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The performance of Defatted Jojoba Seeds for the removal of toxic high concentration of the aqueous ferric ion

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ABSTRACT

This study has focused on the performance of Defatted Jojoba Seeds (DJS) for the removal of ferric (Fe^{3+}) ion from the aquatic systems using a batch operation system. Equilibrium of sorption has been implemented through the influence of ferric ion initial concentration, the dosage amount of DJS, and temperature. The maximum removal of ferric ion was 96% (approx.) by using a high-level concentration of ferric ion ($400\,\mathrm{mg\,L^{-1}}$) and high dosage amount of DJS ($60\,\mathrm{g\,L^{-1}}$). Freundlich model has successfully analyzed the equilibrium of isotherms with $R^2 = 1$. Negative thermodynamic parameter ΔG ($= -12.954\,\mathrm{kJ\,mol^{-1}}$) indicates to the spontaneous process. Adsorption reaction kinetic models, such as pseudo-first-order and pseudo-second-order, and adsorption diffusion model, such as Weber-Morris intra-particle diffusion model, have been used to describe the adsorption rate and mechanism of the ferric ion onto the DJS surface. Adsorption of ferric ion on the DJS has achieved Lagergren pseudo-second-order model ($R^2 = 1.0$ approx.) more than Lagergren pseudo-first-order model. The kinetic parameters, rate constant, and sorption capacities have been calculated.

Keywords: Ferric; Jojoba; Dynamic isotherm; Freundlich isotherm; Pseudo-second-order

1. Introduction

The removal of toxic heavy metals from water is considered as an environmental priority, especially in poorer countries with limited water resources. Water is used in many industrial processes such as in the manufacture of steel goods. As a result, the quantities of industrial and wastewater contain iron ions as a by-product. In terms of chemistry, iron ion presents in water in the form of ferric (Fe^{3+}) or ferrous (Fe^{2+}) ion; and this depends on the pH and dissolves oxygen concentration. In most of the surface water, ferric ion form predominates. Although the iron in the water is

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essential for life, it becomes toxic at high levels of concentrations and it may cause serious problems to both the environment and human health [1–3]. One of the primary concerns for the presence of iron ion in drinking water is its objectionable taste. Furthermore, the presence of iron ion in a large aqueous concentration causes anorexia, oliguria, diarrhea, hypothermia, dysphasic shock, and metabolic acidosis [3]. As we can see, that's why we find the newly scientific research that focused on the removal of heavy metals from aquatic systems, especially iron ion.

A wide range of biological, chemical, and physical processes are available in the removal of heavy metal ions, which exists with unhealthy levels in aquatic systems, especially for human drinking water. For example, chemical precipitation, ion exchange and solvent extraction, ultra-filtration, reverse osmosis, and biosorption through microorganisms of bacteria are among the common processes in this field [4–10]. It is known that the use of conventional methods for removing heavy metals from aquatic or sewage systems often considered as expensive [11,12]. Therefore, the search is always underway to find a low-cost process to use, for example, the adsorption process.

Currently, adsorption process is considered as one of the most efficient methods for the removal of heavy metals from aquatic and sewage systems [13,14]. In many cases, activated carbon has been widely used as a good adsorbent. But the usage of the activated carbon remains expensive adsorbents, especially in developing countries. The removal of ferric ion and heavy metals from the aquatic systems using different low-cost adsorbents was studied by many researchers. For example, granular activated carbon and activated tea waste [15–19], pulp and paper industrial waste [20], thioglycolic acid-modified oil palm [21], wild cocoyam biomass [22], coconut husk [23], chitosan-coated oil palm shell charcoal [24], lignite [25], chitosan [26], Bengal gram husk powder [27], zeolite [28], activated carbon [29–31], olive cake [1], quartz, and bentonite [32] were utilized to remove iron ion and other heavy metals from the aquatic systems.

Jojoba [Simmondsia Chinensis or Simmondsia californica Nutt] is a plant that can grow in semi-arid areas. This evergreen dessert shrub is native to arid hills of Arizona, southern California, and adjacent parts of Mexico. Jojoba yields a crop of seeds that contain 50% oil [33]. Oil content can be isolated through the use of cold-pressing process leaving a huge quantity of industrial residues of Jojoba (defatted Jojoba). This residue could convert into raw low-cost materials and locally available adsorbents, which can be used as an adsorbent to remove ferric ion from the aquatic system. Residual Jojoba has low fat content and high protein content [34]. Fat can be removed from the residues by washing jojoba seeds in *n*-Hexan. This process leaves abundant proteins and cellulose. Furthermore, it increases the cellulosic pore concentrations and then increases the surface active sites in Defatted Jojoba Seeds (DJS) adsorbent. Wherein, the adsorbent includes –OH, $-COO^-$, –CN, and $-NH_2$ functional groups that can take part in heavy metal ion binding.

Studies on Jojoba residue as an adsorbent for heavy metal are very limited. Only one recent research investigated by using the Jojoba residue as an adsorbent for cadmium removal [33]. In particular, iron ion could be adsorbed by DJS using two suggesting sorption mechanism: (i) physi-absorption of ferric ion in the cellulosic pores, and (ii) chemi-sorptions of ferric ion in the –OH, $-COO^-$, –CN, and $-NH_2$ functional groups of the DJS adsorbent. To the best of our knowledge, no study has been reported to remove the ferric ion from aquatic systems using DJS. The main objective of this study is to use the DJS as a low-cost adsorbent to remove the ferric ion from a solution model of polluted aquatic systems. Since the performance of any biosorbent depends on the characteristics of biomass and the microenvironment of the target iron solution, the effects of different physical–chemical parameters on the adsorption process by DJS were investigated. These parameters included a dose of adsorbent, initial concentration of ferric ion in the solution, temperature, and time of exposure. The sorption process is modeled by thermodynamic (e.g. Langmuir and Freundlich) and kinetic (pseudo-first-order and pseudo-second-order) models.

2. Materials and methods

2.1. Jojoba preparation

The residue of Jojoba seeds (DJS) used in this study was taken from Jordan University of Science and Technology (Jordan). Jojoba oil was extracted from the seeds using Soxhelt extractor and n-hexane as a solvent. Details of the extraction method and chemical characterization of Jojoba seeds were also previously reported [33,34]. The dried DJS was crushed and sieved to 0.425 mm mesh size.

2.2. Reagents

All chemicals were used as analytical grade. The metal salt of $Fe(NO_3)_{3.}6H_2O$ was purchased by commercial providers from Fluka Chemika. Others, such as NaOH, HNO_3, and HCl, were purchased from Merck. Stock solution ($1,000\,mg\,L^{-1}$) of ferric ion was prepared by dissolving exact amount of metal salt (±0.01 g) in

1,000 mL ultrapure deionised water (18 Ω cm). The standard model solutions of 50–400 mg L^{-1} were prepared by appropriate dilution. The initial pH of the solution was adjusted using 1% HNO_3 for all experiment to run.

2.3. Apparatus and instruments

Atomic Absorption Spectrophotometer, AAS, (Model AA 100, Perkin-Elmer) was used to analyze the iron ion concentration in aqueous solution. The pH of all the solutions was recorded by pH meter (Oiron 520). The temperature was controled using a temperature controler (Gefellschaft Funn 1003, ±0.1°C). Isothermal shaker was also used (Gefellschaft Fur 978). Analytical balance is used with ± 0.0001 mg (Sartorius, CP324-S/ management system certified according to ISO 9001).

2.4. Equilibrium studies

The removal amount of ferric ion was calculated from the mass balance, which was stated as the amount of ferric ions adsorbed onto the DJS. It is equal to the amount of ferric ion that removed from the aqueous solution. Mathematically, it can be expressed by Eqs. (1) and (2) [35]:

$$q_e = \frac{(C_i - C_e)}{S} \tag{1}$$

$$q_t = \frac{(C_i - C_t)}{S} \tag{2}$$

where q_e is ferric ion amount adsorbed on DJS surface at equilibrium (mg g^{-1}); q_t is ferric ion amount adsorbed on DJS surface at a specific time (mg g^{-1}); C_i is initial concentration of ferric ion in the aqueous solution (mg L^{-1}); C_e is Equilibrium concentration or final concentration of ferric ion in the aqueous solution (mg L^{-1}); and C_t is the final concentration of ferric ion in the aqueous solution (mg L^{-1}) at a specific time.

The dosage (slurry), S, concentration of DJS is expressed by Eq. (3):

$$S = \frac{m}{v} \tag{3}$$

where v is the initial volume of ferric ion solution used (L) and m is the mass of DJS adsorbent.

The percent adsorption (%) and the distribution coefficient (K_d) are calculated by using Eq. (4):

$$\%\ \text{adsorption} = \frac{C_i - C_e}{C_i} \times 100\% \tag{4}$$

The simplest and most common method of estimating contaminant retardation is based on the distribution coefficient, K_d. The K_d parameter is a factor related to the partitioning of a contaminant (Fe^{3+}) between the solid (DJS) and aqueous phases. The distribution coefficient, K_d, is defined as the ratio of the quantity of the ferric ion adsorbed per mass of DJS to the amount of the ferric ion remaining in the solution at equilibrium. For the reaction:

$$\mathrm{Fe^{3+} + X - DJS \rightarrow Fe^{3+} \leftarrow X - DJS}$$

$$\mathrm{X = COO^-,\ CN\ and\ NH_2}$$

The mass action expression for K_d is calculated by using Eq. (5):

$$K_d = \frac{\text{Amount of ferricion in DJS}}{\text{Amount of ferricion in solution}} \times \frac{1}{S}\ (\text{ml/g}) \tag{5}$$

The percent adsorption and K_d (L g^{-1}) can be correlated by Eq. (6) [36]:

$$\%\ \text{adsorption} = \frac{100K_d}{K_d + 1/S} \tag{6}$$

2.5. Effect of dosage

Adsorption measurements were made by a batch technique at a temperature of 30°C (±1°C). Different doses of DJS (10, 20, 30, 40, 50, and 60 g L^{-1}) were used. The initial concentration of ferric ion was C_i = 400 mg L^{-1}. The solutions were shaken vigorously using thermostatic mechanical shaker for 2 h. The agitation speed (300 rpm) was kept constant for each run to ensure equal mixing. At the end of the equilibrium, the flasks were removed from the shaker and then the solution was filtered using filter paper (Whatman No. 41). The filtrate samples were analyzed. All reported results were the average of triplicate measurements.

2.6. Effect of ferric ion concentration

Adsorption measurements were made by a batch technique at a temperature of 30°C (± 1°C). The stopper plastic flasks containing 50 mL of different initial concentrations (C_i = 50, 200, 300, and 400 mg L^{-1}) of ferric ion and 10 g L^{-1} of DJS were shaken vigorously using thermostatic mechanical shaker for 2 h. The agitation speed (300 rpm) was kept constant for each run. At the end of the equilibrium time, the flasks were removed from the shaker and then DJS was filtered using filter paper (Whatman No. 41). The filtrate samples were analyzed. All the reported results were the average of triplicate measurements. Afterwards, the experiments of the isotherms were conducted.

2.7. Effect of the temperature

The adsorption experiments were carried out by shaking vigorously the stopper plastic flasks containing 50 mL of 400 mg L^{-1} of ferric ion and 60 g L^{-1} of DJS using thermostatic mechanical shaker at constant contact time (2 h) and agitation speed (300 rpm) with varying temperatures (20, 30, and 40°C). At the end of the equilibrium time, the flasks were removed from the shaker and then DJS was filtered using filter paper (Whatman No. 41). The filtrate samples were analyzed. All the reported results were the average of triplicate measurements.

2.8. Effect of contact time

Adsorption measurements were made by a batch technique at a temperature of 30°C (± 1°C). The stopper plastic flasks containing 50 mL of initial concentrations ($C_i = 400$ mg L^{-1}) of ferric ion and 60 g L^{-1} of DJS were shaken vigorously using thermostatic mechanical shaker (300 rpm) for a known period in the interval of 5 to 120 min with increment of 10 min from 10 to 60 min then 30 min from 60 to 120 min, and then 60 min from 120 min to 180 min. At the end of the predetermined interval, the flasks were removed from the shaker and then DJS was filtered using filter paper (Whatman No. 41). The filtrate samples were analyzed. All the reported results were the average of triplicate measurements. Afterwards, the experiments of the kinetic models were conducted.

3. Results and discussions

3.1. Dosage effects

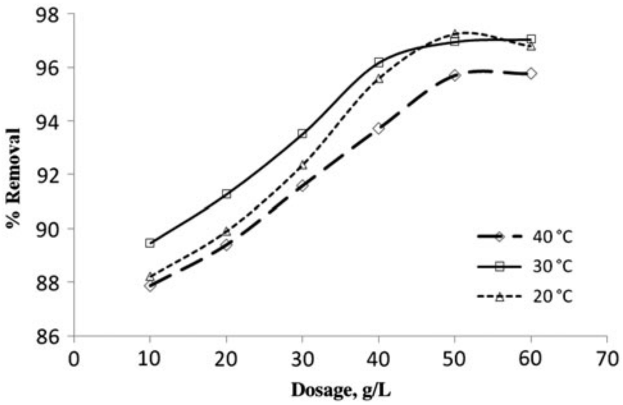

Fig. 1. The effect of DJS adsorbent dosage (10, 20, 30, 40, 50 and 60 g L^{-1}) on the removal of ferric ion from the high-level aqueous solution at constant contact time (2 h), temperature (20, 30, and 40°C), agitation speed (300 rpm), $C_i = 400$ mg L^{-1}.

Fig. 1 shows the removal percentage of ferric ion from the aqueous solution using different doses of DJS (10, 20, 30, 40, 50, and 60 g L^{-1}). This removal experiments were applied using three temperature values ($T = 20$, 30, and 40°C). The percentage removal increases by increasing the DJS doses. It has been observed that the maximum removal of ferric ion can be achieved using 60 g L^{-1} of the DJS doses at 30°C. This is because of an increase in the number of active sites, chemical functional group in the DJS adsorbent which enhances the removal of ferric ion. This was taken as the highest removal rate as function of temperature for removing aqueous ferric ion. At a temperature of 30°C, it was observed that the removal percentage was 88% using 10 mg L^{-1} of DJS, while it was 96% using 60 mg L^{-1}. This can be explained by the fact that more mass available, i.e. the more contact active sites offered to the adsorption. These results are qualitatively in a good agreement with the similar reported studies [1,2,28,32,37].

The effect of varying the dosage of the adsorbent on the distribution coefficient, K_d is shown in Fig. 2.

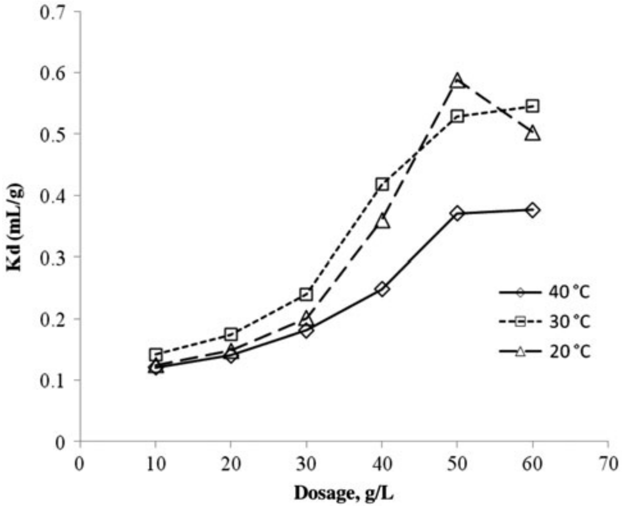

Fig. 2. The effect of DJS adsorbent dosage (10, 20, 30, 40, 50, and 60 g L^{-1}) on the distribution coefficient of ferric ion from the high-level aqueous solution ($C_i = 400$ mg L^{-1}) at constant contact time (3 h), temperature (20, 30, and 40°C), agitation speed (300 rpm).

The K_d values increase with the increasing dosage concentration over the three temperature values (20, 30, and 40˚C). The maximum K_d value was 0.0975 L g^{-1} at 20˚C using 50 mg L^{-1}of the DJS doses. Higher values of K_d indicates that the DJS has high sorption capacity for adsorbing ferric ion. While, low K_d indicates that most of the metal ions remain in solution where they are available for transporting. Thus, we can conclude that higher amounts of DJS are preferred for adsorbing more numbers of ferric ions.

3.2. *Effect of initial ferric ion concentration*

Actually, the variation of the removal percentage of heavy metal ions through changing the initial heavy metal concentration does not show in regular trends. In this study, the removal percentage using the doses of DJS vs. different concentrations of ferric ion (50, 100, 200, 300, and 400 mg L^{-1}) is shown in Fig. 3. We have noticed that the removal percentage increases by increasing the initial ferric ion concentration. This could be an indication for a weak interaction between ferric ion and DJS adsorbent. This means that the high concentration of ferric ions will create and activate some new activation sites on the DJS adsorbent surface. Furthermore, this behavior is connected with the noncompetitive diffusion process of the ferric ions through the microchannel and pores in DJS. This could guide us for the presence of large size of pore inlets on the adsorbent surface. This could allow more number of ferric ions to pass deeply inside the DJS adsorbent.

This result does not compatible with those results founded in the literatures through the use of natural zeolite [28], olive cake [1], bentonite [32], chitosan [38], and chitin [2]. But, it is compatible with other studies concerning the adsorption of the cationic methylene blue dyes on DJS [39] as well as the adsorption of ferric ion on the natural quartz [32].

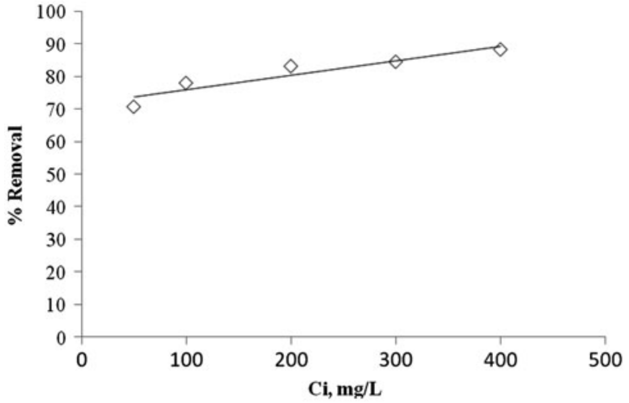

Fig. 3. The effect of initial concentration namely 50, 200, 300, and 400 mg L^{-1} of ferric ion at constant contact time (3 h), adsorbent dosage 60 g L^{-1} of natural DJS, temperature (30˚C), and agitation speed (300 rpm).

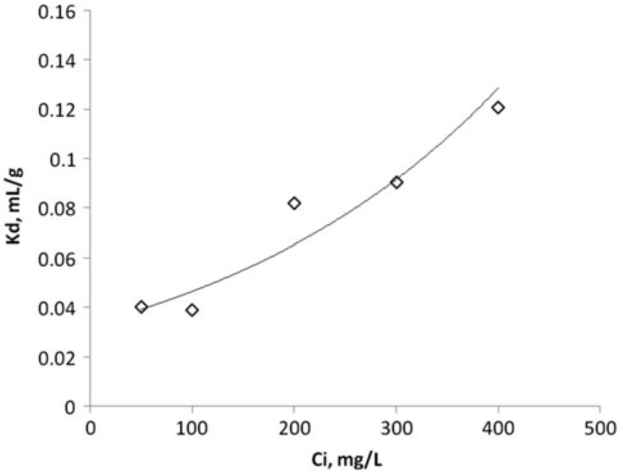

Fig. 4. Variation of ferric ion on DJS as a function of initial concentration: dosage = 60 g L^{-1}, t = 3 h, and T = 30˚C.

Fig. 4 illustrates K_d as a function of ferric ion concentrations. The K_d values increase with increasing concentration of ferric ion. This result indicates that energetically high favorable active sites, chemical functional group, become involved with increasing metal concentrations in the aqueous solution.

3.3. *Effect of temperature*

Fig. 5 indicates the temperature effect for the removal of aqueous ferric ion using DJS. There has been a slight change in the percentage removal of

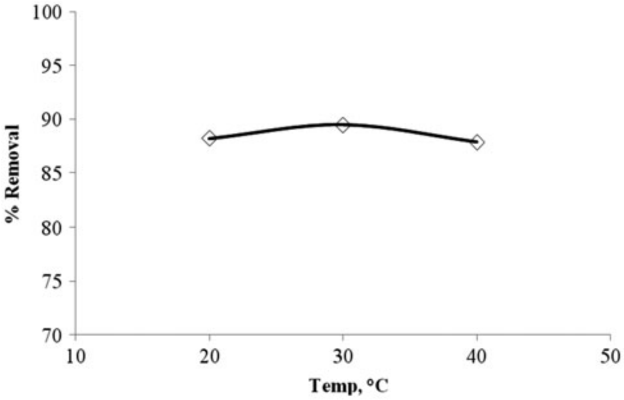

Fig. 5. The effect of temperature between 20 to 40˚C for the removal of Fe^{3+} ions from the aqueous solution at constant initial concentration (400 mg L^{-1}), contact time (3 h), adsorbent dosage 60 g L^{-1} of natural Jojoba (DJS), and agitation speed (300 rpm).

ferric ion by increasing the temperature values in this study. This study has achieved the maximum removal of ferric ion at a temperature of 30℃ reaching 90%. While, this percentage was 88% at a temperature value of 20 or 40℃. This behavior may be due to the following interpretations: (i) the higher temperatures do not activate the ferric ion for enhancing the adsorption on the active sites in the DJS adsorbent [40–42]; (ii) high temperatures do not accelerate the slow step of chemisorption mechanisms and do not create some new activation sites in the DJS surface [43,44]. This result is in a good agreement with our study regarding the adsorption of the cationic methylene blue dyes on DJS [39] as well as the adsorption of ferric ion on the natural quartz [32].

3.4. Isotherms models

In this study, the experimental data for the isotherm set are fitted by using Langmuir and Freundlich isotherms, which are the most common isotherms describing the equilibrium of adsorption. The Langmuir isotherm is based on the theoretical principle that only a single adsorption layer exists on an adsorbent. It represents the equilibrium distribution of metal ions between the solid and liquid phases. The basic assumption of the Langmuir adsorption process is the formation of a monolayer from the adsorbate (Fe^{3+}) on the outer surface of the adsorbent (DJS), and afterward no further adsorption takes place. The Langmuir isotherm for pure component adsorption is described in Eq. (7) [45]:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{1}{q_{\max}} C_e \tag{7}$$

where $q_{\max}$ is the maximum removal of the ferric ion per unit mass of the DJS adsorbent (mg g^{-1}), which relates to the adsorption capacity of DJS. The b is Langmuir constant (L mol^{-1}), which is exponentially proportional to the heat of adsorption. It relates to the adsorption intensity, which indicates to the interaction forces between DJS surface. Therefore, a plot of C_e/q_e vs. C_e gives a straight line of slope $1/q_{\max}$ and intercept $1/(q_{\max} b)$ as shown in Fig. 6.

The Freundlich adsorption isotherm assumes an exponentially decaying function of site density with respect to the heat of adsorption. The Freundlich isotherm is expressed as in Eq. (8) [46]:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{8}$$

The Freundlich isotherm is an indicator of the heterogeneity extent of the adsorbent surface. The Freundlich constants K_f and n indicate the adsorption capacity and the adsorption intensity, respectively. Wherein, they have been calculated by the intercept and slope of the $\ln q_e$ vs. $\ln C_e$ plot as shown in Fig. 7.

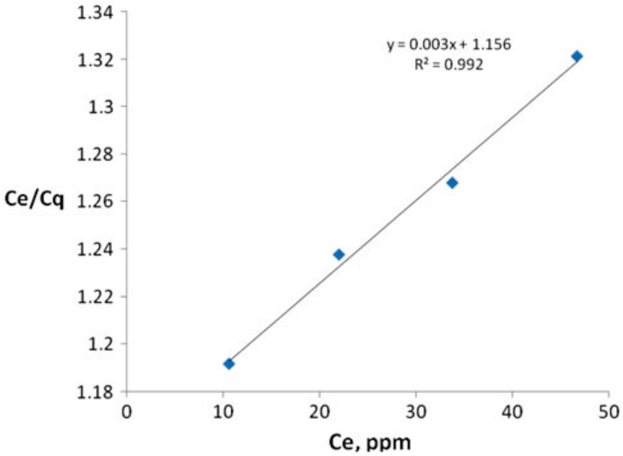

Fig. 6. The linearized Langmuir adsorption isotherms for the ferric ion on the DJS at a temperature 30℃, (initial concentration: 400 mg L^{-1}, 300 rpm, and contact time: 3 h).

The calculated results of the Langmuir isotherm constants are present in Table 1. The maximum removal of the ferric ion per unit mass of the DJS ($q_{\max}$) is 333.33 mg g^{-1}. The calculated b value is equal to 0.0026 L mg^{-1}, which is consistent with the higher ionic potential of the ferric ion [31].

The R^2 values that were obtained from both Langmuir and Freundlich models were above 0.99, indicating a very good agreement with the data. The experimental data for the isotherm set were well described by Freundlich isotherms. This is due to the higher value of the correlation regression coefficient

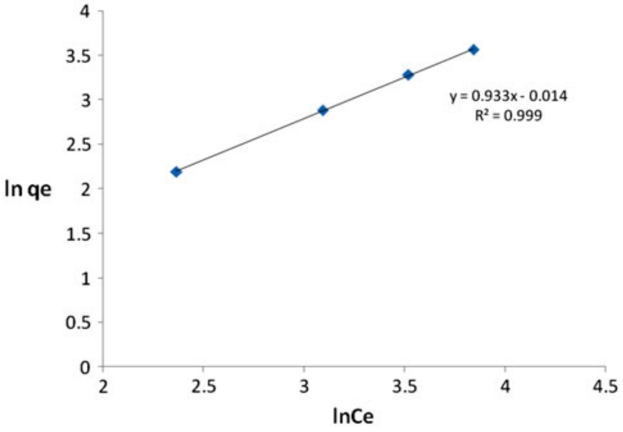

Fig. 7. The linearized Freundlich adsorption isotherms for ferric ion adsorption by DJS at constant temperature 30℃. (C_i: 400 ppm, 1% HNO_3 aqueous solution, 300 rpm, contacts time: 3 h).

Table 1
Langmuir and Freundlich parameters

	T/℃	$q_{\max}$ ($\mathrm{mg\,g^{-1}}$)	b ($\mathrm{L\,mg^{-1}}$)	R^2	ΔG° ($\mathrm{kJ\,mol^{-1}}$)	K ($\mathrm{L\,mol^{-1}}$)
Langmuir	30	333.33	0.0026	0.992	−12.954	145.197
	T/℃	n	K_f	R^2		
Freundlich	30	1.0718	0.986	0.995		

from the Freundlich model ($R^2 = 0.999$) as shown in Fig. 7. The empirical formula of this model was found $\ln q_e = 0.933 \ln C_e + 0.014$ with $R^2 = 0.999$. This indicates the formation of heterogeneous layers of the ferric ion around DJS adsorbent and surface. This can be supported from the value of the K_d (see Fig. 2). Freundlich model has been widely applied to describe the adsorption of several ferric ions onto several adsorbents like natural bentonite, natural quartz, olive cake, and chitin (see Table 2).

The Freundlich constants K_f and n indicate the adsorption capacity and the adsorption intensity, respectively. They have been calculated by the intercept and slope of the $\ln q_e$ vs. $\ln C_e$ plot as shown in Fig. 7. The values of the K_f and n were also listed in Table 1. The magnitudes of K_f and n show easy separation of ferric ion from the aqueous solution and they indicate favorable adsorption. The intercept K_f value is an indication of the adsorption capacity of the adsorbent; the slope $1/n$ indicates the effect of concentration on the adsorption capacity and represents adsorption intensity or surface heterogeneity. It becomes more heterogonous as its value gets closer to zero. A value below unity implies chemisorptions process. As seen, n value was found high enough for separation.

The apparent Gibbs free energy of sorption (ΔG^0) is the fundamental criterion of spontaneity. Reaction occurs spontaneously at a given temperature, if ΔG^0 is negative in value. The standard Gibbs free energy change (ΔG^0) for the adsorption of ferric ion by DJS can be calculated using the thermodynamic Eq. (9):

$$\Delta G^0 = -RT \ln k_L \tag{9}$$

wherein, T is the absolute temperature in Kelvin and R is the gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$). The equilibrium constant (k_L) can be calculated by Eq. (10):

$$k_L = b \times \mathrm{MA} \tag{10}$$

where MA is the molar weight of sorbate, and b is the Langmuir constant, $b = 0.0026$. The calculated equilibrium constant (k_L) equals to $145.197\,\mathrm{L\,mol^{-1}}$. The value of standard Gibbs free energy change calculated at 30° C is found to be $-12.96\,\mathrm{kJ\,mol^{-1}}$. The negative sign for ΔG^0 indicates to the spontaneous adsorbing nature of ferric ion adsorption on the DJS.

The effect of isotherm shape is discussed from the direction, predicting whether adsorption system is "favorable" or "unfavorable". This can be predicted by dimensionless separation factor "R_L", which is defined as:

$$R_L = 1/(1 + bC_i)$$

Table 2
List to compare the isotherm parameters for the adsorption of ferric ion on the DJS with other natural adsorbent

Adsorbents	Langmuir				Freundlich			Refs.
	$q_{\max}$ ($\mathrm{mg\,g^{-1}}$)	b ($\mathrm{L\,mg^{-1}}$)	ΔG ($\mathrm{kJmol^{-1}}$)	R^2	K_f	$1/n$	R^2	
Natural bentonite (NB)	20.96	0.005	−13.90	0.938	0.202	0.775	0.992	[32]
Natural quartz (NQ)	14.49	0.004	−13.40	0.961	0.115	0.780	0.996	[32]
Olive cake (OC)	58.48	0.015	−16.87	0.96	2.164	0.628	0.992	[1]
Natural zeolite (NZ)	7.35	0.014	−16.98	0.998	3.353	0.106	0.954	[28]
DJS	333.33	0.0026	−12.96	0.992	1.795	0.672	0.999	This study
Others								
Carbon	6.14	0.274		1.00				[29–31]
Eggshells	5.991	1.285		0.983	3.0	0.608	0.982	[47]
Chitosan	90.09	2.413		0.999	55.3	0.301	0.995	[38]
Chitin	1.3982	0.259	−4.52	0.975	2.45	0.672		[2]

where b is the Langmuir constant and C_i is the initial concentration of ferric ion. The calculated R_L was 0.490, indicating for the favorable adsorption.

To justify the validity of DJS as a good adsorbent to remove ferric ion from the aqueous solution, the adsorption potentials of DJS have been compared with the other adsorbents like olive cake (OC) [1], natural zeolite (NZ) [28], natural bentonite (NB) [32], natural quartz (NQ) [32], activated carbon [30,31], and eggshell [47]. The obtained results from this study suggest a preference to use the DJS adsorbent compared with all previous natural adsorbents as shown in Table 2. The preference is determined in terms of the highest removal efficiency ($q_{\max} = 333\,\mathrm{mg\,g^{-1}}$). In addition, the adsorption capacity of DJS adsorbent is better than natural zeolites, bentonite, and quartz. In terms of adsorption intensity (n), its value is found similar for other reported adsorbents as listed in Table 2.

3.5. Kinetic models

Kinetic models of sorption govern the rate, especially using batch sorption systems. Kinetic models of the pseudo-first-order and pseudo-second-order are used to describe the rate and transporting of the ferric ion onto DJS adsorbent surface. Evidently, this rate controls the residence time of ferric ion at the solid–liquid interface. Therefore, the required time for the removal of ferric ion to complete the sorption is important and gives insight into a sorption process. This can provide information on the minimum time that required for the adsorption on the DJS. In addition, it controls the diffusion mechanism between ferric ions as it moves from the bulk solution towards the DJS surface.

3.5.1. Effect of contact time

The role of contact time on sorption was studied under the shaking conditions, such as 300 rpm, $60\,\mathrm{g\,L^{-1}}$ dosage of DJS, 40°C of temperature, and $400\,\mathrm{mg\,L^{-1}}$ of ferric ion solution. The effect of contact time is shown in Fig. 8. Samples were collected at regular intervals and then analyzed after filtration. At the initial stage, the removal rate is high and is associated with uncontroled rate, especially during the first 5 min of sorption. This behavior may be due to the availability of a huge number of the uncovered active sites on DJS surface. For example, the removal of ferric ion was 90% (approx.) at the first 5 min of sorption. This stage shows that the external active sites on the DJS surface are covered before 5 min. Afterward, smooth and continual plot is observed leading to the saturation. This is due to the gradual decline of the few remaining active sites on the DJS. In this stage, the final equilibrium of sorption starts after 40 min (approx.), where ferric ion is slowly transported and linked into the DJS active sites. The maximum removal of ferric ion has been calculated 96% at all temperatures that are used in this study, see Fig. 8. We have seen such results and behavior in many of the studies such as using of the olive cake [1], Zeolite, [28] and natural bentonite [32] adsorbents.

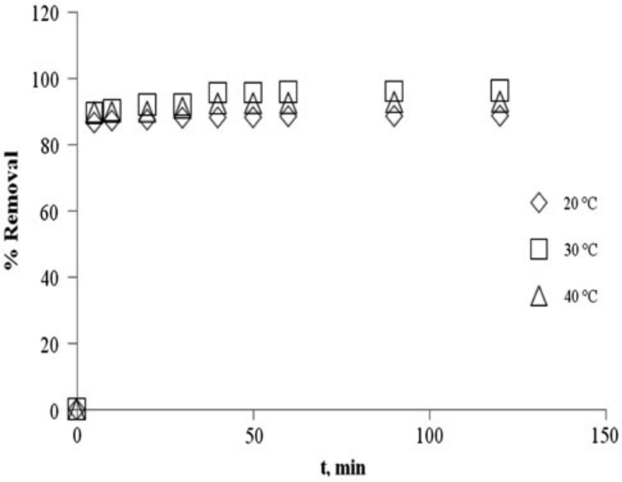

Fig. 8. The effect of contact time on the removal of $400\,\mathrm{mg\,L^{-1}}$ of ferric ion in the interval of 5 to 120 min (with increment of 10 min from 10 to 60 min, and then using 30 min from 60 to 120 min) at constant adsorbent dosage ($60\,\mathrm{g\,L^{-1}}$) of natural Jojoba (DJS), and agitation speed (300 rpm).

3.5.2. Kinetic modeling

In order to investigate the mechanism of sorption, adsorption reaction kinetic models, such as pseudo-first-order (Fig. 9) and pseudo-second-order (Fig. 10), and adsorption diffusion model, such as Weber-Morris intra-particle diffusion model, were used to describe the adsorption rate and mechanism of the ferric ion onto the DJS surfaces.

The pseudo-first-order kinetic model and its integral can be expressed by Eq. (11) [48]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{11}$$

where q_e and q_t ($\mathrm{mg\,g^{-1}}$) are the amounts of adsorbed ferric ion at equilibrium and at any time t, respectively, k_1 ($\mathrm{min^{-1}}$) is pseudo-first-order rate constant, and t (min) is contact time. The values of the model parameters, k_1 and q_e, can be determined by plotting $\ln(q_e{-}q_t)$ vs. t to produce a straight line of slope k_1 and intercept $\ln q_e$, which are listed in Table 3. The fitting of the experimental data to the pseudo-first-order (Fig. 9) was not

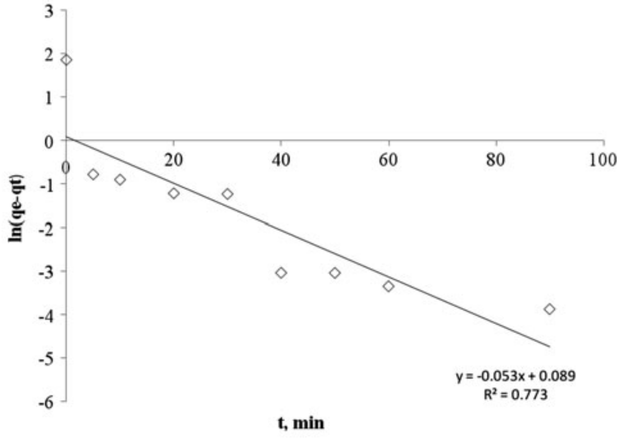

Fig. 9. Legergen pseudo-first-order of initial ferric ion concentration on $60\,g\,L^{-1}$ dosage, temperature of 30°C, 120 min, 1% HNO_3 aqueous solution, 300 rpm, and constant initial concentration ($400\,mg\,L^{-1}$).

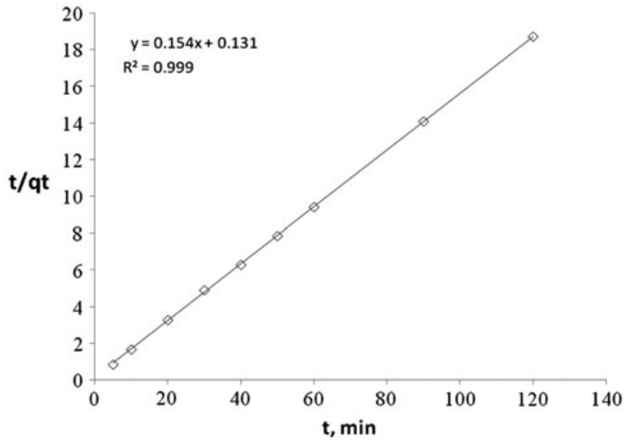

Fig. 10. Pseudo-second-order of initial ferric ion concentration on $60\,g\,L^{-1}$ dosage, 30°C, 120 min, initial pH of 1% HNO_3, 300 rpm, and constant initial concentration ($400\,mg\,L^{-1}$).

so good rather than low R^2 value. Therefore, the experimental q_e values for the pseudo-first-order model were much remarkably deviated from the calculated values for all studied temperatures.

The goodness degree of linear plot is applied by the pseudo-second-order kinetic model and its integral form. This model is expressed by Eq. (12) [49]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{12}$$

where k_2 is the equilibrium rate constant of the pseudo-second-order kinetic model ($g\,mg^{-1}\,min^{-1}$). The value of k_2 can be determined by plotting t/q_t vs. t to obtain a straight line of slope $1/q_e$ and intercept of $1/(k_2)$, which were listed in the Table 4.

Table 3
The calculated and experimental data of the pseudo-first-order model

T (°C)	k_1 (min^{-1})	$q_{e,\ cal}$ ($mg\,g^{-1}$)	$q_{e,\ Exp}$ ($mg\,g^{-1}$)	R^2
20	0.014	5.92	1.177	0.225
30	0.053	5.92	1.09	0.773
40	0.022	5.92	0.92	0.392

The goodness degree of a linear plot t/q_t vs. t can be judged from the determination coefficient values (R^2) of the plot, which can also be regarded as a criterion in the determination of the adequacy of kinetic model. Based on the R^2 values in Table 4, adsorption of ferric ion on the DJS is regarded as pseudo-second-order rather than pseudo-first-order. Furthermore, the adsorption of ferric ion is faster at 20°C, which binds easily with the active sites on the DJS surface.

Apparently, the pseudo-second-order model explains the adsorption of ferric ion onto DJS well. It was considered that the interaction of ferric ion with active sites on the DJS surface was found to be rate limiting and controling step of adsorption reaction. This means that ferric ion is chemisorbed with two functional groups in the DJS adsorbent. The similar results were observed using olive cake (OC) [1], natural zeolite (NZ) [28], natural bentonite (NB) [32], natural quartz (NQ) [32], activated carbon [30,31], and eggshell [47] and chitosan [38]. In general, based on the various conditions of the previous experiments (see Table 2), it could be said that DJS has high adsorbing rate for removing aqueous ferric ion compared to the natural olive cake, zeolite, carbon, and chitosan (Table 5).

The pseudo-first-order and pseudo-second-order kinetic models could not identify the diffusion mechanism. Thus, to determine the diffusibility of the ferric ions into the pores of the adsorbent, Weber-Moris intra-particle diffusion model [50] was used in the form of the following equation:

Table 4
The calculated and experimental data to the pseudo-second-order model

T (°C)	k_2, g/(mg min)	$q_{e,\ cal}$ ($mg\,g^{-1}$)	$q_{e,\ Exp}$ ($mg\,g^{-1}$)	R^2
20	0.724	5.92	5.95	1
30	0.181	5.92	6.45	0.999
40	0.346	5.92	6.25	1

Table 5
List to compare the kinetic parameters for the adsorption of ferric ion on the DJS with other natural adsorbent

Adsorbents	Pseudo-first order		Pseudo-second order			Refs.
	k_1 (min^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e	R^2	
Bentonite (NB)	0.066	0.89	0.337	0.649	0.99	[32]
Quartz (NQ)	0.057	0.76	0.552	0.746	0.99	[32]
Olive cake (OC)	0.061	0.89	0.018	15.97	0.99	[1]
Zeolite (NZ)	0.045	0.88	0.040	20.00	1.0	[28]
DJS	0.053	0.773	0.181	6.45	1.0	This study
Others						
Carbon			0.048	13.04	1.0	[29–31]
Eggshells			0.403	1.92	1.0	[47]
Chitosan	0.0306	0.96	0.032		1.0	[38]

$$q_t = k_{\text{int}} t^{0.5} + C$$

where C is constant, q_t is the amount of metal ions adsorbed at time (mg g^{-1}) and k_{int} is the intra-particle diffusion rate constant (mg g^{-1} min$^{-0.5}$). A plot of q_t vs. $t^{0.5}$ giving straight line confirms intra-particle diffusion sorption as shown in Fig. 11. The plot is not totally linear and moreover does not pass through the origin. This is indicative of some degree of boundry layer control, and this further show that the intra-particle diffusion could not be the only mechanism involved. This plot presents multilinearity which indicates that two or more steps occur. The first, sharper portion (ca. $t^{0.5}$ range from 0.87 to 0.94 min$^{0.5}$; i.e. from 0 upto 5 min of adsorption period) is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage (ca. $t^{0.5}$ range from 0.94 to 0.98 min$^{0.5}$; i.e. from 5 upto 30 min of adsorption period), where the intra-particle diffusion is rate-controled. The third portion is final equilibrium stage where the intra-particle diffusion starts to slow down due to extremely low solute concentrations in the solution and chemisorptions stage is taken part on the DJS surface and pores (which already has been successfully explained by pseudo-second-order kinetic model from 30 to 120 min of adsorption period). Moreover, what we notice is that the temperature does not significantly affect the diffusibility of ferric ion over the first 5 minutes of adsorption compared to the last time of adsorption (see Fig. 11).

Film diffusion mass transfer rate equation presented be Boyd et al. [51] is

$$\ln\left\{1 - \frac{q_t}{q_e}\right\} = -kt$$

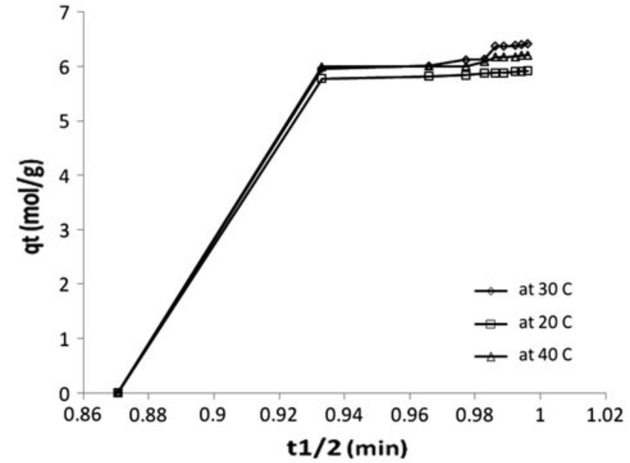

Fig. 11. Weber-Moris intra-particule diffusion kinetic model for adsorption of ferric ion on DJS starting from 0 to 180 min equilibrium contact time.

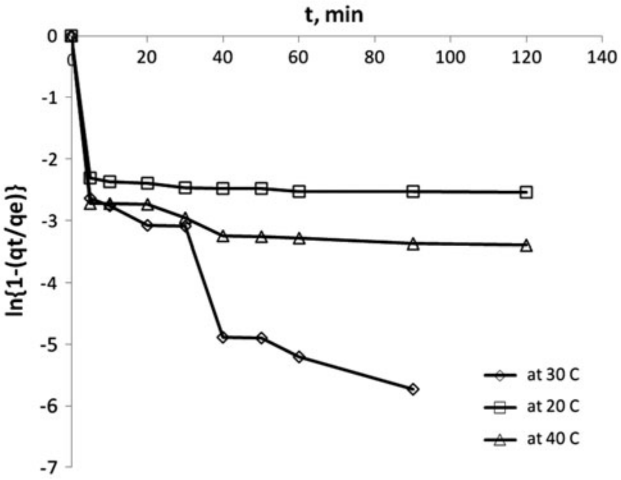

Fig. 12. Film diffusion mass transfer rate model presented by Boyd et al. [51].

where k (min^{-1}) is the liquid film diffusion constant. A plot of $\ln\left\{1 - \frac{q_t}{q_e}\right\}$ vs. t should be a straight line with a slope $-k$ if the film diffusion is the rate-limiting step. Fig. 12 shows the film diffusion mass transfer stage. Therefore, this stage cannot be considered as rate controling and limiting step.

4. Conclusion

DJS are found to be a very effective and low-cost adsorbent for the removal of the aqueous ferric ion. The maximum removal has been found by applying several parameters such as 400 mg L^{-1} of ferric ion solution, 60 g L^{-1} doses of DJS, 30˚C of temperature, 120 min, solution acidity adjusted by 1% HNO_3, and 300 rpm. The final equilibrium of sorption starts after 40 min, yielded a maximum removal of 96%. The equilibrium data have been yielded excellent fits within the Freundlich isotherm. The kinetic studies show that the removal rate is high, and is associated with uncontroled rate, especially during the first 5 min of sorption. Kinetic models of the pseudo-second-order are good model to describe the removal rate of the ferric ion onto DJS surfaces. Ferric ion can be spontaneously, favorably, and heterogeneously chemisorbed onto the DJS adsorbent.

Based on the thermodynamic parameters, this study suggests a preference to use the DJS adsorbent compared with some previous natural adsorbents that have been used for the removal of iron ion from aquatic systems such as natural zeolite, bentonite, quartz, olive cake, and chitosan, carbon, and eggshells. Based on the kinetic studies, this sorption on DJS adsorbent is faster than the use of the natural olive cake, zeolite, carbon, and chitosan. But, it is as slower compared to the use of bentonit, quartz, and eggshells adsorbents. Therefore, we suggest applying this study to manage and prevent pollution of the aquatic system or to reclaim the water for reuse especially in the poor countries.

References

[1] Z.A. Al-Anber, M.A. Al-Anber, Thermodynamics and kinetics studies of iron (III) adsorption by olive cake in a batch system, J. Mex. Chem. Soc. 52(2) (2008) 108–115.

[2] G. Karthikeyan, N.M. Andal, K. Anbalagan, Adsorption studies of ferric on chitin, J. Chem. Sci. 117(6) (2005) 663–672.

[3] G.J. Kontoghiorghes, E.D. Weinberg, Iron: Mammalian defense systems, mechanisms of disease, and chelation therapy approaches, Blood Rev. 9 (1995) 33–45.

[4] M.M. Matlock, B.S. Howerton, D.A. Atwood, Chemical precipitation of heavy metals from acid mine drainage, Water Res. 36 (2002) 4757–4764.

[5] S.J. Al-Bazi, A. Chow, Platinum metals-solution chemistry and separation methods (Ion-exchange and solvent extraction), Talanta 31(10A) (1984) 815–836.

[6] S. Rengraraj, K.H. Yeon, S.H. Moon, Removal of chromium from water and wastewater by ion exchange resins, J. Hazard. Mater. 87(1–3) (2001) 273–287.

[7] L. Yurlova, A. Kryvoruchko, B. Kornilovich, Removal of Ni (II) ions from wastewater by micellar-enhanced ultrafiltration, Desalination 144 (2002) 255–260.

[8] Y. Benito, M.L. Ruiz, Reverse osmosis applied to metal finishing wastewater, Desalination 142 (2002) 229–234.

[9] G.M. Michalakos, J.M. Nieva, D.V. Vayenas, G. Lyberatos, Removal of iron from potable water using a trickling filter, Water Res. 31 (1997) 991–996.

[10] F. Masood, A. Malik, Bisorption of metal ions from aqueous solution and tannery effluent by *Bacillus* sp. FM1, J. Environ. Sci. Health, Part A 46 (2001) 1667–1674.

[11] C.P. Huang, M.H. Wu, Chromium removal by carbon adsorption, J. Water Pollut. Control Fed. 47 (1975) 2437–2445.

[12] O.I. Oboh, E.O. Aluyor, The removal of heavy metal ions from aqueous solutions using sour soup seeds as biosorbent, Afr. J. Biotechnol. 7(24) (2008) 4508–4511.

[13] M.J. Zamzow, J.E. Murphy, Removal of metal cations from water using zeolites, Sep. Sci. Technol. 27 (1992) 1969–1984.

[14] R. Souag, D. Touaibia, B. Benayada, A. Boucenna, Adsorption of heavy metals (Cd, Zn and Pb) from water using keratin powder prepared from Algerian sheep hoofs, Eur. J. Sci. Res. 35(3) (2009) 416–425.

[15] R.L. Ramous, P.E. Flores, A.A. Pina, J.M. Barron, R.M. Coronado, Adsorption of cadmium (II) from aqueous solution onto activated carbon cloth, Sep. Sci. Technol. 40 (2005) 2079–2094.

[16] S.K. Ouki, R.D. Neufeld, R. Perry, Use of activated carbon for the recovery of chromium from industrial wastewaters, J. Chem. Technol. Biotechnol. 70(1) (1997) 3–8.

[17] L. Monser, N. Adhoum, Modified activated carbon for the removal of copper, zinc, chromium, and cyanide from wastewater, Sep. Purif. Technol. 26(2–3) (2002) 137–146.

[18] D.S. Kim, Adsorption characteristics of Fe(III) and Fe(III)–NTA complex on granular activated carbon, J. Hazard. Mater. 106B (2004) 67–84.

[19] M.K. Mondal, Removal of Pb(II) ions from aqueous solution using activated tea waste: Adsorption on a fixed bed column, J. Environ. Manage. 90 (2009) 3266–3271.

[20] S. Suthepong, S. Siranee, Utilization of pulp and paper industrial wastes to remove heavy metals from metal finishing wastewater, J. Environ. Manage. 90 (2009) 3283–3289.

[21] J.O. Akaninwor, M.O. Wegwu, I.U. Iba, Removal of iron, zinc, and magnesium from polluted wastewater samples using thioglycolic acid modified oil-palm, Afr. J. Biochem. Res. 1(2) (2007) 011–013.

[22] M. Horsfall, Jnr, I.S. Ayebaemi, Studies on the effect of pH on the sorption of Pb^{+2} and Cd^{+2} ions from aqueous solutions by *Caladium bicolor* (Wild cocoyam) biomass, Environ. Biotechnol. 7(3) (2004) 1–11.

[23] O.A. Oyedeji, G.B. Osinfade, Removal of copper (II), iron (III), and lead (II) ions from mono-component simulated waste effluent by adsorption on coconut husk, Afr. J. Environ. Sci. Technol. 4(6) (2010) 382–387.

[24] S.F. Nomanbhay, K. Palanisamy, Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal, Electron. J. Biotechnol. 8(1) (2005) 44–53.

[25] D. Mohan, S. Chander, Removal and recovery of metal ions from acid mine drainage using lignite—a low cost sorbent, J. Hazard. Mater. 137(3) (2006) 1545–1553.

[26] A. Burke, E. Yilmaz, N. Hasirci, O. Yilmaz, Ferric ion removal from solution through adsorption on chitosan, J. Appl. Polym. Sci. 84(6) (2002) 1185–1192.

[27] P. Senthil Kumar, R. Gayathri, R. Prabhu Arunkumar, Adsorption of Fe(III) ions from aqueous solution by Bengal gram husk powder: Equilibrium isotherms and kinetic approach, Electron. J. Environ. Agric. Food Chem. 9(6) (2010) 1047–1058.

[28] M. Al-Anber, Z. Al-Anber, Utilization of natural zeolite as ion-exchange and sorbent material in the removal of iron, Desalination 225(1–3) (2008) 70–81.

[29] Z. Zawani, C.A. Luqman, Th.S.Y. Choong, Equilibrium, kinetic and thermodynamic studies: Adsorption of removal black 5 on the palm kernel shell activated carbon (PKS-AC), Eur. J. Sci. Res. 37 (2009) 63–71.

[30] K.C. Lakshminarayanan Rao, K. Krishniah, A. Ashutosh, Colour removal from dye stuff industry effluent using activated carbon, Indian J. Chem. Technol. 1 (1994) 13–19.

[31] A. Edwin Vasu, Adsorption of Ni(II), Cu(II) and Fe(III) from aqueous solution using activated carbon, E-J. Chem. 5 (2008) 1–9.

[32] M. Al-Anber, Removal of high-level Fe^{3+} from aqueous solution using Jordanian inorganic materials: Bentonite and quartz, Desalination 250 (2010) 885–891.

[33] M. Allawzi, S. Al-Asheh, H. Allaboun, O. Borini, Assessment of the natural Jojoba residues as adsorbent for removal of cadmium from aqueous solutions, Desalin. Water Treat. 2(1–3) (2010) 60–65.

[34] M.F. Gayol, D.O. Labuckas, J.C. Oberti, C.A. Guzmán, Chemical characterization of Jojoba seeds (Simmondsia chinensis (Link) Schneider) from "Baado De Los Pantanos", La Rioja Argentina, J. Argent. Chem. Soc. 92 (2004) 59–63.

[35] N. Kannan, T. Veemaraj, Removal of lead(II) ions by adsorption onto bamboo dust and commercial activated carbons—a comparative study, E-J. Chem. 6(2) (2009) 247–256.

[36] S.A. Khan, R. Ur-Reman, M.A. Khan, Adsorption of Cs(I), Sr(II) and Co(II) on Al_2O_3, J. Radioanal. Nucl. Chem. 207 (1996) 19–37.

[37] B.A. Siddique, P.P. Sharma, S. Mohamad, Adsorption studies on phosphate treated sawdust: Separation of Cr(VI) from Zn (II), Ni(II), Cu(II) and their removal and recovery from electroplating waste, Ind. J. Environ. Prot. 19(11) (1999) 846–852.

[38] W.S. Wan, S. Ab Ghani, A. Kamari, Adsorption behaviour of Fe (II) and Fe(III) ions in aqueous solution on chitosan and cross-linked chitosan beads, Bioresour. Technol. 96 (2005) 443–450.

[39] Z.A. Al-Anber, M.A. Al-Anber, M. Matouq, O. Al-Ayed, Defatted Jojoba for the removal of methylene blue from aqueous solution: Thermodynamic and kinetic studies, Desalination 276 (2011) 169–174.

[40] V.J. Inglezakis, M.D. Loizidou, H.P. Grigoropoulou, Ion exchange studies on natural and modified zeolites and the concept of exchange site accessibility, J. Colloid Interf. Sci. 275 (2004) 570–576.

[41] B.B. Johnson, Effect of pH, temperature and concentration on the adsorption of cadmium on goethite, Environ. Sci. Technol. 24 (1990) 112–118.

[42] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: A review, J. Hazard. Mater. B97 (2003) 219–243.

[43] N. Khalid, S. Ahmad, S.N. Kiani, J. Ahmed, Removal of mercury from aqueous solutions by adsorption to rice husks, Sep. Sci. Technol. 34 (1999) 3139–3153.

[44] N. Khalid, S. Ahmed, S.N. Kiani, J. Ahmed, Removal of lead from aqueous solutions using rice husk, Sep. Sci. Tech. 33 (1998) 2349–2362.

[45] I. Langmuir, The constitution, fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[46] H. Freundlich, Über die Adsorption in Losungen [Adsorption in solution], Z. Phys. Chem. 57 (1906) 384–470.

[47] N. Yeddou, A. Bensmaili, Equilibrium and kinetic of iron adsorption by eggshells in a batch system: Effect of temperature, Desalination 206 (2007) 127–134.

[48] S. Lagergren, K.S. Vetenskapsakad, Zur theorie der sogenannten adsorption geloester stoffe, Kungliga Svenska Vetenskapsakad. Handl. 24 (1898) 1–39.

[49] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[50] W.J. Weber, Jr, F.O. Digiano, Process Dynamics in Environmental System; Environmental Science and Technology Series, John Wiley and Sons, New York, NY, pp. 89–94 1996.

[51] G.E. Boyd, A.W. Adamson, L.S. Myers, The exchange adsorption of ions from aqueous solutions by organic zeolites. II. Kinetics, J. Am. Chem. Soc. 69(11) (1947) 2836–2848.