

## Thermodynamic Adsorption of Co(II) from Aqueous Solution onto Fine Powered Limestone

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**Abstract:** Powdered limestone has been investigated as an adsorbent for the removal of cobalt from aqueous solutions. Batch experiments were carried out to investigate the effect of pH, The favorable pH for maximum cobalt adsorption was at 7.0. The adsorption capacity calculated by Langmuir equation was 2000 mgg<sup>-1</sup> at pH 7. The adsorption capacity increased with temperature and the kinetics followed a First-order rate equation. The enthalpy change ( $\Delta H^0$ ) and entropy change ( $\Delta S^0$ ) was 5.542 kJ mol<sup>-1</sup> and 53.2 J mol<sup>-1</sup> K<sup>-1</sup>, which substantiates the endothermic and spontaneous nature of the cobalt adsorption process. All of the results suggested that the LS with strong and could be excellent adsorbents for cobalt contaminated water treatment.

**Key words:** Cobalt • Limestone • Adsorption isotherm • Thermodynamic parameter.

### INTRODUCTION

Cobalt(II) is a toxic heavy metal ion in industrial wastewater. Trace amount ( $\mu\text{g L}^{-1}$ ) of cobalt is required and necessary for some organisms as cofactors for the enzymatic activities. However, for most of the organisms, concentrations at ppm ( $5\text{mg L}^{-1}$ ) level are known to be toxic because of irreversible inhibition of some enzymes by the heavy metal ions [1]. In Humans, cobalt deficiency has never been reported, but the toxic effects of excess cobalt, however, have been fully described as the excess intake will cause acute poisoning by mouth in man produces gastro-intestinal upsets, chronic absorption may cause abnormalities in skin, heart, blood or lungs [2]. Due to the mobility and toxicity in natural water ecosystems, the presence of Co(II) ions in surface water and groundwater poses a major inorganic contamination problem. Up to now, there are various technologies for removing heavy metal ions from solution, including filtration, surface complexation, chemical precipitation, ion exchange, adsorption, electrode position and membrane processing [3-5].

Most of these processes are unacceptable owing to their high cost, low efficiency, disposal of sludge, inapplicability to a wide range of pollutants [6].

Adsorption, on the other hand, is one of the most recommended physico-chemical treatment processes that is commonly used and applied for heavy metals removal from water samples and aqueous solutions. In addition, adsorption process is well recognized as one of the most efficient methods for removal of heavy metals from their matrices. Adsorption is mainly based on the utilization of solid adsorbents from either organic, inorganic, biological or low cost materials [7,8]. Heavy metal removal via adsorption by organic adsorbents is usually accomplished by the applications of polymeric ion-exchangers in which the binding and interaction of metal species with these adsorbents is favored via ion-exchange mechanism or by applications of chelating polymers where as the target metal ions are directly attached to this kind of adsorbents via chelating or complex formation mechanism [9-12]. Naturally occurring materials, either modified or unmodified, organic adsorbents such as chitosan and cross linked carboxymethyl-chitosan, polysaccharide-based materials and lignocellulosic fibers with their surface characteristic functional groups in the form of hydroxyl or carboxyl were also found great research interests [13-15]. Biological adsorbents, referred as biosorbents, are commonly derived from biological components such as bacteria, fungi and algae

that are characterized and capable of complex formation and/or ion-exchange reactions with metal ions via their functional groups in a process known as biosorption [16, 17].

Removal and extraction of heavy metals based on applications of biosorption approach are commonly performed owing to the major advantages of various biosorbents such as the economical nature, eco friendly behavior, regeneration for multiple uses and high selectivity toward different metals [6]. Low cost adsorbent materials originated from industrial products or wastes are also known as biosorbents and widely used for removal of heavy metals from water samples and these include components of plants, wood, grasses, compost, peat moss and carbon materials [18-24].

Inorganic solid adsorbents as novel silica gel matrix [25]; alumina with immobilized 1-nitroso-2-naphthol [26]; nano-TiO<sub>2</sub> [27] and bentonite adsorbent [28] are well characterized by their high mechanical properties and strong resistivity to thermal degradation as compared to other biosorbents or organic adsorbents.

In recent years there has been interest in the development of new products have minimal environmental impact for restoration or remediation of natural resources [29], Limestone (LS) which is produced in large quantities in many countries (among them is Egypt) is a low-cost reactive medium that can be used for the retaining of heavy metals and the subsequent clean up of industrial effluents, leachates and contaminated ground water [30-33]. Hence, the objective of the present work was to study the possibility of utilizing LS (which is naturally occurring or readily available and cheap) as a sorbent for removing lead ions from aqueous solutions and natural waters. The different parameters influencing the adsorption of lead ions onto powdered limestone were optimized and the results are presented in this paper.

## MATERIAL AND METHODS

**Samples:** The Limestone (LS), CaCO<sub>3</sub>, samples used in this study were obtained from the Al-Mokattam area in Cairo (Egypt) where some private and governorate quarries are located. The samples were crushed and pulverized in the laboratory and those with a mean size of ca. 12.5 mm were used in the experiments.

The sample contained 92% calcite and 3% dolomite (as found by chemical analysis) as has been described [32], with the remainder being composed of common minor constituents such as silica, clay, feldspar, pyrite and sedrite [33]. The samples were dried for 2 h in an oven at

125°C, packed into stoppered bottles and stored in a desiccator for future use. Functional groups of LS were characterized through infrared analysis.

The LS spectrum coincided with pure CaCO<sub>3</sub>. The surface area and porosity of LS was measured using Brunauer, Emmett, Teller (BET) method. LS presented no BET porosity and its measured surface area was 0.50 m<sup>2</sup>.g<sup>-1</sup>. The pH values of points of zero charge (pH<sub>pzc</sub>) were 9.1 (not aged), 6.2 (aged 60 min) and 8.3 (aged several days) and this agree with the previously reported data [34]. Stirring the LS sorbent with distilled water (pH = 6.8) for 1 h decreases the suspension pH to 5.8 decreases, confirming the positive charge of the LS surface. Also, the concentration of calcium ion in the solution was measured before and after adsorption in order to confirm that cation exchange was involved.

**Reagents:** All the solutions were prepared from certified reagent grade chemicals. A aluminum sulphate stock solution of 1 molar concentration was prepared and the working solutions were made by diluting the former with doubly distilled water. Aqueous solutions of HNO<sub>3</sub> and NaOH were used for pH adjustments.

**Apparatus:** A Perkin-Elmer 2380 Atomic Absorptions spectrophotometers (AAS) with air-acetylene flame was used for the determination of lead concentration at 217.0 nm. The infrared analyses were undertaken via a Mattson 5000 FT-IR spectrophotometer using KBr disc method. The pH was measured using Jeanway 3311 pH meter. The stirring of the solutions was performed with a magnetic stirrer Model VEHP, Scientifica, Italy.

**Procedure:** Unless stated otherwise, all batch sorption experiments were conducted at room temperature (ca. 25°C). Known volumes of Co(II) solutions with concentrations ranging from 2 to 100 mg.L<sup>-1</sup> were pipette into quick-fit glass bottles containing 0.1 g of LS sorbent in 100 ml aqueous solution. Since the pH of any of the resulting solutions was ca. 7.0, no further control was necessary since it was suitable for most adsorption experiments. The resulting solutions were then stirred with a magnetic stirrer at 250 rpm and the samples were taken at fixed time periods (0.0, 0.3, 0.8, 1.0 5.0, 10, 20, 30,60 and 90 min) in order to study the kinetics of the adsorption process. Preliminary experiments showed that this time length was sufficient for adsorption of Co(II) ion onto LS. The samples were subsequently filtered off and the residual Co(II) ion concentrations in the filtrate were analyzed using AAS.

**Experimental Data Analysis:** The percentage adsorption of Co(II) ion from the solution was calculated from the relationship

$$\% \text{Adsorption} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where  $C_i$  corresponds to the initial concentration of Co(II) ion and  $C_f$  is the residual concentration after equilibration. The metal uptake  $q$  (mg/g) was calculated as

$$q = \frac{(C_i - C_f) \cdot V}{m} \quad (2)$$

where  $m$  is the quantity of sorbent (mg) and  $V$  the volume of the suspension (ml).

As a standard parameter for studying the behavior of the metal adsorption at the adsorbent surface using Mories-Weber equation [35].

$$q = K_d(t)^{1/2} \quad (3)$$

where  $q$  is the amount of Co(II) ions adsorbed (mg/g).

The order of the adsorption may be examined using the Lagergren equation, as cited by Gupta and Shukla [36].

$$\text{Log}(q_e - q) - \text{log}q_e = -K_{ads} t / 2.303 \quad (4)$$

where  $q_e$  is the amount of Co(II) ions adsorbed at equilibrium (mg/g),  $K_{ads}$  is the first order rate constant for Co(II) ions adsorption onto LS ( $\text{min}^{-1}$ ), while  $q$  and  $t$  have been defined previously where  $q_e$  is the amount of Co(II) ions adsorbed at equilibrium (mg/g),

The amount of the metal which may introduce into the pores may be investigated by using Bangham equation [37].

$$\text{Log} \log [C_i / (C_i - q/m)] = \log (K_o m / 2.303V) + \alpha \log t \quad (5)$$

where  $q$ ,  $m$ ,  $V$  and  $C_i$  have been defined above,  $t$  is the time (min),  $K_o$  is the proportionality constant and  $\alpha$  is Bangham equation constant.

Adopted isotherm models were Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models were applied to describe the sorption data.

The Langmuir model is widely used for modeling equilibrium data to indicate then monolayrity of the LS surface from the following equation [38].

$$1/q_e = 1/K_L + (1/K_L \cdot b) \cdot 1/C_e \quad (6)$$

where  $K_L$  is the monolayer adsorption capacity and  $b$  which is the Langmuir constant which is a binding constant relates to the heat of sorption.

The Freundlich expression is an empirical equation describing sorption to heterogeneous surface [39]. The Freundlich equation is presented as:

$$\ln q_e = \ln K_F + n \ln C_e \quad (7)$$

where  $K_F$  ( $\text{mol}^{1-n} \text{L}^n \text{g}^{-2}$ ) represents the sorption capacity when metal ion equilibrium concentration equals to 1 and  $n$  represents the degree of dependence of sorption with equilibrium concentration.

The D-R isotherm is more general than the Langmuir, because it does not assume a homogeneous surface or constant sorption potential. The D-R equation is expressed as [40]:

$$\ln q = \ln q_e - \beta \epsilon^2 \quad (8)$$

$$\epsilon = RT \ln(1 + 1/C_e) \quad (9)$$

where  $\beta$  is the activity coefficient related to mean sorption energy ( $\text{mol}^2 \text{kJ}^{-2}$ );  $\epsilon$  is the Polanyi potential;  $R$  is the ideal gas constant ( $8.3145 \text{ Jmol}^{-2} \text{K}^{-2}$ ) and  $T$  is the absolute temperature in Kelvin(K).  $E$  ( $\text{kJ mol}^{-2}$ ) is defined as the free energy change required to transfer 1mol of ions from solution to the solid surfaces, which equals to:

$$E = 1/(2\beta)^{1/2} \quad (10)$$

The magnitude of  $E$  is useful for estimating the type of sorption reaction. If  $E$  is in the range of 8-16  $\text{kJ mol}^{-2}$ , the sorption is governed by chemical ion-exchange. In the case of  $E < 8 \text{ kJ mol}^{-2}$ , physical forces may affect the sorption. On the other hand, sorption may be dominated by particle diffusion if  $E > 16 \text{ kJ mol}^{-2}$  [41].

Thermodynamic parameters, the enthalpy change ( $\Delta H^\circ$ ) and the entropy change ( $\Delta S^\circ$ ), were calculated from the slope and intercept of the plot of  $\ln K_d$  against  $1/T$ , respectively [42-44],

$$\ln K_d = \Delta S^\circ / R - \Delta H^\circ / RT \quad (11)$$

The other thermodynamic parameter, Gibbs free energy ( $\Delta G^\circ$ ) was calculated by

$$\Delta G^\circ = -RT \ln K_d \quad (12)$$

where R is the universal gas constant ( $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ ) and T is the temperature(K).

The last identification of a suitable isotherm model for the Al(III) ion adsorption onto LS was done by using chi-square test ( $\chi^2$ ) test which measure the difference between the data, as it smaller, it mean the nearest the data from each other [45].

$$\chi^2 = \frac{\sum(q_e - q_{em})}{q_{em}} \quad (13)$$

## RESULTS AND DISCUSSION

**Effect of pH:** The pH value of the solution plays an important role in the sorption of Co(II) on LS. The sorption of Co(II) LS increases from ~20% to ~90% in the pH ranging from 4 to 7 and then maintains high level with increasing pH values (Fig. 1). Similar results were also reported for Cu(II) sorption to TiO<sub>2</sub> [46] or on Al<sub>2</sub>O<sub>3</sub> [47]. The pH values of the solution after sorption equilibrium changes a little to the acidic region, which indicates that H<sup>+</sup> is released during the sorption process. In aqueous systems, the surface groups of LS can be protonated in different extents. Therefore, the concentrations of surface species of LS change under different pH values. With increasing pH, the negative charged groups or deprotonated groups increase and the hydrolysis of Co(II) also increases. As can be seen, below pH 2, the removal of Pb<sup>2+</sup> ions reaches zero which may be attributed to the complete solubility of LS (consists mainly from CaCO<sub>3</sub> and MgCO<sub>3</sub>), thereby hindering the sorption of lead ions. Above pH2, the removal efficiency increases, reaching a maximum value (ca~90%) over the pH range 6-7 followed by decrease.

The removal of the Co(II) ions at pH value,5 may be attributed to a possible ion-exchange mechanism between Co(II) ions and calcium containing LS in similar manner to that reported [48, 49]. Also, this was confirmed by measuring the concentration of calcium ion in the solution before and after adsorption where its value was increased. Adsorbed Co(II) ions generally occupy calcium sites within the calcite lattice [50]. The enhanced removal of metal ion as the solution pH is increased (more than 5) can be attributed to adsorption of hydrolytic product  $\text{Co}(\text{OH})_2^+$  [51] and/or surface precipitation of the metal as the insoluble carbonates,  $\text{CoCO}_3$ , forming successive layers on the sorbent surface [52] which may be explained in the following equation [49].

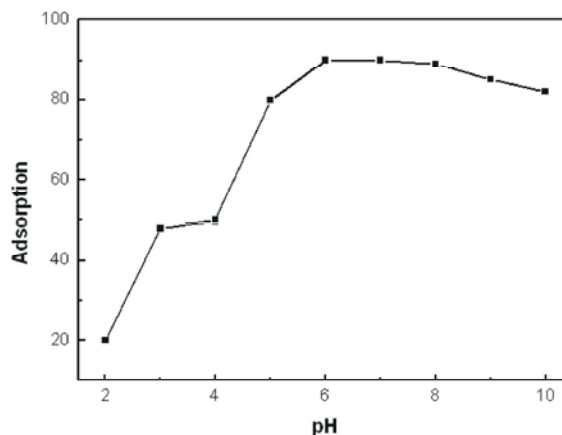
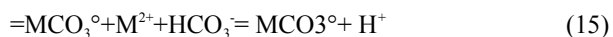


Fig. 1: Adsorption (%) of Co(II) ions ( $6 \text{ mg.L}^{-1}$ ) by LS ( $1000 \text{ mg.L}^{-1}$ ) vs. pH.



The decrease in the removal efficiency at high pH values. 8 may be attributed to the fact that the negative species of cobalt,  $\text{Co}(\text{OH})_3^-$  and  $\text{Co}(\text{OH})_4^{2-}$  are not capable of a combination with the negative surface of LS, as determined by ZPC ( $\text{pHZPC} = 6.2$  after which the surface is negative). Moreover, this finding was confirmed by stirring LS with distilled water and the pH of its suspension was always decreased from 6.8 to 5.8. Therefore, pH 7 was recommended throughout all the other experiments.

**Sorption Model:** Adsorption kinetics is one of the most important characters which represent the adsorption efficiency. The adsorption rate of cobalt adsorption on the LS surface, as a function of the initial cobalt concentration, is shown in Fig. 2. Due to faster adsorption kinetics with smaller particles [53], the cobalt adsorption was initially rapid, after which it decreased. The time required to reach equilibrium was 60 min for all cobalt concentration. The initial rapid adsorption was presumably due to electrostatic attraction. The slow adsorption in the later stage represented a gradual uptake of fluoride at the inner surface by complexation or ion-exchange or due to the decrease in the number of adsorption sites having affinity toward cobalt(II) ions [54].

When the results depicted in Fig. 2 were re-plotted against the square root of the stirring time, the obtained linear correlations (Fig. 3) may verify the Morris-Weber equation (3), which show that an initial linear portion which may be due to the boundary layer effect [55] and a

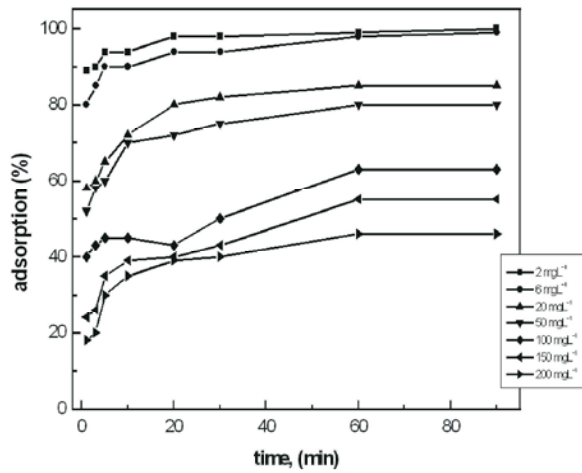


Fig. 2: Influence of stirring time on the adsorption of various concentrations of Co(II) ions by LS (1000 mg.L<sup>-1</sup>) at pH 7.

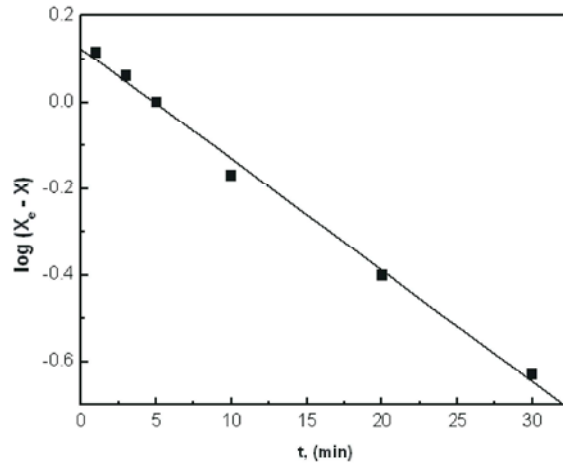


Fig. 4: Plot of  $\log (X_e - X)$  vs. stirring time for Co(II) ions adsorption onto LS.

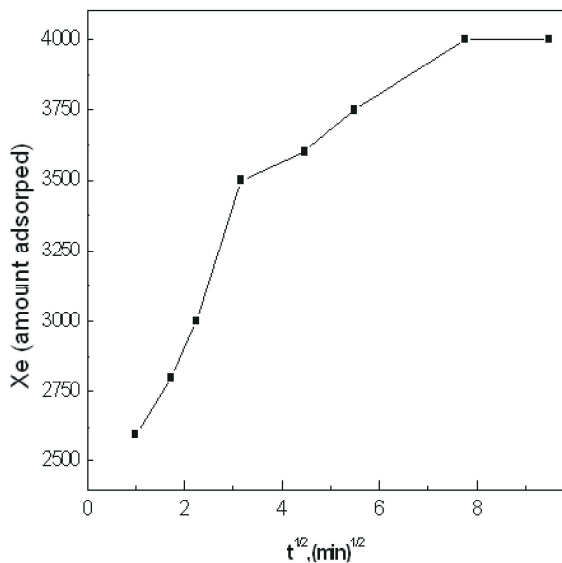


Fig. 3: Plot of the amount of Co(II) ions adsorbed onto LS (1000 mg. L<sup>-1</sup>) vs. square root of time at pH 7.

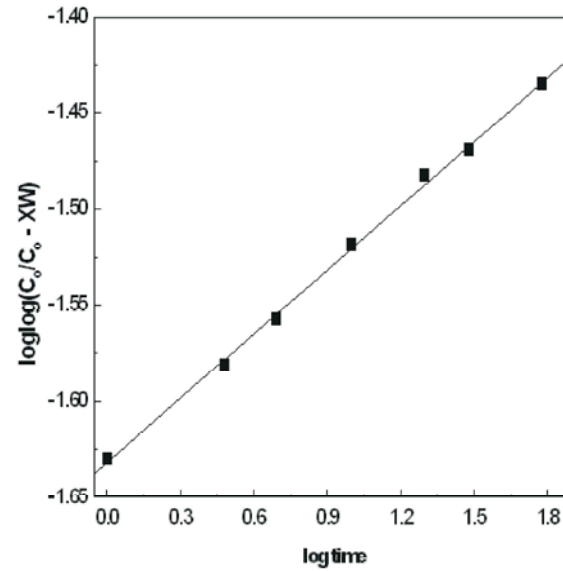


Fig. 5: Plot of  $\log [C_i/(C_i - q_m)]$  vs.  $\log t$  for the adsorption of Co(II) ions by LS (1000 mg. L<sup>-1</sup>) at pH 7.

second portion which may be due to the intraparticle diffusion effect [56]. The value of the rate constant for the intrapore diffusion  $K_d$  was evaluated as 486.1 (mg/g min<sup>-1</sup>) which give indication about the mobility of the Co(II) ions toward the LS surface.

Again when the kinetic data obtained in Fig. 2 for Co(II) ion adsorption by LS were tested by Lagergren equation(4), The linear plot of  $\log (q_e - q)$  vs.  $t$  (Fig. 4) shows the appropriateness of the above equation and consequently the first-order nature of the process involved. The value of  $K_{ads}$  was calculated to be 0.027 min<sup>-1</sup>.

Again the kinetic data (Fig. 2) of the adsorption of Al(III) ions by LS was examined by Bangham equation (5). These results show that the diffusion of Co(II) ions onto LS pores played a role in the adsorption process [57]. The value of  $K_o$  and  $\alpha$  constants deduced were 10588,0.11 respectively.

**Isotherm Model:** The sorption of Co(II) onto LS at pH values of 7. Langmuir, Freundlich and D-R isotherm models are conducted, to simulate the sorption data of Co(II) LS (Fig. 6). It is clear that the Langmuir isotherm

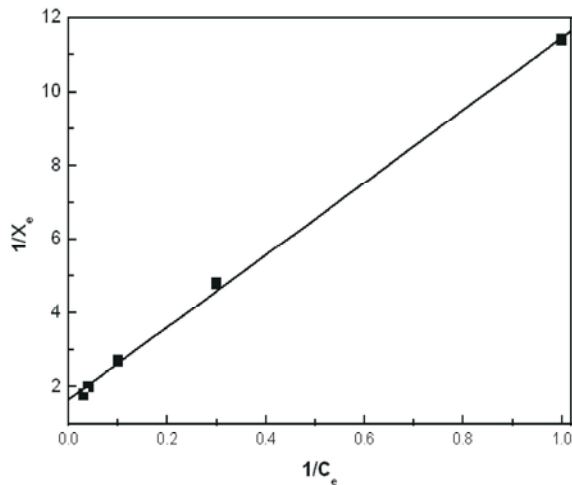


Fig. 6: Langmuir plot for Co(II) ions adsorption onto LS (1000 mg. L<sup>-1</sup>).

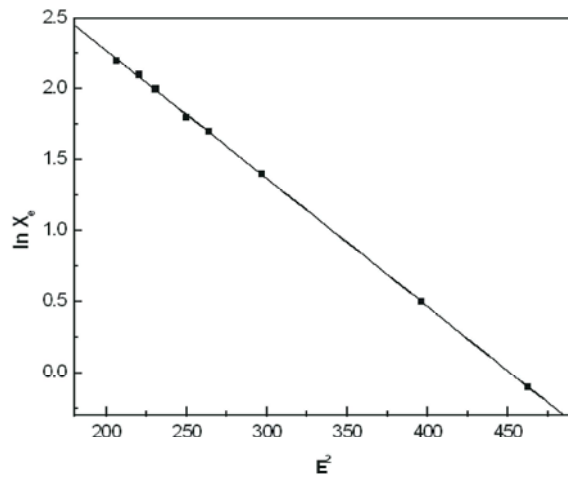


Fig. 8: The D-R isotherm of Co(II) ions adsorption onto LS (1000 mg.L<sup>-1</sup>).

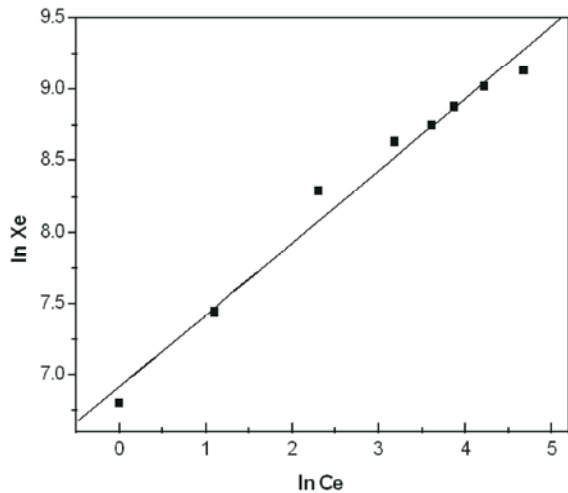


Fig. 7: Freundlich plot for Co(II) ions adsorption onto LS (1000 mg.L<sup>-1</sup>).

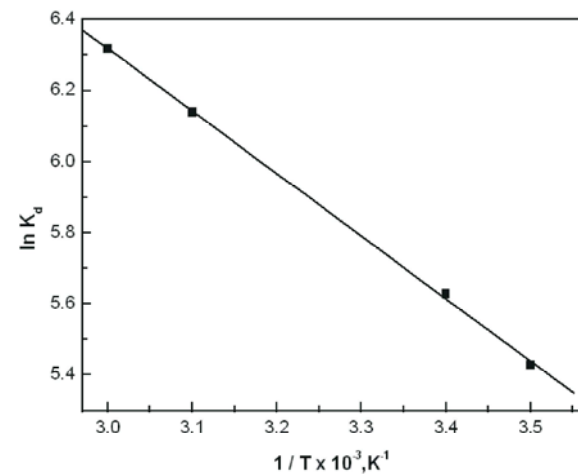


Fig. 9: Thermodynamic distribution coefficient (K<sub>d</sub>) calculated for adsorption of Co(II) onto LS.

model fits the experimental data very well. where  $K_L$  is the monolayer adsorption capacity and it is 0.5 (mg/g) and  $b=2000$  (ml/mg) which is the Langmuir constant.

The Freundlich adsorption isotherm can be used successfully for modeling the equilibrium data in metal-surface systems.

This equation (6) was applied to the experimental data depicted in Fig. 2 with a linear plot being obtained (Fig. 7). This demonstrates the applicability of the Freundlich model to Co(II) ions adsorption onto LS. The parameters  $n$  and  $K_F$  for adsorption of Co(II) ions onto LS were calculated from the slope and intercept of the figure giving values of 2.43 and 1002.2 L/g. Favorable adsorption was demonstrated by the fact that the value of  $n$  is greater than unity [58].

Table 1: Distribution coefficient (K<sub>d</sub>) values calculated for the adsorption of Al(III) ions onto LS at different temperatures.

Temperature	288	298	313	323
(K <sub>d</sub> )	186	400	426	525

From the results of D-R model simulation (Fig 8),  $E$  value is 7.6 kJ mol<sup>-1</sup> which in the range of 8-16 kJ mol<sup>-1</sup>, indicating that sorption is governed by chemical ion-exchange according to the theory of D-R model or sorption may considered as physical-chemical adsorption [41].

#### Effect of Temperature and Thermo Dynamic Parameters:

In order to investigate the effect of temperature on the adsorption of Co(II) ions onto LS, the distribution coefficient,  $K_d$  (L.g<sup>-1</sup>), was calculated at the temperate 288,

298, 313 and 323 K by using the equation (11), the  $K_d$  value increase with increasing temperature and revealing the adsorption of metals onto LS to be endothermic.

Thermodynamic parameters, the enthalpy change ( $\Delta H^\circ$ ) and the entropy change ( $\Delta S^\circ$ ), were calculated from the slope and intercept of the plot of  $\ln K_d$  against  $1/T$ , as shown in Figure (9).

The other thermodynamic parameter, Gibbs free energy ( $\Delta G^\circ$ ) was calculated by equation (11) The enthalpy change,  $\Delta H^\circ$  has a value of 5.5 kJ mol<sup>-1</sup>. The positive  $\Delta H^\circ$  exhibited that the adsorption of Co(II) onto LS was endothermic. The entropy change ( $\Delta S^\circ$ ) was calculated to be 53.2 mol<sup>-1</sup>, The positive sign mean that the adsorption of Co(II) onto LS is random reaction, Also the negative sign of the  $\Delta G^\circ$  indicate that the adsorption of Co(II) onto LS is feasible and spontaneous thermodynamically. In addition, the reaction proceeded physically because  $\Delta G^\circ$  values was 14.9 kJ mol<sup>-1</sup> [53]. This results was in well agreement with that obtained from the D-R isotherm.

The last identification of a suitable isotherm model for the Co(II) ion adsorption onto LS was done by using chi-square test ( $\chi^2$ ) test which give a value equal to 0.31 which an indication about the nearest value from others.

## CONCLUSIONS

The experimental results indicate that LS can be successfully used for the adsorption of Co(II) ions from aqueous solutions. The equilibrium data well followed the Langmuir and Freundlich models. The value of mean sorption energy,  $E$  obtained from the D-R isotherm indicated that the adsorption of the metals on the LS was feasible and spontaneous. The negative  $\Delta H^\circ$  value depicted that the adsorption of Co(II) onto LS was an endothermic process and the increase in  $K_d$  values with increasing temperature also supported this conception. The positive  $\Delta S^\circ$  values revealed that the randomness of the adsorbed system. On the basis of all results, it can be calculated that limestone (LS) can effectively be used for the removal of metal cations from wastewater using adsorption method. The limestone presents a major advantage of giving low cost recovery processes making it useful for use in water purification.

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