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Kinetic Study of Pb(II) Adsorption on Food-grade κ-Carrageenan Beads

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Abstract
Heavy metal contamination in open waters is one of the most urgent environmental problems that needs to be addressed. Pb(II) ion is a toxic heavy metal ion and is often found contaminating nature. Adsorption is one of the methods that is widely used to overcome heavy metal ion pollution such as Pb(II). One source of material that is low-cost, environmentally friendly, and readily available for use as an adsorbent is carrageenan. Carrageenan is an anionic polysaccharide and is a biopolymer that is widely found in the red algae *Rhodophyceae*. In this research, the adsorbent of κ-carrageenan beads made from food-grade κ-carrageenan cross-linked with K^+ ions was successfully made for the adsorption of Pb(II) ions which was confirmed using FTIR. The adsorbent swelling degree was 25.57% in aqua dm and 83.44% in 100 ppm Pb(II) solution. The results of the adsorption kinetics study show that adsorption follows a pseudo-second order kinetic model with a rate constant of 0.03399 g mg^{-1} min^{-1} and an adsorption capacity of 5.48 mg/g.
Keywords: *adsorption, Pb(II), κ-carrageenan, kinetic study*

Abstrak
Salah satu masalah lingkungan yang mendesak untuk ditanggulangi adalah kontaminasi logam berat di perairan. Ion Pb(II) merupakan salah satu ion logam berat yang beracun dan sering ditemukan mencemari alam. Adsorpsi merupakan salah satu metode yang banyak digunakan untuk mengatasi pencemaran ion logam berat seperti Pb(II). Salah satu sumber material yang murah, ramah lingkungan, dan mudah diperoleh untuk digunakan sebagai adsorben adalah karagenan. Karagenan polisakarida yang bersifat anionik dan merupakan biopolimer yang banyak terkandung dalam alga merah *Rhodophyceae*. Pada penelitian ini, telah berhasil dibuat adsorben bulir κ-karagenan berbahan baku κ-karagenan *food-grade* terikat silang ion K^+ untuk adsorpsi ion Pb(II) dan telah dikonfirmasi menggunakan FTIR. Swelling degree adsorben yang diperoleh adalah sebesar 25,57 % dalam aqua dm dan 83,44 % dalam larutan Pb(II) 100 ppm. Hasil studi kinetika adsorpsi menunjukan adsorpsi mengikuti model kinetika orde dua semu dengan tetapan laju 0,03399 g mg^{-1} min^{-1} dan kapasitas adsorpsi sebesar 5,48 mg/g.
Kata Kunci: *adsorpsi, Pb(II), κ-karagenan, studi kinetika*

1. Introduction

One of the urgent environmental issues that needs to be solved is heavy metal contamination in open waters. Heavy metal ions pollution is usually carried through water flow. Heavy metal ions are commonly very toxic even at low concentrations. e.g. Cd(II), Hg(II), and of course Pb(II) ions. The acceptable limit for Pb(II) consumption for humans, as per the World Health Organization (WHO), is set at 0.025 mg/kg body weight per week [1]. The extensive use of lead metal has resulted in significant Pb(II) contamination in aquatic environments. Humans use lead in gasoline, paint, batteries, and other applications. Lead is dangerous because it can poison the nervous system, affect hematologic functions, and impair kidney performance [2]. These risks can be mitigated by employing an environmentally friendly method that effectively and efficiently removes heavy metal ions such as adsorption [3]. One of the sources of low-cost, *green*, and easily obtained is algae biomass. Algae contain hydrocolloid polysaccharides that can function as adsorbents [4]. One of the least-used marine polysaccharides used as adsorbent is carrageenan.

Carrageenan is a biopolymer widely found in red algae (*Rhodophyceae*). Carrageenan is an anionic biopolymer consisting of D-galactopyranose units alternately linked by β-1,4-glycosidic and α-1,3-glycosidic bonds containing ester sulfate groups [5]. Carrageenan belongs to the galactose polysaccharides naturally containing calcium, magnesium, and sodium bound to the ester sulfate groups of galactose and the copolymer 3,6-anhydro-galactose [6]. Carrageenan is mainly found in three groups i.e. κ-, ι-, and λ-

carrageenan, based on the number and the position of the ester sulfate groups. As for κ-carrageenan, it has good gel-forming properties and is commercially available. Therefore, κ-carrageenan has many applications in food, cosmetics, pharmaceuticals, and biotechnology, with its production reaching 100,000 MT annually [7]. In addition, κ-carrageenan especially has the potential and has already been explored to be used as an adsorbent for heavy metal cations and cationic dyes due to its anionic nature.

Previous studies have demonstrated the efficiency of κ-carrageenan in adsorbing Pb(II) ions from aqueous solutions. For instance, Kalaiselvi et al. investigated the use of porous kappa-carrageenan/cellulose hydrogels for the adsorption of Pb(II) ions, achieving a promising maximum adsorption capacity of 486 ±28.5 mg/g with the Freundlich isotherm model [8]. The applications of carrageenan as an adsorbent become another added value besides commonly researched applications in medicine, such as antifungal agents, drug encapsulation, drug transport, and wound dressings [9]. However, high-purity carrageenan powder normally used in scientific adsorption research is relatively costly. Therefore, in this research, the use of food-grade κ-carrageenan as an adsorbent is explored as it would lower the overall cost of the adsorbent production. In addition, the adsorption effectivity is further explored through a kinetic study.

2. Material and Methods

Material

The materials used in this work include commercial κ-carrageenan powder (refined and semi-refined food-grade powder) purchased from a local market, high purity κ-carrageenan powder (Aldrich), potassium chloride (Merck), nitric acid (Merck), sodium hydroxide (Aldrich), and distilled water. All chemicals were used as received without further purification.

Preparation of κ-carrageenan beads

One gram of refined κ-carrageenan powder was weighed and dissolved in 40 ml of distilled water. The mixture was heated to 80 °C and stirred until fully dissolved. Afterwards, the temperature of the κ-carrageenan solution was adjusted to 60 °C. The κ-carrageenan solution was dropped into 1 M of KCl solution (room temperature) using a pipette to form beads. The mixture was further stirred for one hour to harden the beads. The beads were washed with distilled water and dried in an oven overnight at 40 °C. This procedure is adapted from the work of Mahdavinia et al [10].

FTIR characterization

The sample of dried κ-carrageenan beads, high purity κ-carrageenan powder (Sigma Aldrich), and food-grade κ-carrageenan powder was characterized using FTIR (Shimadzu IRPrestige-21). At first, 20 mg of the sample was mixed with 180 mg of KBr and ground until homogeneous. Using a hydraulic press, the mixture was pressured for five tons for 2 minutes to form a pellet. The resulting pellet was analyzed using an FTIR spectrometer in the 400–4000 cm^{-1}.

Swelling Degree test

The swelling degree was determined by weighing 0.1 grams of dry κ-carrageenan beads. The dry κ-carrageenan beads were then immersed in 50 ml of Pb(II) solution or 50 ml of water for 24 hours. After reaching equilibrium, the κ-carrageenan beads were weighed again. The Equilibrium Degree of Swelling (EDS) is calculated using Equation (1):

$$\boldsymbol{EDS = \frac{W_s - W_i}{W_i} \times 100\%} \qquad \textbf{(1)}$$

where W_i and W_s are the initial weight of the adsorbent and its weight after swelling (g), respectively.

Adsorption Experiments

Erlenmeyer flasks were filled with 20 ml of 100 ppm Pb(II) solution at pH 4 and 0.1 g dry κ-carrageenan beads. The adsorption was conducted for 15, 30, 45, 60, 90, 120, and 240 minutes, assisted with a shaker at 130 rpm. The concentration of Pb(II) after adsorption (C_e) was determined using Flame Atomic Absorption Spectrometry (FAAS, Agilent AA 280 FS).

The adsorption capacity of each sample, q_e (mg/g), was determined using Equation 2:

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

where C_0 and C_e are the initial and equilibrium concentrations of the adsorbate Pb(II) in the solution (mg/L), respectively, V is the volume of the solution (L), and m is the mass of the adsorbent (g).

3. Results and Discussion

Adsorbent Preparation

The κ-carrageenan adsorbent was made by adding κ-carrageenan solution into KCl drop by drop. By utilizing the electrostatic interaction of K^+ and anionic surface of κ-carrageenan, physical crosslinked hydrogel beads are obtained. These interactions connect κ-carrageenan polymer chains through reversible ionic interactions. In this case, K^+ ions from the KCl solution interact with the ester sulfate groups on the κ-carrageenan structure, forming a sturdy and robust hydrogel [11]. κ-carrageenan can create a thermo-reversible natural gel, classified as a natural polymer hydrogel [12]. Therefore, having a high concentration and homogenous solution of κ-carrageenan is necessary in order to promote the formation of sturdy beads. Consequently, the making of κ-carrageenan beads was preceded by solubility experiments on κ-carrageenan powders in water at selected temperature, the results are presented in **Table 1**.

Table 1. Solubility of κ-carrageenan powder in water

Types of κ-carrageenan powder	Concentration (w/v)	Temperature (°C)	Result	Remarks
Semi-refined	2%	60	Not dissolved	Dilute mixture
Semi-refined	2%	80	Not dissolved	Dilute mixture
Refined	2%	60	dissolved	Thick solution
Refined	2,5%	60	Not dissolved	Very thick mixture
Refined	2,5%	80	dissolved	Very thick solution
High purity	2%	80	dissolved	Thick solution
High purity	2,5%	80	dissolved	Very thick solution

According to works presented in **Table 1**, semi-refined κ-carrageenan powder did not produce a homogenous solution. The obtained result might be caused by the relatively high impurities in the powder, indicated by the color of the powder itself i.e. darker than others. The resulting semi-refined mixture is very dilute and unable to form beads with the KCl solution, instead, it dissolves completely with the KCl solution. However, beads can be formed using the refined κ-carrageenan solution at appropriate temperatures. As shown in Table 1, for the use of 2% refined κ-carrageenan, the solution can dissolve perfectly at 60 °C with a stirring speed of 600 rpm. In contrast, a 2.5% refined carrageenan solution does not dissolve perfectly at 60 °C with a stirring speed of 600 rpm. A higher temperature i.e. 80 °C is required to dissolve the 2.5% κ-carrageenan solution. By having higher temperatures, the contact between the solute and the solvent becomes more effective, thus making the solute more easily dissolved at high temperatures [13]. As for beads from the high purity κ-carrageenan powder was also successfully made from its solutions. However, it is not further investigated in this research.

FTIR characterization

The κ-carrageenan powder and beads were analyzed using FTIR to detect functional groups present in its chemical structure. The functional group analysis of the samples is performed by comparing the peaks observed on the infrared spectrum using the FTIR correlation table and the spectrum of a reference compound i.e. high purity κ-carrageenan powder from Aldrich. The structure of κ-carrageenan consists of α(1,3)-D-galactose-4-sulfate and β(1,4)-3,6-anhydro-D-galactose alternating connected by β-1,4-glycosidic and α-1,3-glycosidic bonds.

In the κ-carrageenan repeating unit, there is a galactose ring and anhydro-galactose ring which contain hydroxide groups. The previously mentioned anhydro-galactose also contains a characteristic C-O-C functional group. There is also an ester sulfate group which is characteristic of carrageenan polymers. These three functional groups are typical peaks for identifying carrageenan polymers. The FTIR spectrum

of refined κ-carrageenan (powder and dry beads) and high purity κ-carrageenan powder can be seen in **Figure 1**.

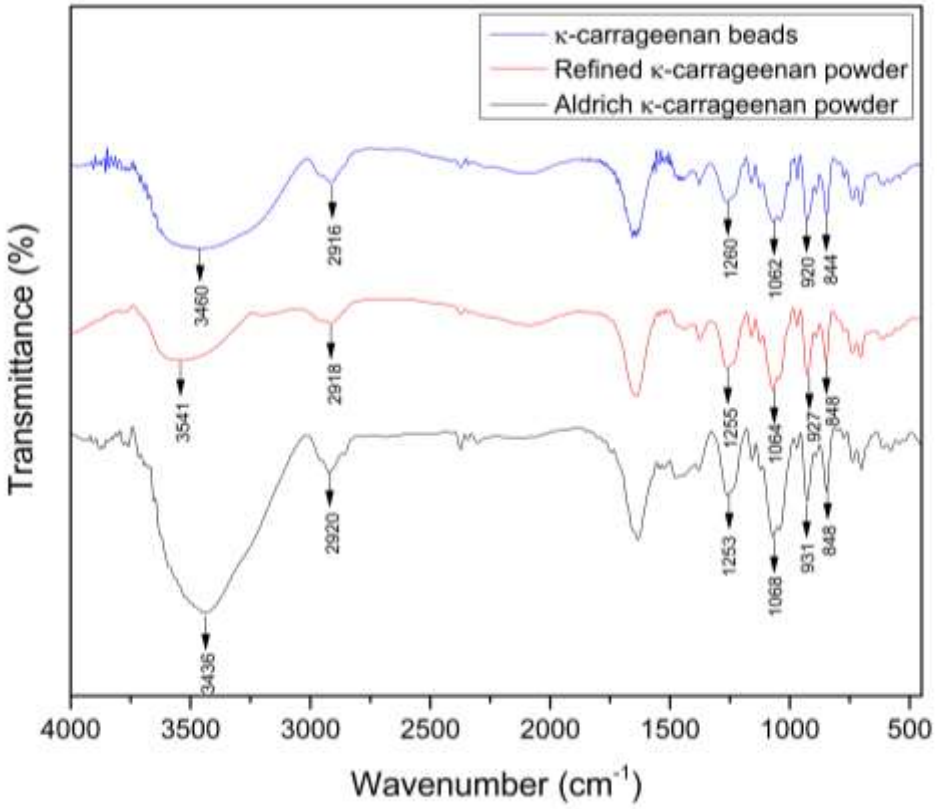

Figure 1. FTIR spectra of κ-carrageenan powder and κ-carrageenan beads.

FTIR characterization of food-grade κ-carrageenan beads, refined κ-carrageenan powder, and high purity κ-carrageenan powder (Aldrich) shows that all three samples contain the same functional groups with several shifts on their peak's wavenumbers. These results confirm that the refined κ-carrageenan powder has comparable purity with the κ-carrageenan from Aldrich. The –OH groups show a broad peak with reasonably high intensity at wavenumbers of 3436 cm^{-1}, 3541 cm^{-1}, and 3460 cm^{-1} for high purity κ-carrageenan powder, refined κ-carrageenan powder, and κ-carrageenan beads, respectively. The C-H group is represented by peaks at 2920 cm^{-1}, 2918 cm^{-1}, and 2916 cm^{-1} for the respective samples. The ester sulfate groups (O=S=O) show peaks at 1253 cm^{-1} for high purity κ-carrageenan powder, 1255 cm^{-1} for food-grade κ-carrageenan powder, and 1260 cm^{-1} for the beads. C–O stretching is indicated by peaks at 1068 cm^{-1}, 1064 cm^{-1}, and 1062 cm^{-1}, respectively. Vibrations in the C-O-C bond of 3,6-anhydro-D-galactose are observed at 931 cm^{-1}, 927 cm^{-1}, and 920 cm^{-1}. Stretching vibrations of $–O-SO_3$ on D-galactose-4-sulfate (G4S) appear at 848 cm^{-1}, 848 cm^{-1}, and 844 cm^{-1} [14]. From the FTIR data, slight shifts in wavenumbers were observed in the κ-carrageenan beads due to the presence and interaction of the crosslinker K^+ with the polymer chains.

Swelling Degree test

Swelling is the process of hydrogel swelling due to the absorption of molecules into the hydrogel structure [15]. In determining the swelling degree, the difference in hydrogel weight before and after absorption is calculated and divided by the dry weight of the hydrogel at a specific pH and temperature. Essentially, swelling occurs due to hydrogen bonds formed between water molecules and hydrophilic groups on the hydrogel polymer chains or interactions between cations/anions and anionic/cationic groups of the hydrogel. Additionally, the crosslinked hydrogel network can trap absorbed molecules within the hydrogel [6].

In general, immersing dry beads with water causes the beads to swell resulting in an increase in size as shown in **Figure 2**. The Equilibrium Degree of Swelling (EDS) of κ-carrageenan beads in water at pH 7 is 25.57%, and the EDS in 100 ppm Pb(II) solution at pH 4 is 83.44%. The EDS value of κ-carrageenan beads in 100 ppm Pb(II) solution at pH 4 is much higher than in water at pH 7. This result might be caused by differences in the strength of interaction between Pb(II) cations with κ-carrageenan which are expected

to be stronger compared to water molecules κ-carrageenan. The presence of Pb(II) ions might disrupt the ion-crosslinked beads thus resulting in higher EDS.

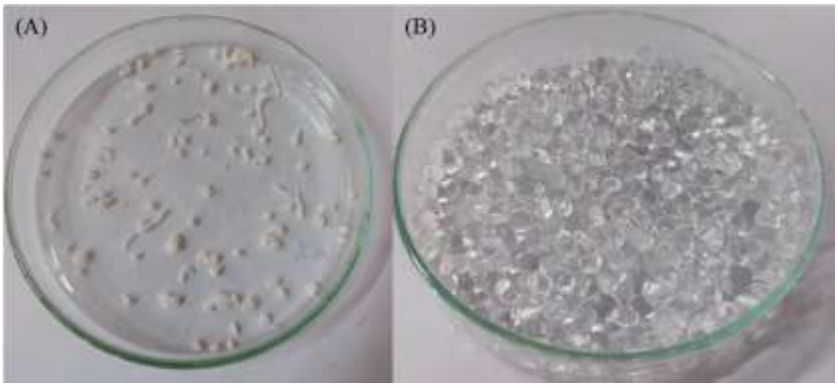

Figure 2. κ-carrageenan beads (A) dry (B) after contact with water for 24 hours

Effect of contact time

Contact time is an essential parameter in the adsorption process because it is related to the adsorption rate and its equilibrium, expressed as the change in adsorption capacity over time. Determining contact time is also used to find the optimal time for adsorption using batch methods based on the adsorption equilibrium. This study used various contact times (i.e. 15, 30, 45, 60, 90, 120, and 240 minutes) to investigate the minimum time needed to reach equilibrium in the adsorption process using κ-carrageenan adsorbent for lead removal from solution.

The results of the contact time test for Pb(II) solution with an initial concentration of 100 mg/L using κ-carrageenan beads adsorbent can be seen in **Figure 3**. Lead adsorption using the adsorbent in the first 15 minutes showed an adsorption capacity of 3.32 mg/g. Then, at 30, 45, and 60 minutes, the adsorption capacity increased significantly to 4.40 mg/g, 5.36 mg/g, and 5.36 mg/g. At 90 minutes, the optimum time was reached, with the highest peak giving an adsorption capacity of 5.48 mg/g. However, in the subsequent minutes, there was a slight decrease, at 120 minutes, the adsorption capacity decreased to 5.19 mg/g. Then, there was an increase at 240 minutes with an adsorption capacity of 5.40 mg/g. These changes were considered as not significant due to the nature of the beads i.e. the size and shape of the beads were not uniform

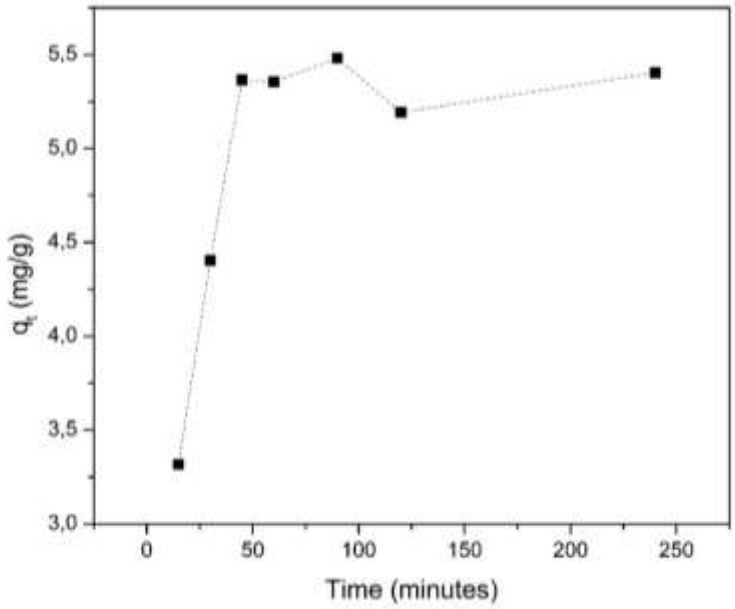

Figure 3. Effects of contact time on adsorption of Pb(II) on refined κ-carrageenan beads

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Adsorption kinetic

The adsorption study of Pb(II) heavy metal ions by κ-carrageenan beads is greatly influenced by pH, requiring an optimum pH for the adsorption system. Tranquilan-Aranilla et al. showed that the optimum pH for Pb(II) ion adsorption is pH 5 [8]. The adsorption rate constant for metal ions using pseudo-first order and pseudo-second order systems is used to investigate the adsorption mechanism.

Two models were used for studying adsorption kinetics: the pseudo-first order Lagergren and the pseudo-second order models. The linear pseudo-first order model is generally expressed as:

$$\ln(q_e - q_t) = \ln q_e - kt \qquad (3)$$

where q_t (mg/g) is the amount of adsorbate which is adsorbed by m grams of adsorbent at time t, q_e is the amount of adsorbate adsorbed by m grams of adsorbent at equilibrium, and $k_{1,ads}$ is the rate constant of adsorption (min^{-1}).

The pseudo-second order model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (4)$$

with q_t (mg/g) as the amount of adsorbate which are adsorbed by m grams of adsorbent at time t, q_e is the amount of adsorbate adsorbed by m grams of adsorbent at equilibrium, and $k_{2,ads}$ are the second order adsorption rate constant.

The determination of the adsorption kinetics model in the pseudo-first order (Eq. **3**) is obtained by plotting the curve of t vs $\log(q_e - q_t)$. As for the pseudo-second order (Eq. **4**), the curve of t vs. t/qt is plotted, as shown in **Figure 4**. It shows the equations and correlation coefficients of each kinetic model in **Table 2**. The pseudo-first order adsorption kinetics of the κ-carrageenan beads adsorbent for Pb(II) ions, based on Equation 3, with a straight-line plot of $\log(q_e - q_t)$ against time t (**Figure 4A)**, yielded the equation of $y = -0.04753x - 1.2481$ with a correlation coefficient of 0.8528. Meanwhile, in **Figure 4B**, the pseudo-second order adsorption kinetics expressed the adsorption kinetics of the κ-carrageenan beads adsorbent for Pb(II) ion adsorption with $y = 0.1803x + 0.9563$ and a correlation coefficient of 0.9973. The results of the kinetic studies showed that the adsorption of Pb(II) ions onto refined κ-carrageenan beads followed the pseudo-second order model. The value of k indicates the speed of the adsorption process; the more significant the k value, the faster the adsorption occurs [16]. Based on the pseudo-first order kinetic model in **Table 2**, the adsorption rate constant for the pseudo-first order kinetic model is 0.00053 min^{-1}. In contrast, the adsorption rate constant for the pseudo-second order kinetic model is 0.03399 g mg^{-1} min^{-1}. The q_e value indicates the amount of adsorbate adsorbed by m grams of adsorbent at equilibrium. The q_e value for the pseudo-first order kinetic model is 3.48 mg/g, while the q_e value for the pseudo-second order kinetic model is 5.55 mg/g which is closer to the experimental results of 5.48 mg/g.

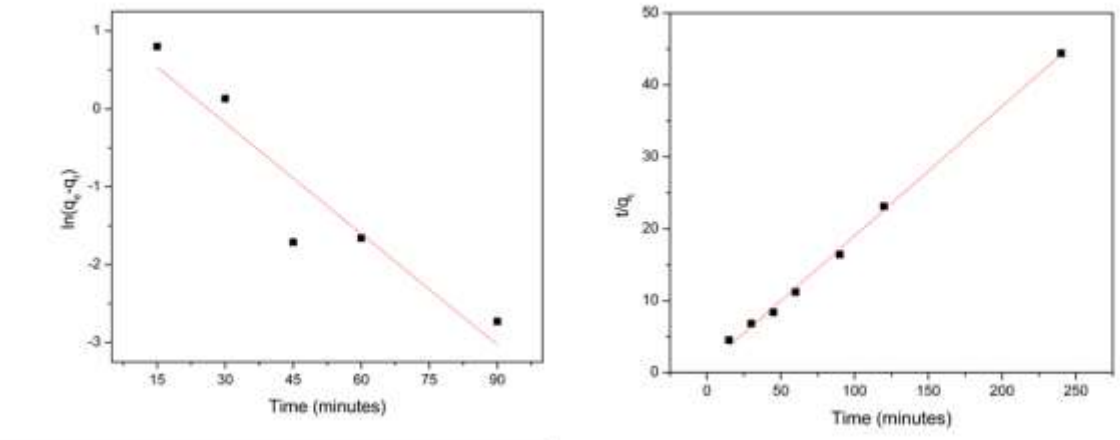

Figure 4. Linear fitting for adsorption kinetics (a) pseudo-first order kinetics (b) pseudo-second order kinetics of adsorption of Pb(II) on refined κ-carrageenan beads

Table 2. Adsorption kinetic parameters for adsorption of Pb(II) on refined κ-carrageenan beads

$q_{e,\,exp}$ (mg/g)	Pseudo-First Order			Pseudo-Second Order		
	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 ($g\ mg^{-1}\ min^{-1}$)	q_e (mg/g)	R^2
5.48	0.00053	3.48	0.8528	0.03399	5.55	0.9973

4. Conclusion

The κ-carrageenan beads made from refined food-grade κ-carrageenan as adsorbents for Pb(II) ion adsorption were successfully carried out. The beads were characterized using FTIR to confirm the presence of their characteristic functional groups. The swelling degree and contact time studies showed that the beads had a higher swelling degree in the Pb(II) solution than in water, with an optimum contact time for adsorption of 90 minutes. The kinetic studies indicated that the adsorption process followed a pseudo-second order model (R^2 = 0.9973). For the pseudo-first order kinetic model, the adsorption rate constant for Pb(II) ions by the κ-carrageenan beads is 0.00053 min^{-1}. In contrast, for the pseudo-second order kinetic model, it is 0.03399 g mg^{-1} min^{-1}. The q_e value, representing the amount of adsorbate adsorbed at equilibrium, is 3.48 mg/g for the pseudo-first order kinetic model and significantly higher at 5.55 mg/g for the pseudo-second order kinetic model. These findings demonstrate the potential of refined κ-carrageenan beads as effective adsorbents for Pb(II) heavy metal ion removal from aqueous solutions.

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