

Absorption Isotherm Study of Mn^{2+} on MnO_2 and FeO - coated zeolite from aqueous solution

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Abstract

The present study is concerned with the removal of Manganese from aqueous solution by adsorption onto low cost adsorbent. Manganese oxide coated zeolite (MOCZ) and iron oxide coated zeolite (FOCZ) were investigated as an adsorbent for the removal of Mn^{2+} . Batch adsorption experiments were performed as a function of pH, contact time and Mn concentration. The optimum conditions for maximum adsorption by MOCZ were attained at pH=7, Mn concentration of 5 mg/L and for FOCZ at pH=8, concentration of 4mg/L. Manganese detection was carried out by Inductive Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES). Furthermore, Results showed that MOCZ had a good adsorption performance for the adsorption of Mn rather than FOCZ, the adsorption capacity of MOCZ was 0.21 mg/g at 15 min. Langmuir, Freundlich, isotherm models were selected to evaluate the adsorption of Mn. It was found that the Langmuir isotherm model with coefficients of determinations (R^2) of 0.97 and 0.94, respectively, best fits the Mn adsorption onto adsorbents. Finally, Obtained results from experiments prove that MOCZ is suitable for removal of manganese from water and it is comparable with FOCZ.

Keywords: *isotherm, manganese oxide, surface-modified, clinoptilolite, Mn^{2+}*

1. Introduction

The contamination of water by heavy metals through the discharge of industrial wastewater is a worldwide environmental problem. Heavy metals may come from various industrial sources such as electroplating, metal finishing, metallurgy, chemical manufacturing, mining and battery manufacturing. Ions like Hg^{+2} , Cr^{+2} , Fe^{+2} and Mn^{+2} are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders[1-2]. For drinking water, the recommended maximum contaminant level of Mn^{2+} by US Environmental Protection Agency is 0.05 mg/L [3-4]. A Mn^{2+} concentration greater than 0.1 mg/L could lead to water discoloration, undesirable taste, and unpleasant odor in the water making it unsuitable for drinking. Mn^{2+} can cause black or brown stains on household utensils, plumbing fixtures and clothing [5]. Current technologies utilized for Mn removal include filtration, membrane processes, adsorption, ion exchange, precipitation, and chemical feed systems [6-7]. Adsorption is an effective process used in water treatment particularly in heavy metal removal. But at present, it is commonly believed that the most rational process for the removal of manganese from water is its oxidation by air oxygen in the presence of catalysts

deposited onto the surface of grained filtering materials. It is known that higher oxides of manganese (Mn_3O_4 , MnO_2) can act as catalysts for Mn (II) oxidation. The grained supports for these catalysts are quartz sand, anthracite, charcoal, natural zeolites such as clinoptilolite [4]. 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+}) [3]. Some reported studies of manganese ions adsorption for different materials such as Granular activated carbon, Na-montmorillonite and Dolomite, est. [3, 8-9]. Although these adsorption capacities correspond to different experimental conditions, they are representative of the solids' tendency to retain Mn^{2+} ions. Clinoptilolite have low ion-exchange capacities, and are commonly treated (Enriching) by chemical or physical methods before use. Ion-exchange with sodium chloride solution is widely employed, because sodium ions can readily remove other cations enhancing the adsorption capacity [10]. In this study, for the formation of surface nanoclusters of MnO_2 and FeO was based on the introduction of Mn^{2+} cations which act as the precursors, into the exchange positions at the external surface of clinoptilolite grains. The oxidation of these cations by potassium permanganate results in the formation of MnO_2 surface nanoclusters. The present work investigates applicability of Iranian clinoptilolite as an adsorbent material for the removal of manganese ions from water was explored under batch conditions, and the sorption kinetics and other related parameters are examined as well.

2. Materials and Methods

2.1. Clinoptilolite and Reagents

The Clinoptilolite used in the present investigation comes from a layer situated in Semnan (Iran). According to its chemical composition it is a clinoptilolite with $(\text{Na}_{0.52}\text{K}_{2.44}\text{Ca}_{1.48})$ $(\text{Al}_{6.59}\text{Si}_{29.41}\text{O}_{72}) \cdot 28(\text{H}_2\text{O})$. Its characterization as clinoptilolite is further supported by the Si/Al ratio, which is equal to 4.46. The powder XRD study showed that zeolite; Ramsdellite, Silicon Oxide and Potassium Aluminum Silicate are present through the tuff whereas the clinoptilolite used in the present study comes from a layer with high clinoptilolite content (70%). Its specific surface area is equal to $12.23\text{m}^2/\text{g}$. Before the test zeolite sample was prepared and sieved with particle diameters (3.8in, 4, 10 Mesh). KMnO_4 – (Scharlau) solution and HCl – (Synth) were used to prepare the MOCZ. $\text{Mn}(\text{NO}_3)_2$ – (Chemlab) was used in the preparation of manganese synthetic solutions for the adsorption study. HNO_3 and NaOH solutions were used for pH adjustment. All solutions were prepared using deionised water and results were obtained in duplicate tests.

2.2. Preparation of MnO_2 – zeolite and FeO – Zeolite

Prior to the coating treatment, the zeolite was converted to its Na form by suspending 30 g of zeolite in 500 ml of a 1 M NaCl solution for a period of 24 h. The zeolite suspension was filtered and washed with deionized water. The resulting Na-zeolite was dried in oven at 100C^0 for 24 h before use. The preparation of MnO_2 coated zeolite was performed as follows: (a) the raw zeolite was sieved to obtain different sets of mesh size; (b) the zeolite was washed with de-ionized water for remove of dust; (c) the latter was ion-exchanged containing potassium permanganate placed in a beaker, followed by drop wise addition of hydrochloric acid (37.5%). After stirring for 1 h, the suspension was filtered, washed several times using distilled water (to remove free potassium and chloride ions); (d) dried in oven at 100C^0 for 24 h and stored in a polypropylene bottle for use. For the preparation of iron oxide-

coated zeolite (a) 30 g clinoptilolite was added to 60 ml of solution containing 2% Fe (NO₃)₃·9H₂O. The pH of the mixture was adjusted to the desired value with NaOH; (b) the mixture was stirred for 1 h; (c) dried at 105 C° for 20 h and (d) then washed with deionized water to remove unattached oxide until the pH of the runoff water was constant (pH 7–8). The solid was dried at 105 C° for 24 h and finally stored in a capped bottle for further use.

2.3. Characterization of Adsorbent

SEM photomicrography of the external surface of uncoated zeolite and manganese oxide coated zeolite was taken using a KYKY (EM-3200) microscope. X-ray diffraction (XRD) analysis was performed on the zeolite (modified) to confirm the crystal structure and determined mineralogical composition of it.

2.4. Methods

Manganese ion concentration was determined using Atomic Absorption Spectrophotometer (Contra 700, Analyticjena) and results were expressed as mg Mn L⁻¹. The solution pH was determined using a Model (WTW, inoLab 720).

2.5. Adsorption Experiments and Isotherm Studies

An isotherm describes the relationship of the concentration of an adsorbate between two separate phases at equilibrium at a constant temperature. So, here is the relationship between the amount of Mn²⁺ ion adsorbed onto MOCZ and FOCZ at given experimental condition in liquid phase described by isotherm [11]. Batch ion-exchange experiments were carried out in glass flasks (0.1 L) using an orbital shaker, at a constant agitation of 400 rpm. Suspensions (1 g of MOCZ and FOCZ with 0.05 L of a 1-5 mg Mn²⁺ L⁻¹ solution) were stirred for different periods of time (5, 15, 30, 60, 120 min). Supernatant aliquots were collected and Centrifuge before chemical analysis. The adsorption studies of Mn²⁺ onto MOCZ and FOCZ were conducted using during 120 min (sufficient for attaining chemical equilibrium) and varying the feed solution concentrations (1, 2, 3, 4, 5 mg L⁻¹). The effect of medium pH in Mn²⁺ adsorption was studied adjusting initial pH values (4, 5, 6, 7 and 8) before agitation in the orbital shaker. All ion-exchange results were averaged values of duplicate tests. The Mn²⁺ uptake (q), expressed as Mn²⁺ removal per unit mass of MOCZ (mg Mn²⁺ g⁻¹), was calculated according to Eq.(1), where C₀ is the initial manganese concentration (mg Mn²⁺ L⁻¹), C_f is the final concentration (mg Mn²⁺ L⁻¹), V is the batch volume (L) and m is the adsorbent mass (g).

$$q = \frac{(C_0 - C_f) \times V}{m} \quad (1)$$

In order to describe the interaction between adsorbate and adsorbent, surface properties as well as the degree of affinity of the adsorbent, various isotherm models were used. The linear form of Langmuir's isotherm model is given by the following Eq. (2):

$$\frac{C_e}{q_e} = \frac{1}{b Q_{\max}} + \frac{C_e}{Q_{\max}} \quad (2)$$

Where Q_{max} is the amount of Mn²⁺ adsorbed at complete monolayer (mg/g) and b is the Langmuir constant related to the binding site (L/mg). The essential characteristics of the Langmuir isotherm commonly known as separation factor or equilibrium parameter (R_L) can be defined as by Eq. (3):

$$R_L = \frac{1}{1 + bC_0} \quad (3)$$

Where b is the Langmuir constant and C_0 is the highest initial concentration of Mn^{2+} ions (mg/L). The value of R_L indicates adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The Freundlich isotherm equation (4) can be written in the linear form as given below:

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (4)$$

Where k_F [$(mg\ g^{-1}) (L/g)^{-1/n}$] and n are the Freundlich constants that are related to the adsorption capacity and intensity, respectively.

3. Results and Discussion

3.1. Characterization Studies

Micrographs shown in Figure 1 were taken at 10000× magnification to observe the changes of the zeolite surface morphology by manganese oxides deposition: raw zeolite (Figure 1a) and MOCZ (Figure 1b).

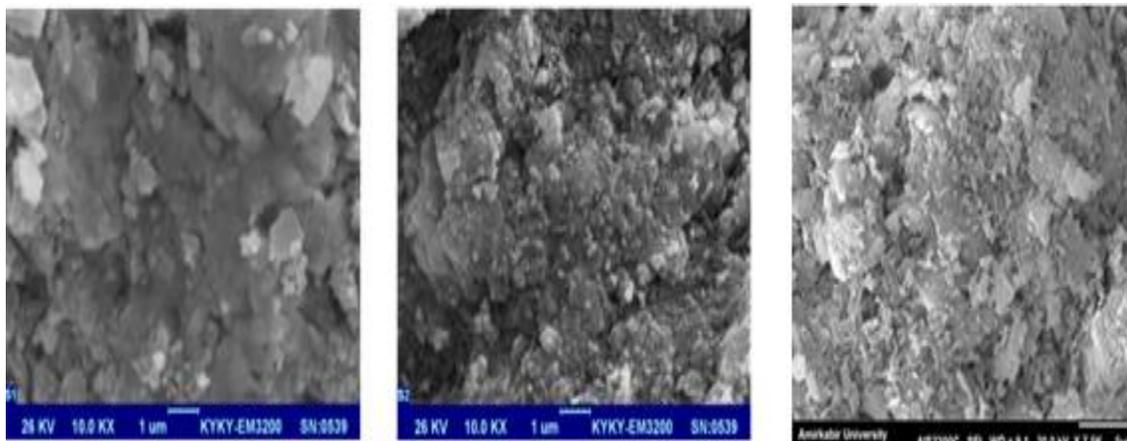


Figure 1. SEM Micrograph of Zeolite Samples. (S₁) Raw Zeolite, (S₂) MOCZ, (S₃) FOCZ

Figure 1(S₂ and S₃) shows that zeolite surface sites were occupied by newborn manganese oxide, and iron oxide which was formed during the coating process. Figure 1(S₂) also shows manganese oxide, formed as clusters onto the zeolite surface. The diffractogram obtained for MOCZ sample is shown in Figure 2 and the main mineral phases present in sample MOCZ are presented in Table 1. The diffractogram of Figure 2 shows that MOCZ has a high crystallinity degree is presented mainly as Clinoptilolite.

Table 1. Mineral Phases Present In Zeolite

Mineral phases present in zeolite	%
Clinoptilolite	70%
Ramsdellite	3%
Silicon Oxide	8%
Potassium	19%
Aluminum Silicate	

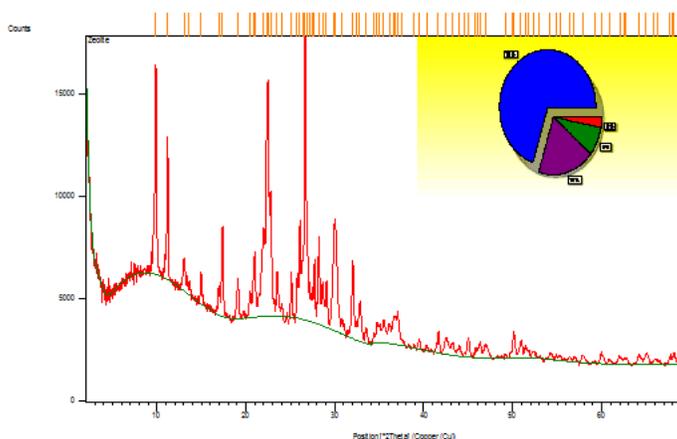


Figure 2. X-ray Diffractogram of the MOCZ Sample

3.2. Effect of pH on the Adsorption of Mn²⁺

The pH has an important effect on Mn²⁺ adsorption since the pH of the medium will control the magnitude of the electrostatic charges that are imparted by ionized manganese. The adsorption capacity (mg g⁻¹) and the removal of Mn²⁺ at different pH by MOCZ and FOCZ are shown in Figure 3. The Mn removal increases with pH from 4 to 8 with FOCZ and optimum pH for MOCZ is 7 with maximum adsorption 0.03 mg/g in 15 min. As pH increases from 4 to 8 the static repulsion force decreases and the Mn adsorption increases [12]. It can be seen that the capacity of MOCZ was higher over a wider range of pH compared to that of FOCZ. In the pH range of 4–8, the surface of MOCZ and FOCZ was negatively charged. In comparison to FOCZ, the more negatively charged surface of MOCZ would have higher affinity towards Mn²⁺ that makes the adsorption more favorable, which resulted to a higher adsorption capacity [13-14]. At high pH values, both ion exchange and aqueous metal hydroxide formation (not necessarily precipitation) may become significant mechanisms in the metal removal process [14].

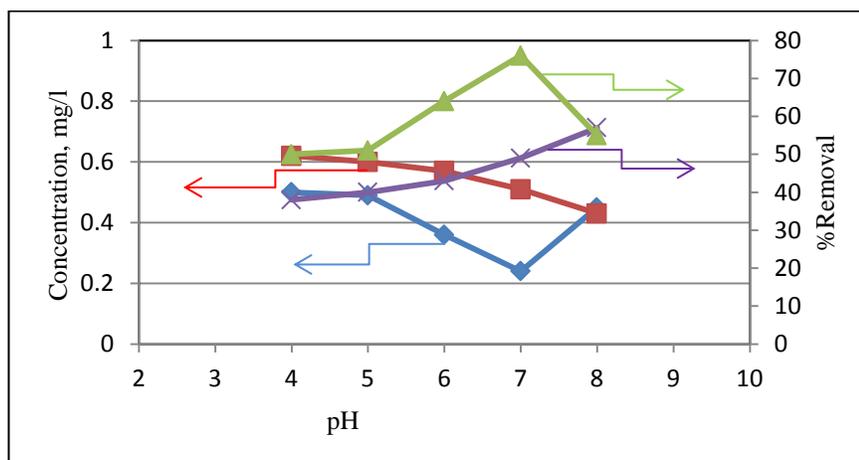


Figure 3. Effect of Initial pH on the Adsorption Capacity with MOCZ and FOCZ

3.3. Effect of Initial Mn Concentration and Contact Time

Figure 4 shows the effect of the initial concentration in the range 1–5 mg/L and contact time (5, 15, 30, 60, 120 min) on the percentage removal of Mn and adsorption capacity of MOCZ and FOCZ for each concentration at 20 C° and pH 7 and 8, respectively. The amount of Mn adsorbed increased with increasing initial Mn concentration. This may be due to the saturation of the adsorption sites at lower Mn concentrations. The initial Mn concentration provides an important driving force to overcome all mass transfer resistance [2]. If the mass of zeolite in the suspension is equal to 1 g, 88.4% of the initial Mn²⁺ with a concentration of 5 mg/L by MOCZ is removed. For example, while the amount adsorbed was 0.01 mg/g at the initial Mn²⁺ concentration of 1 mg/L, it increased to 0.21 mg/g at the initial Mn²⁺ concentration of 5 mg/L. In other hand, the maximum removal percent by FOCZ at 4 mg/L is equal 76.75%. The results given in Figure 4 showed that the adsorption of Mn²⁺ has gradual increase with contact time until 15 min then the removal percent became constant (*i.e.*, equilibrium is attained). The adsorption rates are quite high towards the beginning of these experiments to 15 min and For contact times longer than 30 min there was no significant increase in the adsorption capacity for the two adsorbents investigated [15].

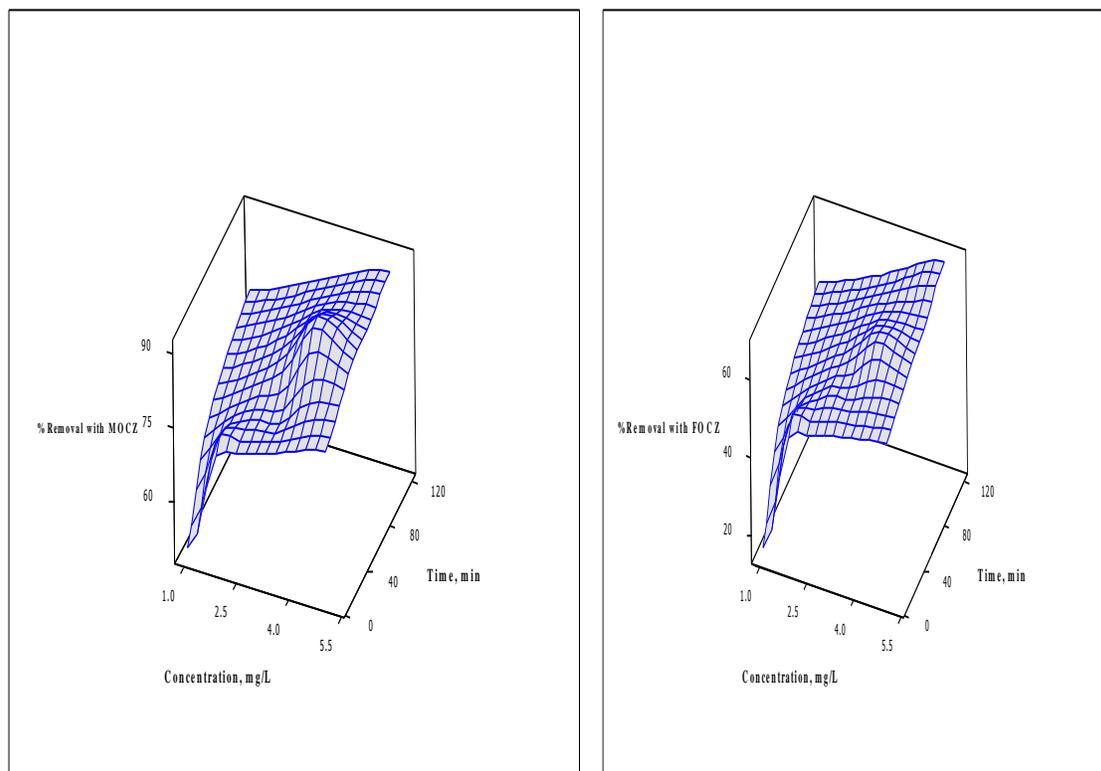


Figure 4. Experimental Mn Adsorption on MOCZ (left) and FOCZ (Right) at Various Concentration and Time

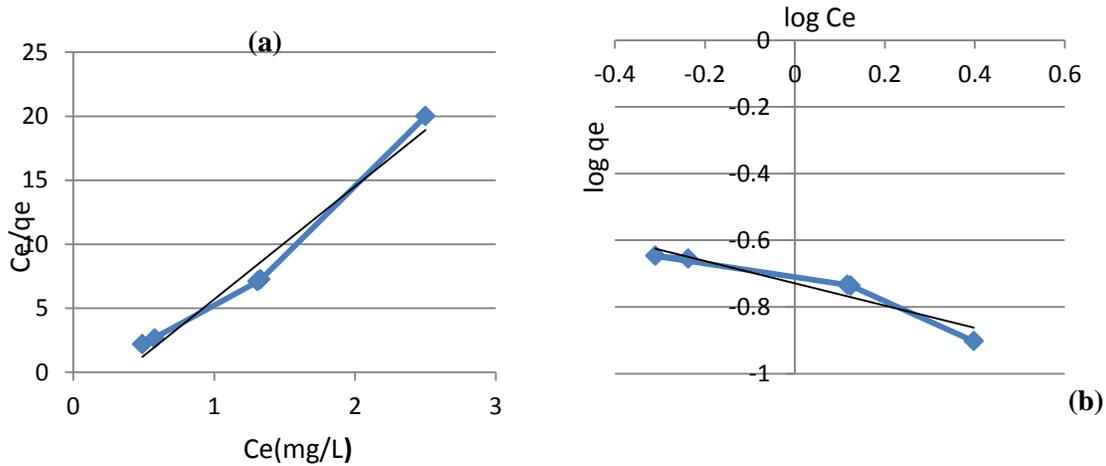
3.4. Adsorption Study

Figure 5 shows the Mn²⁺ adsorption isotherms with MOCZ and FOCZ. The adsorption performances associate with chemical features to the solute and the properties of the adsorbent [16]. The equilibrium adsorption data were best represented by the Langmuir

isotherm by two adsorbents, indicating monolayer adsorption on a homogenous surface and the adsorption capacity was found to be 0.21 mg/g at 20C°. The Langmuir equation is applicable to homogenous adsorption where adsorption process has equal activation energy, based on the following basic assumptions [17]: (i) molecules are adsorbed at a fixed number of well-defined localized sites; (ii) each site can hold one adsorbate molecule; (iii) all sites are energetically equivalent; (iv) there is no interaction between molecules adsorbed on neighboring sites. The Freundlich isotherm model is derived by assuming a non-ideal adsorption on heterogeneous surface with a multilayer adsorption [18]. The fitted result of Langmuir isotherm was presented in Fig. 5 and Table 2. The correlation coefficient ($R^2=0.97$) of Langmuir equation was high, using MOCZ as adsorbent, which suggested that the Langmuir isotherm model was suitable. The q_{max} parameter is related to the sorption capacity with respect to a specific solute, and in the case of Mn, the values obtained in this study are closed to those of literature [19-20]. It can be seen in Table2 that the sorption capacity (q_{max}) of Mn for MOCZ is almost three and three times bigger than FOCZ. In contrast, the Langmuir isotherm contains the heterogeneity factor (b) which is related to the affinity of the adsorbing surface. For the MOCZ amount of the b is equal 0.113 and higher than FOCZ as adsorbent (see Table 2).

Table 2. Absorption Parameters for Mn²⁺ Adsorption onto the MOCZ and FOCZ Zeolite

Adsorbent	Freundlich		Langmuir			
	R ²	n	k	R ²	b	Q(max)
MOCZ	0.89	2.99	-0.137	0.97	0.113	2.825
FOCZ	0.92	0.638	0.334	0.94	0.0051	0.004



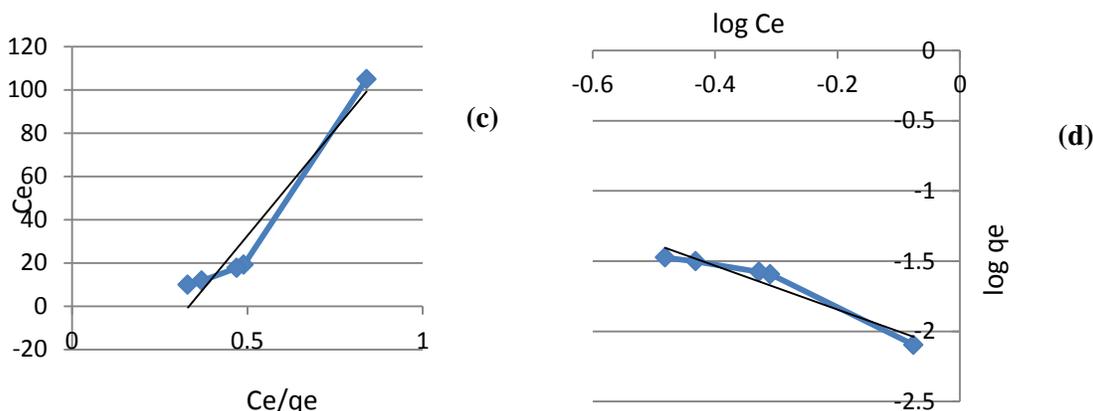


Figure 5. The Fitting of (a) Langmuir and (b) Freundlich Model for Adsorption of Mn^{2+} on MOCZ and (c) Langmuir and (d) Freundlich Model by FOCZ

Data presented in Table 2 shows that the sorption capacity obtained by MOCZ in this work for Mn^{2+} ions onto the optimal sorbent under study, is comparable with the sorption capacity of FOCZ. Thus, MOCZ has good sorption properties. In the same time, the cheaper sorbents like natural materials (i.e. Clinoptilolite) are use sorbents [5].

4. Conclusions

The adsorption of Mn^{2+} using MOCZ and FOCZ was investigated. The adsorption of Mn^{2+} was found to be dependent on the pH solution, initial Mn^{2+} concentration and contact time. The maximum removal of Mn was attained at pH 7, using Mn concentration of 5 mg/L by MOCZ. The equilibrium adsorption data were best represented by the Langmuir isotherm, indicating monolayer adsorption on a homogenous surface and the adsorption capacity was found to be 0.21 mg/g at $20C^{\circ}$. The observed Mn ion uptake is thought not only a simple ion-exchange process but also ion exchange, complex formation and surface adsorption mechanisms play important role in the whole adsorption process of Mn^{2+} . The chemical interaction may also play a role in the process. From a dimensionless equilibrium parameter (R_L) it is conclude that desorption is favorable. In addition, the adsorption process was controlled by physical mechanism rather than chemical mechanism.

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