the absolute values of zeta potential indicating the development of novel negatively charged sites onto stevensite particles. This is due to the deprotonation of the broken-end hydroxyls bonded to the particles edges ({010} and {110} planes) of the stevensite particles. As in principle there are no aluminol surface groups present on the edges of a smectite grain [2], we deduce that only silanol (>SiOH) deprotonation could occur for stevensite according to the reaction:

$$>Si\text{-}OH \rightarrow >Si\text{-}O^- + H^+ \tag{1}$$

Beyond pH 10.5, the solution is so basic that all silanol surface groups of particles edges of the stevensite are likely totally neutralized so that the zeta potential value stabilizes at -35 mV.

3.2 Adsorption

Fig. 2 shows UV-visible absorption spectra recorded from the stevensite-dye mixtures after different contact times. It shows that absorption spectra of orange G (Fig. 2a) remain unchanged after all contact times. This result indicates that the initial OG concentration doesn't decrease; so there is no evidence for OG adsorption onto the stevensite. This is likely due to repulsive forces between negatively charged stevensite layers and anionic dye. In contrast, absorption spectra of MB indicate they become flattened after a contact time around 20 mn (Fig. 2b). This denotes that almost all initial MB amount was retained by the stenvensite particles. These results demonstrate that the stevensite particles exhibit a great

affinity for cationic MB reagent by contrast to anionic OG dye. Moreover, this ability is well evidenced by the colourless of aqueous solution of the stevensite clay. In accordance with the above microelectrophoresis results, the higher uptake of MB by the stevensite could be explained by the intensive electrostatic interactions between positive MB species and the negatively charged sites of stevensite layers [4]. Indeed, it's generally reported that the MB species, evolved in different uptake mechanisms (cationic exchange or adsorption or aggregation) that could occur, are commonly cationic either such as monomers (MB^+) for diluted MB solutions or dimers ($MB^+)_2$, trimers ($MB^+)_3$ and/or protonated species (MBH^{2+}) for high MB concentrations [4].
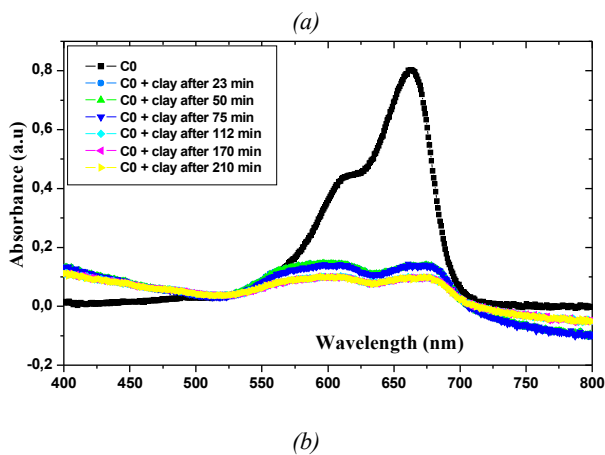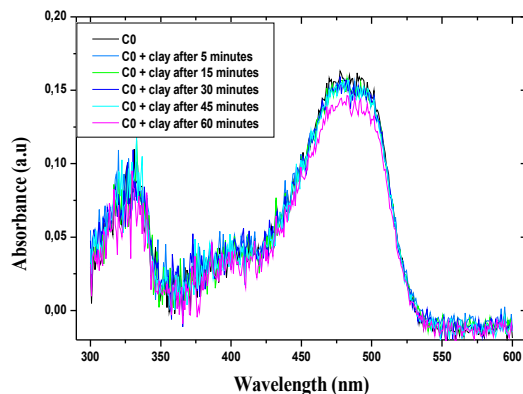

(a)

(b)

Fig. 2. UV absorption spectra of orange G (a) and methylene blue (b) versus adsorption time onto stevensite.

The variation of MB amount adsorbed onto stevensite particles as a function of pH is depicted in Figure 1. The overall examination of this curve shows that, like zeta potential, the adsorption of dye from aqueous solution onto surfaces particles of stevensite is highly dependent on the pH of the solution. So, to make correlation between both phenomena, we also report in the figure 1 the variation of zeta potential versus pH for this series. As far as pH increases, the number of negatively charged surface sites of the stevensite increases and the retained MB amount increases. The slope is low for pH ranging from 2

to 9 due likely to the fact that the surface charges density of the clay is constant in this range. Thereafter, the adsorbed MB amount strongly increases for reaching 240 mg/g at pH = 11. This increase could be explained by the development of supplementary active negative surface sites of the stevensite as a result of the deprotonation of the edges silanol sites of the clay as evidenced by microelectrophoresis measurements.

4. Conclusions

This study demonstrates the usefulness in identifying the nature and the density of surface charges of clay minerals in order to predict the magnitude of the adsorption of ionic organic dyes onto these silicates. Indeed, strong correlation was established between ionic organic dyes adsorption onto Moroccan stevensite Jbel Rhassoul clay and the nature of surface charge of this silicate. For pH ranging from 2 to 12, stevensite particles are formed of negatively charged layers responsible of strong retention of cationic methylene blue dye by contrast to anionic Orange dye via columbic attractions. Predominant permanent negative structural charges, which are insensitive to pH variation, extend over the pH range 2 – 7.5 and correspond to active sites distributed onto basal surfaces bearing siloxane –O-Si-O- groups. Over this pH range, the MB uptake slightly increases. Beyond pH = 7.5 till 10.5, supplementary active sites are developed, as a result of deprotonation of silanol hydroxyls (Si-OH) bonded on the surface edges. As a consequence, The MB retention in this pH range is stronger for reaching the highest capacity value around 240 mg/g at pH strongly basic (pH = 12).

References

[1] M. Rautureau, S. Caillère, S. Hénin, Les argiles, Edition Septima, 21, 2004.
[2] P. Leroy, A. Revil,, Journal of Colloid and Interface Science **270**, 371 (2004).
[3] I. Sondi, J. Biscan, V. Pravdic, Journal of Colloid and Interface Science. **178**, 514 (1996).
[4] C. H. Weng, Y.-F. Pan, Journal of Hazardous Materials **144,** 355 (2007).
[5] B. Rhouta, H. Kaddami, J. Elbarqy, M. Amjoud, L. Daoudi, F. Maury, F. Senocq, A. Maazouz, J.-F. Gerard, Clay minerals **43,** 393 (2008).
[6] A. R. Mermut, G. Lagaly, Clays and Clay Minerals

49, 393 (2001).

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