# Examination of an Algerian Clay in the Retention of Zinc Ions Charged in Brackish Water

**Ammar Fadel[†] and Saci Nacef***

*Department of industrial Chemical, University of Biskra, ALGERIA*
*\*Laboratory of Chemical Process Engineering (LGPC), Department of Chemical Engineering, Ferhat Abbas University of Setif, Algeria*

**Abstract** – We studied the removal of zinc ions from synthetic brackish water by an adsorption method using natural Algerian Bentonite (NAB). The effect of the main physico chemical parameters-contact time, pH, temperature, ionic strength, clay weight and initial metal ion concentrations on the removal of $Zn^{+2}$- were investigated. The results showed that equilibrium was attained within 10 min of stirring time. The retention capacity of $Zn^{+2}$ increased with the increase of pH, the adsorbent dose and ionic strength. A modelization study showed that the adsorption follows Langmuir isotherm, while its kinetics was pseudo-second-order. Based on the results, it was concluded that NAB, which is natural and available, could be used as an alternative for the removal of zinc from saline aqueous solutions.

Key words: Zinc removal, Brackish water, Adsorption, Bentonite

## 1. Introduction

Zinc is one of the most important heavy metal contaminants for surface and ground water despite the fact that trace amounts are considered as an essential element for life acting as a micronutrient [1]. Industrial activities such as mining, mineral processing, and extractive metallurgy of zinc, lead, and cadmium ores, steel production, coal burning, and waste incineration are the main causes for zinc pollution. Free zinc ion in solution is highly harmful to plants and invertebrates. Trace amounts of free zinc ions can cause heavy damage to the environment and even kill some organisms. Moreover, excessive intake of zinc can promote deficiency in other dietary minerals [2]. The World Health Organization (WHO) recommends the maximum acceptable concentration of zinc in drinking water as 3 mg/l [3]. Therefore, it is necessary to remove this hazardous metal ion from liquid wastes at least to the limit accepted by national and international regulatory agencies before its discharge to the environment [4].

Literature survey concerning the treatment of water containing heavy metals by the electrodialysis technique shows that in most cases the effluents treated contain high concentrations of metal ions [5]. In this study, prior to electrodialysis, a pretreatment process which consisted of an adsorption on local clay using high concentrations was prepared from an aqueous model solution containing a fixed amount of sodium chloride salt.

Clays are particularly noteworthy nanoparticles because of their ubiquity and their reactivity. Their nanometric size and sheet structure provides a large specific surface area for adsorption and gives them a crucial role in the retention of a large number of industrial pollutants, The interest in these materials is justified by the importance of their developed surface, by the presence of charges on their surface, and their ability to exchange cations and a wide availability in nature [6,7]. Though all clay minerals have similar compositions, bentonite is superior with its unique cation chemistry and surface area. It is mainly composed of montmorillonite with a chemical composition of $SiO_2$, $Al_2O_3$, CaO, MgO, $Fe_2O_3$, $Na_2O$, $K_2O$ [8]. The selection of using raw bentonite is justified by the fact that it is both a low cost and environmentally friendly adsorbent material. The influence of key physico-chemical parameters such as stirring time, stirring rate, mass of the adsorbent, temperature, initial feed concentration, initial pH and ionic strength on the removal of zinc from adsorption process was studied.

## 2. Materials and Methods

### 2-1. Bentonite

The bentonite used, which is rich in montmorillonite, was obtained from Hammam Boughrara mine (Maghnia, west Algeria).The characteristics of this sodium based bentonite which were determined by the laboratory analysis carried out by the Bentonite Unit of the National Company of non-ferrous mineral products are summarized in the Table 1.

**Table 1. Physical and chemical characteristics of bentonite of Maghnia**

| Surface area (m²/g) | pH | Exchangeable cation (meq/100g) | | | |
|---|---|---|---|---|---|
| | | $Ca^{2+}$ | $Mg^{2+}$ | $Na^+$ | $K^+$ |
| 80 | 6.2 | 30.6 | 12.8 | 36.2 | 9.5 |

[†]To whom correspondence should be addressed.
E-mail: am.fadel@univ-biskra.dz

## 2-2. Preparation of stock solutions

A stock solution of 1000 mg of $ZnCl_2$ (7646-85-7) and 3 g NaCl (7647-14-5) in 1 L of distilled water was prepared. This mother solution was then diluted with distilled water in order to prepare solutions of lower concentrations used in the tests.

## 3. Equilibrium Isotherms

Equilibrium isotherm experiments were carried out using the optimum concentration of all the adsorbents and the optimum pH of $Zn^{+2}$ solutions for each adsorbent. 250 mL $Zn^{2+}$ ion solutions with different initial concentrations (11.25, 23.5, 47 and 94 mg/L) and containing the optimum adsorbent weight and the optimum pH of solution. The bottles were stirred at a fixed speed of 250 rpm in a rotating stirrer water bath at different temperatures of 30, 35 and 40 °C for 2 hours. The solutions were then filtered and the remaining $Zn^{+2}$ ion concentrations in the filtrate were determined by using the atomic-absorption spectrophotometer.

The adsorption of metal ions onto the adsorbent surface at a specific time was estimated from the mass balance equation [9]. The amount of zinc adsorbed by bentonite mass unit was calculated by the following formula:

$$q_t = \frac{(Co - Ce).v}{m}$$

where $q_t$, $C_0$, Ce, v and m are the amount adsorbed at time t (mg/g), initial metal ion concentration (mg/L), equilibrium metal ion concentration (mg/L), volume of the solution (L) and mass of the adsorbent (g), respectively. The results may be expressed in percentage removal as given by the following formula [10].

$$E(\%) = \frac{(Co - Ce)}{Co} \cdot 100$$

## 4. Results and Discussion

The study of the adsorption of $Zn^{+2}$ ions on Maghnia bentonite requires knowledge of the parameters that influence this phenomenon: temperature, ionic strength, stirring rate, stirring time, initial concentration, pH and adsorbent concentration.

## 4-1. Effect of temperature

The temperature dependence of $Zn^{+2}$ by adsorption on natural bentonite was investigated with a constant concentration of metal zinc ions of 23.5 mg/L at different temperatures (293.15 K, 303.15 K and 313, 15 K). The results, which are shown in Fig. 1, show that the efficiency of the adsorption of $Zn^{+2}$ decreases with increasing temperature. For example, for an increase in temperature from 293.15 K to 313.15 K, the adsorption rate decreased from 84% to 55%.

The percentage decrease of adsorption with the temperature may be due to the desorption caused by an increase of the thermal energy available. The increase in temperature induces greater mobility
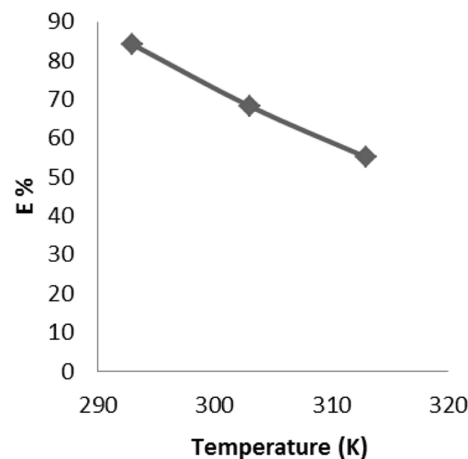
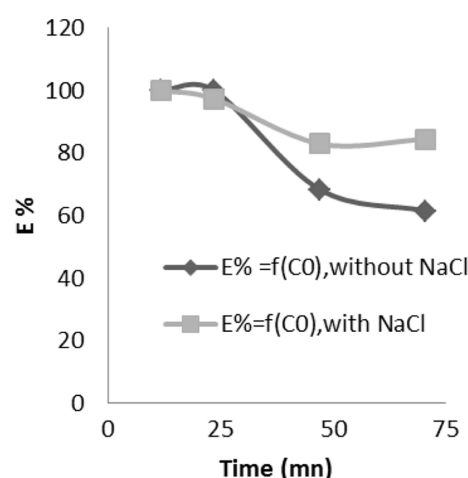Fig. 1. Variation of elimination rate with temperature.



Fig. 2. Variation of elimination rate with ionic Strength.

desorption. This indicates that the adsorption process is spontaneous and exothermic.

## 4-2. Effect of ionic strength

According to Fig. 2, the rate and adsorption capacity of zinc by the bentonite in a chloride solution were better than those in a non-saline medium. This is explained by the activation of the bentonite adsorption sites by the $Na^+$, leading to the creation of new adsorption sites. Since this effect was more pronounced with increasing the initial concentration of zinc, we can therefore conclude that the adsorption capacity increased with increasing the ionic strength of the solution.

## 4-3. Effect of the stirring rate

As shown in Fig. 3, the removal rate and the adsorption capacity of zinc by sodium bentonite increase with the increase of the agitation rate; this effect is attributed to the fact that the resistance to transfer from the liquid phase to the surface of the solid decreases with stirring.

## 4-4. Effect of the stirring time

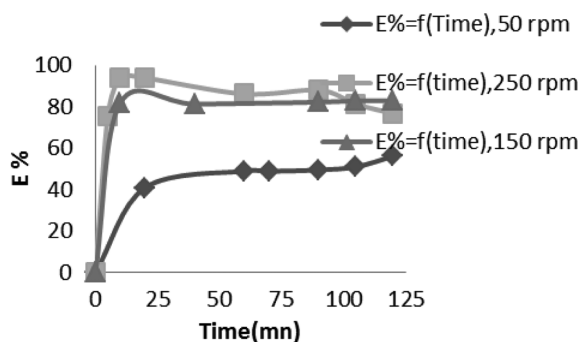The zinc adsorption kinetics was monitored for an initial zinc con-

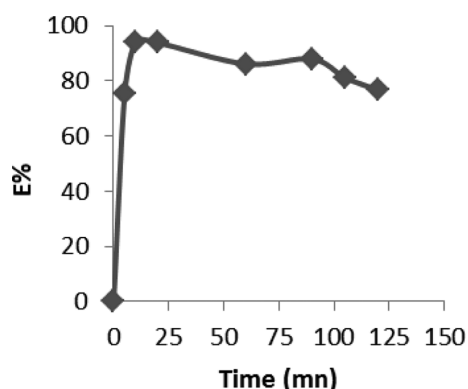Fig. 3. Variation of elimination rate with stirring speed.



Fig. 4. Variation of elimination rate with time.



Fig. 5. Variation of elimination rate with initial solute concentration.



Fig. 6. Variation of elimination rate with pH.

tent of 23.5 mg/L and to a constant weight of the adsorbent (1 g/L) and a pH equal to 6. The results (Fig. 4) show that the zinc removal efficiency varies with stirring time and the maximum efficiency was obtained after 10 minutes. Indeed the maximum value of elimination corresponding to this time was 94.24 %, for a stirring speed of 250 rpm, above which the adsorption rate became practically very slow and started decreasing after 90 min, The difference in the degree of adsorption may be due to the fact that at the beginning of adsorption, all the sites of the surface of the adsorbent are clear and the solute concentration gradient is relatively high. Accordingly, the degree of zinc removal decreased with increasing contact time, which depends on the number of vacant sites on the surface of the bentonite.

### 4-5. Effect of initial solute concentration

The effect of the solute concentration was investigated for an initial zinc content ranging from 11.25 to 94 mg/L and a concentration of the bentonite introduced of 1 g/L. The results presented in Fig. 5 show that the efficiency gradually decreased with increasing the initial zinc content of Maghnia bentonite. Note that Zhang et al. 2011 [11] also found a reduction in processing efficiency by varying the initial content of $Zn^{+2}$ between 30 and 250 mg/L and setting the concentration of bentonite to 1 g/L.

### 4-6. Effect of pH

The results of variation of the zinc ions removal rate by bentonite at 17 °C and a fixed concentration of zinc solution (23.5 mg/L) as a
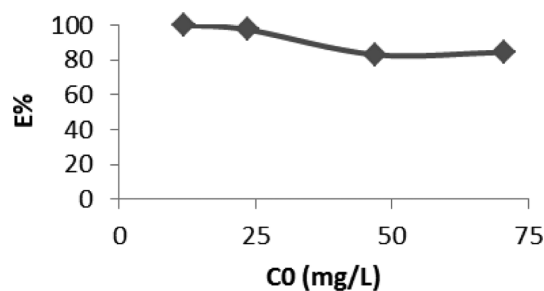
function of pH are shown in Fig. 6. The zinc adsorption tests were carried out in the presence of a constant dose of the adsorbent equal to 1 g/L and the pH of the solutions was adjusted to 3, 4, 6, 7, 9 and 12 using (0.1 N) NaOH (1310-73-2) and (0,1N) HCl (7647-01-01) solutions. The results which are presented in Fig. 6 show that the elimination rate of Zn ions increases when the pH increases. It appears that the elimination rate of Zn ions was affected by the surface charges of the adsorbent, which are variable depending on the pH. For Maghnia bentonite the highest efficiency was obtained in a basic medium, and the best performance was achieved at a pH of 7 and 10, with an elimination rate equal to 100 %. Mohammadi - AZIZI et al. 2013 [12] reported an increase in the zinc removal efficiency of bentonite with increasing pH. On the other hand, Gupta and Battacharyya, 2008 [13] reported also that the adsorption of metal ions on a sodium bentonite decreases with decreasing pH.

According to Abollino et al. 2003 [14], the low amounts of ions adsorbed at pH lower than 4 are due to the repulsive competition between the Zn ions in solution and the more mobile hydronium ions to interact with adsorption sites available. In addition to the Si-O- and Al-O- group less deprotonated and hardly form complexes with divalent and trivalent ions have shown that the elimination of Zinc using bentonite as adsorbent is strongly dependent on pH. The percent removal increases with increasing pH from pH from 1 to 4.

Then decreases from 72 to 59% in the pH range between 4 and 6; this decrease may be due to the reduction of the amount of negative charges on the surface of the clay. The positively charged metallic ions are retained on the surface of the clay by the Coulomb forces. It is explained by the increase of hydroxyl sites of the water that could attach to the silicon atoms of the incomplete tetrahedrons and the SiOH groups formed.
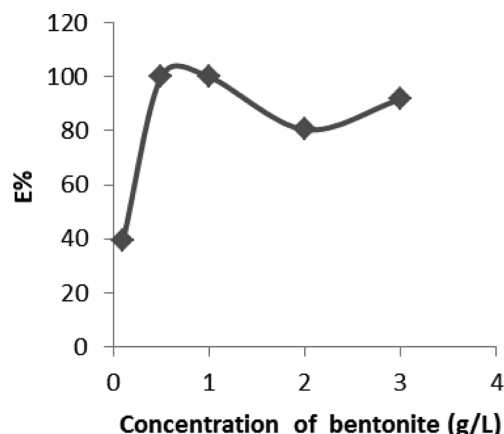
**Fig. 7. Variation of elimination rate with concentration of bentonite.**

By increasing the pH, the number of negative charges sites increases, which facilitates the adsorption of more Zn ions at pH > 7. Precipitation of Zn $(OH)_2$ plays the main role in the elimination of zinc. Accordingly, the predominant ionic species is $Zn^{2+}$ for pH < 7, but $Zn^{2+}$ is present mainly and to a less important amount as $Zn (OH)^+$ at a pH between 8 and 9. Since all experiments were performed at a maximum pH of 7, $Zn^{2+}$ species would be present predominantly in solution and adsorbed onto the bentonite surface.

### 4-7. Effect of adsorbent concentration

We followed the evolution of the removal efficiency of zinc at a constant initial concentration of zinc (23.5 mg/L) and varying bentonite concentration from 0.1 to 3 g/L.

The residual zinc content for each treated sample was measured after 2 hours contact time with bentonite.

From the results shown in Fig. 7, we can see that the zinc removal efficiency increases with the increase of the introduced amount of the adsorbent (bentonite of Maghnia) until the optimal dose 0.5 g/l at which the performance achieved 100% and then decreases slightly. According to Zhang *et al.* 2011 [11], zinc removal efficiency (100 mg/L) increases with increase of the bentonite dose (0.2 to 2 g/L).

## 5. Adsorption Isotherms of Zinc Ions on the Bentonite

We used the results according to the linear form of the model of Freundlich, Langmuir and Temkin, considering the following operating conditions:

Initial concentration of zinc of 23.5 mg/L, mass of the bentonite used equal to 1 g/L, stirring speed 250 rpm, pH=6, contact time equal to 2 hours and temperature=15.2 °C. The curves obtained with a good coefficient of correlation showed that with our experimental conditions, based on the correlation coefficient $R^2$ (Table 2), it can be concluded that the Langmuir model yields a better fit to the experimental data than the Freundlich and Temkin models.

## 6. Zinc adsorption kinetics

To determine the constants of adsorption rate, kinetic data were analyzed using two kinetic models [15]: the model of Lagergren pseudo-first-order, which is expressed as:

$$\log \frac{qe - qt}{qe} = -\frac{K_1 \cdot t}{2.3}$$

And the pseudo-second-order model, which is expressed as:

$$\frac{t}{qt} = \frac{1}{2 \, K_2 qe^2} + \frac{t}{qe}$$

The most representative data model was selected based on the correlation coefficient $R^2$, as shown in Table 3.

Accordingly, the kinetic model of pseudo-second-order is very suitable for the adsorption of zinc ions on the bentonite.

## 7. Conclusions

The results obtained in this study confirm the interest of the use of the Algerian clay (bentonite of Maghnia) for the adsorption of polluting metallic cations from an aqueous solution.

The zinc elimination efficiency increased with the increase of the introduced dose of adsorbent (bentonite of Maghnia) up to the optimal dose of 0.5 g/L at which performance achieved 100%. It also increased when the pH increased. The best performance was obtained at pH 7 and 10, with an elimination rate equal to 100%.

The removal efficiency, which increased with increasing agitation speed, exhibited a maximum value of 94.24% after 10 minutes for a rate of 250 rpm.

The elimination rate of Zn ions decreased gradually with increasing the initial zinc content in the bentonite and decreased also with increasing temperature, meaning that the adsorption process was exothermic.

**Table 2. Isotherm Constants for Adsorption of $Zn^{+2}$ onto Maghnia bentonite**

| Langmuir | | | | Freundlich | | | Temkin | | |
|---|---|---|---|---|---|---|---|---|---|
| $q_m$ (mg/g) | b (L/mg) | $R_L$ | $R^2$ | n | K (mg/g) | $R^2$ | B (J/mol) | A (L/g) | $R^2$ |
| 16.94 | 2.35 | 0.018 | 0.996 | 6.80 | 23.5 | 0.95 | 2.957 | 0.00037 | 0.962 |

**Table 3. Values of the coefficients of the two linearized kinetic models with experimental results**

| Kinetics of the pseudo-first-order | | | Kinetics of the pseudo-second-order | | | |
|---|---|---|---|---|---|---|
| $q_{e.cal}$ (mg/g) | $K_1$ (L·min$^{-1}$) | $R^2$ | $q_{e.cal}$ (mg/g) | $K_2$ (g·mg$^{-1}$·min$^{-1}$) | h (mg/g.min) | $R^2$ |
| not calculated | not calculated | 0. 069 | 18.86 | 0.021 | 0.398 | 0.993 |

The rate and adsorption capacity of zinc by the bentonite in a chloride solution were better than those in a non-saline medium.

The experimental results were in accordance with the Langmuir model and the kinetics revealed its compliance with the pseudo-second-order model.

## List of symbols

A : Temkin isotherm equilibrium binding constant [L/g]

b : Affinity parameter of Langmuir [L/mg]

B : Constant related to heat of sorption [J/mol]

$C_0$ : Initial solute concentration [mg/L]

$C_e$ : Concentration of solute at time t [mg/L]

E : Elimination rate [%]

h : Initial rate of adsorption [mg/g·min]

k : Freundlich adsorption capacity [mg/g]

$K_1$ : Rate constant of the pseudo first order adsorption [L·min$^{-1}$]

$K_2$ : Second order rate constant of the pseudo-order adsorption [g·mg$^{-1}$·min$^{-1}$]

m : Mass of the adsorbent [g]

n : Freundlich adsorption intensity

$q_t$ : Amount adsorbed at time t [mg/g]

qe : Amount of solute adsorbed per unit weight of adsorbent at equilibrium [mg/g]

$q_m$ : Maximum capacity [mg/g]

$R_L$ : Separation factor

$R^2$ : Correlation coefficient

t : Time [mn]

V : Volume of the solution [L]

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