

Adsorption of cadmium and copper onto natural clay: isotherm, kinetic and thermodynamic studies

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Abstract

Clay of the Middle Atlas Mountains region, Morocco, was used to investigate the removal of heavy metals ions (Cadmium and Copper) from aqueous solutions with respect to several experimental conditions including pH, contact time, initial solute concentrations, temperature and ionic strength. Kinetic study revealed that metal ions uptake was fast with 90% or more of the adsorption occurring within first 30 min of contact time. Adsorption rate increased with the increasing initial metal ions concentrations and the sorption rate was well fitted by the pseudo-second-order rate model. The data according to mass transfer and intraparticle diffusion models confirmed diffusion of solutes inside the clay particles as the rate-controlling step and more important for the adsorption rate than the external mass transfer.

The suitability of the adsorbent was tested by fitting the adsorption data with Langmuir and Freundlich isotherm models. Equilibrium and kinetic adsorption data showed that clay displays a high selectivity with an affinity order of $Cd > Cu$. Thermodynamic parameters including the Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) changes indicated that the present adsorption process was feasible and endothermic in the temperature range of 25–45 °C.

Keywords: Adsorption, Moroccan clay, heavy metals, kinetics, isotherm.

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 (Al-Degs *et al.*, 2006, Inghui and Caoc, 2009). These metals enter the environment due to various industrial procedures including melting, extraction and purification. Presence of heavy metals and their compounds, even in small amounts, in industrial wastewater is very dangerous and must be removed.

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, electro-dialysis, coagulation and adsorption (Fu

and Wang, 2011). Of all the various water-treatment techniques, adsorption is undoubtedly the most important of the physicochemical processes responsible for the uptake of inorganic and organic substances in the aqueous environment. It has been found to be superior to other techniques for wastewater treatment in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Factors such as pH, nature and concentration of substrate and adsorbing ion, ionic strength, and the presence of competing and complex ions affect the extent of adsorption.

The most commonly used adsorbent in industrial wastewater treatment systems is activated carbon because of their high specific surface area, microporous characteristic, and the chemical nature of their surfaces. However, they are expensive, and their regeneration cost is also high. So, there is a dire need for low-cost and readily available materials for the removal of toxic pollutants from water (Crini, 2006).

Natural clays as the adsorbent have received much attention on organic and inorganic pollutants sorption from contaminated water. The use of these materials is becoming popular due to their low-cost, abundant availability, non-toxicity and potential for ion exchange. A number of clay materials: bentonite (Bereket *et al.*, 1997), kaolinite (Jiang *et al.*, 2010), illite (Echeverria *et al.*, 2005), sepiolite (Lazarević *et al.*, 2007), perlite (Alkan and Doagan, 2001), montmorillonite (Ijagbemi *et al.*, 2009) and pyrophyllite (Gupta *et al.*, 2009) have been investigated for removal of pollutants. These clay minerals are of interest according to their variety of structural and surface properties, high chemical stability, high specific surface area and high sorption capacity.

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 metal ions by these sorbents. Some of these mechanisms are chemisorption, physical adsorption and micro-precipitation which involve (i) an ion exchange reaction at permanent-charge sites and, (ii) formation of complexes with surface hydroxyl groups at edge-sites (Kraepiel *et al.*, 1999, Bradbury and Bayens, 1999). The adsorption capacity of clay minerals can be

enhanced by replacing the natural exchangeable cations with organic molecules forming the so called "organoclays" (Stathi *et al.*, 2007).

In this work, we attempt to investigate the potential of Moroccan clay, called locally Ghassoul, as an adsorbent. This mineral clay comes from the only deposit in the world, located at the Middle Atlas, Morocco. 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) and Benhammou *et al.*, (2009). 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 $\text{Si}_{3.78}\text{Al}_{0.22}\text{Mg}_{2.9}\text{Fe}_{0.09}\text{Na}_{0.08}\text{K}_{0.08}\text{O}_{10}(\text{OH})_{2.4}\text{H}_2\text{O}$ (Chahi *et al.*, 1999, Benhammou *et al.*, 2009). At pH 2–12, Ghassoul particles are formed of negatively charged layers responsible via Coulombic attractions of the strong retention of cationic pollutants (Bouna *et al.*, 2010).

This Moroccan clay has been the subject of several recent studies in order to develop new industrial applications. Bejjaoui *et al.* (2010) were interested in the development of cordierite ceramics by mixing andalusite and Ghassoul clay. El Ass *et al.*, (2010, 2011) studied the use of this mineral clay for removal of cationic dyes from aqueous solution.

The main objective of the present study was to evaluate the applicability of Ghassoul clay in removal heavy metals ions (Cadmium and Copper) from aqueous solutions by batch adsorption process. Therefore, the effects of pH, contact time, initial metal 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

Ghassoul 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 (El Ass *et al.*, 2010). The solid sample was parched at 70 °C for 24 h and ground then sieved to pass 140 μm mesh (140 μm mesh was proved an appropriate size in the pre-experiment) before being used as adsorbent.

The reagents used to prepare solutions of metal ions were all extra pure analytical grades. The stock solutions of the metals of 1000 mg L^{-1} were prepared by dissolving weighed

quantities of nitrate salts ($\text{Cd}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$) in twice-distilled water. The pH of solution was adjusted by using 0.1 M (NaOH) and/or 0.1 M (HNO_3). The concentration of Cadmium and Copper were determined using an atom adsorption spectrophotometer (AA300, Perkin Elmer, USA).

2.2 Methods

Batch adsorption experiments were performed on a rotary shaker at 110 rpm using 125 mL capped polyethylene bottles containing 100 mL of solutions and 0.1 g of adsorbent. Experiments were performed at room temperature ($\sim 25^\circ\text{C}$) and at solutions pH, except those in which the effects of temperature and pH were investigated. An adsorbent dose of 1 g/L was kept constant for all of the adsorption experiments. 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 4000 rpm for 10 min and the supernatant was kept for analyses. Various conditions, including the contact time, the pH, the initial solute 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:

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

where C_0 (mg L^{-1}) is the initial concentration, C_e (mg L^{-1}) is the equilibrium concentration 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 adsorption amount onto Ghassoul clay.

Blanks containing no pollutants were used for each series of experiments. Each experimental point was an average of three independent adsorption tests.

3. Results and discussions

3.1 Characterization of the Ghassoul clay

Mineralogical identification of adsorbent was performed by a Siemens D5000 X-ray diffraction instrument with filtered $\text{Cu K}\alpha$ radiation ($n = 1.5418 \text{ \AA}$).

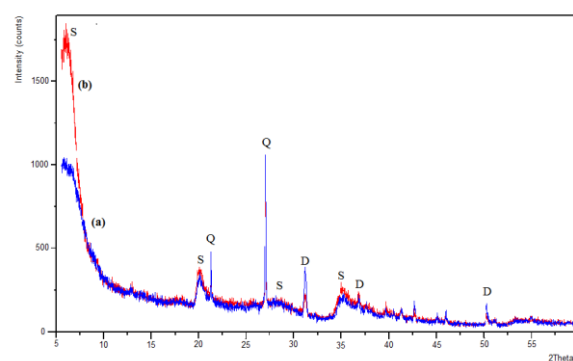


Figure 1. XRD diagrams of (a) the raw sample and (b) the separated fine fraction of Ghassoul clay

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.

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 SiO₂ (58.16 wt.%) and MgO (27.44 wt.%). Al₂O₃ 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).

The surface area of fine mineral fraction, measured by the N₂-BET method, is 137m²/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}=2.1, the same result was found by Bouna *et al.*, (2010) and Benhammou, *et al.*, (2005). The cation exchange capacity is 79 meq/100 g, relatively large, compared to the values for natural stevensite, reported by Faust and Murata, (1953) and Takahashi *et al.*, (1997) to be 37.6 and 41 meq/100 g, respectively. It is noted that the prevalent exchangeable element is Mg²⁺, 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 ₂ O ₃	2.87	4.48
Fe ₂ O ₃	1.44	1.92
MgO	24.64	27.44
CaO	12.13	1.88
Na ₂ O	1.12	0.17
K ₂ O	0.85	1.05
Total	96.36	95.20

3.2 The effect of solution pH

pH is one of the most important factors which control the adsorption capacity of pollutants on clay surfaces. Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface-active sites.

The effect of solution pH on the equilibrium up-take capacity of Ghassoul clay was studied at initial concentrations of 400mg L⁻¹ for Cd(II) and 200 mg L⁻¹ for Cu(II) 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 interactions of cationic metal ions with the negatively charged surface. At the pH interval of the experiments, the surface of Ghassoul clay is predominantly negative, due to silanol (SiOH⁻) and aluminol (AlOH⁻) groups (Stumm, 1997), which is in accordance with the value of the zeta potential (pH_{ZPC} 2.1) for this mineral (Bouna *et al.*, 2010). Similar results were observed using natural kaolinite clay for the adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) (Jiang *et al.*, 2010) and for adsorption of Pb(II) and Cd(II) ions on tripolyphosphate-modified kaolinite clay (Adebowale *et al.*, 2008).

At very low pH, the number of H₃O⁺ ions exceeds that of metal ions by several times and the metal ions can hardly compete with H₃O⁺ ions for the binding sites on the clay adsorbents and thus, electrostatic repulsion occurred between the metal ions (M²⁺) and the edge groups with positive charge (SiOH₂⁺) on the surface as follows:

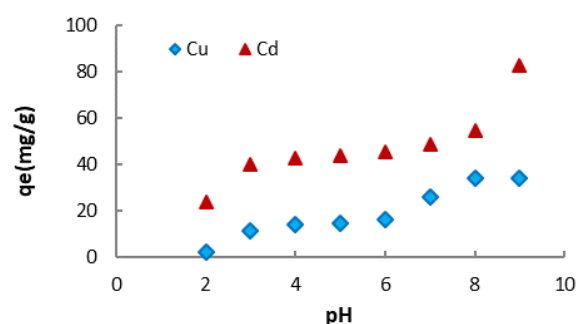
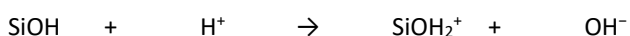
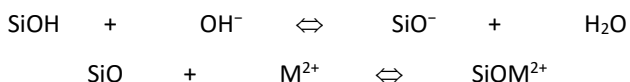


Figure 2. The effect of initial solution pH on the removal of Cd(II) and Cu(II) onto Ghassoul clay

With an increase in pH, the concentration of H₃O⁺ ions decreases and some of the sites become available to the metal ions. As the acidity decreases, more and more H₃O⁺ ions on the clay surface are replaced by metal ions and metal species such as Cd²⁺, Cd(OH)⁺, and Cd(OH)₂ (Lai *et al.*, 2002) and Cu²⁺, Cu(OH)⁺, and Cu₂(OH)₂²⁺ (Bosso and Enzweiler, 2002). This happens at lower pH (~6.0) for Cu(II) (Nuhoglu and Oguz, 2003), while the adsorption could be safely carried out to pH (~9.0) for Cd(II) (Mathialagan and Viraraghavan, 2002). Experiments were not conducted beyond pH 6.0 for Cd(II) and Cu(II) to avoid the precipitation of metal ions.

In an alkaline medium, the surface of Ghassoul clay becomes negatively charged and electrostatic repulsion decreases with raising pH due to reduction of positive charge density on the sorption edges thus resulting in an

increase metal adsorption. This mechanism can be shown as follows:



A similar theory was proposed by several earlier workers for metal adsorption on different adsorbents (Sari *et al.*, 2007).

3.3 Effect of ionic strength

The ionic strength of the solution is one of the factors that control both electrostatic and non-electrostatic interactions between the adsorbate and the adsorbent surface. The influence of ionic strength on the adsorption of Cd(II) and Cu(II) ions was investigated using NaCl and CaCl₂ solutions. It was observed that when ionic strength of both electrolyte increased from 0.01 to 0.1 mol L⁻¹, the total decrease in percentage removal of 400 mg L⁻¹ Cd(II) and 200 mg L⁻¹ Cu(II) was 34.17 and 19.41, respectively, for Ca-electrolyte and 23.87 and 15.33, respectively, for Na-electrolyte. This suggests that with increase in the concentration of chloride anions in metal ion solution, there is a possibility for the formation of uncharged species and negatively charged chloride complexes (MCl₂, MCl₃⁻ and MCl₄²⁻) that will invariably reduce the adsorption capacity of the adsorbent for positively charged cations. It was also observed that the adsorbents show stronger preference for Ca²⁺ (a divalent cation) than for Na⁺ (a monovalent cation) with the resultant effect of a further drop in monolayer adsorption capacities of the adsorbents for the metal ions when Ca-electrolytes were used.

Similar results were found by several earlier workers for metals adsorption on different adsorbents (Jiang *et al.*, 2010, Adebowale *et al.*, 2006, Ozdes *et al.*, 2011).

Adebowale *et al.*, (2006) have reported that the presence of electrolyte (NaCl and CaCl₂) and their increasing concentration reduced the adsorption capacities of both unmodified and p-modified kaolinite clay for the metal ions. They have demonstrated that Ca-electrolytes had more negative effect on the adsorption capacities of the adsorbents than Na-electrolytes. Ca-electrolytes reduced adsorption capacities of the adsorbents for Pb and Cd ions.

The NaCl, KCl, NaNO₃, and Na₂HPO₄ salts were chosen as electrolytes by Ozdes *et al.*, (2011) to investigate the effect of ionic strength on Pb(II) and Cd(II) adsorption onto Turkish illitic clay. They have observed that there was a decrease in the adsorption capacities of clay for Cd(II) and Pb(II) ions with increasing the concentration of electrolytes. These results can be attributed by these reasons: (i) the competition between cations of the salts and metal ions for the active adsorption sites of clay (ii) the active adsorption sites of the clay may be blocked in the presence of these salts.

3.4 Adsorption isotherms and equilibrium

3.4.1 Effects of initial metal ions concentration

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 for Cd(II) and in the range of 25–400 mg L⁻¹ for Cu(II). 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 Cd(II) and Cu(II) increased from 11.5 to 73,55 mg g⁻¹ and from 5.93 to 15,19 mg g⁻¹ whereas adsorption percentage decreased from 92 % to 36.77 % and from 94.83 % to 15.75 %, respectively.

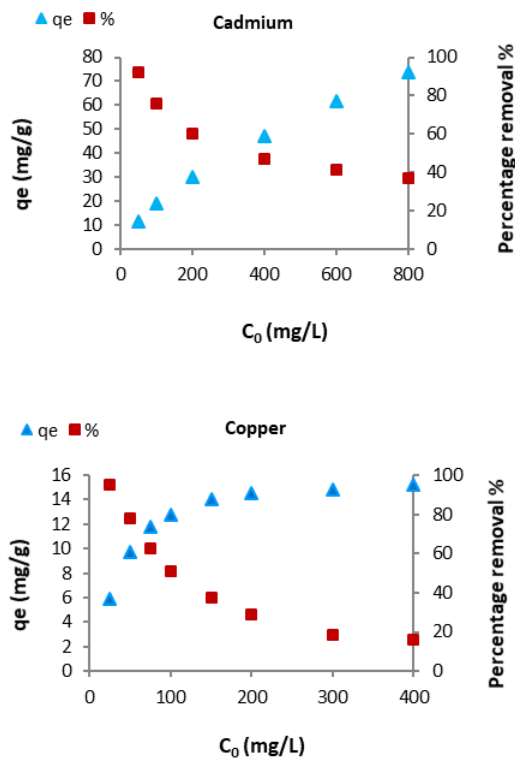


Figure 3. Effect of initial metal concentration on the adsorption of Cd(II) and Cu(II) onto Ghassoul clay

Similar observations for metal ions uptake on different adsorbents have been reported earlier by Ozdes *et al.*, (2011) and Sdiri *et al.*, (2011). It appears that, at low Cd(II) and Cu(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 (Bhattacharyya and Gupta, 2011). 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.

3.4.2 Adsorption isotherms

Generally, adsorption isotherms provide vital information in optimizing the use of adsorbents. The two most commonly employed models are the Langmuir and Freundlich isotherms, which have shown to be suitable for

describing short-term and mono-component adsorption of metal ions by different materials.

The physical and mathematical explanations of the adsorption and interpretation of the monolayer adsorption isotherms measured on homogeneous surfaces was started by Langmuir in 1916. This theory is based on the dynamic character of adsorption. At equilibrium, the numbers of adsorbed and desorbed molecules in unit time on unit surface are equal. Langmuir's theory does not take the lateral interactions and horizontal mobility of the adsorbed molecules into account (Langmuir, 1918). The Langmuir equation can be written in the form:

$$q_e = q_m \left[\frac{K_L \cdot C_e}{1 + K_L \cdot C_e} \right]$$

where C_e is the equilibrium concentration of the solution (mol L^{-1}), q_e the amount of adsorbed per unit mass of adsorbent (mol g^{-1}), and q_m is the monolayer capacity (mol g^{-1}); K_L is the constant related to the energy of adsorption (L mol^{-1}). The steepness of the isotherm is determined by K_L . K_L can be considered to be a measure of the affinity of the adsorbate for the surface. The value of q_m is the upper limit for q_e and represents the maximum adsorption of adsorbate determined by the number of reactive surface adsorption sites. The parameters q_m and K can be calculated from adsorption data by converting the Langmuir equation into the linear form (Langmuir *et al.*, 1918):

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

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 (Yang, 1998).

The Freundlich equation has the form:

$$q_e = K_F \cdot C_e^{1/n}$$

The linear form of Freundlich equation obtained, by the logarithmic linearization of the 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 analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes.

Fig. 4 show the Langmuir ($1/q_e$ versus $1/C_e$) and Freundlich ($\ln q_e$ versus $\ln C_e$) plots, respectively, for the removal of the

Cd(II) and Cu(II) onto Ghassoul clay. 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 (Jiang *et al.*, 2010).

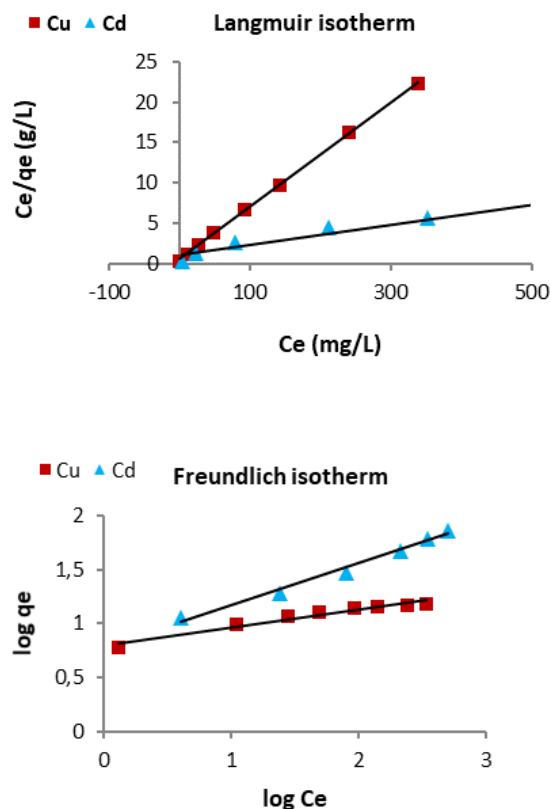


Figure 4. Adsorption isotherm models of Cd(II) and Cu(II) adsorption onto Ghassoul clay

The calculated values of the constants in Langmuir and Freundlich equations and the regression correlation coefficients (R^2) are given in Table 2. The Freundlich coefficient, n obtained in the present study for both metal ions are greater than unity, n values between 2.5 and 6 indicate that the adsorption of Cd(II) and Cu(II) onto Ghassoul clay under studied conditions was favorable (Unuabonah *et al.*, 2008).

According to the Langmuir isotherm model, the maximum monolayer adsorption capacity of Ghassoul clay for Cd(II) was found to be higher than for Cu(II) ions indicating that Ghassoul clay showed stronger preference for Cd(II) than for Cu(II). The monolayer adsorption capacity was found as 86.34 and 15.41 mg g^{-1} for Cd(II) and Cu(II) respectively. Jiang *et al.*, (2010) and Lv *et al.*, (2005) have reported the same affinity order: Cd(II) > Cu(II).

Table 2. Langmuir and Freundlich isotherm parameters for the adsorption of Cd(II) and Cu(II) onto Ghassoul clay.

	Langmuir constants			Freundlich constants			
	q_m (exp) (mg g ⁻¹)	q_m (cal) (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2	n	K_F (mg g ⁻¹)	R^2
Cd(II)	73.55	86.34	0.011	93.73	2.55	5.86	98.46
Cu(II)	15.19	15.41	0.136	99.94	5.90	11.07	95.26

3.5 Adsorption kinetics

3.5.1 Effect of contact time and initial concentration

The effect of contact time on the sorption of metal ions was analyzed kinetically over a range of 5–180 min. Adsorption was carried out at initial concentrations range of 200–600 mg L⁻¹ and 100–400 mg L⁻¹ for Cd(II) and Cu(II), respectively. As can be seen in Fig. 5, the equilibrium adsorption was very fast and maximum uptake was reached within 30 min, thereafter, the amount of adsorption remained almost constant. Increasing concentration gradient, acts as increasing driving force, and in turn leads to an increasing equilibrium sorption until sorbent saturation is achieved. The same results were reported by other investigators (Sdiri *et al.*, 2011, Potgieter *et al.*, 2006), who found that the equilibrium time clays was short.

3.5.2 Kinetics studies

The experimental data were fitted through three kinetics models including pseudo-first order, pseudo-second order kinetic models and intraparticle diffusion models.

The pseudo first-order equation (Lagergren’s equation) describes adsorption in solid–liquid systems based on the sorption capacity of solids (Lagergren, 1898, Ho, 2006) The Lagergren's first-order reaction model is expressed as follows:

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

where q_t is the amount of adsorption at time t (mg g⁻¹); k_1 is 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 is based on the assumption of chemisorption of the adsorbate on the adsorbent. This model as described by Ho, (2006) 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.

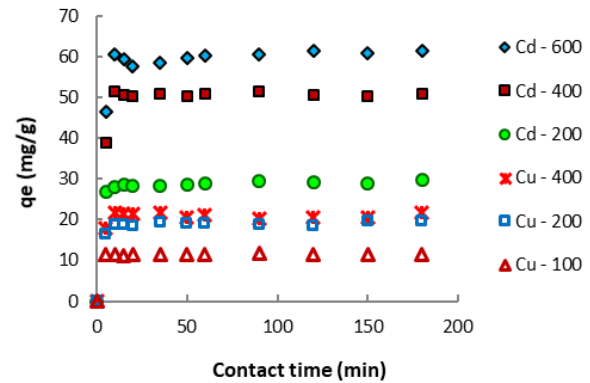


Figure 5. Effect of contact time on the adsorption of various concentrations of Cd(II) and Cu(II)

The form of the intraparticle diffusion model described by Weber and Morris, (1963) is:

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

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⁻¹) is the intercept, which represents the thickness of the boundary layer (Furusawa and Smith, 1974).

By testing the plots of $\log(q_e - q_t)$ versus t and (t/q_t) versus t (Fig. 6), for the adsorption of Cd(II) and Cu(II) onto Ghassoul clay at various concentrations, the rate constants k_1 and k_2 , and correlation coefficients can be calculated, the results are shown in Table 3.

As seen from Table 3, 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 Cd(II) and Cu(II) adsorption process appeared to be controlled by the chemical process (Chen and Wang, 2007). Similar results were found by Sdiri *et al.*, (2011) who studied the adsorptive capacity of montmorillonitic and calcareous clays on the removal of several heavy metals and by Jiang *et al.*, (2010) who studied the removal of Pb(II), Cd(II), Ni(II) and Cu(II) ions onto natural clay.

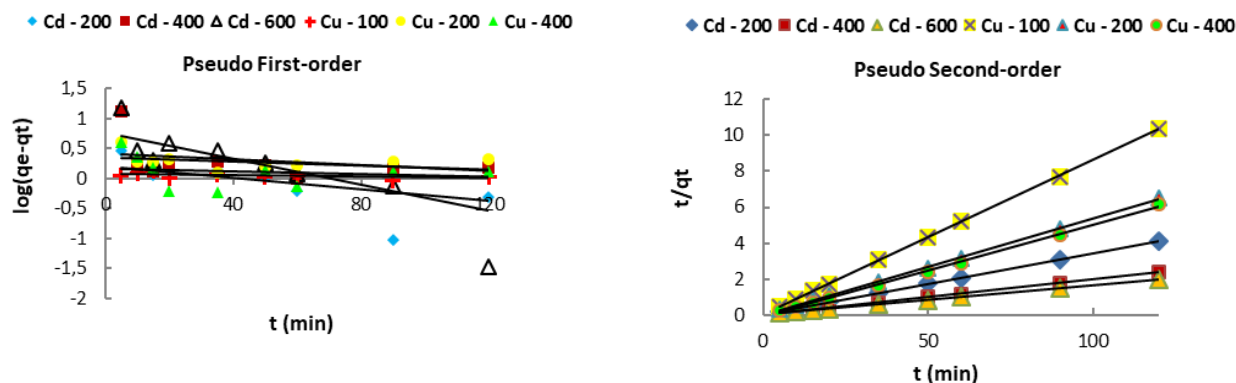


Figure 6. Pseudo First-order and Pseudo second-order plots for the adsorption of Cd(II) and C(II) at various concentrations

Table 3. Kinetics parameters for the adsorption of Cd(II) and Cu(II) onto Ghassoul clay at various concentrations.

	Cd (mg L ⁻¹)			Cu (mg L ⁻¹)		
	200	400	600	100	200	400
$q_{e(\text{exp})}$ (mg g ⁻¹)	29,0	50,9	61,3	11.6	19.5	21.7
First-order kinetics model						
$k_1 \cdot 10^2$ (min ⁻¹)	-1,19	-0,55	-2,46	-0.11	-0.41	0.27
$q_{e(\text{cal})}$ (mg g ⁻¹)	1,87	2,54	5,63	1.17	2.27	1.60
R^2	39,29	14,47	59,49	27.6	28.5	29.0
Pseudo-second-order model						
$q_{e(\text{cal})}$ (mg g ⁻¹)	29,4	50,7	61,7	11.6	19.4	20.9
$k_2 \cdot 10^2$ (g mg ⁻¹ min ⁻¹)	3,66	6,16	1,33	39.1	4.02	8.69
R^2	99,9	99,9	99,9	100	99.8	99.6

According to Weber and Morris model, the plots of q_t versus $t^{1/2}$ (Fig. 7), for the adsorption of Cd(II) and C(II) onto Ghassoul clay at various concentrations, show that intraparticle diffusion occurred in two stages for both the metal ions.

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.

Table 4. Kinetics parameters for the adsorption of Cd(II) and Cu(II) onto Ghassoul clay at various concentrations.

	Cd (mg L ⁻¹)			Cu (mg L ⁻¹)		
	200	400	600	100	200	400
K_{1d} (mg g ⁻¹ min ^{-1/2})	2,51	13,55	15,25	1,21	2,35	3,09
C_1	10,09	8,47	12,28	7,54	11,3	11,02
R^2	1	1	1	1	1	1
K_{2d} (mg g ⁻¹ min ^{-1/2})	0,19	0,03	0,42	0,034	0,02	0,161
C_2	17,28	50,37	56,55	11,27	18,9	22,12
R^2	72,75	69,4	84,57	87,71	79,4	71,68

For the first sharper portion, i.e. from 0 to 10 min, its rates, k_{1d} (2.51–15.25 mg g⁻¹ min^{-1/2} for Cd(II) and 1.209–3.097 mg g⁻¹ min^{-1/2} for Cu(II)), shows that the adsorption process is very fast. The second portion with k_{2d} (0.19–0.42 mg g⁻¹ min^{-1/2} for Cd(II) and 0.034–0.161 mg g⁻¹ min^{-1/2} for Cu(II)) 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 Cd(II) and Cu(II) onto Ghassoul clay.

The same type results were also given in some works (Sari *et al.*, 2007, Ozdes *et al.*, 2011, Chen *et al.*, 2007).

The intraparticle rate constants for the first phase (k_{1d}) and second phase (k_{2d}) and C parameters were given in Table 4.

3.6 Thermodynamic studies

3.6.1 Effect of temperature

The removal efficiency of metal ions was investigated in the temperature range of 25–45 °C at initial concentrations of 400 and 200 mg L⁻¹ for Cd(II) and Cu(II) respectively (Table 5).

The adsorption efficiency increased from 61.87 to 69.88 mg g⁻¹ for Cd(II) and from 18.86 to 22.03 mg g⁻¹ for Cu(II), when the temperature was increased from 25 to 45 °C, indicating that the adsorption process for both metal ions 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 (Adebowale *et al.*, 2008). Similar observations have been reported earlier by Bhattacharyya and Gupta, (2011) for removal of Cu(II) by natural and acid-activated clays.

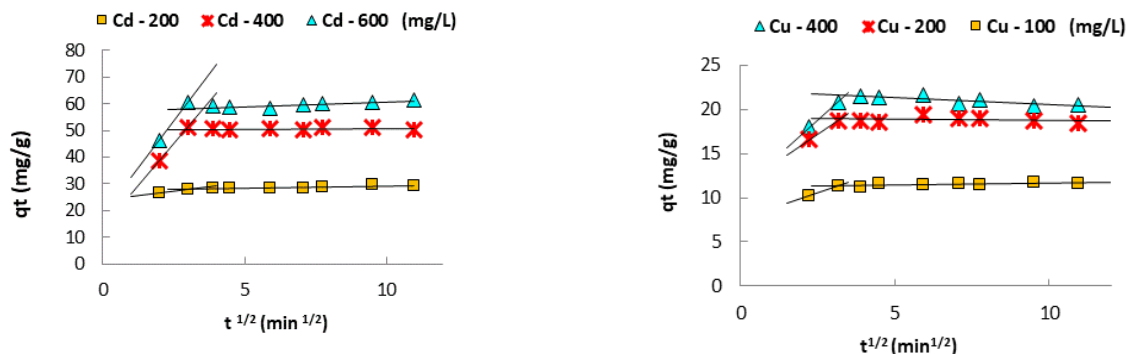


Figure 7. Intra-particle diffusion plots for the adsorption of Cd(II) and C(II) onto Ghassoul clay at various concentrations

Table 5. Adsorptive capability of metal ions onto Ghassoul clay at different temperatures

	Temperature °C		
	25	35	45
Cd	61.87	64.07	69.88
Cu	18.86	20.43	22.03

3.6.2 Thermodynamic parameters

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 (Ramesh *et al.*, 2005):

$$\Delta G = RT \ln K$$

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

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

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 pollutant 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.

Thermodynamic parameters of the adsorption of metal ions onto Ghassoul clay are shown in Table 6. Gibbs free energy (ΔG) was calculated using lnK values for different temperatures (25, 35 and 45°C). ΔG , values obtained were all small and positive which suggests that the adsorption of Cd(II) and Cu(II) onto Ghassoul clay require some small amount of energy to convert reactants into products (Scheckel and Donald, 2001). 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 , (1.715 and 3.691 kJ mol⁻¹ for Cd(II) and Cu(II) respectively), suggests that the adsorption reactions of Cd(II) and Cu(II) onto Ghassoul clay adsorbents are endothermic in nature meaning that increasing temperature will favour the adsorption of both metals. Endothermic adsorption of Cd(II) and Cu(II) ions has been observed by Bhattacharyya and Gupta, (2011) and Adebowale *et al.*, (2008). Data of ΔS obtained for the adsorption of metal ions onto Ghassoul clay are shown in Table 6. It was found that adsorption of Cd(II) and Cu(II) has a negative ΔS (-20,22 and -33,74 J mol⁻¹ respectively). Other investigators were reported a value range of negative ΔS for the adsorption of heavy metals onto clays (Unuabonah *et al.*, 2008, Gupta *et al.*, 2004). The negative values obtained indicate a stable configuration of the metal ion on the Ghassoul clay adsorbent surface (Gupta and Bhattacharyya, 2006).

Table 6. Thermodynamic parameters for the adsorption of Cd(II) and Cu(II) onto Ghassoul clay at various temperatures

	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹)	ΔG_{298} (kJ mol ⁻¹)	ΔG_{308} (kJ mol ⁻¹)	ΔG_{318} (kJ mol ⁻¹)
Cu	3.691	-33,74	13.746	14.084	14.421
Cd	1.715	-20,217	7.740	7.942	8.144

4. Conclusion

In the present work, Moroccan clay, without any previous activation treatment, has identified as a potentially attractive adsorbent for the treatment of metal ions in

aqueous solutions. The empirical values of the adsorption showed that Langmuir and Freundlich isotherm models were more suitable for modeling the adsorption of heavy metals. It was in conformity with the existence of different

types of possible adsorption sites on clay surface with considerable difference in energy. The adsorption capacity, determined with the Langmuir isotherm, was found as 86.34 and 15.41 mg g⁻¹ for Cd(II) and Cu(II) respectively. Experimental kinetic data indicated that 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. The high adsorption ability, wide pH range and thermodynamic stability of Ghassoul clay revealed that this Moroccan clay can be used as low-cost alternative adsorbents for removal of heavy metals in industrial wastewater.

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