Characterization and electrokinetic properties of montmorillonite

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The determination of surface properties of montmorillonite clay is an important criterion for establishment of its adsorption ability against anionic and cationic species from wastewaters. In this study, electrokinetic surface properties of montmorillonite were investigated using the microelectrophoresis technique. The zeta-potential (ζ) analysis of the montmorillonite was done by streaming potential measurements as a function of salt concentration and equilibrium pH of solution. It was found that the zeta potential of the clay particles was negative for monovalent cations (KCl, LiCl, NaCl) added to solution phase. Divalent cations ($CaCl_2$, $Ca(NO_3)_2$, $Pb(NO_3)_2$) could provide a neutral charge at just maximum concentrations. In addition, montmorillonite had a negative charge even at pH 2 and only trivalent cations ($Fe(NO_3)_3$, $FeCl_3$) provided positive surface charge at just maximum concentration. The characterization of the montmorillonite was performed by using XRD, XRF, FTIR, SEM imaging, and N_2-BET analyses. The determined porous structure and strong negative surface charge of the montmorillonite showed that this clay would be used effectively in removal of cationic species from waters.

Keywords: Montmorillonite; XRD; Electrokinetic; Zero charge point; SEM; FTIR

INTRODUCTION

Clay is a soil particle smaller than 2 μm. Clays have a high specific surface area which mainly influences the soil colloidal properties as well as the stability of soil structure. Besides, clays have a high stability in both wet and dry conditions. Colloid is a particle which may be a molecular aggregate with a diameter changing from 0.1 to 0.001μm. Clay and soil organic matter are often called as soil colloids because they have particle sizes that are within, or approach to the colloidal dimensions. Clay minerals which are hydrous aluminum silicates have a large interlayer space that can retain significant amounts of water. Clays are encompassed of large surface area that allow swelling and shrinking [1, 2].

Montmorillonite is a very soft phyllosilicate mineral that typically forms in microscopic crystals. Montmorillonite, a member of the smectite family, is 2:1 layered clay and it has 2 tetrahedral sheets sandwiching a central octahedral sheet. The montmorillonite particles are plate-shaped with an average diameter of approximately 1 micrometer. The particle thickness is extremely small (~1 nm).

It is the main constituent of the volcanic ash weathering product, bentonite. The water constent of montmorillonite is variable and it increases greatly in volume when it absorbs water. Chemically it is hydrated sodium calcium aluminum magnesium silicate hydroxide $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH).nH_2O$. Potassium, iron, and other cations commonly substitutes with structural cations of the monmorillonite and the exact ratios of cations vary based on the clay deposit [3-5].

Montmorillonite is used in the oil drilling industry as a component of drilling mud to make the mud slurry viscous which helps in keeping the drill bit cool and in removal of drilled solids. Montmorillonite is also used as a soil additive in dry soils to hold soil water content at maximum ratio. Montmorillonite is preferred in construction of earth dams to prevent the leakage of fluids. It is also used as a component of foundry sand and as a desiccant to remove moisture from air and gases. Montmorillonite clays have been extensively utilized in catalytic processes for over 60 years. Other acid based catalysts also utilize acid treated montmorillonite clays [6].

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The clay samples shows different surface charge density and cation content based on its mined deposit. Therefore, the characterization and surface properties of the montmorillonite samples belonging to different regions should be determined as separately. Also, the purity of the montmorillonite samples changes from a deposit to another. For these reason, in this work, we investigated the effect of the mono- and multivalent salts including NaCl, KCl, LiCl, CaCl$_2$, Ca(NO$_3$)$_2$, Pb(NO$_3$)$_2$, Fe(NO$_3$)$_3$, and FeCl$_3$ on the electrokinetic behavior of montmorillonit. The effects of clay concentration, initial pH, and electrolyte type on the zeta potential were also investigated. In addition, the structure and properties of the montmorillonite were examined by XRD, XRF, SEM, FT-IR and N$_2$-BET analysises.

MATERIAL AND METHODS

Characterization of Montmorillonite

The montmorillonite sample was obtained from Süd-Chemie Clay Processing Plants located in Balikesir in Turkey. Before being used in the experiments, the montmorillonite sample was treated as follows: the bulk solution containing 10 g L^{-1} montmorillonite was mechanically stirred for 24 h, and the bulk solution delayed for about two minutes and then the supernatant suspension was filtered through a what-man filter paper (Φ = 12.5 cm (diameter of filter paper)). The clay sample was dried at 110 $^\circ$C for 24 h, and then sieved by 45-90-mesh sieve. The sample of montmorillonite was characterized by using X-ray diffraction (XRD), X-ray fluorescence (XRF), infrared (FT-IR), scanning electron microscopic (SEM) and BET N$_2$ adsorption technique.

Zeta Potential

The zeta potential of samples were measured using a Zeta Meter 3.0 (Zeta Meter Inc.) equipped with a microprocessor unit. The unit automatically calculates the electrophoresis mobility of the particles and converts it to the zeta potential using the Smoluchowski equation. This equation is the most elementary expression of zeta potential and gives a direct relation between zeta potential and electrophoresis mobility of particles;

$$\zeta = \frac{4\pi V_t}{D_t} EM \qquad (1)$$

Where, *EM* is electrophoresis mobility at actual temperature, V_t is viscosity of the suspending liquid, D_t is dielectric constant, π is constant and ζ is zeta potential. A 0.15 g montmorillonite amount was conditioned in 100 ml distilled water for 3 h. Each data point is an average of approximately 10 measurements. All zeta potential measurements were carry out at natural pH of the suspension except those in which the effect of pH was investigated. The pH of the suspension was adjusted using diluted HCl and NaOH. The electrolyte concentrations of the solutions were adjusted using 1 M electrolyte solutions containing different salts. Electrolyte concentrations of the solutions were adjusted with an automatic pipette.

RESULTS AND DISCUSSION

Characterization of Montmorillonite Clay

XRD, XRF, N$_2$-BET, SEM and FT-IR analysis. The XRD pattern of the montmorillonite is shown in Figure 1 and the crystallographic parameters are evaluated by measuring the (001) and (080) peaks. The peaks marked as montmorillonite are indicative of 2:1 swelling clay and confirm the characteristics of the montmorillonite type clay. The other peaks are impurities corresponding to quartz. Montmorillonite exhibits a diffraction peak of the (001) plane at 2θ = 19.733, which corresponds to its basal spacing of 4.99 Å. The (080) reflection at 2θ = 68.823 indicates that montmorillonite has a dioctahedral structure [7, 8].
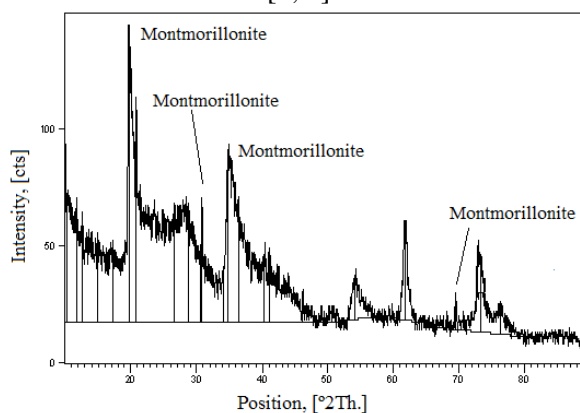

Fig. 1. XRD pattern of montmorillonite clay.

X-ray fluorescence (XRF) method has been used to identify the major minerals and chemical compounds present in the clays. The specific surfaces area of montmorillonite (measured by N$_2$-BET) was 95.36 m^2 g^{-1}. The chemical compositions and some index properties of the montmorillonite sample were given in Table 1.

SEM image of the montmorillonite is given in Figure 2. The surface morphology of montmorillonite demonstrates a layered surface with some large flakes, which is the typical structure for montmorillonite. When this image was analyzed, it could be observed that surface of the

Table 1. Chemical composition of montmorillonite (a) and physicochemical properties of montmorillonite (b).

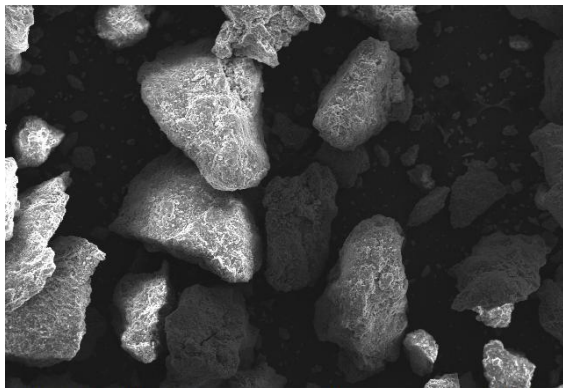|	Component	Weight (%)
	SiO_2	49.40
	Al_2O_3	19.70
	MgO	0.27
(a)	CaO	1.50
	Fe_2O_3	0.30
	Na_2O	1.50
	H_2O	25.67
	Parameters	Value
	Color	White
	Density (g cm^{-3})	$2.3 - 3$
(b)	Transparency	Semi-transparent and opaque
	Brightness	Matt
	Surface Area (m^2 g^{-1})	95.36
	Reflective index	$1 - 2$

Fig. 2. SEM picture of montmorillonite particles.

clay didn't have homogenous dispersion. In addition, clay structure has pores which randomly distributed with different sizes. Surface images of montmorillonite clay sample used in this study are similar to the literature [9, 10].

In the FT-IR spectrum (Fig. 3) of montmorillonite the broad band centered near 3495 cm^{-1} is due to the –OH stretching mode of the interlayer water. The overlaid absorption peak in the region of 1654 cm^{-1} is assigned to the –OH bending mode of adsorbed water. The characteristic peak at 1127 cm^{-1} is due to the Si–O–Si stretching and out of plane Si–O–Si stretching mode for montmorillonite. The band at 1048 cm^{-1} is assigned to the Si–O–Si stretching (inplane) vibration for layered silicates. The band in the region of 873 cm^{-1} is due to the Si–O–Al stretching mode for montmorillonite. The FT-IR peaks at 531 cm^{-1} and 472 cm^{-1} are assigned to the Si–O–Al and Si–O–Si bending vibration, respectively [11, 12].
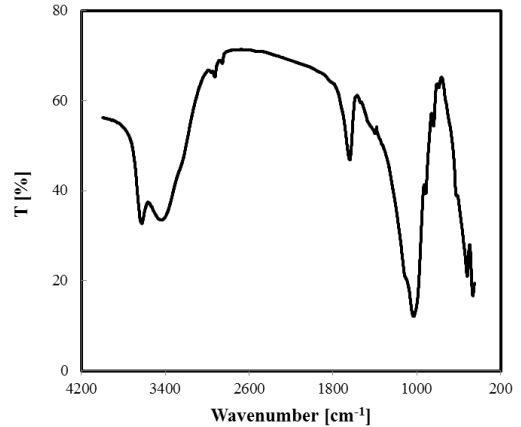

Fig. 3. FT-IR spectra of montmorillonite.

Measurement of Zeta Potential and pH profiles of montmorillonite

The pH profiles of montmorillonite in a 1.5 wt % suspension as a function of time is presented in Fig. 4 at natural, acidic and basic pHs. When montmorillonite was added to distilled water of pH 5.45, the suspension pH raised to 8.15 in 45 min and to 7.7 after 75 min and then remained almost constant upon reaching to the equilibrium pH of 7.7. The reason for the rapid rise in the suspension pH in the first 45 min can be ascribed to the rapid adsorption of H$^+$ ions in water both onto the negatively charged montmorillonite surface and as potential determining ions (pdi) in the electrical double layer (EDL) in order to provide electroneutrality. In addition, the H$^+$ ions in solution exchanged with some of the cations in the montmorillonite lattice leading to the consumption of H$^+$ ions in suspension. When the initial pH was adjusted to 4.00, after montmorillonite addition, the suspension pH raised to 6.20 in 30 min, and then increased till it reached equilibrium around pH 7.24.
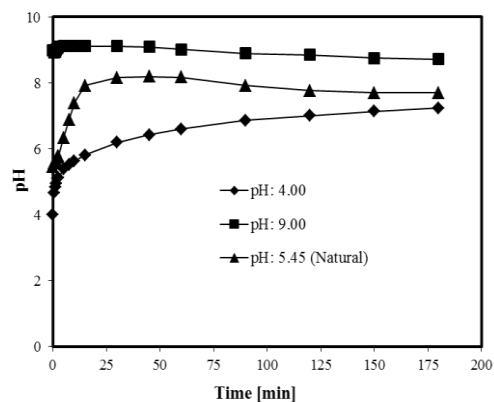

Fig. 4. The pH variation of montmorillonite suspension at different pHs.

The reasons for the rapid rise in pH are the same as above. When the initial pH was adjusted to 9.00, after montmorillonite addition, the suspension pH decreased to 8.89 in 90 min, and reached its equilibrium at pH 8.72 in about 180 min. The decrease of the suspension pH can be attributed to the adsorption of OH ions onto the positive sites on the montmorillonite surface. Thus, montmorillonite suspensions exhibited a buffer pH around pH 8 [13, 14].

Effect of solid concentration

The solid concentration in solution is a major parameter governing the surface charge generation. To determine the effect of solid-to-solution ratio on the zeta potential, different montmorillonite dispersions were prepared at concentrations between 0.01–0.50 g/100 mL in distilled water and their zeta potentials were measured (Fig. 5). It was observed that there is no significant effect of the solid concentration on the zeta potential of montmorillonite suspensions. Thus, subsequent experiments were carried out at 0.15 g/100 mL solid-to-solution ratio [15].
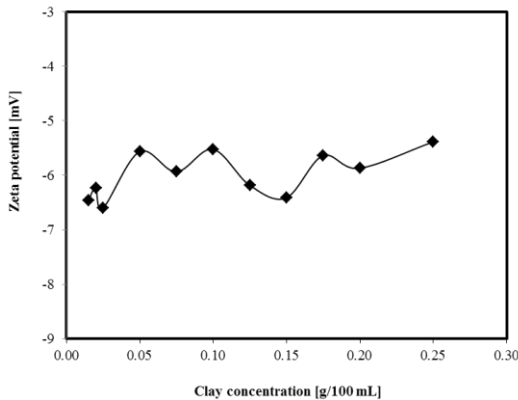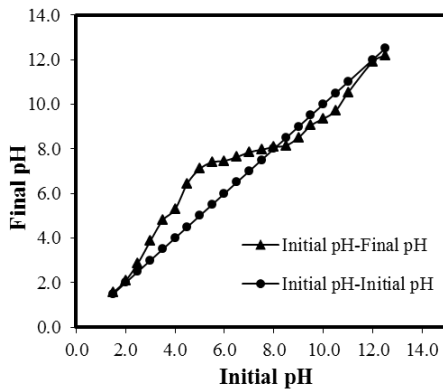

Fig. 5. Zeta potential of montmorillonite as a function of solid concentration.

Figure 6. Zeta potential of montmorillonite as a function of pH

Zero point charged of montmorillonite

The zeta potential of montmorillonite particles was plotted as a function of the dispersion pH (Figure 6). Zeta potential has low negative value for pH values less than pH 8.04 and it is essentially pH independent at pH range of 2 and 8.04. But, zeta potential has more negative value for pH values higher than pH: 8.04. In this figure, two different types of charge on the montmorillonite particle surface are apparent. The decrease in zeta potential at pH>8.04 was mainly due to the adsorption of OH$^-$ on the positive edges of the clay particles, which acquire negative charge. At the lowest pH values, the zeta potential analysis indicated lower negative values owing to the H$^+$ adsorption on the negative charged sites on the particle surface [17]. The montmorillonite particles dissolved at pH values lower than 2 and this resulted in more negative surface charge.

Effect of metal salts on the zeta potential of montmorillonite

The results obtained at natural pH of the medium with monovalent electrolytes such as NaCl, KCl and LiCl and were shown in Figure 7. The increasing concentrations of monovalent cations (NaCl, KCl and LiCl) converted the negative surface charge to less negative value. This result can be explained in the following manner: the monovalent ions added to the solution are known as indifferent electrolytes except their ion exchange tendency [18]; they cannot adsorb specifically onto montmo-rillonite, and are not capable of causing a charge reversal. Fig. 7 showed the zeta potential of montmorillonite in the presence of various divalent electrolytes such as. $CaCl_2$, $Ca(NO_3)_2$ and $Pb(NO_3)_2$.
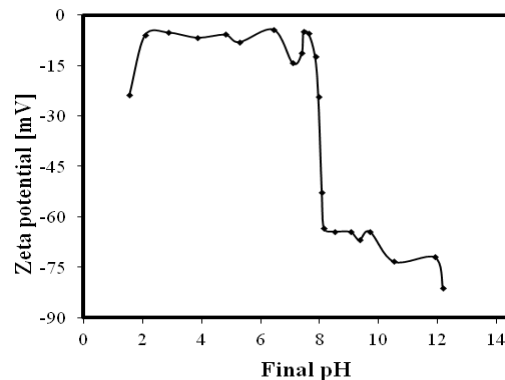
As the concentration of divalent electrolytes ions increase in the solution, the zeta potential of montmorillonite decreases (becomes less negative). $CaCl_2$, $Ca(NO_3)_2$ and $Pb(NO_3)_2$ electrolytes species were selected as divalent ions because natural water normally contains an appreciable quantity of them. It was found that montmorillonite were negatively charged each of the three electrolyte concentrations less than 1×10^{-2} M. In each of the three types of salt, at 1×10^{-1} M concentration montmorillonite surface of the electrolyte concentration is almost zero charged [15]. Fig. 7 has shown the effect of trivalent electrolyte ions such as $FeCl_3$ and $Fe(NO_3)_3$ on the zeta potential of montmorillonite sample. Addition of $FeCl_3$ and $Fe(NO_3)_3$ reduces the zeta potential of montmorillonite suspensions steadily starting from 1×10^{-5} to 1×10^{-1} M. Zeta potentials of montmorillonite samples were positive in the presence of $FeCl_3$ and $Fe(NO_3)_3$ at concentration of more than 1×10^{-3} M and 1×10^{-2} M, respectively [14]
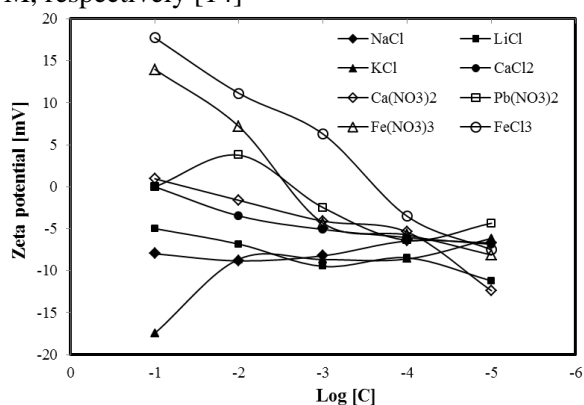

Figure 7. The variation of zeta potential of montmorillonite samples with monovalent, divalent and trivalent electrolytes at various concentrations.

CONCLUSIONS

The main results of the present study can be given as follows:

- The characterization of the montmorillonite was performed by using XRD, XRF, FTIR, SEM imaging, and N_2-BET analysis
- Montmorillonite suspensions exhibit a buffer pH around pH 8.
- It was observed that there is no significant effect of the solid concentration on the zeta potential of montmorillonite suspensions.
- Natural montmorillonite particles didn't have point of zero charge even at pH 2.
- In presence of monovalent electrolytes (NaCl, KCl and LiCl), the surface is, at first, more negatively charged, and then the negative charge decreases as the concentration of electrolyte

increases. While the divalent cations such as Ca^{2+} and Pb^{2+} provided neutral charge at 1×10^{-1} M concentration, iron ions caused the charge reversal from the negative to positive at 1×10^{-1} M concentration.

- The results of characterization and elektrokinetic experiments showed that montmorillonite clay would be used effectively in removal of cationic species from waters. The strong negative surface charge and porous structure of montmorillonite will enable to adsorb more organic and inorganic cations to its interior.

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ОХАРАКТЕРИЗИРАНЕ И ЕЛЕКТРОКИНЕТИЧНИ СВОЙСТВА НА МОНТМОРИЛОНИТ

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(Резюме)

Определянето на повърхностните свойства на монтморилонитови глини е важен критерий за адсорбционните му способности спрямо аниони и катиони, съдържащи се в отпадъчни води. В настоящата работа са изследвани електро-кинетичните му повърхностни свойства използвайки микроелектрофореза. Анализът на ζ-потенциала е извършен чрез измервания на електро-кинетичния потенциал като функция на концентрацията на соли и равновесното pH на разтворите. Намерено е, че ζ-потенциалът на частиците е отрицателен за едновалентни катиони (KCl, LiCl, NaCl), добавени към разтвора. Двувалентните катиони (CaCl$_2$, Ca(NO$_3$)$_2$, Pb(NO$_3$)$_2$) могат да доведат до неутрален заряд при максимални концентрации. В допълнение, монтморилонитът има отрицателен заряд дори при pH 2 и сам тривалентни катиони (Fe(NO$_3$)$_3$, FeCl$_3$) осигуряват положителен заряд на повърхността при високи концентрации. Охарактеризирането на монтморилонит е извършено чрез XRD, XRF, FTIR, SEM образи и N$_2$-BET-анализи. Определената порьозна структура и силният отрицателен повърхностен заряд показват, че тази глина може да се използва успешно за отстраняването на катиони от водите.