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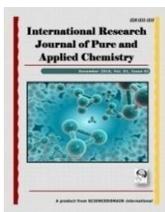


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Maize Stalks as a Cheap Biosorbent for Removal of Fe (II) from Aqueous Solution

Gamal O. El-Sayed^{1*}, Ragaa El-Sheikh² and Nora H. Farag³

¹Faculty of Science, Benha University, Benha, Egypt.

²Faculty of Science, Zagazig University, Zagazig, Egypt.

³Holding Company of Potable Water and Wastewater, Zagazig, Egypt.

Authors' contributions

This work was carried out in collaboration between all authors. Author GOES designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors RES and NHF managed the analyses of the study. Author NHF managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The evaluation of the ability of maize stalks to remove Fe(II) ions from aqueous solution was carried out. Different parameters affecting Fe(II) removal were investigated in batch experiments to optimize the removal method. These parameters include contact time, initial metal concentration, adsorbent dose, stirring rate, pH and temperature. Langmuir and Freundlich isotherm models were applied to the equilibrium data. The developed method showed high applicability to Langmuir isotherm model ($R^2=0.9806$) compared with Freundlich model ($R^2=0.8293$) for the adsorption of Fe(II) on maize stalks. Maximum saturated monolayer sorption capacity of maize stalks for Fe(II) was 5.14 mg/g. Adsorption process was performed at different temperatures to evaluate the thermodynamic parameters. The negative ΔG^0 values at various temperatures confirms that biosorption processes is spontaneous. The adsorption process was endothermic ($\Delta H^0 = 6.174$ KJ/mol) and the randomness at the adsorbent/solution interface increases during the sorption

*Corresponding author: Email: gamaloelsayed@yahoo.com;

process ($\Delta S^\circ = 22.622 \text{ J/mol k}$). The removal efficiency is a maximum at slightly acidic media. The proposed method could be applicable for removal of low concentrations of Fe(II) ions from aqueous solutions.

Keywords: Maize stalks; metal removal; iron; adsorption isotherms.

1. INTRODUCTION

Groundwater pollution can result from various sources ranging from natural or geochemical contamination to leaks in pipes and leachates from landfills. It can be divided into three main contamination categories: by microorganisms, organic compounds and by inorganic (mineral) pollutants. It can be divided into three main contamination categories, by organic compounds, by microorganisms, and inorganic pollutants. Some regions in Egypt suffer from the contamination of ground water with high concentration of iron and manganese, which threat human health and leading to chronic diseases. The most common sources of iron in groundwater are naturally occurring, for example from weathering of iron bearing minerals and rocks. Industrial effluent, acid-mine drainage, sewage and landfill leachate may also contribute iron to local groundwater. The contamination of ground water with metals or inorganic pollutants constitutes dangerous environmental problem due to the fact that metals are not biodegradable and can cause severe adverse effects on human health [1].

Biosorption is a fast and reversible reaction of the heavy metals with biomass. The by-products obtained from biomaterial production are a cheap source of biosorbents. Several agricultural waste materials have been studied and developed for the effective removal of heavy metals and some examples are: maize bran [2], coffee husks [3], rice straw [4], sugar peat pulp [5], olive pomace [6], apple wastes [7], palm kernel fibre [8], peanut hull [9], almond shell [10], hazelnut husks [11], oak sawdust [12] and grape stalks [13].

Maize is an economical crop in Egypt and is cultivated in vast areas of land within the country.

The aim of the present study is to examine the ability of maize stalks as cheap bio-adsorbent for removal of Fe(II) ions from aqueous solutions. The different factors affecting adsorption process were evaluated as time of contact, initial concentration of the metal, solution pH, temperature and adsorbent dosage.

Furthermore, equilibrium and thermodynamic studies on the adsorption of Fe(II) ions onto the maize stalks were also carried out for the design of adsorption process and to optimize the method. The advantage of using maize stalks as adsorbent is the ability of using the dry biomass after removal process in the manufacture of a cheap type of artificial wood by special treatment.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Solutions

Stock solution of divalent iron was prepared in bi-distilled water using the analytical reagent grade ferrous nitrate $\text{Fe}(\text{NO}_3)_2$. The initial metal concentration was 1000 mg/L. The concentrated solutions were kept in a refrigerator in order to avoid undesirable bacterial growth in the feed medium. The desired concentrations of metal ions were prepared by suitable dilution of stock solution using double-distilled water.

2.1.2 Biosorbent

Maize stalks were collected and used as sorbent for the biosorption of Fe(II). The maize stalks sample was collected from Sharqiya Governorate region of Egypt. Samples were washed several times using double-distilled water to remove extraneous and dust. They were then dried in an oven at 105 °C for 24 h. The dried biomass was chopped and filtered. The resulting powder was sieved to a particle size of 100 μm which was used for the adsorption studies. The chemical properties of the maize stalks were characterized by Fourier-transform infrared (FTIR) spectroscopy using a FTIR spectrometer (FTIR 2000, PerkinElmer) using a KBr disk containing 1% of finely ground sample by averaging in the range of 400–4000 cm^{-1} .

2.1.3 Adsorption studies

Batch adsorption experiments were carried out at room temperature ($25^\circ\text{C}\pm 1$). Exactly 50 ml of Fe (II) solution of different concentrations (10-50 mg/L) was put in different beakers and 0.1 g of

the adsorbent added to each of them and they were subsequently agitated at a stirring rate of 200 rpm with a magnetic stirrer for a period of 90 min. The pH values of the solutions were adjusted to the required value by adding either 1M HCl or 1M NaOH solution. After equilibrium, the final concentration (C_e) was measured spectrophotometrically [14] using absorbance values with Varian Cary 100 (UV-Vis) Spectrophotometer and the values compared with the standard (calibration curve). Experiments were carried out in duplicate and mean values are presented. The percentage removal of Fe(II) were calculated using the following relationship:

$$\%Metal\ Removal = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e are the initial and final (equilibrium) concentrations of the synthetic solution of ferrous solution (mg/L), respectively. Blanks containing only distilled water were used for each series of experiments as controls. The amount of the synthetic solution of Fe(II) adsorption per unit mass of maize stalks at equilibrium, q_e (mg/g) was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where V is the volume of the synthetic solution of ferrous solution (L) and W is the weight of maize stalks (g) added to volume V .

3. RESULTS AND DISCUSSION

3.1 FTIR Spectra of Biosorbent

In order to provide qualitative information of the characteristic functional groups exist in the maize stalks structure, the FTIR spectra was taken (Fig. 1). The vibration observed at 3423 cm^{-1} was assigned to the stretching vibration of $-\text{OH}$ group [15]. The peak at 2922 cm^{-1} corresponded to the stretching vibration of $-\text{CH}$ in saturated aliphatic hydrocarbons, while the peaks at 1728 cm^{-1} and 1634 cm^{-1} were attributed to the stretching vibrations of $\text{C}=\text{O}$ that may be attributed to the lignin aromatic groups [16]. The peak at 1046 cm^{-1} is due to the $\text{C}-\text{O}$ stretching vibration of the cellulose [16]. Finally, the peak at 824 cm^{-1} was assigned to the bending modes of aromatic compounds [16].

3.2 Determination of Point of Zero Charge (pH_{ZPC})

Point of zero charge of an adsorbent surface is the pH at which that surface has a net neutral charge. This value was evaluated by adding 0.1g of maize stalks to 50 mL of water with varying pH from 2 to 12.2 and stirred for 24 h. The initial pH was adjusted by adding either HCl or NaOH solutions and the final pH of the solution was plotted against the initial solution pH (Fig. 2). pH_{ZPC} for maize stalks is determined as pH 5.1.

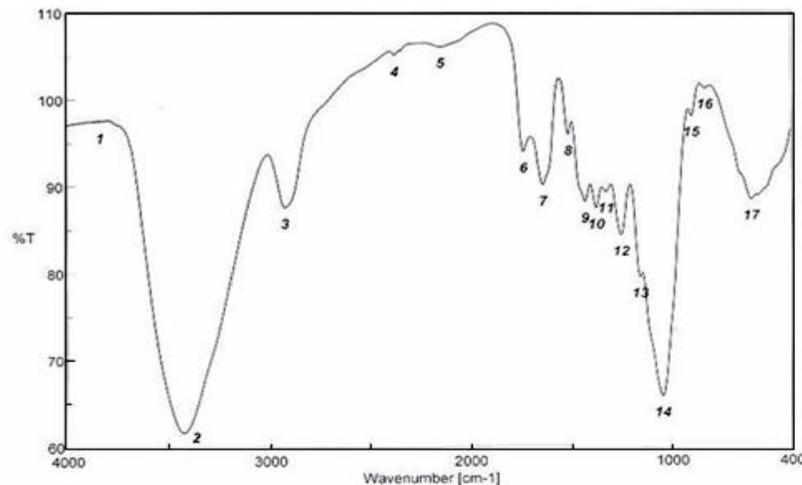


Fig. 1. FTIR spectra of maize stalks

3.3 Effect of contact time and metal ion concentration

The effect of contact time on the percentage removal of Fe (II) ion from the synthetic aqueous solution was investigated at different initial concentrations of Fe (II) (10-40 mg/L) and the plot is shown in Fig. 3. The adsorption equilibrium of iron onto maize stalks was completed within 75 min. The contact time required for the metal ions to reach the

equilibrium was relatively short which indicated the economical availability for the real practical applications. It is clear from Fig. 3 that the percentage removal decreases with increase in initial concentration of Fe (II) ion. The metal ion uptake were found to be 81.0%, 35.2%, 21.3%, and 13.1% for initial metal concentrations of 10, 20, 30, and 40 mg/L, respectively. This was due to the saturation of the adsorption sites of the adsorbent by the metal ion [17].

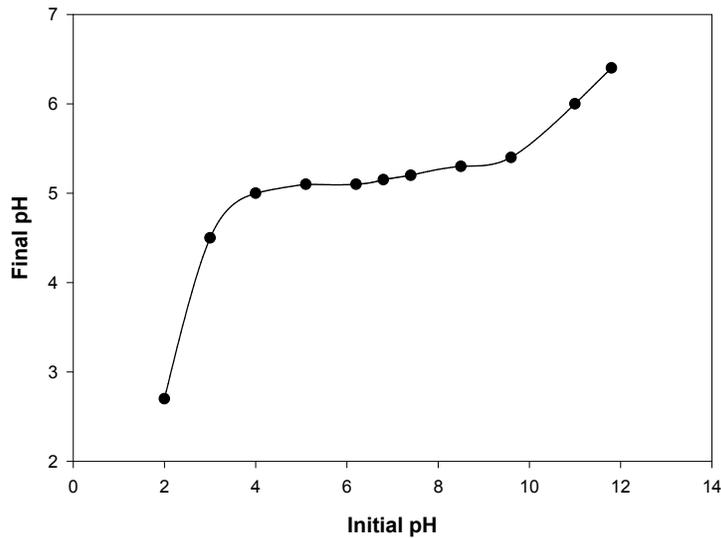


Fig. 2. Point of zero charge (pH_{ZPC}) of maize stalks used for the adsorption experiments

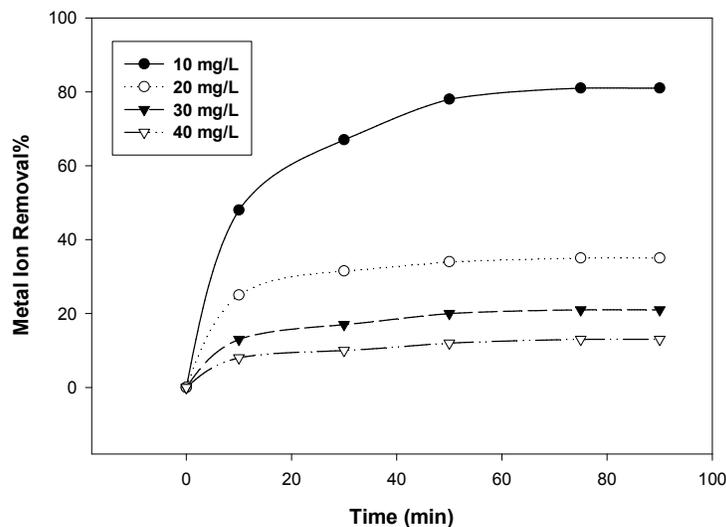


Fig. 3. Effect of contact time and initial metal concentration on the removal of Fe(II) by maize stalks [adsorbent dose = 2 g/L, pH = 5]

3.4 Effect of pH

The pH of the solution plays an important role in the adsorption capacity. The effect of initial pH of Fe(II) solution on the percentage removal was studied by varying the initial pH under constant process parameters (2 g/L of adsorbent at initial metal concentration 20 mg/L). The results are shown in Fig. 4. The metal adsorbed by maize stalks was higher at higher pHs. Maximum removal of Fe (about 22.5%) was achieved at pH 6. As the pH was decreased from 6 to 2.1, the removal percent decreased to 18.1%. This behavior can be explained on the basis of zero point charge for maize stalks which lie at around a pH 5.1. At lower pH values below this point of zero charge, the hydroxonium ions, H_3O^+ compete effectively with the Fe (II) cations, thus leading to a decrease in the percentage removal. At a slightly higher pH above this zero point charge, the surface of biomass gets negatively charged, which enhances the positively charged metal cations through electrostatic force of attraction [18].

3.5 Effect of Adsorbent Dose

The influence of adsorbent dosage on Fe (II) removal by maize stalks is presented in Fig. 5. The percentage of removal of Fe increased from 28.5% to 49% as the adsorbent dose was increased from 1 to 5 g/L. The increased removal at high dosages is expected, because of the increased adsorbent surface area and availability of more adsorption sites.

3.6 Effect of Stirring Speed

The effect of agitation speed on Fe (II) adsorption at the adsorbent dose of 2 g/L and initial iron concentration of 20 mg/L at a pH 5 is shown in Fig. 6. The increase of stirring speed causes a corresponding increase in metal ion removal. As a result of increasing the stirring speed, the diffusion rate of metal ions from the bulk liquid to the liquid boundary layer surrounding particles became higher because of an enhancement of turbulence and a decrease of the thickness of the liquid boundary layer. Under these conditions, the value of the external diffusion coefficient became higher [19].

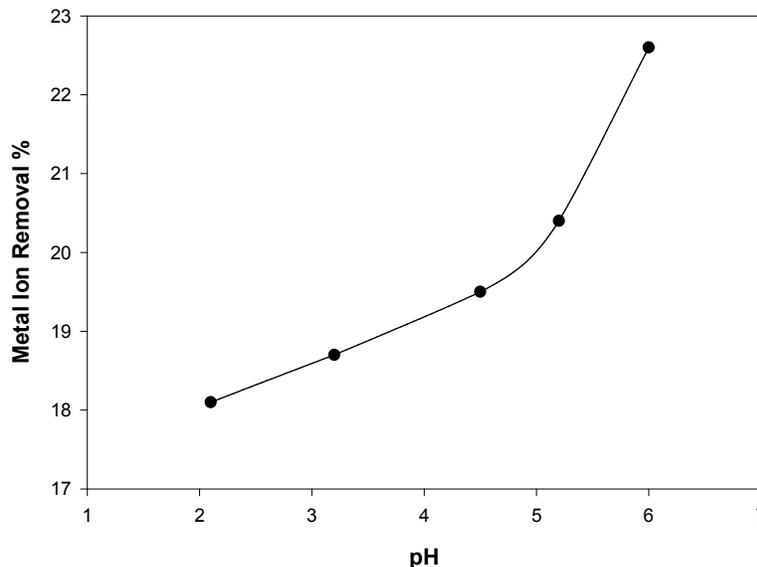


Fig. 4. Effect of initial pH on the removal of Fe (II) by maize stalks [adsorbent dose = 2 g/L, initial metal concentration = 20 mg/L]

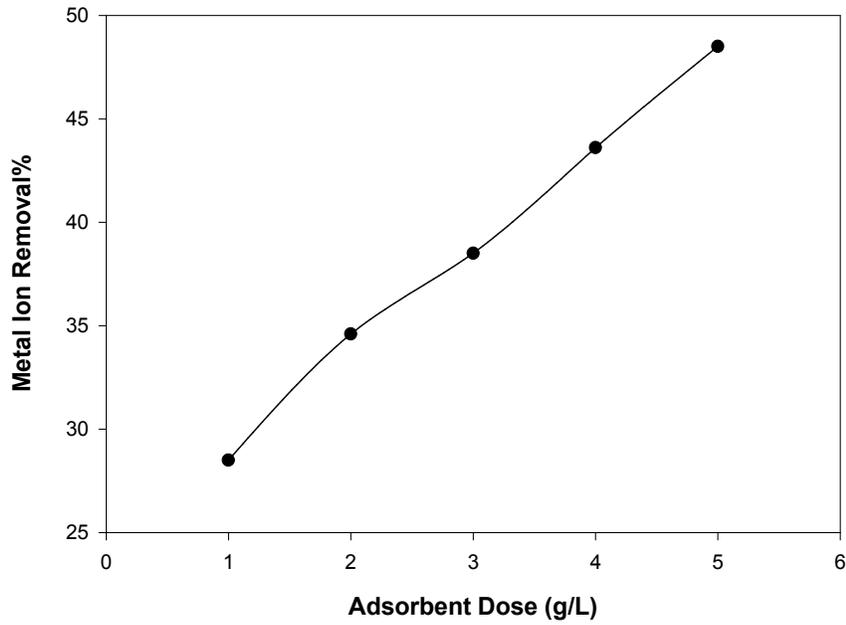


Fig. 5. Effect of adsorbent dose on the removal of Fe (II) by maize stalks [metal concentration = 20 mg/L, pH = 5]

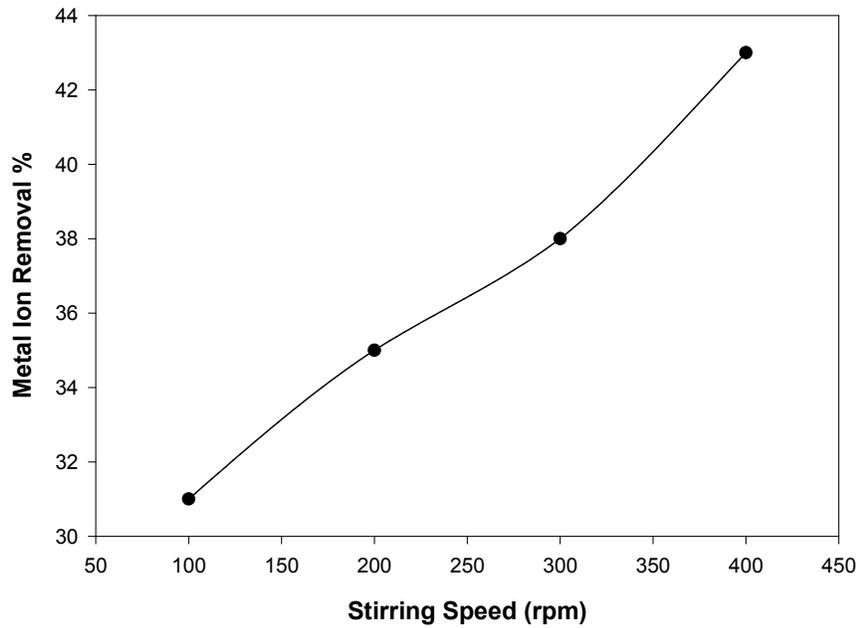


Fig. 6. Effect of stirring speed on the removal of Fe(II) by maize stalks [adsorbent dose = 2 g/L, metal concentration = 20 mg/L, pH = 5]

3.7 Effect of Temperature and Thermodynamic Parameters

Experiments were performed at different temperatures (23, 33, 43 and 53 °C) while keeping the other conditions constant. The percentage of adsorption increased from 19.1 to 23.2 with the increase of temperature from 23 to 53°C at concentration 20 mg/L and pH 5, as indicated from Fig. 7. Therefore, higher temperature facilitated the adsorption of Fe(II) on maize stalks (i.e. endothermic process). This may be a result of increasing the mobility of the metal ion with increasing temperature [20]. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the biosorbent enabling more Fe(II) ions to penetrate further [21]. In order to evaluate the thermodynamic feasibility of the adsorption process and to confirm its nature, thermodynamic parameters such as change in Gibbs free energy (ΔG^0 : kJ/mol), enthalpy (ΔH^0 : kJ/mol) and entropy (ΔS^0 : kJ/mol K) were determined using the following equations [22]:

$$K_c = C_A / C_S \quad (3)$$

$$\ln K_c = \left(\frac{\Delta S^0}{R} \right) - \left(\frac{\Delta H^0}{RT} \right) \quad (4)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

where R (8.314 J/mol K), T (K), C_A , C_S and K_c (L/g) are the gas constant, the absolute temperature, the amount of Fe(II) adsorbed on the adsorbent of the solution at equilibrium (mol/L), the equilibrium concentration of the metal ion in the solution (mol/L) and the standard thermodynamic equilibrium constant, respectively. By plotting a graph of $\ln K_c$ versus $1/T$ ($R^2 = 0.9227$), the values ΔH^0 and ΔS^0 can be estimated from the slopes and intercepts, respectively (Fig. 8).

The data in Table 1 shows the negative values of ΔG^0 and positive ΔH^0 and ΔS^0 . The change in free energy for physisorption and chemisorption are between -20 and 0 kJ/mol and -80 to -400 kJ/mol, respectively. The values of ΔG^0 are within the range of -20 and 0 kJ/mol indicating that the mechanism of the adsorption process was by physisorption [23]. The positive value of ΔH^0 indicates the presence of an energy barrier in the adsorption process and further reveal an endothermic process [24]. The positive value of ΔS^0 suggests an increase in randomness at the solid/solution interface.

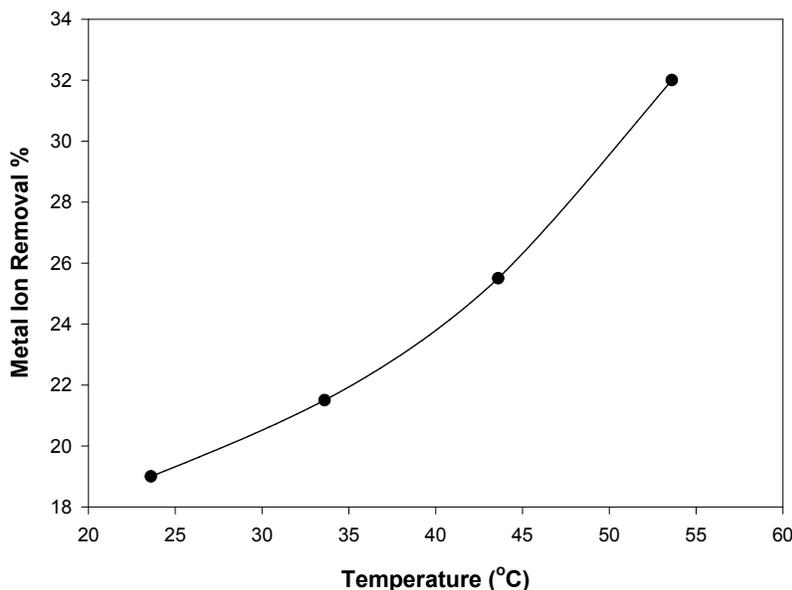


Fig. 7. Effect of temperature on the removal of Fe(II) by maize stalks [adsorbent dose = 2 g/L, metal concentration = 20 mg/L, pH = 5]

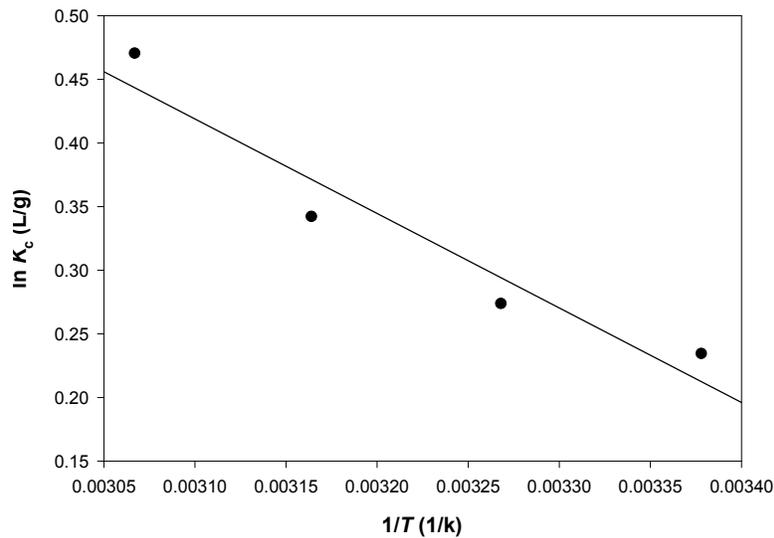


Fig. 8. Plots $\ln k_c$ versus $1/T$ for adsorption of Fe(II) on maize stalks

Table 1. Thermodynamic parameters of Fe(II) adsorption on maize stalks

Temperature (T)	Thermodynamic Parameters		
	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)
296	-0.522	6.174	22.622
306	-0.748		
316	-0.974		
326	-1.200		

The data in Table 1 shows negative values of ΔG^0 and positive values of ΔH^0 and ΔS^0 .

3.8 Adsorption Isotherms

Adsorption isotherms describe how adsorbates interact with adsorbents. For this reason, two isotherm models were applied to this adsorption study. The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface where all sorption sites are identical. The theory assumes the uniform energies of adsorption onto the adsorbent surface. The linear form of Langmuir isotherm equation is given as follows [25]:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (6)$$

where q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium, C_e (mg/L) is the final concentration at equilibrium, q_m (mg/g) is the maximum adsorption at monolayer coverage and b (L/mg) is the constant related to the extent of adsorption. The plots of specific adsorption (C_e/q_e) versus equilibrium concentration (C_e) at

different temperatures are shown in Fig. 9 and the related parameters are listed in Table 2. Due to the high correlation coefficient obtained from Langmuir plot, the Langmuir model might be suitable for the interpretation of the adsorption data. The essential features of Langmuir can be expressed in terms of dimensionless constant called separation factor or equilibrium parameter (R_L) which is calculated using the following equation [26]:

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

where C_0 (mg/L) is the initial concentration of the adsorbate. The values of R_L indicate the shapes of isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$). In the present investigation the equilibrium parameter (Table 2) was found to be in the range $0 < R_L < 1$ (between 0.053-0.183) indicating that the adsorption process was favorable and the Langmuir isotherm was applicable ($R^2 = 0.9806$).

The Freundlich isotherm assuming that the adsorption process takes place on heterogeneous surfaces and the adsorption capacity is related to the concentration of the adsorbent. The Freundlich model is based on the following expression [27]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

By plotting $\ln q_e$ vs $\ln C_e$ (Fig. 10), the values of n and K_F could be evaluated from the slope and

intercept, respectively. The data obtained from this plot are shown in Table 2.

By comparing the correlation coefficients (R^2) obtained from the two isotherms plots (Table 2), it can be concluded that Langmuir model can be applied successfully to the adsorption of Fe(II) on maize stalks more than Freundlich model.

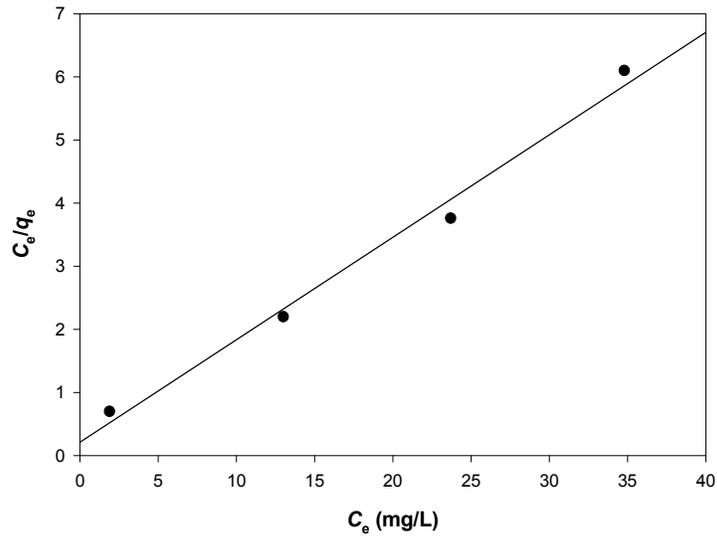


Fig. 9. Langmuir plot for adsorption of Fe(II) on maize stalks

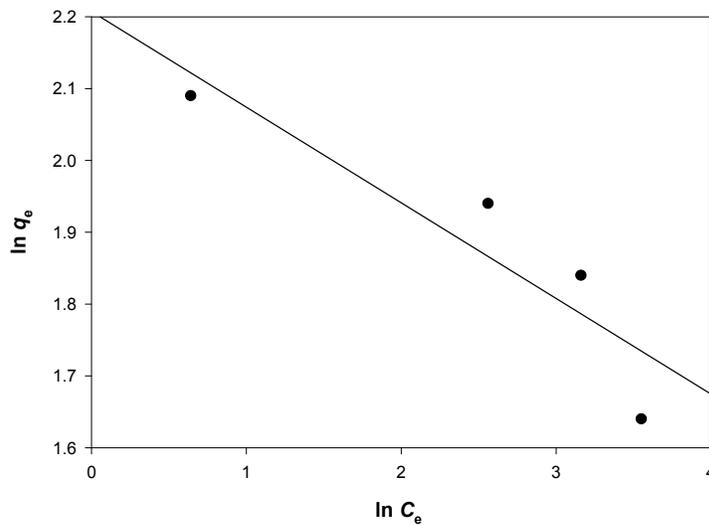


Fig. 10. Freundlich plot for adsorption of Fe(II) on maize stalks

Table 2. Langmuir and Freundlich isotherms parameters for adsorption of Fe(II) on maize stalks

Langmuir isotherm			Freundlich isotherm			
q_m (mg/g)	B (L/mg)	R_L (L/mg)	R^2	K_F	n	R^2
5.14	0.446	0.053-0.183	0.9806	9.097	-7.507	0.8293

4. CONCLUSION

The biosorption of Fe(II) on maize stalks was investigated. It was found that the adsorption process is dependent on metal initial concentrations and pH of the metal solution and temperature. The equilibrium adsorption was attained in less than 90 min. The results indicate that the optimum pH for maximum removal of Fe (II) ion is 6.0. The adsorption process was found to be endothermic. Langmuir adsorption model can be applied successfully to the adsorption of Fe(II) ions compared to Freundlich. The adsorption capacity corresponding to monolayer coverage is 5.14 mg/g according to Langmuir model. Maize stalks which are an agricultural waste material can be used for industrial water treatment to eliminate low concentrations of ferrous ions.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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