

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/



Adsorption of Zn (II) and Cd (II) from Aqueous Solution using Natural Clay: Equilibrium, Kinetic Studies and Effect of Thermal Activation of Adsorbent on Adsorption Capacity

Salah Bahah *

Department of Environmental Engineering, Faculty of Science and Technology, University Mohamed El Bachir El Ibrahimi of Bordj Bou Arreridj, Algeria.

Electrochemistry and Environment Laboratory, Department of Environmental Engineering, Faculty of Science and

Technology, University Mohamed El Bachir El Ibrahimi of Bordj Bou Arreridj, Algeria.

Laboratory of Chemical Processes Engineering (LGPC), Department of Process Engineering, Faculty of Technology,

University Ferhat Abbas Setif-1, 19000 Sétif, Algeria.

Abstract

Natural clay containing some metal oxides and dolomite was used as an effective adsorbent to remove heavy metals such as cadmium and zinc. Thermal activation of natural clay was exploited as an efficiency method to improve and increase its effectiveness in removing these metals. The maximum removal efficiency value of natural clay for zinc and cadmium ions were 21.3 (mg.g⁻¹) and 33.33 (mg.g⁻¹) respectively. This clay had a maximum zinc and cadmium removal capacity at pH above 4, contact time 25 min and 5 min for zinc and cadmium respectively, and adsorbent mass 4 (g.l⁻¹). Thermal activation of natural clay at 900 °C increases this capacity to 83.33 (mg/g) and 90.909 (mg/g) for Zinc and Cadmium respectively. The pseudo second order model and the equations of Freundlich and Langmuir are the most adequate to represent the experimental data of kinetics and isotherms of adsorptions of Zn (II) and Cd (II) by natural clay respectively. The Langmuir model maintain the most adequate equation to represent the isotherm of adsorption of zinc and cadmium by thermal activated natural clay.

Keywords: Natural Clay, Zinc, Cadmium, Adsorption. Thermal activation.

1. Introduction

Environmental pollutants of all kinds are now concern for the whole world because of their direct effects on the environment, humans and animals. If water pollution produces many risks due to its direct association with the lives of all organisms in general, it is very important that this element be constantly under our control. Heavy metals are classified among the most dangerous inorganic pollutants for humans and the environment. The sources of these pollutants are natural (soil erosion, volcanic eruption, forest fires...) or anthropogenic (energy production by combustion, pyrometallurgy, waste incineration, and agriculture sector, textile, plastic, pharmaceutica) [1-3]. These pollutants are considered inorganic pollutants, and they are characterized by their resistance to decomposition, which leads to their presence for long periods of time in the environment, which may affect some of their chemical properties such as solubility, which makes them available to plants [4,5]. These elements such as Zn^{2+} , Cd^{2+} , Cr^{2+} , Co^{2+} ,...etc., present a danger to human health or the environment [6]. Several methods are used to remove these pollutants from water, among them chemical precipitation [7], membrane filtration [8], ion exchange [9], and adsorption [10]. This last technique is among the easiest and most used methods. Many natural materials are used as adsorbents to remove heavy metals including, for example, clays, activated carbon, and zeolite.

Each metal has different effects on human health. Some of these elements are extremely toxic to human beings, even at very low concentrations [6]. For example, organic lead strongly disrupts the nervous system. Zinc and its salts cause respiratory and intestinal problems. As for cadmium, in exposure to it, various types of cancer can affect humans such as breast, lung, prostate, nasopharyngeal, pancreatic and kidney cancer [11]. In addition, cadmium has a significant effect on the enzymatic systems of cells [12,13]. Cadmium and zinc are a subgroup (IIb) metals in the transition series in the periodic table of elements. These two heavy elements are commonly found at the contaminated sites. Therefore, the removal of Zn^{2+} and Cd^{2+} from waters is important to protect public health [10]. Natural clays are ranked among the most abundant natural adsorbents in the world. Due to

their low cost, and their effectiveness in removing heavy metals from water, they are widely documented in the literature.

Several research works that use natural clays as adsorbents to remove cadmium and zinc have attempted to improve its adsorption capacity by modifying the clay mineral with other chemical reagents. However, this is not without many negatives related to the increase in the cost of using clay in addition to the environmental problems due to the addition of more chemicals and their impact on the environment. On the other hand, these chemicals added to the adsorbent may constitute a major obstacle in it regeneration.

The use of natural clay adsorbent to treat heavy metal ions, such as Zn^{2+} and Cd^{2+} from water, has been the subject of several studies.

The purpose of this study is the determination of clay adsorption capacity of zinc and cadmium ions in water. Note that this clay is used for the first time for the elimination of Zn^{2+} and Cd^{2+} ions. The natural clay used was applied after pre-treatment, without any chemical modifications. In order to know the impact of thermal activation on the adsorption capacity of this clay, the adsorbent is thermally activated and used for the elimination of these two inorganic ions (zinc and cadmium)

The adsorption of cadmium and zinc ions by natural clay was made by studying the influence of several factors, such as pH, adsorbent dose, temperature, contact time and effect of the presence of another ion in the solution (Pb^{2+}). Regarding the adsorption of zinc and cadmium by thermally activated clay, the study focuses only on the adsorption of these two ions at different concentrations at room temperature, solution pH, same mass of adsorbent, and stirring speed.

2. Materials and methods

2.1. Pretreatment of natural clay sample

The natural adsorbent used is a local clay from east of Algeria. The raw material was subjected to a pretreatment step including drying, grinding and sieving. The solid obtained was added to distilled water, the mixture was agitated for 3 hours. In order to remove the organic matter contained in the adsorbent, the solid was treated with hydrogen peroxide (H_2O_2). The clay washing was realized by distilled water. The obtained sample was dried at 80 °C for 24 hours.

2.2. Methods

2.2.1. Thermal activation of natural clay

The pretreated natural clay was calcined at 900 °C for 6 hours in a type Nabertherm furnace under open air conditions. The obtained natural clay activated was allowed to cool to room temperature and then collected in a suitable bottle for further use in the adsorption process.

2.2.2. Metal ion solutions $(Zn^{2+}, Cd^{2+} and Pb^{2+})$

Mono- and bi-metallic adsorption experiments were carried out to obtain the adsorption characteristics of (Cd^{2+}, Zn^{2+}) and $(Zn^{2+} + Pb^{2+})$ in aqueous solutions.

A metallic solution of Zn^{2+} and Pb^{2+} with a concentration of 1000 mg.l⁻¹ was prepared by dissolving the appropriate quantities of heavy metal salt of $Zn(NO_3).4H_2O$ (Merck) and $Pb(NO_3)_2$ (Merck) in distillated water. The used solutions were prepared by dilutions of the stock solution. NaOH and HCl reagents were purchased from Merck Company. The same solution preparation protocol was followed for the preparation of cadmium solutions from Cd(NO_3)_2.4H_2O (Sigma-Aldrich).

2.2.3. Adsorption Experiments

To each 50 mL of Zn (II) solution prepared in several beakers, we added a known mass of natural, all solutions are stirred at 400 rpm, by a magnetic stirrer at room temperature. The solution was then thoroughly mixed, allowing sufficient time for equilibrium. Analysis of the solutions was done by an atomic absorption apparatus (AAS), type PG-990. The same protocol was followed for binary-metal adsorption of metals $(Zn^{2+} + Pb^{2+})$ by natural clay.

In the case of cadmium, we used 25 ml of Cd(II) solution, and the same procedure was followed as for zinc and binary-metal adsorption of metals $(Zn^{2+} + Pb^{2+})$ by natural clay. The number of ions adsorbed on the surface of natural clay is determined through the following equation:

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

689

Where, \mathbf{q}_e , \mathbf{C}_i , \mathbf{C}_e , \mathbf{m} and \mathbf{V} are the quantity of metal adsorbed at equilibrium (mg/g), the initial concentration of the metal ion (mg.l⁻¹), the final ion concentration (mg. l⁻¹), the mass of the clay (g), and the volume of the aqueous solution (l), respectively.

The removal efficiency was determined by the formulae in Eq. (2)

Adsorption (%) =
$$\frac{C_0 - C_t}{C_0} * 100$$
 (2)

Where C_0 and C_t are the initial concentration and concentration at time *t*, respectively.

2.3. Characterization

A Bruker D8 diffractometer with CuK α radiation (λ = 0.15406 nm) was used to study the structural properties of the clay. Scanning electronic microscopy instrument S-4800, Hitachi model, and Fourier transform infrared spectroscopy, Perkin-Elmer model, were used to study the surface properties and functional group of the adsorbent. Moreover, this last technique was used to examine the influence of retention of Zn²⁺ on the different bands of the functional groups after adsorption. FTIR spectra were recorded between 400 to 4000 cm⁻¹. The zeta potential can be measured by the technique of micro-electrophoresis. This technique consists in measuring the speed of individual particles in a suspension when they are subjected to an electric field. The device used to measure the zeta potential is a Malvern Zeta Sizer.

3. Results and Discussion

3.1. Adsorbent characterization by XRD

The diffractogram of the clay natural studied is presented in the figures 1. Several peaks that characterize the kaolin and illite phases were present in the XRD patterns, as shown in Figure 5; in addition, the X-ray diffraction pattern indicates the presence of dolomite as secondary phase. As for the impurities found in this natural clay, we note the existence of quartz as the major phase among the other impurities such as calcite.



Figure 1: X-ray diffraction pattern of natural clay

3.2. FTIR spectroscopic studies

As shown in Figure 2. There are 3 main regions, below 1000 cm^{-1} , between 1000 cm^{-1} and 3000 cm^{-1} and above 3000 cm^{-1} . The first less than 1000 cm^{-1} which itself contained four essential bands at 472.563 cm¹⁻, 526.088 cm¹⁻, 776.354 cm¹⁻ and 873.763 cm⁻¹ is the band Si–O or Si-O-Si deformation, Si-O-Al stretching or FeO or Fe₂O₃, Si-O quartz [14,15], and CO₃²⁻ [16] respectively.

The second region also contained three essential bands at 1028.06 cm¹⁻, 1436.79 cm¹⁻ and 1653.008 cm¹⁻, which were assigned to Si-O [15], CO_3^{2-} of Dolomite and the bending vibrations of the OH group of H₂O.

In the third region, two remarkable bands at 3630.061 cm⁻¹ and 3447.304 cm⁻¹can be noticed. The first band represented the OH stretching of layer hydroxyl and the last band was assigned to the interlayer water (H-O-H), respectively **[15]**.

3.3. Potential zeta

The curve below Figure 3, shows the zeta-potential of natural clay depending on pH values. Above pH 3, the curve shows a change in the concentration of H^+ ions, i. e. OH^- in the electrical double layer takes place, this may give the substance a high adsorption capacity for heavy metals, including zinc, lead and cadmium. In the pH range between 0 and 4.6 potential zeta increased from 0 to -19 mv.

In addition, the zeta potential was negative above pH 3, showing a negative charge of the natural clay particles above pH 3, and thus complete adsorption of Zn (II) was achieved in this pH range. These results are in agreement with those found by other researchers such as Chai et al [17].

As the mineral surface was not homogeneously composed of identically charged particles, more or less variable values of zeta potentials can be observed **[18]**.



Figure 2: FTIR Spectrum of natural clay



Figure 3: Zeta potential of natural clay

3.3. Characterization of natural clay particles by SEM

The SEM images in figure 4a show large particles with different sizes and thickness, some particle characterized by surface lamellar plates and aggregates of stacked nanosheets. We also observed pseudo-hexagonal plates of different sizes as shown in the figure 4a. These particles are characterized by heterogeneous surfaces (roughness).



Figure 4a: SEM images of natural clay with different amplification

After calcination of natural clay at 900 °C for 6 h (Figure 4b) the particle size was greatly reduced according to images figure 4b and the porosity increased. It is also observed that the particles agglomerate and appear more compared to the images of natural clay of the same amplification (Figure 4a).



Figure 4b: SEM images of thermal activated natural clay with different amplification

During the calcination process of clays, dehydration, dehydroxylation, decarbinization and other volatile compounds take place and lead to the formation of new phases that have different physicochemical properties of high reactivity. This calcination process promotes the division of clay particles and aggregates and makes them smaller, less dense and more porous with ample active sites, which increases the specific surface area of the adsorbent, giving it a high adsorption capacity.

3.4. Investigation of Adsorption

3.4.1. Effect of pH on the Removal Zn^{2+} and Cd^{2+} ions

Due to its direct effect on surface load, the influence of pH on the retention of zinc and cadmium on natural clay has been examined in the range of 2 to 9. In this case, the mass of natural clay and the volumes of the solutions are 50 ml and 25 ml for zinc and cadmium respectively. The concentration of each of them is equal to 25 (mg.l⁻¹) and 50 (mg.l⁻¹) for zinc and cadmium respectively. The pH of the solutions was adjusted with HCl and NaOH solutions. The stirring time is 4 hours.

The adsorption of Zn^{2+} and Cd^{2+} ions are strongly depending on the pH as presented in figure 5a and 5b. At low pH (pH less than or equal to 3), the percentage of elimination of Zn^{2+} was relatively low and did not exceed 53%, conversely for Cd^{2+} , where the Cd^{2+} elimination rate was 72% at pH 2. At pH 4 or higher, the percentage of Zn^{2+} and Cd^{2+} removal increased considerably and reached 98% and 84 %, respectively. The decrease in the quantity of Zn^{2+} and Cd^{2+} ions at pH less than or equal to 4 is due to the competition of H_3O^+ with them on the active sites [19].

Also, The Cd²⁺ shows higher removal efficiency (72%) compared to Zn²⁺ (53%) at pH 2. this could be due to hydration energies, or specific interactions with the clay surface.

In the range of pH higher than 4, the concentration of H_3O^+ ions decreases and there is a large and sufficient number of active sites on the natural clay surface that react with Zn^{2+} and Cd^{2+} ions, respectively. In addition, several mechanisms can contribute simultaneously to the fixation of Zn^{2+} and ions such as, the precipitation of Zn^{2+} , either in the presence of calcium, or at a pH ≥ 6 on the pores or on the clay surface, the adsorption of Zn^{2+} on active sites of the clay surface and the exchange of anions. These results are in agreement with those of potential zeta, which shows that from pH 3 the concentration of OH⁻increased, which favors the adsorption of Zn (II) ions. The mechanism of removal of Zn (II) by precipitation at pH greater than or equal to 6 can be explained by the following reaction [20] (Sdiri et al. 2014):

$$M(II) + 2 OH \Leftrightarrow M(OH)_2$$

M is Zn (II).

Cadmium in aqueous solution is formed from Cd^{2+} in the pH range of 2 to about 9, therefore, the main mechanism of elimination of Cd^{2+} is the adsorption of Cd^{2+} on active sites of the natural clay surface. By precipitation at pH greater than or equal to 8.5. Knowing that, the Cd^{2+} ions will precipitate at pH of about 8.5 [21].



Figure 5: Effect of initial pH on removal percentage of: (a) Zn (II), (b) Cd (II) on natural clay

3.4.1.1. Adsorption Isotherms by Natural clay

The study of isotherms has often been considered the best approach in the study of the theoretical aspects of any adsorption systems [22]. Typically, isotherm data are used to determine the amount of adsorbate retained by the selected adsorbent [23]. Solutions of varying concentration of Zn^{2+} and Cd^{2+} were prepared.

The adsorption of Zn^{2+} and Cd^{2+} of all solutions was carried out at the pH of the solution, room temperature, 3 hours of stirring speed of 400 rpm, and 0.2 g of natural clay. The adsorption isotherms of Zn^{2+} and Cd^{2+} as a function of the resulting concentration of zinc and cadmium in the aqueous solution are presented in figure 6a and 6b.

First, it is clear from the adsorption isotherms that the amounts of adsorbed zinc and cadmium increased with increasing Zn^{2+} and Cd^{2+} concentrations (Figure 6a and 6b). Adsorption is carried out by the different active sites located on the external surface of natural clay, dolomite and probably the small quantities of traces of metal oxides such as manganese oxides, which has an affinity between these oxides and certain metal ions [24,25]. This adsorption on different types of active sites is governed by several parameters such as clay structure, texture, and surface heterogeneity. The participation of different active sites can be confirmed by the infrared technique of natural clay before and after adsorption of Zn^{2+} figure 6. knowing that, the infrared technique is an important technique often used to elucidate changes in chemical structures [26].



Figure 6: Adsorption isotherms: (a) Zn²⁺ and (b) Cd²⁺ by natural clay of natural clay at pH of solution

Spectrum peaks (Figure 7) provide the surface functional groups that participate in the adsorption processes on the natural clay surface. As presented in the figure 7, it is very clear that there are several functional groups of the adsorbent involved in the elimination of Zn^{2+} . The intensity of these peaks decreased and shifted after adsorption of zinc and this decrease and offset were enhanced with the increase of the concentration of zinc and the appearance of other bands near the essential bands after adsorption.

These two last remarks accounted markedly for the trends observed at high concentrations of Zn^{2+} , namely at 17.5 (mg.L⁻¹) and above. The intensity of the peaks, which decreased, concerns those of the oxides of metals between 400 cm⁻¹ and 1100 cm⁻¹, carbonate band at 1436.79 cm¹⁻and hydroxyl layers of natural clay between 3400 cm⁻¹ and 3800 cm⁻¹.Due to the presence of CO_3^{2-} (contain in dolomite) at 1436.79 cm⁻¹ and 876.73 cm⁻¹as presented in the IR spectra (Figure 6), Zn^{2+} was removed due to the precipitation as metal carbonate (zinc carbonates) [20]. As mentioned by Sdiri and Higashi, the removal of Zn (II) can also be carried out through the interaction of metal cations with reactive sites at the surface of the sorbent after calcite dissolution [20,27]:

$$CaCO_{3(S)} \leftrightarrow Ca^{2+}_{(aq)} + Ca^{2-}_{3(aq)}$$
$$Ca^{2-}_{3(aq)} + M^{2+}_{(aq)} \leftrightarrow MCO_{3(S)}$$

Due to the presence of dolomite, it can also contribute to the fixation of Zn (II) according to the following reaction:

$$CaMgCO_{3(S)} \leftrightarrow Ca^{2+}_{(aq)} + Mg^{2+}_{(aq)} + CO^{2-}_{3(aq)}$$
$$Ca^{2-}_{3(aq)} + M^{2+}_{(aq)} \leftrightarrow MCO_{3(S)}$$

Where M = Zn (II).

Figure 5 indicates a considerable increase of adsorbed zinc by natural clay at high concentration of Zn^{2+} . This increase can be assigned to zinc precipitation as explained by AL-DEGS, Yahya S. et al. which showed that adsorption by precipitation of zinc on soil was improved when Zn^{2+} concentration is high [28].

Most of the Zn^{2+} removing is due to the interaction with the reactive site of the hydroxyl layers on the sorbent surface. The possible removal mechanisms that can take place as proposed by Bahia et al, Srivastava et al and Sari et al [29-31] are as follows:

$$SiOH + OH^{-} \rightleftharpoons SiO^{-} + H_2O$$
$$SiO^{-} + M^{2+} \rightleftharpoons SiO^{-}, M^{2+}$$

Where $M = Zn^{2+}$

As presented in figure 7, the shift which accompanied by a decrease in the intensity of the peak which corresponds to the quartz (around 1028.06 cm⁻¹), is explained by the participation of the latter in the adsorption of Zn^{2+} ions.

In general, the high adsorption capacity, which characterizes this clay, is reflected by the great heterogeneity of the active sites of natural clay.



Figure 7: FTIR Spectrum of natural clay: Before and after removal of Zn²⁺ of various concentrations

The models of Langmuir, Freundlich and Temkin model the adsorption of Zn^{2+} and Cd^{2+} . The corresponding linear forms are [26, 32-33]:

$\frac{1}{q_e} = \frac{1}{K_L, q_{max}, C_e} + \frac{1}{q_{max}}$	(3)
$Log q_e = Log K_F + \frac{1}{n} Log C_e$	(4)
$q_e = \frac{RT}{b} \ln C_e + \frac{RT}{b} \ln K_T$	(5)

For the Langmuir model, q_e and q_{max} are the quantities adsorbed at equilibrium and maximum respectively. b is the Langmuir constant (L.mg⁻¹). C_e is the equilibrium metal concentration. The adsorption equilibrium term R_L is given by equation (6):

The adsorption equilibrium term R_L which exhibits the essential characteristics of the Langmuir isotherm, is given by the following equation [33,34]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{6}$$

Equation (2) presents the Freundlich model. K_F and *n* are the Freundlich constants. When the values of *n* are between 0 and 10 the adsorption is said to be favorable. In the Temkin model, K_T and b are constants that exhibit equilibrium binding and energy of adsorption, respectively. R represents the ideal gas constant (R= 8.314 j.k⁻¹.mol⁻¹), and T is the temperature in kelvin (K). $B_T = \frac{RT}{b}$ is a constant related to adsorption heat (J.mol⁻¹).

The adsorption mechanism and the adsorption capacity of natural clay related to the concentration of cadmium and zinc are analyzed through these models.

The obtained results are presented in the table.1, Figure (8a, 8b, 8c) and Figure (9a, 9b, 9c); According to the values of the regression coefficients (R^2), we find that the adsorption of zinc and cadmium in clay follows the Langmuir and Freundlich models.

The maximum adsorption capacity of Cd^{2+} and Zn^{2+} on natural clay calculated from Langmuir model was 21.73 (mg.g⁻¹) and 33.33 (mg.g⁻¹) respectively. According to the initial Zn^{2+} concentrations between 10 until 250 (mg.L⁻¹), the dimensionless separation factor (R_L) values calculated from relation (7) were between 0.11 and 0.005 for zinc and between 0.45 and 0.064, indicating favorable adsorption. The Freundlich constants (n) which were equal to 1.66 and 2.22 for zinc and cadmium respectively, also confirmed the results of Langmuir related to favorable adsorption.



Figure 8: Linearized adsorption isotherm of Langmuir (a), Freundlich (b) and Temkin (c) adsorption isotherm of Zn (II) by natural clay



Figure 9: Linearized adsorption isotherm of: (a) Langmiur, (b) Freundlich, and (c)Temkin of Cd (II) by natural clay

Ions		Zn ²⁺	Cd ²⁺
Model		Model Parameters	
	$Q_m(mg.g^{-1})$	21.73	33.33
Langmuir	$K_L(L.mg^{-1})$	1.12	0.048
8	R ²	0.84	0.96
Freundlich	n	1.66	2.22
	$K_F(mg.g^{-1})(L.mg^{-1})^{1/n}$	7.84	3.22
	\mathbb{R}^2	0.96	0.98
Temkin	<i>b</i>	684.08	552.72
	$B (J.mol^{-1})$	3.66	4.59
	$K_T(L.mg^{-1})$	30.09	1.39
	R^2	0.82	0.88

Table 1. Constants of adsorption isotherms of Zn^{2+} and Cd^{2+} .

3.4.1.2. Adsorption isotherms by thermal activated natural clay

The results of adsorption of used pollutants by thermal activated clay at 900°C are presented in the figure (10a and 10b) and table (2). According to the adsorption isotherm curves and following the adsorption data, the results show that the adsorption capacity of zinc and cadmium increases significantly after thermal treatment of the adsorbent. According to the Langmuir model (Figure 11a and 12a), the maximum adsorption capacity of zinc and cadmium increases from 21.73 (mg/g) and 33.33 (mg/g) to 83.33 (mg/g) and 90.909 (mg/g) for zinc and cadmium respectively (table 1 and 2).

The data of cadmium adsorption by activated clay are well represented by the Freundlich model compared to those found in Zinc (table 2 and figure 11b and 12 b). The K_1 values found increase compared to those calculated before activated, which indicates the increase in the adsorption capacity after thermal activation (table 1 and 2).



Figure 10: Adsorption isotherms: (a) Zn^{2+} and Cd^{2+} by thermal actives natural clay at pH of solution.

Table 2. Constants of adsorption isotherms of Zn^{2+} and Cd^2 adsorbed by thermal activated clay.

Ion		Zn ²⁺	Cd ²⁺
Model	Model Parameters		
	Qm(mg.g ⁻¹)	83.33	90.909
Langmuir	K _L (L.mg ⁻¹)	0.057	0.687
	R ²	0.986	0.96
Freundlich	n	0.897	1.121
	$K_F(mg.g^{-1})(L.mg^{-1})^{1/n}$	13.001	43.551
	R ²	0.853	0.95
Temkin	b	105.51	144.285
	B (J.mol ⁻¹)	23.49	17.18
	K_T (L.mg ⁻¹)	1.992	10.989
	R ²	0.39	0.88



Figure 11: Linearized Langmuir (a), Freundlich (b) and Temkin (c) adsorption isotherm of Zn (II) by thermal activated natural clay



Figure 12: Linearized adsorption isotherm of : (a) Langmuir, (b) Freundlich (c)Temkin of Cd (II) by thermal activated natural clay

3.4.2. Contact time effect

The effect of contact time on the adsorption process by natural clay was studied at 12.5 and 25 (mgl⁻¹) for zinc and at 25 (mg.l⁻¹) and 50 (mg.l⁻¹) for cadmium are shown in the figure 13a and 13b. Adsorption equilibrium was reached after 25 min for both concentrations of zinc (Figure 13a) before 5 min for both concentrations of cadmium (Figure 13b). The faster adsorption of cadmium compared to zinc can be explained by the presence of oxide element that has a greater affinity for cadmium than zinc and reacts more rapidly with it, or plays a role as a catalyst, increasing the rate of cadmium fixation in surface clay compared to zinc. The adsorption efficiency of Zn^{2+} ions decreased with increasing initial ion concentration from 12.5 to 25 (mg.l⁻¹). The same remark was observed for cadmium. The quantities of adsorbed zinc ions at equilibrium were 3.13 (mg.g⁻¹) and 5.23 (mg.g⁻¹), for 12.5 (mg.g⁻¹) and 25 (mg.g⁻¹), respectively. In addition, the elimination rate obtained at equilibrium was higher at 12.5 (mg Zn (II) / 1), above 99%, if compared to that obtained at 25 (mgZn(II) / 1), 83.57%.

These results can be explained by the availability of adsorption sites to adsorb more Zn^{2+} at 12.5 (mg.l⁻¹) than at 25 (mg.l⁻¹) **[35,36]**. The same remark was observed for cadmium, where the percentage of removal of Cd (II) at 25 (mg.l⁻¹), 97.66 % (3.05 (mg.l⁻¹)) is higher than that observed at 50 mg.l⁻¹, 85.28 % (5.33 mg.g⁻¹) (Figure 14b).



Figure 13 (b): Adsorption kinetics curves of cadmium on natural clay.

3.4.3. Adsorption mechanism

To investigate the mechanism that controls the adsorption of Zn^{2+} and Cd^{2+} on natural clay three models were used. The pseudo-first and second order and intra-particle diffusion models were used to test the experimental data (Table 3) [37,38].

The linear form of these three models is expressed by the following equations [33, 34, 37-39-40]: $ln(q_e - q_t) = ln(q_e) - K_1 t$ (7)

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$
(8)
$$q_t = K_i t^{1/2} + C$$
(9)

 q_e and q_t (mg.g⁻¹) are the adsorbed quantities at equilibrium and at time (t). k_1 ((min⁻¹)) and k_2 (g/mg/min) the first order and the second order rate.

The lines drawn from these three linear equations are presented in the figures 14 a, 14b, 14c, the figures 15 a, 15 b, and 15c.



Figure 14: Kinetic models of zinc: (a) pseudo first -order, (b) pseudo- second and (c) and (c) intra-particle diffusion



Figure 15: Kinetic models of cadmium pseudo first-order, (b) pseudo- second order and (c) intra-particle diffusion

Table 3 present the constants of the used kinetic models, the values of q_e calculated and obtained experimentally for the adsorption of Zn^{2+} and Cd^{2+} on natural clay. The high values of the correlation coefficient of the pseudo-second order model (R²) for the two Zn^{2+} concentrations (12.5 and 25 (mg / l)), and Cd²⁺ for the concentrations 25 (mg.l⁻¹) and 50 (mg.l⁻¹) namely higher than those of the other models. This last model is the most adequate to represent the experimental data of adsorption of zinc and cadmium on natural clay. In addition, the qe values acquired by the equation (7) were not in agreement with the experimental values, contrarily to those given by equation (8) (Table 3). According to the model presented by equation (9), the Zn^{2+} and Cd^{2+} ions form chemical bonds with the adsorption sites located on the surface of the natural clay [**37**]. Figure 14c and 15c show that, the lines do not pass through zero, which shows that the adsorption process of Zn^{2+} and Cd^{2+} is limited by the diffusion of the film.

Zinc									
Concentration	Pseudo First		Pseudo second		Intra-particle				
Zn (II)		order order		diffusion					
	qe	K ₁	R ²	qe	K ₂	R ²	Ki	С	R ²
12.5 (mg/l)	1.205	0.101	0.94	1.37	1.39	0.99	0.171	2.005	0.94
25 (mg/l)	0.138	1.944	0.99	5.235	3.722	1	0.022	5.085	0.90
Concentration		Cadmium							
25 (mg/l)	0.0007	0.009	0.09	3.05	41.12	1	0.0032	3.04	0.23
50 (mg/l)	0.16	0.115	0.50	5.36	1.47	1	0.042	5.046	0.21

Table. 3. Kinetic model parameters.

3.5. Binary-metal adsorption of metals by natural clay

To study the effect of the presence of another cation, such as Pb^{2+} in our case, 0.2 g of natural clay was shaken in 50 mL of a solution containing a mixture of 12.5 (mg.l⁻¹) of Zn²⁺, and different concentration of Pb^{2+} . The solution was shaken at room temperature for 3 hours. The results obtained are presented in figure 17.

From the figure 16, the retention of Zn (II) by natural clay showed that the retention of the latter can be influenced by the presence of another cation like Pb^{2+} in the solution. In addition to that, it can be noted that the percentage of Pb^{2+} removal was higher than that of Zn^{2+} for the various tested Pb^{2+} concentrations (Figure 16), i.e. presence of Pb^{2+} can reduce the adsorption of Zn^{2+} . This is most likely due to the high electronegativity and the lower hydrated ionic radii of Pb^{2+} than Zn^{2+} , since the electronegativity are 2.33 and 1.69 and the hydrated ionic radii values are 0.401 and 0.426 forlead and zinc, respectively [41]. Except for the initial concentration of 10 mg/l, increasing the initial concentration of (Pb^{2+}) from 20 to 50 (mg/l) increased the reduction of Zn^{2+} adsorption (Figure 16).

Moreover, an increase in the percentage of Pb^{2+} elimination was observed with the increase of the initial concentration of Pb^{2+} , from 91.50 % at 10 (mg/l) to 97.50 % at 100 (mg/l). For Zn²⁺, the percentage of elimination was in the range 60-77% for Pb^{2+} in the range 10 to 80mg/L Pb^{2+} .

It can be noted that the capacity of elimination of Zn^{2+} and Pb^{2+} by this clay is very high, since the percentage of elimination of Zn^{2+} was between (60.43% up to 77.08%), and between (91% up to 98.16) for Pb^{2+} . The adsorption of lead is higher over zinc in binary system because of the higher selectivity for Pb^{2+} by clay, and its higher relative binding strength and lower ionization potential. In addition, These results can be explained by the presence of a very high number of active sites on the surface of this clay.



Figure 16: Comparison of adsorption capacity between Zn²⁺ and Pb²⁺

3.6. Effect of temperature

Figure 17 a and 17b, shows the influence of the temperature on the adsorption. In the case of zinc, the increase in temperature from 28°C to 50°C was accompanied by an increase in the percentage of zinc elimination from 89.58% to 99.9%, then remained constant above this temperature. For cadmium, which is characterized by a high initial concentration compared to zinc, the percentage of elimination of cadmium increases with the increase in temperature.

The increase in temperature from 28°C to 60°C is accompanied by an increase in the cadmium adsorption capacity from 82.32 % to 89.28%. Based on these results, the temperature factor can be used as a significant parameter to increase the removal capacity of Zn^{2+} and Cd^{2+} ions.



Figure 17: Influence of temperature for the adsorption of: (a) Zn^{2+} and (b) Cd^{2+} on natural clay

3.7. Thermodynamic Parameters

Due to the relationship between temperature and thermodynamic parameters, data of temperature effect on adsorption are used to calculate free energy change (ΔG), enthalpy change (ΔH) and entropy (ΔS), these parameters are determined according to the following equations [42]:

$$ln K_{d} = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

$$K_{d} = \frac{q_{e}}{C_{e}}$$

$$\Delta G_{ads} = -RT ln K_{d}$$
(10)
(11)
(12)

The slope and intercept of equation (10) are used to calculate ΔS and ΔH . All thermodynamic parameters are shown in table (4).

All the ΔG values obtained in this work were negative, confirming the spontaneity and the feasibility of the adsorption process [26, 43-45].

For zinc, the value of ΔH was positive (Table. 4), indicating that, the adsorption process of natural clay is endothermic. Positive values for ΔS indicate the random adsorption of zinc on the surface of the natural clay and thermal activated natural clay respectively (Table. 4) [46].

Conversely compared to zinc, the ΔH value of cadmium is negative (Table 4), indicating that, the adsorption process of natural clay is exothermic and the adsorption is physical with electrostatic interaction between adsorption sites and the cadmium [47]. The negative entropy change (table 4) indicated a decreased randomness at adsorbent-sorbate interface during the adsorption of Cd²⁺ ions onto the clay [48].

These results are in agreement with other studies on the adsorption of cadmium by some types of natural clays, such as the studies cited on the following references [48-51]. The decrease in ΔG values from positive to negative values as a function of temperature shows that the adsorption process becomes a spontaneous process for high temperatures.

Metal	Temp (K)	K _D (L/g)	ΔG (kj/mol)	ΔH (kj/mol)	ΔS (kj/mol)	
	301.15	2.15	-1.915	106.05		
Zinc	323.15	128.35	-13.04		0.36	
	337.15	155.22	-14.14			
	301.15	0.58	1355.18951			
Cadmium	322.15	0.85	430.36448	-0.00015	-49.97	
	333.15	1.04	-111.41502			

Table. 4. Thermodynamic parameters

3.8. Mass of adsorbent effect

The different masses of the used natural clay for the adsorption of zinc are 0.05 mg, 0.15 mg, 0.2 mg and 0.3 mg. the zinc concentration was fixed at 12.5 mg/l. Figure 18a, shows that the percentage of zinc removal increases proportionally with the mass of the natural clay. The increase in the mass of natural clay gives an increase in zinc adsorption sites. In addition, the maximum adsorption capacity of Zn^{2+} was observed for 0.2 g of adsorbent and beyond.

For cadmium, the effect of adsorbent mass for cadmium removal was studied at 0.1 mg, 0.2 mg, 0.3 mg and 0.4 mg of adsorbent. The cadmium concentration has been fixed at 50 mg/l.

Figure 18b, shows that the increase in clay mass from 0.1 g to 0.2 g is accompanied by an increase in cadmium removal from 85.2 % to 86.9 %. From 0.2 g, a slight increase in cadmium removal is observed from 86.9 % at 0.2 g up to 87.55% at 0.4 g. From these results, it can be seen that the optimum mass to remove Zn^{2+} and Cd^{2+} was 0.2 g.



Figure 18: Mass effect on Zn^{2+} (a), Cd^{2+} (b) removal by natural clay.

4. Conclusions

This work confirms the great efficiency of elimination of Zn^{2+} and Cd^{2+} by this clay, either in their raw state or by thermal activation. This clay is considered as one of the most abundant materials on earth and does not present any toxicity, which is in favor of its use as a tool to eliminate or reduce the percentage of heavy metals in water. Zeta potential showed that the adsorption sites are mainly from OH functional groups. SEM also showed the presence of a wide distribution of particles of different sizes, with porous surfaces.

The optimum operating conditions for Zn^{2+} and Cd^{2+} adsorption were 0.2 g of clay in 50 ml of solution, the solution pH and ambient temperature.

The equilibrium times of adsorption of Zn^{2+} and Cd^{2+} on natural clay are obtained after 25 min and 5 min respectively. The percentage of removal of Zn^{2+} reached almost 98 % and 83% for 12.5 (mg/l) and 25 (mg/l) initial Zn^{2+} amount, respectively. In the case of cadmium, the percentage of removal reaches 97.66 % and 85.28 % for the concentrations of 25 and 50 mg/l, respectively.

This natural clay also showed a high adsorption capacity of Zn^{2+} and Cd^{2+} from pH 4 and above, and this capacity was favorably impacted by an increase of the mass of clay.

Zinc and Cadmium ions are removed either by adsorption of zinc and cadmium ions on the active sites on the natural clay surface, or by precipitation at pH above 7.

On the other hand, this clay shows a high percentage of Zinc and Cadmium removal at room temperature.

In the presence of lead ion, the zinc and lead removal rate did not fall below 60 % and 90 % regardless of the lead concentration.

Through the isotherm and the used kinetic models, the results provided a good agreement with Langmuir and pseudo-second order kinetic models for the adsorption of Zn (II) and Cd (II) on natural clay. In addition, the adsorption process is controlled by intra-particle diffusion.

Based on ΔG , ΔH and ΔS , the zinc adsorption is spontaneous, exothermic and randomness. For cadmium, the thermodynamic parameters of ΔH and ΔS , shows that, the cadmium adsorption process is endothermic ($\Delta H>0$) and decreased randomness during the adsorption of Cd^{2+} ions onto the clay ($\Delta S<0$). According to the values of ΔG , the adsorption process becomes a spontaneous process for high temperatures.

5. Compliance with Ethical Standards

Conflict of Interest: The author declare that they have no conflict of interest.

Funding: This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

6. References

- H. Deng, Y. Tu, H. Wang, Z. Wang, Y. Li, L. Chai, & Z. Lin. Environmental behavior, human health effect, and pollution control of heavy metal (loid) s toward full life cycle processes. Eco-Environment & Health, 1(4) (2022) 229-243.
- [2] W. M. Ibrahim, A. F. Hassan, Y. A Azab. Biosorption of toxic heavy metals from aqueous solution by Ulva lactuca activated carbon. Egyptian journal of basic and applied sciences, 3(3)(2016) 241-249.
- [3] N. Semwal, D. Mahar, M. Chatti, A. Dandapat, & M. C. Arya. Adsorptive removal of Congo Red dye from its aqueous solution by Ag-Cu-CeO₂ nanocomposites: adsorption kinetics, isotherms, and thermodynamics. Heliyon, 9(11) (2023).
- [4] M. I. Al-Wabel, A. R. Usman, A. H. El-Naggar, A. A. Aly, H. M. Ibrahim, S. Elmaghraby, & A. Al-Omran. Conocarpus biochar as a soil amendment for reducing heavy metal availability and uptake by maize plants. Saudi journal of biological sciences, 22(4) (2015) 503-511.
- [5] P. Gupta, B. Diwan. Bacterial exopolysaccharide mediated heavy metal removal: a review on biosynthesis, mechanism and remediation strategies. Biotechnology Reports, 13(2017) 58-71.
- [6] A. H. Abd El Hameed, W. E. Eweda, K. A. Abou-Taleb, H. I. Mira. Biosorption of uranium and heavy metals using some local fungi isolated from phosphatic fertilizers. Annals of Agricultural Sciences, 60(2) (2015) 345-351.
- [7] Y. Zhang, X. Duan. Chemical precipitation of heavy metals from wastewater by using the synthetical magnesium hydroxy carbonate. Water Science and Technology, 81(6) (2020) 1130-1136.
- [8] K. C. Khulbe, & T. Matsuura. Removal of heavy metals and pollutants by membrane adsorption techniques. Applied water science, (8)1 (2018) 1-30.
- [9] A. Bashir, L. A. Malik, S. Ahad, T. Manzoor, M. A. Bhat. G. N. Dar, & A. H. Pandith. Removal of heavy metal ions from aqueous system by ion-exchange and biosorption methods. Environmental Chemistry Letters, 17 (2) (2019) 729-754.

- [10] A. Bahloul, H. Zouaoui, A. Diafat, A. Meribai, Y. Noufel, M. Derrardja, & B. Nessark. Study on Removal of Heavy Metal Ions (Pb 2+, Cd 2+ and Cu 2+) by Coriandrum sativum (Coriander). Journal of Water Chemistry and Technology. 42 (2020) 157-163.
- [11] G. Genchi, M. S. Sinicropi, G. Lauria, A. Carocci, & A. Catalano. The effects of cadmium toxicity. International journal of environmental research and public health. 7 (11) (2020) 3782.
- [12] M. M. Brzóska, & J. Moniuszko-Jakoniuk. Interactions between cadmium and zinc in the organism. Food and Chemical Toxicology, 39(10) (2001) 967-980.
- [13] S.J. Stohs, D. Bagchi. Oxidative mechanisms in the toxicity of metal ions. Free Radical Biology and Medicine 18 (1995) 321–336.
- [14] K. G. Akpomie, & F. A. Dawodu. Potential of a low-cost bentonite for heavy metal abstraction from binary component system. Beni-suef university journal of basic and applied sciences, 4(1) (2015) 1-13.
- [15] B. J. Saikia, & G. Parthasarathy. Fourier transform infrared spectroscopic characterization of kaolinite from Assam and Meghalaya, Northeastern India. J. Mod. Phys, 1(4) (2010) 206-210.
- [16] Veerasingam, S., & Venkatachalapathy, R. (2014). Estimation of carbonate concentration and characterization of marine sediments by Fourier Transform Infrared Spectroscopy. Infrared Physics & Technology, 66, 136-140.
- [17] W. Chai, Y. Huang, S. Su, G. Han, J. Liu, & Y. Cao. Adsorption behavior of Zn (II) onto natural minerals in wastewater. A comparative study of bentonite and kaolinite. Physicochemical Problems of Mineral Processing, 53 (1) (2017) 264-278.
- [18] A. Serrano-Lotina, R. Portela, P. Baeza, V. Alcolea-Rodríguez, M. Villarroel, & P. J. C. T. Ávila. Zeta potential as a tool for functional materials development. Catalysis Today. (2023) 423, 113862.
- [19] R. Gonte, & K. Balasubramanian. Heavy and toxic metal uptake by mesoporous hypercrosslinked SMA beads: Isotherms and kinetics. Journal of Saudi Chemical Society, 20 (2016) 579-590.
- [20] A. T. Sdiri, T. Higashi, & F. Jamoussi. Adsorption of copper and zinc onto natural clay in single and binary systems. International Journal of Environmental Science and Technology, 11 (4) (2014) 1081-1092.
- [21] A. Khosravan, & B. Lashkari. Adsorption of Cd (II) by dried activated sludge. Iranian Journal of Chemical Engineering, 8(2) (2011) 41-56.
- [22] I. Ghorbel-Abid, & M. Trabelsi-Ayadi. Competitive adsorption of heavy metals on local landfill clay. Arabian Journal of Chemistry, 8(1) (2015) 25-31.
- [23] M. M. Majd, V. Kordzadeh-Kermani, V. Ghalandari, A. Askari, & M. Sillanpää. Adsorption isotherm models: A comprehensive and systematic review (2010–2020). Science of The Total Environment, 812 (2022) 151334.
- [24] T. Deschamps, M. Benzaazoua, B. Bussière, T. Belem, & M. Mbonimpa. Mécanismes de rétention des métaux lourds en phase solide: cas de la stabilisation des sols contaminés et des déchets industriels. VertigO-la revue électronique en sciences de l'environnement, 7 (2) (2006).
- [25] C. Blanchard. Caractérisation de la mobilisation potentielle des polluants inorganiques dans les sols pollués., Thesis, Doctoral dissertation, Lyon, INSA, (2000).
- [26] K. S. Shabani, F. D. Ardejani, K. Badii, & M. E. Olya. Preparation and characterization of novel nano-mineral for the removal of several heavy metals from aqueous solution: Batch and continuous systems. Arabian Journal of Chemistry, 10 (2017) 3108-3127.
- [27] A. Sdiri, & T. Higashi. Simultaneous removal of heavy metals from aqueous solution by natural limestones. Applied Water Science, 3(1) (2013) 29-39.
- [28] Y. S. Al-Degs, M. I. El-Barghouthi, A. A. Issa, M. A. Khraisheh, & G. M. Walker. Sorption of Zn (II), Pb (II), and Co (II) using natural sorbents: equilibrium and kinetic studies. Water research, 40 (14) (2006) 2645-2658.
- B. Meroufel, O. Benali, M. Benyahia, M., Zenasni, A., Merlin, & B. George. Removal of Zn (II) from aqueous solution onto kaolin by batch design. Journal of Water Resource and Protection,5 (7) (2013)
 669-680.
- [30] V. C. Srivastava, I. D. Mall, & I. M. Mishra. Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA. Journal of hazardous materials, 134(1-3) (2006) 257-267.
- [31] A. Sari, M. Tuzen, D. Citak, & M. Soylak. Equilibrium, kinetic and thermodynamic studies of adsorption of Pb (II) from aqueous solution onto Turkish kaolinite clay. Journal of hazardous materials, 149 (2) (2007) 283-291.
- [32] A. Demirbas, A. Sari, & O. Isildak. Adsorption thermodynamics of stearic acid onto bentonite. Journal of hazardous materials, 135(1-3) (2006) 226-231.
- [33] S. Golkhah, H. Zavvar Mousavi, H., Shirkhanloo, & A. Khaligh. Removal of Pb (II) and Cu (II) Ions from Aqueous Solutions by Cadmium Sulfide Nanoparticles. International Journal of Nanoscience and Nanotechnology, 13(2) (2017) 105-117.
- [34] H. E Karce, S. Boumessaidia, A. Bahloul, B. Lal, A. Saravanan, A. Ouakouak, A., ... & C. Prakash. Efficient removal of methylene blue by a biochar from neem tree shell wastes using adsorption technology. Biomass Conversion and Biorefinery, (2024) 1-16.
- [35] P. C. Mishra, & R. K. Patel. Removal of lead and zinc ions from water by low cost adsorbents. Journal of hazardous materials, 168(1) (2009) 319-325.
- [36] P. Kampalanonwat, & P. Supaphol. The study of competitive adsorption of heavy metal ions from aqueous solution by aminated polyacrylonitrile nanofiber mats. Energy Procedia, 56 (2014) 142-151.
- [37] A. M. Azzam, S. T. El-Wakeel, B. B. Mostafa, & M. F. El-Shahat. Removal of Pb, Cd, Cu and Ni from aqueous solution using nano scale zero valent iron particles. Journal of Environmental Chemical Engineering, 4 (2) (2016) 2196-2206.
- [38] W. J. Weber Jr, & J. C. Morris. Kinetics of adsorption on carbon from solution. Journal of the sanitary engineering division, 89(2) (1963) 31-59.

- [39] A. F. Ali, A. S. A. Ahmed, A. A. Gahlan, & A. A. Y. El-Sayed, A. A. Y. (2024). Biochar derived from peanut husks as an adsorbent to ammonium ions remediation from aqueous solutions. Egyptian Journal of Chemistry, 67(12), (2024) 231-244.
- [40] A. A. El-Sayed, S. A. Abdel Ghani, A. H. Shobier, & M. A. Aly-Eldeen. Factorial Experimental Design for the Elimination of Cationic Dye Stuff from Aqueous Solution via a Novel sediment–alga–silver Nanocomposite. Egyptian Journal of Chemistry, 68(5), (2025) 283-299.
- [41] S. Huang, S. Jin, Y. Wang, J. Liu, J., Yu, D. Liu, & R. Chi. Selective adsorption of heavy metal ions from aqueous solution by modified bagasse. Chemistry and Ecology, 36 (9) (2020) 839-854.
- [42] B. Nagy, C. Mânzatu, A. Măicăneanu, C. Indolean, L. Barbu-Tudoran, & C. Majdik. Linear and nonlinear regression analysis for heavy metals removal using Agaricus bisporus macrofungus. Arabian Journal of Chemistry, 10 (2017) 3569-3579.
- [43] C. P. Jordão, R. B. A. Fernandes, K., de Lima Ribeiro, B. de Souza Nascimento, & P. M. de Barros. Zn (II) adsorption from synthetic solution and kaolin wastewater onto vermicompost. Journal of hazardous materials, 162(2-3) (2009) 804-811.
- [44] B. Houari, S. Louhibi, K. Tizaoui, L. Boukli-hacene, B. Benguella, T. Roisnel, & V. Dorcet. New synthetic material removing heavy metals from aqueous solutions and wastewater. Arabian journal of chemistry, 12 (8) (2019) 5040-5048.
- [45] R. M. Ali, H. A. Hamad, M. M., Hussein, & G. F. Malash. Potential of using green adsorbent of heavy metal removal from aqueous solutions: adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis. Ecological Engineering, 91 (2016) 317-332.
- [46] S. Mustapha, M. M. Ndamitso, A. S. Abdulkareem, J. O. Tijani, A. K. Mohammed, & D. T. Shuaib. Potential of using kaolin as a natural adsorbent for the removal of pollutants from tannery wastewater. Heliyon, 5(11) (2019) 02923.
- [47] N. T. Abdel-Ghani, & G. A. Elchaghaby. Influence of operating conditions on the removal of Cu, Zn, Cd and Pb ions from wastewater by adsorption. International journal of environmental science & technology, 4(4) (2007) 451-456.
- [48] A. Sari, & M. Tuzen. Cd (II) adsorption from aqueous solution by raw and modified kaolinite. Applied Clay Science, 88 (2014) 63-72.
- [49] E. I. Unuabonah, B. I. Olu-Owolabi, K. O. Adebowale, & L. Z. Yang. Removal of lead and cadmium ions from aqueous solution by polyvinyl alcohol-modified kaolinite clay: a novel nano-clay adsorbent. Adsorption Science & Technology, 26(6) (2008) 383-405.
- [50] R. Bassam, A. El Hallaoui, M. El Alouani, M. Jabrane, E. H. El Khattabi, M. Tridane, & S. Belaaouad. (2021). Studies on the removal of cadmium toxic metal ions by natural clays from aqueous solution by adsorption process. Journal of Chemistry, 1 (2021) 7873488.
- [51] N. N. Mladenović, M. M. Ivanović, L. M., Kljajević, J. Gulicovski, S. S. Nenadović, & K. Trivunac. K. Adsorption study of cadmium ions on kaolinite modified by histidine and cysteine. Tehnika, 74 (1) (2019) 15-22.