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Adsorption of Zn(II), Pb(II), Cr(III) and Mn(II) from water by Jordanian bentonite

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ABSTRACT

Jordanian bentonite from Al-Azraq has been purified using centrifugation technique. Both raw and purified bentonite were characterized by FTIR, XRD, XRF and SEM. Adsorption of Zn(II), Pb(II), Cr(III) and Mn(II) on purified bentonite was studied using batch technique as a function of bentonite dosage, contact time, pH and temperature. The variation of distribution coefficient with bentonite weight was also studied. The isothermal behaviors of the metal ions uptake onto the surface of purified bentonite were investigated. The metal ions uptake properties on the bentonite fit Langmuir better than Freundlich and Dubinin–Radushkevich adsorption isotherms. Purified bentonite showed high-metal ion uptake capacity toward Pb(II) and moderate ion uptake toward Cr(III), while Zn(II) and Mn(II) had relatively low adsorption capacity toward bentonite. The order for increasing adsorption capacity was as the following: Pb(II)>Cr(III)>Zn(II)>Mn(II). Thermodynamic functions, ΔG^*, ΔH^* and ΔS^*, were determined for each metal ion; ΔG^* values indicated that the adsorption process of these metal ions on bentonite is favorable while ΔH^* values indicated that this process is endothermic. On the other hand, the process has positive entropy which means that the adsorption process increases the disorder of the system. Column experiment was used effectively for the determination of metal ion loading capacity. Desorption studies were done using column experiments where 0.1 N HNO_3 was used in order to regenerate bentonite.

Keywords: Jordanian bentonite; Adsorption; Heavy metals; Thermodynamic functions; Column

1. Introduction

Pollution by heavy metals is one of the most serious environmental problems facing life and earth; they are stable and persistent environmental pollutants since they cannot be degraded or destroyed. Because of this, the concentration of these heavy metals must be reduced to the maximum permissible concentration [1]. Heavy metals are introduced into the environment through natural phenomena and human activities such as agricultural practices, transport, industrial activities and waste disposal. When heavy metals are present in waste streams, they can be absorbed by marine animals and enter the human food chain [2]. The most conventional methods of heavy metals removal from industrial wastewater are chemical precipitation, ion exchange, solvent extraction, ultrafiltration, reverse osmosis and adsorption. Each method has it's inherit advantages and limits of applications [3].

Many mechanisms have been postulated for heavy metals adsorption such as: cation exchange, surface complexation (inner sphere and outer sphere surface complexation), surface – induce precipitation, surface – co precipitation, colloid formation at the surface and diffusion into particle micro pores [4]. Activated carbon has broadly applied for wastewater

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treatment as one of the most effective adsorbents to remove a variety of contaminants, but relatively high cost, difficulty of preparation, loss of adsorption capacity and need of regeneration limit its application as adsorbent [5].

Bentonite is a 2:1 type of clay, which means that the montmorillonite clay mineral is composed of units of two silica tetrahedral sheets with a central alumina octahedral sheet. All tips of tetrahedrons point in the same direction and toward the center unit. These layers are held together by weak Van der Waals forces, which ease the penetration of water molecules between the layers. The isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} or Zn^{2+} for Al^{3+} in the octahedral layer results in a net negative surface charge on the clay. This negative charge is balanced by the presence of exchangeable cations (e.g. H^+, Na^+ and Ca^{2+}) at the clay surface. Compared with other clay types, bentonite has excellent sorption properties and possesses sorption sites available within its interlayer space as well as on the outer surface and edges [6]. Bentonite is considered one of the most promising candidates for use in decontamination of high level heavy metals waste due to its physical and chemical properties. Bentonite has high specific surface area, cation exchange capacity, and adsorptive affinity for organic and inorganic ions [7]. Removal of Pb(II) ions from wastewater effluents seized upon scientist interest, so many adsorbents have been used for this purpose. Montmorillonite, Kaolinite and Zeolite were used extensively to remove Pb(II) from wastewater, it was determined that the adsorption capacity of Pb(II) is greater on montmorillonite [8]. Natural bentonite and expanded perlite have been evaluated for the removal of Cr(III) from aqueous solutions, this study showed that bentonite (96% Cr(III) removed) is more efficient and rapid for removing Cr(III) from aqueous solutions than expanded perlite (40% Cr(III) removed) [7]. Smectite clays, as montmorillonite, are widely used as industrial adsorbents in the removal Mn(II) ions from industrial effluents. The removal efficiency of Mn(II) ions is dominated by pH value [9]. Physical and chemical treatment of bentonite can increase its adsorption capacity toward zinc; there was an investigation showed that the adsorption capacity of zinc is improved by heat treatment of bentonite, and the adsorption of sodium-enriched bentonite is higher than natural bentonite in all physical and chemical changes [10].

The aim of this work is to use raw Jordanian bentonite from Al-Azraq as adsorbent of heavy metals from aqueous solution, the heavy metals which will be studied are: Pb(II), Cr(III), Zn(II) and Mn(II). Purification of bentonite will be done in order to increase its ability to adsorb these heavy metals. The adsorption of these heavy metals on purified bentonite will be studied as a function of contact time, pH, temperature, and concentration variation.

The data will be analyzed based on adsorption models such as: Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) adsorption isotherms. In order to determine the nature and characteristic of the adsorption process, thermodynamic functions will be determined.

2. Materials and methods

2.1. Materials used

All chemicals used in this study were analytical grade. Samples of Jordanian bentonite from Azraq were obtained from Natural Resources Authority (NRA–Amman-Jordan). These natural bentonite rocks were grounded gently using glass rod, and then they were sieved to remove particles greater than 120 mesh (<250 μm). The bentonite portions of particle size less than 120 mesh were used in further purification to be used in this investigation.

2.2. Methods used

Infrared adsorption spectra of bentonite samples were recorded using (SHIMADZU-IR Prestige-21) FTIR spectrophotometer at (4,000–400) cm^{-1} infrared region. X-ray diffraction was performed using (SHIMADZU-XRD-6000) diffractometer with nickel filtered copper X-ray radiation (CuKα, $\lambda = 1.5406$ Å), where Cu is the target material that produces primary X-rays at 30.0 kV voltage and 30.0 mA current. Scanning was done according to the following sets: 2.000–80.000 2Θ scanning range, 2.000 (deg/min) speeds, and the receiving slit width was 0.3000 mm. The chemical composition of bentonite samples was done using X-ray fluorescence spectrometer (SHIMADZU-XRF-1800). The shape and surface morphology of bentonite samples were also studied with (Shimadzu–SEM SUPER SCAN SSX Series). The concentrations of metal ions were determined using ICP (SHIMADZU-ICPS-7510) under the following conditions: Radio frequency power = 1.2 kW, coolant gas flow = 14.0 L/min, plasma gas flow = 1.20 L/min and carrier gas flow = 0.70 L/min.

2.3. Purifications process

Purifications process was done using the following steps: the bentonite samples of particle size less than 250 μm were mixed with distilled water and then the suspension was centrifuged at 750 rpm to obtain particles less than 2 μm. Carefully, these particles were separated in large bottles. The centrifugation was repeated for further five times more. The centrifuged (pure) bentonite samples were dried in an oven at 105°C for 4 h and stored in polyethylene bottles.

2.4. Adsorption of metals on purified bentonite

2.4.1. Studying bentonite dosage effect on metal ion adsorption on bentonite

A 50.0 ml of 100 mg/l standard solutions of studied metal ions were added to variable bentonite weights at fixed pH, temperature, and shaking time. The temperature of the water bath was adjusted to 25°C and the contact time fixed at 30 min. For Zn(II), the amount of bentonite was varied from 0.10 to 0.80 g and the solution was shaken at pH 7.0. In the case of Pb(II), studying weight effect was started with 0.03 g and ended with 0.10 g, this was done at pH 5.0. A 0.05–0.30 g range of weights were examined for Cr(III) uptake capacity after equilibration by shaking at pH 5.0. On the other hand, Mn(II) was also studied using the same manner, but the weights of bentonite were ranging from 0.20 to 2.00 g at pH 4.0.

2.4.2. Studying pH effect on metal ion adsorption on bentonite

Metal ions of 50.0 ml in volume and 100 mg/l in concentration at 25°C were shaken for 30 min with a certain amount of bentonite at different pH ranges; the pH was adjusted either with diluted nitric acid (HNO_3) or sodium hydroxide (NaOH). For Zn(II), the studied pH values were 4.0, 6.0 and 7.0; this study was done on 0.60 g of bentonite, but 1.00 g of Mn(II) was taken to study pH effect ranging from 2.0 to 4.0. A 3.0–5.0 pH range was studied for both Pb(II) and Cr(III) using different bentonite dosage, 0.07 g for Pb(II) study and 0.10 g for Cr(III).

2.4.3. Studying contact time effect on metal ion adsorption on bentonite

In order to study the effect of contact time on the adsorption of metals ion on bentonite, 50.0 ml of 100 mg/l standard solutions of metal ions at fixed pH value were added to a certain weight of bentonite, the solution was then shaken for different time periods at 25°C water bath temperature. Zn(II) solution pH was adjusted to 7.0, and then shaken for 5–120 min. The studied time intervals for Mn(II) solutions were from 5 to 30 min, this study was done at pH 4.0. Both Pb(II) and Cr(III) solutions were adjusted to pH 5.0, and contact time effect was investigated at the period of 5–120 min.

2.4.4. Batch adsorption experiments

Studying adsorption Isotherms for each studied metals on purified bentonite were done using batch equilibrium technique according to the following procedure; 50.0 ml of 100 mg/l solutions of investigated metal ions were added to an exact weight of purified bentonite at different pH values and temperatures. The pH was adjusted either with diluted nitric acid (HNO_3) or sodium hydroxide (NaOH). The mixture was shaken on a thermostated shaker for a fixed period of time. The solution was then filtered and the concentrations of metal ions before and after adsorption were measured using Inductively Coupled Plasma (ICP). All the measurements were repeated twice.

2.4.5. Column adsorption and desorption experiments

The adsorption and desorption of Pb(II), Zn(II), Cr(III) and Mn(II) ions was carried under column conditions, where the bentonite was loaded with each metal ion. A glass column of 150 mm length and 10 mm interior diameter was used. The column was packed with certain amount of dried bentonite; 1.000 g ± 1 mg was taken for Cr(III) and Pb(II), 10.000 g ± 1 mg was taken for Mn(II) and 6.000 g ± 1 mg was used for Zn(II) experiment. Samples of 50.0 ml of 1000 mg/l of Pb(II), Zn(II), Cr(III) and Mn(II) were adjusted at the favorable pH, and then passed through the column at (1.0 ml/min) flow rate. The eluate was collected and the concentration of metal ions was determined using ICPS. After that a 50.0 ml of 0.1 HNO_3 was used for elution of the sorbed metal ion, keeping the flow rate at (1.0 ml/min), and eluate was collected and metal ions concentrations were measured using ICPS. Elution with 0.1 HNO_3 was repeated several times until the collected samples were free from heavy metals ions, and then metal ion uptake by the packed bentonite was repeated following the same steps described before.

3. Results and discussion

3.1. X-ray diffraction patterns

X-ray diffraction is a non destructive analytical technique which reveals information about crystallographic structure. This technique is widely used in the characterization of clays. The XRD patterns for raw bentonite and purified bentonite are shown in Fig.1. Raw Jordanian bentonite consists of montmorillonite (M) as major clay mineral, whereas quartz (Q) and calcite are present as impurities [12]. Fig. 1 shows that the percent of SiO_2 decreases significantly after purification process while the percent of montmorillonite in purified bentonite is increased.

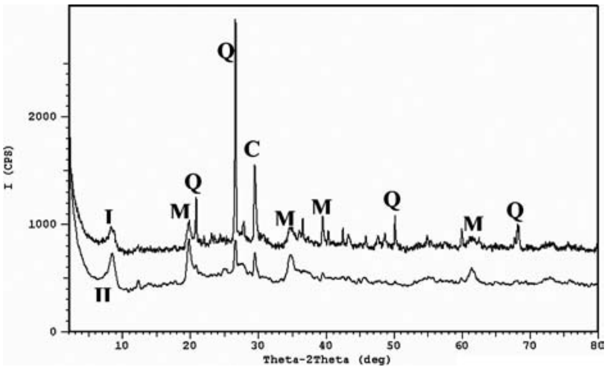


Fig. 1. XRD patterns for (I) Raw bentonite and (II) Purified bentonite, M: montmorillonite, Q: Quartz and C: calcite.

3.2. The XRF analysis

According to XRF analysis, bentonite is a type of clay which mainly consists of silica, alumina and appreciable quantities of iron, alkalis and alkali earth metals. Bentonite having (Na^+) as the exchangeable ions typically has very high swelling capacities and forms gel-like masses when added to water. Other type of bentonite is calcium bentonite, which the exchangeable (Ca^{2+}) is more dominant than other ions; this type has much lower swelling capacity than sodium bentonite. A third type of bentonite is calcium-sodium, or called mixed bentonite, which tends to swell moderately and forms gel of lesser volumes than equal masses of sodium type. According to Table 1, the XRF of raw bentonite shows that the Jordanian bentonite is of intermediate swelling capacity since it contains both calcium (CaO ~ 1.24%) and sodium (Na_2O ~ 2.98%), and the percent of these two cations are reduced after loading bentonite with Pb(II) ions. On the other hand, the amount of SiO_2 decreased significantly after purification from 60.86% to 45.72%; this result strongly indicates that the centrifugation removed large amounts of silica from bentonite.

Table 1
The XRF for raw and purified bentonite.

Compound (%)	Raw bentonite	Purified bentonite	Purified bentonite loaded with Pb(II)
SiO_2	60.86	45.72	46.63
Al_2O_3	13.03	13.57	13.96
Fe_2O_3	6.51	8.54	8.88
TiO_2	1.10	0.88	0.88
P_2O_5	0.12	0.09	0.10
CaO	1.24	2.78	1.56
MgO	3.08	4.76	4.60
K_2O	2.98	3.11	2.99
Na_2O	2.85	3.61	2.11

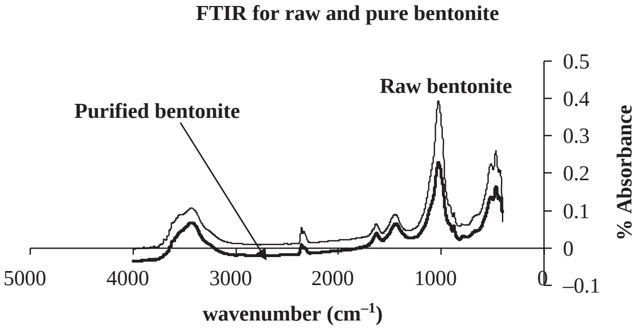


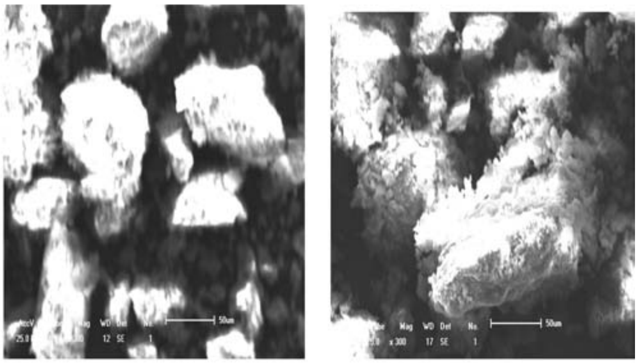
Fig. 2. FTIR for raw and purified bentonite.

3.3. FTIR spectra

Bentonite was characterized by FTIR. This technique could be used to identify the major functional groups consisting bentonite. From the wave number of the molecular vibrations modes, a good explanation of the chemical structure could be obtained. As illustrated in Fig. 2, the characteristic IR band of montmorillonite appeared at 3,468 cm^{-1}. This band represents the fundamental stretching vibrations of different –OH groups present in Mg–OH–Al, Al–OH–Al, and Fe–OH–Al units in the octahedral layer [11]. The strong peak appears at 1,035 cm^{-1} is related to the stretching vibrations of Si–O groups, while the bands at 533 and 476 cm^{-1} are due to Al–O–Si and Si–O–Si bending vibrations, respectively [12]. The peak at 848 cm^{-1} is assigned to O–Si–O asymmetric stretching, while the peak at 450 cm^{-1} is due to O–Si–O bending mode [11]. On the other hand, the peak at 1,647 cm^{-1} is for H–O–H bending whereas the peak at 890 cm^{-1} is due to OH bending bounded to Fe^{3+} and Al^{3+} [12]. Fig. 2 gives strong indication that the aim of purification process is achieved. According to this figure, the intensity of absorbance at 1,035 cm^{-1} peak, which relates to Si–O groups, decreased after purification. This can be explained by the fact that the SiO_2 amount decreases after purification process.

3.4. The SEM observations

To observe the surface morphology of raw bentonite, Scanning Electron Microscope (SEM) of gold-coated samples were taken under liquid nitrogen. Fig. 3 clearly illustrates the presence of cavities in the raw bentonite. The images indicate that there are abundant pores distributed on the surface. The existence of these pores would provide convenient diffusion channels for metal ions into the interior of bentonite when it is immersed with metal ions aqueous solutions. Purified bentonite appears as corn



a) b)

Fig. 3. The SEM images for (a) Raw bentonite and (b) Purified bentonite (Magnification = 300 times).

flake like crystals with fluffy appearance revealing its extremely fine platy structure [12,13].

3.5. Adsorption study of metal ions on purified bentonite

The adsorptions of Pb(II), Zn(II), Cr(III) and Mn(II) on purified bentonite surface were studied by determination of metal ion concentration remaining in the adsorbate solution.

3.5.1. Metal ion uptake by raw and purified bentonite

The percentage uptake for each metal ion at optimized pH value is done for raw and purified bentonite in order to evaluate the importance of purification process in increasing the metal ion uptake on to the surface of bentonite. Table 2 presents the percent of metal ion uptake for each metal ion at the favorable pH value.

According to Table 2, the purified bentonite has the superior advantage in increasing the percent of metal ion uptake comparing with raw bentonite.

3.5.2. Effect of contact time on the adsorption of metal ions on purified bentonite

The time dependence behavior of each metal ion was measured by varying the equilibrium time between the adsorbate and adsorbent in the range of 5–120 min and the concentration of each metal ion was kept 100 mg/l at fixed bentonite dosage. The results of these experiments are presented in Table 3 and shown in Fig. 4

Table 2
Uptake comparison between raw and purified bentonite at 100 mg/l concentration and 25°C

Bentonite state	% Zn(II) uptake at pH 7.0	% Pb(II) uptake at pH 5.0	% Cr(III) uptake at pH 5.0	% Mn(II) uptake at pH 4.0
Raw	77.87	84.16	82.65	73.16
Purified	96.45	93.50	94.73	93.00

It can be seen that the adsorption of each metal ion on bentonite increases with increasing time and reaches maximum value after 30 min, and thereafter it remains constant (plateau). The removal of these metal ions occurs quickly and this 30 min shaking time is enough to achieve the adsorption equilibration, so it was used in all subsequent measurements. At this equilibrium time, the percent uptake of Zn(II), Pb(II), Cr(III) and Mn(II) were 96.62%, 93.42%, 94.63% and 93.11%, respectively.

3.5.3. Effect of bentonite dosage on the adsorption of metal ions on purified bentonite

The effect of bentonite dosage on the adsorption of Pb(II), Zn(II), Cr(III) and Mn(II) was studied as described later. The solution pH, temperature, and contact time were adjusted for each metal ion, and the percent uptake was determined at different bentonite masses.

The results of these experiments are presented in Table 4 and shown in Fig.5.

The adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for given initial concentration of the adsorbate. The above results show that the percentage of adsorption increases with increasing bentonite weight. This increase is explained by an increase in the surface area of bentonite samples. With increasing bentonite content, the available sites for binding each metal ion increases and thereby enhances the adsorption from solution to bentonite.

3.5.4. Effect of pH value on the adsorption of metal ions on purified bentonite

The effect of varying pH values on metal uptake was studied using batch procedure for fixed contact time of 30 min. The results are presented in Table 5 and shown in Fig.6.

The pH dependence on the adsorption of each metal ion on bentonite surface was carried in the range that will avoid hydrolysis and found to increase with pH. This can be explained in a similar manner to what has been reported in the following references as follows. The effect of the pH on Zn(II) adsorption by bentonite was studied in the pH region between 2.0 and 7.0. At low pH values (under 4.0), there is an excess of H_3O^+ ions in the solution, which make a competition between the positively charged hydrogen ions and

Table 3
Metal ion uptake by bentonite as a function of contact time at 100 mg/l concentration, 25°C and favorable pH value

Zn(II)		Pb(II)		Cr(III)		Mn(II)	
Time (min)	% Uptake	Time (min)	% Uptake	Time (min)	% Uptake	Time (min)	% Uptake
5	94.70	5	90.10	5	77.73	5	91.80
10	95.12	10	90.60	10	85.12	10	93.00
15	96.55	15	92.90	15	89.57	15	93.07
30	96.62	30	93.42	30	94.63	30	93.11
60	96.78	60	93.55	60	95.12		
120	96.79	120	93.62	120	95.22		

Zn(II) ions for the available adsorption sites on the negatively charged bentonite surface [2]. The basic mechanism that governs the adsorption characteristics of bentonite at pH ranging between 4.0 and 7.0 is adsorption and ion exchange. At these pH levels, exchangeable cations present at the exchangeable sites are exchanged for Zn^{2+} cations in the aqueous solutions. Optimum removal of Zn(II) is achieved at pH 7.0 [14]. Adsorption of Pb(II) on bentonite occurred by the same manner between pH= 1.0 and 5.0. At low pH values, surface complexation contributes mainly to the adsorption of Pb(II) on bentonite. As the pH increases, the competition between protons and Pb(II) for surface sites will decrease and Pb^{2+} ion is the predominating species and it will be attracted to the surface of bentonite by columbic forces [4]. From pH 1.0 to 5.0, the chromium exists as Cr^{3+} ions in aqueous solution and reach its maximum adsorption at pH 5.0 [15]. The effect of pH on the adsorption of Mn(II) was studied in the range 2.0–8.0. The maximum uptake was achieved at pH 4.0. As expected, the adsorption of Mn(II) decreases with decreasing pH because the aluminol and silanol groups are more protonated and, hence, they are less available to retain Mn(II). From pH 4.0 to 8.0, a plateau was noted and there was negligible difference in the sorption of Mn(II) onto the bentonite within this range [9].

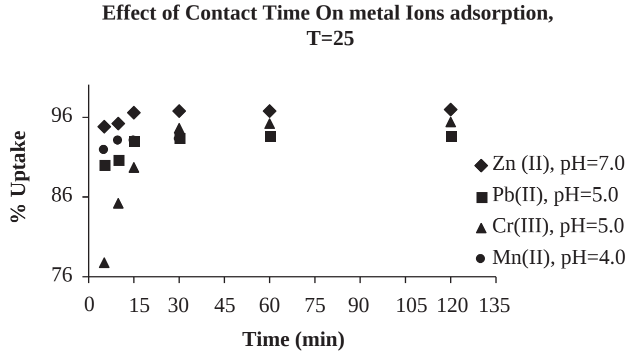


Fig. 4. Effect of contact time on metal ions adsorption on bentonite.

Based on the above, the optimum pH values where for Zn(II), pH 7.0, Pb(II) and Cr(III), pH 5.0 and for Mn(II), pH 4.0.

3.6. Distribution coefficient (K_d)

As mentioned previously, the distribution coefficient is defined as the final concentration of metal ion in the sorbed form on the bentonite divided by its final concentration in solution. It is regarded as a standard parameter in the assessment of the physicochemical behavior of metal ions between solid and liquid phases. It is calculated by the following equation [16].

$$K_d = \frac{(C_o - C_{eq}) \times V}{C_{eq} \times m}. \qquad (1)$$

The effect of bentonite dosage on the distribution coefficient is presented in Table 4 and shown in Fig. 7.

It can be seen that the distribution coefficient (K_d) decreases logarithmically with the increase of bentonite content as shown in Fig. 7. The decrease of K_d value with increasing solid content may be attributed to the competition among the functional groups at the surface of bentonite which decreases the adsorption and complexation ability of bentonite, and thereby results in the decrease of K_d values [4].

3.7. Adsorption isotherms of bentonite

The adsorption isotherms were determined for Zn(II), Pb(II), Cr(III) and Mn(II) at different pH values and different temperatures in the range of concentrations from 10 to 160 mg/L as shown in Fig. 8 for example at optimum pH, $T = 25$°C and 30 min contact time. Adsorption isotherms results are presented in Table 6.

Table 4
Bentonite dosage vs. metal ion uptake and distribution coefficients at 100 mg/l concentration, 25°C and optimized pH value (for Zn(II), pH 7.0, Pb(II) and Cr(III), pH 5.0 and for Mn(II), pH 4.0)

Zn (II)			Pb(II)			Cr(III)			Mn(II)		
Weight (g)	% Uptake	K_d (cm^3/g)	Weight (g)	% Uptake	K_d (cm^3/g)	Weight (g)	% Uptake	K_d (cm^3/g)	Weight (g)	% Uptake	K_d (cm^3/g)
0.10	49.32	85.63	0.03	59.21	492.07	0.05	51.73	466.56	0.20	43.51	64.92
0.20	63.88	47.12	0.05	85.64	119.77	0.1	94.48	29.21	0.40	64.14	27.95
0.40	88.14	11.21	0.07	93.68	48.19	0.15	98.90	5.56	0.60	79.61	12.81
0.50	92.30	6.95	0.08	99.10	6.49	0.20	99.60	2.01	0.80	87.40	7.21
0.60	96.60	2.93	0.10	99.22	5.62	0.25	99.72	1.40	1.00	93.00	3.76
0.70	99.12	0.74				0.30	99.80	1.00	1.20	96.46	1.83
0.80	99.41	0.49							1.40	97.12	1.48
									1.60	98.00	1.02
									1.80	99.13	0.44
									2.00	99.25	0.38

3.7.1. Langmuir adsorption isotherm

The Langmuir adsorption isotherm model was chosen for the estimation of the maximum adsorption capacity corresponding to the saturation of the bentonite surface using linearized forms of Langmuir isotherms.

The second form of linearized Langmuir adsorption isotherm is described as the following:

$$1/q = (1/(q_mK))1/c + 1/q_m \qquad \text{(linear form II)} \qquad (2)$$

Plots of $1/q$ versus $1/c$ gives a straight line of slope $(1/q_mK)$ and intercept $1/(q_m)$ as shown in Fig. 9 for example at optimum pH, $T = 25°C$ and 30 min contact time.

The q_m and K_L is Langmuir constants related to the adsorption capacity and adsorption energy respectively. Maximum sorption capacity (q_m) represents monolayer coverage of the bentonite with the metal ion [4].

The estimated parameters; q_m and K_L of the adsorption isotherms for the three forms of linearized Langmuir equations were calculated from the intercept and slopes of the corresponding linear plots for Zn(II), Pb(II), Cr(III) and Mn(II) adsorption onto bentonite at different temperatures and pH values. The values of these parameters for Langmuir Model form (II) with their correlation coefficients (R^2) at 140 mg/l are given in Table 6.

According to Tables 6, q_m values for Pb(II), Zn(II), Cr(III) and Mn(II) are increasing generally in the following order:

$$\mathrm{Pb(II)} > \mathrm{Cr(III)} > \mathrm{Zn(II)} > \mathrm{Mn(II)}. \qquad (3)$$

This trend of increasing q_m values is the same trend for increasing K_d values. According to Table (6), the K_d values for each metal ion are ordered as the following:

$$\mathrm{Pb(II)} > \mathrm{Cr(III)} > \mathrm{Zn(II)} > \mathrm{Mn(II)}. \qquad (4)$$

As the value of K_d increases, the affinity of the metal ion toward bentonite surface increases, which in turn increases the maximum adsorption capacity of the metal ion on bentonite.

Many postulates can be introduced to explain this trend of increasing q_m.

Higher atomic weight and ionic radius, give smaller hydrated radius, which effects significantly in increasing q_m values.

This trend can be also explained by hard and soft acids and bases (HSAB) theory, in which hard acids

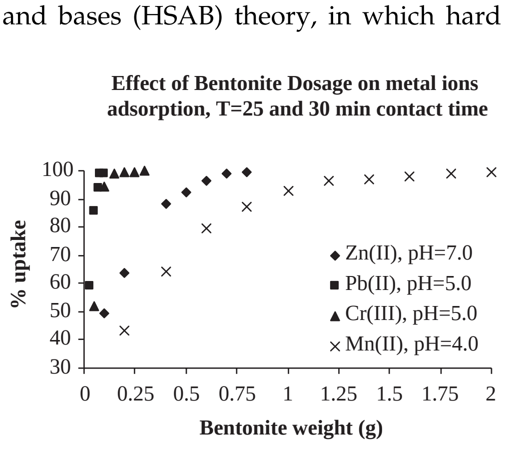


Fig. 5. Effect of bentonite dosage on metal ions adsorption.

Table 5
Metal ion uptake by bentonite as a function of pH value at 100 mg/l concentration and 25°C

Zn(II)		Pb(II)		Cr(III)		Mn(II)	
pH	% Uptake	pH	% Uptake	pH	% Uptake	pH	% Uptake
2	19.59	1.00	1.02	1	15.15	2	46.47
3	55.14	2.00	12.12	2	30.76	3	78.37
4	89.27	3.00	33.59	3	41.37	4	92.67
5	93.00	4.00	78.99	4	74.35	5	92.70
6	93.79	5.00	93.45	5	94.73	6	92.75
7	96.45					7	92.77
						8	93.00

tend to associate with hard bases, and soft acids with soft bases [17].

According to HSAB theory, Cr(III) is hard metal ion while Pb(II) and Zn(II) ions are in the borderline and Mn(II) is classified as soft metal, so Cr(III) and Pb(II) will have higher tendency to make complexes with the hard surface of bentonite. Pb(II) also has 2 valence electrons in its 6s atomic orbital (and empty p-orbital of only slightly higher energy), which can form, depending on the Pb-oxygen symmetry, molecular orbital with oxygen p-atomic orbital originating from the oxide surface. This orbital overlap stabilizes the Pb-O complex. On the other hand, the other metal ions have a filled 4d valence atomic orbital, which participates minimally in electron sharing with oxygen p-atomic orbital from oxide surfaces [18].

The correlation coefficient is a mathematical expression which reveals the favorability of the adsorption process. Since R^2 values for Langmuir isotherm are very close to 1, monolayer adsorption is obtained and the process becomes highly favorable. The high fitness of Langmuir isotherm for the adsorption process shows that the adsorption is homogenous and no interaction occurred between the adsorbed species [2].

As mentioned before, the maximum adsorption capacity (q_m) is determined form Langmuir adsorption isotherm. In bentonite, the metal ions seem to reach saturation which means that the metal ion had filled the possible available sites, so the adsorption efficiency increases to a certain level, and then remained constant as the concentration increases, as a result, no metal ions

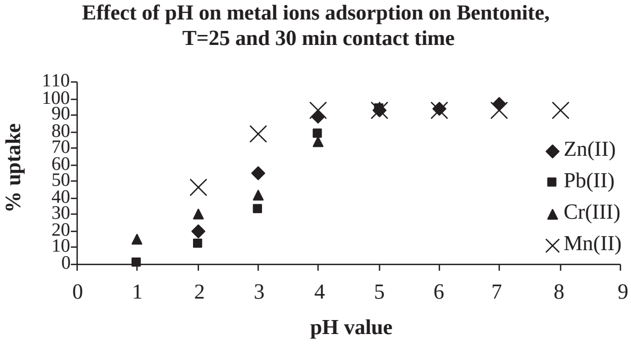


Fig. 6. Effect of pH on metal ion adsorption on bentonite.

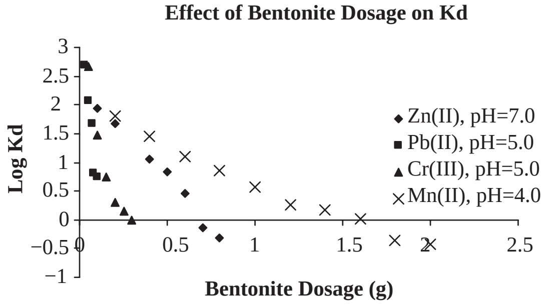


Fig. 7. Effect of bentonite dosage on distribution coefficient.

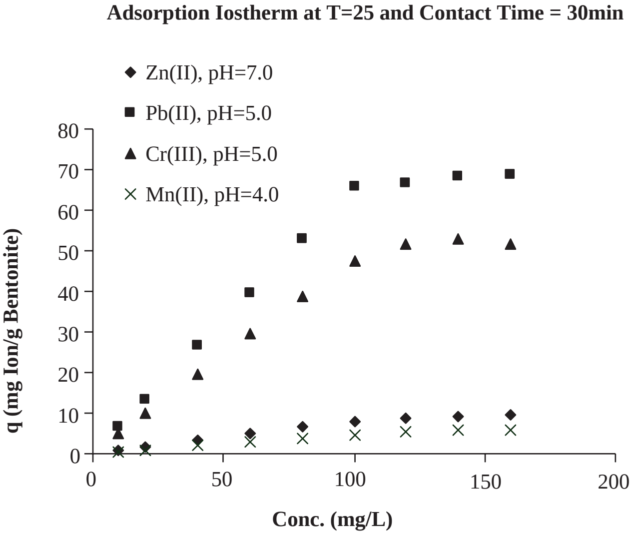


Fig. 8. Adsorption Isotherm for Zn(II), Pb(II), Cr(III) and Mn(II) at $T = 25°C$ and 30 min contact time.

Table 6
Langmuir (II), Freundlich and (D-R) adsorption isotherms parameters at T=25°C.

Metal ion	Langmuir (II) parameters			Freundlich parameters			(D–R) parameters			
	R^2	q_m (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2	β (mol^2/kJ^2)	$q_m{}^{/}$ (mg/g)	E (kJ/mol)
Zn(II)										
pH 4.0	0.9991	9.05	1.2657	0.9805	2.6014	2.6810	0.9942	0.1137	15.19	2.0970
pH 6.0	0.9996	9.26	1.3952	0.9756	2.7530	2.6645	0.9929	0.1164	17.97	2.0726
pH 7.0	0.9994	9.55	1.3510	0.9754	2.7214	2.6709	0.9660	0.1185	19.03	2.0541
Pb(II)										
pH 3.0	0.9999	83.33	0.0398	0.9802	4.5269	1.5623	0.9785	0.9770	21504.12	0.7154
pH 4.0	0.9994	76.34	0.0912	0.9834	7.1187	1.8797	0.9895	0.5808	2118.36	0.9278
pH 5.0	0.9942	105.26	0.1174	0.9782	11.3136	1.9201	0.9868	0.3983	826.42	1.1204
Cr(III)										
pH 3.0	0.9985	24.88	0.1037	0.9924	2.9765	2.1659	0.9834	0.7607	2471.30	0.8107
pH 4.0	0.9997	37.31	1.0114	0.9875	9.6672	2.9291	0.9940	0.1459	90.63	1.8500
pH 5.0	0.9997	52.08	1.3152	0.9772	22.7353	1.8376	0.9928	0.1220	106.62	2.0244
Mn(II)										
pH 2.0	0.9932	2.98	0.1468	0.9947	0.4427	2.1858	0.9912	0.5758	108.06	0.9319
pH 3.0	0.9990	4.90	0.1763	0.9861	0.7101	1.8426	0.9942	0.3988	55.30	1.1208
pH 4.0	0.9966	6.05	0.4837	0.9836	1.3210	1.9948	0.9907	0.1890	17.27	1.6265

can be adsorbed. Table 6 also shows that the adsorption capacity (q_m) increases as the temperature and pH values increase for all investigated metal ions. On the other hand, the (K_L) values increase with increasing temperature at the same pH value.

3.7.2. *Freundlich and Dubinin–Radushkevich (D–R) Isotherm*

The linearized form of Freundlich adsorption isotherm can be expressed as the following:

$$\log q = \log K_F + 1/n \log c. \tag{5}$$

A plot of log q versus **c** gives a straight line with a slope of $(1/n)$ and intercept of (log K_F) as shown in Fig. 10 for

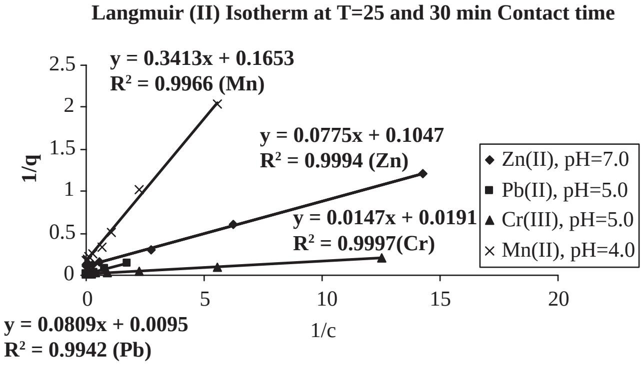


Fig. 9. Langmuir adsorption isotherm form (II) for Zn(II), Pb(II), Cr(III) and Mn(II) at $T = 25$°C and 30 min contact time.

example at optimum pH, $T = 25$°C and 30 min contact time. Both K_F and n are Freundlich constants, being indicative of the adsorption capacity and the adsorption intensity respectively. High value of n indicates that adsorption is good over the entire range of concentration studied, while small values of **n** means that the adsorption is good at high concentrations but much less at lower concentrations. A greater value of K_F indicates a higher capacity for the adsorption than smaller values [3].

Freundlich isotherm does not predict any saturation of the metal ions by bentonite, since it indicates a multilayer sorption of the surface and used for the adsorption on heterogeneous surfaces [3].

The linear form for Dubinin–Radushkevich (D–R) isotherm has the following expression:

$$\ln q = \ln q_{\max} - \beta \varepsilon^2, \tag{6}$$

$$\varepsilon = RT \ln\left(1 + 1/C_{eq}\right). \tag{7}$$

The values of β and $q_{\max}$ are evaluated from the slope and intercept of the linear plot of ln q versus ϵ^2 as shown in Fig. 11 for example at optimum pH, $T = 25$°C and 30 min contact time, where $q_{\max}$ is related to the adsorption capacity and β is the constant related with the adsorption energy [4].

The adsorption free energy (E) is defined as the free energy change required for transferring one mole of

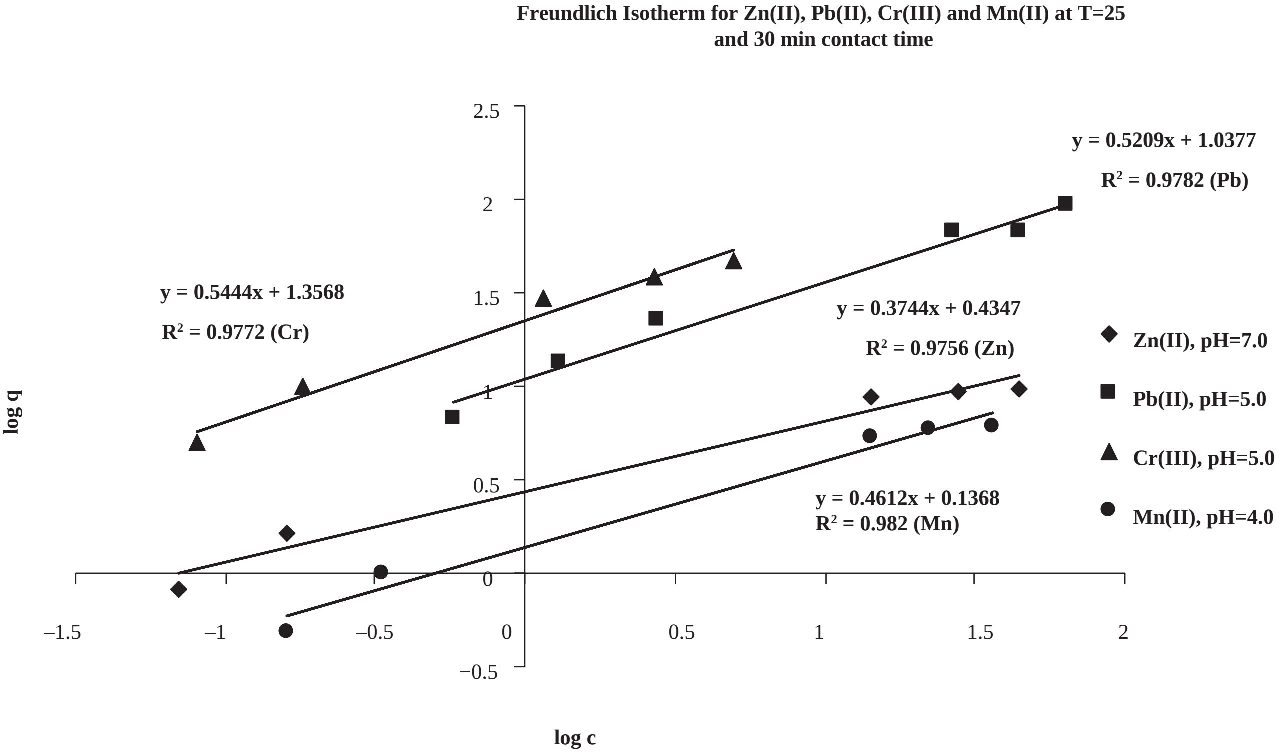


Fig. 10. Freundlich adsorption isotherm for Zn(II), Pb(II), Cr(III) and Mn(II) at $T = 25°C$ and 30 min contact time.

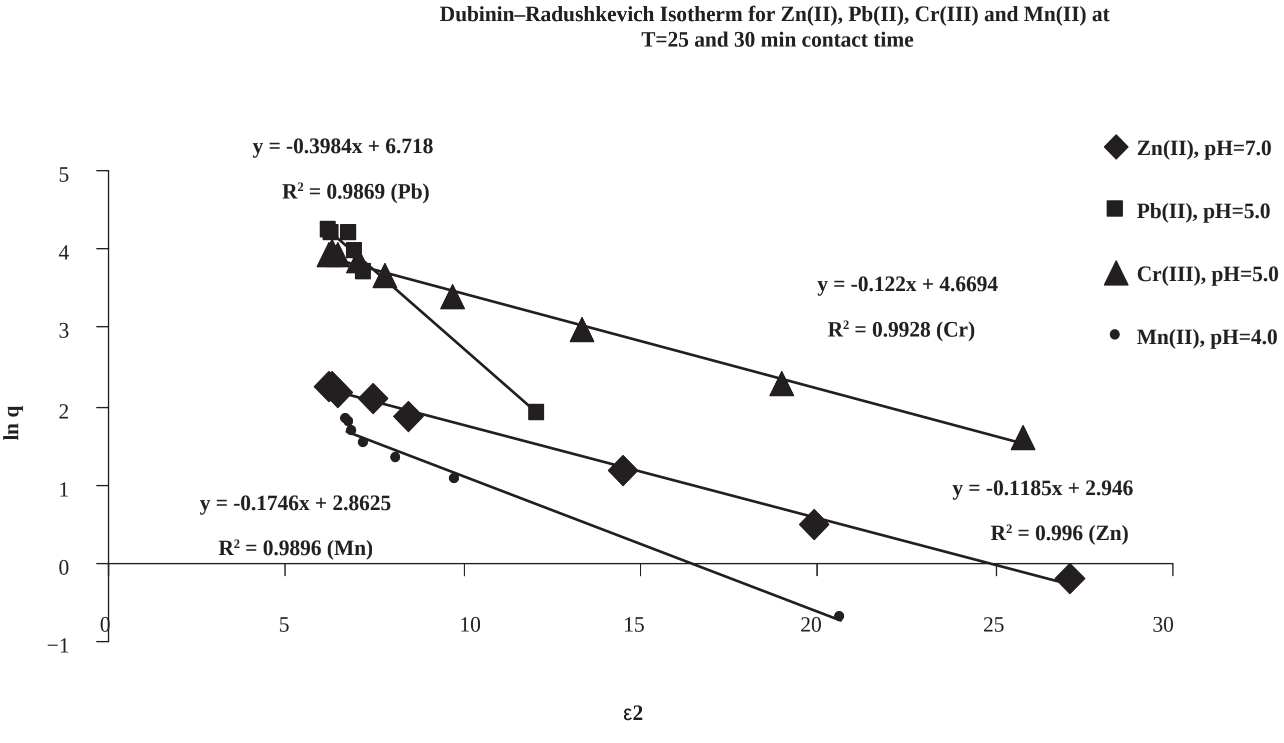


Fig. 11. Dubinin-Radushkevich adsorption isotherm for Zn(II), Pb(II), Cr(III) and Mn(II) at $T = 25°C$ and 30 min contact time.

Table 7
Δg % for Zn(II) at pH 7.0, $T = 25°C$

Eq. Conc.	Q_e^{exp}	q_e^{cal}	$Q_e^{exp} - q_e^{cal}$	$[q_e^{exp} - q_e^{cal}/q_e^{exp}]^2$
0.07	0.828	0.825	0.003	1.31×10^{-5}
0.16	1.653	1.698	0.045	7.41×10^{-4}
0.36	3.303	3.125	0.178	2.90×10^{-3}
0.56	4.953	4.114	0.839	2.87×10^{-2}
1.84	6.513	6.811	0.298	2.09×10^{-3}
3.58	8.035	7.915	0.120	2.23×10^{-4}
14.21	8.816	9.078	0.262	8.83×10^{-4}
27.95	9.338	9.305	0.033	1.25×10^{-5}
44.64	9.613	9.395	0.218	5.14×10^{-4}

ions from solution to solid surface, this energy is calculated as following:

$$E = 1/(2\beta)^{-0.5}. \tag{8}$$

The value of E gives information about the physical and chemical features of the adsorption. Low values of adsorption energy (E) show that the adsorption has a physical nature [4].

The D–R isotherm model is more general than Langmuir isotherm as it rejects the homogenous surface or constant adsorption potential [4].

The values of K_F, n, β, $q_m{}'$ and E for Zn(II), Pb(II), Cr(III) and Mn(II) are summarized in Table 6 at $T = 25°C$ and different pH values.

Since the values of n are in the range between 2.0 and 10.0, the adsorption of each metal ion on bentonite surface is favorable [15]. The values of R^2 for Freundlich isotherm is not close to 1.0 as obtained for Langmuir, which indicates that homogenous adsorption describe the process more than heterogeneous adsorption. K_F is a parameter which is related to the temperature, as the temperature of solution increases, K_F value will increase at the same solution pH.

As illustrated in Table 6, the values of E are less than 8.00 kJ/mol; this indicates that physical forces may affect the adsorption [3]. It is interesting to note that the difference of q_{max} derived from the Langmuir and $q_m{}'$ derived from D–R models is quite large. The difference may be attributed to the different definition of q_{max} in the two models. In Langmuir model, q_{max} represents the maximum adsorption of metal ions at monolayer coverage, whereas it represents the maximum adsorption of metal ions at the total specific micropore volume of the sorbent in D–R model. Thereby, the value of q_{max} derived from Langmuir model is lower than that derived from D–R model [4].

A comparison between the adsorption q_{max} of Zn(II), Pb(II), Cr(III) and Mn(II) at optimum pH and $T = 25°C$ on purified Jordanian bentonite with other bentonite from different locations in the world will be discussed. The maximum adsorption capacity for Pb(II) is (105.26 mg/g), which is higher than French bentonite (68.55 mg/g) [4], Pakistani bentonite (19.20 mg/g) [19] and Turkish bentonite (14.50 mg/g) [3]. While the maximum adsorption capacity for Cr(III) is (53.00 mg/g), which is higher than Moroccan bentonite (9.60 mg/g) [7] and Pakistani bentonite (49.75 mg/g) [15].

On the other hand, the adsorption of Zn(II) is not efficient comparing with bentonite from other origins; the maximum adsorption capacity for Zn(II) is (9.54 mg/g), while this capacity is (52.91 mg/g) for Algerian bentonite [20], (35.18 mg/g) for Indian bentonite [21] and (80.64 mg/g) for Turkish bentonite [8]. The purified Jordanian bentonite adsorption capacity toward Mn(II) (6.05 mg/g) is close to Pakistani bentonite (7.14 mg/g) [22] and Brazilian bentonite (6.80 mg/g) [9].

3.8. The validity of adsorption isotherm

It was observed that the value of R^2 is higher than 0.98 in Langmuir adsorption isotherms, this emphasis the fitness of this model to represent the isotherm data. In order to prove the validity of the Langmuir model isotherm equations more definitely, a normalized standard deviation, Δg %, can be used. Δg % is calculated as following:

$$\Delta g\% = 100 \times \left(\left(\sum [q_e^{exp} - q_e^{cal}/q_e^{exp}]^2\right)/N - 1\right)^{0.5}, \tag{9}$$

where superscripts 'exp' and 'cal' show the experimental and calculated values for q_m obtained form Langmuir adsorption isotherm and **N** is the number of measurements [11].

Table 8
% uptake at the optimum pH against temperature for 140 mg/l Zn(II), Pb(II), Cr(III) and Mn(II)

% uptake of Mn(II) at pH 4.0	% uptake of Cr(III) at pH 5.0	% uptake of Pb(II) at pH 5.0	% uptake of Zn(II) at pH 7.0	Temperature (°C)
81.94	75.41	68.14	80.04	25
83.95	78.39	70.56	87.20	35
86.20	83.11	78.03	94.92	45

Table 7 shows the calculation needed to determine Δg % for Zn(II) ion at the favorable pH value and $T = 25°C$ as an example.

The Δg % for Zn(II) is 6.33%, for Pb(II) at pH 5.0 is 19.81%, for Cr(III) at pH 5.0 is 3.79% and for Mn(II) at pH 4.0 is 17.93%. Based on Δg % values, it is noted that Langmuir equation gives the best fit over the entire range of concentrations [11].

3.9. *The effect of temperature on the uptake*

The effect of varying temperature on the % uptake of metal ions was also investigated. The results are obtained by plotting % uptake at the optimum pH against temperature are presented in Table 8.

The results obtained show that the adsorption process of Zn(II), Pb(II), Cr(III) and Mn(II) onto the surface of bentonite is an endothermic process since the % of uptake is increased as the temperature increases at the same pH value.

3.10. *Thermodynamics of adsorption on bentonite*

In order to understand the possible adsorption mechanism involved in the removal process, thermodynamic functions for the system, including changes in Gibbs free energy (ΔG^*), change in enthalpy of adsorption (ΔH^*) and changes in entropy of adsorption (ΔS^*), were calculated using the following equation

$$\ln K_\mathrm{d} = \Delta S^*/R - \Delta H^*/RT, \tag{10}$$

where K_d is the equilibrium constant, R is the gas constant and T is the temperature in Kelvin.

The plot of ln K_d against $1/T$ for each metal ion gives a linear relationship as shown in Fig. 12, where the values of enthalpy (ΔH^*) were entropy (ΔS^*) are obtained from the slope and intercept of ln K_d vs. $1/T$ plots [4].

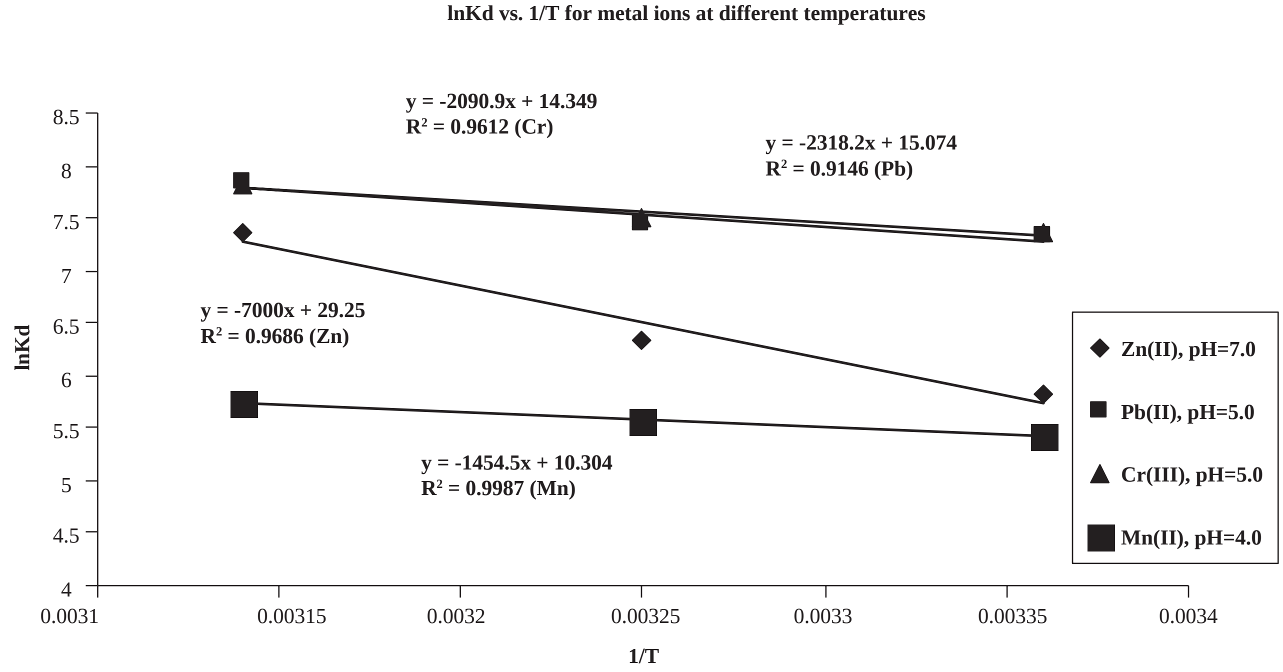


Fig. 12. Plots of ln K_d vs. $1/T$(K) for metal ions at different temperatures.

Table 9
Thermodynamic functions for Zn(II), Pb(II), Cr(III) and Mn(II)

Metal ion	ΔG^* (kJ/mol) T (K) 298	pH	ΔH^* (kJ/mol)	ΔS^* (kJ/mol.K)
Zn(II)	−14.28	4	31.37	0.1532
	−14.37	6	32.50	0.1573
	−14.27	7	58.20	0.2432
Pb(II)	−17.34	3	17.38	0.1165
	−17.15	4	27.97	0.1514
	−18.07	5	19.27	0.1253
Cr(III)	−13.82	3	19.65	0.1123
	−15.90	4	15.12	0.1041
	−18.17	5	17.38	0.1193
Mn(II)	−9.38	2	10.20	0.0657
	−11.79	3	6.42	0.0611
	−13.45	4	12.09	0.0857

ΔG^* was calculated at each temperature using the following equation:

$$\Delta G^* = \Delta H^* - T\Delta S^*. \tag{11}$$

Table 9 presents the thermodynamic functions for Zn(II), Pb(II), Cr(III) and Mn(II).

The negative value of ΔG^* indicates the degree of favorability of the adsorption process, so the values of ΔG^* presented in Table 9 indicate that the adsorption of Zn(II), Pb(II), Cr(III) and Mn(II) is a favorable process.

According to Table 9, the values of ΔG^* for Zn(II) are about −14 kJ/mol at pH values of 4.00, 6.00, and7.00. This indicates that the ion exchange mechanism is predominant (ΔG^* from 8.00 to 16.00 kJ/mol). The values of ΔG^* for Pb(II) and Cr(III) are raised above 16.00 kJ/mol as pH value increases, which indicates that the electrostatic interaction between the adsorptive sites of bentonite and the metal ion occurred. In the case of Mn(II), the values of ΔG^* are in the range of ion exchange mechanism [5]. The positive values of ΔH^* show that the adsorption of metal ion is endothermic. This means that the energy of dehydration exceed the exothermicity of the metal ions bonded to bentonite surface. The positive value of ΔS^* suggests that the entropy of the system is increased. This fact emphasizes the endothermicity of the adsorption process when the water molecules of hydration are separated from the metal ion before they attach on the bentonite surface. During the adsorption process, the metal ions become associated on the surface of the bentonite resulting in the loss of a degree of freedom while releasing water of hydration which explains the increases in the value of this function [3]. On the other hand, these positive values of entropy indicate that the adsorption process is irreversible and favors complexation and stability of sorption.

3.11. Column experiments

3.11.1. Metal ion uptake by bentonite

The investigation of metal ion uptake by bentonite using column experiments for Zn(II), Pb(II), Cr(III) and Mn(II) were determined at the optimum pH for each metal ion with initial concentration of 1000 mg/l (50.0 mL) at 25°C and flow rate of 1.0 ml/min. The results are expressed as percent metal uptake by the column and are presented in Table 10.

It is observed that the % of uptake in column experiment is larger than those obtained in batch experiment for Zn(II), Pb(II), Cr(III) and equal for Mn(II) (Table 11) due to the relatively high contact time (50 vs. 30 min).

Table 10
The percent of metal ion uptake by bentonite using column experiment at 50 min contact time

Metal ion	pH	Initial Conc. (mg/l)	Final Conc. (mg/l)	Loaded Conc. (mg/l)	% Uptake
Zn(II)	7.0	1000	134.6	869.4	86.5
Pb(II)	5.0	1000	112.1	887.9	88.8
Cr(III)	5.0	1000	99.8	900.2	90.0
Mn(II)	4.0	1000	203.6	796.4	79.6

Table 11
Desorption of Zn(II), Pb(II), Cr(III) and Mn(II) and the regeneration process

Metal ion on bentonite	% Recovery (first washing)	% Recovery (second washing)	% Recovery (third washing)	% Cumulative recovery	% Uptake for loaded bentonite
Zn(II)	49.7	7.6	0.94	58.2	61.8
Pb(II)	57.5	7.9	0.71	66.2	66.3
Cr(III)	60.9	11.2	0.51	72.6	70.0
Mn(II)	40.1	6.3	0.15	46.6	53.6

3.11.2. Desorption studies

One of the aims of this study is to determine the capability of bentonite to be regenerated for further uses. A 50 ml of 0.1 N HNO_3 was used for the removal of metal ions and regeneration of bentonite, keeping flow rate of elution 1.0 ml/min. The bentonite sample in column was washed with this eluting reagent several times until the collected potions is free from metal ion, then a second column experiments is done to determine the efficiency of loaded bentonite to absorb the metal ions. The results are of these experiments are presented in Table 11.

From Table 11, the eluting reagent (HNO_3) which was used for desorption studies made cumulative percent recovery in the following order:

$$\mathrm{Cr(III)} > \mathrm{Pb(II)} > \mathrm{Zn(II)} > \mathrm{Mn(II)} \tag{12}$$

It is clearly observed that the efficiency of Jordanian bentonite to adsorb metal ions for the second time is decreased significantly when desorption of the first time is done; this fact indicated that the washing of bentonite with HNO_3 regenerates bentonite but the regeneration is not complete, since bentonite loses significant efficiency to adsorb metal ions for the second adsorption process.

Since the percent of cumulative recovery and the percent of loaded uptake bentonite are almost close to each other, bentonite can be easily used to remove these metal ions from wastewater. This process is cheap and easy and could be used widely in many environmental applications.

4. Conclusion

The present work has focused on the purification of Jordanian bentonite and then studying its adsorption characteristics toward Zn(II), Pb(II), Cr(III) and Mn(II). Raw and purified bentonites were characterized by FTIR, XRD, XRF and SEM. The adsorption characteristics for Zn(II), Pb(II), Cr(III) and Mn(II) ions from aqueous solutions were examined under various experimental conditions and techniques (batch and column). The effective desorption of the metal ions was also studied and the coefficients of recovery of sorption ability were also investigated.

The following remarks are concluded:

- The influence of bentonite dosage on metal ions uptake showed that the metal ions uptake increases as the bentonite weight increases.
- As pH value increases, the uptake of each metal ion on bentonite surface increases, but at higher values, precipitation of metal ions is observed.
- The equilibrium for each metal ion on the surface of bentonite occurs quickly and 30 min is enough to achieve maximum uptake.
- The obtained adsorption isotherm data showed fittings for Langmuir, Freundlich and Dubinin–Radushkevich adsorption isotherms models with almost similar correlation coefficients.
- The maximum adsorption capacity of the investigated metal ions on the bentonite surface are increasing as the following order:
- Pb(II)>Cr(III)>Zn(II)>Mn(II). On the other hand, the adsorption capacity of the bentonite increases as the temperatures increases.
- A glass column packed with bentonite exhibits good adsorption properties toward metal ions. The regeneration process of bentonite was done using 0.1 N HNO_3 and the results shows that this process is effective for environmental applications.
- The thermodynamic functions obtained for the adsorption process shows that this process is favorable.
- The maximum adsorption capacity (q_m) for purified Jordanian bentonite is relatively high for Pb(II) and Cr(III) comparing with other types of bentonite from different origins.

List of symbols

C	Equilibrium concentration of metal ion remained in solution.
C_0	Initial metal concentration

C_{eq}	The residual concentration of the metal ion in solution after equilibrium(mg/l).
D–R	Dubinin-Radushkevich.
Eq. Conc.	Equilibrium concentration.
E	Adsorption free energy.
FTIR	Fourier Transform Infrared.
HSAB	Hard and Soft Acids and Bases theory.
ICP	Inductively Coupled Plasma.
I	Emission intensity.
K_{L}	Langmuir constant.
K_{F}	Freundlich constant relates to adsorption capacity.
K_{d}	Distribution coefficient.
m	Mass of bentonite(g).
M	Montmorillonite.
n	Freundlich constant relates to adsorption intensity
Q	Quartz.
q	Metal ion adsorbed in (mg) per gram of adsorbent.
q_{m}	Monolayer adsorption capacity.
$q_{\mathrm{m}}^{/}$	Maximum adsorption capacity derived from D–R models.
R^2	Correlation coefficient.
R	The ideal gas constant (8.3145 J.mol^{-1}.K^{-1}).
SEM	Scanning Electron Microscope.
T	The absolute temperature (Kelvin).
V	Volume of the solution (L).
XRD	X-Ray Diffraction.
XRF	X-Ray Fluorescence.
β	The activity coefficient related to mean sorption energy.
ϵ	The Polanyi potential.
ΔG^*	Change in Gibbs free energy.
ΔH^*	Change in enthalpy of adsorption.
ΔS^*	Change in entropy of adsorption.

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