Sorption of Zn(II), Pb(II), and Co(II) using natural sorbents: Equilibrium and kinetic studies

Yahya S. Al-Degsa, Musa I. El-Barghouthia, Ayman A. Issaa, Majeda A. Khraishehb, Gavin M. Walkerc

a Chemistry Department, The Hashemite University, P.O. Box 150459, Zarqa, Jordan
b Department of Civil and Environmental Engineering, University College of London, Gower Street, London WC1E 6BT, UK
c School of Chemistry and Chemical Engineering, Queen’s University Belfast, David Keir Building, Stranmillis Road, Belfast, Northern Ireland, UK

ABSTRACT
Natural Jordanian sorbent (consisting of primary minerals, i.e., quartz and aluminosilicates and secondary minerals, i.e., calcite and dolomite) was shown to be effective for removing Zn(II), Pb(II) and Co(II) from aqueous solution. The major mineral constitutions of the sorbent are calcite and quartz. Dolomite was present as minor mineral and palygorskite was present as trace mineral. The sorbent has microporous structure with a modest surface area of 14.4 m² g⁻¹. pH of zero point charge (pH of zero point charge) of the sorbent was estimated by alkaline–titration methods and a value of 9.5 was obtained. The sorption capacities of the metals were: 2.860, 0.320, 0.076 mmol cation g⁻¹ for Zn(II), Pb(II) and Co(II) at pH 6.5, 4.5 and 7.0, respectively. The shape of the experimental isotherm of Zn(II) was of a "L2" type, while that of Pb(II) and Co(II) was of a "L1" type according to Giles classification for isotherms. Sorption data of metals were described by Langmuir and Freundlich models over the entire concentration range. It was found that the mechanism of metal sorption was mainly due to precipitation of metal carbonate complexes. The overall sorption capacity decreased after acid treatment, as this decreased the extent of precipitation on calcite and dolomite. The effect of Zn(II) ions concentration on sorption kinetics was investigated. Kinetic data were accurately fitted to pseudo-first order and external diffusion models which indicated that sorption of Zn(II) occurred on the exterior surface of the sorbent and the contribution of internal diffusion mechanism was insignificant. Furthermore, the sorption rate of Zn(II) was found to be slow, where only 10–20% of the maximum capacity was utilized in the first 30 min of interaction.

1. Introduction
The existence of heavy metals in the aquatic system can be detrimental to a variety of living species. Many industrial processes discharge aqueous effluents containing heavy metals (Allen and Brown, 1995). Heavy metals are non biodegradable and tend to accumulate in living organisms, causing various disorders for living organisms. Accordingly, improved and innovative methods of water and wastewater treatment are continuously being developed to treat water-containing metals (Bailey et al., 1999). Precipitation and ion-exchange are the most widely used methods for cleaning water contaminated with metal pollutants. However these methods are unable to achieve the standards which are
Nomenclature

\begin{tabular}{ll}
\textbf{A/V} & the external sorption area to the total solution volume, cm² cm⁻³  \\
\textbf{b} & energy related constant in Langmuir equation, dm³ mmol⁻¹  \\
\textbf{C₀} & the initial concentration of solute in solution, mmol dm⁻³  \\
\textbf{Cₑ} & concentration of solute in solution, mmol dm⁻³  \\
\textbf{Cₜ} & concentration of solute in solution at time, t, mmol dm⁻³  \\
\textbf{k₁} & the rate constant of pseudo-first order reaction, 1/min  \\
\textbf{k₂} & the rate constant of pseudo-first order reaction, 1/min  \\
\textbf{k₆₀} & internal diffusion constant, mmol g⁻¹ min⁻¹/2  \\
\textbf{k₉} & external diffusion constant, cm s⁻¹  \\
\textbf{k₇} & Ferndlich constant, mmol g⁻¹  \\
\textbf{k₉₉} & sorption capacity at equilibrium, mmol g⁻¹  \\
\textbf{k₉₉₃₀ₐₘ} & sorption capacity at 300 min, mmol g⁻¹  \\
\textbf{Qₘₐₓ} & the maximum sorption value, mmol g⁻¹  \\
\textbf{r.p.m} & revolution per minute  \\
\textbf{SSE} & the sum of square errors squared  \\
\textbf{t} & time, h  \\
\end{tabular}

recommended by international water standards bodies (Garcia-Sanchez et al., 1999). In recent years, many natural adsorbents have been investigated for the removal of heavy metals from water. A review of more than 70 natural and synthetic adsorbents and their potential uses for metal removal has been reported (Bailey et al., 1999). Calcite, magnesite and dolomite (which are classed as carbonate minerals or secondary soil minerals) were investigated for use as potential adsorbents for the removal of heavy metals and radio-active metals from solution (Brady et al., 1999; Zachara et al., 1991; Papadopoulos and Rowell, 1988; Papadopoulos and Rowell, 1989). Carbonate minerals are effective in removing heavy metals with the mechanism of interaction found to be a combination between ion-exchange and precipitation on the carbonate surface (Garcia-Sanchez and Alvarez-Ayuso, 2002; Comans and Middelburg, 1987. Brady et al., 1999) have effectively applied carbonate minerals for the removal of Ca²⁺, Mg²⁺, UO₂²⁺, Am³⁺, NpO₂⁴⁺, and PuO₂⁴⁺ from solution (Brady et al., 1999). Natural silicate minerals, of which clays are a typical form, have been also investigated as potential low-cost sorbents for removing toxic heavy metals (Bailey et al., 1999; Al-Degs et al., 2003; Yavuz et al., 2003; Sheta et al., 2003; Coles and Yong, 2002; Sanchez et al., 1999).

In addition to high mechanical strength, natural clay minerals have good porosity and high surface area (Sanchez et al., 1999). Natural adsorbents; silicate minerals, carbonate minerals and metal oxides (like SiO₂, Fe₂O₃ and Al₂O₃) are not present in soil as pure components, but are usually found in nature as admixtures (Hajjaji et al., 2001; Frimmel and Huber, 1996). Therefore, the determination of the exact type of mechanism for metal sorption by complex-adsorbents like natural adsorbents is a complex procedure (Frimmel and Huber, 1996).

In Jordan, large deposits of clay minerals have been found in several locations. These deposits however, are not homogeneous. The predominant clay types in these deposits are: illite, montmorillonite, muscovite, kaolinite, pylogorskite, with quartz, calcite and dolomite found as minor constituents (Al-Degs et al., 2003; Mahmoud et al., 2003). In this work the chemical, mineralogical, and textural characteristics of a new discovered natural clay deposit were investigated. The feasibility of Jordanian natural silicate minerals—as low cost sorbents—for removing Zn(II), Pb(II) and Co(II) from solution was assessed in this study. Furthermore, the effect of acid washing the adsorbents on metal sorption was assessed and the mechanism of metal sorption determined. The sorption kinetics and the rate limiting step(s) of zinc sorption were also investigated.

2. Experimental method and procedures

2.1. The sorbent

The sorbent was obtained from the Natural Resources Authority (Amman, Jordan). The sample was washed with deionized water several times with constant stirring, to remove soluble inorganic salts and any adhering materials. It was observed that the supernatant showed little turbidity even after leaving the solution overnight. In order to keep the fine clay particles, the supernatant solution was filtered and the obtained solid material returned to the original sample.

After drying at 105°C for 24 h, the sample was crushed, and separated into different particle size ranges. Sorption tests were conducted on a size range of <100 𝜇m. Most sorption studies conducted on clays start by the removal of non-clay minerals (like carbonate minerals and quartz) in order to concentrate the clay minerals and improve the sorption properties of the adsorbent. These procedures are employed either by collecting the small fractions down to 2 𝜇m of the sample (Hajjaji et al., 2001) or by washing the sample with a strong acid (Li et al., 2001). In this work, the sorbent was washed with HNO₃ to leach the non-clay materials as follows: A 12.0-g sample of dried clay deposit was added to 250 ml distilled water. The mixture was heated to 90°C, acid (250.0 cm³ of 0.1 M HNO₃) was gradually added to the clay solution. The mixture was stirred for 2 h. After completion of acid treatment, the sorbent was thoroughly washed with deionized water until the pH of the washings remained constant.

2.2. Physical and chemical characteristics of the adsorbent

The mineral constitution of the adsorbents (raw and treated samples) was determined using X-ray diffraction techniques (PANalytical, ExpertPro, equipped with Xlerator detector). X-ray fluorescence analysis for the adsorbents is shown in Table 1. The IR-spectra were recorded in the range...
The textural characteristics and the pH zpc are presented in Table 1.

Metal ion solutions of different concentrations were prepared from their pure metal salts (ZnSO₄, Pb(NO₃)₂, and CoSO₄·7H₂O) and then transferred into the sample bottles. The sorption isotherms of Zn(II), Pb(II), and Co(II) were measured, respectively, at concentration ranges: 0–0.0153 mol dm⁻³, 0–4.83 x 10⁻³ mol dm⁻³ and 0–2.56 x 10⁻³ mol dm⁻³. The sample bottles were placed in a shaker bath for 24 h at 25 ± 1 °C. Blank solutions containing no clay were also included. To prevent the precipitation of metal cations from solution, the pH of the solution was maintained at pH less than the pH̴ precip (pH precip) for each single metal (see Table 3). pH adjustment was employed by adding dilute HNO₃ solution. After attainment of equilibrium, about 10 cm³ sample was withdrawn and filtered for analysis. The initial and equilibrium concentration of metal ions were determined by inductively coupled plasma atomic emission spectrophotometry (Perkin-Elmer 400 series).

The measured liquid phase concentrations were then used to calculate the sorption capacity, qₑ (mol g⁻¹ or mmol g⁻¹) of the sorbent using the following mass balance equation:

\[ qₑ = \frac{bQ_{\text{max}}C_e}{1 + bC_e} \]

where \( C_o \), \( C_e \), \( V \), and \( m \) are initial metal concentration (mol dm⁻³), metal concentration at equilibrium (mol dm⁻³), total volume (dm³) and weight (g) of sorbent, respectively. All the reagents used in this research were of analytical reagent grade and supplied from Riedel-de Haeën chemicals.

### 2.4. Verification of sorption mechanism

The following sorption tests were employed to verify the nature of the sorption mechanism. Initially, an exact weight (0.0500±0.0001 g) of the dried sorbent (treated and untreated) was agitated with 50.0 cm³ of metal solution. The initial concentrations of Zn(II), Pb(II), and Co(II) were 0.01, 0.004, and 0.002 mol dm⁻³. The pH of the solution was adjusted to pH 5–6 after adding the sorbent using dilute HNO₃ solution. The test bottles were placed in a temperature controlled shaker bath for 24 h at 25 ± 1 °C to attain equilibrium.

### 2.5. Kinetic experiments

Kinetic studies were carried out in an agitated batch sorption system, which consisted of a 2.0 dm³ glass vessel, of diameter 0.13 m, filled with 1.7 dm³ of aqueous solution. A six-flat-blade impeller driven by an electric motor (Heidolph-motors, Germany) with a speed adjustable from 100 to 700 revolutions/min (r.p.m) was used to achieve homogeneity within the reactor. This kinetic sorption vessel design has been used by previous investigators (Cheung et al., 2000).

The effect of initial concentration of Zn(II) on sorption rate was studied at the following conditions: Initial Zn(II) concentration: 11.47, 10.10, 7.20, and 4.05 mmol dm⁻³. Mass of sorbent: 3.400 g. Volume of solution: 1.7 dm³. Stirring speed: 500 rpm pH: 7 and particle size: <100 µm.

### 3. Theoretical background

#### 3.1. Sorption isotherms of heavy metals

Two of the most commonly used isotherm theories have been adopted in this work, namely, the Langmuir and Freundlich equilibrium isotherm theories. The form of Langmuir equation can be represented by the following Eq. (1):

\[ qₑ = \frac{bQ_{\text{max}}C_e}{1 + bC_e} \]

or in the linear form

\[ \frac{qₑ}{C_e} = \frac{1}{bQ_{\text{max}}} + \frac{C_e}{Q_{\text{max}}} \]

where \( C_o \) is the equilibrium concentration of remaining metal in the solution (mmol dm⁻³), \( qₑ \) is the amount of a metal adsorbed per mass unit of sorbent at equilibrium (mmol g⁻¹), \( Q_{\text{max}} \) is the amount of adsorbate at complete monolayer.
coverage (mmol g\(^{-1}\)). \( b \) (dm\(^3\) mmol\(^{-1}\)) is a constant that relates to the heat of adsorption. Freundlich isotherm model has the following form (Allen and Brown, 1995; Sanchez et al., 1999): 

\[
q_e = k_r C_e^n
\]  

(3)

or in the linear form 

\[\log q_e = \log k_f + n \log C_e\]

(4) 

where, \( k_f \) (mmol\(^{-1}\) g\(^{-1}\) L\(^n\)) represents the sorption capacity when metal equilibrium concentration equals to 1, and \( n \) represents the degree of dependence of sorption with equilibrium concentration.

3.2. Sorption kinetic Models

Sorption kinetic models can be divided into two main types: reaction-based models and diffusion-based models (HO et al., 2000).

3.3. Reaction-based models

A simple kinetic analysis of Zn sorption can be employed using pseudo-first-order equation (HO and McKay, 1998):

\[
\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}.
\]

(5)

In addition, a pseudo-second-order equation based on sorption equilibrium capacity may be written in the form (HO and McKay, 1998; Chiron et al., 2003):

\[
\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t.
\]

(6)

where, \( q_e \), \( q_t \), \( k_1 \), \( k_2 \), and \( t \) are the surface concentration at equilibrium (mmol g\(^{-1}\)), surface concentration at time \( t \) (mmol g\(^{-1}\)), pseudo-first-order rate constant (1/min), pseudo-second-order rate constant (g mmol min\(^{-1}\)), and time of reaction (min). Eqs. (5) and (6) have been applied to many sorption systems (HO et al., 2000).

3.4. Diffusion-based models

3.4.1. External diffusion model

If external-diffusion of metal cations (within the diffuse layers outside the sorbent) is the rate-limiting step then it has been shown that Eq. (7) can be fitted into sorption data with some success (Lee et al., 1999):

\[
\ln \frac{C_t}{C_0} = -k_f \frac{A}{V} t.
\]

(7)

where \( C_0 \), \( C_t \), \( A/V \), and \( t \) are the initial metal concentration, concentration at time \( t \), the external sorption area to the total solution volume, and sorption time, respectively. The external diffusion coefficient \( k_f \) (cm s\(^{-1}\)) can be calculated from the slope of the straight line obtained from Eq. (7).

3.4.2. Internal diffusion model

When the diffusion (internal surface and pore diffusion) of metal cations inside the sorbent is the rate-limiting step, then sorption data can be presented by the following equation (HO et al., 2000):

\[q_t = k_d t^{1/2},\]

(8)

where \( q_b \), \( k_d \), and \( t \) are surface concentration of adsorbate at time \( t \) (mmol g\(^{-1}\)), internal diffusion coefficient (mmol g\(^{-1}\) min\(^{-1/2}\)), and sorption time (min). The kinetic models outlined above were applied to kinetic data of Zn(II) sorption on the natural sorbent.

4. Results and discussion

4.1. Characterization of adsorbent

X-ray diffraction (XRD) analysis confirmed the presence of calcite 2\([\text{CaCO}_3]\) and quartz \([\text{SiO}_2]\) as major minerals as indicated from their high intensities (Fig. 1a). Dolomite \([\text{CaMg(CO}_3\text{)}_2]\) is present as minor mineral while palygorskite 2\([\text{MgAl}_2\text{Si}_8\text{O}_{20}\text{(OH)}_2\cdot8\text{H}_2\text{O}\]) is present as trace material. A similar mineral composition was found in Moroccan natural clay deposits (Hajji et al., 2001). The non–clay minerals (calcite and dolomite) were eliminated after acid treatment as indicated in Fig. (1b). The removal of non-clay components increased the concentration of clay minerals like palygorskite, muscovite \([4\text{KAl}_3\text{Si}_3\text{O}_{10}\text{(OH)}_2]\) and quartz as indicated in Fig. (1b). A reduction of 60% was observed in sorbent weight after acid treatment, which indicates that the percentage of clay mineral and quartz is about 40% (w/w) in the sample. Acid treatment of the sorbent has no effect on silica. Silica has a poor capacity for heavy metals sorption and elimination of this material requires more complex procedures (Vanloon and Duffy, 2000).

A chemical assay of the sorbents is shown in Table 1. The results indicate that the natural sorbent contains a large fraction of Ca-minerals (which is mainly calcite, from XRD). In
is known that CaCO₃ minerals are usually present in most ground and surface soils (Fuller and Davis, 1987). Hajjaji et al. (2001) reported that carbonate minerals (calcite 38% and dolomite 12%) are the major minerals present with the natural Moroccan clay (Hajjaji et al., 2001). The chemical composition was significantly affected upon acid treatment. The data indicate that the percentage of silica increased from 15.00% to 49.75% (w/w), with a significant increase in the mass fraction of aluminum and iron. The data also indicate a reduction in the mass fraction of CaO after acid treatment, decreasing from 46.85 % to 1.39% (w/w). These data were expected, as calcium present as CaCO₃ or CaMg(CO₃)₂ is easily removed by acid washing. Previous research has indicated that Al(III) ions are easier to release than Si(IV) ions from silicate adsorbents after acid washing (Suraji et al., 1998). Therefore, to determine the extent of Al(III) release, an estimation of Si/Al (w/w) ratio is essential. The Si/Al ratio for the raw sorbent was found to be 4.2 while that for treated sorbent was 4.5. Thus it can be concluded that relatively small amounts of Al(III) ions have released from the sorbent by the action of the nitric acid. In a similar study, (Flessner et al., 2001) reported an increase in Si/Al ratio from 7 to 16 after a long acid treatment of the sample (Flessner et al., 2001).

The acid–base characteristics of the adsorbents and the pHₚₑcac are reported in Fig. (2). The pHₚₑcac of the natural clay deposit and after acid treated sample are 9.5 and 4.0 respectively. The pHₚₑcac was determined using a standard technique (Babić et al., 1999). The pHₚₑcac of natural clay reported in this work is unusually high when compared to the literature data (García–Sanchez et al., 1999; Coles and Yong, 2002; Mellah and Chegrouche, 1997). The pHₚₑcac of treated clay is close to that of natural clay samples free of carbonate minerals (García–Sanchez et al., 1999). The high shift in pHₚₑcac after acid treatment is mainly due to the elimination of alkaline carbonate minerals like calcite and dolomite (Coles and Yong, 2002).

Infrared techniques have been used by previous researchers for identification of soil and clay minerals (Gadsden, 1975). Fig. 3 depicts the IR-spectra of the natural adsorbent. Fig. 3(a) shows the characteristic bands of calcite at 1428.76, 873.66, and 712.68 cm⁻¹. The IR peaks appearing at 1798.41 and 2513.52 cm⁻¹ are also an indication of the presence of calcite and dolomite (Gadsden, 1975). The high intensity of the peak appearing at 1428.76 cm⁻¹ is an indication of the high content of calcite in the sample. The strong band at 1029.22 cm⁻¹ (due to Si–O stretching) is the main characteristic band for quartz. Quartz also gives two other characteristic bands at 800 and 780 cm⁻¹ (Gadsden, 1975). However, these two bands did not appear in the spectra. The bands at 515.71 and 468.97 cm⁻¹ are assigned, respectively, to Si–O–Al and Si–O–Si bending vibrations (Madejova, 2003). These functional groups are present in silicate minerals like palygorskite which is identified by XRD in the natural sample (Fig. 1a). The band at 3424.21 cm⁻¹ is assigned to stretching vibrations of adsorbed water molecules. Another characteristics band for bending vibrations of adsorbed water usually appears at 1650–1600 cm⁻¹ as a medium band (Gadsden, 1975). This band is overlapped by the very strong absorption band of calcite (at 1428.76 cm⁻¹). The stretching vibrations of the surface hydroxyl groups (Si–Si–OH, or Al–Si–OH) are found at 3543.57 and 3614.29 cm⁻¹ (Hajjaji et al., 2001; Madejova, 2003). The short bands appearing at 2920.00 cm⁻¹ are mainly attributed to the C–H stretching vibrations of natural organic matters present in the sample (Hajjaji et al., 2001). Fig. 3(b), depicts the IR-spectra of the sorbent after treatment with HNO₃ solution. It is obvious that the characteristic bands of calcite and dolomite have completely disappeared. The frequency of most remaining bands have changed slightly, this is attributed to the action of the acid. This also indicates that the acid treatment had negligible affect on the structure of silicate materials present in the adsorbent. Fig. 3(b) indicates a new band in the spectra, 1630.34 cm⁻¹, which can be attributed to the bending vibrations of adsorbed water. It is to be expected that the porosity and surface area have increased after treatment, therefore the amount of adsorbed water is also likely to have increased.

### 4.2. Sorption characteristics of N₂ sorption on the sorbent

The textural characteristics and pHₚₑcac of the sorbent are given in Table 1. The sorbent has a relatively low surface area when compared to the surface areas of pure clay adsorbents (Sanchez et al., 1999). It was noted that that the sorbent is mainly microporous in structure with microporosity accounting for 70% of the total pore volume (Table 1). Fig. 4 shows the pore size distribution of the natural sorbent and the acid treated adsorbent. The data indicate that the dv/dr ratio (ratio of the change in volume to the change in radius) doubles (from 0.04 to 0.08 cm³ g⁻¹ nm⁻¹ at about 2 nm pore radius) after acid treatment. It is evident from Fig. 4 that both adsorbents are microporous with the average pore radius for both approximately 2.0 nm.

### 4.3. Sorption isotherms of heavy metals

Sorption isotherms of Zn(II), Pb(II) and Co(II) ions are shown in Fig. 5(a–c). The sorption data were described using the Langmuir and Freundlich isotherm models. The results of these analyses, using linear regression procedures, are shown in Table 2. The shape of Zn(II) isotherm is of “L2” type, while that of Pb(II) and Co(II) is “L1” type according to Giles classification for isotherms (Giles and Smith, 1974).
The shape of the L2 type isotherm (Fig. 5a) for the sorption of Zn(II) indicated that the data have reached a maximum value, resulting in the presence of the plateau. This was not the case for the L1 type curves, of Pb(II) and Co(II), where only the initial part of the isotherm is present and the plateau is not entirely represented (Fig. 5d and c). Another important difference between these isotherms is that the slope of L2 isotherm is steeper than that of L1 isotherm (Giles and Smith, 1974). L-isotherm type (or Langmuir isotherm type) is usually associated with ionic substrates (e.g., metal cations) sorption with weak competition from the solvent molecules (Giles and Smith, 1974).

4.4. Langmuir isotherm

Table 2 indicates that Langmuir model has a limited application for Pb(II) sorption with a regression coefficient, $r^2 = 0.819$. A better description for Co(II) sorption data was evident ($r^2 = 0.910$). The best fit to the Langmuir model was obtained for Zn(II) adsorption, with a correlation coefficient, $r^2 = 0.984$. 

![Infrared spectra. (a) natural sorbent; (b) acid-washed sorbent; (c) the sorbent after Zn(II) sorption.](image-url)
Using the Langmuir model, the maximum sorption capacity for the metals can be estimated as: Zn (2.860 mmol g\(^{-1}\) or 187.0 mg g\(^{-1}\)) > Pb (0.320 mmol g\(^{-1}\) or 66.2 mg g\(^{-1}\)) > Co (0.076 mmol g\(^{-1}\) or 4.5 mg g\(^{-1}\)).

4.5. Freundlich isotherm

Table 2 indicates that there is a slight deviation from linearity using the Freundlich isotherm model for describing Pb(II) and Co(II) sorption (\(r^2 = 0.937\) and 0.984 for Pb(II) and Co(II), respectively). The model gives a poor presentation for Zn(II) sorption behavior (\(r^2 = 0.850\)). Freundlich parameters (\(k_F\) and \(n\)) indicate whether the nature of sorption is either favorable or unfavorable (Frimmel and Huber, 1996). The intercept is an indicator of sorption capacity and the slope is an indicator of sorption intensity. A relatively slight slope \(n < 1\) indicates that sorption intensity is good (or favorable) over the entire range of concentrations studied, while a steep slope \((n > 1)\) means that sorption intensity is good (or favorable) at high concentrations but much less at lower concentrations (Frimmel and Huber, 1996; McKay, 1980). A high value of the intercept, \(K_F\), is indicative of a high sorption capacity (McKay, 1980). In the three sorption systems, \(n\) values are all less than unity which indicates that sorption intensity is good (or favorable) over the entire range of concentrations studied.

The \(1/n\) values for the three systems studied fall in the range: 2–10, which again indicates a favorable sorption process (McKay, 1980). The \(k_F\) values, reported in Table 2, can be used to indicate the relative sorption capacity of the system (Mohan and Singh, 2002). It was noted that \(k_F\) values show the same trend as that of \(Q_{\text{max}}\) for the metals studied, see Table 2.

4.6. Interaction of metals with Calcite (CaCO\(_3\))

The sorbent used in this study has a number of constituents, the presence of which, may explain the variation in the metal adsorptive capacities. In terms of electronegativity, conventional theory states that metals of higher electronegativity should adsorb more readily (McBride, 1994). This convention is partially observed where Zn(II) and Pb(II) show a higher adsorptive capacity than Co(II). However, Zn(II) shows a higher adsorptive capacity than Pb, which possesses a greater electronegativity (electronegativities of metals are presented in Table 3). Furthermore, the conventional sorption theory on solid surfaces would suggest that metals of higher hydrolysis constants have increased adsorptive capacity (McBride, 1994). The reverse of this convention was observed in this study, Pb(II) adsorbed less than Zn(II) (hydrolysis constants are presented in Table 3).

As calcite is a principal component of the adsorbent, the differences between metal sorption capacities may be due to their affinity to the surface of calcite.

The theoretical analysis of metal sorption on calcite surface is complex. However, the following generalisations can be considered as guidelines for prediction of metal sorption on calcite surface (Papadopoulos and Rowell, 1988; Papadopoulos and Rowell, 1989): (a) ionic radius of M(II) cations; metals of ionic radius close to that of Ca(II) adsorb stronger (i.e., stronger displacement) than other metals; (b) solubility of the carbonate complexes formed after sorption of M(II); metals that form less soluble complexes with carbonate adsorb stronger than metals which form more soluble complexes. The first convention can give a reasonable explanation for the higher capacity of Zn(II) and Pb(II)
compared to Co(II). The ionic radius for Co(II) is much smaller than Ca, while the ionic radii of Zn(II) and Pb(II) are much closer to that of Ca(II) (ionic radii are presented in Table 3). However, the convention does not explain the preferential sorption of Zn(II) compared to Pb(II) where the latter has a radius more similar to Ca(II). According to the second convention, Pb(II) should have the highest sorption capacity of the metals studied, however, this was not found to be the case, where Zn(II) of higher solubility was adsorbed to a greater extent than Pb(II) which possesses lower solubility constant (see Table 3 for metals–carbonate solubility constants). The data, however, do show some correlation with convention indicating a high affinity of Pb(II) compared to Co(II) (Table 3). In general the poor correlation with conventional theories for the sorption of metals on calcite may be attributed to the heterogeneous nature of the adsorbent.

### 4.7. Mechanisms of metals sorption

It was found that the sorbent had a significant ion exchange capacity as indicated in Table 1. However, the calculated CEC of the sorbent is 17.8 cmol+/kg (or 0.178 mmol+/g), which indicates that the intrinsic ion exchange capacity of the sorbent, was not high enough to remove large amounts of the heavy metals via ion-exchange mechanism. As indicated in Table 4, the sorption value of Zn(II) is 2.75 mmol Zn2+/g. If one assumed that all Zn(II) ions were removed via ion-exchange mechanism, then the CEC value should be 5.50 mmol+/g (2.75 × 2) or more to facilitate the removal of all Zn(II) ions from solution. This analysis suggests that only 3% of adsorbed Zn(II) was removed via an ion-exchange mechanism. For the Pb(II) system, the amount of metal removed (0.30 mmol Pb2+/g or 0.60 mmol+/g) is higher than the CEC value (0.178 mmol+/g) which would indicate that precipitation is the predominant removal pathway. However, ion-exchange mechanisms are also involved in a range of sorption processes. Even though the retention capacity of Co(II) (0.08 mmol Co2+/g or 0.16 mmol+/g) is relatively close to CEC value (0.178 mmol+/g), the entire sorption process may involve a precipitation mechanism. It has been shown that the removal of heavy metals from solution by calcite surfaces can occur via precipitation mechanisms at high metal concentrations, and can occur via ion exchange at very low metal concentrations (Zachara et al., 1991; Papadopoulous and Rowell, 1989; McBride, 1980) showed that Cadmium Cd(II) is the metal cation which replaces more easily Ca(II), due to the similitude of their ionic radii, for the rest of metal cations ion exchange will occur in much lesser extent. Therefore, most of the amount of Zn(II), Pb(II) and Co(II) retained by calcite may be due to a precipitation process. The precipitation of metals on the surface of sorbents or even in solution is probable considering the dissolution of calcite into solution under the conditions of this study. Ksp of calcite is 4.5 × 10⁻⁹ at 25.0 °C (Harris, 1995). Based on this, the carbonate (CO₃²⁻) content in solution is equal to \sqrt{Ksp} = 6.71 × 10⁻⁷ mol·L⁻¹. Also, the initial concentration of Zn(II), Pb(II), and Co(II) are 0.01, 0.004, and 0.002 mol·L⁻¹ are, respectively. At these concentrations, the precipitation of ZnCO₃, PbCO₃, and CoCO₃ is possible where the concentration product [M⁺]²[CO₃²⁻] is much higher than the corresponding solubility product constants Ksp (Table 3). It can be calculated that the formation of metal hydroxycarbonates (M₂(OH)₂CO₃) is not possible for these metals under the experimental conditions of this study, as follows.

**Hydrolysis of Zn(II) ions by water can be presented as (Wulfsberg, 1987):**

\[
\text{Zn}^{2⁺}(aq) + \text{H}_2\text{O}(L) \rightarrow \text{Zn(OH)}^+ (aq) + \text{H}^+(aq)
\]

This reaction has a pKₐ₁ = 9.6 (or Kₐ₁ = 2.5 × 10⁻¹⁰). The equilibrium expression can be expressed as:

\[
K_{a1} = \frac{[\text{H}^+] [\text{Zn(OH)}^+]}{[\text{Zn}^{2⁺}]}.
\]

The value of [H⁺] at equilibrium can be calculated from pH eql. For Zn(II) sorption system, pH eql = 6.5 or [H⁺] = 3.2 × 10⁻⁷ M. Using the values of [H⁺] and pKₐ₁ in the equilibrium expression one can obtain

\[
2.5 \times 10^{-10} = \frac{[3.2 \times 10^{-7}][\text{Zn(OH)}^+]}{[\text{Zn}^{2⁺}]}.
\]

The ratio: [Zn²⁺]/([Zn(OH)⁺]) can be calculated from the above equation:

\[
\frac{[\text{Zn}^{2⁺}]}{[\text{Zn(OH)}^+]} = 1280.
\]

This indicates that the concentration of free divalent Zn(II) is much higher than Zn(OH)⁺ at pH = 6.5. At pH ini (5.5), the ratio ([Zn²⁺]/([Zn(OH)⁺])) is much higher and becomes 12,800. The ratio becomes unity (i.e. 50% of metal concentration is present as Zn(II) and the remaining is present as Zn(OH)⁺) at pH = 9.6. At solution pH higher than 9.6 the concentration of Zn(OH)⁺ becomes more than Zn(II) in solution. In light of the above analysis, the formation of Zn hydroxycarbonate complexes is not possible at pH ≤ 6.5. Therefore, the following reactions are not possible under the experimental conditions employed due to the concentration of Zn(OH)⁺ being insignificant:

\[
\text{Zn(OH)}^+ (aq) + \text{CO}_3^{2⁻}(aq) = \text{Zn(OH)CO}_3(aq)
\]
**Table 3 – Ionic properties, solubility, and acidity constants for the studied metals**

| Metal   | Ionic radius (pm)
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(II)</td>
<td>137</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>175</td>
</tr>
<tr>
<td>Co(II)</td>
<td>125</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>197</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>1.6</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>1.9</td>
</tr>
<tr>
<td>Co(II)</td>
<td>1.0</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>–</td>
</tr>
<tr>
<td>$pK_{sp}$ for MCO$_3$</td>
<td>10.0</td>
</tr>
<tr>
<td>$pK_{sp}$ for M(OH)$_2$</td>
<td>15.5</td>
</tr>
<tr>
<td>$pH_{ppt}$</td>
<td>7.1</td>
</tr>
<tr>
<td>$pK_a$</td>
<td>9.6</td>
</tr>
<tr>
<td>$pH_{equi}$</td>
<td>6.5</td>
</tr>
<tr>
<td>Hydration enthalpy (kJ mol$^{-1}$)</td>
<td>$-2044$</td>
</tr>
<tr>
<td>Second ionization enthalpy (kJ mol$^{-1}$)</td>
<td>1734</td>
</tr>
</tbody>
</table>

- **Metal Ionic radius (pm)**: Data were taken from McMurry and Fay (1995). pm: picometer.
- **Electronegativity (Pauling)**: For the reaction: MCO$_3$(s) $\rightarrow$ M$^{2+}$(aq) + CO$_3^{2-}$(aq) Harris (1995).
- **$pK_{sp}$ for M(OH)$_2$**: For the reaction: M(OH)$_2$(s) $\rightarrow$ M$^{2+}$(aq) + 2OH$^-$(aq) Harris (1995).
- **$pH_{ppt}$**: pH after which a precipitation by OH$^-$ ions occurs. These values were calculated from the following equation:

$$pH_{ppt} = 14 - \log \sqrt{\frac{M^{2+}_{eq}}{K_{sp}}}$$

K$_{sp}$ are given in the table (column 5), $M^{2+}$ are the metals concentrations (in mol dm$^{-3}$). $pH_{ppt}$ values of Zn(II) and Pb(II) were calculated at initial concentrations of 0.0153 and 4.83 × 10$^{-3}$ mol L$^{-1}$. For Co(II) ions, $pH_{ppt}$ was calculated at 2.56 × 10$^{-3}$ mol L$^{-1}$.
- **$pK_a$**: For the reaction: M$^{2+}$(aq) + H$_2$O$L_2$ $\rightarrow$ M(OH)$^+$(aq) + H$^+$ (aq) Wulfsberg (1987).
- **$pH_{equi}$**: pH values after establishment of equilibrium. pH of metal solution before adding the sorbent (pH$_{initial}$) are 5.5, 3.5, and 6.0 for Zn(II), Pb(II), and Co(II), respectively.
- **Hydration enthalpy (kJ mol$^{-1}$)**: Data obtained from Wulfsberg (1987).
- **Second ionization enthalpy (kJ mol$^{-1}$)**: Data obtained from Wulfsberg (1987).
The concentration of Zn(II) is much higher in comparison with Zn(OH)+ concentration, therefore, the following reaction is more likely to occur:

\[ \text{Zn}^{2+} + \text{CO}_3^{2-} \rightarrow \text{ZnCO}_3(s) \]

Adopting a similar analysis for Pb(II) and Co(II) ions, the following ratios can be determined at equilibrium pH:

\[ \frac{[\text{Pb}^{2+}]}{[\text{Pb(OH)}^+]^3} = 320, \]
\[ \frac{[\text{Co}^{2+}]}{[\text{Co(OH)}^+]^3} = 400. \]

The formation of metal hydroxycarbonates complexes of Pb(II) [Pb2(OH)2CO3] or Co [Co2(OH)2CO3] is not possible under the experimental conditions in this study.

Based on the above analysis, the sorption mechanism of metals by the sorbent can be represented by the following surface reactions:

Dissolution of calcite that is present in the sorbent:

\[ \text{CaCO}_3(s) \rightarrow \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq). \]  

Interaction between the free metal (M2+) in solution and CO3\(^2\) in solution:

\[ \text{M}^{2+}(aq) + \text{CO}_3^{2-}(aq) \rightarrow \text{MCO}_3(s). \]

Deposition of MCO3 on the sorbent surface:

\[ -\text{S} - \text{CaCO}_3(s) + \text{MCO}_3(s) \rightarrow [-\text{S} - \text{CaCO}_3] - \text{MCO}_3(s), \]

where M\(^{2+}\) represents the free metal cation in solution.

Fig. 3(c) shows the IR spectra of the sorbent after sorption of Zn(II). The characteristic bands of calcite were greatly affected after zinc sorption, in that the band at 712.68 cm\(^{-1}\) shifted to 708.42 cm\(^{-1}\) and the bands at 873.60 and 1798.41 cm\(^{-1}\) were completely removed. The evidence of formation of a new material on the surface was recognized from the significant split in the band at 1428.76 cm\(^{-1}\) and the formation of a new band at 835.10 cm\(^{-1}\) (Gadsden, 1975). Several studies have indicated that the sorption of zinc on pure calcite occurs by formation of hydroxo, and carbonate complexes of zinc within the crystal structure of calcite (Papadopoulos and Rowell, 1989; Garcia-Sanchez and Alvarez-Ayuso, 2002). In this work, it has been shown that Zn(II) sorption on calcite occurs by formation of ZnCO3 complexes. Regarding Pb(II) and Co(II) sorption
mechanisms, the obtained IR spectra (not shown) were identical to the spectra of the sorbent (Fig. 3a) and no new bands were observed. This would indicate that amount of new precipitated phases (PbCO3 and CoCO3) are very low with respect to the amount of mineral sample, and therefore the intensity of the corresponding bands is not high enough to be detected.

The data presented in Table 4 suggest that the Zn/Ca ratio is very high (>50) in the case of the treated adsorbent. This indicates that other cations such as Mg(II) and K(I) may exchange with Zn(II) ions. Other adsorption processes, such as retention by means of terminal OH groups of clays, may also be involved. The precipitation mechanism is unlikely in this case due to the absence of calcite. It is proposed that the primary silicate minerals (muscovite, palygorskite) are responsible for Zn(II) sorption from solution. Table 4 indicates the importance of primary minerals (calcite and dolomite) for metal adsorption. Sorption of Zn(II) has been significantly affected by the acid treatment process, as the treated sorbent was ineffective for Pb(II) and Co(II) removal from solution.

4.8. Kinetics of Zn(II) sorption by natural sorbent

As has been shown the metal with the highest adsorptive capacity was Zn(II), in light of this, kinetic studies and modeling were undertaken with this particular sorbate. The assessment of the employed models for fitting the sorption data was made by calculating the sum of square errors squared (SSE). Lower values of SSE show better fit to sorption data.

\[
SSE = \sum (q_{t,\text{exp}} - q_{t,\text{theo}})^2,
\]

where \( q_{t,\text{exp}} \) and \( q_{t,\text{theo}} \) are the experimental sorption capacity of Zn(II) (mmol g\(^{-1}\)) at time \( t \) and the corresponding value which is obtained from the kinetic models.

4.9. Pseudo-first-order and second-order models

Kinetic data of Zn(II) sorption were analyzed using pseudo-first order and second order models (Eqs. (4) and (5)). In order to use these models, the equilibrium capacity (\( q_e \)) needs to be determined. Some researchers (Cheung et al., 2001) have used a trial and error procedure to determine the value of \( q_e \) that best describes the kinetic data, however, other researchers have used Langmuir isotherm to determine the value of \( q_e \) (Chiron et al., 2003). In this work, the values of \( q_e \) were calculated from Langmuir equation with modification of Eq. (1) shown below.

The equilibrium concentration \( (C_e) \) can be presented as in the following equation:

\[
C_e = C_0 - C_{\text{surface}},
\]

where \( C_0 \) and \( C_{\text{surface}} \) are, respectively, the initial concentration (mol dm\(^{-3}\)) and the surface concentration at equilibrium (mol g\(^{-1}\)). The ratio of the sorbent mass to the volume of the solution can be presented as:

\[
m = \frac{\text{mass}(g)}{\text{volume}(dm^3)}.
\]

The surface concentration \( (C_{\text{surface}}) \) is equal to \( m q_e \), accordingly, Eq. (14) becomes:

\[
C_e = C_0 - m q_e.
\]

Combining Eqs. (1) and (15), Eq. (16) can be obtained:

\[
q_e = \frac{b Q_{\text{max}} (C_0 - m q_e)}{1 + b (C_0 - m q_e)}.
\]

By rearranging Eq. (16), Eq. (17) is obtained:

\[
b m q_e^2 - [1 + b C_0 + m b Q_{\text{max}}] q_e + b Q_{\text{max}} C_0 = 0.
\]

Eq. (17) was applied to determine the values of \( q_e \) at the experimental conditions used in this study. In these systems, the solution to Eq. (17) is possible and gives reasonable values for \( q_e \). The use of Eq. (17) is novel to this study, however, similar expressions have been derived for estimating the equilibrium capacity \( (q_e) \) for sorption of heavy metals on grafted silica (Chiron et al., 2003). Table 5 summarizes the solution of \( q_e \) values obtained from Eq. (17) for this system.

It is noted in Table 5 that sorption mass transfer is required to cease before the attainment of an equilibrium state, where \( q_{t,\text{theo}} > q_{300,\text{min}} \); taking into account that \( q_{t,\text{theo}} \) is the true equilibrium capacity. As shown in Table 5, the values of \( q_{t,\text{theo}} \) were higher than the capacities calculated (assuming that all Zn(II) ions were removed from solution), indicating that \( q_{t,\text{theo}} \) does not represent the true equilibrium capacity. In the following discussion \( q_{t,\text{theo}} \) is simply referred to as \( q_e \).

The effect of Zn(II) ion concentration on sorption rate is depicted in Fig. 6. The parameters of pseudo-first order model

Table 5 – The results of the solution of Eq. (17)

<table>
<thead>
<tr>
<th>Initial Zn(II) concentration mmol dm(^{-3}) (C0)</th>
<th>mass of adsorbent (g)</th>
<th>m (g dm(^{-3}))</th>
<th>( q_{300,\text{min}} ) mmol g(^{-1})</th>
<th>( q_{t,\text{theo}} ) mmol g(^{-1})</th>
<th>( q_{e1} ) mmol g(^{-1})</th>
<th>( q_{e2} ) mmol g(^{-1})</th>
<th>( q_{e} ) ( ^a ) mmol g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.47</td>
<td>3.400</td>
<td>2.0</td>
<td>0.74</td>
<td>2.40</td>
<td>6.83</td>
<td>5.74</td>
<td></td>
</tr>
<tr>
<td>10.10</td>
<td>3.400</td>
<td>2.0</td>
<td>1.26</td>
<td>2.32</td>
<td>6.23</td>
<td>5.05</td>
<td></td>
</tr>
<tr>
<td>7.20</td>
<td>3.400</td>
<td>2.0</td>
<td>1.26</td>
<td>2.03</td>
<td>5.06</td>
<td>3.60</td>
<td></td>
</tr>
<tr>
<td>4.05</td>
<td>3.400</td>
<td>2.0</td>
<td>0.91</td>
<td>1.41</td>
<td>4.11</td>
<td>2.03</td>
<td></td>
</tr>
</tbody>
</table>

\( q_{300,\text{min}} \) is the sorption capacity at 300 min from the start of the sorption test. \( q_{e1} \) and \( q_{e2} \) are the equilibrium capacities which represent the solutions of Eq. (17).

\( a \) \( q_e \) is the capacity assuming that all Zn(II) ions were removed from the solution.
are shown in Table 6. The model adequately fits the data over the entire course of the experiment, with high correlation coefficients obtained (Table 6). The values of rate constants \(k_1\) should be consistent if the whole process is controlled by a first order mechanism. However, the value of the first order rate constant varied in this study. This phenomenon has attributed to the heterogeneous nature of the sorbent surface (Sparks, 1989). The sorption capacity after 30 min \(q_{30\text{ min}}\) of interaction was calculated with the results presented in Table 6. It appears that the process was slow, with 10–20% of the available capacity achieved in the first 30 min. Furthermore, 30–100% of the sorbent capacity was utilized after 300 min. The analysis of sorption data were recalculated by neglecting the initial stage of interaction (0–30 min). The obtained \(k_1\) value was close to those reported in Table 6. This is an indication that the initial stage of sorption was rapid and has a slight effect on the process. The high correlation of this model to the sorption data is an indication that Eq. (17) gives an accurate estimation for the equilibrium capacity.

The parameters of second order model are shown in Table 6. This model was not as effective as the pseudo-first order model in describing the kinetic data, with the correlation coefficients obtained lower than those obtained from the pseudo-first order model.

4.10. External diffusion model

It is probable that the sorption of Zn(II) occurred only on the external surface of the adsorbent, it follows therefore, that an external diffusion model should describe the sorption data. The parameters for external diffusion model are shown in Table 7. The external diffusion model shows excellent correlation with the sorption data, with high correlation coefficients obtained. This would indicate that the sorption of Zn(II) is probably a surface process occurring on the exterior of the sorbent particle. As shown in Table 7, \(k_f\) values increase.

### Fig. 6 – Effect of Zn(II) initial concentration on sorption rate. Mass of sorbent: 3.400 g, volume of solution: 1.7 dm³, stirring speed: 500 rpm, pH: 7 and particle size: <100 μm.

### Fig. 7 – Plots of internal diffusion model for Zn(II) adsorption. Mass of sorbent: 3.400 g, volume of solution: 1.7 dm³, stirring speed: 500 rpm, pH: 7 and particle size: <100 μm.

#### Table 6 – Pseudo first and second order model parameters for the sorption of Zn(II)

<table>
<thead>
<tr>
<th>(C_0) (mmol dm(^{-3}))</th>
<th>mass (g)</th>
<th>(m^a) (g dm(^{-3}))</th>
<th>(k_1) (l/min)</th>
<th>(r^2)</th>
<th>(k_2) (g mmol (^{-1}) min(^{-1}))</th>
<th>(r^2)</th>
<th>(q_{30\text{ min}}) (mmol g(^{-1}))</th>
<th>(q_{300\text{ min}}) (mmol g(^{-1}))</th>
<th>(q_{e})(^b) (mmol g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.47</td>
<td>3.400</td>
<td>2.0</td>
<td>0.00138</td>
<td>0.9331</td>
<td>0.0009</td>
<td>0.9300</td>
<td>0.20</td>
<td>0.71</td>
<td>2.32</td>
</tr>
<tr>
<td>10.10</td>
<td>3.400</td>
<td>2.0</td>
<td>0.00276</td>
<td>0.9685</td>
<td>0.0021</td>
<td>0.9498</td>
<td>0.25</td>
<td>1.19</td>
<td>2.00</td>
</tr>
<tr>
<td>7.20</td>
<td>3.400</td>
<td>2.0</td>
<td>0.00346</td>
<td>0.9842</td>
<td>0.0027</td>
<td>0.9327</td>
<td>0.21</td>
<td>1.31</td>
<td>2.0</td>
</tr>
<tr>
<td>4.05</td>
<td>3.400</td>
<td>2.0</td>
<td>0.00507</td>
<td>0.9277</td>
<td>0.0051</td>
<td>0.9162</td>
<td>0.20</td>
<td>1.12</td>
<td>1.14</td>
</tr>
</tbody>
</table>

| \(a\) Volume of solution in all experiments is 1.7 dm³. 
| \(b\) Calculated from Eq. (17). |

#### Table 7 – External and internal diffusion models parameters for Zn(II) adsorption

<table>
<thead>
<tr>
<th>(C_0) (mmol dm(^{-3}))</th>
<th>mass (g)</th>
<th>(k_f) cm s(^{-1}) (\times 10^{-6})</th>
<th>(r^2)</th>
<th>(k_d) (mmol g(^{-1}) min(^{-1/2}))</th>
<th>(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.47</td>
<td>3.400</td>
<td>1.736</td>
<td>0.9272</td>
<td>0.0811</td>
<td>0.9673</td>
</tr>
<tr>
<td>10.10</td>
<td>3.400</td>
<td>2.777</td>
<td>0.9768</td>
<td>0.0813</td>
<td>0.9788</td>
</tr>
<tr>
<td>7.20</td>
<td>3.400</td>
<td>4.861</td>
<td>0.9930</td>
<td>0.0930</td>
<td>0.9809</td>
</tr>
<tr>
<td>4.05</td>
<td>3.400</td>
<td>9.027</td>
<td>0.9728</td>
<td>0.0856</td>
<td>0.9622</td>
</tr>
</tbody>
</table>
with a decrease in the initial Zn(II) concentration. For example, a 5-fold increase was observed in the $k_f$ value when the zinc concentration decreased from 11.47 to 4.05 mM. The reason for this behavior can be attributed to the lower competition for the sorption surface sites at lower concentration. At higher concentrations, the competition for the surface active sites will be high and consequently lower sorption rates are obtained.

### 4.11. Internal diffusion mechanism

Theory indicates that external diffusion is the dominant process, if the straight line obtained from Eq. (8) does not pass through the origin (HO et al., 2000). This is shown to be the case in Fig. 7, indicating the presence of external diffusion at the earlier stages of interaction. Due to the heterogeneous nature of the adsorbent, and the presence of active materials, i.e., calcite and clay minerals, the molecular movement of Zn(II) deep inside the sorbent particles is unlikely. However, the process of migration of Zn(II) ions inside the sorbent can not be totally excluded. The linear plots shown in Fig. 7 indicate the presence of internal diffusion with this mechanism involved in the process at $t > 25$ min. Prior to this, the process appears to be entirely controlled by an external diffusion mechanism. The external diffusion model shows good correlation with the sorption data at $t > 25$ min, where the obtained correlation coefficients for all systems are higher than 0.95 as shown in Table 7. It is noted that the changes in $k_f$ values, due to variations in experimental conditions, are much greater than those in $k_d$ values. This would indicate that external diffusion was the controlling mechanism during Zn(II) sorption. This in fact gives further evidence that the reduction in aqueous phase Zn(II) by the adsorbent is a surface process and that the contribution of internal diffusion is less significant under the studied experimental conditions.

### 5. Conclusions

Natural Jordanian sorbent containing silicate and carbonate minerals is an effective sorbent for removing Zn(II), Pb(II), and Co(II) ions from solution. The equilibrium sorption capacities of the metals were: 2.860, 0.320, 0.076 mmol cation g$^{-1}$ for Zn(II), Pb(II) and Co(II) at pH 6.5, 4.5 and 7.0, respectively. Acid-treatment of the sorbent reduces the sorption capacity with this attributed to elimination of carbonate minerals (calcite and dolomite) from the adsorbent. It was found that the mechanism of metal sorption is mainly precipitation as metal carbonate complexes. Furthermore, the natural sorbent is especially suited to retaining Zn, as Zn is generally considered to be more mobile than Pb. The rate of Zn(II) sorption was found to be slow, with only 10–20% of available sorbent capacity utilized in the first 30 min of interaction. Kinetic data showed good correlation to a pseudo-first order and external diffusion models which indicated that sorption of Zn(II) occurred on the external surface of the sorbent with internal diffusion less significant under the experimental systems investigated.

### References


