Performance evaluation of immobilized micro green algae for heavy metals removal from water

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ABSTRACT

Biosorption and sequestration by living plants provide an environmentally and economically favorable method for removing heavy metals from natural waters, on the other hand, groundwater would provide an alternative drinking water resource. The groundwater treatment is necessary for it to be safe to drink. The influence of contact duration and pH on the removal of heavy metals (Mn(II) and Fe(II)) contaminants from groundwater was studied in this study. The Isotherms were utilized to investigate their adsorption properties. The percent absorption of Mn(II) and Fe(III) ions by algae rose virtually in lockstep with contact duration, reaching 83.7% and 76.5% at 60 min for Mn(II) and Fe(III), respectively. Reduced acidity improves the percentage of heavy metal ions taken up by algae; at the maximum pH 5.5, manganese ions are removed 92.35% of the time, whereas iron ions are taken up 99.38% of the time. The Langmuir adsorption isotherm model is believed to be the best for modelling the monolayer chemisorption process on homogeneous adsorption sites on algae surfaces. Pseudo-first-order and pseudo-second-order kinetic models were tested with experimental data to better understand the kinetics of Fe(III) and Mn(II) removal by algae. The results showed that the adsorption of Fe(III) and Mn(II) ions onto algae followed pseudo-second-order kinetics rather than pseudo-first-order kinetics.

Keywords: Biosorbed; Adsorption isotherms; Algae; Groundwater; Manganese; Iron

1. Introduction

Heavy metals are released in large quantities into surface and groundwater, soils, and eventually the biosphere, because of human activities such as industrial production, mining, agriculture, and transportation. One of the most important concerns with heavy metals is groundwater contamination; some of these heavy metals are poisonous when their allowed levels are exceeded [1]. Because low concentrations of iron and manganese in aqueous solutions produce physiological effects and illnesses over time, many techniques for removing iron and manganese from aqueous solutions are available. The influence of potassium permanganate on manganese removal in drinking water was explored by Zhang et al. [2]. When the addition ratio was 3.9, the findings showed that $KMnO_4$ could successfully remove manganese from drinking water,

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with a manganese removal effectiveness of 98%. Similarly, Kwakye-Awuah et al. [3] reported that zeolite Y might be used as an adsorbent for the removal of iron and manganese from groundwater, with data revealing that zeolite Y can remove 98% of iron and 97% of manganese in an hour. Other research investigated how ozone may be used to remove iron from groundwater. The three factors tested were pH (6.0–8.0), hardness (300–500 mg/L as CaCO$_3$), and removal time (10–60 min). In addition, the optimal pH was 6.99, with a hardness of 300 mg/L CaCO$_3$ liters of unclean water. A Master Flex pump with 0.5 horsepower per hour electrical power was used in this experiment and a reaction time of 10 min. The best setting for confirming the model's iron removal efficiency accuracy was 98.45%, according to the experiment. According to the research, ozone has the capacity to remove iron from groundwater [4]. Because of heavy metal absorption and toxicity, algae have been employed to identify regions of trace metal pollution [5,6]. To bring these findings together, it's worth noting that heavy metal buildup isn't necessarily linked to toxicity. *Scenedesmus* and Chlorella, two green algae, have been shown to be tolerant to heavy metals. *Scenedesmus actus* isolates that were Cr-tolerant were also Cu-tolerant, but not Zn-tolerant [7].

Algae are the most frequent and diversified category in the aquatic environment. These creatures exist in a wide range of sizes and forms, and they live in some of the world's most hostile settings. Algae can be classified into numerous functional, taxonomic, and ecological groupings. Phytoplankton, for example, are algae that float in the water column; periphyton, on the other hand, are mixed populations of algae, moss, fungus, and bacteria that grow on rocks, macrophytes vascular plants, and sediment surfaces [8]. Pollutant sensitivity varies by algae. Some are more sensitive than others. Toxicity tests have been performed on the most susceptible ones [9]. Several algae, on the other hand, are very resistant to certain metals and can sequester extremely high metal concentrations. Algae biomass has a high volatile solids concentration and a balanced biological makeup (lipid, protein, and carbohydrates). Biosorption is a fast-moving phenomenon in which non-growing biomass/adsorbents sequester metals. It offers several benefits over traditional processes, including cheap cost, high efficiency, minimal chemical and/or biological sludge, no extra fertilizer demand, bio sorbent renewal, and the possibility of metal recovery [10]. For single analytes, many empirical isotherm models have been discussed (i.e., Freundlich, Langmuir, Temkin, Sips, and Redlich–Peterson). The Freundlich and Langmuir models are the most frequent and commonly utilized isotherm models in numerous investigations. The pseudo-first-order and pseudo-second-order kinetic models are still widely used for researching the rate absorption of heavy metals and their bio adsorption from aqueous solutions. The pseudo-second-order kinetic model is preferable than the pseudo-first-order model in the chemisorption process because it addresses the interaction of adsorbent and adsorbate through their valence forces. The objective of this study is to investigate utilizing of green algae as a bio-adsorbents for the removal of heavy metal (Mn(II) and Fe(III)) from groundwater. The effect of contact time and pH on the

removal of heavy metals were also explored. The isotherms were used to study their nature of adsorption.

2. Materials and methods

2.1. Groundwater and heavy metals

Iron is dissolved in almost every rock and soil. Under oxidizing circumstances and groundwater temperature, iron in groundwater rapidly oxidizes and creates a reddish-brown precipitate, which has a disagreeable taste and promotes the development of iron bacteria. Manganese is similar to iron in that its oxidized state generates dark brown or black stains. A significant amount of manganese can be detrimental to humans. Groundwater samples were collected at El-Kenayat, El-Sharkia Government, Egypt, for this study. To characterize the groundwater, total solids (TS), total dissolved solids (TDS), and chemical oxygen demand (COD) were assessed using the usual procedures [11]. The concentrations of Mn(II) and Fe(III) were determined under room temperature working circumstances using an automated adsorption system. The pH was measured with a pH meter. (Pocket-size pH meter, HI 98107). The samples were collected and kept at room temperature in polypropylene containers. After each stage, the samples are put in sealed plastic vials for automated adsorption analysis. The measured parameters are listed in Table 1. The impact of contact time and pH on heavy metal removal was investigated.

2.2. Ethylenediamine tetraacetic acid

Ethylenediamine tetraacetic acid (EDTA) is an amino polycarboxylic acid with the formula [CH$_2$N(CH$_2$CO$_2$H)$_2$ as illustrated in Fig. 1. Iron and calcium ions are typically bound with this water-soluble white solid. It binds to these ions as a hexadentate ("six-toothed") chelating agent. Disodium EDTA, sodium calcium edetate, and tetrasodium EDTA are some of the salts available. It inhibits metal ion contaminants, notably Mn(II), from causing disproportionation.

After each run, the concentration of Mn(II) and Fe(III) on the algae media surface was determined using an EDTA solution of 1 M concentration, whereas the residue was adsorbed interior media algae, indicating that most of the iron and manganese ions were adsorbed interiorly and the residue on the surface was low in concentration, so it was only used to make washing for the other runs. To achieve a 1 molar concentration, chemicals such as

Table 1
Characteristics of raw groundwater

Parameter	Values
Fe(III), ppm	3.2
Mn(II), ppm	1.5
pH	7.2
COD, ppm	450
TS, ppm	1,000
TDS, ppm	767

Fig. 1. Chemical structure of EDTA.

Table 2
Algae characteristics

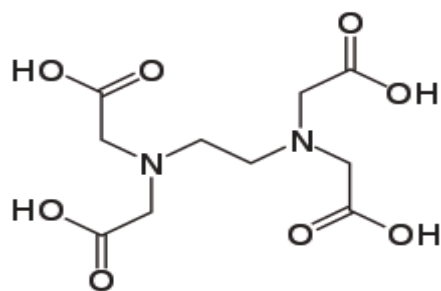| Parameter	Algae
pH	7.10
TS (%)	1.70
TDS (%)	73.40
C (%)	12.96
N (%)	2.40
K (%)	0.53
P (%)	0.66
C/N	5.4

EDTA were used. The samples were obtained at a location where iron and other ferrous elements were extensively contaminated. The samples were evaluated utilizing an automated adsorption machine under room temperature working conditions.

2.3. Algae

Scenedesmus (sp.) microalgae were obtained at the lab of Zagazig University's Faculty of Science. 5 Erlenmeyer flasks holding 100 mL sterile BG-11 medium were prepared according to [12]. *Scenedesmus* was administered to this group (5 mL for each flask). The inoculum of organisms was the same and had the same effect (0.6 nm). Under aseptic conditions, a 250 mL Erlenmeyer flask containing 100 mL sterile BG-11 medium according to Stanier and an adequate incolumn of *Scenedesmus* (5 mL) was infected. For 14 d all flasks were incubated at 28°C with a photoperiod of 16 light/8 dark. Algal cells were extracted by centrifuge unit at 5,000 rpm at the conclusion of the incubation time. The cells were collected, and distilled water washed twice before being stored. Fig. 2 depicts the *Scenedesmus* algae sector, while Table 2 lists the algae characteristics.

Scenedesmus algae were prepared using 0.5 g and exposed to light for 15 d with 300 mL blank media accumulated by 2 mL *Chlandy domeros* (microgreen algae),

followed by closed continuous circulation of bulk algae solution into the column by downflow pumping, the algae were trapped between sponge slides as shown in Fig. 3, and then left for 48 h to be ready for use [13]. The major important economic aspects of biosorption technology are [14]:

- The biomass used must be natural and cheap (low cost and large availability).
- The selectivity elimination of heavy metal must be under a wide range of pH, temperature, and rapid kinetics of adsorption and desorption.
- The high surface to volume ratio of microorganisms must be found, and
- Superior capability to detoxify heavy metals.

Several important parameters that affect the performance of living biosorbent must be considered; these are [15]:

- The physiological state of the organism,
- The age of the cells, the availability of micronutrients during their growth, and
- The environmental conditions during the biosorption process such as pH, temperature, and the presence of certain ions.
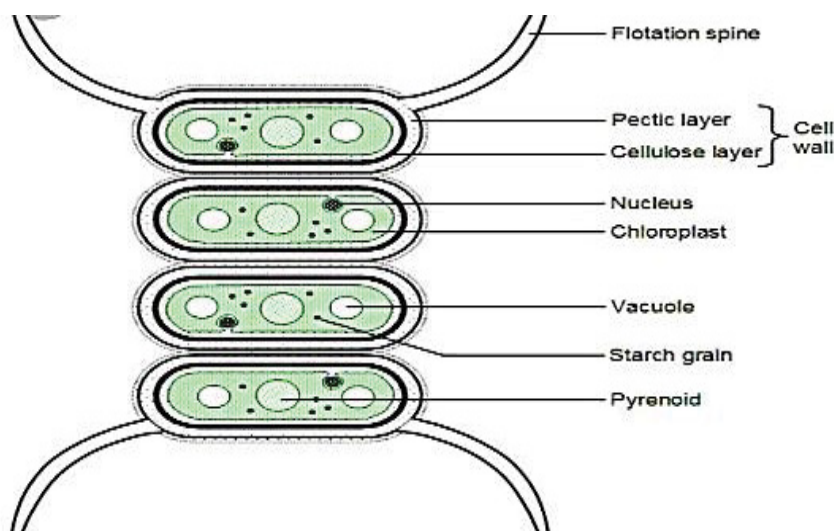

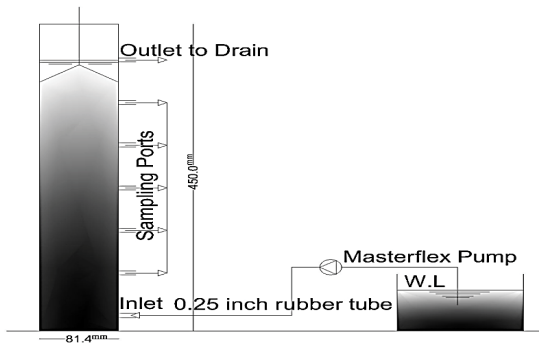Fig. 2. Sector of *Scenedesmus* algae adopted from Salman et al. [13].

Fig. 3. Schematic diagram of the designed model.

Fig. 4. Effect of contact time on the removal efficiency of Mn(II).

The used microalgae species *Scenedesmus* (sp.) are affordable and simple to make in the Arab Republic of Egypt; the cost of the model is to filter iron and manganese ions for every 0.6 L of unclean water. A Master Flex pump with 0.5 horsepower per hour electrical power was used in this experiment.

2.4. Bench scale model

A laboratory-scale reactor was constructed in the Science Laboratory, Faculty of Science, Zagazig University, Egypt. The reactor was 81.4 mm (inner diameter) plastic acrylic pipe with 2.0 m height. A schematic diagram of the model is shown in Fig. 3.

3. Results and discussions

3.1. Effect of contact time

The influence of contact time and pH on heavy metal removal has been investigated. Table 3 demonstrates the association between different contact durations and the removal of manganese and iron ions from a 600 mL groundwater sample at room temperature.

The percent absorption of Mn(II) ions by algae rose with contact time, reaching 83.7% within 60 min and 76.5% for iron ions at the same time (with EDTA). This is related to the composition of algae and the behavior of heavy metal ions near the surface, which are attracted to the algae negative group. The negative group on the algae's surface accepts positive ions from contaminated groundwater, according to its features. Manganese removal efficiency is 92.3% after 60 min of contact time (without
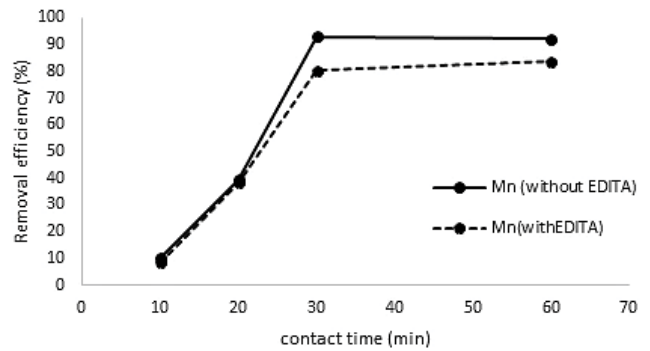
EDTA), whereas iron removal efficiency is 71.2% after 60 min. It indicates that heavy metals and algae have a phi chemisorption process. Fig. 4 depicts the influence of contact time on Mn(II) removal efficiency (with and without EDTA), whereas Fig. 5 depicts the effect of contact time on Fe(III) removal efficiency (with and without EDTA).

Table 3 clearly shows that the data obtained without EDTA at the same time are regarded the true adsorption process. Fig. 6 shows that manganese ions are removed at a rate of 92.3%, whereas iron ions are removed at a rate of 71.25%.

3.2. Effect of pH

The most essential component that affects the adsorption process is pH; as pH rises, so does the biosorption of heavy metal ions, since H^+ ions improve electrostatic interaction with heavy metal ions in a variety of biosorption systems [16]. A pH rises of up to 5 resulted in a 98% increase in biosorption capacity, whereas a pH increase of more than 5 resulted in a reduction in capacity. Protonation and deprotonation of functional groups are controlled by the pH of the medium, which affects the biosorption capacity: at low pH, carboxylic groups, being acidic, exist in a protonated state due to the presence of excess H^+ and H_3O^+; therefore, repulsive forces of these protonated groups with positively charged heavy metal ions are responsible for the lower biosorption capacity at low pH. Deprotonation exposes functional groups like amine, carboxyl, and hydroxyl groups when pH rises, enhancing electrostatic interaction with heavy metal ions owing to a negative charge [17]. The creation of hydroxide anionic complex is caused by a substantial increase in

Table 3
Relation between different contact times and the removal efficiency of metals

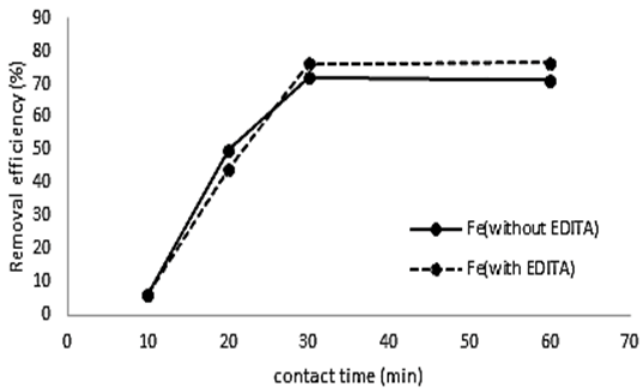| Time (min)	Mn uptake with EDTA	Fe uptake with EDTA	Mn uptake without EDTA	Fe uptake without EDTA
10	8.3%	6.25%	10%	10.25%
20	38.3%	44.3%	39.41%	50%
30	80.4%	76.3%	92.94%	71.88%
60	83.7%	76.5%	92.35%	71.25%

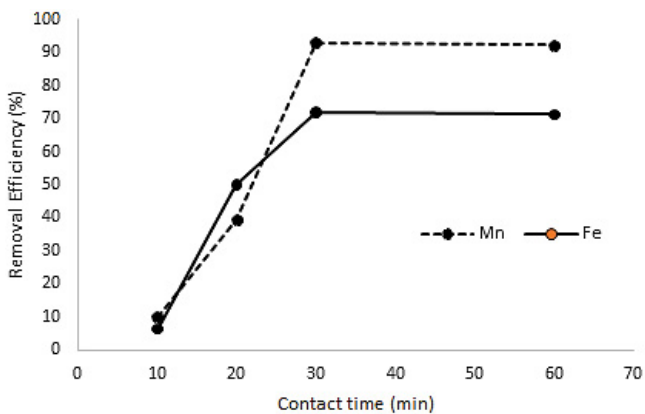Fig. 5. Effect of contact time on the removal efficiency of Fe(III).

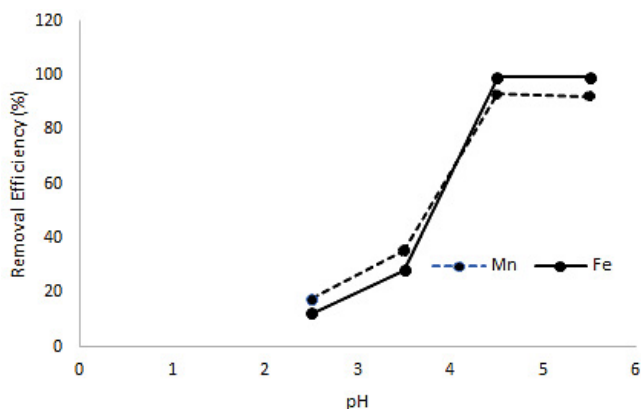Fig. 6. Effect of contact time on the removal efficiency of Fe(III) and Mn(II) without EDTA.

Fig. 7. Effect of pH on the adsorption of Fe and Mn without EDTA.

pH, and the increase in acidity impacts the percentage of heavy metal ions taken up by algae. According to the findings, increasing pH enhanced the removal effectiveness of metals (Mn(III) and Fe(II)) up to 4.5 pH, after which the removal efficiency in both metals remained nearly constant, as shown in Fig. 7. Manganese ions were removed with 92.35% efficiency at pH 5.5, whereas iron ions were

removed with 99.38% efficiency at the same pH. This is due to ion exchange in the bulk between hydrogen ions and positive ions. Because of the solubility and activity of heavy metal ions, there is a variation in their removal. As can be observed, iron ions have a lower percent absorption than manganese ions due to their lower solubility, which causes them to precipitate as iron hydroxide.

The optimum pH lies between 4.5–5.5. According to [18] the ideal pH range is 5 to 8.5, with the highest elimination of iron and manganese occurring at pH 5.5. (97% and 40%). As the acidity rises, H+ ions behave like any other cations, competing with other metals in the solution and stripping them from the solution. This result is less than the condition of pH 9.3- and 20 d contact time using *Cladophora* algae [19], also less than the condition of contact time 120 min and pH 3 when using *Sargassum vulgare* algae [20].

3.3. Effect of contact time on the removal of TDS and TS

It was discovered that increasing contact time improved TDS removal efficiency, but TS removal efficiency remained virtually constant at 10 and 20 min before increasing with contact time and following the same pattern as TDS removal efficiency. As demonstrated in Figs. 8 and 9, the maximum efficiency of TS removal was 80% at 60 min, whereas the best efficiency of TDS removal was 65% at the same contact time.

3.4. Adsorption description

The Langmuir isotherm is a mathematical formula for interpreting hyperbolic adsorption data. The adsorption of ions to a finite number of ligand sites in a single layer on the cell surface is described by the same equation used to explain Michaelis–Menten enzyme kinetics [21]. Another popular model with no theoretical foundation is the Freundlich isotherm [22]. The adsorption curve's form, on the other hand, is determined by the constants K_d and N.

3.4.1. Iron isotherms

The data will be described mathematically using Langmuir for homogenous adsorption. The Langmuir formula is as follow:

$$Q_e = \frac{K_l C_e}{\left(1 + a_L C_e\right)} \tag{1}$$

where Q_e: the adsorption density at equilibrium (mg adsorbate/g of adsorbent); C_e: the residual adsorbate concentration in the solution (mg/L) at equilibrium; K_l: the relative adsorption capacity; a_L: Langmuir constant correlated to the adsorption energy (1/mg adsorbate).

Freundlich equation:

$$Q_e = K_f C_e \frac{1}{b_f} \tag{2}$$

where Q_e: the adsorption density at equilibrium (mg adsorbate/g of adsorbent); C_e: the residual adsorbate concentration
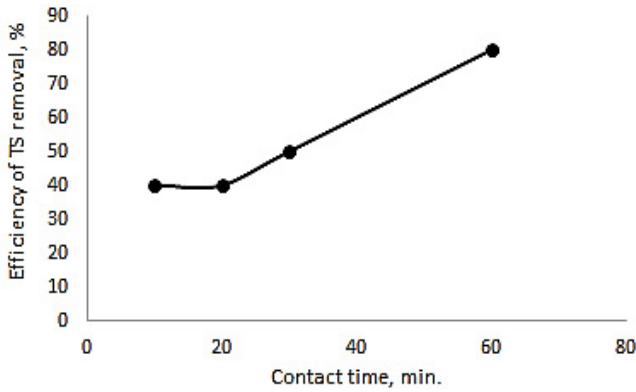
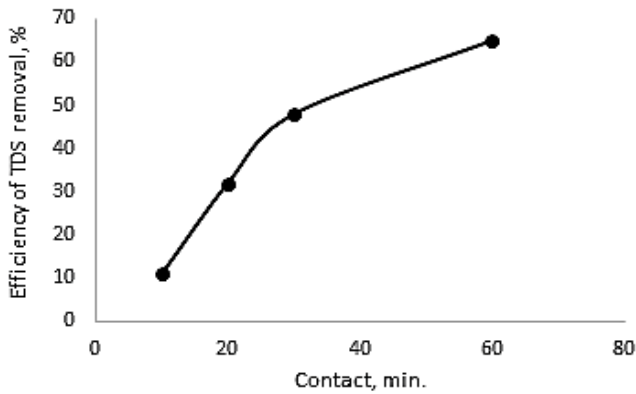Fig. 8. Effect of contact time on the efficiency of TS removal.

Fig. 9. Effect of contact time on the efficiency of TDS removal.

in the solution (mg/L) at equilibrium; K_f: the relative adsorption capacity; b_f: Langmuir constant correlated to the adsorption energy (1/mg adsorbate).

The formation of monolayer coverage of manganese on the outer surface of algae, as shown in the following figures plotting both isotherms for adsorption of heavy metals Iron and manganese; it is clearly shown that the algae signifies dual adsorption mechanisms, as shown in the following figures plotting both isotherms for adsorption of heavy metals iron and manganese [23]. Iron adsorption occurs in two stages: physisorption and chemisorption. R is a constant with no dimensions.

$$R = (1 + a_L C_e) \tag{3}$$

Values of Rs type of isotherm
Rs > 1 Unfavorable
Rs = 0 Linear
0 < Rs < 1 Favorable
Rs < 0
As shown in Figs. 10 and 11, the value of R is 0 < R < 1.

3.4.2. Manganese isotherm

The Langmuir adsorption isotherm model, which describes monolayer chemisorption on homogeneous adsorption sites on algae surface, is regarded the best for characterizing monolayer chemisorption on heterogeneous
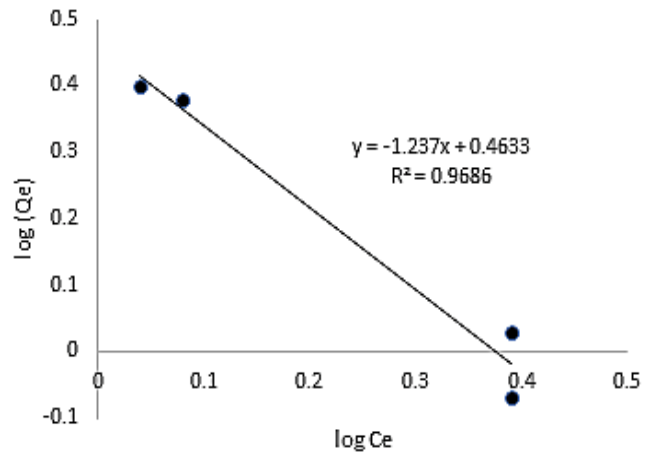

Fig. 10. Langmuir isotherms of the adsorption of Fe(III) on *Scenedesmus* algae.
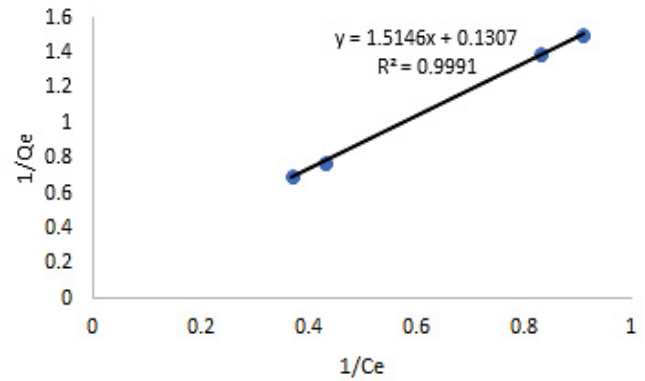

Fig. 11. Freundlich isotherm of the adsorption of Fe(III) on *Scenedesmus* algae.

adsorption sites on the adsorbent surface, as illustrated in Figs. 12 and 13.

3.4.3. Adsorption kinetics

The experimental data was used to evaluate pseudo-first-order and pseudo-second-order kinetic models to better understand the kinetics of Fe and Mn removal by *Scenedesmus*. Pseudo-first-order kinetics models were:

$$\text{Pseudo-first-order: } \log(q_e - q_t) = \log(q_{1st}) - \frac{K_1}{2.303}t \tag{4}$$

where q_t, is the experimental adsorption capacity at time (t), q_{1st} is the adsorption capacity from the pseudo-first-order model (mg/g), k_1 (min⁻¹) is the rate constant of pseudo-first-order models.

Pseudo-second-order kinetics models were:

$$\text{Pseudo-second-order: } \frac{t}{q_t} = \frac{1}{K_2 q_{2nd}^2} + \frac{1}{q_{2nd}}t \tag{5}$$

where q_t is the experimental adsorption capacity at time (t), q_{2nd} is the adsorption capacity from the pseudo-second-order
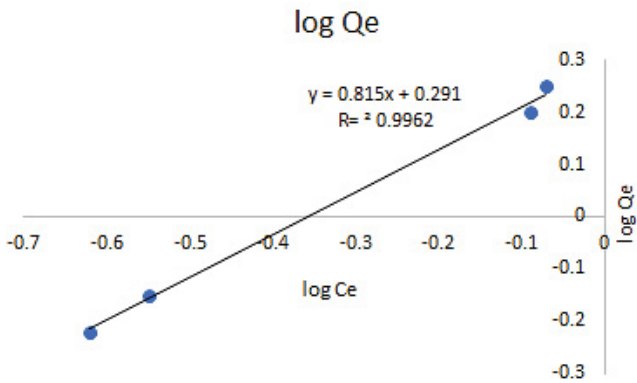
Fig. 12. Langmuir isotherm of the adsorption of Mn(II) on *Scenedesmus* algae
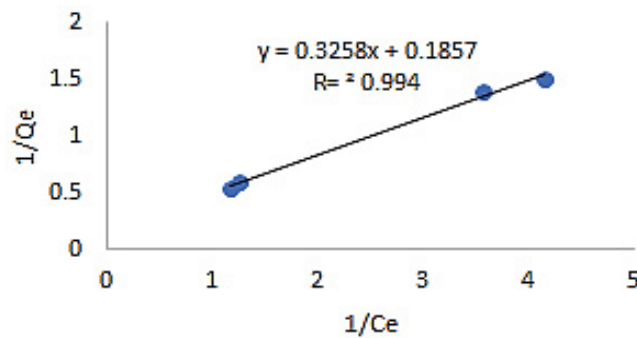

Fig. 13. Freundlich isotherm of the adsorption of Mn(II) on *Scenedesmus* algae.

Table 4
Pseudo-first and second-order kinetics models of iron ions

Time (min)	$\log(q_e - q_t)$	q_t	t/q_t
10	0.55	1.28	7.8
20	0.28	1.92	10.4
30	0.025	2.76	12.5
60	–0.5	2.74	21.9

Table 5
Pseudo-first and second-order kinetics models manganese ions

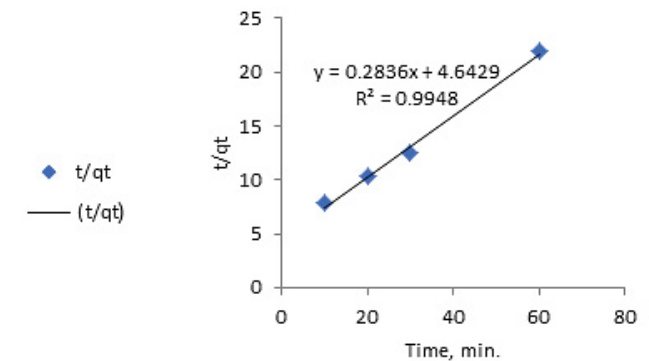| Time (min)	$\log(q_e - q_t)$	q_t	t/q_t
10	0.5	1.22	8.2
20	0.25	1.89	10.6
30	0.02	2.68	12.4
60	–0.5	2.69	22.3

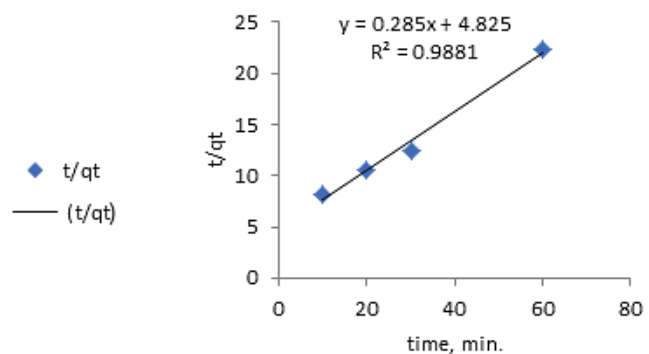Fig. 14. Pseudo-second-order model for Fe(III) ions adsorption by *Scenedesmus* algae.

Fig. 15. Pseudo-second-order model for Mn(II) ions adsorption by *Scenedesmus* algae.

models (mg/g), k_2 (g/mg min) is the rate constant of pseudo-second-order models. Tables 4 and 5 show the pseudo-first-order kinetics models and pseudo-second-order kinetics models of iron and manganese, respectively.

Plotting of (t/q_t) against (t) gave straight lines with slopes and intercepts from the following figures the goodness of the model may be tested from the value of regression coefficients and the consistency of the calculated value (q_{calc}) with the experimental one, as shown in Figs. 14 and 15, while Figs. 16 and 17 show the relation between $\log(q_e - q_t)$ against time. The results indicated that the adsorption of Fe and Mn ions onto algae followed the pseudo-second-order rather than pseudo-first-order kinetics. This implies that the rate of adsorption of heavy metals ions on the used adsorbents depends on the properties of both adsorbate and adsorbent.

The Freundlich plots properly suit the experimental data produced in this investigation, according to the examination of the results.

3.5. Scanning electron microscopy product

The scanning electron microscopy (SEM) photos for this technique's output primarily reveal info well about sample's surface morphology as shown in Fig. 18. The metal removed are found, while the schematic representation of

the mechanisms involved in the biosorption of potentially toxic elements [24,25]. First, the metal ions are adsorbed to the surface of the cells by the interaction between metal and functional groups found on the surface of the wall. Second, due to active biosorption, metal ions penetrate the
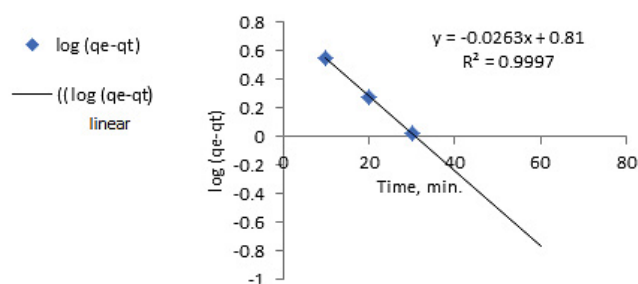
Fig. 16. Pseudo-first-order model for Fe(III) ions adsorption by *Scenedesmus* algae.
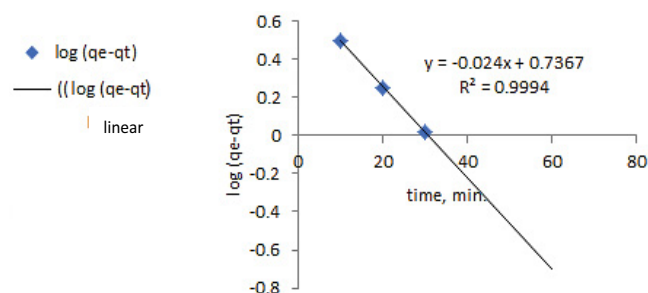

Fig. 17. Pseudo-first-order model for Mn(II) Ions adsorption by *Scenedesmus* algae.
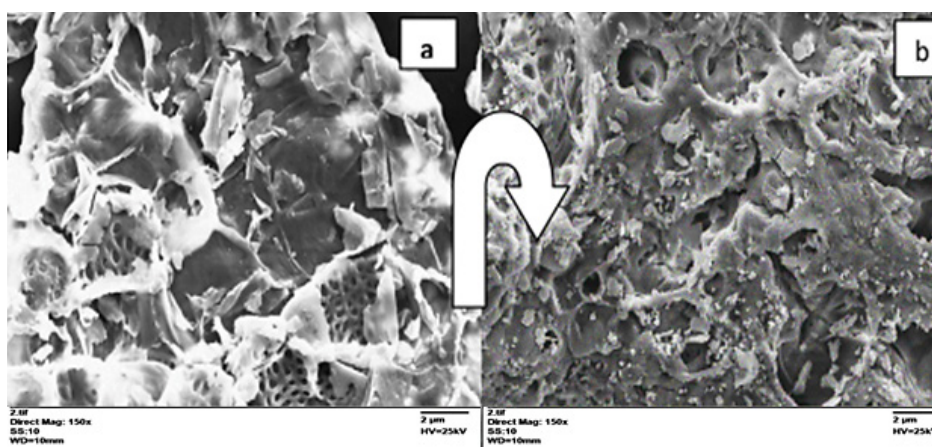

Fig. 18. Product of SEM for algae media: (a) before treatment and (b) after treatment

cell membrane and enter the cells. Active mode is metabolism-dependent and related to metal transport and deposition. Iron and manganese enter algae cells, cross the membrane. The ions compete for binding to multivalent ion carriers enter the cell by active transport [26,27].

4. Conclusions

The primary purpose of this study was to determine the concentrations of several heavy metals as well as some chemical factors such as pH and hardness of water collected from groundwater, as well as the concentrations of Mn(II) and Fe(III). Also, the algae *Scenedesmus* was utilized as an adsorbent, and the results demonstrate that when the pH rises, the percentage of contaminants removed rises as well. Mn(II) and Fe(III) removal were measured below WHO permitted levels. According to the findings, the procedure may be scaled up to larger capacity. Iron adsorption tends to fit the Freundlich adsorption isotherm preferentially, implying monolayer coverage of adsorbed molecules. Second-order kinetics governs the adsorption process. Adsorption was shown to be endothermic and spontaneous in temperature experiments.

Acknowledgment

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