

## Effects of Algerian Clays Properties on the Adsorption of Cd (II)

Fatima Zohra CHOUMANE \* <sup>1,2</sup>, Belkacem BENGUELLA <sup>1</sup>

1. Laboratory of Inorganic Chemistry and Environment, Department of Chemistry, Faculty of Sciences, University of Tlemcen, B.P 119 Tlemcen, Algeria
2. Department of chemistry, Faculty of Science and the technology, University of Saïda, Algeria

Corresponding Author Email: [chimief@yahoo.fr](mailto:chimief@yahoo.fr)

### Abstract:

In this work, Cd (II) adsorption from aqueous solutions was studied on three Algerian clays :bentonite, kaolin and clay of djebal Debbagh; using batch process, these materials were characterized by different methods infrared spectroscopy, x -ray fluorescence, measure of Cation Exchange Capacity (CEC) and specific area, the Adsorption tests were carried out at room temperature. The uptake of cadmium ions from aqueous solutions to the clays has been studied depending on contact time, temperature, agitation speed and pH, which was regarded as a principal factor in the analysis of the adsorption process. the contact time for the maximum adsorption required is 240m. The kinetics was correlated well with the pseudo second-order model. The results show that the uptake of Cd(II) increases with the pH increasing in the pH range of 2.0–12.0. The increase of the temperature influences negatively the process of the adsorption, what shows the phenomenon of the physisorption of cadmium ion on the materials tested. The studies of the retention of cadmium ion showed that it is mainly influenced by the physico-chemical properties of used clays. Results show that sorption of cadmium ion was higher by bentonite clay than for others clays. In consequence, the tests allowed us to choose the bentonite as the material, which presents a capacity raised for the adsorption.

**Keywords:** clays, bentonite, heavy metals, cadmium, Adsorption

### 1. Introduction

Environmental pollution with heavy metal gained lately much concern because of their general and specific toxicities. The most toxic heavy metals, namely lead, mercury, nickel, zinc, copper and cadmium can be distinguished from other pollutants, because they cannot be degraded naturally but accumulates in living organisms. Therefore they cause different diseases and disorders even in lower concentrations [1–4]. The major important sources of heavy metal pollution in water are wastewaters and agricultural sources. The presence of heavy metals in the wastewater from various industries is accumulating in the ecosystem which causes serious risk to the environment and endangers public health.

Cadmium may be found in wastewater discharges from the electroplating industry, the manufacture of nickel–cadmium batteries, fertilizers, pesticides, pigments, dyes and textile operations [5,6]. In humans, nausea and vomiting has been recorded at levels of 15 mg Cd<sup>2+</sup>/L with no adverse effects at 0.05 mg Cd<sup>2+</sup>/L. Severe toxic, but non fatal, symptoms are reported at concentrations of 10–326 mg Cd<sup>2+</sup>/L of cadmium. The kidneys are the critical target organs after ingestion (renal dysfunction, hypertension and anemia) [7,8].

Therefore, various methodologies have been used for the removal of heavy metals from industrial wastewater such as electro chemical, ion exchange, membrane filtration, reverse osmosis and chemical coagulation, etc., however each method has its own shortcomings and limitations [9-11]. Adsorption is one of the efficient methods due to its simplicity, sludge free operation; easiness in handling, availability of various adsorbents, adsorbent can be regenerate and more efficient in removal of heavy metals at lower concentration levels [12].

The clay minerals, being important constituents of soil, have been playing this role, by acting as a natural scavenger of pollutants from water through both ion exchange and adsorption Mechanisms. The high specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), Bronsted and Lewis acidity, etc., have made the clays excellent materials for adsorption [13]. Adsorption of metal ions on clay minerals may occur via two mechanisms: outer-sphere adsorption, which occurs primarily on the basal planes existing in the interlayer of the clay minerals, and inner-sphere adsorption, which occurs at the amphoteric ligand sites existing on the edges of clay minerals [14].

The objective of this study is to study adsorption of cadmium onto three types of Algerian clays and to investigate the influence of various experimental conditions. The adsorption kinetics was determined quantitatively by pseudo-first order and pseudo-second order models and the adsorption mechanism of Cd (II) on clays was discussed.

## **2. Materials and Methods**

### **2.1. Chemicals**

A stock solution of Cd(II) was prepared by dissolving required amount of Cd(NO<sub>3</sub>)<sub>2</sub>.4 H<sub>2</sub>O in double distilled water.

### **2.2. Clays**

These clays were chosen according to their different chemical and mineralogical characteristics to represent substantially the different behaviour regarding the heavy metal sorption. Three Algerian clays minerals, bentonite, kaolin and Djebel Debbagh clay. The bentonite used during our work is extracted from the deposit of Hammam-Boughrara to Maghnia (Tlemcen). It was supplied to us by the company (ENOF), Tlemcen. The used kaolin results from the deposit of Tamazert (Mila), and the clay of Djebel Debbagh extracted from the deposit of Ain Barbar (Guelma), these clays were supplied to us by the company of ceramic of Ghazaouet (Tlemcen). The three natural's clays were finely crushed. Physico-chemical properties of each material are given in Table 1.

All materials were used as received without other treatment apart from drying at 100 °C for 1 h to remove excess moisture, and then kept in a desiccator until analysed water.

### **2.3. Batch adsorption studies**

In each experiment, a 300 mL metal ion (100 mg /l) was continuously stirred at 500 rpm with 1 g of clay at ambient temperature. The contact time was ranged from 5minTo 360mn.The concentrations of the cadmium ions in the solution were determined at given time intervals. After agitation, the suspensions were centrifuged at 2500rpm for 10min and the cadmium ions concentration in the supernatants was measured by atomic absorption spectrophotometer. Quantity  $q_t$  (mg/g) of the cadmium ion fixed per gram of the adsorbent was determined as follows:

$$q_t = [(C_0 - C_t) \times V] / m$$

Where,

$C_0$  (mg/l) = the initial concentration of metal ions

$C_t$  (mg/l) = concentrations of metal ions at t time

$V$  (l) = the volume of cadmium ion solution

$m$  (g) = the mass of adsorbent used.

## **3. Results and Discussion**

### **3.1. Adsorbents characterization**

#### **3.1.1. Chemical composition**

Table 1 presents chemical composition of natural clays used as adsorbent in this study. We found that these clays contain a large ratio of  $\text{SiO}_2$ . The report  $\text{SiO}_2 / \text{Al}_2\text{O}_3$  for the bentonite is in agreement with the one of the montmorillonite understood between 2 and 5.5. [15,16]. We notice that the chemical composition of our kaolinite comes closer a lot that the one of the Indian kaolinite. [17]

**Table (1): Chemical analysis, specific area and cation exchange capacities CEC of the natural clays**

% mass	Bentonite	Kaolin	Djebel Debbagh clay
SiO <sub>2</sub>	65.97	50.82	46.29
Al <sub>2</sub> O <sub>3</sub>	16.20	37.50	43.73
Na <sub>2</sub> O	2.86	0.17	0.23
CaO	4.53	3.01	3.33
K <sub>2</sub> O	2.15	2.60	1.80
MgO	2.89	0.71	0.60
Fe <sub>2</sub> O <sub>3</sub>	3.39	3.16	2.02
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	4.07	1.35	1.05
Specific area (m <sup>2</sup> /g)	23.76	22.71	49.69
CEC (meq/100g)	80	5.2	13.8

### 3.1.2. Specific area

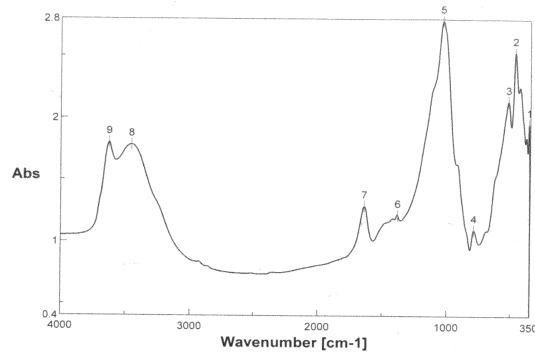
The measured specific area of the three adsorbents are given in Table 1. The specific area of Djebel Debbagh Clay was increased to 49.69 m<sup>2</sup>/g. The bentonite had a specific area of 23.76 m<sup>2</sup>/g and 22.71m<sup>2</sup>/g for the Kaolin.

### 3.1.3. Cation exchange capacity (CEC)

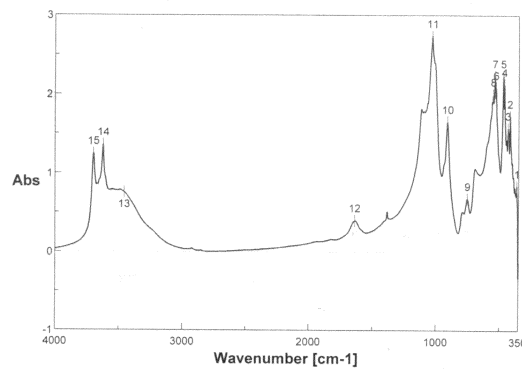
Bentonite has a very large CEC (Table 1) compared to that of kaolin and Djebel Debbagh Clay, the values obtained being 5.2 meq/100g (kaolin), 13.8 meq/100g and 80 meq/100 g (bentonite). The CEC of the djebel Debbagh clay is situated inside the interval for clay of type illite or chlorite the values found in the literature concerning CEC of bentonite and kaolin confirm our obtained results. [15]

### 3.1.4. Infrared spectra analysis

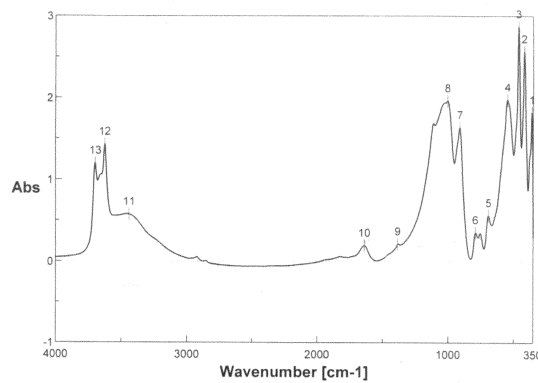
The infrared spectrums of the clays are given in figures 1, 2 and 3. While the band assignments of Bentonite, Djebel Debbagh Clay and Kaolin are shown in Table 2.



**Figure 1.** Infrared spectra of bentonite



**Figure 2.** Infrared spectra of Djebel Debbagh Clay



**Figure 3.** Infrared spectra of Kaolin

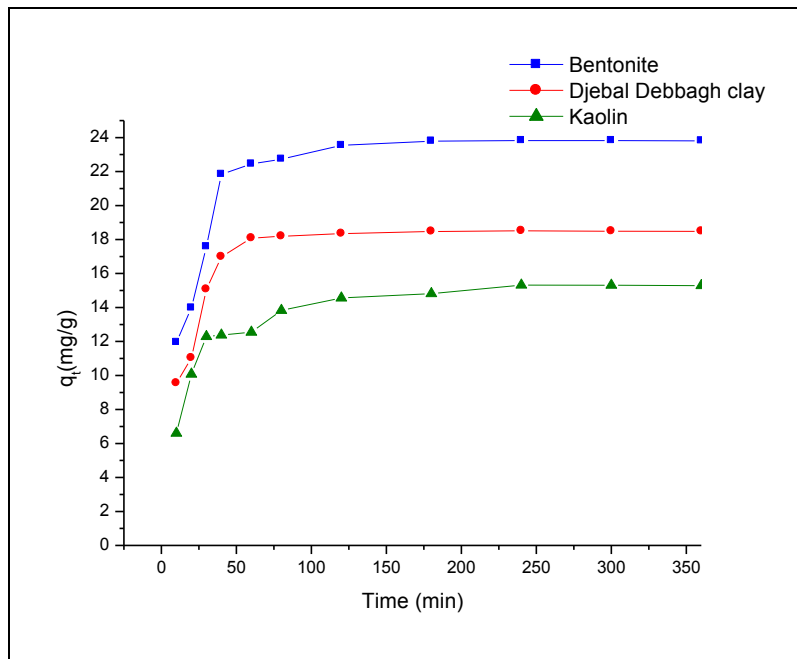
FTIR spectrum was recorded in the region of 400–4000  $\text{cm}^{-1}$ . There is a group of absorption peaks between 3440 and 3695  $\text{cm}^{-1}$ , which is due to stretching bands of the OH groups. The band at 1639  $\text{cm}^{-1}$  is assigned to the OH deformation of water on natural clays (see Fig. 1, 2 and 3). The 1029, 1033  $\text{cm}^{-1}$  component of the Si–O stretching band, assigned to the Si–O vibrations within the layer. The band at 521 and 461  $\text{cm}^{-1}$  was from the Si–O–Al (where Al is an octahedral cation).

**Table ( 2 ) : Infrared data of of Bentonite, Djebel Debbagh Clay and Kaolin**

Clays Bands assignments	IR Frequencies ( $\text{cm}^{-1}$ )		
	Bentonite	Kaolin	Clay of djabal debbagh
$\nu_{\text{OH}}$ stretching vibration ( $\text{H}_2\text{O}$ )	3623, 3452	3695,3622, 3439	3694, 3619, 3455
$\nu_{\text{OH}}$ deformation ( $\text{H}_2\text{O}$ )	1639, 1378	1639,1385	1637
$\nu_{\text{SiO}}$ stretching vibration	1033,	1006	1029
quartz	790	913, 792,694	911,754
$\delta_{\text{Si-O-M}}^{\text{VI}}$ ( M= Al, Mg, Fe)	521, 468, 360	548,461, 418, 360	551,538,529, 472, 462, 433, 417, 365

### 3.2. Kinetics study

Fig.4 shows the adsorption kinetic curve of Cd(II) on clays sample, the adsorption amount initially increases rapidly and then it slows down as equilibrium is approached. The adsorption of the cadmium ions shows that the equilibrium was attained only after 240 min with a rate of 79.4 % adsorption.



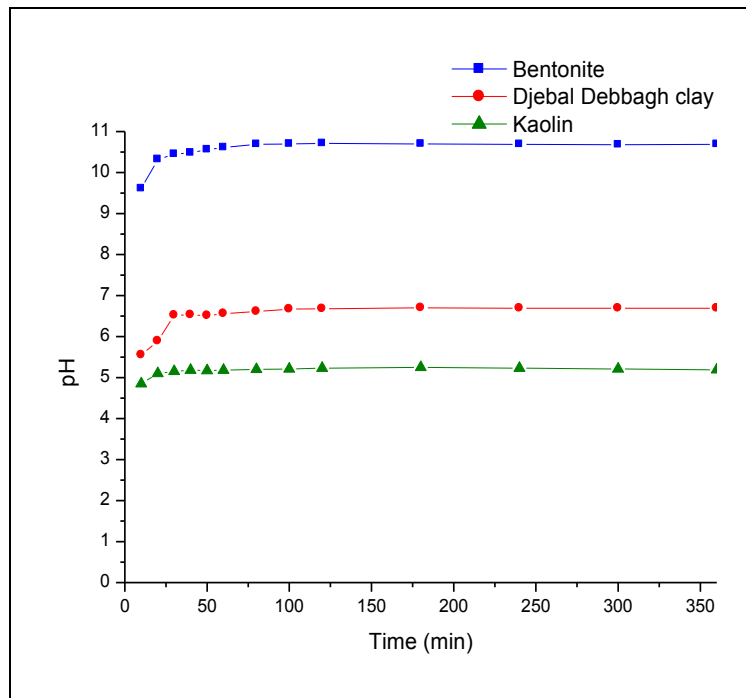
**Figure 4.** Adsorption kinetic of cadmium ions on clays.

The values of  $q_t$  by using the bentonite as adsorbing are increased with regard to the other clays. At the equilibrium, the bentonite fixes more cadmium ions than the kaolin and clay of djebal Debbagh. The results obtained are summarizing in Table 3.

**Table (3): Results obtained with equilibrium**

Clays	Cadmium ions mass equilibrium(mg/g)
Bentonite	23.82
Djebal Debbagh Clay	18.51
Kaolin	15.32

At the same time as the kinetic study of adsorption of cadmium ions on these clays, we followed the evolution of the initial pH of the solutions, which is represented on Fig 5. Therefore, the results of the final pH for the cadmium ions with three clays are grouped in the Table 4.



**Figure 5.** Evolution of pH of cadmium ions in the presence of clays

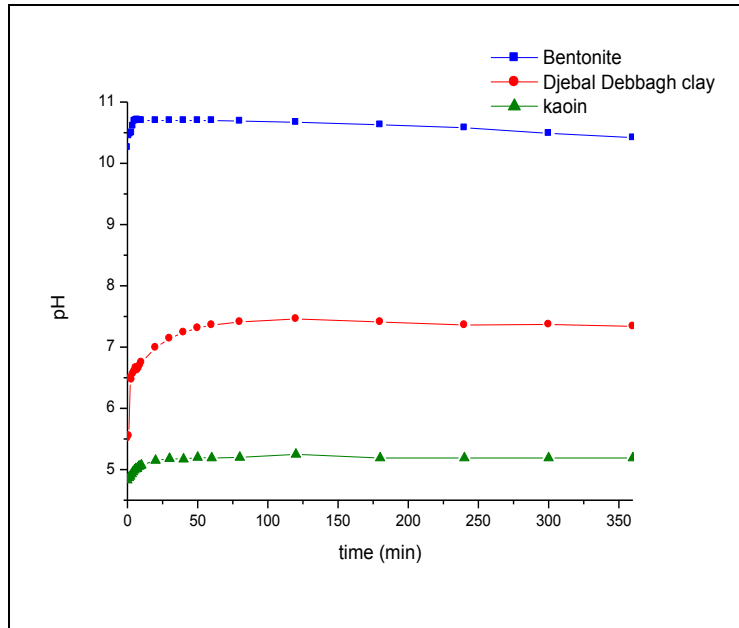
**Table ( 4).** Values of the final pH of cadmium ions in the presence of studied clays

Clays / pH	Cadmium ions	Distilled water
Bentonite	10.70	10.42
Clay of Djebel Debbagh	6.69	7.34
Kaolin	5.23	5.19

For better understanding of this phenomenon, we studied the evolution of the pH of a distilled exempt water of cadmium ions in touch with the bentonite, clay of Djebel Debbagh and the kaolin in the same operating conditions as previously. The Fig 6 shows a fast and important



increase of the initial pH of the water distilled in the case of the bentonite. For the clay of Djebel Debbagh and the kaolin, this increase is low, what justifies that the bentonite adsorbs more the acid species than the clay of Djebel Debbagh and the kaolin.



**Figure 6.** Evolution of the pH of distilled water exempt from cadmium ions in presence clays.

In order to optimize the design of an adsorption system to remove the cadmium ions, it is important to establish the most appropriate correlation for the kinetic data for each system. Several kinetic models can be used to express the adsorption rate constant of solutions on solids. The adsorption kinetics was tested with the following well-known models:

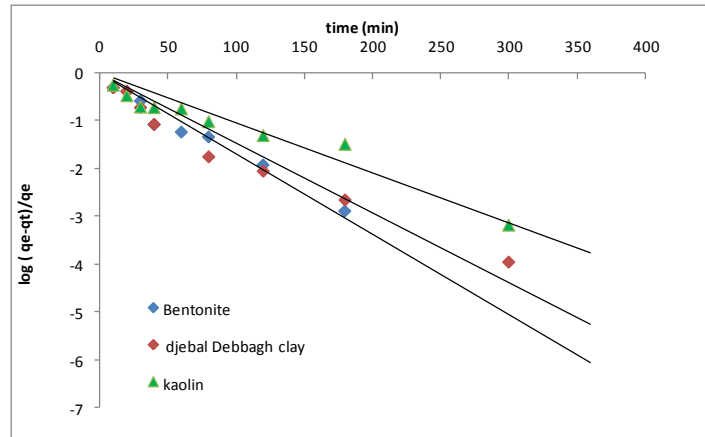
Pseudo-first order kinetics by using the Lagergren equation [18, 19]

$$\log \frac{(q_e - q_t)}{q_e} = -\frac{K_v t}{2,3}$$

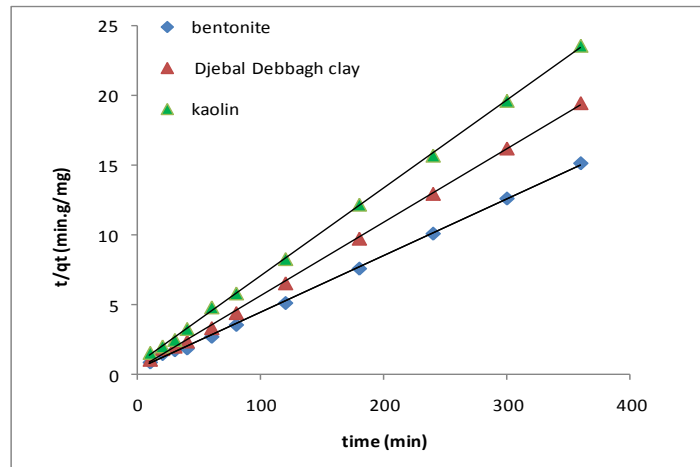
For the pseudo-second order kinetics [20, 21], if the pseudo-first order kinetics does not properly account for the kinetics of the adsorption process, pseudo-second order kinetics may be applied by the linear equation,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where  $k'$  is the pseudo-second order adsorption rate constant. The kinetic models are shown in Figs. 7, 8.



**Figure 7.** Linearization of cadmium ions adsorption kinetics by clays for the first-order rate.



**Figure 8.** Linearization of cadmium ions adsorption kinetics by clays for the pseudo second order rate.

The kinetics of clay-Cd (II) interactions was tested with different models. The pseudo second order kinetic plots of  $t/q_e$  versus  $t$  are of better linearity. The uptake of Cd (II) was the most rapid in case of bentonite and the slowest for kaolin and djebal debbagh clay. A comparison of  $q_e$  values (experimental and those obtained from the slopes of the pseudo second order plots) shows a much better agreement (Table 6), kinetic data fit this model with a correlation coefficient higher than 0.99.

**Table (5). First-order rate constants**

Parameters of first-order	$k_v(\text{min}^{-1})$	$R^2$
Bentonite	0.036	0.949
Djebal Debbagh Clay	0.032	0.910
Kaolin	0.023	0.913

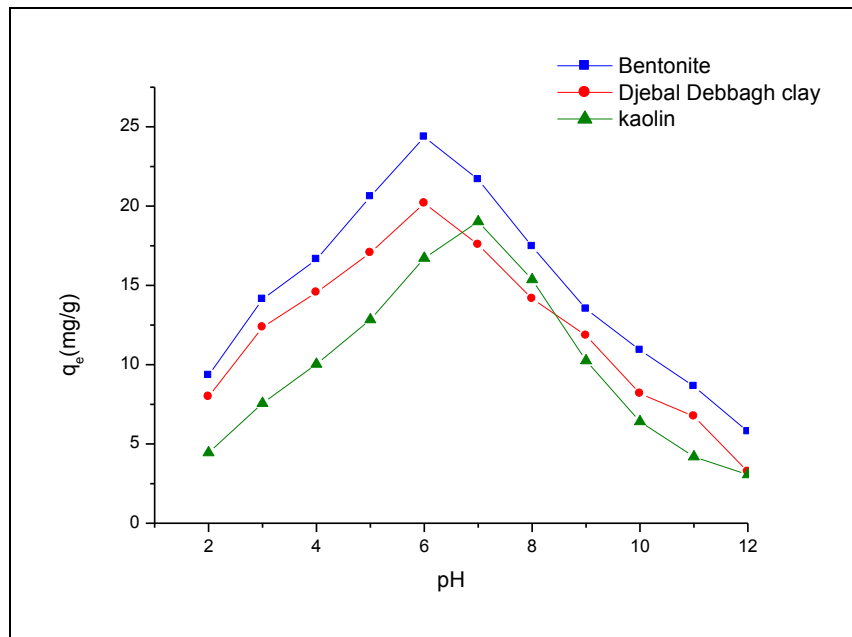
**Table (6). Pseudo second-order rate constants**

Parameters of pseudo second-order	$q_e$ (mg/g)	$k_v$ ( $\text{min}^{-1} \cdot \text{g}/\text{mg}$ )	$R^2$
Bentonite	25.00	0.0023	0.999
Djebal Debbagh Clay	19.23	0.0037	0.999
Kaolin	16.13	0.0025	0.999

## 4. Effects of operating factors

### 4.1. Effect of pH

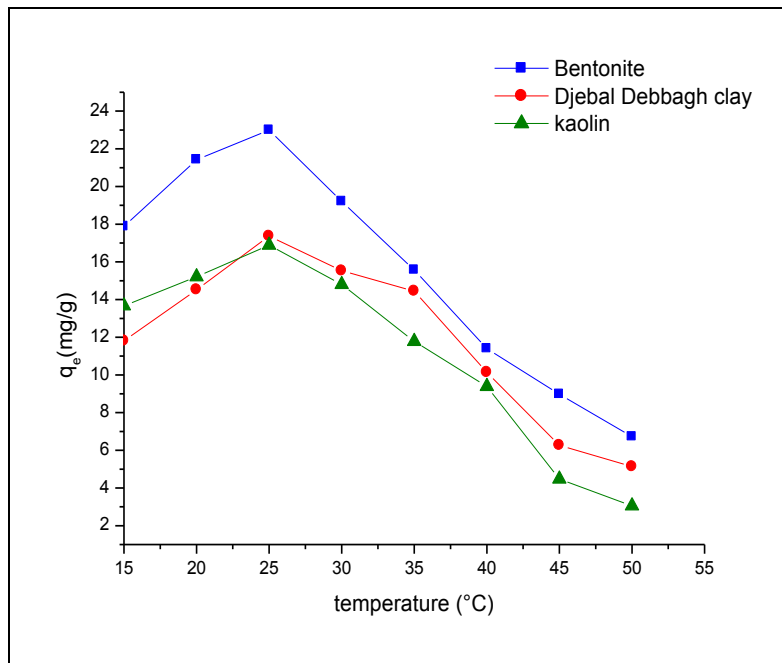
To determine the effect of pH on adsorption of cadmium ions by clays, different pH levels (2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12) were prepared by adjusting the pH to desired initial pH value using 0,1N HCl or 0,1N NaOH before mixing the adsorbent. Fig 9 show that adsorption of metal ions was increased with an increase in pH up to a certain value and there after decreased. The maximum adsorption for Cd (II) took place surrounding pH 6-7, then decreases from this pH. An increase in pH increases the negatively charged nature of the sorbent surface. The decrease in the removal of metal ions at a lower pH is due to the higher concentration of H<sup>+</sup> ions present in the reaction mixture which compete with the Metal ions for the sorption sites on the sorbent surface. Mean- While the observed decrease in sorption at higher pH is due to the formation of insoluble hydroxyl complexes of the metal ions. [22, 23]



**Figure 9.** Influence of the pH on adsorption kinetics of cadmium ions on clays

#### 4.2. Effect of temperature

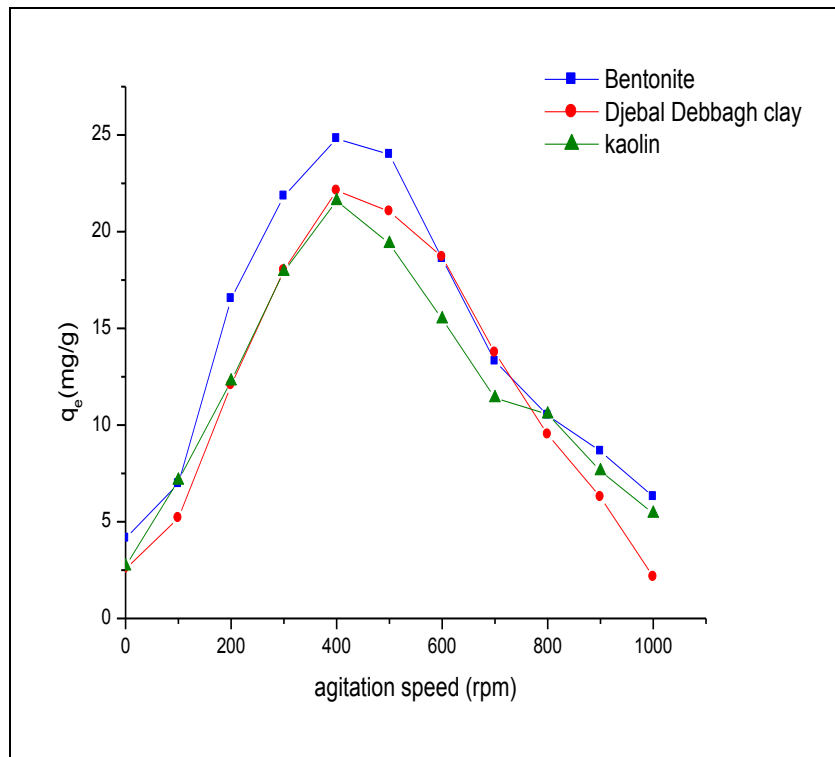
Temperature has vital effect on adsorption process as it can influence the process by an increase or decrease in the amount of adsorption. The effect of temperature on the adsorption of metal ions by using different clays was studied in the range of 15–55 °C. The results (Fig 10) show that the quantity of the cadmium ions adsorbed decreases with the increase of the temperature, what suggests that we are in the presence of a phenomenon of exothermic adsorption.



**Figure 10.** Influence of the temperature on adsorption kinetics of cadmium ions on clays

### 4.3. Effect of agitation speed

To study the influence of the agitation speed on clays, we chose the range of agitation speeds of 0-1000 rpm. The capacity of adsorption of cadmium ions is obtained with agitation speed of 400 rpm (Fig 11), which assures a good distribution of adsorbates towards clays.



**Figure 11.** Influence of the agitation speed on adsorption kinetics of cadmium ions on clays

In the case of the high agitation speeds, we notice a decrease of the adsorption capacity of adsorbats. While, for the absence of agitation speed, we notice a very significant decrease of the capacity of adsorption of adsorbats.

In conclusion, clay minerals (bentonite, kaolin, and djebel debbagh clay) are cable to remove Cd (II) from an aqueous solution. This study investigates the factors affecting the adsorption of cadmium ions on clays, the adsorption capacities also depend on the type of clay used. Increasing pH of metal ion solutions increased the amount of the metal ions adsorbed. The adsorption mechanism of Cd (II) on clays may be explained in two aspects: the chemical binding between Cd (II) ions and surface hydroxyl groups; and the electrostatic binding between Cd (II) ions and the permanent negatively charged sites of clays. The adsorption kinetics is in better agreement with pseudo-second order kinetics. The kinetics of adsorption of Cd(II) on clays allowed us to choose the bentonite as the best adsorbing.

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## 5. References

- [1] A.F. Shaaban, D.A. Fadel, A.A. Mahmoud, M.A. Elkomy, S.M. Elbahy (2013). Synthesis and characterization of dithiocarbamate chelating resin and its adsorption performance toward Hg(II), Cd(II) and Pb(II) by batch and fixed-bed column methods, article in press, *J. Environ. Chem. Eng.*, <http://dx.doi.org/10.1016/j.jece.2013.04.014> G Model JECE-25; No. of Pages 10
- [2] S. Babel, T.A. Kurniawan (2003). Low-cost adsorbents for heavy metal uptake from contaminated water: a review, *J. Hazard. Mater.* 97, 219–243.
- [3] M.M. Saeed, M. Ahmed (2004). Retention, kinetics and thermodynamics profile of cadmium adsorption from Iodide medium onto polyurethane foam and its separation from zinc bulk, *Anal. Chem. Acta* 525, 289–297.
- [4] L.R.B. Sanchez, B.S.V. de la Riva, J.M.C. Fernandez, R. Pereiro, A.S. Medel (2001). Determination of lead and mercury in sea water by preconcentration in a flow injection system followed by atomic adsorption spectrometry detection, *Talanta* 55, 1071–1078.
- [5] R. Salim, M.M. Al-Subu, E. Sahrhage (1992). Uptake of Cadmium from water by beech leaves, *J. Environ. Sci. Health* 27, 603–627.
- [6] C.W. Cheung, J.F. Porter, G. McKay (2000). Elovich equation and modified second-order equation for adsorption of cadmium ions onto bone char, *J. Chem. Technol. Biotechnol.* 75, 963–970.
- [7] J.D. Zuane (1990), *Handbook of Drinking water quality standards and controls*, Van Nostrand Reinhold, New York, pp. 64–69.
- [8] C.W. Cheung, J.F. Porter, G. McKay (2001). Adsorption kinetic analysis for the removal of cadmium ions from effluents using bone char, *Water Res.* 35, 605–612.
- [9] Sivaraju Sugashini, Khadhar Mohamed Meera Sheriffa Begum (2013). Performance of ozone treated rice husk carbon (OTRHC) for continuous adsorption of Cr (VI) ions from synthetic effluent, *Journal of Environmental Chemical Engineering* 1, 79–85
- [10] M. Oswald, M.K. Aroua, W.A.D. Wan Daud, S. Baroutian (2009). Removal of hexavalent-contaminated water and wastewater: a review, *Water Air Soil Pollut.* 200, 59–77.
- [11] S. Sugashini, K.M. Meera, S. Begum (2012). Optimization using central composite design (CCD) for the biosorption of Cr (VI) ions by cross linked chitosan carbonized rice husk (CCACR), *Clean Technol. Environ. Policy*, <http://dx.doi.org/10.1007/s10098-012-0512-3>.

- [12] L. Monser, N. Adhoum (2002). Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater, *Sep. Purif. Technol.* 26, 137–146.
- [13] Tanabe, K. (1981). Solid acid and base catalysis. In: Anderson, J.R.,
- [14] J.C. Echeverria, E. Churio, J. Garrido (2002). *Clays Clay Miner.* 50 ,614.
- [15] Jozja N., Baillif P., Touray J. S., Pons C.H., Muller F., Burgevin C. (2003). Impacts « multi-echelle » d'un échange (Mg, Ca) – Pb et ses conséquences sur l'augmentation de la perméabilité d'une bentonite. *Comptes Rendus Géoscience*, 335, 729 – 736.
- [16] Gungor N and Karaoglan S. (2001). Interaction of polyacrylamide polymer with bentonite in aqueous systems. *Materials Letters*, 48, 168 – 175.
- [17] Krishna B. S., Murty D.S.R., Jai Prakash B. S. (2001). Surfactant modified clay as adsorbent for chromate. *Applied Clay Science*, 20, 65-71.
- [18] Y.S. Ho, G. McKay, *Water Res.* 33 (1999) 578.
- [19] O. Keskinan, M.Z.L. Goksu, M. Basibuyuk, C.F. Forster (2004). *Biores. Technol.* 92 ,197.
- [20] Y.S. Ho, G. McKay (1999). *Trans. I. Chem. E. B* 77 165.
- [21] Y.S. Ho, J.C.Y. Ng, G. McKay (2001), *Sep. Sci. Technol.* 36 ,241.
- [22] Riddish R. Bhatt, Bhavna A. Shah (2013). Sorption studies of heavy metal ions by salicylic acid formaldehyde–catechol terpolymeric resin: isotherm, kinetic and thermodynamics article in press, *Arabian Journal of Chemistry*, <http://dx.doi.org/10.1016/j.arabjc.2013.03.012> .
- [23] Shah, B.A., Shah, A.V., Bhandari, B.N., Bhatt, R.R. (2008). *J. Iran. Chem. Soc.* 5, 252–261.