



Adsorption of Fe ions by modified carrageenan beads with tricarboxy cellulose: kinetics study and four isotherm models

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ABSTRACT

In this work, we have studied the kinetics of Fe ions adsorption from aqueous solutions by modified carrageenan beads with tricarboxy cellulose. The steps employed in this study involved the extraction of cellulose from bagasse and subsequently, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) oxidation followed by periodate-chlorite oxidation. Different adsorption conditions were investigated such as; time intervals (5–120 min), Fe ions concentrations (25, 50, 80, 120 and 160 ppm), adsorbent weight (0.1, 0.2, 0.3, 0.4 and 0.5 g), and pH (3–9). Two kinetic models including; pseudo second-order and intra-particle diffusion model have been applied. The conclusion is that, the adsorption kinetics of Fe ions removal using modified carrageenan beads followed pseudo second-order model. Also, four isotherm models namely; Freundlich, Langmuir, Temkin, and Dubinin–Radushkevich were fitted with this study.

Keywords: Beads; Carrageenan; Tricarboxy cellulose; Dubinin–Radushkevich; Freundlich; Kinetic models; Langmuir; Temkin

1. Introduction

In the recent years, water contamination by metals have become an essential topic for studying from the viewpoint of environmental scientists. Metals are present in water not only, from natural sources such as volcanoes, weathering and ore deposits but also, from anthropogenic activities for instance industries, mining, agriculture activities and waste water irrigation [1,2].

Iron (Fe) is one of the most common transition earth metals; occur naturally in the aquatic environment as several different forms of dissolved ions. This element has widespread uses, such as metallurgical applications and as

coagulants in water treatment [3]. Although iron is essential element to humans and relatively non-toxic, ions of this element in water often cause mild to severe aesthetic problems, such as discolored water, precipitation, scaling, staining, resuspension in the distribution system and metallic water taste [4]. Therefore, iron removal from the contaminated water is necessary. In general, there are traditional methods for metal removal such as evaporation, chemical precipitation, flocculation, electrolysis, membrane separation, and ion exchange, which are often costly or ineffective. Adsorption has been considered as one of the most effective and feasible method for metals removal [4–6].

Among the adsorbents that used around the world for this purpose is the activated carbon fiber, but the disadvantages of its use are the high cost and low selectivity.

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Therefore, searching for alternative adsorbents should be considered by a vigorous study. As an example, fruit peel [7,8], combination of natural zeolite–kaolin–bentonite [9], chitosan [10–12], anaerobic granular sludge [13,14], and natural bentonite have been used as an adsorbent for metal [15,16].

Recently, research interest has increased in terms of the use of natural adsorbents to overcome the environmental pollution [17]. Supplementary efforts have been made to use cheap and available natural bi-products (agriculture wastes) such as sugar cane bagasse, coconut shell, orange peel, rice husk, peanut husk, pecan shells, jackfruit, maize cob, apple waste, and sawdust as adsorbents to remove metals from water [18,19]. The major composition of these wastes is cellulose.

Cellulose as an adsorbent is a naturally existing biopolymer characterized by its renewability, biocompatibility, biodegradability, nontoxicity, low cost and environmentally friendly in comparison with conventional polymers [20]. On the other hand, the disadvantages of using native cellulose as adsorbent refer to its poor physical stability and low adsorption capacity. So, it should be chemically modified to achieve efficient ion-exchange capacity [21]. Adding chemical modification such as grafting to nanotechnology offers an improvement to the efficiency of the bio-adsorbent. Among the cellulosic nanomaterials, cellulose nanocrystals have gained a great deal of attention because of their high surface area, excellent mechanical strength, good aqueous colloidal stability, rigid rod-shaped nanostructure and favorable surface modification [22]. These features increase the applicability of cellulose nanocrystals in water purification.

One of the most important methods to convert cellulose into value-added derivative is the oxidation of cellulose. Recently, 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO)-mediated oxidation is one of the most used chemical methods for surface modification of cellulose to convert the primary hydroxyl groups (C6) to carboxylic groups [23]. While periodate oxidation cleaves C2–C3 bonds of glucopyranose ring and form 2,3 dialdehyde groups along the chains of cellulose [24]. The tricarboxylic cellulose was prepared by Ragab et al. through TEMPO oxidation followed by periodate-chlorite oxidation. They found that, the prepared tricarboxylic cellulose had high efficiency for scavenging of Cu, Ca and Pb ions from water due to its high surface area and high surface charge [25].

In the recent decades, researchers have been devoted their activities for developing polymeric hydrogel beads containing numerous functional groups as promising adsorbent materials. Since, tricarboxy cellulose is anionic polyelectrolyte material which is sensitive to a change in solution pH, and ionic strength, etc. Tricarboxy cellulose beads may be crosslinked but purely crosslinked tricarboxy cellulose beads have a weak mechanical stability and limited swelling degree. Thus, it was favorable to modify via blending, grafting, forming an interpenetrating network and composites with other polymers, or immobilizing clays and metals [26].

Similar to tricarboxy cellulose, carrageenan is a linear sulfated polysaccharide obtained from red seaweed. In addition, carrageenan based nanocomposite has been developed and used as adsorbent [27,28].

In this study, we have studied the kinetics of Fe ions adsorption from aqueous solution by modified carrageenan beads with tricarboxy cellulose under different adsorption conditions including; time intervals, Fe ions concentrations, adsorbent weight, and pH.

2. Materials and methods

2.1. Materials

Bagasse raw material was supplied from Quena Company of Paper Industry, Egypt. The chemical composition of the bagasse raw material was determined according to Tappi standards. The results were 22, 44.4, 28.1, and 1.4% for Klason lignin, Pentosan, α -cellulose, and ash content respectively. Dissolved bagasse pulp was prepared as reported in our previous work [21]. Through prehydrolysis with 2% H_2SO_4 based on the raw material followed by alkali treatment using 5% NaOH giving unbleached pulp. This pulp was bleached by sodium chlorite giving dissolving bagasse pulp with cellulose content (96%), hemicellulose (3%) and very low content of lignin. *K*-carrageenan, Sodium metaperiodate ($NaIO_4$), NaBr and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) were purchased from Sigma Aldrich. Additional chemicals needed for the different analytical methods were bought from Sigma-Aldrich and used with no further purification.

2.2. Sorbent preparation

As described in our previous work, TEMPO oxidation of cellulose which extracted from dissolved bagasse pulp followed by periodate-chlorite oxidation giving tricarboxy-cellulose were carried out [25]. It can be briefly explained as follows; dissolving pulp was dispersed in distilled water with TEMPO and sodium bromide. Then sodium hypochlorite solution was added with stirring and adjusted the pH to 10. At the end of the reaction the pH was adjusted to 7 and the product was centrifuged at 7000 rpm followed by further purification by repeated adding water, dispersion, and centrifugation. Finally, the product was purified by dialysis using deionized water.

Sodium metaperiodate was added to the suspended TEMPO oxidized cellulose solution and the reaction container was covered with aluminum foil to avoid photo-induced decomposition of the periodate. The reaction was stopped after 3 h by washing the resulting dialdehyde carboxy cellulose with distilled water and filtering it in a funnel. In the next step, aqueous sodium chlorite solution with acetic acid was added slowly to dialdehyde carboxy cellulose suspended solution. Again, the resulting product tricarboxyl cellulose was washed with deionized water and filtered.

2.3. Modification of carrageenan with tricarboxy cellulose

Carrageenan was dissolved in distilled water with 2% (w/v) concentration, through heating it on a 70°C water bath. Then 50 mL of carrageenan with 10 mL of tricarboxy cellulose solutions was vigorously stirred using mechanical stirrer for 2 h at 70°C. The modified carrageenan beads with

tricarboxy cellulose were prepared by dropping the solutions through a nozzle of 700 μm to a magnetically stirred 2% KCl solution using the Encapsulator to prepare a uniform gel modified carrageenan beads with tricarboxycellulose (diameter 2 mm). The modified carrageenan beads with tricarboxy cellulose were left in the KCl solution till using them [29].

2.4. Sorption study

2.4.1. Metal removal study

The batch equilibrium experiment was employed at room temperature to remove Fe ions from 100 ml aqueous solutions (prepared by dissolving FeCl_3 in distilled water) at 300 rpm. Different adsorption conditions were investigated such as; (i) various time intervals (5–120 min) at pH = 3.3 using 0.5 g of dry modified carrageenan beads with tricarboxy cellulose and 50 ppm of Fe ions, (ii) different concentrations of Fe ions (25, 50, 80, 120 and 160 ppm) were investigated at pH 3.3 and 0.5 g of dry modified carrageenan beads with tricarboxycellulose for 30 min, (iii) different adsorbent weight (0.1, 0.2, 0.3, 0.4 and 0.5 g) at pH = 3.3 and 50 ppm of Fe ions for 30 min, and (iv) at different pH (from 3 to 9) using 50 ppm of Fe ions and 0.5 g of dry modified carrageenan beads with tricarboxy cellulose for 30 min, where the pH of the solution was adjusted by NaOH and HCl. The sorbent was next filtered from the solution. After that, the Fe ions concentration was measured by atomic absorption spectrophotometry (Perkin Elmer 3110, USA). The removal efficiency percent (R%) of the adsorbent was calculated by the following relation:

$$R\% = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

The amount of the Fe ions uptake (q) within the adsorbent was calculated by the following equation:

$$q = (C_o - C_t) \times \frac{V}{M} \quad (2)$$

where C_o is the initial Fe ions concentration (mg/L), C_t is the remaining Fe ions concentration after a period of time (t) (mg/L), V is the volume of solution (ml), and M is the mass of the adsorbent added (g).

2.4.2. Kinetic study

2.4.2.1. The pseudo-second-order reaction

The pseudo-second-order reaction was used to determine the sorption rate constant.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \left(\frac{1}{q_e} \right) t \quad (3)$$

where q_t is the sorption capacity (mg/g) at any given time (t , min), q_e is the equilibrium sorption capacity (mg/g), and k is the rate constant of the second order reaction (g/mg min).

The following expression denoted the sorption rate h (mg/g min) [30].

$$h = k q_e^2 \quad (4)$$

2.4.2.2. Intraparticle diffusion model

Sorption data for the metals were described based on the intraparticle diffusion model that can be expressed as:

$$q_t = k_p (t)^{0.5} + c \quad (5)$$

where k_p is the intraparticle diffusion rate, t is the time interval (min), and C is the constant [31].

2.4.5. Isotherm study

Four adsorption isotherms were used to analyze the adsorption data: Freundlich, Langmuir, Temkin, and The Dubinin–Radushkevich isotherm (D–R).

2.4.5.1. Freundlich isotherm

The Freundlich isotherm is expressed by the following equation:

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

where q_e is the equilibrium sorption capacity (mg/g), C_e is the equilibrium concentration of metal ion (mg/L), and (k_f and n) are the Freundlich isotherm constants [31].

2.4.5.2. Langmuir isotherm

The Langmuir isotherm suppose monolayer adsorption of the adsorbate onto a limited number of active sites of the adsorbent surface. The following represents the linearized Langmuir isotherm equation:

$$q_t / q_{max} = b C_t / (1 + b C_t) \quad (7)$$

where q_e is the equilibrium sorption capacity (mg/g), C_e is the equilibrium concentration of metal ion (mg/L), q_{max} is the maximum sorption capacity (mg/g), and b is the Langmuir constant (L/mg), which correlates to the adsorption energy.

2.4.5.2.1. Separation factor

The essential characteristics of the Langmuir isotherm can be expressed in terms of separation factor R_L which is defined as:

$$R_L = 1 / (1 + b C_o) \quad (8)$$

$R_L > 1$ represents an unfavorable adsorption, $R_L = 1$ represents linear adsorption, $R_L = 0$ translates into irreversible, whereas R_L values between 0 and 1 indicate favorable adsorption [32].

2.4.5.3. Temkin isotherm

The Temkin isotherms suppose that, the energy of sorption during the sorption process decreases linearly with increasing sorption site saturation. The Temkin isotherm can be given in the following forms [33]:

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \quad (9)$$

Or can be linearized as:

$$q_e = B \ln A + B \ln C_e \quad (10)$$

where q_e is the equilibrium sorption capacity (mg/g), C_e is the equilibrium concentration of metal ion (mg/L), B is constant related to the heat of sorption $B = RT/b$, b is the Temkin constant related to the sorption energy, A is the equilibrium binding constant (L/mg), R (0.00813 kJ/mol-K) is the gas constant, and T (K) is temperature.

2.4.5.4. The Dubinin–Radushkevich isotherm (D–R)

The Dubinin–Radushkevich isotherm (D–R) can be used to differentiate between chemical vs. physical nature of sorption. The D–R isotherm model can be expressed as [34]:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (11)$$

where q_m (mg/g) is the maximum adsorption capacity onto adsorbent, β is the activity coefficient and ε is the Polanyi potential, which is defined as:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (12)$$

where; R is the gas constant (J/mol-K) and T is the temperature (K).

2.4.5.4.1. Sorption energy

It is the energy (E) of sorption when the sorbate transferred to the surface of the sorbent from the solution which can be expressed as:

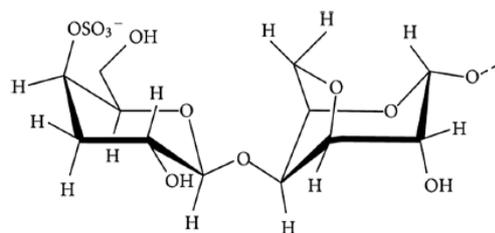
$$E = \frac{1}{(2\beta)^{0.5}} \quad (13)$$

3. Results and discussion

3.1. Predictable mechanism of oxidation

The first step of tricarboxy cellulose preparation was the oxidation of cellulose by TEMPO in the presence of sodium bromide and sodium hypochlorite. This oxidation is a selective oxidation for primary hydroxyl groups (C6) which considered more reactive than secondary hydrox-

yls in C2 and C3. This followed by selective cleavage at the C2 and C3 vicinal hydroxyl groups to yield a product with 2,3-dialdehyde units along the polymer chain. Further oxidation with chlorite yielded tricarboxy cellulose. Fig. 1 illustrates the reaction mechanism of the consecutive oxidation processes.



Carrageenan structure

The modified carrageenan with tricarboxy cellulose beads with diameter 2 mm were prepared and characterized. The capability of these modified beads toward removing of Cu^{2+} , Pb^{2+} , Ca^{2+} , Mg^{2+} , and Fe^{2+} from aqueous solution was studied, as reported in our earlier publication [29].

In this study the kinetic adsorption of the modified carrageenan beads with tricarboxy cellulose toward removing of Fe ions was studied by studying the effect of; contact time, concentration of Fe ions, adsorbent weight, and pH on removing activity.

3.2. Effect of contact time

Fig. 2 displays the effect of contact time on the removal of Fe ions by modified carrageenan beads with tricarboxy cellulose at an ambient temperature ($20 \pm 5^\circ\text{C}$) and $\text{pH} \approx 3.3$. For about the first 5 min, equilibrium between amount of Fe ions adsorbed by beads and the amount of Fe ions remaining in the solution not achieving due to the active side of the adsorbent beads was not fully bind Fe ions.

The optimum contact time of Fe ions adsorption happened at 15 min, where the amount of Fe ions adsorbed by beads and remained in the solution were in equilibrium and the monolayer forms of the adsorbed material get exhausted. Beads as an adsorbent has bond Fe ions from solution to its surface-active site and initially a large numbers of vacant surface sites are available [35]. At 15 min of contact time; the prepared beads remove Fe ions by concentration 50 mg L^{-1} until 81.1%. The equilibrium at higher concentration may be due to that there are no free binding active sites on adsorbent to absorb more Fe ions from the solution [36].

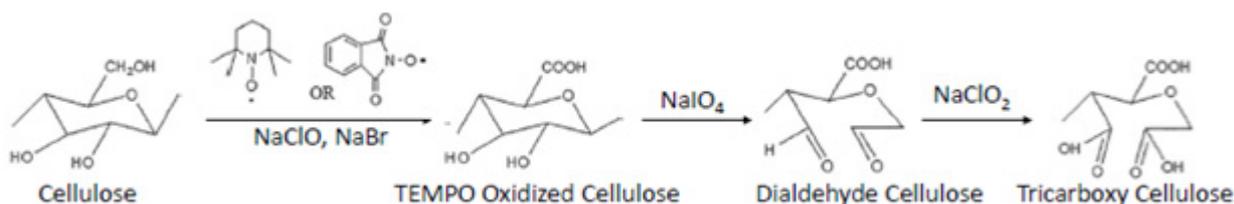


Fig. 1. Oxidation of cellulose to tricarboxy cellulose.

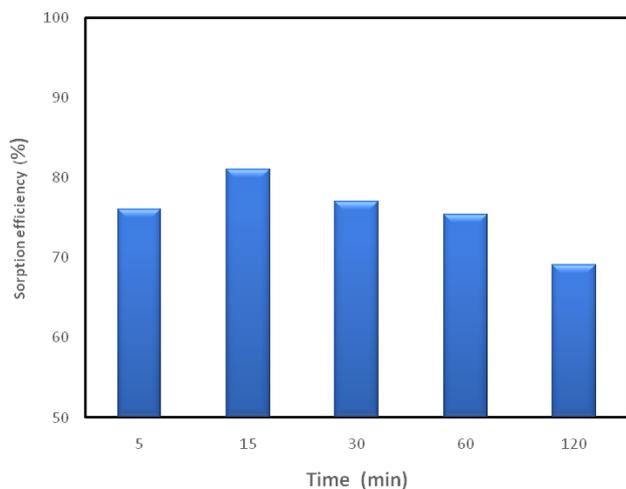


Fig. 2. Effect of contact time on the sorption efficiency of Fe ions by the modified carrageenan beads with tricarboxy cellulose.

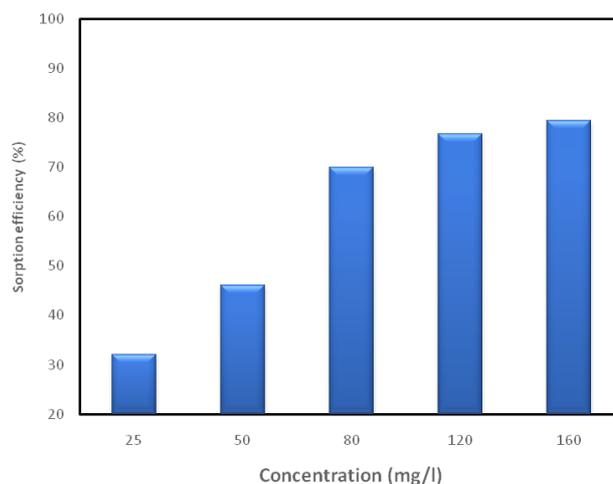


Fig. 3. Effect of the initial concentration on the removal of Fe ions by the modified carrageenan beads with tricarboxy cellulose.

3.3. Effect of the initial Fe ions concentration

Initial concentration of Fe ions is one of the effective factors on adsorption efficiency and the Fe ions concentration may be different in water samples. So, the experiments were carried out with variable initial Fe ions concentrations (25, 50, 80, 120 and 160 ppm) at pH 3.3 and 0.5 g/100 mL solution of dry modified carrageenan beads with tricarboxy cellulose for 30 min (Fig. 3). It can be observed from the experimental results that, the rate of Fe ions removal increased with the increased of initial Fe ions concentration. The sorption efficiency of Fe ions on the prepared beads increased from 32 to 46% as the initial concentration of Fe ions increased from 25 to 50 mg/L. Further increasing of Fe ions, increasing the sorption efficiency of beads. However, after a certain amount of Fe ions removal percentage no longer increases as the sorption efficiency increased from 76.6 to 79.4% with increased Fe ions from 120 to 160 ppm. This may be due to that the initial concentration delivers an important driving force to overcome all mass transfer resistances between the solid and liquid phases [37].

3.4. Effect of pH

pH value of the surrounding environment is one of the most important factors influencing the removal of metal ions. So, the effect of pH on the adsorption of Fe ions by the modified carrageenan beads with tricarboxy cellulose was studied over the pH range of 3–11 (Fig. 4). It is obviously found that pH is closely related with the adsorption capacity of Fe ions on the beads. In general, with increasing pH of the solution, the adsorption amount of Fe³⁺ ions was increased and the effect of pH on the kind of this adsorption was in linearity of surface adsorbent acidity condition. Long contact of adsorption was conducted at optimum contact time yielded before i.e. at 15 min. The pH can influence the removal of Fe ions on beads by changing the surface charges of the adsorbent and Fe ions species present at different pH. At acid condition (pH ≈ 3–5), beads could remove Fe ions species from 81.2 to 86.2% which attributed to a competition between H⁺ and Fe²⁺ and Fe³⁺ ions to be

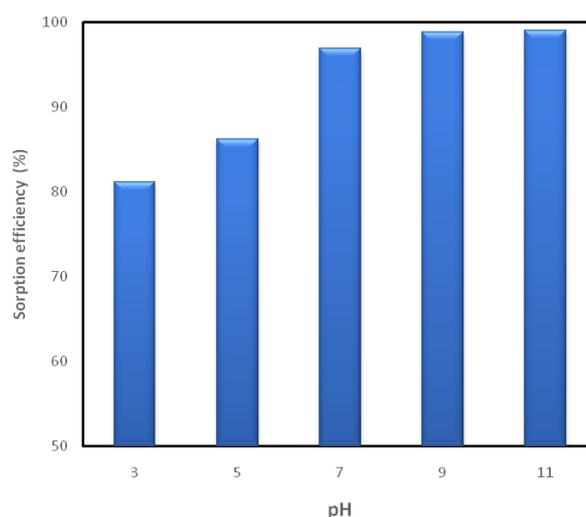


Fig. 4. Effect of the pH of the solution on the removal of Fe ions by the modified carrageenan beads with tricarboxy cellulose.

adsorbed on the adsorbent sites [38]. As pH raised to 7, where the capability of beads to adsorb Fe ions was 96.9%, the H⁺ competition disappeared and the positively charged iron species (Fe(OH)⁺ and Fe(OH)²⁺) can easily attach to the free binding sites [39]. At pH higher (>8.0) the removal of Fe ions was 98.8 and 99.0% which related to the precipitation of metal ion-hydroxides (Fe(OH)₃) [40]. It means that, the modified carrageenan beads with tricarboxy cellulose needs a basic condition to adsorb Fe ions.

3.5. Adsorbent dosage

In addition to, contact time, initial Fe ions concentration, and pH; adsorbent weight can influence the adsorption process. Fig. 5 shows the effect of modified beads dosage on the removal of Fe ions using different amounts of beads (0.1, 0.2, 0.3, 0.4 and 0.5 g) under ambient lab conditions (20 ± 5°C) at pH = 3.3 and 50 ppm of Fe ions for 30 min.

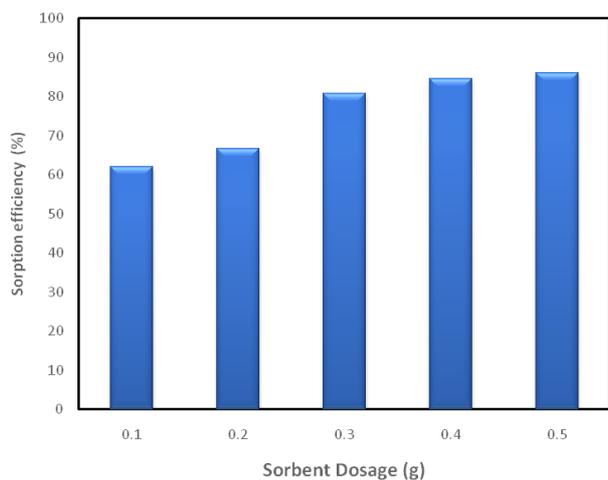


Fig. 5. Effect of modified carrageenan beads with tricarboxy cellulose dosage on the removal of Fe ions.

As expected, the sorption efficiency of Fe ions increased with increasing the modified carrageenan beads with tricarboxy cellulose added. The results can be explained as with increasing the adsorbent amount, further active sites were exposed to Fe ions and the removal percentage increased. However, after a certain amount of adsorbent, removal percentage no longer increased [41].

3.6. Kinetic study

To identify the sorption kinetics of Fe ions removal using modifying carrageenan with tricarboxy cellulose beads as a bio-sorbent, two kinetic models namely pseudo second-order, and intra-particle diffusion model have been discussed. The pseudo-second order as a kinetic model was studied by plotting t/q_t vs. time (Fig. 6A), which suggested that; the metals adsorption involving valance forces through sharing or exchange of electrons between adsorbate and adsorbent [42]. The intra-particle diffusion model was studied by plotting q_t vs. $t^{1/2}$ (Fig. 6B), which suggested that; the adsorbate was transported from the bulk of the solution into the adsorbent through an intraparticle diffusion process [43]. The two kinetic models' constants and correlation coefficients were calculated and listed in Table 1 which indicated that; the sorption kinetics of Fe ions removal using modified carrageenan beads with tricarboxy cellulose as a bio-sorbent follows pseudo second-order model due to the higher correlation coefficient (R^2) value.

3.7. Isotherm study

Adsorption isotherms illustrate how the adsorbate molecules interact with the bio-sorbent particles and in the current study, experimental data were fitted by applying four isotherm models, namely; Freundlich, Langmuir, Temkin and Dubinin–Radushkevich (D–R).

Freundlich isotherm is assuming that the sorption process on a heterogeneous surface is in the form of multilayers [44]. A linear plot between $\log q_e$ and $\log C_e$ (Fig. 7A) gives a slope ($1/n$), where $1/n$ is a function of the

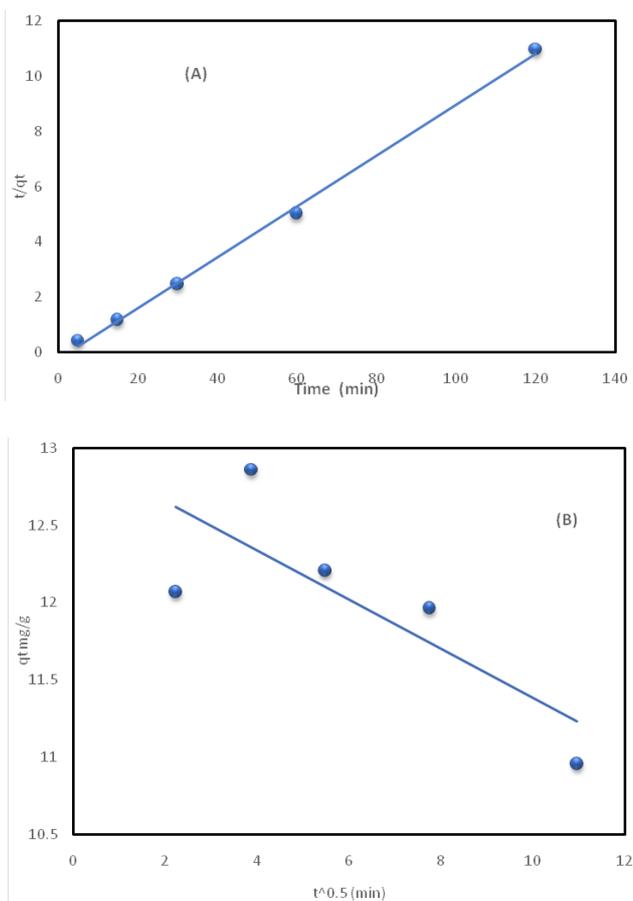


Fig. 6. Pseudo-second-order (A), and intra-particle diffusion model (B) for the adsorption of Fe ions onto modified carrageenan beads with tricarboxy cellulose.

Table 1

Pseudo-second-order and intra-particle diffusion model constants for the adsorption of Fe ions onto modified carrageenan beads with tricarboxy cellulose

Pseudo second-order				Intra-particle diffusion model		
K	q_e	h	R^2	K_p	C	R^2
0.037	10.87	27	0.9981	0.1593	12.973	0.6319

strength of adsorption [45]. If $1/n = 1$ it indicates the partition between the two phases is concentration independent, if $1/n < 1$ it indicates normal adsorption, and if $1/n > 1$ indicates cooperative adsorption [46]. While Langmuir isotherm describes the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. This isotherm studies by plotting C_e/q_e vs. C_e (Fig. 7B). The dimensionless separation factor, R_L was calculated and noted to be always in the range $0 < R_L < 1$ which confirmed that favorable adsorption of Fe ions on modified carrageenan beads with tricarboxy cellulose under these conditions.

The Temkin isotherm assumes that; the sorption energy during the sorption process decreases linearly with increas-

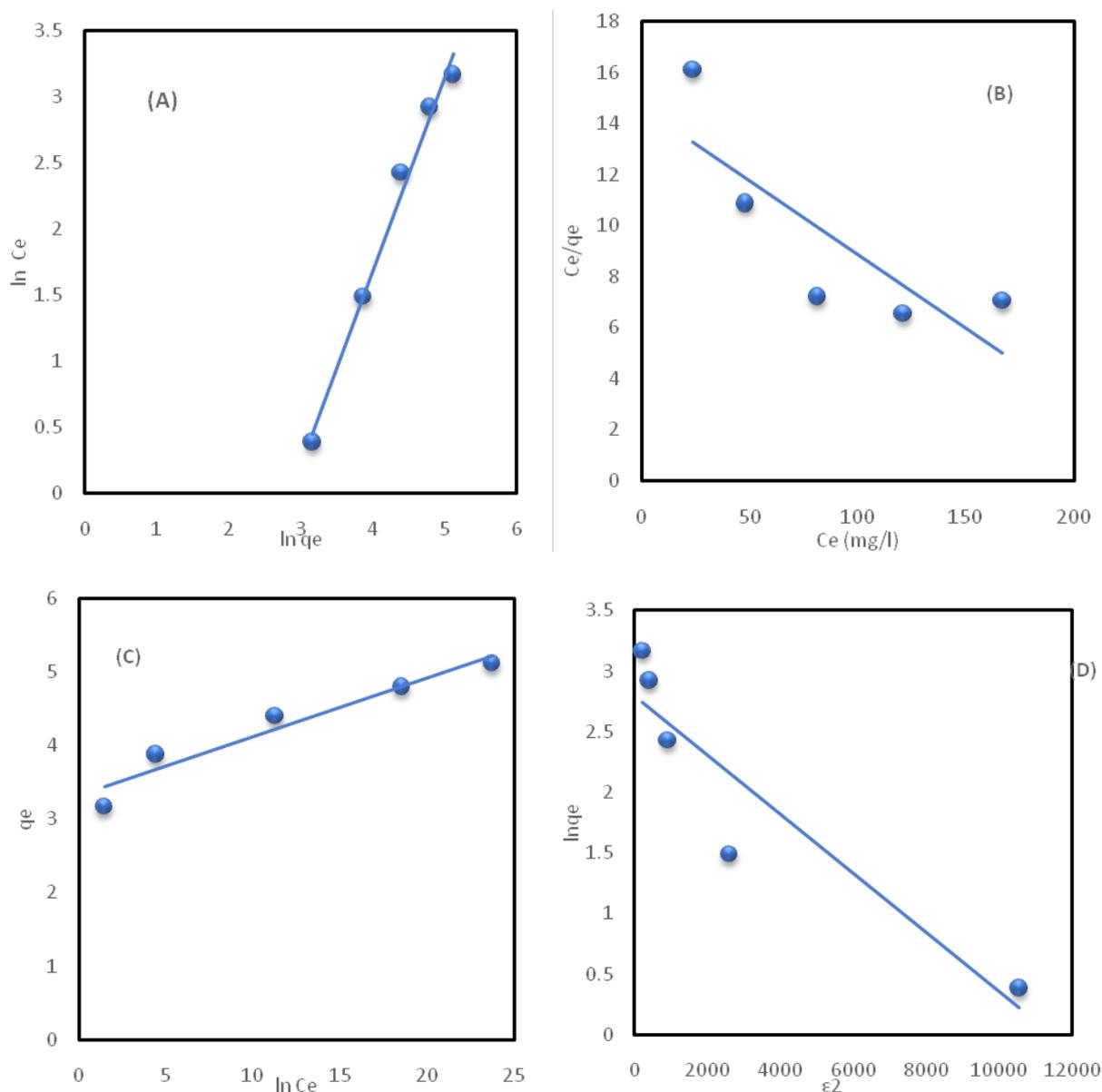


Fig. 7. Freundlich (A), Langmuir (B), Temkin (C), and (D–R) (D) adsorption isotherms for the adsorption of Fe ions onto modified carrageenan beads with tricarboxy cellulose.

ing sorbent dose [47]. For our data, the slope obtained from a linear plot of q_e vs. $\ln C_e$ (Fig. 7C), if (b) has a positive value that means your adsorption process is exothermic one but if it has a negative value, it is endothermic. Note that a value of the constant $b > 8$ kJ/mol indicates a strong interaction between adsorbent and adsorbate [48]. Dubinin–Radushkevich (D–R) isotherm uses to differentiate between physical vs. chemical nature of the sorption process [49]. A linear plot of $\ln q_e$ vs. ϵ^2 gives β (Fig. 7D). The β gives the energy of sorption (E), where a value E is >8 reveals to that; the sorption process follows chemical sorption [50]. The four isotherms models' constants and correlation coefficients were calculated and listed in Table 2. The results indicated that; the reaction of the sorption followed the Freundlich adsorption isotherm due to the higher correlation coefficient

Table 2
Freundlich, Langmuir, Temkin, and (D–R) adsorption isotherms constants for the adsorption of Fe ions onto modified carrageenan beads with tricarboxy cellulose

Freundlich adsorption isotherm			Langmuir adsorption isotherm		
$1/n$	K_f	R^2	q_{max}	b	R^2
1.46	66.5	0.988	17.5	0.004	0.665
Temkin adsorption isotherm			(D–R) adsorption isotherm		
b	A	R^2	β	q_{max}	R^2
30.9	1.04	0.935	0.0002	16.3	0.86

Table 3

A comparison of adsorption capacity for Fe ions by several sorbents at room temperature

Sorbents	Adsorption capacity, (mg/g)	Reference
Granular activated carbon	3.601	48
Coffee ground activated carbon	7.68	49
Modified carrageenan beads with tricarboxy cellulose	17.5	Present work

cient (R^2) value which assumes a multilayers adsorption of the Fe ions onto active sites of the beads surface. The value of $1/n > 1$ in Freundlich, $b > 8$ in Temkin, and $E > 8$ in (D-R) indicating that the adsorption was strong interaction.

The sorption capacities of Fe ions by modified carrageenan beads with tricarboxy cellulose was compared to other sorbent materials (Table 3) and the comparison showed the excellence of carrageenan beads with tricarboxy cellulose for Fe ions removal [51,52].

4. Conclusion

In this study the kinetic adsorption of modified carrageenan beads with tricarboxy cellulose toward removing of Fe ions was studied by studying the effect of contact time, concentrations of Fe ions, adsorbent weight, and pH on removing activity. The data presented in this work revealed a quick removal of Fe ions within the first 15 min followed by decreasing due to the sorption of Fe ions taken place at the active site on the adsorbent surface that initially large numbers were available. The sorption efficiency increased with increasing initial concentration of Fe ions because of the initial concentration delivers an important driving force to overcome all mass transfer resistances between the solid and liquid phases. The sorption efficiency increased with increasing the pH of the solution that attributed to large numbers of protons were available at low pH that may saturate the adsorbent sites. As pH values rose to 4, the H^+ competition disappeared and the positively charged Fe ions can easily attach to the free binding sites. At pH higher than 8.0 precipitations of metal ion-hydroxides could occur. The sorption efficiency of Fe ions increased with increasing the amount of modified carrageenan beads with tricarboxy cellulose added. This attributed to increasing the number of available adsorption sites.

To identify the sorption kinetics of Fe ions; two kinetic models namely pseudo-second-order and intra-particle diffusion model have been discussed and indicated that the sorption kinetics of Fe ions removal follows pseudo second-order model due to the higher correlation coefficient (R^2) value.

Conflict of Interests

The authors declare that they have no conflict to interests.

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