



Adsorption of iron (III) by spent bleaching earth (SBE)-chitosan composite

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ABSTRACT

Spent Bleaching Earth (SBE) is a solid waste generated from the crude palm oil (CPO) bleaching process. SBE has potential as an adsorbent; however, its adsorption capacity is relatively limited and requires enhancement. In this study, the adsorption capacity of SBE was improved by compositing it with chitosan. The research aims to find the best composition of SBE and chitosan and then test its adsorption on Fe (III) which includes pH, contact time, isotherm study and calculation of adsorption capacity. Analysis Fe were measured using Atomic Absorption Spectrophotometer (AAS). The results of the study show that composite ratio variation SBE/Chitosan for Fe (III) adsorption is 4:1, as it exhibited the highest percentage removal of 93.34 %. Adsorption of Fe (III) on the SBE-chitosan composite showed optimal performance at pH 7. with equilibrium time achieved in 50 min. The adsorption follows the Langmuir and Freundlich isotherm, the maximum adsorption capacity determined from Langmuir model was 34.01 mg.g⁻¹.

1. Introduction

The global escalation of heavy metal pollution, particularly iron (Fe), has resulted in significant contamination of soil and water resources [1,2]. Due to their toxicity, persistence, and tendency to bioaccumulate, these ions pose a severe threat to all life forms during prolonged exposure [3,4]. Assessments of various Indonesian rivers indicate widespread heavy metal presence in both water and sediment, with Fe consistently showing higher pollution indices than other metals [5,6]. High concentrations of Fe are linked to skin cell degradation and premature aging; furthermore, systemic accumulation can lead to ulcers, cognitive decline, and organ damage in the liver and brain [4]. Consequently, developing effective methods to sequester Fe from water supplies is a public health necessity. To reduce heavy metal pollution, especially Fe in acidic coal mine water, an adsorbent that is resistant to acidic conditions and can absorb metals is needed.

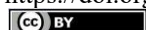
One promising adsorbent material is Spent Bleaching Earth (SBE), a waste product from the decolorization process in Crude Palm Oil (CPO) refining. SBE is the

largest waste stream in the industry, accounting for 0.5–2.0 % of the total processed CPO mass. However, SBE has limited adsorption capacity and thus requires reactivation to enhance its adsorption performance [7,8].

Previous research on SBE adsorption of methylene blue produced a maximum adsorption capacity 40.485 mg/g, and adsorption isotherm analysis showed that the adsorption mechanism was in accordance with the Langmuir isotherm model [9]. The dye tartrazine yellow adsorption efficiency of 48 %, and Elovich models [10]. The CO₂ adsorption capacity of 344.98 mg/g, and regeneration study revealed that the spent Chi-BE was recycled 10 times [11]. Tetracycline hydrochloride (TCH) removal efficiency Fe0/SBE carbon + PS system 78.2 % [12]. The adsorption capacity of SBE/C was independent on pH (5-12), Combined with characterization analysis, the adsorption mechanism likely includes electrostatic interaction, hydrogen bonding, hydrophobic interaction, halogen bonding and π - π interaction. Overall, this exploration of SBE/C might open a window to the design of an efficient and low-cost adsorbent for Eosin Y dye elimination from wastewater [13]. The CO₂ adsorption capacity on RSBE produced by

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heat treatment followed by nitric acid treatment was shown to be more effective than RSBE produced by direct heat treatment. RSBE₅₀₀HNO₃ offered highest surface area (192.81 m².g⁻¹) and give highest CO₂ adsorption capacity of 86.67 mg CO₂/g [14]. The absorbent SBE was effective to remove methylene blue from aqueous solution with removal efficiency 99.97 % in 120 min, and it was found that Langmuir isotherm fitted to data of experiment with adsorption capacity 0.5 mg/g [15].

The best Spent Mushroom Substrate (SMS)-SBE material comparison was found at a composition of 75 %:25 %, which was further characterized. The materials of SMS, SBE, and composite adsorbent have surface areas of 836.62 m².g⁻¹, 788,82 m².g⁻¹, and 812,721 m².g⁻¹. Based on the FTIR spectrum, the presence of hydroxyl groups, alkanes, ketones, amides, esters, carboxyl, and aromatic compounds on the SMS, and SBE consisting of OH groups, amine, Si-O, as well as composite adsorbent have hydroxyl, NH, and P-OH groups as a heavy metal binder [16]. The use of SBE as an adsorbent requires reactivation, and its performance can be enhanced by compositing the SBE material with chitosan. Chitosan is a material derived from crustacean shell waste. Its highly varied uses are based on the numerous amine groups along the chitosan polymer chain, which increase chitosan's adsorption capacity [17]. This is based on the presence of hydroxyl and amino groups in the chitosan polymer chain, which makes it effective in binding organic cations and heavy metal ions [18,19].

2. Materials and Methods

2.1. Materials and tools

The equipment used includes analytical balance, filter paper, 100-mesh sieve, mortar and pestle, standard laboratory glassware, universal indicator, oven, furnace, Soxhlet apparatus, hotplate, Fourier Transform Infrared (FTIR 8201PC Shimadzu) Spectrophotometer, X-Ray Fluorescence (XRF), and Atomic Absorption Spectroscopy (AAS-GBC Avanta Ω). The materials utilized comprised Spent Bleaching Earth (SBE), commercial chitosan (degree of deacetylation 97.03 %), 16 M nitric acid (HNO₃), distilled water, technical grade acetone, concentrated acetic acid (99 %), FeCl₃, 37 % hydrochloric acid (HCl), solid sodium hydroxide (NaOH).

2.2. Preparation of spent bleaching earth (SBE)

SBE was ground using a mortar and pestle and sieved to obtain particles passing through a 100-mesh sieve. Oil extraction was performed using a Soxhlet apparatus with acetone as the solvent. Specifically, 50 gs of the ground SBE were placed into a thimble, which was subsequently inserted into the Soxhlet extractor. Approximately 500

mL of acetone was added, and the extraction process was conducted at 72 °C for 8 h.

2.3. Activation of Spent Bleaching Earth (SBE)

The activation process involved treatment with 0.8 M HNO₃ solution. A mixture of SBE and HNO₃ solution at a ratio of 1:10 (g.mL⁻¹) was stirred using a magnetic stirrer at 70°C and 300 rpm for 1 hour. The resulting solid residue was thoroughly washed with distilled water and dried in an oven at 105 °C for 24 h. Subsequently, the material underwent carbonization in a furnace at 500 °C for 2 h [19]. Characterization of SBE before and after activation was conducted using FTIR and X-Ray Fluorescence (XRF).

2.4. Synthesis of Spent Bleaching Earth (SBE)-Chitosan Composite

The composite preparation was carried out with variations in the SBE: Chitosan ratio (w/w) in grams, namely 1:1, 2:1, 3:1, and 4:1. For the 1:1 and 2:1 ratio variations, 1 gram of chitosan was dissolved in 10 mL of 1 % acetic acid solution. For the 3:1 and 4:1 ratio variations, 1 gram of chitosan was dissolved in 25 mL of 1 % acetic acid solution. The SBE/Chitosan composite that had formed was then dried in an oven at 70–80 °C. After drying, the composite was ground until it reached a homogeneous particle size of 100 mesh.

2.5. Effect of pH on adsorption

2 g adsorbent and 40 ppm Fe solution were placed into separate 100 mL beakers and stirred using a magnetic stirrer for 30 min. The solution was then filtered, and the obtained filtrate was measured using Atomic Absorption Spectroscopy (AAS). The pH determination was carried out using a 40 ppm Fe solution with pH variations of 2, 3, 4, 5, 7, and 9. The solution pH was adjusted using 0.1 M HCl and 0.1 M NaOH solutions.

2.6. Effect of contact time

2 g adsorbent and 40 ppm Fe solution were placed into separate 100 mL Erlenmeyer flasks and stirred using a magnetic stirrer with contact time variations of 30, 50, 70, 90, and 110 min, conducted at the optimum pH. The solution was then filtered, and the obtained filtrate was measured using Atomic Absorption Spectroscopy (AAS).

2.7. Kinetics of adsorption

In order to obtain a suitable rate equation and investigate the controlling mechanism of adsorption process, the two main types of sorption kinetic models, pseudo-first and pseudo-second order models were considered. The pseudo-first-order reaction equation of Lagergren is widely used for the adsorption of liquid/solid system on the basis of solid capacity. This

model assumes that the rate of change of surface site concentration is proportional to the amount of surface sites remaining unoccupied. Its linearized form is given as Eq. (1):

$$\log(qe - qt) = \log qe - \left(\frac{k_1}{2.303t}\right) t \quad (1)$$

where qe and qt are the amounts of adsorbed metal ions per unit mass of biosorbent at the equilibrium (mmol/g) and at time t , respectively and k_1 is the Lagergren rate constant of the first-order adsorption (min^{-1}). The pseudo-second-order model assumes that the rate is proportional to the square of the number of remaining free surface sites [39]. The linearized second-order kinetic model is given as Eq. (2):

$$\frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{t}{qe} \quad (2)$$

where k_2 is the rate constant for the second-order adsorption kinetics ($\text{g.mmol}^{-1}.\text{min}^{-1}$).

2.8. Adsorption thermodynamic studies

Adsorption standard enthalpy change (ΔH°), standard free energy change (ΔG°) and standard entropy change (ΔS°) are thermodynamic parameters that can be obtained by the Eq. (3):

$$\Delta G^\circ = RT \ln K_e \quad (3)$$

where ΔG° is the standard Gibbs free energy change (J), T is the absolute temperature (K), R is the universal gas constant ($\text{J.mol}^{-1}.\text{K}^{-1}$), and K_e is an equilibrium constant defined as Eq. (4-6):

$$K_e = CA_e / C_e \quad (4)$$

$$CA_e = C_0 - C_e \quad (5)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (6)$$

where C_e and CA_e correspond to the equilibrium concentration of heavy metal ions on the solution and on the adsorbent, respectively.

According to thermodynamics, the Gibbs free energy change is also related to the entropy change and heat of adsorption at constant temperature by the following equation.

2.9. Determination of adsorption capacity

The determination of adsorption capacity was carried out at the optimum pH and contact time. Fe solutions with concentration variations of 25, 50, 75, 100, 150, and 200 ppm were prepared and adjusted to the previously determined optimum pH and contact time. 2 g adsorbent and the Fe solution were placed into separate 250 mL Erlenmeyer flasks and stirred using a magnetic stirrer for 50 min. The solution was then filtered, and the obtained filtrate was measured using Atomic Absorption Spectroscopy (AAS).

The Langmuir adsorption isotherm equation can be

written as Eq. (7):

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{1}{q_{\max}} C_e \quad (7)$$

where qe (mg.g^{-1}) is the amount of adsorbate adsorbed at equilibrium, C_e (mg.L^{-1}) is the equilibrium concentration of the solution, K_L (L.mg^{-1}) is the Langmuir constant related to the adsorption energy, which is determined from the slope and intercept of the linear plot of C_e/q_e versus C_e , and $q_{\max}$ (mg.g^{-1}) represents the maximum adsorption capacity of the adsorbent. The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L which is used to predict if an adsorption system is “favorable” or “unfavorable”. The separation factor, R_L is defined by Eq. (8):

$$R_L = \frac{1}{1 + b C_0} \quad (8)$$

The Freundlich adsorption isotherm equation is expressed as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (9)$$

where qe (mg.g^{-1}) is the amount of adsorbate adsorbed at equilibrium, C_e (mg.L^{-1}) is the equilibrium concentration of the solution, and K_F and $1/n$ are the Freundlich constants representing the adsorption capacity and adsorption intensity, respectively.

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3. Results and Discussion

3.1. Activation of spent bleaching earth (SBE)

Adsorption is one of the effective and widely used water treatment processes for reducing heavy metal concentrations. Several factors such as surface area, particle size, pore number, and functional groups on the surface influence adsorption capacity. Adsorbents can be modified to enhance their ability to remove metal ions from solution, for example through activation to increase their adsorption capacity [20]. Spent Bleaching Earth (SBE) is a porous material classified as bentonite clay. The use of SBE in metal adsorption is still limited; therefore, an activation process is required. The activation stage in this study was carried out using acid treatment and heating. The use of 1 M HNO_3 solution can produce an adsorbent with higher adsorption capability, while the heating stage aims to remove water bound within the molecular pores, thereby increasing its porosity [21]. The measurement data of Spent Bleaching Earth (SBE) before and after activation using X-Ray Fluorescence (XRF) and Fourier Transform Infrared (FT-IR) are presented in Table 1. Based on Table 1, the silica

(SiO₂) content in the activated SBE increased by 41.74 %, while the alumina (Al₂O₃) content also increased by 4.37 %. This research is in accordance with previous research, where the content of Al and Si as the main components of SBE is shown in Table 2.

Table 1. Analysis SBE before and after activation by X-Ray Fluorescence (XRF)

Parameter	SBE before activation	SBE after activation
Silika (SiO ₂)	26.45 %	68.19 %
Alumina (Al ₂ O ₃)	3.71 %	8.08 %

Table 2. Chemical compositions (mass %) of spent bleaching earth (SBE) [22].

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Reference
79.8	8.7	1.9	3.2	0.7	[23]
56.9	9.24	8.27	4.32	3.9	[24]
37.45	8.01	0.83	1.28	0.78	[25]
65-75	15-20	2	2.5	0.5	[26]

The results of the FTIR analysis of Spent Bleaching Earth (SBE) powder, Soxhlet-extracted SBE, and Activated SBE are shown in (Fig. 1 Supp.). The identification of each functional group in the infrared spectra of raw SBE powder, Soxhlet-extracted SBE, and activated SBE (c) can be seen in Table 3.

The infrared spectrum results on the characteristics of SBE powder have symmetric O-H stretching vibration functional groups between layers at wave numbers 3,400-3,650 cm⁻¹.

At 2,921.20 cm⁻¹ and 2,852.10 cm⁻¹ are symmetric aliphatic CH₂ and asymmetric stretching vibrations, after the calcination process, these absorption bands disappear, which is direct evidence that the remains of organic matter have been converted into carbon species during the heating process. At 1,743.89 cm⁻¹ to 1,455.48 cm⁻¹ indicate the presence of C=O bonds and C=C or O-H bonds, which represent unsaturated vegetable oils in SBE [27].

These peaks disappear in the soxhleted SBE, as shown

in Figure 1(b), due to the soxhlet extraction of oil residues in SBE from the surface and inner pores of SBE.

The aliphatic CH₂ group during soxhletation decreased in intensity and disappeared upon activation. This is because the aliphatic group was activated using HNO₃ to remove organic impurities and heated in a furnace at 500°C, causing the aliphatic CH₂ to evaporate and become undetectable in the infrared spectrum in Figure 3(c). The characteristic peaks of bleaching earth are present at 1,016.16 cm⁻¹ and 798.04 cm⁻¹ and indicate the silicate (Si-O-Si) and silica/quartz (Si-O bending vibration in kaolinite) matrices are maintained throughout the sample, respectively, as shown in Figure 1, confirming that bleaching earth maintains its core matrix during extraction [27].

FTIR results also show a characteristic absorption peak at 1,640 cm⁻¹, indicating the presence of structural water in the matrix or hydroxyl bending vibrations. This research is in accordance with FTIR SBE, wave numbers 3,620.54 cm⁻¹ and 3,694.81 cm⁻¹ indicate the stretching vibration of the N-H group.

The wave number of 1,710.93 cm⁻¹ indicates the presence of an amine group that functions as a metal binder. The presence of a wide absorption band at a wave number of 1,033.89 cm⁻¹ indicates the characteristics of Si-O-Si or SiO₂. Besides that, the Si-O-Al vibration is also observed at a wave number of 798.56 cm⁻¹ [16].

3.2. Synthesis of chitosan-SBE composite

Chitosan is a potential biosorbent containing numerous hydroxyl (-OH) and amino (-NH₂) functional groups that can bind metal ions. However, pure chitosan as an adsorbent has limitations due to its low surface area, tendency to agglomerate, and high solubility in acidic conditions; therefore, it requires modification. Chitosan also has low mechanical strength and stability, so its performance in binding metal ions simultaneously needs to be improved.

Improved performance of chitosan can be achieved by combining it with other materials, such as inorganic natural materials, such as SBE [27,28].

Table 3. Identification of functional groups in the infrared spectra of Spent Bleaching Earth (SBE), Soxhlet-extracted SBE, and activated SBE.

Spent Bleaching Earth (SBE) (cm ⁻¹)	Spent Bleaching Earth (SBE) -0.8M HNO ₃	Spent Bleaching Earth (SBE) 0.8M HNO ₃ , 500 °C	Reference wavenumber (cm ⁻¹)	Functional group
3534.44	3550.03	3390.34	3412-3100	Symmetric stretching vibration O-H
2921.20 & 2852.10	2925.20 & 2854.28	-	2924-2855	Symmetric stretching vibration CH and acymetric CH ₂ aliphatic
1743	-	-	1745-1700	C=O
1650.90	1644.52	1632.79	1650-1600	O-H
976.69	1349.69	1016.16	1040-1070	Si-O-Si
796.81	797.33	798.04	780-797	Silica amorf

An example of an inorganic natural material that also possesses adsorptive properties is SBE, which has a porous structure. The composite was prepared with variations in the SBE: Chitosan ratio (in grams), namely 1:1, 2:1, 3:1, and 4:1. The determination of the best SBE/Chitosan composite variation was carried out by contacting a 40 ppm Fe solution, and the obtained filtrate was measured using Atomic Absorption Spectroscopy (AAS).

Based on Table 4, the results show that the best composite ratio variation for Fe (III) adsorption is 4:1, as it exhibited the highest percentage removal of 93.34 %.

Table 4. Adsorption Fe (III) composite SBE/chitosan

Concentration Fe (ppm)	% adsorption				
	1:0	1:1	2:1	3:1	4:1
18.32 ppm	60.43	67.41	73.43	84.11	93.34

The obtained results indicate that the performance of the SBE/Chitosan composite is very good, as evidenced by the removal percentage approaching 100 %. This is very likely due to the higher SBE content, which allows greater metal uptake through its porous structure. SBE is an alumina silicate material, meaning that Al is present within the silica framework. The +3 charge of Al creates a negatively charged framework. This enables it to bind with metal cations, thereby enhancing the metal adsorption capacity of the composite as the SBE to chitosan ratio increases. The hydroxyl and amino groups along the chitosan polymer chain make it highly effective in binding cations from both organic substances and heavy metal ions. The interaction between chitosan and metal cations occurs through the formation of coordination chelates involving the N atom of the amino group and the O atom of the hydroxyl group [30]. This is why chitosan is frequently utilized as an adsorbent for heavy metals, through the protonation of free amino groups ($-\text{NH}_2$) into cationic amino groups ($-\text{NH}_3^+$). This cationic property forms the basis of most chitosan applications [31].

Characterized Fourier Transform Infrared (FTIR) shown in (Fig. 2 Supp.). Identification of functional groups in the infrared spectra of SBE and SBE Chitosan composite can be seen in Table 5.

Table 5. Identification of functional groups in the infrared spectra of SBE and SBE Chitosan composite

SBE	SBE-Chitosan	Reference wavenumber (cm^{-1})	Functional group
3390.34	3242.81	3412-3100	Symmetric stretching vibration O-H
1632.79	1632.79	1650-1600	O-H
	1582.38	1640-1540	N-H
1016.16	1013.88	1040-1070	Si-O-Si
798.04	776.00	780-797	Silica amorf

In (Fig. 2 (a) Supp.), the IR spectrum of the SBE–chitosan composite shows an absorption peak at a wave number of 3390.34cm^{-1} , corresponding to the stretching vibration of hydroxyl groups ($-\text{OH}$). When the SBE–chitosan composite. Wave number 1016.16 cm^{-1} and 798.04 cm^{-1} , which are attributed to Si–O stretching and Si–O bending vibrations of silicate and silica/quartz. (Fig. 2 (b) Supp.) an absorption peak at a wave number 3242.81 cm^{-1} corresponding to the stretching vibration of hydroxyl groups ($-\text{OH}$), peak at 1582.38 cm^{-1} is assigned to the N–H bending and stretching vibrations of amine groups ($-\text{NH}_2$) present in chitosan. Characteristic bands corresponding to the Spent Bleaching Earth (SBE) matrix are observed at 1013.88 cm^{-1} and 776.00 cm^{-1} , which are attributed to Si–O stretching and Si–O bending vibrations of silicate and silica/quartz frameworks, respectively[32].

3.3. Effect of pH on adsorption

The effect of pH was determined by using a 4:1 adsorbent variation, then contacting it with Fe solution at pH 2, 3, 4, 5, 7, and 9. The filtrate obtained was measured using Atomic Absorption Spectroscopy (AAS). The data from the measurement of Fe(III) are shown in the following Figure 1.

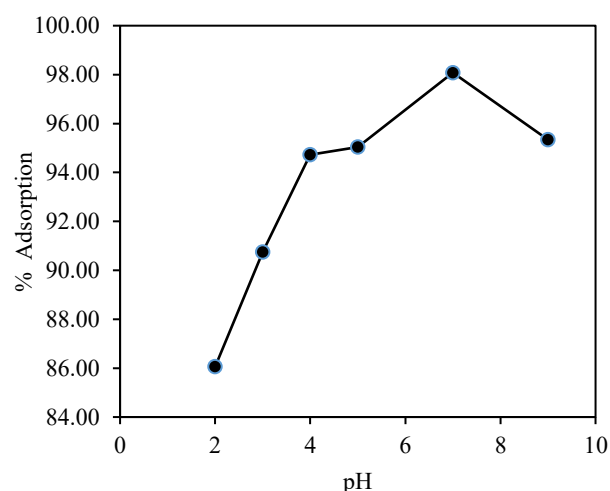


Fig. 1. Effect of pH on % adsorption Fe(III)

The results of the study showed that the highest adsorption percentage occurred at pH 7, with an adsorption rate of 98.08 %. Meanwhile, the lowest adsorption percentage was observed at pH 9, at only 94.34 %. Based on Figure 1, the adsorption of Fe(III) decreased from pH 1 to 3, and then increased from pH 3 to 5. This is due to the decreasing number of H^+ protons in the solution, allowing more Fe(III) ions to bind to the epichlorohydrin-crosslinked SBE–chitosan composite. The highest adsorption capacity was observed when the solution was at pH 5. This research is in line with adsorption of Cu(II), Cd(II) and Pb(II) the optimum pH values for the chitosan crosslinked with epichlorohydrin-triphosphate as the adsorbent were 6.0, 7.0 and 5.0 [33].

Adsorption of methylene blue and reactive red 120 dyes composite chitosan-epichlorohydrin/zeolite at pH 9 optimum for methylene blue and pH 6 for reactive red 120 [34].

In acidic conditions, there are a large number of H^+ protons that can bind to active groups ($-NH_2$) of chitosan and hydroxyl active groups, leading to competition between Fe(III) ions and hydrogen ions for access to the amine and hydroxyl active sites. H^+ protons, being harder Lewis acids than Fe(III), reduce the likelihood of Fe(III) binding to the adsorbent, thus decreasing the efficiency of Fe(III) ion removal.

On the other hand, at $pH > 8.5$, Fe(III) precipitates completely as pH increases, the concentration of OH^- ions also increases, strengthening the interaction between Fe(III) ions and OH^- [35]. At pH values below 5, the high concentration of H^+ ions leads to protonation of the active groups in the epichlorohydrin-crosslinked SBE-chitosan adsorbent, particularly the protonation of $-NH_2$ (amine) to $-NH_3^+$ [36].

The higher the H^+ concentration, the greater the tendency for active group protonation, reducing Fe(III) adsorption due to the lack of free electron pairs available for bonding. At pH 5, Fe(III) is believed to have higher affinity for binding with the adsorbent's active groups, leading to increased ion adsorption. This result is consistent with finding [37]. Subsequently, the amount of Fe(III) adsorbed decreases as the solution pH continues to rise. This is due to the reduced solubility of the metal in solution, as Fe(III) remains in the form of $Fe(OH)_3$ [38], under alkaline conditions, the Iron(III) hydroxide that is formed will precipitate so that the concentration of dissolved Fe^{3+} decreases, so that true adsorption is reduced.

3.4. Effect of time contract

The adsorption of Fe(III) on SBE-Chitosan to determine the adsorption equilibrium time was carried out at contact times of 30, 50, 70, 90, and 110 min. The variation in contact time can be seen in Figure 2.

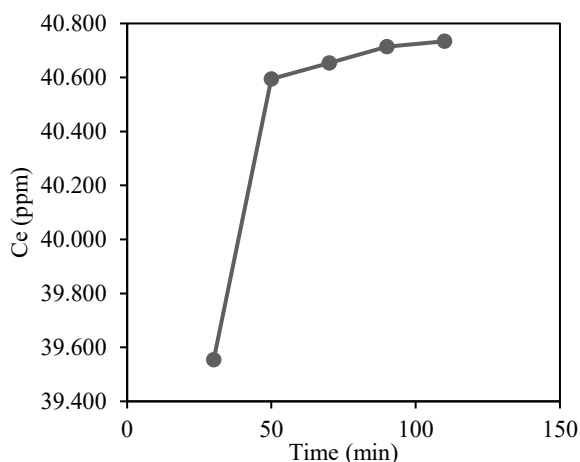


Fig. 2. Effect of time contract on % adsorption Fe(III)

The results of the study show that optimal adsorption was already achieved at a contact time of 50 min, with no significant increase thereafter. The peak adsorption was reached at 110 min, with a value of 99.538 %. Between 50 and 110 min, the adsorption level gradually increased not significant.

When adsorbate molecules come into contact with the surface of the adsorbent, some molecules bind to the surface, while others are repelled. At the beginning of the contact time, the interaction is quite strong due to the abundance of available active sites on the adsorbent surface, resulting in a rapid increase in the adsorption rate. However, as contact time continues, the process approaches equilibrium and eventually stabilizes. Adsorption of humic acid from aqueous solutions on crosslinked chitosan-epichlorohydrin beads, after 50 min, it can be observed that the adsorption capacity remained constant and this implies that adsorption has reached the equilibrium state [39], removal of copper(II) ions from aqueous solution on chitosan and cross-linked chitosan beads [40], adsorption behavior of Fe(II) and Fe(III) ions in aqueous solution on chitosan and cross-linked chitosan beads [17].

3.5. Kinetics of adsorption

The results of calculations using two types of sorption kinetic models, pseudo-first and pseudo-second order models using equations (1) and (2), found that the adsorption of Fe(III) on the SBE-chitosan composite follows pseudo-second order models. Where R^2 is 1 (Figure 3).

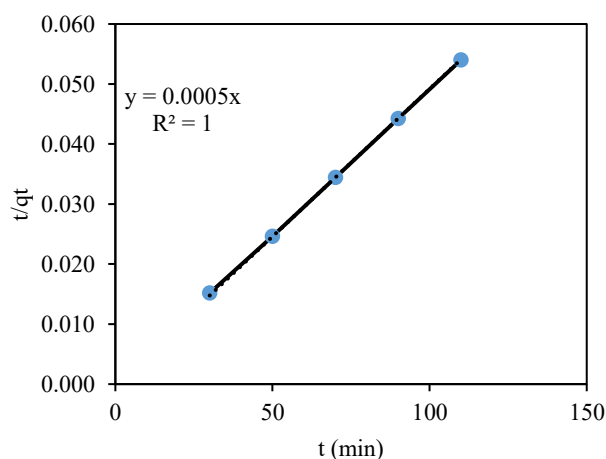


Fig. 3. Pseudo-second-order kinetics of the uptake adsorption Fe(III) on SBE chitosan composite

Whereas, the second-order kinetic model assumes that the rate-limiting step may be chemical adsorption. In many cases, the second-order equation correlates well to the adsorption studies. It is more likely to predict that the adsorption behavior may involve valency forces through sharing of electrons between transition metal cations and adsorbent.

3.6. Adsorption thermodynamic studies

The thermodynamic adsorption studies SBE-chitosan composite, were carried out at pH 7, with an initial concentration of 41,334 ppm at a solution volume of 100 ml and an adsorbent weight of 2 g, where the room temperature was 32 °C. Calculations using equations 3 to 6 produce the results following.

$$CA_e = 0.740$$

$$K_e = 54.857$$

$$\Delta G^\circ = -RT \ln K_e = -10155.074 \text{ J/mol}$$

$$= -10.155074 \text{ KJ/mol}$$

Shows, the adsorption process is spontaneous, adsorption can occur naturally without additional energy.

3.7. Determination of adsorption capacity

The adsorption capacity of the SBE and SBE-chitosan composite for Fe(III) was determined at pH 7 and a contact time of 50 min. The equations used to describe the liquid adsorption process on solid surfaces are the Langmuir and Freundlich isotherms. The use of adsorption isotherms aims to illustrate the interaction between the adsorbent and the adsorbate [39]. To observe the adsorption isotherm that occurs in the adsorption process of the SBE chitosan ECH composite, it is calculated using equations 1 and 2. The adsorption

isotherm plots of the Langmuir and Freundlich models for Fe(III) on SBE and SBE-Chitosan composite can be seen in Figures 4 and 5. Figures 4 and 5 shows that the adsorption follows the Langmuir and Freundlich isotherm, the maximum adsorption capacity SBE determined from Langmuir model was 22.22 mg.g⁻¹, and SBE-Chitosan was 34.01 mg.g⁻¹. This is research that has been conducted by study using methylene blue following the Langmuir isotherm model and the maximum adsorption capacity of 40.485 mg.g⁻¹ [9]. Clay activated carbon adsorbent obtained by activation of spent bleaching earth and its application for removing Pb(II) ion, adsorption capacity (206.65 mg.g⁻¹) and the adsorption follows the Langmuir and Freundlich isotherm [42,43]. Adsorption mechanism of Cu (II) by SBE is in accordance with the Langmuir isotherm model [41]. Adsorption capacity of chitosan-epichlorohydrin (ECH) beads towards humic acid, the adsorption isotherm was fitted well by Langmuir and Freundlich models and the maximum adsorption capacity determined from Langmuir model was 44.84 mg.g⁻¹ [39]. Chitosan was used in combination of Fe₃O₄ magnetite nanoparticles (MNPs) for the preparation of a magnetic composite (Fe₃O₄-chitosan) isotherm was fitted well by Freundlich model and maximum adsorption capacity was 9.43 mg.g⁻¹ [21,45].

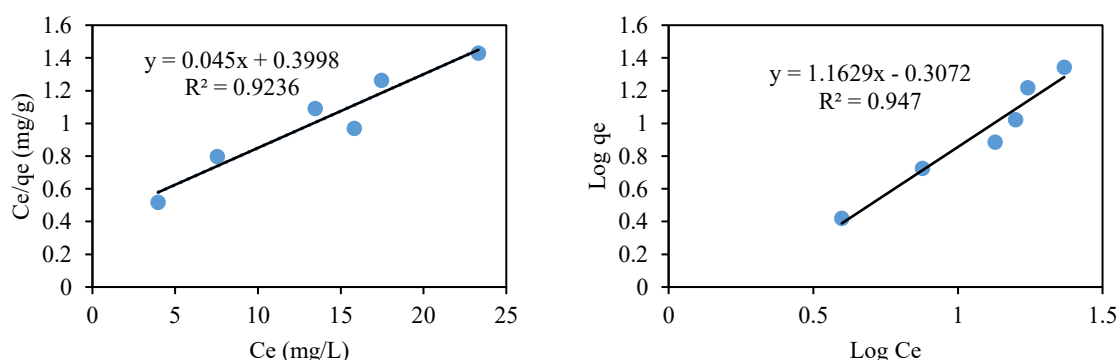


Fig. 4. Isotherm Langmuir and Freundlich for Fe(III) SBE

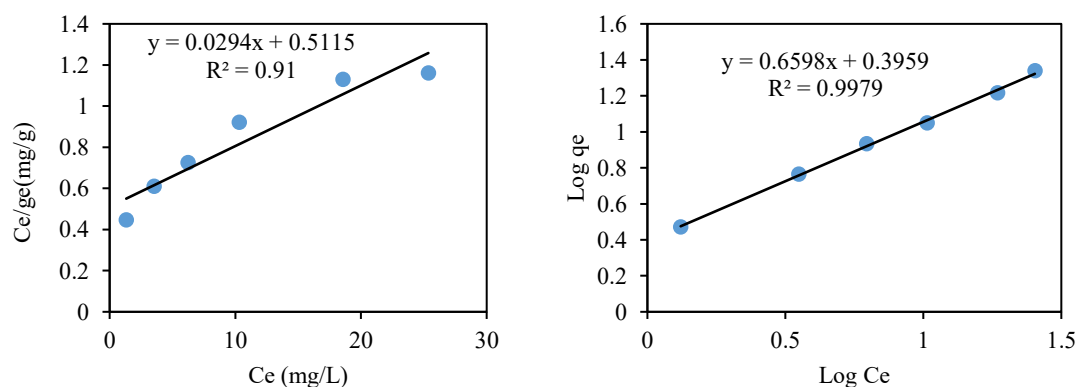


Fig. 5. Isotherm Langmuir and Freundlich for Fe(III) SBE-Chitosan

Adsorption Metilen Blue dye from wastewater by clay-chitosan composite, the Langmuir model was suitable for modeling the adsorption and adsorption capacities were 97.08 mg.g^{-1} [31]. Chitosan composite of metal-organic framework (CS/MOF-235) synthesized by solvo-thermal process shows adsorption capacity of 2833 mg.g^{-1} methylene orange (MO) and 2467 mg.g^{-1} metylen blue (MB), and isotherm was fitted well by Langmuir isotherm model [46]. Adsorption of chitosan for the removal of Fe(II) ions from aqueous phase, the adsorption isotherm were well fitted with Langmuir–Freundlich model, with maximum capacity of 28.7 mg.g^{-1} with removal efficiency of 92.9 % [47]. Chitosan/Fe-sludge particles (CHFS) were prepared to absorbanti in water by backwashing iron sludge with chitosan embedding.

Adsorption isotherm was Freundlich and Langmuir models. The maximum adsorption capacity of CHFSf or Sb(III) was 24.38 mg.g^{-1} [48]. This study shows that the production of chitosan SBE composites can increase adsorption capacity. Adsorption on SBE with Fe(III) is likely to occur physical adsorption (physisorption), occurs through Van der Waals forces, where metal ions are trapped within the micropores of SBE, as in the SBE framework at Figure 6 [41], or ion exchange, that metal ions in the solution exchange with cations originally present on the surface or within the structure of SBE, such as Si^{2+} and Al^{3+} .

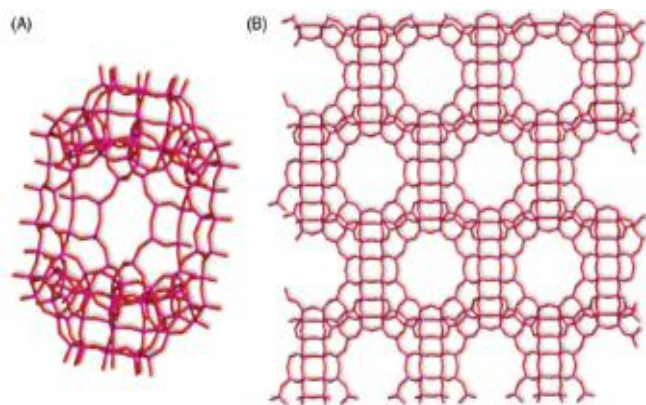


Fig. 6. SBE framework (A) unit cell/supercage and (B) view along

The results of the R_L parameter calculations in equation 8 show the results as shown in the Table 6.

Table 6. R_L parameter SBE and SBE- chitosan composite

Concentration Fe(III) (ppm)	R_L SBE	R_L SBE-Chitosan composite
25	0.471	0.576
50	0.308	0.405
75	0.229	0.312
100	0.182	0.254
150	0.129	0.185
200	0.100	0.145

Based on the effect of separation factor on isotherm shape, the R_L values are in the range of $0 < R_L < 1$, which indicates that the adsorptions of Fe(III) on SBE and SBE-chitosan are favorable. Thus, SBE and SBE-chitosan are favorable adsorbers. As mentioned earlier, SBE and SBE-chitosan are microporous biopolymers, therefore pores are large enough to let Fe (III) ions through. The mechanism of ion adsorption on porous adsorbents may involve three steps (i) diffusion of the external surface of adsorbent; (ii) diffusion of ions into the pores of adsorbent; (iii) adsorption of the internal surface of adsorbent. The first step of adsorption may be affected by metal ion concentration and agitation period. The last step is relatively a rapid process. [49,50]. The following are the details of the SBE–chitosan adsorption mechanism: physical adsorption (physisorption) and ion exchange by SBE and complex formation (chelation), that amine ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) groups on the chitosan polymer chains act as active sites that Fe(III) ions through coordination bonds, or electrostatic interactions, acidic pH the amine groups of chitosan become protonated into $-\text{NH}_3^+$. This allows electrostatic interactions between positively charged chitosan and metal ions, or ion exchange, that adsorbed Fe(III) ions often exchange positions with ions (such as H^+) bound to the chitosan surface. This is possible because the adsorption that occurs in the composites is due to chemical adsorption between chitosan and Fe (III). Interaction between metal and chitosan can be seen in Figure 7 [51].

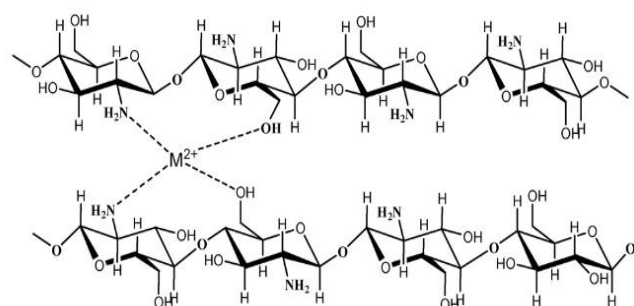
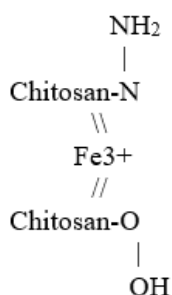


Fig. 7. Interaction between metal and chitosan

Identification of functional groups in the infrared spectra of SBE-chitosan composites and SBE-chitosan composites after adsorption Fe(III), can be seen in (Fig. 3 Supp.). Identification of each functional group in the infrared spectra of the SBE-chitosan composite and the SBE-chitosan composite after adsorption Fe(III) can be seen in Table 7. The absorption band at 1582.38 cm^{-1} , associated with $-\text{NH}_2$ groups, interaction between the SBE–chitosan composite and Fe(III) ions is indicated by a wavenumber shift from 1582.38 cm^{-1} to $1,602.28 \text{ cm}^{-1}$, showing that the $-\text{NH}_2$ groups interact with Fe(III). This is due to the lone pair electrons on the $-\text{NH}_2$ group that can coordinate with Fe(III) cations through coordinate bonding. The interaction between chitosan and Fe(III) is as Figure 8.

Table 7. Identification of each functional group in the infrared spectra of the SBE-chitosan composite, and the SBE-chitosan composite after adsorption Fe(III)

SBE-Chitosan	SBE-Chitosan-Fe	Reference wavenumber (cm ⁻¹)**	Functional group**
3242.81	3242.81	3412-3100	symmetric stretching vibration O-H
1632.79	1632.79	1650-1600	O-H
1582.38	1602.28	1640-1540	N-H
1013.88	1013.88	1040-1070	Si-O-Si
776.00	776.00	780-797	Silica amorf

**Fig. 8.** Interaction Fe with Chitosan.

4. Conclusion

FTIR analysis results indicate that the soxhlet extraction and activation of SBE were effective in removing unsaturated vegetable oils and organic contaminants. In addition, FTIR also shows the successful formation of interactions between SBE-chitosan. The best composite ratio variation SBE-Chitosan for Fe (III) adsorption is 4:1, as it exhibited the highest percentage removal of 93.34 %. The successful adsorption of Fe(III) by this composite is characterized by the shift in wave numbers at specific functional groups, indicating interactions between Fe(III) and the composite. Based on the research conducted, it was found that the adsorption of Fe(III) on the SBE-chitosan composite showed optimal performance at pH 7, with equilibrium time achieved in 50 min. The adsorption follows the Langmuir and Freundlich isotherm, the maximum adsorption capacity determined from Langmuir model was 34.01 mg.g⁻¹.

Supplementary files

Supplementary file 1.

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