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Equilibrium ion exchange studies of Zn^{2+}, Cr^{3+}, and Mn^{2+} on natural bentonite

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ABSTRACT

Bentonite is a clay mineral often used in ion exchange processes due to its high ion exchange capacity. In the present study, a commercially available in Greece market bentonite was obtained and characterized by XRD, XRF, FTIR, BET, and TG/DTA analysis. Monmorillonite was the main component of bentonite sample (>80%). Ion exchange equilibria of Zn^{2+}, Cr^{3+}, and Mn^{2+} on bentonite was examined by use of batch equilibrium isotherms, distribution coefficients, and maximum exchange levels (MELs) under the same normality for all metals (0.01 N) at 25 ± 2˚C. The equilibrium isotherms for the metals studied exhibit a favorable-type isotherm. Selectivity series deduced from equilibrium isotherms are $Cr^{3+} > Zn^{2+} > Mn^{2+}$, and the same occurs for MELs. The Langmuir and Freundlich models were applied and fitted the equilibrium data for the metal ion uptake. A detailed literature review on heavy metals-bentonite equilibrium is provided.

Keywords: Bentonite; Ion exchange; Adsorption; Heavy metals; Manganese; Chromium; Zinc

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1. Introduction

Intense industrial activity results in contamination of wastewater with several heavy metals. The pollution of water from heavy metals is a major problem because they are toxic and persistent in nature, nonbiodegradable and they bio-accumulate in the food chain. Chromium is commonly used in acid electroplating, tanning, painting, dye, manufacturing, and petroleum refining. Cr^{3+} is more stable and less toxic than Cr^{6+} but in the presence of mild oxidizing agents, Cr^{3+} can be oxidized into Cr^{6+}, which is highly toxic, causing several forms of cancer, kidney diseases, liver, gastric damage, and even death [1,2]. Zinc is released into the aquatic environment through several industrial activities, such as mining, metal coating, battery production. It can be found in paints, ceramics, wood,

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fabrics, drugs, sun blocks, and deodorants [3]. Zinc is associated with short-term "metal-fume fever", nausea, diarrhea, depression, lethargy, and neurological signs, such as seizures and ataxia. Manganese major applications are found in metallurgical alloy industry. Manganese is toxic mainly because of its organoleptic properties, while it has been associated with increased intellectual impairment and reduced intelligence quotients in school-age children [4].

Several processes are currently available to treat effluents containing heavy metals; chemical precipitation, evaporation, ion exchange, membrane technologies, sorption processes, etc. [5]. Among wastewater treatment methods, adsorption and ion exchange are superior to the other methods for removal of heavy metals, in terms of cost, simplicity of design and operation, good removal efficiency while it does not result in the formation of harmful substances like most of the other techniques [4,6]. The removal of heavy metals through ion exchange processes with the use of natural minerals and especially zeolites has been investigated thoroughly in the literature due to their low cost, safety in use (environmental friendly), worldwide abundance, high exchange capacity, and selectivity properties [7,8]. Clays, though, have higher cation exchange capacity than zeolites and are becoming more promising in heavy metal removal in batch reactors in relation to zeolites [9–14]. Currently, the smectite clays are among the most investigated clays for heavy metal removal [15]. Smectites is one of the four main groups of clay minerals that are characterized by a phyllosilicate structure and more specifically by a sheet structure which is composed by two layers of silica tetrahedrons and one central dioctahedral or trioctahedral layer. One of the most abundant smectite mineral is the di-octahedral montmorillonite which is the predominant mineral (>50%) of commercially available clay rock known as bentonite.

Activated carbon has been found to be a very effective adsorbent for the removal of metals from solution but its high cost limits its wide spread use, especially in developing countries [4]. As a result, research has been focusing on low-cost adsorbents as agricultural waste and biomass materials, clays, zeolites, fly ash, bentonite, and others. In the majority of cases, bentonites are formed by the alteration of volcanic ash and rocks after intense contact to water [16]. Heavy metal adsorption on montmorillonite is achieved through (a) exchange of cations in the interlayers resulting from the interactions between ions and negative permanent charge and (b) formation of inner-sphere complexes through Si–O^- and Al–O^- groups at the clay particle edges [17].

The available equilibrium studies on heavy metals–bentonite system are presented in Table 1. As bentonite is a natural mineral, its characteristics vary which means that in order to compare different metals the same sample should be used. According to the literature review, there are two studies on the equilibrium of Zn^{2+}, Cr^{3+}, and Mn^{2+}; these of de Pablo et al. [18] and Al-Jariri and Khalili [19]. Al-Jariri and Khalili recognize ion exchange as predominant uptake mechanism, however for the equilibrium studies they are using the same concentration for all metals, a typical flaw found in the related literature. The dependence of equilibrium isotherms and selectivity upon the concentration of the solution in ion exchange systems are well known and in order to compare different metals, based on equilibrium isotherms, the same constant normality for all metals should be used (although this is not the case in most of equilibrium studies), which either use the same constant concentration or even variable concentration for the same metal [10]. The reason for that is that the mechanism of the heavy metals removal by bentonite is frequently considered to be adsorption while is known that ion exchange is frequently the prevailing mechanism. De Pablo et al. [18] are using the same normality, but the difference to the current study is that they are interested on binary metal-Ca^{2+} systems. Furthermore, they are not using normalized isotherms, i.e. there is not an independent measurement of the maximum exchange level (MEL) of the metals on bentonite [20]. The present study comes to complement the existing experimental studies and provides a solid protocol for better understanding ion exchange systems involving bentonite.

The aim of this study is to present equilibrium experimental data and apply simplified isotherm models for Zn^{2+}, Cr^{3+}, and Mn^{2+} exchange on natural bentonite by a rigorous experimental protocol. Also, full characterization of the material is provided by use of X-ray Diffraction (XRD), X-ray fluorescence analysis (XRF), Fourier Transform Infrared (spectroscopy) (FTIR), Brunauer–Emmett–Teller (BET) surface and Differential Thermal Analysis (DTA) and Thermo-Gravimetric Analysis (TGA, as well as DTG) methods.

2. Materials and methods

2.1. Samples and characterization

Bentonite samples were supplied by S&B Industrial Minerals SA (Greece) (<90 μm). The elemental composition of the materials was obtained through XRD and XRF analysis with the use of an ARL Advant XP sequential XRF. The minerals were used without any chemical pretreatment. Samples before experimental

Table 1
Available equilibrium studies on heavy metals–bentonite systems

Metal(s)	Solution	Bentonite type	Refs.
Zn^{2+}	Single component	Natural Na-enriched	[21]
	Single component	Natural	[13]
	Single component	Natural	[22]
	Single component Comparison between Zn^{2+} and Mn^{2+}	Natural	[23]
	Single component Comparison between Zn^{2+} and Fe^{3+}	Natural	[24]
	Single component Binary Pb^{2+}/Zn^{2+}	Natural	[25]
	Single component Comparison between Zn^{2+} and Cd^{2+}	Na-enriched	[26]
	Comparison of Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, and Cr^{3+}	Na-bentonite Ca-bentonite	[27,28]
	Bimodal metal + Ca^{2+} solutions Comparison of Pb^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}, Ba^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, and Cd^{2+}	Montmorillonite Ca-Montmorillonite	[18]
	Single component Comparison of Zn^{2+}, Cr^{3+}, Mn^{2+}, and Pb^{2+}	Natural	[19]
	Comparison of Zn^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+}	Natural	[9]
Cr^{3+}	Single component	Acid activated	[29]
	Single component	Natural	[2]
	Single component Comparison between Cr^{3+}, Cr^{6+}, and Ag^{+}	Natural	[12]
	Cr^{3+} in tannery wastewater	Natural	[30]
	Comparison of Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, and Cr^{3+}	Na-bentonite Ca-bentonite	[27,28]
	Single component Comparison of Zn^{2+}, Cr^{3+}, Mn^{2+}, and Pb^{2+}	Natural	[19]
	Bimodal metal+Ca^{2+} solutions Comparison of Pb^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}, Ba^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, and Cd^{2+}	Montmorillonite Ca-Montmorillonite	[18]
Mn^{2+}	Single component Comparison between Zn^{2+} and Mn^{2+}	Natural	[23]
	Binary Mn^{2+}/Ni^{2+}	Natural	[4]
	Single component Comparison between Mn^{2+} and Fe^{2+}	Natural	[31]
	Single component Comparison of Zn^{2+}, Cr^{3+}, Mn^{2+}, and Pb^{2+}	Natural	[19]
	Bimodal metal + Ca^{2+} solutions Comparison of Pb^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}, Ba^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, and Cd^{2+}	Montmorillonite Ca-Montmorillonite	[18]
Pb^{2+}	Single component Binary Pb^{2+}/Zn^{2+}	Natural	[25]
	Single component	Natural	[32]
	Bimodal metal + Ca^{2+} solutions Comparison of Pb^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}, Ba^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, and Cd^{2+}	Montmorillonite Ca-Montmorillonite	[18]
	Single component Comparison of Zn^{2+}, Cr^{3+}, Mn^{2+}, and Pb^{2+}	Natural	[19]
	Comparison of Zn^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+}		[9]
Cr^{6+}	Single component Comparison between Cr^{3+}, Cr^{6+}, and Ag^{+}	Natural	[12]
Ag^{+}	Single component Comparison between Cr^{3+}, Cr^{6+}, and Ag^{+}	Natural	[12]
	Bimodal metal+Ca^{2+} solutions Comparison of Pb^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}, Ba^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, and Cd^{2+}	Montmorillonite Ca-Montmorillonite	[18]

(*Continued*)

Table 1 (*Continued*)

Metal(s)	Solution	Bentonite type	Refs.
Ni^{2+}	Single component	Natural	[28]
	Binary Mn^{2+}/Ni^{2+}	Natural	[4]
	Single component	Natural	[20]
	Binary Ni^{2+}/Cd^{2+}		
	Bimodal metal + Ca^{2+} solutions	Montmorillonite	[18]
	Comparison of Pb^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}, Ba^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, and Cd^{2+}	Ca-Montmorillonite	
	Comparison of Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, and Cr^{3+}	Na-bentonite	[28]
		Ca-bentonite	
Cu^{2+}	Binary Cu^{2+}/Cd^{2+}	Natural	[6]
	Single component	Montmorillonite	[18]
	Comparison of Zn^{2+}, Cr^{3+}, Mn^{2+}, and Pb^{2+}	Ca-Montmorillonite	
	Comparison of Zn^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+}		[9]
	Comparison of Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, and Cr^{3+}	Na-bentonite	[28]
		Ca-bentonite	
	Single component	Montmorillonite	[33]
	Bimodal metal + Ca^{2+} solutions	Montmorillonite	[18]
	Comparison of Pb^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}, Ba^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, and Cd^{2+}	Ca-Montmorillonite	
Cd^{2+}	Binary Cu^{2+}/Cd^{2+}	Natural	[6]
	Single component	Natural	[20]
	Binary Ni^{2+}/Cd^{2+}		
	Single component	Na-enriched	[26]
	Comparison between Zn^{2+} and Cd^{2+}		
	Bimodal metal+Ca^{2+} solutions	Montmorillonite	[18]
	Comparison of Pb^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}, Ba^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, and Cd^{2+}	Ca-Montmorillonite	
	Comparison of Zn^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+}		[9]
	Comparison of Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, and Cr^{3+}	Na-bentonite	[28]
		Ca-bentonite	
Fe^{3+}	Single component	Chemically treated	[34]
	Single component	Natural	[24]
	Comparison between Zn^{2+} and Fe^{3+}		
Fe^{2+}	Single component	Natural	[31]
	Comparison between Mn^{2+} and Fe^{2+}		
Co^{2+}	Single component	Acid activated	[35]
Hg^{2+}	Bimodal metal + Ca^{2+} solutions	Montmorillonite	[18]
	Comparison of Zn^{2+}, Ba^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, and Cd^{2+}	Ca-Montmorillonite	
Ba^{2+}	Bimodal metal + Ca^{2+} solutions	Montmorillonite	[18]
	Comparison of Pb^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}, Ba^{2+}, Hg^{2+}, Ni^{2+}, Mn^{2+}, and Cd^{2+}	Ca-Montmorillonite	

investigation were air-dried at 80˚C for 24 h and stored in desiccators for further use. The specific surface area and the pore characteristics for the solid materials were measured by N_2 adsorption at 77 K using an Autosorb-1 Quantachrome nitrogen porosimeter with krypton upgrade. An FTIR spectrophotometer (Perkin Elmer 880 spectrometer) was used to measure the infrared absorption on the three mineral samples. The FT-IR spectra in the 4,000–400/cm range were recorded for all minerals at room temperature. Samples were prepared by the standard KBr pellets method. Solid samples have been milled together with potassium bromide (KBr) to form a very fine powder which is then uniaxially compressed into a thin pellet which can be further analyzed. DTA, TGA and DTG were obtained at the same time, by means of a Mettler Toledo 851 thermal analyzer at a heating rate of 10˚C/min, using air atmosphere. The samples were heated in a platinum crucible in the temperature range 25–1,200˚C.

2.2. Batch experiments

2.2.1. Equilibrium isotherms

A measured quantity of bentonite (0.1–14 g) was added to a vessel containing 100 ml of metal solution (Mn^{2+}, Zn^{2+} or Cr^{3+}) under a normality of 0.01 N. Every

10–20 d, the solution was analyzed for metal concentrations until no further uptake from the minerals was observed. Total sampling volume was 2% of the total solution volume. The exchange temperature was kept constant during the batch reaction time at 25 ± 2℃. Final pH was recorded and in all cases, it was found to be lower than 5, indicating that no precipitates were formed. All chemicals used were analytical grade reagents and high-purity deionized water. pH was initially adjusted to 4 in order to avoid precipitation during all ion exchange experiments by using HNO_3. The concentration of metal ions was measured by Atomic Absorption Spectroscopy (AAS), using a Perkin–Elmer Model 2380 spectrophotometer. The mean standard error of concentration measurements was 1.5 ± 1%.

2.2.2. Maximum exchange level

MEL of ion-exchange materials was measured using the repeated equilibrations method [8]. MEL studies (repeated batch equilibrations) were conducted as follows: a measured quantity of mineral (0.2–1.0 g) was added in a vessel containing measured volume of metal solutions (100 ml) at initial concentration of 0.01 N, with pH initial adjustment, as above. Every 7 d, the solution was analyzed for metal concentrations and then replaced with fresh solution of the same metal, until no further uptake from the mineral was observed. The term "MEL" is introduced for the upper limit (saturation) equilibrium loading [36].

2.2.3. Sorption isotherms

For the purposes of simplified equilibrium modeling in adsorption and ion exchange systems, Langmuir equilibrium equation is used [37]:

$$\frac{q_e}{Q_M} = \frac{K \cdot C_e}{1 + K \cdot C_e} \Longleftrightarrow \frac{1}{q_e} = \frac{1}{Q_M \cdot K} \cdot \frac{1}{C_e} + \frac{1}{Q_M} \tag{1}$$

where q_e is the solid-phase concentration in equilibrium with liquid-phase concentration C_e, Q_M is the ultimate sorptive capacity (mg/g) and K is an equilibrium constant (L/mg).

Freundlich isotherm equation is also frequently used, especially in liquid-phase systems [37]:

$$\frac{q_e}{Q_M} = k \cdot C_e^{Fr} \Longleftrightarrow q_e = K_F \cdot C_e^{Fr} \Longleftrightarrow \ln q_e = Fr \cdot \ln C_e + \ln K_F \tag{2}$$

where q_e is the solid-phase concentration in equilibrium with liquid-phase concentration C_e, Q_M is the ultimate sorptive capacity, k and Fr are equilibrium constants and $K_F = (Q_M k)$.

It is important to distinguish the values of (q_{max}) and (Q_M). The first is the solid-phase concentration in equilibrium with the initial fluid-phase concentration, while (Q_M) is higher, representing the maximum adsorption capacity, which typically is achieved in higher fluid-phase concentrations. Following the terminology of Inglezakis (2005), for ion exchange (q_{max}) corresponds to the MEL, while (Q_M) corresponds to the real exchange capacity (REC) [36]. MEL-normalized equilibrium curves should be used with caution. As mentioned above, REC which refers to the amount of the actual total amount exchangeable cations of the solid phase and is a characteristic constant of the ion exchanger. MEL on the other hand depends on the temperature and normality. MEL and REC could be equal for "ideal" ion-exchange systems, i.e. systems where complete exchange is achieved, which is not the case of zeolites [36]. While MEL-normalized equilibrium curves are useful for equilibrium modeling and derivation of thermodynamic properties, selectivity series is better investigated either by REC-normalized equilibrium curves or by use of distribution coefficients. The distribution coefficient (λ_i, mL/g), for cation (i) is defined by [38]:

$$\lambda_i = \frac{C_{s.i}}{C_{l.i}} \tag{3}$$

where $C_{s,i}$ and $C_{l,i}$ are the solid and liquid cation concentrations in (mg/g) and (mg/mL), respectively. In general, the selectivity series derived from MEL-normalized equilibrium curves agree with those derived from distribution coefficients but the later method is preferred [36,38].

3. Results and discussion

3.1. Sample characterization

XRD analysis showed that bentonite samples were consisted mainly of the clay mineral monmorillonite (>80%) (Fig. 1). The XRD pattern of the natural bentonite (Fig. 1) shows reflection peaks at about $2\theta = 7.28^\circ–13.29^\circ–19.91^\circ–28.5^\circ$, corresponding to a basal spacing of 12.13–6.66–4.46–3.13 Å. These reflections are attributed to montmorillonite, which is the main component of the mineral, with concentration up to ~80% wt. Small amounts of mica/illite, dolomite ($2\theta = 31.120^\circ–d = 2.87$) [$CaMg(CO_3)_2$], calcite ($2\theta = 29.74^\circ–d = 3$) [$CaCO_3$], quartz ($2\theta = 26.921^\circ–d = 3.30915$) [$SiO_2$], anatase ($2\theta = 25.55^\circ–d = 3.48$) [$TiO_2$] and pyrite ($2\theta = 33.3^\circ–d = 2.69$) [$FeS_2$] have been also identified.

The XRF analysis of cation oxides in bentonite sample does not give a clear characterization of

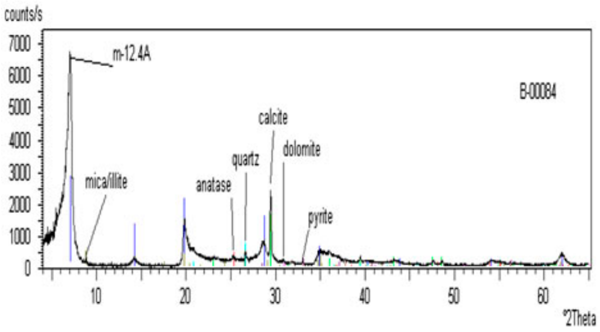

Fig. 1. XRD analysis of bentonite samples.

bentonite as Ca- or Na-bentonite, as Ca and Na percentages are similar (Table 2). Bentonite shows Si/Al ratio lower than 4, while $SiO_2 + Al_2O_3$ is higher than 65%.

BET surface area of bentonite is 41.87 m^2/g, within the limits found in the literature for natural bentonites, between 20 and 69.34 m^2/g [2,4,5,12]. Fig. 2 shows that they belong to the Type IV isotherms. This type of isotherm exhibits a hysteresis loop, which is associated with capillary condensation taking place in mesopores, and has a limiting uptake over a range of high P/P_0. The initial part of the type IV isotherm is attributed to a monolayer–multilayer adsorption since it follows the same path as the corresponding part of a type II isotherm obtained with the given adsorptive on the same surface area of the adsorbent in a non-porous form. Type IV isotherms are characteristic of many mesoporous industrial adsorbents. It is well known that hysteresis loops are connected to pore structure and thus, its assessment is useful for the analysis of the results. Bentonite under research follows similar hysteresis loop patterns, in particular of type H3. According to IUPAC classification, this type of loop is usually given by the aggregates of platy particles or adsorbents containing slit-shaped pores. The presence of a broad hysteresis loop in the desorption isotherms (Fig. 2) reveals the existence of limited ordered meso-macroporosity [32].

Table 2
Bentonite chemical analysis (XRF)

Oxide	% w/w
SiO_2	55,9
Al_2O_3	18,0
Fe_2O_3	3,85
CaO	3,63
MgO	3,53
Na_2O	3,52
K_2O	0,611

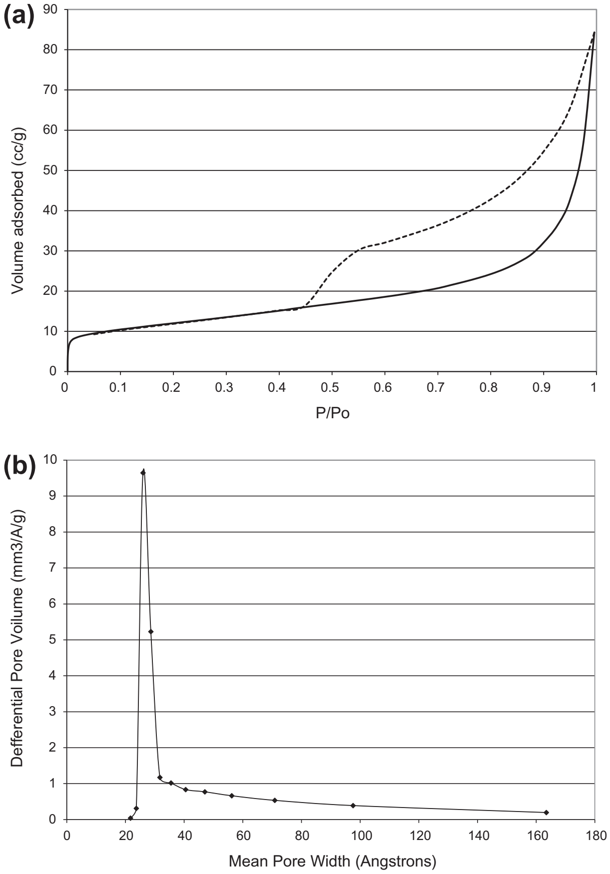

Fig. 2. Sorption—desorption isotherm curves (bentonite).

Fig. 3 shows the FTIR spectra of bentonite. In the bentonite band, the vibrations given at 469 and 522 cm^{-1} are due to the absorption of the characteristic bond of Si–O–Si and Si–O–Al^{vi}, whereas the vibrations given at 878 and 916 cm^{-1} and 3,628 cm^{-1} are due to the bonds of Al^{vi}–OH–R^{vi}, (where R: A1^{3+}, Mg^{2+}, Fe^{3+} or Fe^{2+}) [39]. The vibration given at 917 cm^{-1} refers to the Al^{vi}–OH–Al^{vi} bond and corresponds to pure montmorillonite. Finally, the wide vibration at 3,446 cm^{-1}, and the sharp vibration at 1,637 cm^{-1} are attributed to the adsorbed water.

Thermal characterization data for bentonite are shown in Fig. 4. In most DTA curves, some endothermic peaks are observed between 100 and 400˚C, which is the result of dehydration. The endothermic peak which results from dehydroxylation and the exothermic peak which results from recrystallization are observed at 600–800˚C. The exothermic peak resulting from the loss of the crystal structure of the 2:1 layers of CaM and recrystallization is observed at 950–1,050˚C [40].

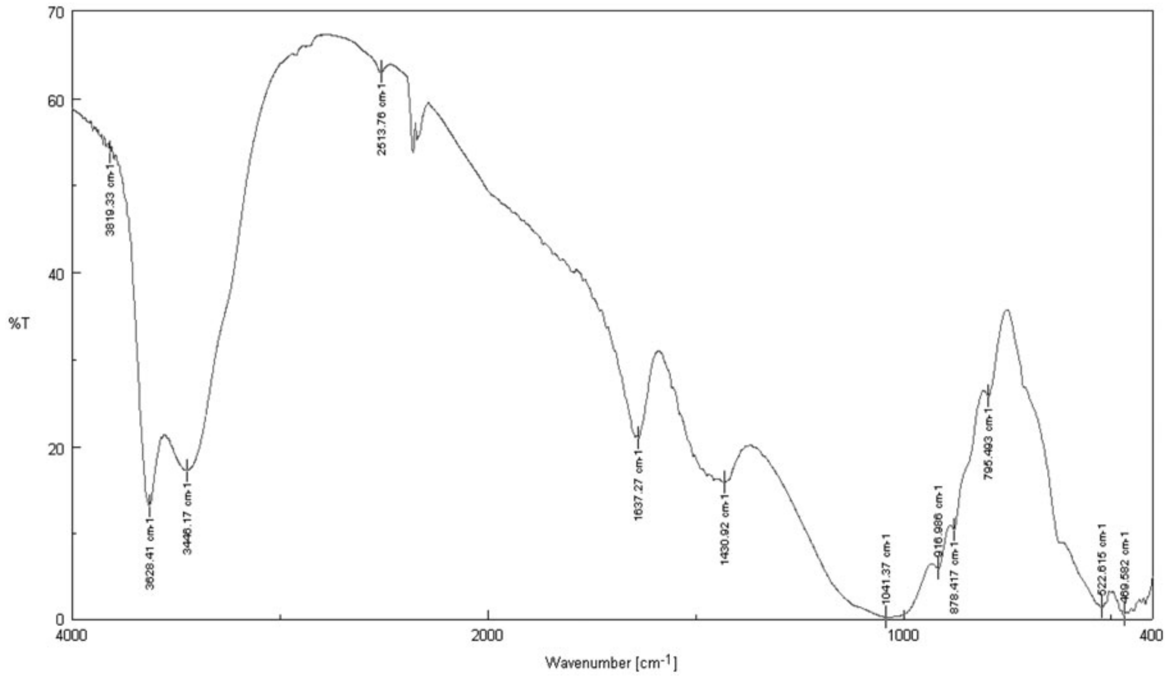

Fig. 3. FTIR spectra of bentonite.

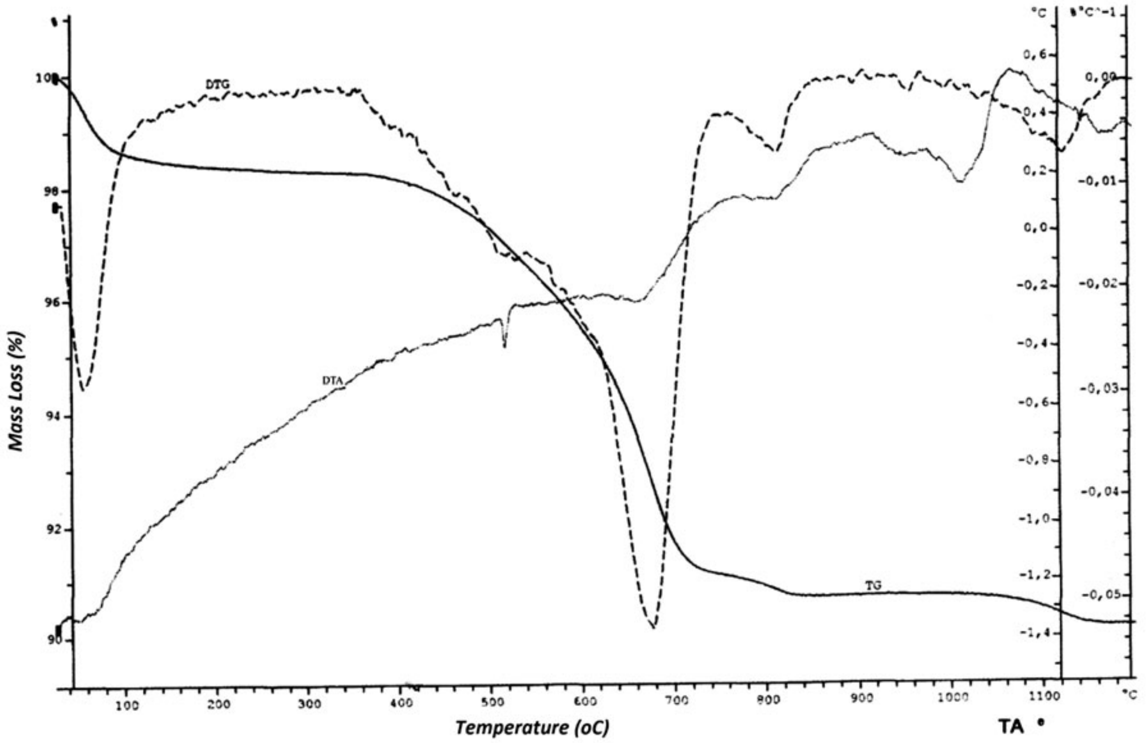

Fig. 4. Thermogravimetric analysis of bentonite.

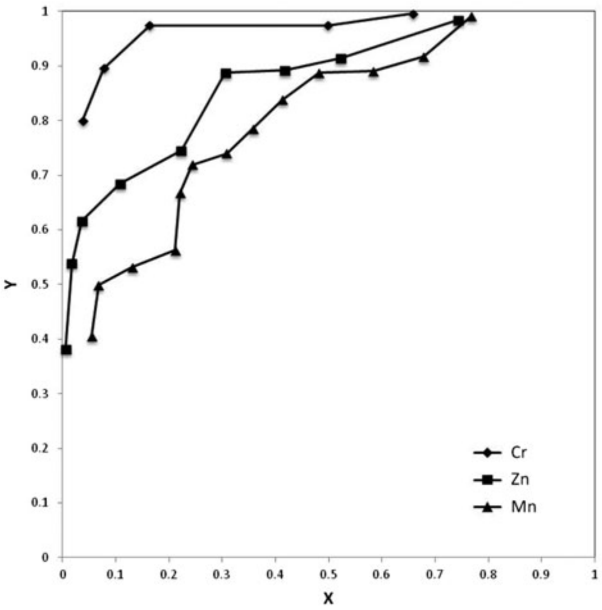

Fig. 5. Bentonite (Mn^{2+}, Cr^{3+}, and Zn^{2+}) equilibrium curves.

3.2. Batch experimental results

3.2.1. Equilibrium Isotherms

The equilibrium isotherms and distribution coefficients for the metals studied are presented in Figs. 5 and 6, respectively, where X ($X = C_{eq}/C_0$) is the reduced concentration of metal in the liquid phase, in respect to initial metal concentration, and Y ($Y = q_{eq}/q_0$) the relative equilibrium concentration of metal in the solid phase, in respect to the MEL for the specific metal. As is evident from Fig. 5, all isotherms are favorable following the order Cr > Zn > Mn.

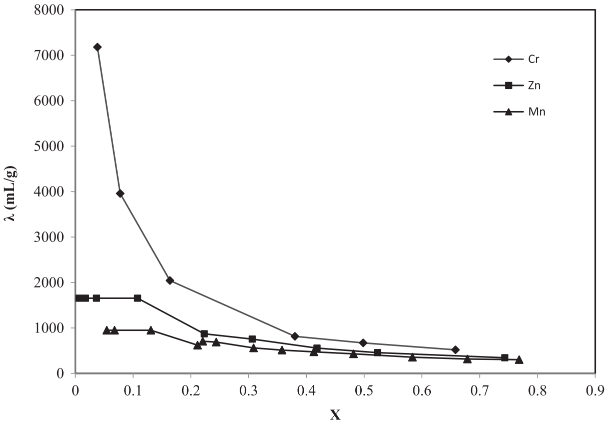

Fig. 6. Bentonite (Mn^{2+}, Cr^{3+}, and Zn^{2+}) distribution coefficients.

According to Al-Jariri and Khalili [19], the maximum adsorption capacity of the investigated metal ions on the bentonite surface is increasing as the following order: $Cr^{3+} > Zn^{2+} > Mn^{2+}$. Higher atomic weight and ionic radius, give smaller hydrated radius, which effect significantly in increasing capacity values. This trend can be also explained by hard and soft acids and bases (HSAB) theory, in which hard acids tend to associate with hard bases, and soft acids with soft bases. According to HSAB theory, Cr^{3+} is hard metal ion while Zn^{2+} ions is in the borderline and Mn^{2+} is classified as soft metal, so Cr^{3+} will have higher tendency to make complexes with the hard surface of bentonite. Iskander et al. [23] studied the equilibrium of Zn^{2+} and Mn^{2+} on natural bentonite and the results showed that the affinity for Mn^{2+} is higher. The opposite result is found by de Pablo et al. [18]. Abollino et al. [17] studied the sorption of seven metals on Na-montmorillonite. The results showed that the total capacity of Na-montmorillonite toward the investigated metals increased in the order: $Zn^{2+} < Mn^{2+} < Cr^{3+}$. Ions with the same valence but with larger ionic radii are adsorbed less on clay, and their introduction in interlayers and complexation with surface sites is limited by steric hindrance and lower electrostatic attraction. Chromium(III) ion has higher charge density than the other ions, and thus the coulombic attraction toward the superficial sites of the clay is greater. For this reason, the total capacity of Na-montmorillonite toward the trivalent ion is considered the highest [17]. Kaya and Oren [21] showed that the difference in the metal ion sorption onto the bentonites may be due to the difference in the mineralogical compositions and associated cations in the exchangeable sites. Sheta et al. [24] investigated the sorption characteristics of natural bentonite via zinc and iron and concluded that heavy metal uptake strongly depends on the mineralogical compositions of materials and kinds of heavy metal used in the tests.

3.2.2. Maximum exchange levels

In Table 3 the MELs of natural bentonite for the three metals studied are presented. The selectivity

Table 3
Minerals MEL

Metal	meq/g	mg/g
Zn	2,61	85.23
Mn	2,34	64.17
Cr	3,40	58.90

series deduced from MEL values follows the order Cr > Zn > Mn and is the same compared to the equilibrium isotherms.

3.2.3. Sorption isotherms

The equilibrium curves are used for the estimation of Langmuir and Freundlich constants and are presented in Table 4, where R^2 is the correlation coefficient of the linear trendline.

As is evident, Langmuir isotherm fits data better for Cr, while Freundlich seems superior for Zn and Mn. It is interesting to note that the ultimate sorptive capacity as estimated by Langmuir isotherm is very close to the MEL value for Cr and Mn and not far for Zn. In Table 5, data on equilibrium isotherms are presented for similar systems (single component and natural bentonite). There is a good agreement in the case of Cr with published data in [19], Zn with [30] and Mn with [32]. However, is evident that there are differences and apart from the bentonite sample characteristics the reason is that different concentrations are used. Thus, literature data should be used with caution, especially when it comes to natural minerals, which exhibit different characteristics from deposit to deposit.

Table 4
Models fit and constants

		Langmuir			Freundlich		
Metal	Concentration (mg/L)	Q_M (mg/g)	K (L/mg)	R^2	Fr	K_F	R^2
Cr	172	59.52	0.59	0.98	0.0678	43.28	0.82
Zn	327	71.43	0.39	0.92	0.18	31.1	0.97
Mn	275	60.24	0.05	0.88	0.32	11.29	0.95

Table 5
Data on equilibrium isotherms in the literature for natural (unmodified) bentonite and single component solutions of metals at ambient temperature

Metal(s)	Isotherm type	Concentration (mg/L)	Constants	Refs.
Zn^{2+}	Langmuir	300	Q_M (mg/g) = 52.91, K (L/mg) = 0.01	[13]
	Freundlich failed			
	Langmuir	10–90	Q_M (mg/g) = 68.39, K (L/mg) = 0.02	[30]
	Freundlich		K_F = 1.4845, Fr = 0.81	
	Langmuir	50–1,000	Q_M (mg/g) = 1.54, K (L/mg) = 0.06	[27]
	Freundlich		Fr = 0.5	
	Langmuir	5–500	Q_M (mg/g) = 3.08, K (L/mg) = 0.04	[29]
	Langmuir	100	Q_M (mg/g) = 9.12, K (L/mg) = 22.08	[31]
	Freundlich		K_F = 1.84, Fr = 0.45	
	Langmuir	100	Q_M (mg/g) = 9.05–9.55, K (L/mg) = 1.27–1.40	[19]
	Freundlich		K_F = 2.60–2.75, Fr = 0.37	
	Freundlich	–	Fr = 0.72	[9]
	Langmuir failed			
Cr^{3+}	Freundlich	0.52–52	K_F = 118–341, Fr = 0.23–0.30	[2]
	Langmuir failed			
	Freundlich	0.052–5.2	–	[12]
	Langmuir	100	Q_M (mg/g) = 24.88–52.08, K (L/mg) = 0.10–1.32	[19]
	Freundlich		K_F = 2.98–22.74, Fr = 0.34–0.54	
Mn^{2+}	Langmuir	50–1,000	Q_M (mg/g) = 1.55, K (L/mg) = 0.044	[27]
	Freundlich		Fr = 0.45	
	Langmuir	100	Q_M (mg/g) = 24.88–52.08, K (L/mg) = 0.10–1.32	[32]
	Freundlich		K_F = 2.98–22.74, Fr = 0.34–0.54	
	Langmuir	100	Q_M (mg/g) = 7.14, K (L/mg) = 0.39	[19]
	Freundlich		Fr = 0.16	

4. Conclusions

Ion exchange equilibria are examined by use of batch equilibrium isotherms and distribution coefficients for three metals (Zn^{2+}, Cr^{3+}, and Mn^{2+}) on natural bentonite. All isotherms are favorable. Selectivity series derived from distribution coefficients is $Cr^{3+} > Zn^{2+} > Mn^{2+}$ and is the same for MEL experiments. The Langmuir and Freundlich models were applied to describe the equilibrium isotherms for the metal ion uptake. According to the results, Langmuir isotherm fits data better for Cr, while Freundlich seems superior for Zn and Mn.

List of symbols

q_e	—	the solid-phase concentration in equilibrium
C_e	—	liquid-phase concentration
Q_M	—	the ultimate sorptive capacity (mg/g)
K	—	equilibrium constant (L/mg)
k and Fr	—	equilibrium constants
$C_{s,i}$	—	solid cation concentrations in (mg/g)
$C_{l,i}$	—	liquid cation concentrations in (mg/mL)
λ_i	—	distribution coefficient (mL/g), for cation (i)

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