Kinetic, equilibrium and thermodynamic studies for the removal of lead ions from aqueous solutions by using low cost adsorbents: a comparative study

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Abstract: *Adsorption and desorption of Pb(II) on two natural minerals (natural calcite and eggshell) were studied. The ability of the natural materials in removal of Pb(II) from aqueous solutions had been examined in a batch adsorption process with respect to several experimental conditions including initial solution pH, contact time, initial metal ion concentration, temperature and adsorbent concentration. The absorption isotherms showed that the adsorption capacity of substrates varied as follows: natural calcite>eggshell. Desorption kinetics show a complete hysteresis testify to the irreversibility of the bonds formed between Pb and the substrates. Thus, the uptake of lead was reproduced by a cation exchange model and by a surface complexation model for the mineral-aqueous solution interface. The thermodynamic study demonstrated that lead adsorption is endothermic for both adsorbents. It is spontaneous and non-spontaneous for natural calcite and eggshell, respectively. All these results indicate that eggshell and natural calcite could be employed as efficient low-cost and eco-friendly adsorbents for lead removal from industrial wastewaters.*
Keywords: Eggshell; lead; natural calcite; sorption-desorption; thermodynamic.

I.   Introduction

Recently, the pollution of heavy metals in various environmental has been of great interest. Owing to their existence in certain concentrations in water, these metals may constitute danger to health (Mirzaeiet *al.* 2011). Lead is one of the most toxic metals from the hazardous heavy metals list. It is widely used in many industrial purposes, including storage battery manufacturing, painting pigment, fuels, photographic materials, coatings, automotiveindustries and hundreds of other products (Lalhruaitluanga et *al.* 2010). Acute lead poisoning usually affects the gastrointestinal track or the nervous system, and sometimes both(Goldstein 1990). World Health Organization (WHO) has set the maximum contaminant level (MCL) of lead in drinking water at $15 \, \mu g \, L^{-1}$.

Several methods are available to remove lead species from wastewater. These include ion exchange (Ahmed et *al.* 1998), precipitation (Eren 2009), coagulation–flocculation (Matlock *et al.* 2002) and flotation (Ghazy et *a*l. 2008). Among them, adsorption technique is found to be the most effective treatment process with selection of a proper adsorbent (Eloussaief & Benzina2010). The significant advantages of the adsorption technique are; high efficiency in removing very low levels of heavy metals from dilute solutions, easy handling, high selectivity, lower operating cost, minimization of chemical or biological sludge, and regeneration of adsorbent (Ahalya et *al.* 2003).

Materials composed mostly of calcite have been tested (Albadarin et *al.* 2012). Calcite is one of the important biominerals and had already been studied for heavy metal ions removal (Al-Degs et *al.* 2006). It is well known that calcite is one of the cheapest materials in nature and harmless to humans. $CaCO_3$ with improved removal performance has become a hotspot of this field. However, the low efficiency on heavy metal adsorption and long time for equilibrium adsorptions significantly limited the practical applications of $CaCO_3$ in water treatment. Moreover, this method is relatively inexpensive compared to other treatment techniques. Also, the usage of eggshell as a biosorbent can be viewed from two standpoints, first, to utilize waste eggshells and second, to solve metal contamination (Daraei et *al.* 2014; Zheng et al. 2007). Eggshells are considered to be of low or no economic value and often dumped as organic wastes in landfills. Hence, efficient utilization of eggshells as a metal biosorbent will be beneficial to egg-based industries to decrease their disposal costs. The potential of eggshell to adsorb heavy metals arises from its chemical composition, the main component is calcite

(94%), which is an effective sorbent of heavy metals. The residual components include the $MgCO_3$ (1%), the $Ca_3(PO_4)_2$ (1%) and an organic matter (4%) (Pramanpol & Nitayapat2006).Several researchers have been worked on synthetic solutions with low initial concentrations of pollutants. In the present study, we have tested synthetic solutions with high initial concentrations of lead. However, the majority of these studies have not characterized the natural adsorbents in detail and missed the investigation on the involved mechanisms.

In the present study, divalent lead cations [Pb(II)] are used as model solute owing to its commercial importance and high toxicity. Our work is aimed to: (i) evaluate and compare the adsorption capacity of two low cost natural adsorbents: eggshell and calcite on lead removal from aqueous solutions by batch adsorption process. Eggshell and calcite were used without any pretreatment. This is one of the significant features of this study with respect to decrease in the cost of the adsorption process, (ii) to contribute to the establishment of a consistent thermodynamic and kinetic data base for solution-mineral interactions in the calcite H_2O-Pb(II) and eggshell-H_2O-Pb(II), and finally, (iii) to gain a better understanding of the possible mechanisms involved in the adsorption of lead by these natural adsorbents.

II. Methods
Preparation of lead solutions and analytical methods
The stock solution of Pb(II) ions was prepared by dissolving required amount of $Pb(NO_3)_2$ (lead nitrate provided by Riedel de Haien) in distilled water. A stock lead solution of 1.000 mg L^{-1} was prepared and used throughout this study. The lead concentrations were determined by flame atomic absorption spectrophotometer (analytic jena novAA 350) by using a cathode lamp, a wavelength of 283.8 nm, an air/acetylene flame.

Preparation of the adsorbents
The eggshells of chickens used in this study were collected from a restaurant located in Tunis. The collected eggshells were washed with tap water several times and after with distilled water. Then they were dried at the ambient temperature for several days. The dried eggshells were crushed powdered to small grain. The residue was washed with distilled water several times and dried at 60°C for 24 h. The residue was finely chopped and screened through a set of sieves to get the target geometrical size. The resulting material was stored in glass bottle for further use without any pretreatment. The natural calcite was coming from a large private marble processing unit and was used in the experiment without any prior treatment.

Adsorbent characterization
The chemical composition of the eggshell and natural calcite samples was obtained by X-ray diffration (XRD) using a Bruker D8 Advance diffractometer equipped with CuK_α (λ = 1.541) X-rays. The surface morphology and elemental composition of the samples were captured by scanning electron microscopy (JEOL, JSM 5400LV). The specific surface area and pore volume of these samples were obtained using a Quantachrome Autosorb1 Sorptiometer BET surface area analyzer. Moreover, the functional groups present in the solid samples were identified using Fourier transform-infrared spectrometry (FTIR) with the KBr disk method (Perkin, Elmer, UK). The particle size distribution was determined using a Microtrac S3500 laser granulometer. The pH of zero-point charge (pH_{ZPC}) is an essential parameter for the comprehension of mechanisms involved in lead adsorption onto the used adsorbents. This parameter was obtained according to the methodology of Wan Ngah and Hanafiah (Wan Ngah&Hanafiah2008) by shaking with a Varimag-poly15 magnetic stirrer (Thermo Fischer Scientific, USA) at 400 rpm for 24 h, 0.2 g of natural calcite or eggshell in 100 mL aqueous solution of NaCl (0.1 M) at different values of initial pH of 2, 4, 6, 8, 10, and 12.

Adsorption equilibrium experiments
Adsorption experiments were carried at different solution pH, adsorbent dosage, contact time, initial lead concentration and temperature in 100 mL Erlenmeyer flasks. The effect of solution pH on the adsorption of Pb(II) onto eggshell and natural calcite were investigated by separately mixing 1 g for natural adsorbents (eggshell and natural calcite) in 100 mL sample having an initial concentration of 50 mg L^{-1} at ambient temperature. The initial pH of the solutions was adjusted to 5.30 ± 0.1 by adding 1 M HCl and 1 M NaOH. The agitation speed was fixed at 400 rpm. The effect of adsorbent dosage on the adsorption of metal ions was determined by separately mixing natural calcite and eggshell with a metal ions ranged concentration of 0.003–3g L^{-1} in 100mL samples with an initial metal ions concentration of 50 mg L^{-1}. The effect of contact time was studied between 1 min and 180 min whereas the effect of initial metal ions concentration was determined in the range of 50–250 mg L^{-1}. After adsorption process, the adsorbents were filtered using membrane filters with pore diameter of 0.45 μm and the filtrates were analyzed for total Pb(II) levels by a flame atomic absorption spectrometer, FAAS (novAA 350). In this study, all experiments were performed in triplicate, and the average values were recorded.

The quantity of lead adsorbed at equilibrium (q_e, mg g^{-1}) was calculated by the following expression Equation (1):

$$q_e = (C_0 - C_e) \, \frac{V}{m} (1)$$

Where C_0 (mg L^{-1}) is the initial metal ion concentration, C_e (mg L^{-1}) is the equilibrium of metal concentration, V (L) is the volume of solution, m (g) is the mass of adsorbent.
For the calculation of lead adsorption percentage R (%), the following expression was used Equation (2):

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Desorption study

After adsorption, the lead desorption from preloaded eggshell and natural calcite at concentrations of 50 mg L^{-1} was performed using calcium chloride solutions (CaCl$_2$). During these experiments, 0.5 g of the lead-loaded adsorbents was shaken in 50 mL of distilled water at different initial pH values of 2, 3, 4, and 5, adjusted with nitric acid (analytical grade) at 20°C for 2 h. As for adsorption studies, the aqueous phase of the triplicate samples were separated from the solid ones by centrifugation before analysis by a flame atomic absorption spectrometer, FAAS (novAA 350). The desorbed leaded amounts q_d (mg g^{-1}) and the corresponding desorption yields were calculated as follows:

$$q_d = \frac{C_d}{m} \times V (3)$$

$$\% \, \text{Desorption} = \frac{q_d}{q_e} \times 100 (4)$$

Where C_d is the Pb desorbed concentration (mg L^{-1}) and q_e is the adsorbed amount of Pb at equilibrium (mg g^{-1}).

III. Results and Discussion

Characteristics of the adsorbents

In this study, some physical and chemical characterization of the adsorbents was performed so that it could help in the interpretation of the results of the batch adsorption studies. These characteristics such as surface area, pore size distribution, particle size distribution, porosity and density of the adsorbents are presented in Table 1. The particle size distribution of natural calcite and eggshell shows that they are heterogeneous porous media since uniformity coefficient was higher than 2 (Table 1). The median pore diameter (d_{50})of eggshell and natural calcite is 212.30 µm and 12.54 µm, respectively. This range between 0.1 µm and 2.5 nm indicates that both materials are mesoporous adsorbents and that they seem to have larger pore diameters than conventional adsorbents (Lorenc-Grabowska & Gryglewicz 2007). The pH$_{ZPC}$ values are 8.38 and 8.20 for natural calcite and for eggshell, respectively. The BET surface area, pore volume and pore size obtained for natural calcite and eggshell are summarized in Table 1. The BET surface area of natural calcite is 12.13 m^2 g^{-1} twice larger than the eggshell with a surface area of 5.24 m^2 g^{-1}. In addition, the pore volume is 0.00363 cm^3 g^{-1} for eggshell and 0.0069 cm^3 g^{-1} for natural calcite.

Table 1: Properties of the used adsorbents (d_x[a]: mesh diameter that allows x% of the adsorbent to pass through, UC[b]: uniformity coefficient: ratio of d_{90}/d_{10}).

Materials	Natural calcite	Eggshell
Grains size distribution		
d_{10}[a] (µm)	2.191	17.70
d_{50}[a] (µm)	12.54	212.30
d_{90}[a] (µm)	15.57	291.2
UC[b]	7.106	16.45
pH$_{ZPC}$	8.38	8.20
Pore structure		
BET surface area (m^2 g^{-1})	12.13	5.24
Pore volume (cm^3 g^{-1})	0.0069	0.00363

FTIR spectroscopy, which could provide some useful information on the structure and conformation of molecules, was employed to investigate the existing state of adsorbents used. The IR spectra of natural calcite and eggshell are shown in Figure1.
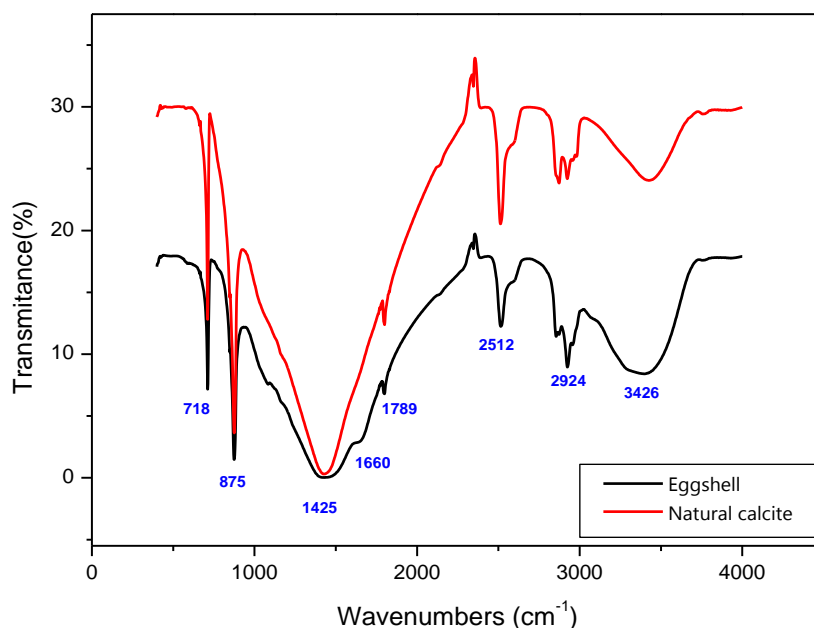

Figure 1. FTIR spectrum of natural calcite and eggshell.

The IR spectrum of natural calcite is well known, with the most intense peak around 1425 cm^{-1}.It can be seen that the adsorbents have vibrations bands at 2924–2872 cm^{-1}, corresponding to the vibration mode of C–H of stearic acid, and also at 718 and 875 cm^{-1} corresponding to an out plane bending and asymmetrical stretching vibration peaks of O-C-O, respectively. IR spectra of natural calcite and eggshell are very similar, but peaks displayed slight shift. Eggshell has an additional low band at 1660 cm^{-1} caused by the C=O stretching vibrations which can be used to differentiate the two materials. IR spectra of the adsorbents used are in agreement with the calcite characteristic vibrations. The X-ray diffraction spectrum of the eggshell and natural calcite were explored in Figure 2 which shows that the natural $CaCO_3$ and eggshell belongs to the calcite Rhombohedral structural type (00-047-1743) and (01-089-1304) respectively. The studied sample diffractions exhibit three characteristic peaks of calcite which localized with 2θ angles of 29.39, 47.50 and 48.49°, corresponding to d-spacing of 3.03, 1.91 and 1.87 respectively. Other peaks from the calcite plane can be observed with minor intensity. This spectrum confirms the presence of calcium carbonate, which represent the main characteristic peak obtained with the XRD for eggshell powder.
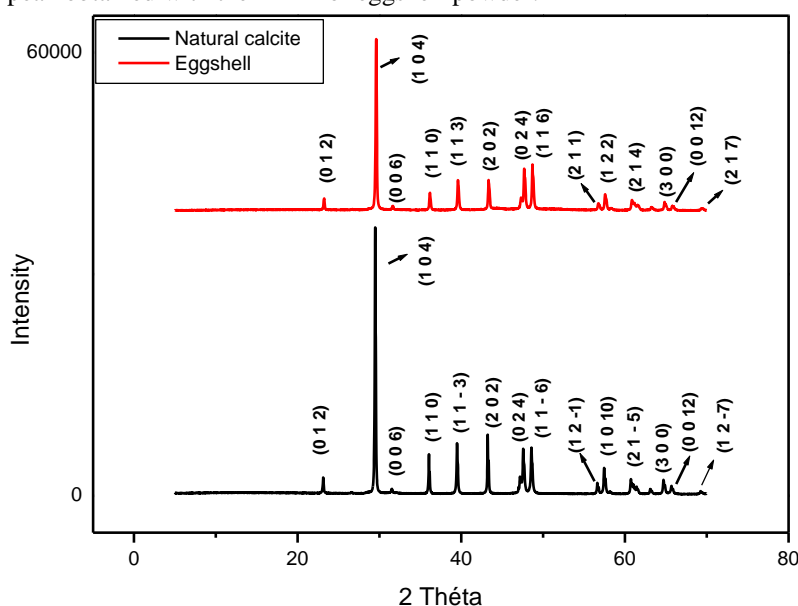

Figure2. XRD patterns of natural calcite and eggshell.

The surface morphology of the adsorbents was examined by scanning electron microscope (SEM). The SEM images from the natural calcite and eggshell are shown in Figure 3 which shows that the morphological aspects of the two adsorbents presented irregular agglomerate particles. According to micrographs, it could be seen that the surface of natural calcite and eggshell have a heterogeneous surface structure. In addition, the natural calcite particles present clearly higher surface and certainly higher porosity than eggshell particles according to results obtained for porosity analysis.
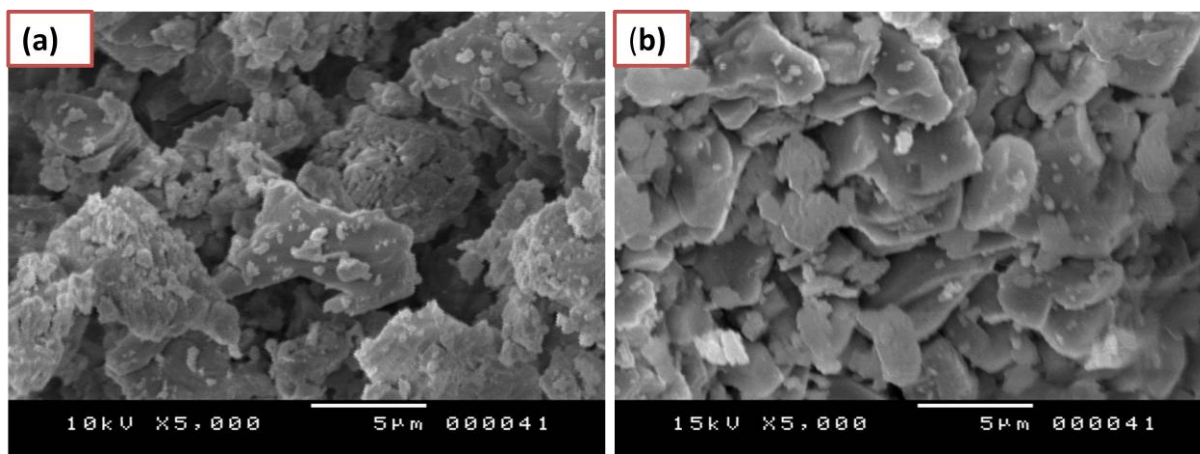

Figure3. SEM images of eggshell (a) and natural calcite (b) at 5µm.

Effect of pH on lead sorption

It seems that pH is the most significant parameter that affects the sorption phenomenon because it affects the sorbent surface charge and the chemistry form of the metal, as well as the physico-chemical conditions and the hydrolysis of the metal (Lopez et *al.* 2000). It has been numerously reported that at acid pH (pH<5), Pb^{2+} ions are the leading species, the more dominating. At higher pH (pH>5), solubility of Pb^{2+} ions decreases (Bradl 2004). At 6< pH<10, Pb^{2+} undergoes hydrolysis to $Pb(OH)^{+}$. At pH=9, solid lead hydroxide $Pb(OH)_2$ is thermodynamically the most stable phase, while $Pb(OH)_3^{-}$ and $Pb(OH)_4^{2-}$ are the predominant species at pH>11. Hence the effects of initial pH on the removal of Pb^{2+} ion were studied with initial Pb^{2+} concentration of 50 mg L^{-1} at concentration of sorbent of 1 g L^{-1} for eggshell and natural calcite, respectively, by varying the pH of the solutions over a range of 2.5–6.

Experiments were not conducted beyond pH 6 owing to lead hydroxide precipitation (Ghazy & Ragab 2007). In the examined pH range of 2.5–6, no precipitation of lead was observed in control experiments. Figure 4 shows that the percentage removal of lead ion increase with increase of pH, to reach a maximum at pH=5, reaching a maximum removal value of 100%. At lower acid pH (2.5 and 3), the experimental results (Fig. 4) showed relatively low Pb(II) removal by the eggshell and natural calcite. This behavior low lead removal may be attributed to: (i) the elevated concentration of protons that will compete with lead cations on the surface sorbent active sites and hence reduce their adsorption; (ii) the dissolution of $CaCO_3$, the principal constituent of the two adsorbents which lowers the adsorption. At higher acid pH (4–6), the important removal of lead in the range can be attributed to the competitive effect (H_3O^{+} vs. Pb (II)) which becomes weaker, increasing the adsorption of Pb(II). Similar results were also reported for Pb(II) adsorption onto eggshell (Vijayaraghavan & Umid 2012) and for Pb(II) adsorption onto powdered marble (Ghazy &Ragab2007). Despite that calcite is the principal component of both sorbents, there is a difference between their Pb (II) sorption capacities versus pH. This may be explained by the fact that eggshells are composed of layers of calcite ($CaCO_3$), containing embedded proteins that make eggshells less prone to dissolution compared to calcite alone (Ahmed et *al.* 2005).
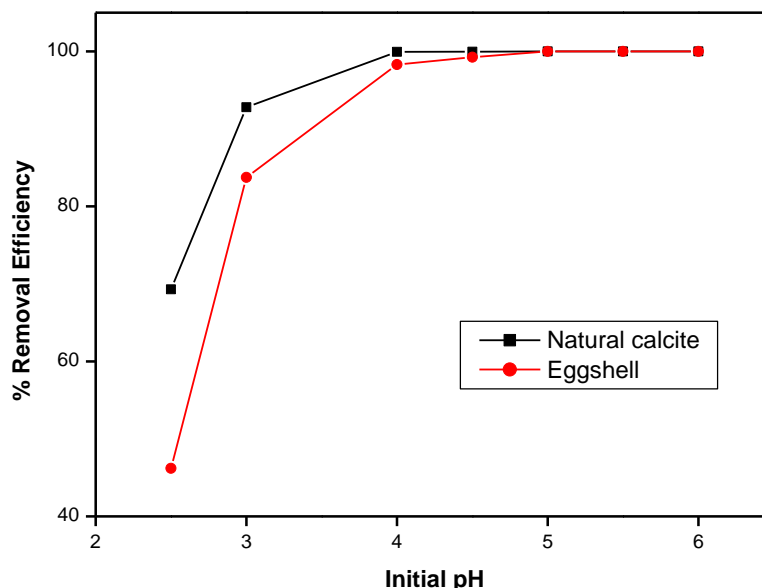
Figure 4. Effect of initial aqueous pH on lead adsorption onto eggshell and natural calcite ($C_0 = 50$ mg L^{-1}, dose = 1 g L^{-1}, contact time = 3 h, temperature = 20 ± 2°C).

Effect of contact time on lead sorption and kinetics models

In order to determine the required adsorption equilibrium time of lead onto eggshell and natural calcite as well as the probable involved mechanisms, a kinetic study was elaborated for contact times varying from 1 to 40 min at an initial lead concentration of 50 mg $L^{-1}$for both tested adsorbents. The adsorption capacity and the time required to reach the equilibrium are indicators of the absorbate transfer kinetics from the liquid phase to the adsorbent surface.

As illustrated in Figure 5, experimental results showed that lead adsorption process is clearly time-dependent. Initially, adsorption of the lead ions was fast and about 99.28% and 98.08% of total uptake capacity was achieved in first 16 min for eggshell and natural calcite, respectively. It was due to high initial concentration of lead ions and empty metal binding sites of adsorbents. After the contact time of 20 min, there was no significant increase in the adsorption capacity because of the equilibrium between the aqueous and solid phase. Therefore, the optimum contact time was selected as 20 min for further experiments. This result is important because the absorbent used in this study look a lesser time to reach equilibrium when compared to most adsorption studies reported in literature (Ahmad et *al.* 2014).
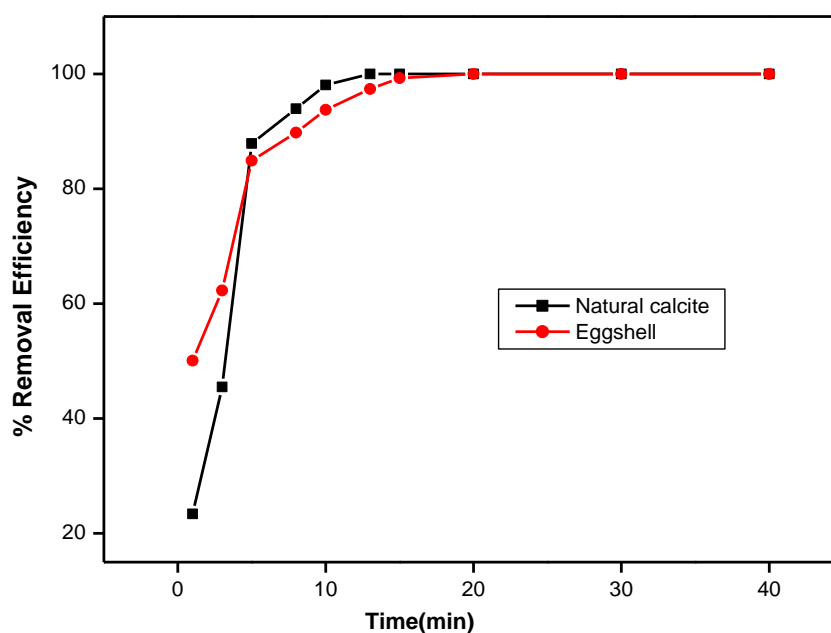

Figure5. Effect of contact time on lead removal ($C_0 = 50$ mg L^{-1}, pH 5.3, dose = 1 g L^{-1}, temperature = 20 ± 2°C)

In order to investigate the kinetics models of Pb(II) ions adsorption onto eggshell and natural calcite, the linear pseudo first order and pseudo-second order kinetics models were tested to fit the experimental data (Ho 2006; Lagergren et *al.* 1898).

The pseudo-first-order model can be expressed as Equation (5):

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \quad (5)$$

Where q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium phase and at time t (min) respectively, K_1 (min^{-1}) is the equilibrium rate constant of Lagargren model. The value of K_1 can be determined from the slope and intercept of the diagrams of $\log(q_e-q_t)$ versus t.

The pseudo-second-order rate is given by Equation (6):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where K_2 (g mg^{-1} min^{-1}) is the rate constant for a pseudo-second order model. The pseudo-second order kinetic model constants K_2 and $q_{e,cal}$ values were determined from the intercept and slope of the plot of t/q_t versus t.

Figure 6 represents the comparison between experimental data with the second order model for eggshell and natural calcite. The corresponding parameters are summarized in Table 2. For eggshell, it was observed that in Figure 6, a good linear plot of t/q_t versus t was presented and the regression coefficient (R^2 = 0.999) was close to 1. As it is shown in table 2, the difference between the calculated value (q_e=2.589 mg g^{-1}) and the experimental value (q_e= 2.4822 mg g^{-1}) was very small in contrast to the correlation coefficient. Also, the trend obtained with the pseudo first-order model is strongly different from the experimental curve. Moreover, a large difference of equilibrium adsorption capacity (q_e) between the experimental and calculation was observed, indicating a poor pseudo-first-order fit to the experimental data (Table 2). Thus, a better correlation between experimental and simulated data and suggest that the pseudo-second order model describe accurately Pb(II) adsorption on eggshell.
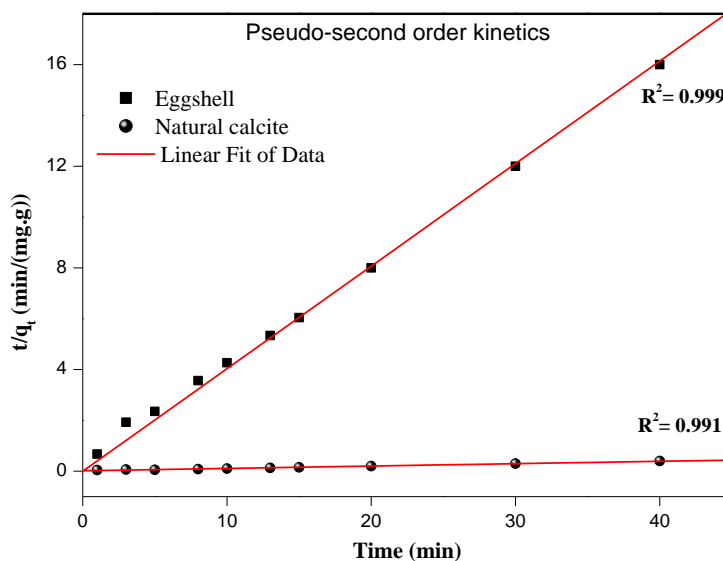

Figure 6. Pseudo-second order kinetic plot for the adsorption of lead by eggshell and natural calcite (C$_0$ = 50 mg L^{-1}, pH=5.3, dose = 1 g L^{-1}, temperature = 20 ± 2°C)

As shown in Figure 6, the behavior of the pseudo second-order adsorption model on natural calcite seems similar to the experimental data comparatively to that of the other model kinetics. Also in this case the obtained correlation coefficients the kinetics of lead adsorption by the natural calcite follows pseudo-second order kinetics with a correlation coefficient (R^2= 0.991). Moreover, the value of R^2 for the pseudo-first-order was not satisfactory. Therefore, it has been concluded that the pseudo-second-order adsorption model is more suitable to describe the adsorption kinetics of lead onto natural calcite. The reason is that the pseudo-first order kinetic model is used only for obtaining K_1 coefficient (mass transfer coefficient in design).

It seems that the pseudo-second-order model describes better adsorption kinetic for the both adsorbents. This suggests that the adsorption of lead by eggshell and natural calcite is controlled by chemisorption process. This gives prediction that the lead sorption onto both adsorbents may involve valence forces through sharing or exchange of electrons between sorbent and sorbate (Namasivayam & Sureshkumar 2008). So, the ion exchange mechanism plays a significant role in the sorption process.

Table 2: Parameters of pseudo-first-order kinetic and pseudo-second-order kinetic models for the adsorption of lead.

Adsorbent	$q_{e,exp}$ (mg g^{-1})	Pseudo first-order			Pseudo second-order		
		K_1 (min^{-1})	$q_{e\ cal}$ (mg g^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2
Natural Calcite	98.08	0.370	128.026	0.977	0.004	107.529	0.991
Eggshell	2.4822	0.254	1.552	0.97	0.357	2.589	0.999

Effect of initial concentration and adsorption isotherms model

The effect of initial sorptive concentration was studied varying the initial concentration of Pb(II) from 50 mg L^{-1} to 250 mg L^{-1} at pH=5.30. The equilibrium sorption data obtained for Pb(II) is displayed in Figure 7. While the initial concentration of lead ions solution increased from 50 to 250 mg L^{-1}, the removal percentage decreases from 98.21% to 50.96% for natural calcite and from 97.36 % to 43.88% for eggshell. Consequently, at lower initial metal ions concentration, sufficient binding sites are available for lead. That is, when initial concentration of lead ions solution was less than 50 mg L^{-1}, the lead ions of the aqueous solution would be fully adsorbed. On the other hand, at higher concentration the amount of lead ions are quite higher compared to available adsorption sites. Hence, the percentage removal of lead ions largely depends on the initial ions concentration and decreases with increase in initial ions concentration.
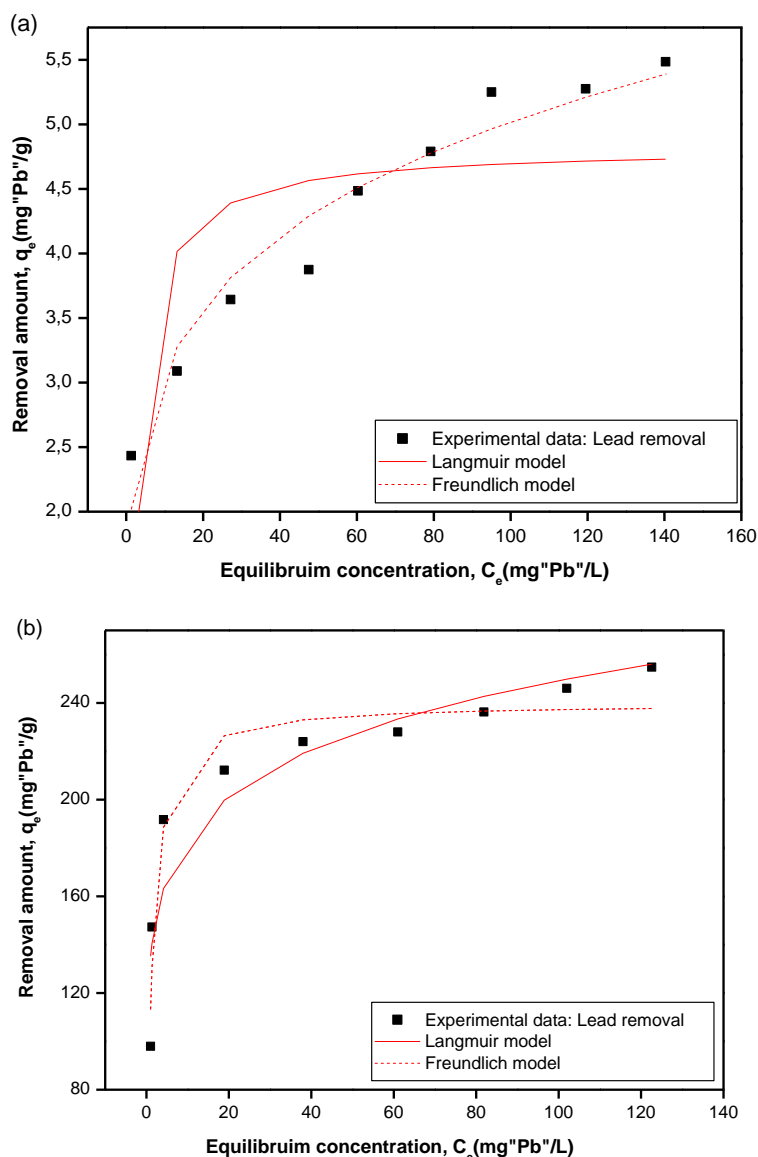

Figure 7. Modeling of equilibrium isotherms for removal of lead from aqueous solutions using eggshell and natural calcite (C$_0$ = 50–250 mg L^{-1}, contact time = 3 h, pH = 5.3, dose = 1 g L^{-1}, temperature = 20 ± 2°C): a) Eggshell, b) Natural calcite.

The equilibrium adsorption isotherms are one of the most important data in order to clarify the mechanism of the adsorption process. In the last decades, several empirical, heuristic or mechanistic models (e.g. Langmuir, Freundlich, Redlich–Peterson, Brunauer–Emmett–Teller, and others) have been successfully used to fit and describe the removal processes, including adsorption, chemisorption, co-precipitation, incorporation, oxidation or photo-oxidation of ions and/or molecules at solid/aqueous solution interfaces.

In this work, the relationship between the amount of Pb(II) ions adsorbed onto the eggshell and natural calcite and their equilibrium concentrations in aqueous solution were evaluated in terms of Langmuir and Freundlich isotherm models.

The Langmuir isotherm model is valid for monolayer adsorption on a surface containing a finite number of identical sites. The Langmuir isotherm model has the following form (Langmuir 1916).

$$q_e = \frac{q_{e,max}\ K_L C_e}{1+K_L C_e} \quad (7)$$

Where q_e (mg g^{-1}) is the amount adsorbed at equilibrium concentration of lead ions in solution C_e, $q_{e,max}$ (mg g^{-1}) is the Langmuir constant representing the maximum adsorption capacity, K_L(L g^{-1}) is the Langmuir constant related to the binding energy of the metal ions to the active site on adsorbent.

The essential feature of the Langmuir isotherm can be expressed by means of R_L a dimensionless constant referred to equilibrium parameter. This was expressed mathematically in Equation (8):

$$R_L = \frac{1}{1+K_L C_0} \quad (8)$$

Where K_L is the Langmuir constant and C_0 is the initial lead concentration, R_L values indicate the type of isothermto be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) (Chen & Zhao 2009).

The Freundlich isotherm model can be applied for modeling the adsorption on heterogeneous surfaces. The model has the form (Freundlich 1906).

$$q_e = K_F C_e^{\frac{1}{n}} \quad (9)$$

Where K_F (L mg^{-1}) a constant related to sorption capacityand $1/n$ is an empirical parameter related to sorption intensity. The value of n varies with the heterogeneity of sorbent and gives an idea for the favorability of sorption process. The value of n should be less than 10 and higher than unity for favorable sorption conditions.

In this work, equilibrium data was applied onto Langmuir and Freundlich isotherm models. All of the isotherm constants and correlation coefficients were calculated from the nonlinear equation of the models and provided in Table 3 as calculated from Figure 7. Here, the $q_{e,max}$ value for natural calcite (239.8 mg"Pb"/g) is taller than $q_{e,max}$ value for eggshell (4.81 mg'Pb"/g), indicating that calcite have a better capacity to trap lead. In the case of eggshell, these values clearly suggest that Freundlich isotherm shows a good correlation with the experimental results. For natural calcite, after the application of the Langmuir model to the adsorption results, the values of the coefficients of determination strongly support that the lead adsorption data closely follow the Langmuir model.

Moreover, according to the initial concentration range of tests, 50–250 mg L^{-1}, R_L or dimensionless constant (Eq.8) was obtained at 0.0219–0.0044 and 0.0512–0.0106 for natural calcite and eggshell, respectively. Since the rate of the parameter for adsorbent was between 0 and 1, indicated that the Pb(II) adsorption onto natural calcite and eggshell were favorable under studied conditions. Furthermore n values, obtained from Freundlich plot are 7.53 and 4.75 for natural calcite and eggshell, respectively. Since the value is greater than 1, it may be concluded that the adsorption process is suitable and heterogeneity of adsorbent surface doesn't have any effect on adsorption process. Furthermore, the natural calcite K_F value is 135.2 g g^{-1} and 71 times higher than the eggshell K_F value (1.903 g g^{-1}). This means that the adsorption capability of natural calcite is higher than that of eggshell.

Table 3: Langmuir and Freundlich isotherm parameters for the adsorption of lead onto natural calcite and eggshell.

Adsorbent	Freundlich			Langmuir		
	K_F(mg g^{-1})	n	R^2	K_L(L mg^{-1})	R^2	$q_{e,max}$(mg g^{-1})
Natural calcite	135.2	7.53	0.88	0.89	0.94	239.8
Eggshell	1.903	4.75	0.94	0.37	0.582	4.81

Table 4 gives comparative equilibrium capacities ($q_{e,max}$) of lead ion on various adsorbents. The sorption capacity shown by various sorbents is varied due to difference in physicochemical properties of adsorbents as well as experimental factors including concentration range of pollutants (Pb), pH, temperature and ionic strength, etc. The result reveals that natural calcite and eggshell were effectives in attenuating lead in aqueous solutions.

Table 4: Comparison of natural calcite and eggshell with other reported adsorbent for Pb(II) adsorption

Adsorbent	$q_{e,max}$ (mg g^{-1})	Reference
Calcium hydroxyapatite	85	(Yasukawa et *al*.2007)
Activated carbon	31.2	(Machida et *al*.2005)
Olive cake	19.53	(Doyurum&Celik 2006)
Turkish bentonite (MTA)	16.66	(Bereket et *al*.1997)
Hierarchical CaCO$_3$-maltose	3242.48	(Ma et *al*.2012)
Montmorillonite	31.05	(Gupta &Bhattacharyya 2005)
Modified kaolinite	23.10	(Gupta &Bhattacharyya 2005)
Natural sorbents (CaCO$_3$)	66.2	(Al-Degs et *al*. 2006)
Natural calcite	239.8	This study
Eggshell	4.81	This study

Effect of adsorbent dose

Adsorbent dose is an important parameter because it determines the capacity of an adsorbent with a known initial concentration of adsorbate at the operating conditions. The adsorbent dose varied from 0.003 to 3 g L^{-1} for eggshell and 0.05 to 3 g L^{-1} for natural calcite. The initial concentration of lead was fixed to 50 mg L^{-1}, the volume of solution to 100 mL and shaking rate to 400 rpm. The effects of adsorbent dose on the adsorption of Pb(II) were presented in Figure 8. The effect of natural calcite and eggshell doses on lead removal from aqueous solutions confirmed that calcite can be considered as a promising and efficient material (Figure 8). Consequently, only 0.05 g L^{-1} of this material was sufficient to ensure a total removal yield of 100%. Thus, a plateau with a constant removal efficiency of more than 100% was observed beyond a dose of 0.05 g L^{-1}. For eggshell, this plateau, with a total efficiency of 100% was observed for doses higher than 2 g L^{-1}. The results obtained could be probably attributed to the increase of the adsorbent surface areas, with the increase of the number of available adsorption sites. The difference between the doses obtained for the both adsorbents can be explained by the difference of their surface areas. Therefore, the obtained results indicate that the number of activated surface sites was more important for natural calcite than those found for eggshell.
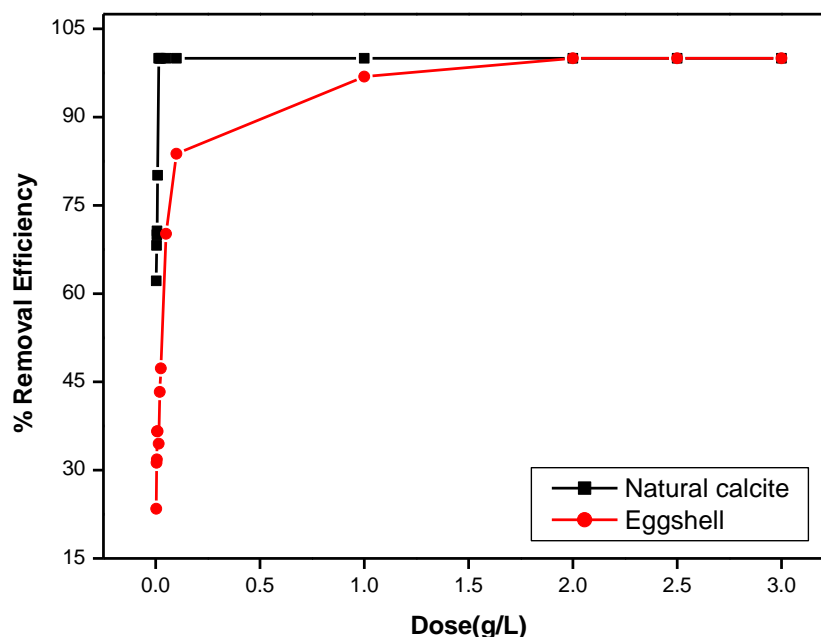

Figure8. Effect of adsorbent dosage on lead adsorption onto natural calcite and eggshell (C$_0$= 50 mg L^{-1}, pH = 5.3, contact time = 3 h, temperature = 20 ± 2°C).

Effect of temperature and thermodynamic parameters

The effect of temperature on the adsorption of Pb(II) by eggshell and natural calcite was investigated in the temperature range of 25-45°C. Curves were determined for an initial Pb(II) concentration of 50 mg L^{-1} and pH=5.30. The thermodynamic parameters of the adsorption of lead by different adsorbents, including the Gibbs free energy change ΔG° (KJ mol^{-1}), enthalpy change ΔH° (KJ mol^{-1}) and entropy change ΔS° (J mol^{-1} K^{-1}) were determined. ΔG° indicates the degree of spontaneity of an adsorption process, and a higher negative value reflects a more energetically favorable adsorption. The thermodynamic parameters were determined by using the Van't Hoff equations:

$$\Delta G° = -RT \ln(K_d) \quad (10)$$

Where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K) and K_d is the distribution coefficient. The K_d value was calculated using following equation (Al-Degs et *al.* 2006).

$$K_d = \frac{q_e}{C_e} \quad (11)$$

Where q_e and C_e are the equilibrium concentration of metal ions on adsorbent (mg g^{-1}) and in the solution (mg L^{-1}), respectively.

The enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) of adsorption were estimated from the following equation:

$$\ln K_d = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \quad (12)$$

According to Eq. (12), the values of enthalpy change $\Delta H°$ and the entropy change $\Delta S°$ were determined from the slope and intercept the plots of $\ln K_d$ of versus $1/T$ yields, respectively (Figure 9).
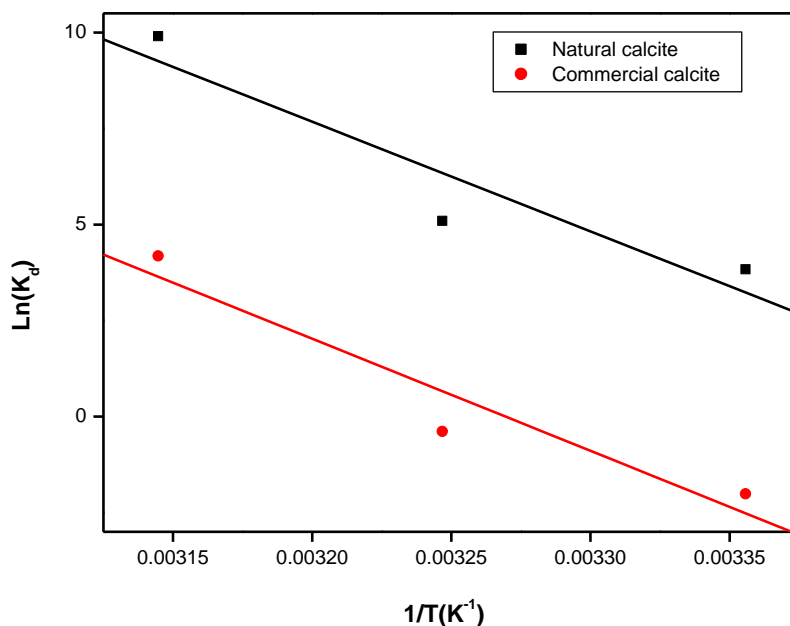

Figure 9. Plot of $\ln K_d$ versus $1/T$ for estimation of thermodynamic parameters for the adsorption of Pb(II) onto eggshell and natural calcite.

As can be seen in table 5, the free energy change ($\Delta G°$) obtained during the adsorption reaction at different temperature were all negative for Pb(II) onto natural calcite, this indicate the reaction are spontaneous and favorable. But, the values of $\Delta G°$ were positive from 25°C to 35°C, but negative at 45°C for Pb onto eggshell. It indicated the process of lead adsorption by the eggshell was non-spontaneous from 25°C to 35°C, and spontaneous process at 45°C. The positive value of $\Delta H°$ indicated the endothermic nature of the adsorption process. The positive values of $\Delta S°$ indicate the increased randomness at the solid–solution interface during the adsorption of lead onto natural calcite and eggshell.

Table 5: Thermodynamic parameters for the adsorption of lead ions onto natural calcite and eggshell

Adsorbent	T (K)	$\Delta G°$ (KJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	$\Delta H°$ (KJ mol^{-1})	R²
Natural calcite	298	-9,50	823,58	237.42	0.886
	308	-13,04			
	318	-26,18			
Eggshell	298	4,978	793.48	244.70	0.919
	308	0,99			
	318	-11,06			

Desorption study

The lead desorption experiments were performed according to the experimental procedure presented in Section 2.5. The results, reported in Figure 10, showed that lead desorption percent yields for both natural calcite and eggshell increase with increasing the acidity of the used solutions. It is important to note that the percentage of desorption represents the reversible mechanisms contribution of the total mass of Pb(II) adsorbed on the adsorbents. If the adsorption is reversible, the percentage of desorption is 100%. For instance, eggshell efficiency increases from 1.88% to 9.72% when decreasing the pH solution from 5 to 2. This behavior may be

explained both by a chemisorption process involving protonated OH groups that are displaced as H_2O molecules and replaced by Pb ions, leading to the formation of inner-sphere metal complexes through a legend exchange process (Elzinga & Sparks 2001).
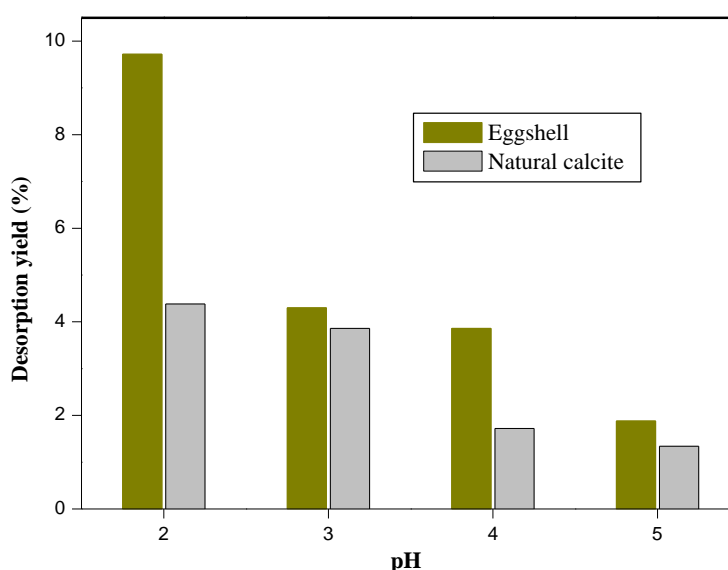

Figure 10. Effect of initial pH on Pb(II) desorption from natural calcite and eggshell (dose = 0.5 gL^{-1}, contact time = 2 h, temperature = 20 ± 2°C).

IV. Conclusions

The present study shows that the natural materials (eggshell and natural calcite) have the ability to remove lead from synthetic wastewater and should be considered as potential low cost adsorbents. We emphasize that the adsorption study showed that the binding of metal ions is dependent on factors such as pH, adsorbent dose, contact time, initial concentration and point of zero charge. Adsorption of Pb(II)was found to follow the pseudo-second-order kinetics model and the equilibrium could be established in 30 min for the two studied adsorbents. The maximum sorption capacities and the adsorption kinetic rate noticed for powdered marble are higher than those of eggshell. Thermodynamic analysis showed that the adsorption process was endothermic and spontaneous onto the two adsorbents (natural calcite). But ΔG° was positive from 25 to 35 °C and negative at 45 °C for Pb(II) onto eggshell. It indicated the process of lead adsorption by the eggshell was non-spontaneous from 25 to 35 °C, and spontaneous process at 45 °C.

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