# Clay Mineral Characterization and Effect of the Particle Size onto Zinc Adsorption Kinetic Studies

A. Laajeb[1,*], A. Addaou[1], A. Lahsini[1], F. Ghomri[1], M. Elfatri[1] and Miguel A. Rodriguez[2]

[1]Equipe Matériaux et Procédés Industrials, Laboratoire des Sciences et du Technologie des Génies des Procédés, Université Sidi Mohamed Ben Abdellah, Ecole Supérieure de Technologie, Fès, Morocco
[2]Instituto de Cerámica y Vidrio (ICV- CSIC), 28049 Cantoblanco, Madrid, Spain

*Corresponding author: E-mail: alilaajeb@yahoo.fr

The mineralogy of clay from the Fez region (Morocco) has been studied by X-ray fluorescence, X-ray diffraction (XRD), BET and sedimentation separation process. Clays have received considerable attention especially as potential adsorbents for environmental research and as membranes supports. This paper describes the clay characterization and the effect of particle size on the process of zinc adsorption from aqueous solution. Adsorption of Zn(II) ions from aqueous solutions was studied in a batch system using different clay material granulometry. The conditions fixed for the adsorption of $Zn^{2+}$ ions from aqueous solution by clay material was investigated by considering the different parameters such as: contact time and particle size of the adsorbent (> 125, 125-20 and < 2 μm) at pH 6,7 at 25 ºC. The adsorption kinetic was consistent with Weber-Morris intra-particle diffusion, Lagergren pseudo first-second order and Elovich kinetic models.

**Key Words: Mineralogy, Particle size, Adsorption kinetic, Zinc ion, Clay mineral.**

## INTRODUCTION

The clay minerals are aluminosilicate with particles size less than 2 μm. It is abundante in the nature associated to other minerals like feldespars, quartz, carbonates and micas.

Pollution from industrial and agricultural sources is responsible to a great extent for high concentration of zinc in surface water. Zinc may also be contributed by the water distribution system due to leaching of zinc from galvanized pipes[1]. Adsorption is one of the important phenomena in water quality control, which may determine transport of pollutants in the aquatic environment. The tremendous increase in the use of heavy metals over the past few decades has resulted in an increased concentration of metals in aquatic systems and has a great significance owing to their toxicity and adsorption behaviour. Thus, in the natural conditions of surface water, suspended load and sediments have an important function of buffering higher metal concentrations of water particularly by adsorption or precipitation. Therefore, the study of sediments and their sorptive properties can provide valuable information relating to the tolerance of a system to increased heavy metal load and may determine the fate and transport of pollutants in the aquatic environment[1].

Zinc adsorption capacity correlates with soil contents of aluminosilicate clays, metal oxides and carbonates. Aluminosilicate clays affect Zn adsorption mainly through their effects on soil cation exchange capacity. Adsorption and or precipitation on surface of soil solids decrease the concentration of Zn in solution phase[2].

The present study examines the fine clay mineral fraction as adsorbent for heavy metals adsorption and that the kinetic studies of best adsorption models is filled.

## EXPERIMENTAL

The clay fraction (< 2 μm) was separated by sedimentation method. From this formula below (1), we can calculate an appropriate time to sample the solution so that all of the fine particles (*i.e.* clay) have been in suspension. The same principle can be used to determine a time to sample so that all of the silt and sand particles have fallen past H.

$$d_{éq} \leq \sqrt{\frac{18\eta}{g(\rho_s - \rho_w)} \frac{H}{t}} \qquad (1)$$

where, H = 0.1 m (height of the suspension); $\eta = 10^{-3}$ Pa.s (viscosity of solution); $\rho_s = 2650$ Kg/m$^3$ (weight specific of clay particle); $\rho_w = 1000$ Kg/m$^3$ (weight specific of water at 25 ºC); g = 9.81 m/s$^2$.

The clay mineral samples were characterized by powder X-ray diffraction analysis, using CuK$_\alpha$ radiation. For the adsorption studies, 1 g of clay mineral, with different granulometry, was equilibrated for contact times ranging between 0

TABLE-1
CHEMICAL ANALYSIS OF CLAY MINERAL (wt.%)

| Oxides | SiO$_2$ | Al2O$_3$ | CaO | Fe$_2$O$_3$ | MgO | Na$_2$O | K$_2$O | TiO$_2$ | MnO | SO$_3$ | L.O.I.[*] |
|--------|---------|----------|-----|-------------|-----|---------|--------|---------|-----|--------|-----------|
| wt (%) | 47.05 | 10.34 | 14.53 | 4.92 | 3.91 | 1.40 | 1.73 | 0.55 | 0.05 | 0.57 | 14.81 |

[*]: Loss on ignition

TABLE-2
MINERALOGY COMPOSITION OF CLAY MINERAL

| Phases | Illite | Kaolinite | Chlorite | Feldspar | Quartz | Calcite | Dolomite |
|--------|--------|-----------|----------|----------|--------|---------|----------|
| wt (%) | 7.15 | 16.43 | 8.65 | 2.28 | 37.15 | 23.08 | 5.26 |

and 90 min, at room temperature (25 ºC) and pH 6.7, in 50 mL of solutions with 200 mg/L of initial concentration of Zn(II), which was prepared with distilled water from standard solutions of 1000 mg/L of Zn(II). At the end, the centrifugation supernatant was drawn off, filtered through 0.45 µm paper and Zn(II) ion was measured by ICP-AES.

## RESULTS AND DISCUSSION

### Clay mineral characterization

**Chemical analysis:** According to the eqn. (1), the clay fractions (d$_{éq}$ < 2 µm) were obtained by sedimentation of raw clay fraction < 200 µm during 7 h 43 min. Chemical analyses were performed according to the procedure described by Jeauroy. Si, Al, Fe, Ti, Mg, Ca, Na and K were analyzed by atomic absorption spectroscopy (Tables 1 and 2). X-ray fluoresence and loss on ignition at 1000 ºC was measured by thermogravimetric analysis (TGA) and specific surface determined by BET method.

**X-ray analysis:** X-ray diffractograms of clay fraction of the four fraction samples under the present investigation have been presented in Figs. 1 and 2.
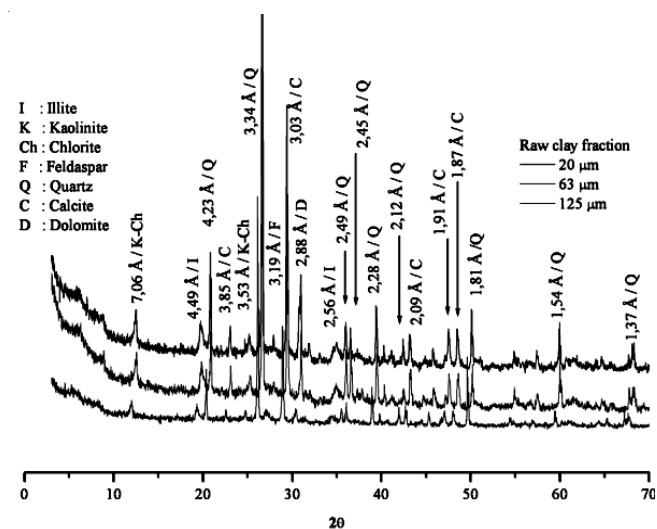

Fig. 1. XRD patterns of clay mineral (Fraction 20, 63 and 125 µm)

The X-ray patterns indicate that quartz and calcite were dominant clay minerals phase. A small quantity of kaolinite and illite (weak peak, Fig. 1) are present in all fraction clays (> 20, > 63 and > 125 µm).

Whereas, in Fig. 2, we can seen that koalinite and illite phases light increase (mean peak) and there is a light dimunition of quartz and calcite after sedimentation process.
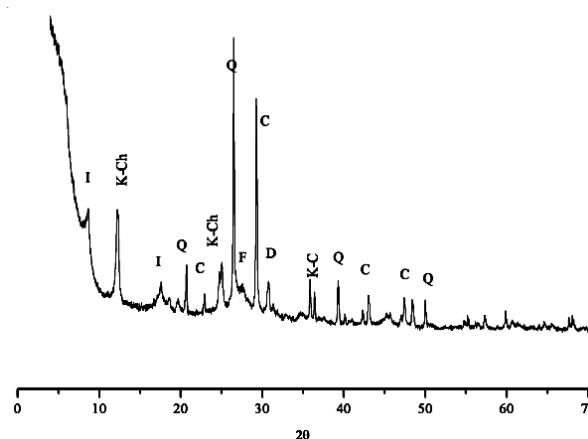

Fig. 2. XRD patterns of clay mineral (Fraction < 2 µm)

In general, this can be explained by the fact that the argillaceous phase are in fine fractions and released by sedimentation process.

**Adsorption kinetic studies:** In order to study the adsorption kinetics of heavy metal ions, the kinetic parameters for the adsorption process were studied for contact times ranging between 0 and 90 min by monitoring the amount of the heavy metals removal by the adsorbent. The data obtained was analyzed with the Lagergren first-order, pseudo second-order kinetic models as shown below.

**Contact time effect:** Fig. 3, shows the contact time and particle size effects. The values of equilibrium contact time were found to be 30 min for all clay fractions. The amounts adsorption of zinc ions by clay mineral with three particle sizes (< 2, > 20 and > 125 µm) are given in Table-3.
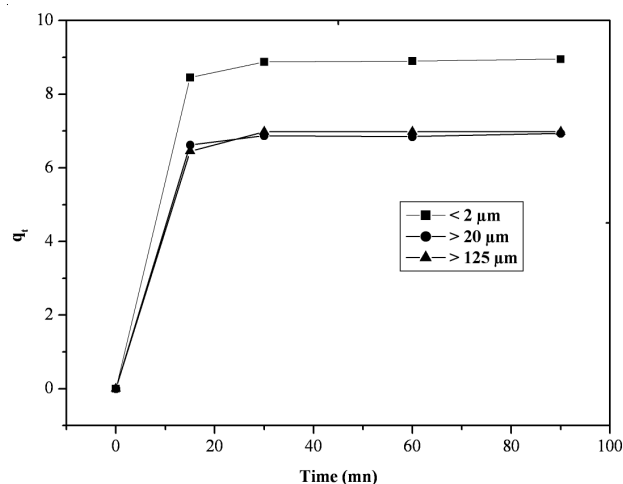

Fig. 3. Contact time and particle size effects of Zn$^{2+}$ adsorption

TABLE-3
SEDIMENTOLOGY STUDY OF CLAY FRACTION < 200 μm

| Clay fractions | wt (%) |
|---|---|
| Clay (< 2 μm) | 7,68 |
| Silt (2- 63 μm) | 74,62 |
| Sand (> 63 μm) | 17,70 |
| OM[*] | 7,2 |

[*] : Organic matter

It is evident that, from the Table-5, the concentration of zinc(II) adsorbed decreases with an increase of the particle size.

In general, the light increase of amount adsorption by clay mineral with small particle sizes is due to the availability of more specific surface area (Table-4) and elimination part of quartz in fine fraction[3].

TABLE-4
SPECIFIC SURFACE OF DIFFERENT CLAY FRACTIONS

| Clay particle size (μm) | Specific surface (m²/g) |
|---|---|
| 2 | 52 |
| 20 | 28.7 |
| 125 | 30.4 |

TABLE-5
EQUILIBRIUM ADSORPTION AMOUT AT DIFFERENT CLAY FRACTION

| Clay particle size (μm) | $q_e$ (mg/g) |
|---|---|
| 2 | 9.03 |
| 20 | 6.99 |
| 125 | 7.09 |

According to Weber and Morris, the breaking of larger particles tends to open tiny cracks and channels on the particle surface of the material resulting in more accessibility to better diffusion, owing to the smaller particle size.

**Adsorption kinetic studies:** In most adsorption studies, the linear method has been widely used in assaying the quality of fit of a kinetic model to an experimental data primarily due to its simplicity and usefulness. However, the different outcomes obtained by linear regression for the same kinetic model show the real complexities and problems in estimating the kinetic parameters by linearization technique[4].

In order to further study the kinetic for the adsorption of $Zn^{2+}$ from aqueous solution, Lagergren models were also used[5-9]. Lagergren first order pseudo second order kinetic are represented by eqs. (2) and (3) respectively.

**First- order model:**

$$\log (q_e - q_t) = \log q_e - K_1.t/2.303 \qquad (2)$$

**Pseudo second-order model:**

$$t/q_t = 1/(K_2.qe^2) + t/qe \qquad (3)$$

**Elovich kinetic model:** The Elovich kinetic model is for general application to chemisorption kinetics. The general explanation for this form of kinetic law involves that the active sites are heterogeneous in nature and therefore exhibit different activation energies for chemisorptions[10]. The Elovich model can be expressed in the following form:
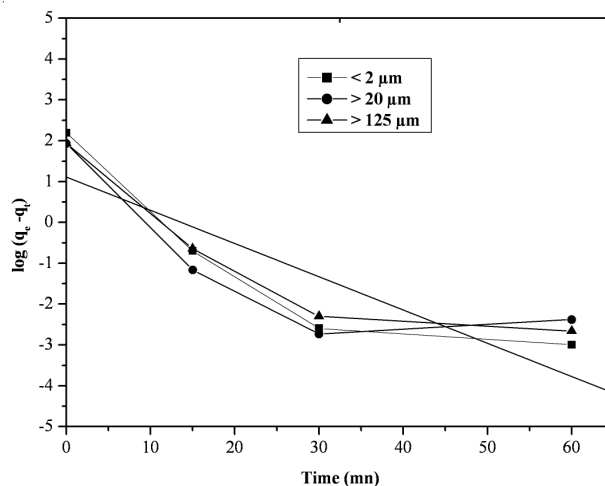
$$q_t = a + b.Ln\ t \qquad (4)$$



Fig. 4. Pseudo second order kinetic model of $Zn^{2+}$ adsorption
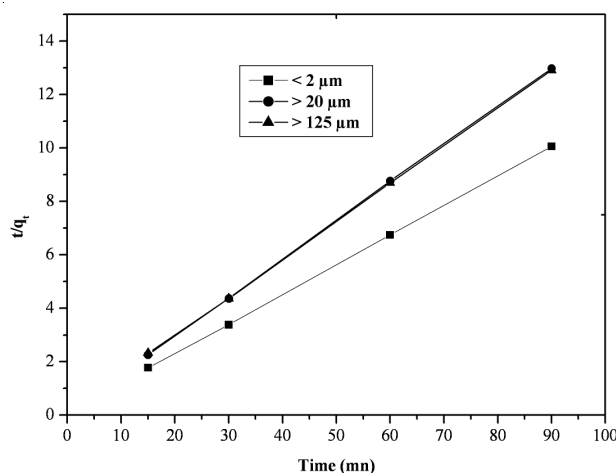


Fig. 5. Pseudo second order kinetic model of $Zn^{2+}$ adsorption

where, $q_t$ and $q_e$ are the amount of $Zn^{2+}$ ion adsorbed at time t and at equilibrium (mg/g) and $k_1$ (mn⁻¹) and $k_2$ (g/mg min) is the pseudo-second-order rate constant for the adsorption process. α is the initial adsorption rate (mg/g⁻¹ mn⁻¹) and β is the desorption constant, which are obtained from the intercept and the slope of a plot of $q_t$ *versus* Ln t. The plot should give a linear relationship for the applicability of simple Elovich kinetics as in Fig. 6.
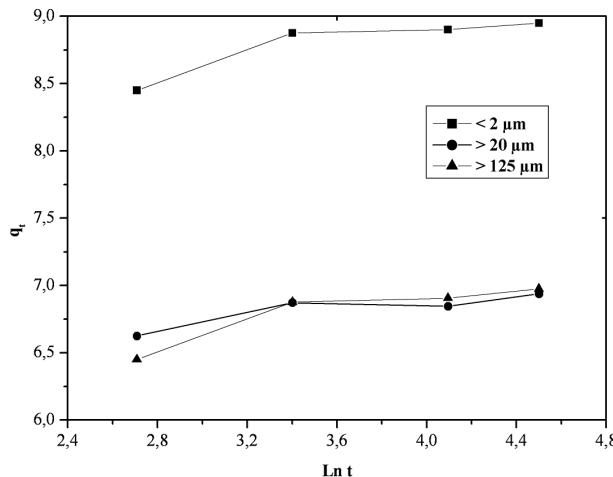


Fig. 6. Elovich Kinetic model of $Zn^{2+}$ adsorption

**Intra particle diffusion:** Adsorption kinetics is usually controlled by different mechanisms but the most limiting ones are the diffusion mechanisms[11-17], which consist of:

• The initial portion representing rapid external diffusion or boundary layer diffusion and surface adsorption.

• The linear portion indicating a gradual adsorption state due to intra particle diffusion.

• A plateau to equilibrium where the intra-particles diffusion starts to decrease due to the low concentration in solution as well as fewer available adsorption sites.

According to Weber and Morris, an intraparticle diffusion coefficient, $K_{id}$ is study by the equation:

$$q_t = K_{id}.t^{0.5} + C \qquad (5)$$

where, $q_t$ is the amount adsorbed per unit mass of adsorbent (mg/g) at time, t and $K_{id}$ is the intraparticle diffusion constant (mg/g mn0.5). Using eqn. (5), a plot of $q_t$ *versus* $t^{0.5}$ :

According to the results, in Fig. 7 and Table-6, the kinetic adsorption data were better fitted with pseudo second order model for zinc ions onto clay mineral.
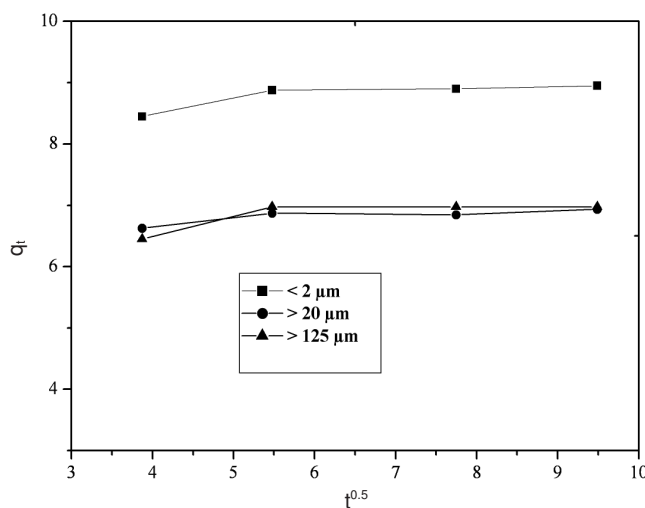


Fig. 7. Intra-particle diffusion Kinetic model of $Zn^{2+}$ adsorption

## Conclusion

Characterization of clay minerals in fine clay fraction and XRD spectras gave consistent results : % of clay material is about 7,68 (Fraction < 2 μm) and, according to chemical composition and X-ray analysis, this clay mineral is a marl, with 23.08 % of calcite and 5.26 % of dolomite. The equilibrium contact time is about 0.5 h and kinetic adsorption efficiency is weak depending on clay mineral paticle size. The pseudo-second order equation was more appropiate for description onto clay mineral than other models. This suggests that chemical adsorption might be rate-limiting step that controls adsorption process. Zinc ion uptake process was controlled by external mass transfer at earlier stages and by intraparticle difffusion at later stage.

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TABLE-6
PARAMETERS OF VARIOUS KINETICS MODELS
FITTED TO EXPERIMENTAL DATA

| Kinetic model | | Parameters with particle size | | |
|---|---|---|---|---|
| | | < 2 μm | > 20 μm | > 125 μm |
| Pseudo 1st Order Lagergren | $K_1$ | 0.1878 | 0.1501 | 0.1662 |
| | $q_e$ | 13.1471 | 4.2299 | 9.5277 |
| | $R^2$ | 0.7797 | 0.6183 | 0.7770 |
| Pseudo 2nd Order | $K_2$ | 0.1331 | 0.1910 | 0.1172 |
| | $q_e$ | 9.0342 | 6.9798 | 7.0656 |
| | $R^2$ | 0.9999 | 0.9999 | 0.9999 |
| Elovich kinetic model | $\alpha$ | 7.84121 | 6.26535 | 5.80402 |
| | $\beta$ | 0.25913 | 0.15089 | 0.27129 |
| | $R^2$ | 0.78090 | 0.76950 | 0.80900 |
| Intra particle diffusion | $K_{id}$ | 0.0774 | 0.0458 | 0.0794 |
| | $C$ | 8.2795 | 6.5153 | 6.3162 |
| | $R^2$ | 0.6843 | 0.6980 | 0.5590 |