



EQUILIBRIUM STUDIES OF MANGANESE REMOVAL FROM AQUEOUS SOLUTION BY ADSORPTION ON NATURAL ZEOLITE

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Introduction

Heavy metals are a common pollutant found in various industrial effluents. They are often encountered in metal plating facilities, electroplating, mining operations, fertilizers, battery manufacture, dyestuffs, chemical pharmaceutical, electronic device manufactures and many others. Most of heavy metals are highly toxic and are non-biodegradable, therefore they must be removed from the polluted streams in order to meet increasingly stringent environmental quality standards.

Removal of these heavy metals can be accomplished by a variety of techniques. Conventional methods typically involve the use of processes such as coagulation, precipitation, ion-exchange, electrochemical methods, membrane processes, extraction, biosorption, adsorption, etc. Among these methods, adsorption is currently considered to be very suitable for wastewater treatment because of its simplicity and cost effectiveness. Some widely used adsorbents for adsorption of heavy metals include activated carbon, clay minerals, biomaterials, industrial solid wastes and zeolites [1].

Zeolite is a natural porous mineral in which the partial substitution of Si^{4+} by Al^{3+} results in an excess of negative charge. This is compensated by alkali and alkaline earth cations (Na^+ , K^+ , Ca^{2+} or Mg^{2+}). Zeolites have been used as adsorbents, molecular sieves, membranes, ion-exchangers and catalysts, mainly because zeolite exchangeable ions are relatively innocuous. Thus, zeolites are particularly suitable for removing undesirable heavy metal ions (e.g. lead, nickel, zinc, cadmium, copper, chromium and/or cobalt), radionuclides as well as ammoniacal nitrogen (ammonia and ammonium) from municipal wastewaters, electroplating effluents and agricultural wastewaters [2].

The aim of this work was to investigate the adsorption of manganese ions onto a natural zeolite (clinoptilolite) whereby the main parameters were the adsorption isotherms.

Experimental

Adsorbent

The natural zeolite - clinoptilolite was used in the recent study as an adsorbent for adsorption of heavy metals, such as manganese. The particle size range of the natural zeolite used in this study was 0.8 to 2.5 mm.

The chemical composition of natural zeolite are presented in Table 1.

Table 1 Chemical composition of zeolite samples

Typical chemical composition in % wt			
SiO_2	69.68	CaO	2.01
Al_2O_3	11.40	Na_2O	0.62
TiO_2	0.15	K_2O	2.90
Fe_2O_3	0.93	H_2O	13.24
MgO	0.87	P_2O_5	0.02
MnO	0.08	ratio Si/Al	4.0-5.2
Cation exchange per cation		K^+	41 meq/100g
		Na^+	16.10 meq/100g
		Ca^{2+}	67.14 meq/100g
		Mg^{2+}	3.88 meq/100g
Total cation exchange capacity		1.8-2.2 meq/g	

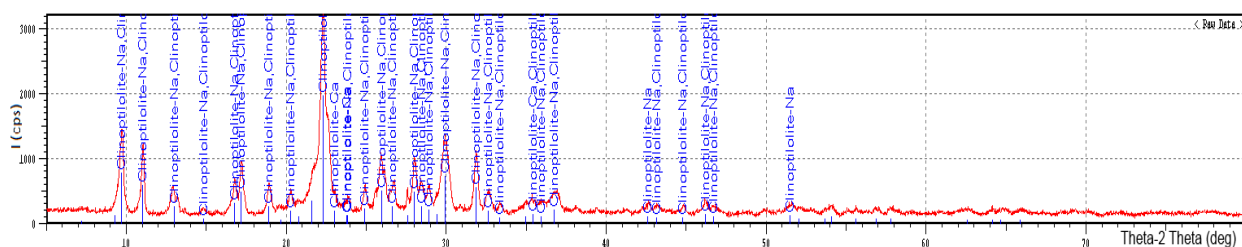


Fig. 1 X-Ray diffraction of natural zeolite

X-Ray Diffractometer 6100 from Snimadzu was used to investigate the mineralogical structure of natural zeolite samples. This technique is based on observing the scattering intensity of an X – Ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. The diffraction data obtained are compared to the database maintained by the *International Centre for Diffraction Data*, in order to identify the material in the solid samples. The results of XRD (Fig. 1) shown that the natural zeolite contained clinoptilolite in the majority.

The surface morphology of natural zeolite was studied using a scanning electron microscope, VEGA3 LMU. This particular microscope is also fitted with an Inca 250 EDS system. EDS, stands for Energy Dispersive Spectroscopy, it is an analytical technique used for the elemental analysis of a sample based on the emission of characteristic X – Rays by the sample when subjected to a high energy beam of charged particles such as electrons or protons.

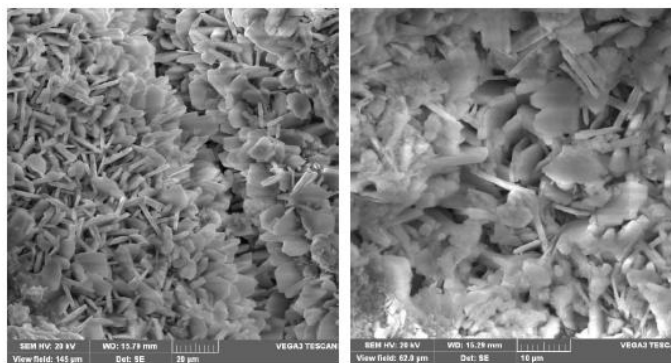


Fig. 2 Micrographs of natural zeolite samples obtained from SEM analysis

Micrographs of natural zeolite samples obtained from SEM analysis are given in Fig. 2. The micrographs clearly show a number of macro-pores in the zeolite structure. The micrographs also show well defined crystals of clinoptilolite.

An electron beam was directed onto different parts of the samples in order to get a more accurate analysis (Fig. 3) and the elemental composition of natural zeolite (clinoptililolite) are presented in Table 2.

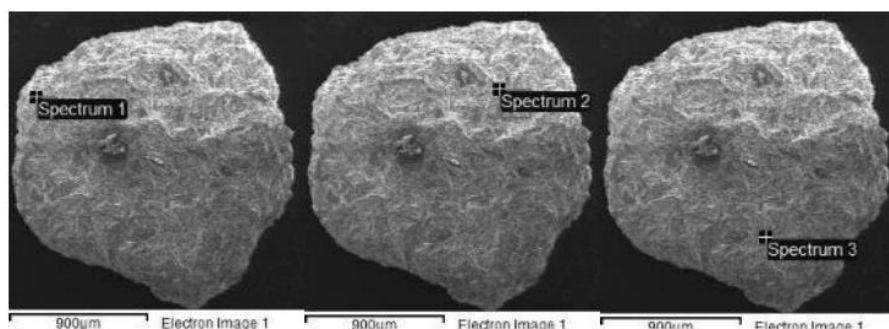


Fig. 3 EDS analysis showing the scanning method for natural zeolite

Table 2 EDS analysis showing the elemental composition for natural zeolite

	O	Na	Mg	Al	Si	K	Ca	Fe	Total
Spectrum 1	58,46	0,27	0,72	5,28	29,55	2,73	1,9	1,1	100
Spectrum 2	55,4	0,15	0,66	5,52	31,36	2,96	2,42	1,53	100
Spectrum 3	58,83	0,3	0,77	5,03	29,47	2,44	1,66	1,5	100
Average	57,56	0,24	0,72	5,28	30,13	2,71	1,99	1,38	100
Std. deviation	1,882	0,079	0,055	0,245	1,068	0,26	0,388	0,24	

Results of EDS analysis showed that the predominant exchangeable cations in natural zeolite (clinoptilolite) structure were Na⁺, Mg²⁺, K⁺ and Ca²⁺.

Adsorbate

The heavy metal, Mn, was used as adsorbate in the recent investigations. Synthetic single component solutions of Mn²⁺ were prepared by dissolving a weighed mass of the analytical grade salt MnSO₄·H₂O in 1000ml distilled water. Initial pH of prepared solutions was adjusted by adding 2% sulfuric acid and controlled by 210 Microprocessor pH Meter.

Experimental procedure

Adsorption of manganese ions on zeolite was performed with synthetic single ion solutions of Mn²⁺ ions with different initial concentration. The experiments were performed in a batch mode in a series of beakers equipped with magnetic stirrers by contacting a mass of zeolite with a certain volume of Mn²⁺ ions solution. Zeolite sample and aqueous phase were suspended by magnetic stirrer at 400 rpm. The agitation time was varied up to 360 minutes. At the end of the predetermined time, the suspension was filtered and the filtrate was analyzed. The final pH value was also measured. The initial and remaining concentrations of metal ions were determined by ISP Emission Spectrometer. All experiments were performed at room temperature on 20±1°C.

Based on material balance, the adsorption capacity was calculated by using the following expression [3]:

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

where: q_e is the mass of adsorbed metal ions per unit mass of adsorbent (mg/g), C_0 and C_e are the initial and final metal ion concentrations (mg/l), respectively, V is the volume of the aqueous phase (l) and m is the mass of adsorbent used (g).

Degree of adsorption, in percentage, is calculated as:

$$AD\% = \left(1 - \frac{C_e}{C_0}\right) \cdot 100 \quad (2)$$

Equilibrium studies

Equilibrium studies generally involve the determination of the adsorption capacity of a given material. This determination is important in accessing the potential of the material as an economic and commercially viable adsorber. The material is contacted with the solute until equilibrium is achieved. The adsorption equilibrium is a dynamic concept achieved when the rate at which molecules are adsorbed onto a surface is equal to the rate at which they are desorbed [4], [5].

Experimental data were also fitted to conventional adsorption mathematical models, namely the Freundlich and Langmuir models. These were used to predict the adsorption performance of natural zeolite. The performance of natural zeolite was also assessed at different initial solution pH levels.

- Langmuir model

The Langmuir isotherm model [6], based on monolayer coverage of adsorbent surfaces by the adsorbate at specific homogeneous sites within the adsorbent, is represented as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where q_e , mg/g, is the amount of solute adsorbed per unit mass of adsorbent at equilibrium; C_e , mg/l, is the residual liquid phase concentration at equilibrium; q_m , mg/g, is the amount of solute adsorbed per unit mass of adsorbent corresponding to complete coverage of available sites, K_L , l/mg, is the Langmuir adsorption coefficient, this constant is related to the affinity between the adsorbent and solute, which is evaluated through linearization of Eq. 3:

$$\frac{1}{q_e} = \frac{1}{k_L q_m C_e} + \frac{1}{q_m} \quad (4)$$

- Freundlich model

The Freundlich isotherm model, based on multilayer adsorption on heterogeneous surfaces with a non-uniform distribution of adsorption heat, is represented as:

$$q_e = k_f C_e^{1/n} \quad (5)$$

where k_f and n are empirical Freundlich constants that are dependent on experimental conditions. k_f is an indicator of adsorption capacity, while n is related to the adsorption intensity or binding strength. Their values were determined from the linear form of the Freundlich equation, given by [7]:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (6)$$

1/n is the heterogeneity factor; values of 1/n << 1 indicate heterogeneous adsorbents, while values closer to or even 1 indicate a material with relatively homogeneous binding sites. Natural zeolite should be a heterogeneous adsorbent due to its porous nature.

Results and Discussion

The main objective of the equilibrium studies was to determine the maximum capacity of natural zeolite towards manganese removal under the studied conditions. Furthermore, the determination of the mechanism involved in removing manganese from solution was carried out, mainly by measuring the amount of exchangeable cations released from the natural zeolite samples at equilibrium.

In order to carry out the equilibrium studies, 5 g of natural zeolite was mixed with 100 ml solution of the manganese cations at different initial pH levels (2.5, 3.5 and 4.5) and concentrations (5, 25, 50, 200 and 400mg/l), and agitated for 360 minutes. The results of equilibrium studies for manganese cation are presented in Table 3 and Figs. 4, 5 and 6.

Table 3 Calculated equilibrium adsorption isotherm constants for the uptake of Mn from solution by natural zeolite

pH	Experimental		Langmuir			Freundlich			
	q_e (mg/g)	C_e (mg/l)	q_m (mg/g)	K_l (l/mg)	R^2	K_f (l/mg)	$1/n$	n (g/l)	R^2
2,5	3,525	223,76	4,5851	0,0122	0,9554	0,0811	0,7225	1,3841	0,9765
3,5	4,0596	197,02	4,2680	0,0382	0,9252	0,2625	0,5339	1,8730	0,8282
4,5	4,107	194,66	4,3365	0,0553	0,9752	0,3080	0,5275	1,8957	0,8644

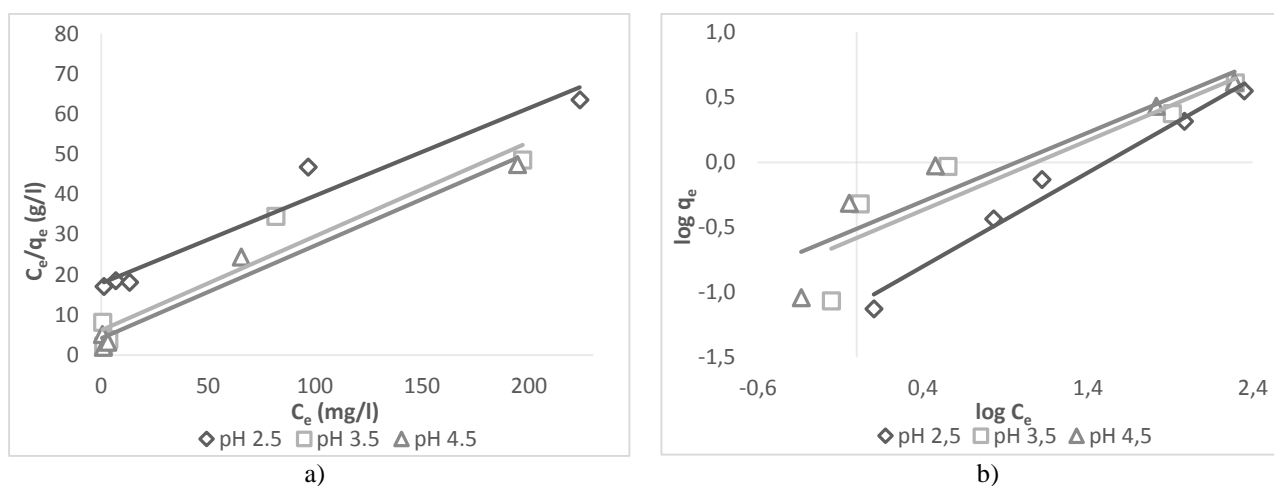
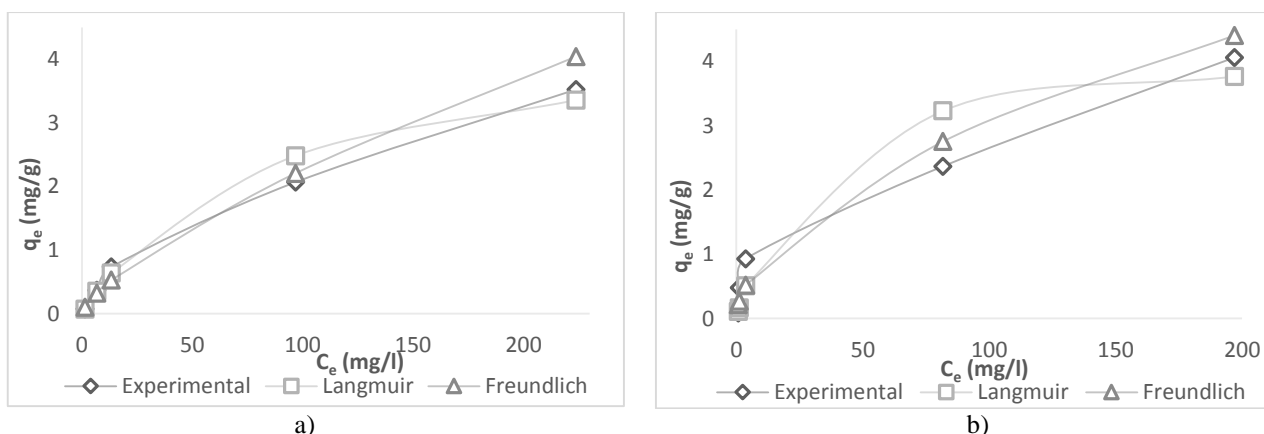


Fig. 4 Adsorption isotherms
a) Langmuir isotherms and b) Freundlich isotherms



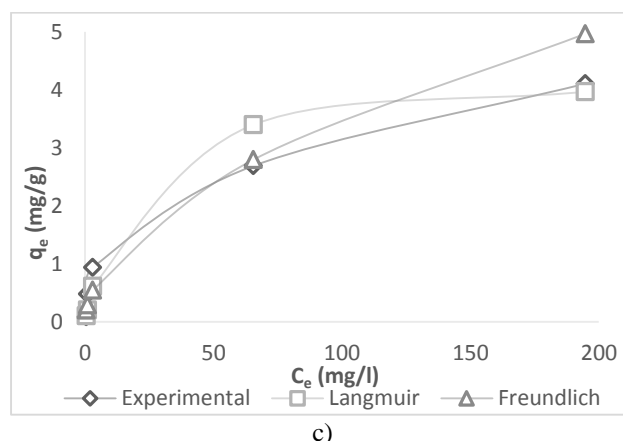


Fig. 5 Equilibrium isotherms for the removal of manganese from solution
a) pH 2.5 b) pH 3.5 c) pH 4.5

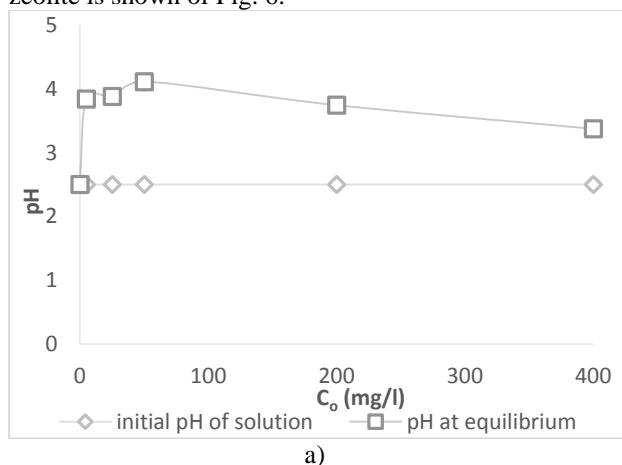
The highest experimental amount of manganese removed, $q_{e \max}$, was 4.1 mg/g, from a solution whose initial pH was 4.5 and the amount of manganese removed from solution increased with an increase in initial solution pH.

This is mainly due to the fact that at high metal concentrations, there is a higher solute concentration gradient, and this provides the necessary driving force for metal ions to displace exchangeable cations on the surface and from the internal micro-pores of natural zeolite [8], [4]. However, this increasing trend is valid up to a point at which the maximum capacity of the natural zeolite samples for the respective heavy metal cation is achieved, that is, its saturation point.

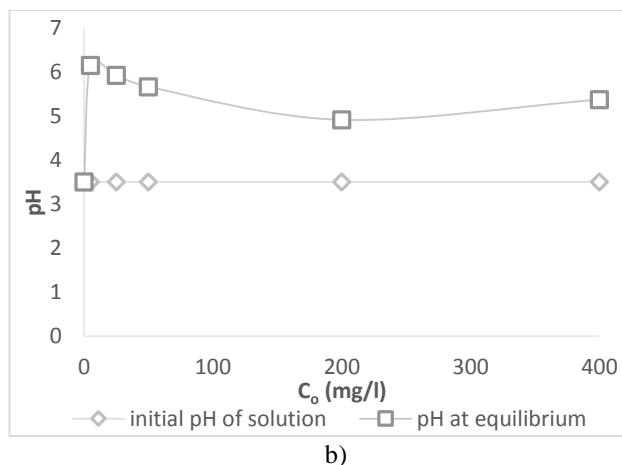
Experimental data obtained from equilibrium experiments were fitted to the Langmuir and Freundlich adsorption isotherms. The values of the parameters for the two isotherms are presented in Table 3.

Table 3 shows that the Langmuir isotherms for the adsorption of manganese from solution gave better fits of the experimental results than Freundlich isotherms. The adsorption capacity, q_e , generally increases from pH 2.5 to 4.5. The fitting of Langmuir and Freundlich models to experimental results for the adsorption of manganese are also shown graphically in Figs. 4 and 5.

Fig. 5 also show the adsorption capacity of natural zeolite for manganese at different initial solution pH levels. It can be observed that there is a general increase in adsorption capacity as the solution pH increases. This is mainly attributed to the decrease in H^+ ion concentration as the initial pH level increases from 2.5 to 4.5. H^+ ions act as competitors for available adsorption sites on the natural zeolite surface, and hence at low pH levels, H^+ ions are more concentrated and thus because of the concentration driving force will be adsorbed in preference to manganese ions, resulting in lower adsorption capacities for manganese ions [9]. The effect of initial solution pH on the adsorption of manganese by natural zeolite is shown of Fig. 6.



a)



b)

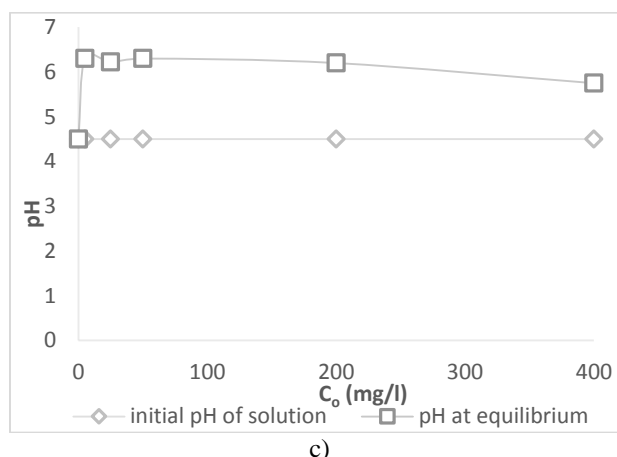


Fig. 6 Equilibrium pH change with respect to various initial copper concentrations. The initial solutions were at different pH values. Error in pH reading is ± 0.2 .
a) Initial pH 2.5 b) Initial pH 3.5 c) Initial pH 4.5

Fig. 6 presents the variation in the equilibrium pH values with respect to initial Mn concentration in each equilibrium study. The equilibrium pH values are greater than the initially adjusted pH values and the difference between equilibrium pH and initial pH exhibits a descending trend with increasing initial Mn concentration. The increase in pH is a result of the adsorption of H^+ ions from solution, but as the initial concentration of manganese increases, the concentration driving force begins to favour the adsorption of Mn^{2+} ions in preference to H^+ ions, thus the descending trend of the equilibrium pH at higher initial manganese concentrations.

The probability of manganese precipitating out of solution is very small since the equilibrium pH ranges up to 6.3, Fig. 6 (c), and this is lower than the minimum pH (10.6) needed for the precipitation of manganese [10].

We can conclude that increase in initial concentration not only results in an increase in the amount adsorbed (q_e) but a decrease in the efficiency of natural zeolite for the removal of Mn from solution. Increases pH value results in an increase in the adsorption capacity. The adsorption of manganese ions from diluted solution onto natural zeolite occurs efficiently.

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