Journal of Materials and
Environmental Sciences
ISSN : 2028-2508
CODEN : JMESCN

J. Mater. Environ. Sci., 2018, Volume 9, Issue 2, Page 487-496

https://doi.org/10.26872/jmes.2018.9.2.52

http://www.jmaterenvironsci.com

# Removal of Pb(II) from aqueous solutions by low cost adsorbent, Equilibrium, kinetic and thermodynamic studies

**K. El Ass[1], F. Erraib[1], M. Azzi[2], A. Laachach[1]**

*[1]Laboratoire de métrologie environnementale, Ecole nationale supérieure des mines de Rabat, Maroc*
*[2]Laboratoire d'électrochimie et de l'environnement, Faculté des Sciences Aïn Chock, Moroc*

*Received 23 May 2017,*
*Revised 06 Jul 2017,*
*Accepted 10 Jul 2017*

*Keywords*

- Adsorption;
- Ghassoul clay;
- heavy metals;
- kinetic;
- isotherm

**K El Ass**
**khelass@gmail.com**
**+212661764544**

## Abstract

The ability of Moroccan clay, called locally Ghassoul, in removal of Pb(II) ions from aqueous solutions has been examined in a batch adsorption process with respect to several experimental conditions including pH, contact time, initial metal ions concentration, temperature, ionic strength. The suitability of the adsorbent was tested by fitting the adsorption data with Langmuir, Freundlich and Dubinin–Radushkevich isotherms. The monolayer adsorption capacity was found as 90.91 mg $g^{-1}$. Kinetic studies revealed that Pb(II) ions uptake was fast with 90% or more of the adsorption occurring within first 30 min of contact time. The kinetic data fits to the pseudo-second-order model. Thermodynamic parameters including the Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) changes indicated that the present adsorption process was feasible, spontaneous and endothermic in the temperature range of 25-45 °C.

## 1. Introduction

Heavy metal has become a public health concern because of their tendency to accumulate in living organisms, and by that find their way into the human body causing various diseases and disorders. Several methods have been applied over the years on the elimination of these metal ions. The usual methods can be ordered as chemical precipitation, ion-exchange, solvent extraction, phytoextraction, ultrafiltration, reverse osmosis, electrodialysis, and adsorption [1]. Of all the various water-treatment techniques, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling and cost effectiveness.

A wide range of low cost adsorbents have been tested for their capacity to eliminate heavy metal ions from aqueous solutions, as documented in recent reviews [1,2]. Among these low cost adsorbents, clay minerals are copious in nature, cost less, have a high specific surface area and exchange capacity and hence are strong candidates as adsorbents. Many kinds of natural clay minerals such as, bentonite [3], kaolinite [4], illite [5], and sepiolite [6] have been used to remove heavy metals from wastewaters.

Adsorption mechanism at clay surfaces is strictly related to the dual nature of the surface charge, both of permanent and variable nature. A number of mechanisms have been supposed to be active in the sorption of heavy metals by these sorbents. Two types of reactions are necessary to explain ion adsorption on clay surfaces. The first one is a cation-exchange mechanism that occurs on the interlayer and basal planes [7]. It originates from the presence of a permanent negative structural charge in the alumino-silicate layer created by isomorphous substitutions in the lattice. The second type of reaction is the pH-dependent specific sorption on the clay edges. On these clay edges, the proton surface charge depends on physico-chemical parameters of the solution (pH, ionic strength) that control the protonation state of the surface [8,9].

In this work, we attempt to investigate the potential of Moroccan clay, called locally Ghassoul, as an adsorbent of heavy metals from aqueous solutions. This mineral clay comes from the only deposit in the world, located at the East side of the Middle Atlas Mountains, in the Moulouya valley, approximately 200 km away from Fes, Morocco [10]. For several centuries, Ghassoul clay has been used in natural cosmetic products (soap, shampoo, skin conditioner). Currently, it is marketed for its detergent and grease-removing properties.

The geochemical characterization and the origin of the Ghassoul clay formation were studied by Chahi et al., (1997, 1999) [11,12] and Benhammou et al., (2009) [10]. The mineralogical composition of Ghassoul clay shows that the raw Ghassoul clay consists mainly of an Mg-rich trioctahedral smectite, stevensite, together with quartz and dolomite. The empirical chemical formula of raw stevensite is :

$Si_{3.78}Al_{0.22}Mg_{2.9}Fe_{0.09}Na_{0.08}K_{0.08}O_{10}(OH)_{2}\cdot 4H_2O$ [10,12].

At pH 2–12, stevensite particles are formed of negatively charged layers responsible via Coulombic attractions of the strong retention of cationic dyes [13].

The main objective of the present study was to evaluate the applicability of Ghassoul clay in removal of Pb(II) ions from aqueous solutions by batch adsorption process. Therefore, the effects of pH, contact time, initial dye concentration, ionic strength, and temperature were investigated. Equilibrium and kinetic analysis were conducted to determine the parameters controlling the rate of adsorption and to find out the possibility of using this material as low cost adsorbent for metal ions removal.

## 2. Materials and methods

### 2.1. *Materials*

Ghasssoul clay comes from the East side of the Middle Atlas Mountains, approximately 200 km away from Fes. Ghassoul clay was treated before using in the experiments as follows: a distilled water suspension of the clay was dispersed for approximately 4 h and then cleaned several times with de-ionized water. The fine fraction was collected by repeated dispersion, sedimentation and siphoning techniques [14]. The solid sample was parched at 80°C for 24 h and ground then sieved to pass 140 µm mesh (140 µm mesh was an appropriate size in the pre-experiment) before being used as adsorbent.

All the chemical compounds used to prepare the reagent solutions were of analytic grade. The stock solutions of the metals used in this study (1000 mg $L^{-1}$) were prepared by dissolving weighed quantities of nitrate salts in twice-distilled water. The pH of solution was adjusted by using 0.1 M (NaOH) and/or 0.1 M ($HNO_3$).

### 2.2 *Methods*

Adsorption study - Batch adsorption experiments were performed on a rotary shaker at 110 rpm using 100 mL capped polyethylene bottles containing 50 mL of metal ion solutions and 0.1 g of adsorbent. Experiments were performed at room temperature (25°C) and pH 5±0.2, except those in which the effects of temperature and pH were investigated. The preliminary experiment revealed that about 60 min was required for the adsorption process to reach equilibrium. Therefore, a contact period of 90 min was finally selected for all of the equilibrium tests. The solution and solid phase were separated by centrifugation at 3000 rpm for 10 min and the supernatant was kept for Pb(II) analyses using an atom adsorption spectrophotometer (AA300, Varian, USA). Various conditions, including the contact time, the pH, the initial metal ions concentration and the ionic strength, were tested. The metal ion concentrations, retained in the adsorbent phase ($q_e$, mg $g^{-1}$), were calculated by using the following equation:

$$q_e = \frac{C_0 - C_e}{m}.V$$

where $C_0$ (mg $L^{-1}$) is the initial metal ion concentration, $C_e$ (mg $L^{-1}$) is the equilibrium concentration of metal ions in aqueous solution, V (L) is the volume of solution, m (g) is the mass of the Ghassoul clay and $q_e$ (mg $g^{-1}$) is the calculated metal ion adsorption amount onto Ghassoul clay.

Adsorption isotherm models - Langmuir adsorption isotherm is applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites and is represented in linear form [15]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{(q_m.K_L)}$$

where $C_e$ is equilibrium concentration of the metal (mg $L^{-1}$) and $q_e$ is the amount of the metal adsorbed (mg) by per unit of the adsorbent (g). $q_m$ and $K_L$ are Langmuir constant relating adsorption capacity (mg $g^{-1}$) and the energy of adsorption (L $g^{-1}$). These constants are evaluated from slope and intercept of the linear plots of $C_e/q_e$ versus $C_e$, respectively.

The Freundlich isotherm is applicable to both monolayer and multilayer adsorption and is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent [16]. The linear form of Freundlich equation is expressed as:

$$log\ q_e = log\ K_F + \left(\frac{1}{n}\right) log\ C_e$$

where $K_F$ (mg $g^{-1}$) and n are Freundlich constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of adsorption. These constants are determined from the intercept and slope of linear plot of log $q_e$ versus log $C_e$, respectively.

The D–R isotherm model is a semi-empirical equation where adsorption follows a pore filling mechanism. It assumes that the adsorption has a multilayer character, involves Vander Waals forces and is applicable for physical adsorption processes [17]. The linear form of D–R isotherm model is expressed as:

$$lnq_e = lnq_d - \beta\varepsilon^2$$

where $q_d$ is the D–R monolayer adsorption capacity (mg $g^{-1}$), β is the activity coefficient related to mean sorption energy and ε is the Polanyi potential which is defined as:

$$\varepsilon = RT.ln\left(1 + \frac{1}{C_e}\right)$$

Adsorption kinetic models - The pseudo first-order equation (Lagergren's equation) describes adsorption in solid–liquid systems based on the sorption capacity of solids [18,19]. The Lagergren's first-order reaction model is expressed as follows:

$$log(q_e - q_t) = logq_e - \frac{k_1}{2.303}t$$

where $q_t$ (mg $g^{-1}$) is the amount of adsorption time t (min); $k_1$, the rate constant of the equation ($min^{-1}$) and $q_e$ is the amount of adsorption equilibrium (mg $g^{-1}$). The adsorption rate constant $k_1$, can be determined experimentally by plotting of ln ($q_e$ −$q_t$) versus t.

The pseudo second-order model, as described by Ho, (2006) [20], is expressed as:

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

where $k_2$ (g $mg^{-1}$ $min^{-1}$) is the rate constant of the second-order equation; $q_e$ and $q_t$ are the amount of adsorption (mg $g^{-1}$) at equilibrium and at time t, respectively.

The intraparticle diffusion model described by Weber and Morris, (1963) [21], is used.

$$q_t = k_{id}t^{1/2} + C$$

where $q_t$ (mg $L^{-1}$) is the amount of adsorption time t (min), $k_{id}$ (mg $g^{-1}$ $min^{-1/2}$) is the rate constant of intraparticle diffusion and C (mg/g) is the intercept..

Thermodynamic study - Thermodynamic parameters can be determined using the equilibrium constant K, which depends on temperature. The change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) associated to the adsorption process were calculated by using following equations [22] :

$$\Delta G = RTlnK$$

$$ln\,K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

$$K = \frac{q_e}{C_e}$$

where R is the universal gas constant (8.314 J $mol^{-1}$ $K^{-1}$) and T is temperature (K), $q_e$ (mg $g^{-1}$) and $C_e$ (mg $L^{-1}$) are the equilibrium concentration of metal ions adsorbed and remained in the solution, respectively.

ΔH and ΔS parameters can be calculated from the slope and intercept of the plot of ln K versus 1/T yields, respectively.

## 3. Results and Discussion

### *3.2. Characterization of the Ghassoul clay*

Mineralogical identification of adsorbent was performed by a Siemens D5000 X-ray diffraction instrument with filtered Cu Kα radiation (n = 1.5418 Å). The XRD pattern of raw Ghassoul clay (Fig. 1a) showed that the dominant phase is the stevensite with the presence of quartz and dolomite. The XRD pattern of the fine fraction (Fig. 1b) shows (i) an increase in the abundance of stevensite, indicating that the clay fraction of the Ghassoul clay consists mainly by phyllosilicates, (ii) significant decrease in the abundance of quartz and disappearance of dolomite.

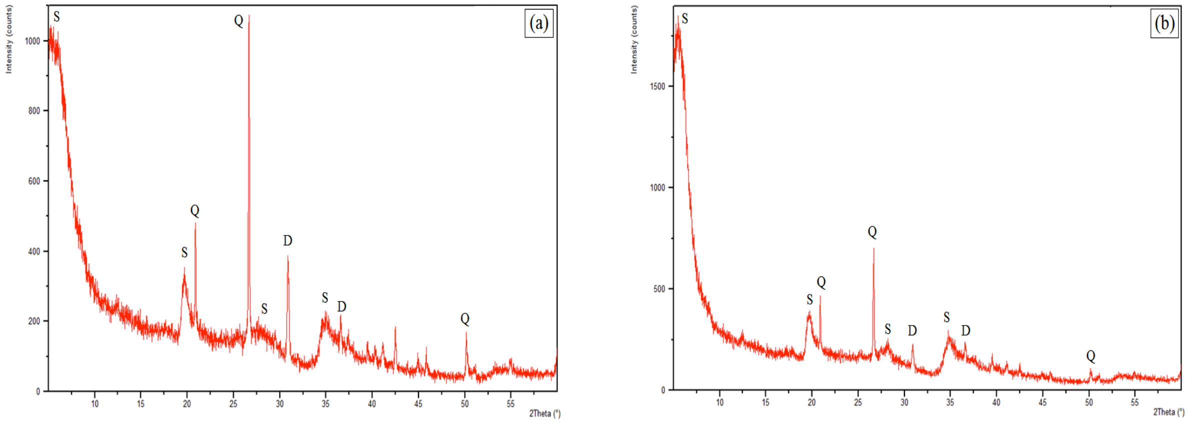

**Figure 1 :** XRD diagrams of (a) the raw sample and (b) the separated fine fraction of Ghassoul clay.

The chemical composition of the raw Ghassoul clay and its fine mineral fraction are presented in Table 1. These results show that the fine fractions are principally made up of $SiO_2$ (58.16 wt.%) and MgO (27.44 wt.%). $Al_2O_3$ is notably concentrated in the fine clay mineral fraction (4.48 wt.%). The large amount of CaO (12.13 wt.%) measured in the raw clay may be ascribed partly to the dolomite recognized in XRD patterns, but particularly to gypsum. Indeed, gypsum has been reported to be present in the Ghassoul clay deposit by Benhammou, (2005) [23]. The surface area of fine mineral fraction, measured by the $N_2$-BET method, is $137 m^2/g$. This high value, compared with other clays, reveals the existence of a high porosity responsible for the strong capacity of this material to fix some cations. The pH of zero point charge $pH_{ZPC}=2.0$, the same result was found by Benhammou, (2005) [23] and Bouna et al., (2010) [13]. The cation exchange capacity is 79 meq/100 g, relatively large, compared to the values for natural stevensite, reported by Faust and Murata, (1953) [24] and Takahashi et al., (1997) [25] to be 37.6 and 41 meq/l00 g, respectively. It is noted that the prevalent exchangeable element is $Mg^{2+}$, which presents 73.11% of the CEC.

**Table 1 :** Chemical composition of the raw Ghassoul clay and its fine mineral fraction.

| Sample Oxides | Raw clay (wt.%) | fine fraction (wt.%) |
|---|---|---|
| $SiO_2$ | 53.31 | 58.16 |
| $Al_2O_3$ | 2.87 | 4.48 |
| $Fe_2O_3$ | 1.44 | 1.92 |
| MgO | 24.64 | 27.44 |
| CaO | 12.13 | 1.88 |
| $Na_2O$ | 1.12 | 0.17 |
| $K_2O$ | 0.85 | 1.05 |
| Total | 96.36 | 95.20 |

### 3.2. *Effect of pH*

The pH is an important factor that can affect the form and the quantity of metals in water, the form and quantity of a mineral's surface sites, and the interaction of the mineral and metals. The effect of solution pH on the equilibrium up-take capacity of Ghassoul clay was studied at initial lead concentrations of 400 mg/L between pH values of 2 and 9. As shown in Fig.2, the amount of adsorbed metals was found to increase with an increase in pH, which can be explained by the electrostatic interaction of cationic metal ions with the negatively charged surface. Indeed at pH 2–12, Ghassoul clay particles are formed of negatively charged layers responsible via Coulombic attractions of the strong retention of cationic metals by contrast to the anionic metals [13].

Increased adsorption of Pb(II) at higher pH values may be due to enhanced ion exchange [26] and surface precipitation [27]. The linear increase of Pb(II) adsorption at pH>6 may be partially due to the decreased solubility of Pb(II) hydroxide with rising pH [28]. Experiments were not conducted beyond pH 6.0 to avoid the precipitation of metal ions. Similar results were observed using natural kaolinite clay for the adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) [4] and for Removal of Pb(II) from water by natural zeolitic tuff [28].

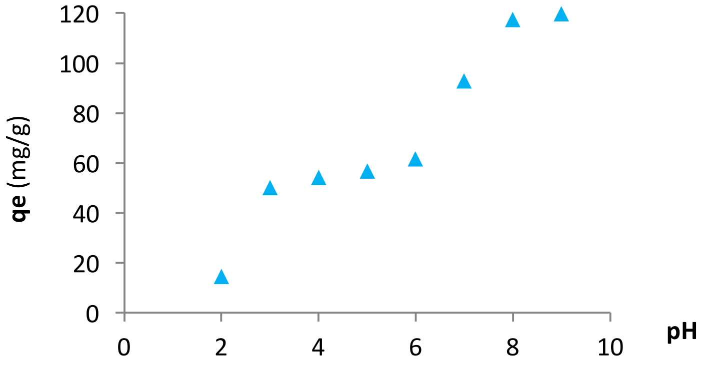

**Figure 2 :** The effect of solution pH on the adsorption of Pb(II) ions onto Ghassoul clay.

### 3.3. *Effect of ionic strength*

The $NaNO_3$, NaCl and $CaCl_2$ were chosen as electrolytes to investigate the effect of ionic strength on Pb(II) adsorption onto Ghassoul clay. Initial lead concentration was 400 mg $L^{-1}$. It was found that when ionic strength of electrolytes increased from 0.01 to 0.1 mol $L^{-1}$, the total decrease in Pb(II) percentage removal were 8.63%, 11.24% and 20.96% for $NaNO_3$, NaCl, and $CaCl_2$, respectively (Table 2).

**Table 2 :** Effect of different electrolytes on Pb(II) ions adsorption onto Ghassoul clay

| | **$NaNO_3$** (mol $L^{-1}$) | | | **NaCl** (mol $L^{-1}$) | | | **$CaCl_2$** (mol $L^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0,01 | 0,05 | 0,1 | 0,01 | 0,05 | 0,1 | 0,01 | 0,05 | 0,1 |
| $q_e$ *(mg $g^{-1}$)* | 59,81 | 58,33 | 54,25 | 58,93 | 55,11 | 51,25 | 57,97 | 51,81 | 44,26 |

This suggests that with increase in the concentration of chloride anions in metal ions solution, there is a possibility for the formation of uncharged species and negatively charged chloride complexes ($PbCl_2$, $PbCl_3^-$ and $PbCl_4^{2-}$) that will invariably reduce the adsorption capacity of the adsorbent for positively charged cations [29]. It was also observed that the adsorbent show stronger preference for $Ca^{2+}$ (a divalent cation) than for $Na^+$ (a monovalent cation) with the resultant effect of a further drop in monolayer adsorption capacities of the adsorbent for the metal ions when Ca-electrolytes were used. Similar results were found by several earlier workers for metals adsorption on different adsorbents [29,30].

These results can be attributed by these reasons: (i) the competition between cations of the electrolytes and metal ions for certain surface sites, (ii) the active adsorption sites of the Ghassoul clay may be blocked in the presence of these salts so metal ions were hindered to bind the surface of the adsorbent [4].

### 3.4. *Adsorption isotherms and equilibrium*

The effects of initial metal ions concentration on the adsorption process were evaluated by varying initial metal ions concentration in the range of 50-800 mg $L^{-1}$. With increasing metal ions loading, the amount adsorbed per unit mass of clay adsorbents ($q_e$) increases gradually (Fig. 3) while the extent of adsorption (%) decreases. As calculated from adsorption data, the amount of Pb(II) increased from 12.13 to 88.04 mg $g^{-1}$ whereas adsorption percentage decreased from 97.01 % to 35.23 %. Similar observations for metal ions uptake on different adsorbents have been reported earlier by Sdiri et al., (2011) [31] and Yun et al., (2006) [32]. It appears that, at low Pb(II) ions concentration, a large number adsorption sites are available to the metal ions and the adsorption is independent of the initial concentration. The situation changes with increasing metal ions concentration and the competition for adsorption sites become strong. Under such circumstances, the unit mass of the adsorbent could take up many more metal ions but the overall percentage adsorption shows a decreasing trend [33]. The adsorption equilibrium is established when the amount of metal ions fixed at the interface solid solution is in dynamic balance with that on surface.

The relationship between the amount of Pb(II) ions adsorbed onto Ghassoul clay and its equilibrium concentrations in aqueous solution was evaluated in terms of Langmuir, Freundlich and Dubinin Radushkevich isotherm models.

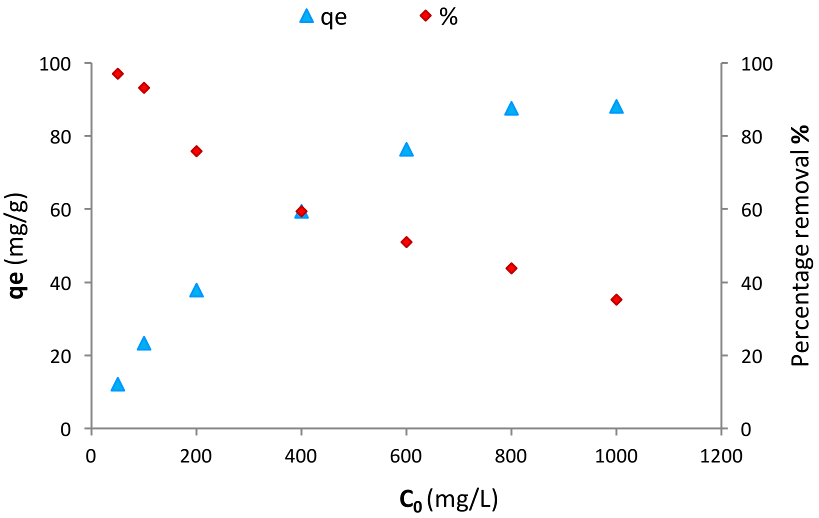

**Figure 3 :** Effect of initial metal concentrations on the adsorption of Pb(II) ions onto Ghassoul clay.

The adsorption pattern of the metals onto Ghassoul clay was well fitted with all the models. This indicated that the adsorption sites were non-uniform and nonspecific in nature. It was in conformity with the existence of different types of possible adsorption sites on clay surface with considerable difference in energy if the site was on an edge or was located in a defect position [4]. The values of the adsorption coefficients, computed from these plots are given in Table 3.

**Table 3 :** Langmuir, Freundlich and Dubinin Radushkevich (D-R) isotherm parameters for the adsorption of Pb(II) ions onto Ghassoul clay.

| Langmuir isotherm model | | | Freundlich isotherm model | | | D-R isotherm model | | | |
|---|---|---|---|---|---|---|---|---|---|
| $q_m$ (mg $g^{-1}$) | $K_L$ (L $mg^{-1}$) | $R^2$ | $K_F$ (mg $g^{-1}$) | n | $R^2$ | $q_d$ (mg $g^{-1}$) | β ($mol^2$ $kJ^{-2}$) | E (kJ $mol^{-1}$) | $R^2$ |
| 90.91 | 0.024 | 97.09 | 6.21 | 2.98 | 99.36 | 165.32 | -0.032 | 3.97 | 98.92 |

The Freundlich coefficient, n obtained in the present study is greater than unity (n = 2.98), indicate that the adsorption of Pb(II) onto Ghassoul clay under studied conditions was favorable [34]. The monolayer adsorption capacity was found as 90.91 mg $g^{-1}$. This is much higher than the adsorption capacity of other adsorbents reported in the literature: natural kaolinite clay 31.75 mg/g [35], Illitic clay 53.76 mg $g^{-1}$ [30], Montmorillonite 31.05 mg $g^{-1}$ [36], Sepiolite 35.19 mg $g^{-1}$ [37], Palygorskite 62.11 mg $g^{-1}$ [38]. From the β values (Table 3) the values of the mean sorption energy, can be calculated by as $E = (2\beta)^{-1/2}$. The calculated E values (Table 3) for Pb(II) adsorption onto Ghassoul clay is 3.97 kJ $mol^{-1}$ indicating the adsorption process may be carried out via physical mechanism [39]. Similar results were previously reported by Sari et al., (2007b) [40] for adsorption of Pb(II) and Cr(III) on Celtek clay and by Sdiri et al., (2011) [31] for the removal of several heavy metals onto montmorillonitic and calcareous clays. The slope and intercept of plots of ln $q_e$ versus $\varepsilon^2$, were used to calculate the D–R isotherm parameters. The $q_d$ values are not consistent with the $q_m$ values previously determined for the Langmuir isotherm.

### 3.5. *Adsorption kinetics*

The effect of contact time on the sorption of lead was analyzed kinetically over a range of 5–120 min. Adsorption was carried out at initial lead concentrations range of 200–600 mg $L^{-1}$.

As can be seen in Fig. 4, the equilibrium adsorption was very fast and maximum uptake was reached within 60 min, thereafter, the amount of adsorption remained almost constant. So, 90 min was fixed as equilibrium time throughout this study. The same results were reported by other investigators [31,38], who found that the equilibrium time for Pb(II) onto minerals, such as nature palygorskite, montmorillonite and calcareous clays was short.

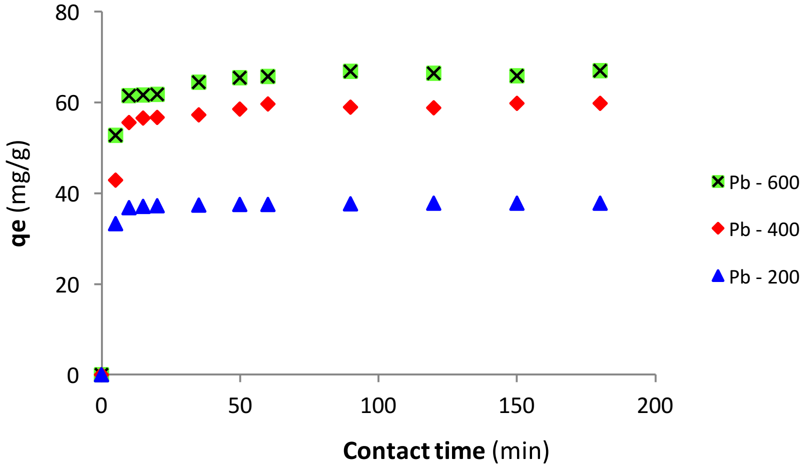

**Figure 4** : Effect of contact time on the adsorption of Pb(II) ions onto Ghassoul clay.

In order to investigate the adsorption kinetics of Pb(II) onto Ghassoul clay, three different kinetic models, pseudo-first order, pseudo-second order, and intraparticle diffusion, have been used to fit experimental data obtained from batch experiments. By testing the plots of $\log(q_e - q_t)$ versus t and $(t/q_t)$ versus t (Fig.5), the rate constants $k_1$ and $k_2$, and correlation coefficients can be calculated and the results are shown in Table 4.

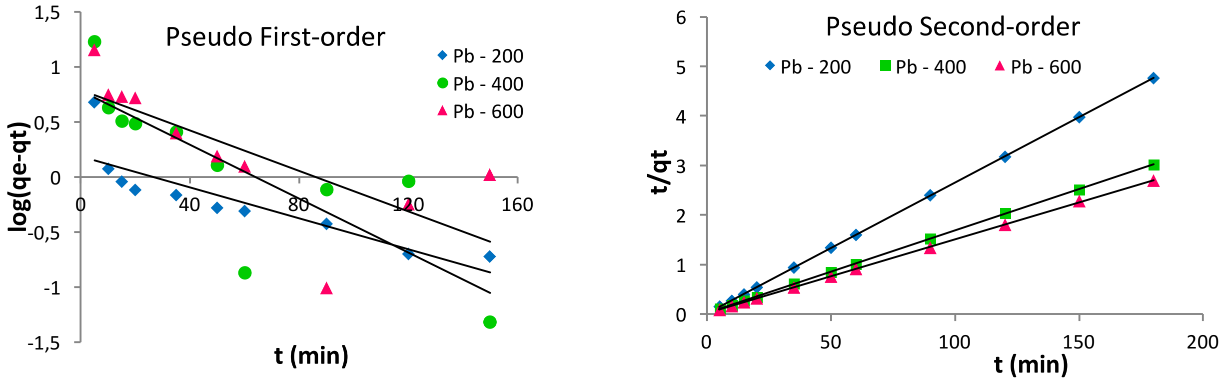

**Figure 5 :** Pseudo First-order and pseudo Second-order plots for the adsorption of Pb(II) ions onto Ghassoul clay at various concentrations.

As seen from Table 4, the correlation coefficients ($R^2$), for the pseudo second-order kinetic model fits, are much higher (>0,99) than those derived from pseudo first-order model fits. Also, the $q_e$ calculated values fit the experimental data. This suggests that the pseudo-second-order adsorption mechanism is predominant and that the overall rate of the Pb(II) adsorption process appeared to be controlled by the chemical process [41].

Similar results were found by Ozdes et al., (2011) [30] who studied the removal of Cd(II) and Pb(II) ions by Turkish illitic clay and by Yun et al., (2006) [32] who studied the removal of Cu(II) and Pb(II) ions onto modified bentonite.

A detailed understanding of adsorption mechanisms facilitates a determination of the rate-limiting step. The Weber–Morris intraparticle diffusion model has often been used to determine if intraparticle diffusion is the rate-limiting step. According to this model, the plot of $q_t$ versus $t^{1/2}$ (Fig 6) shows that intraparticle diffusion occurred in two stages. The first phase is attributed to the diffusion of metal ions through the solution to the external surface and the second phase indicates the intraparticle diffusion of metal ions into the pores of Ghassoul clay. The intraparticle rate constants for the first phase ($k_{1d}$) and second phase ($k_{2d}$) and C parameters were given in Table 4. For the first sharper portion, i.e. from 0 to 10 min, its rates, $k_{1d}$ (2.79-13.72 mg $g^{-1}$ $min^{-1/2}$), shows that the adsorption process is very fast. The second portion with $k_{2d}$ (0.09-0.77 mg $g^{-1}$ $min^{-1/2}$) can be rate controlling. However the intraparticle diffusion model is not the only rate limiting mechanism since the line did not pass through the origin. From the above analysis, it can be concluded that both film diffusion and intra-particle diffusion were simultaneously operating during the process of the adsorption of Pb(II) onto Ghassoul clay. The same type results were also given in some works [30,35,41].

**Table 4:** Kinetics parameters for the adsorption of Pb(II) ions onto Ghassoul clay at various concentrations

| | Pb (mg $L^{-1}$) | 200 | 400 | 600 |
|---|---|---|---|---|
| | $q_{e\ (exp)}$ (mg $g^{-1}$) | 37,49 | 59.74 | 66.92 |
| First-order kinetics model | $\mathbf{k_1}$*$10^2$ ($min^{-1}$) | -1.612 | -2.809 | -2.119 |
| | $q_{e\ (cal)}$ (mg $g^{-1}$) | 1.538 | 6.044 | 6.156 |
| | $R^2$ | 94.28 | 66.93 | 54.71 |
| Pseudo-second-order model | $q_{e\ (cal)}$ (mg $g^{-1}$) | 23,86 | 60.24 | 67.11 |
| | $k_2$ *$10^2$ (g mg $^{-1}min^{-1}$) | 6,45 | 1.25 | 1.13 |
| | $R^2$ | 100 | 99.99 | 99.99 |
| Intraparticle diffusion model | $K_{1d}$ (mg $g^{-1}$ $min^{-1/2}$) | 2,79 | 9,41 | 13,72 |
| | $C_1$ | 13,98 | 31,60 | 12,09 |
| | $R^2$ | 98,74 | 97,93 | 99,68 |
| | $K_{2d}$ (mg $g^{-1}$ $min^{-1/2}$) | 0,09 | 0,39 | 0,77 |
| | $C_2$ | 22,76 | 55,23 | 59,13 |
| | $R^2$ | 97,97 | 96,23 | 97,57 |

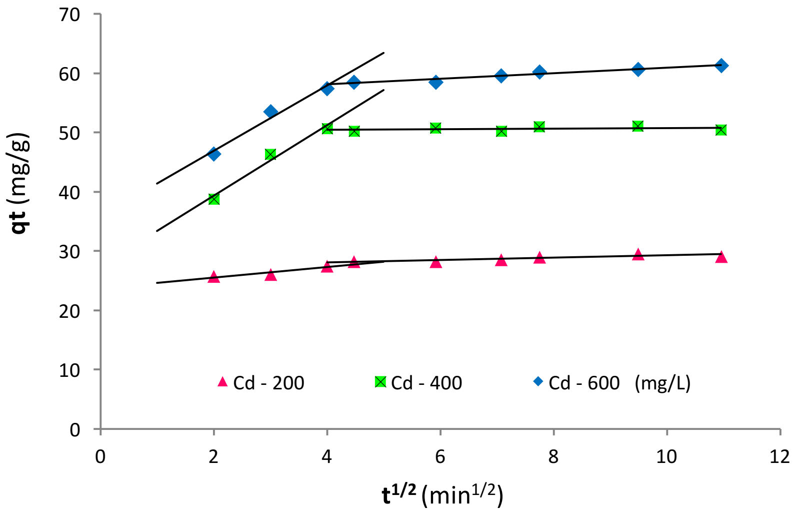

**Figure 6 :** Intra-particle diffusion plots for various initial Pb(II) concentrations.

### 3.6. *Thermodynamic studies*

The effect of temperature on the removal efficiency was investigated in the temperature range of 25-45 °C by using initial lead concentration of 400 mg $L^{-1}$. The adsorption efficiency increased from 71.5 to 73.25 mg $g^{-1}$, when the temperature was increased from 25 to 45 °C, indicating that the adsorption process was endothermic in nature. The increase in the adsorption capacity of Ghassoul clay with temperature may be attributed to either increase in number of available active surface sites on the Ghassoul clay surface or increase in the mobility of metal cations [42]. Similar observations have been reported earlier by Bhattacharyya and Gupta, (2011) [33] for removal of Cu(II) by natural and acid-activated clays.

In any adsorbate-adsorbent system, the values of thermodynamic adsorption parameters are important indicators for practical application of a process. The results of thermodynamic calculations are shown in Table 5.

**Table 5** Thermodynamic parameters for the adsorption of Pb(II) ions onto Ghassoul clay at various temperatures

| | $\Delta H$ *(kJ mol$^{-1}$)* | $\Delta S$ *(J mol$^{-1}$)* | $\Delta G_{298}$ *(kJ mol$^{-1}$)* | $\Delta G_{308}$ *(kJ mol$^{-1}$)* | $\Delta G_{318}$ *(kJ mol$^{-1}$)* |
|---|---|---|---|---|---|
| Pb | 1.14 | -6.60 | 3.11 | 3.18 | 3.24 |

Gibbs free energy change of adsorption (ΔG) was calculated using ln K values for different temperatures (298, 308 and 318 K). ΔG, values obtained were all small and positive which suggests that the adsorption of Pb(II) onto Ghassoul clay require some small amount of energy to convert reactants into products [43]. Ozcan and Ozcan, (2004) [44] have suggested that positive values for ΔG are quite common with ion-exchange mechanism of adsorption of metal ions because of the activated complex of the metal ion formed with the adsorbent in the excited state. On the other hand the magnitude of ΔG increased with increasing the temperature indicated that a better adsorption is actually obtained at higher temperatures. The positive values of ΔH (1.14 kJ mol$^{-1}$), indicated that the endothermic nature of adsorption. The low ΔH values mean that there are weak interactions between the metal ions and the functional group (Si–O−) on the surface of clay mineral [40]. Endothermic adsorption of Pb(II) ion has been observed on tripolyphosphate-modified kaolinite clay by Adebowale et al., (2008) [42] and on illitic clay by Ozdes et al., (2011) [30]. Exothermic adsorption of lead on natural and acid-activated clays has also been reported [45]. It was found that adsorption of Pb (II) has a negative ΔS (-6.057 J mol$^{-1}$). Gupta et al., (2004) [46] reported a value range of negative ΔS for the adsorption of $Cd^{2+}$ and $Pb^{2+}$ by Duolite C-433 synthetic resin. The negative values obtained indicate a stable configuration of the metal ion on the Ghassoul clay adsorbent surface [47].

## Conclusion

The potential usage of Ghassoul clay mineral in removal of Pb(II) ions from aqueous solutions was tested in presented study. One of the essential features of this study was to use the clay mineral without any previous activation treatment. Adsorption characteristics of Pb(II) ions onto Ghassoul clay was found to be influenced by initial pH of aqueous solution, contact time, initial metal ions concentration, temperature, and ionic strength. The empirical values are evaluated according to the Langmuir, Freundlich and D–R isotherms that are generally used to describe the adsorption processes. It is stated that Langmuir and Freundlich isotherm models fit very well. The monolayer adsorption capacity of Ghassoul clay was found to be 90.91 mg g$^{-1}$. Moreover, in the D–R isotherm, adsorption energies are calculated to state the physical and chemical characteristics of adsorption. The magnitude of the mean free energy of adsorption, E for lead adsorption is 3.97 kJ mol$^{-1}$. These low values of adsorption energy show that the adsorption has a physical nature. The pseudo-second-order model gives the good agreement between model fit and experimentally observed equilibrium adsorption capacity in addition to the large correlation coefficients. Both film diffusion and intra-particle diffusion were simultaneously operating during the process of the adsorption of Pb(II) onto Ghassoul clay. The ΔH and ΔG values indicated that the adsorption of Pb(II) ions onto Ghassoul clay was spontaneous and endothermic in nature. The negative ΔS values indicated a more stable formation of adsorbent-adsorbate complex. As a result of this study, it can be concluded that Ghassoul clay can be utilized as a low cost and effective adsorbent in removal of Pb(II) ions from aqueous solutions.

## References

1. F. Fu, Q. Wang, *J. Environ. Manage.* 92 (2011) 407
2. S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, *Water Res.* 33 (1999) 2469
3. G. Bereket, A.Z. Aroguz, M.Z. Ozel, *J. Colloid Interf. Sci.* 187 (1997) 338
4. M. Jiang, X. Jin, X. Lu, Z. Chen, *Desalination*, 252 (2010) 33
5. J.C. Echeverria, I. Zarranz, J. Estella, J.J. Garrido, *Appl. Clay Sci.* 30 (2005) 103
6. S. Lazarević, I. Janković-Častvan, D. Jovanović, S. Milonjić, D. Janaćković, R. Petrović, *Appl. Clay Sci.* 37 (2007) 47
7. F. Ayari, E. Srasra, M. Trabelsi-Ayadi, *Desalination,* 206 (2007) 270
8. A.M.L. Kraepiel, K. Keller, F.M.M. Morel, *J. Colloid interf. Sci.* 210 (1999) 43
9. M.H. Bradbury, B. Bayens, *Geochim. Cosmochim. Ac.* 63 (1999) 325
10. A. Benhammou, B. Tanouti, L. Nibou, A. Yaacoubi, J.P. Bonnet, *Clay. Clay Miner.* 57 (2009) 264
11. A. Chahi, B. Fritz, J. Duplay, F. Weber, J. Lucas, *Clay. Clay Miner.* 45 (1997) 378
12. A. Chahi, Ph. Duringer, M. Ais, M. Bouabdelli, F. Guathier, B. Fritz, *J. Sediment. Res.* 69 (1999) 1125
13. L. Bouna, B. Rhouta, M. Amjoud, A. Jada, F. Maury, L. Daoudi, F. Senocq, *Appl. Clay Sci.* 48 (2010) 527
14. K. El Ass, A. Laachach, A. Alaoui, M. Azzi, *Appl. Ecol. Env. Res.* 8 (2010) 153
15. I. Langmuir, *J. Am. Chem. Soc.* 40 (1918) 136
16. C.H. Yang, *J. Colloid Interf. Sci.* 208 (1998) 379
17. N.D. Hutson, R.T. Yang, *Adsorption*. 3 (1997) 189
18. S. Lagergren, *K. Sven. vetensk.akad. handl.* 24(1898) 1
19. Y.S. Ho, *Scientometrics*, 59 (2004) 171

20. Y.S. Ho, *J. Hazard. Mater.* 136 (2006) 681
21. W.J. Weber, J.C. Morris, *J. Sanit. Eng. Div.* 89 (1963) 31
22. A. Ramesh, D.J. Lee, J.W.C. Wong, *J. Colloid interf. Sci*. 291 (2005) 588
23. A. Benhammou, PhD Thesis, (2005) Cadi Ayyad University, Marrakesh, Morocco.
24. G.T. Faust, K.J. Murata, *Am. Mineral.* 38 (1953) 973
25. N. Takahashi, M. Tanaka, T. Satoh, T. Endo, Shimada M., *Micropor. Mat.* 9 (1997) 35
26. D.K. Singh, D.P. Tiwari, D.N. Saksena, *Indian J. Environ. Health.* 35 (1993) 169
27. Y. Al-Degs, M.A.M. Khraisheh, M.F. Tutunji, *Water Res.* 35 (2001) 3724
28. M. Karatas, *J. Hazard. Mater.* 199– 200 (2012) 383
29. K.O. Adebowale, I.E. Unuabonah, B.I. Olu-Owolabi, *J. Hazard. Mater.* 134 (2006) 130
30. D. Ozdes, C. Duran, H.B.Senturk, *J. Environ. Manage*. 92 (2011) 3082
31. A. Sdiri, T. Higashi, T. Hatta, F. Jamoussi, N. Tase, *Chem. Eng. J.* 172 (2011) 37
32. L. Yun, S. Xing, X. Qiming, C. Haidong, Z. Huixian, G. Shixiang, *J. Hazard. Mater.* 137 (2006) 1149
33. K.G. Bhattacharyya, S.S. Gupta, *Desalination*. 272 (2011) 66
34. E.I. Unuabonah, K.O. Adebowale, B.I. Olu-Owolabi, L.Z. Yang, L.X. Kong, *Hydrometallurgy*. 93 (2008) 1
35. A. Sari, M. Tuzen, M. Soylak, D. Citak, *J. Hazard. Mater.* 149 (2007a) 283
36. S.S. Gupta, K.G. Bhattacharyya, *Appl. Clay Sci.* 30 (2005) 199
37. R. Celis, M.C. Hermosın, J. Cornejo, *Environ. Sci. Technol.* 34 (2000) 4593
38. J.H. Potgieter, S.S. Potgieter-Vermaak, P.D. Kalibantonga, *Miner. Eng.* 19 (2006) 463
39. B.P. Bering, M.M. Dubinin, V.V. Serpinsky, *J. Colloid Interf. Sci*. 38 (1972) 185
40. A. Sarı, M. Tuzen, M. Soylak, *J. Hazard. Mater.* 144 (2007b) 41
41. H. Chen, A. Wang, *J. Colloid Interf. Sci*. 307 (2007) 309
42. K.O. Adebowale, E.I. Unuabonah, B.I. Olu-Owolabi, *Chem. Eng. J.* 136 (2008) 99
43. K.R. Scheckel, L. Donald, *Soil Sci. Soc. Am. J.* 65 (2001) 719
44. A.S. Ozcan, A. Ozcan, *J. Colloid Interf. Sci*. 276 (2004) 39
45. M. Eloussaief, M. Benzina, *J. Hazard. Mater.* 178 (2010) 753
46. V.K. Gupta, P. Singh, N. Rahman, *J. Colloid Interf. Sci*. 275 (2004) 398
47. S.S. Gupta, K.G. Bhattacharyya, *J. Colloid Interf. Sci*. 295 (2006) 21

(2018) ; http://www.jmaterenvironsci.com