Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2023.29990

311 (2023) 67–75
November

Biosorption of Cd(II) ions by *Chlorella* microalgae: isotherm, kinetics processes and biodiesel production

Israa M. Rashid[a,*], Abeer I. Alwared[b], Hala N. Abdelkareem[b]

[a]*Biochemical Engineering Department, Al-Khwarizmi College of Engineering, University of Baghdad, Baghdad 47024, Iraq, email: israa_msc2018@kecbu.uobaghdad.edu.iq*
[b]*Department of Environmental Engineering, College of Engineering, University of Baghdad, Baghdad 47024, Iraq, emails: dr.abeer.wared@coeng.uobaghdad.edu.iq (A.I. Alwared), halan1988@yahoo.com (H.N. Abdelkareem)*

Received 25 July 2023; Accepted 21 September 2023

ABSTRACT

This study aims to remove Cd(II) ions from simulated wastewater by using *Chlorophyceae* algae (CA). Different parameters were studied to show their effects on the biosorption efficiency of CA. These parameters are: the effect of pH 3–7, initial metal ion concentration 20–200 mg/L, sorbent dosage 0.05–2 g/L, contact time 5–180 min, and agitation speed 100–300 rpm. We found that both the Langmuir and Freundlich models appropriate for characterizing the metal removal process. The biosorption data fit best with the results of the pseudo-second-order kinetic model, demonstrating that the chemisorption process is the dominant mechanism controlling the removal. CA was characterized using the scanning electron microscopy test, prior to and post biosorption. Furthermore, the resulting Cd(II) ions-loaded CA was reused for the production of biodiesel. The resulting chromatogram of the methyl ester peaks was typically found in a biodiesel sample production from the algae feedstock before contaminant.

Keywords: Cd(II) ions; Batch biosorption; *Chlorophyceae* algae; Isotherm; Biodiesel

1. Introduction

The growing consumption of energy as well as the increasing environmental pollution have become two major issues that need to be addressed and the best solution to overcome these problems requires the best use of resources and the new sustainable strategies evolution, to transform this biomass to green energy [1–3]. Some heavy metals such as Pb(II), Cu(II), Cd(II), Zn(II) ions and other metal ion contaminants are present in many industries' aqueous waste streams, which contaminates the environment via the effluents discharge, primarily because of inadequate wastewater treatment, metallurgy industries, battery factories, and electroplating factories [4,5].

Even in low concentrations, these metals pose a threat to the environment and can cause health complications. Therefore, thorough removal of these contaminants from industrial wastewater prior to disposal is critical [5,6]. Different conventional methods are used for eliminating heavy metal ions from wastewater, such as electrochemical methods, chemical precipitation, ion exchange, solvent extraction, and membrane processes, which are considered to be expensive and require high energy consumption [7,8]. In comparison, for removing heavy metal ions from industrial wastewater, biosorption is considered a favorable alternative. This includes the retention of heavy metal ions on the surface of solid materials [8–10].

Biosorption has many economical and useful features to eliminate heavy metal ion concentrations to very low levels in an environment-friendly manner. To this end, an adsorbent of low cost is needed, which has led to the biological and agricultural origin material search, as potential metal

---

* Corresponding author.

1944-3994/1944-3986

sorbents, called biosorbents, such as bacteria, yeast, fungi, algae, and industrial and agricultural waste [11,12]. Algae have been shown to have greater heavy metal biosorption capacities than fungus and yeast due to their cell walls, which are composed of a fiber-like structure and an amorphous embedding matrix of various polysaccharides [13].

In general algae grow in lakes, ponds, and slow-moving streams when the water is warm and enriched with nutrients like phosphorus and/or nitrogen. In addition, algae can be grown on effluents, runoff water from municipal and agricultural wastewater, and are also considered to be inexpensive and sustainable vectors for removing toxic waste that is loaded in industrial wastewater. Algae offer a good solution for the treatment of industrial wastewater that contains heavy metals, in a natural manner [14,15]. Biosorption and bioaccumulation occur in two stages, metal ions are taken up [16]. The metal ions are first passively adsorbed on the cell surface (of both living and non-living biomass) in a matter of seconds or minutes, after which they are lingeringly conveyed within the cell membrane, where they accumulate intracellularly. However, only living cells may accumulate metal ions, which are moved over the cell membrane barrier and subsequently bonded to cytoplasmic proteins or polysaccharides, or to specialized cellular structures like vacuoles or polyphosphate bodies. biosorption encompasses the two processes described, which involve both biosorption and bioaccumulation by living and/or dead microorganisms. Algae have excellent biosorption capacity for metal ions. Some cyanobacteria and microalgae are metal stress-tolerant and large surface areas, high binding affinity, and possess a high resistance toward metal toxicity [15]. Nowadays, there are many research studies that deal with algae biomass ability to extract heavy metal ions from wastewater, such as, studies by [17–22]. Currently, algae have obtained a lot of attention for being good sources of biomass for the production of renewable energy in the form of biodiesel and as a feedstock for other types of fuel, as it contains mainly carbohydrates and lipids [23]. Biodiesel production from microalgae entails reusing and integrating carbon resources from the natural environment, which can contribute to achieving the long-term goal of replacing petroleum use and reducing environmental pollution, thereby contributing significantly to the global carbon neutrality endeavour [24].

Biodiesel production by transesterification of lipids [25], biogas production through anaerobic digestion [26], bioethanol production through algal biomass fermentation [27], and bio-crude production through thermochemical conversion are some of the several methods for converting microalgae into biofuel [28,29]. Biodiesel is a low-emission fuel produced from waste lipids and renewable biomass and is an alternative to petroleum-based diesel [30]. Several conversion biomass processes have been investigated for the generation of renewable diesel from macroalgae and microalgae [31]. This study's objective was to assess the microalgae's effectiveness in removing the targeted pollutant, Cd(II) ions. In this line, this study examines for the first time the possibility of the generation of biodiesel from microalgae loaded with Cd(II) ions as a new method for sustainable waste handling.

The batch-vessel adsorption system has been utilized in this study for the removal of Cd(II) ions from simulated wastewater by the variation of four experimental conditions, which are initial pH, contact time, sorbent dose, and initial concentration of Cd(II) ions.

2. Materials and methods

2.1. Materials

In the present study, a single class of *Chlorophyceae* microalgae (Fig. 1), denoted as *Chlorophyceae* algae (CA), was selected as a model of adsorbent, in their non-living form, with a particle size of up to 74 μm and was supplied by www.buyalgae.com and subsequently stored in their original tightened polyethylene containers. All the chemicals used were of analytical grade. Cadmium ions, $Cd(NO_3)_2{\cdot}2H_2O$ (Purchased from BDH Company, England) was chosen as the contaminant model, and the pH value of solutions has been controlled by the experiments by addition of 0.1 M NaOH or HCl. For biodiesel production KOH was chosen as the catalyst. Methanol high-performance liquid chromatography (HPLC grade, 99.9%) and methyl heptadecanoate (purity 99%) were used as the internal standard for gas chromatography (GC), and *n*-hexane (HPLC grade, 99%) was used as a solvent for gas chromatography.

2.2. Methods

2.2.1. Biosorption experiments

The elimination of Cd(II) ions from simulated wastewater has been achieved in different batch experiments; these experiments were carried out in 250 mL conical flasks. Each flask was saturated with 100 mL of Cd(II) ions solution and the selected sorbent amount. Several parameters were studied to examine their effect on the removal process including initial pH value 3–7, agitation speed 100–300 rpm, contact time 0–180 min, sorbent dosage 0.05–2 g/L, and initial metal concentration ranging between 20 and 200 mg/L. The flasks were shaken for a defined time using an incubator shaker (Model: LIS-3016A, No. B110416002, Korea). 0.1 mL aliquots of each solution were extracted, filtered, centrifuged, and then measured for Cd(II) ions concentration using a flame atomic absorption spectrophotometer at a set time interval during each test.

Fig. 1. SOM01. *Chlorella* algae.

2.2.2. Biodiesel separation from algae

2.2.2.1. Extraction of oil

This experiment was achieved by using the chemical extraction process using the n-hexane method. The Cd(II) ions–loaded algae were dried and then mixed with hexane in a Soxhlet extractor for 8 h, according to [32]. The acidity of oil was calculated using the American Oil Chemists' Society (AOCS) method and calculated by using Eq. (1), while the free fatty acid percentage was calculated using Eq. (2) [30,33].

$$\%\,\text{Acid Value}\left(\frac{\text{mg KOH}}{\text{gm}}\right)=\frac{56.1\times C\times V}{\text{weight of loaded CA algae}} \tag{1}$$

$$\%\text{ Free Fatty Acid}=\frac{28.2\times C\times V}{\text{weight of loaded CA algael}}\times 100 \tag{2}$$

where C represents the potassium hydroxide solution concentrate, (mol/L); V represents volume of potassium hydroxide solution used, (mL); 56.1 represents molecular mass of potassium hydroxide.

The average molecular weight of this oil was calculated according to Eq. (3) [25]:

$$\text{MW}=\frac{56.1\times 3}{\text{SV}-\text{AV}}\times 1000 \tag{3}$$

where SV and AV represent the value of saponification and the value of acid, respectively. To determine SV, the sample is completely saponified with an excess of alkali, which excess is then determined by titration (in mg·KOH/g) [31]. The AV is determined by directly titrating the oil/fat in an alcoholic medium against standard potassium hydroxide/sodium hydroxide solution.

2.2.2.2. Transesterification reaction

The most common method to reduce the viscosity and produce biodiesel is by transesterification, which was achieved in a 50 mL three-necked flask with a round bottomed. 5 mL of extracted oil was heated to 60°C, and then a required amount of methanol and KOH catalyst were added in a flask equipped with a reflux condenser and a mechanical stirrer (PHOENX, RSO 20D). The mixture was stirred at 300 rpm and heated to the desired temperature to ensure a homogenous mixture. The reaction time was noted till the temperature reached the desired reaction temperature. The operation parameters were, a methanol: oil ratio of 30:1, catalyst loading (5%), and 3 h of reaction time. The liquid mixture was put in a separating funnel after the transesterification reaction was completed, and the two-phase system was carefully Isolated. The bottom layer of the system consisted of glycerine, while the top layer was made up of a mixture of methyl esters and unreacted methanol.

2.2.3. Characterization of the CA

The surface images of the CA were described via scanning electron microscopy (SEM) (TESCAN, Vega III, Czech Republic) for the detection of the morphological specifications of before and after interacting with the Cd(II) ions.

2.2.4. Experimental parameters for biodiesel analysis

- Ion concentration of Cd(II) ions was determined using an atomic absorption spectrophotometer device (AAS, Sens AA, Australian). Duplicate measurements of the samples were done for a more accurate result, and then the ion concentration was calculated from the following relationship [6]:

$$\text{Removal percentage}=\frac{C_0-C_e}{C_0}\times 100\% \tag{4}$$

where C_o and C_e represent initial and residual concentration of Cd(II) ions after biosorption, respectively.

The equilibrium adsorption capacity of active carbon for Cd(II), q_e (mg/g), was calculated using Eq. (5) [6].

$$q_e=\frac{\left(C_0-C_e\right)V}{m} \tag{5}$$

where q_e is Cd(II) adsorbed amount (mg/g); V is the volume of the sample (mL) and m is the quantity of the adsorbent added (g).

- Biodiesel compounds were identified by using gas chromatography-mass spectrometry (GC-MS), which is one of the common mechanisms to allow the identification and quantification of components in fats and oils. It is a very dependable mechanism, easy to conduct, fast, and extensively used to analyze the contents of fats and oils. FAMEs, which were in the upper phase, were analyzed by GC according to (EN 14103,2003). The GC was equipped with a flame ionization detector (FID-2010 Plus) and a capillary column (DN-WAX; length: 30 m, ID: 0.32 mm, and film thickness: 1 μL). Methyl heptadecanoate was used as an internal standard. A sample of 1 μL volume was injected and the FAME composition was calculated by using Eq. (6) [30,33]:

$$\text{FAME\%}=\frac{\sum A-A_{\text{EI}}}{A_{\text{EI}}}\times\frac{C_{\text{EI}}\times V_{\text{EI}}}{M}\times 100 \tag{6}$$

where $\sum A$ represents total peak areas of the methyl ester in C_{14} of that in $C_{24:1}$; A_{EI} – methyl heptadecanoate peak; C_{EI}, V_{EI} and M represent the concentration (mg/mL), volume of the methyl heptadecanoate solution (mL), and sample weight (mg), respectively.

The quantities of FAME, which were obtained practically were checked by GC analysis, it compared with the theoretical quantities obtained from the chemical equation.

3. Results and discussions

3.1. Scanning electron microscopy

The fundamental morphological characteristic of the CA was studied by using SEM micrographs prior and following Cd ion biosorption. The images of SEM are presented in

Fig. 2a. For unloaded CA, it showed that it consisted of many spherical particles, which did not seem to be agglomerated and separated, and their surfaces were coarse in nature, although upon reacting with Cd(II) ions, the surface properties of the CA particles changed remarkably, Fig 2b. Furthermore, in comparison with the unloaded CA particles, the SEM micrographs of the CA particles loaded revealed that their surfaces had become brighter and less coarse.

3.2. Biosorption results

3.2.1. Influence of pH

Several researches reveal that pH is a supreme parameter affecting the biosorption of heavy metals [4], due to their affection for the protonation of functional groups on the biomass, as well as their metal chemistry. In this study, pH values of 3, 4, 5, 6, and 7 were investigated, and the findings are given in Fig. 3. This figure shows that the removal percentage increases by increasing the initial pH value till it reaches a maximum value at pH 6, and then it decreases. The biosorption capacity decreases at a lower pH value, which may be a result of the competition between the metal ions and the hydrogen in the solution, and the destabilizing of the expectant complexation that occurs between the acidic functional group and metal ions [34]. The algal cell reactive groups on the cell surface protonate in the acidic condition. In this case, the protons had occupied the allowable binding cited for metal removal, thus a slump occurs in the metal biosorption by the algae. However, the biosorption percentage decreases gradually when pH > 6. The Cd(II) ions can hydrolyze and lead to cadmium deposition at high pH [35]. In order to attain a higher removal capacity, a pH value of 5 has been chosen for the next experiment.

3.2.2. Influence of biomass dosage

The biomass dose is an important metric for determining a biosorbent's capacity for a given beginning concentration [36]. The Cd(II) ion biosorption uptake on the CA content has been tested under constant initial metal ions concentration, pH, agitation speed, and reaction time at 50 mg/L, 5, 200 rpm, for 120 min, respectively. Fig. 4 displays the outcome of the experiment, indicating that the increase in the adsorbent content from 0.05 to 1 g/100 mL improves the removal efficiency of metal from 66.55% to 92%, respectively, and then slightly increases after that. When the biomass of algae is raised, it may be able to fully adsorb the pollutants or reach an equilibrium state where it reaches a plateau at a fixed concentration of each pollutant. This is because

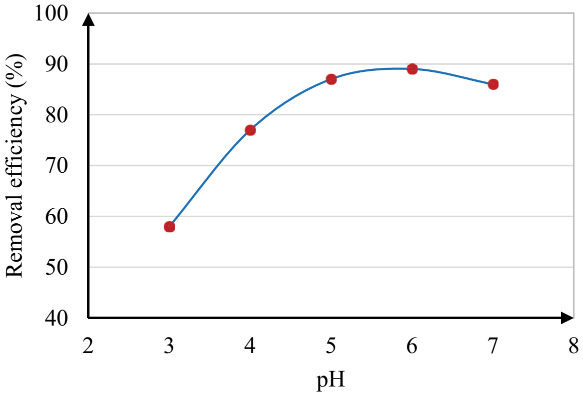

Fig. 3. Profiles of Cd(II) ion removal at different pH values.

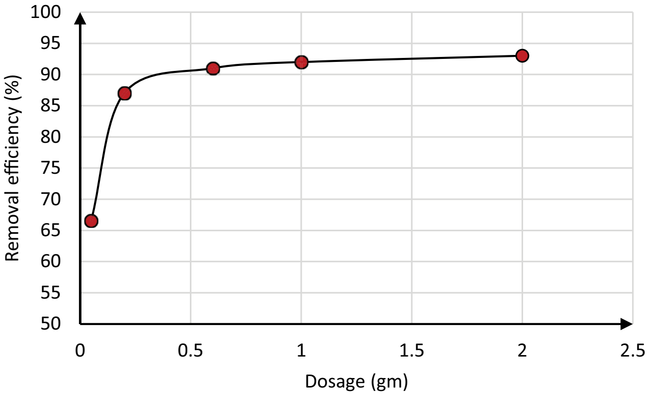

Fig. 4. Profiles of Cd(II) ion removal at different dosages of *Chlorophyceae* algae.

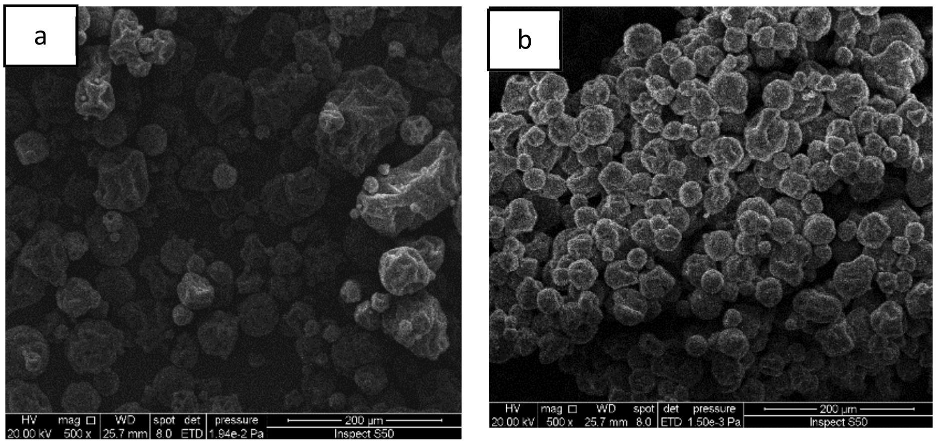

Fig. 2. Scanning electron microscopy photomicrographs of *Chlorophyceae* algae (a) with and (b) without Cd(II) ions.

increasing the adsorbent dosage will increase the active sites of adsorbents in the solution. These results worked well with [37]. The optimum values for biomass dosage 1 g/L.

3.2.3. Influence of initial ion concentration with time

Fig. 5 presents the effect of the various initial concentrations of Cd(II) ions 20, 50, 100, and 200 mg/L on the removal percentage of CA, even as the other parameters are kept constant. It is obvious from this figure that there is a decrease in the uptake rate of metal 94.5%–80% with raising the initial metal concentration from 20 to 200 mg/L. The reduction in the efficiency is explained by the saturation of the available reactive biosorption sites on the sorbent surface, while increasing the initial metal concentration [18]. The contact time is one of the most important parameters impacting biosorption effectiveness, modeling, and engineering of the biosorption process in the industry. In this graph, it can be seen that the removal of Cd(II) by the AC increased as the contact duration increased. The adsorption of Cd(II) was rapid for the first 50 min because there were accessible binding sites on the AC. The adsorption reached equilibrium within 90 min, and the removal percent reached 94.5% for Cd(II). Therefore, the adsorption of Cd(II) by AC took place for 90 min. The initial rapid removal occurs due to surface adsorption on the adsorbent. Then, the removal percentage remains nearly constant beyond that. This conclusion is consistent with Sari and Tuzen's findings [18].

3.2.4. Influence of agitation speed

Different agitation speeds (100, 200, and 300 rpm) were applied to find out their effect on the removal efficiency. This was investigated using CA, although all other parameters were kept constant. Which illustrates that about 92% of Cd(II) were removed, and the uptake increased with the increase in shaking rate to 94% at 300 rpm. This can be attributed as; the film around the solid surface is thicker and the film diffusion seems to be rate-limiting, increasing the agitation speed will reduce the thickness of the boundary layer, which in turn reduces the resistance to the mass transfer of the adsorbate, and hence increase the uptake process. This behavior is in agreement with [38].

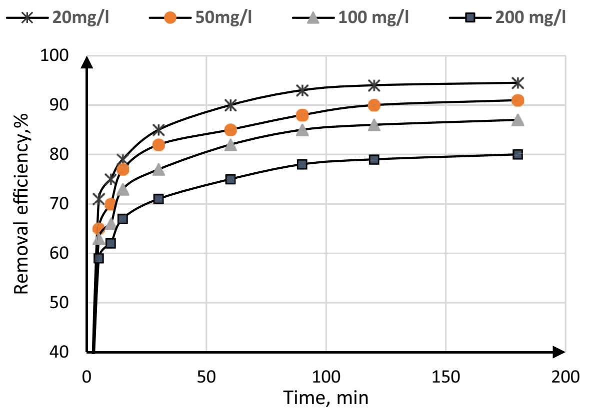

Fig. 5. Effect of initial concentration and time on the removal efficiency of Cd(II) ions by *Chlorophyceae* algae.

3.3. Isotherm study

The obtained experimental data was fitted to the two most commonly used isotherm models: Langmuir and Freundlich isotherms. The correlation coefficient (R^2) was used to judge the fitting of biosorption data into the isotherms.

In this investigation, the commonly used isotherm models Langmuir [Eq. (7)] and Freundlich [Eq. (8)] were employed to represent the data acquired from Cd(II) ions biosorption experiments by CA. For additional detail on the physical background of the use of these two formalisms in pollutant biosorption research, one might refer to the following papers [39,40].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{7}$$

$$q_e = K_F C_e^{1/n} \tag{8}$$

where q_e denotes the metal ions sorbed, q_m (mg/g) denotes the maximum biosorption capacity of the used biosorbent for the target pollutant (uptake), K_L (L/mg) is a Langmuir model constant; and n (g/L) and K_F (mg/g) are biosorption process intensity and biosorbents capacity, respectively, the two Freundlich equation constants denoting the toward non-linear isotherm models were used to examine the experimental data.

Fig. 6 illustrates a comparison of these two isotherm models using experimental data, and Table 1 lists the isotherm parameters for each model as determined using linearized plots. In comparison to the Freundlich isotherm model, the correlation coefficient of 0.992 shows that the Langmuir model is more appropriate for characterizing the

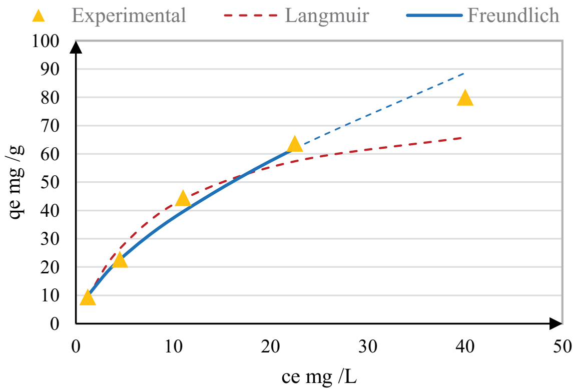

Fig. 6. Equilibrium of Cd(II) ions biosorption onto *Chlorophyceae* algae.

Table 1
Equilibrium biosorption isotherm parameters for Cd(II) ions biosorption onto *Chlorophyceae* algae

Langmuir			Freundlich		
q_m (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
81.071	0.1077	0.992	8.836	1.6	0.991

experimental results of Cd(II) biosorption onto AC. This shows that Cd(II) ions cover the biosorbents outer surface in a monolayer, and the maximum biosorption capacity ($q_{\max}$, mg/g) required to form such a monolayer is 81.071 mg/g.

3.4. Kinetic study

Pseudo-first-order [Eq. (9)] and pseudo-second-order models [Eq. (10)] were utilized to correlate the kinetics data [41]. To determine the parameters for each model, the linearized form of these models was fitted against a set of experimental data, as illustrated in Fige. 7. Fig. 7 shows a good agreement and their constant are illustrated in Table 2. Based on correlation coefficients, pseudo-second-order kinetic model gave better representation for the biosorption process.

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{9}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{10}$$

where q_e (mg/g) represents equilibrium amount of Cd(II) ions onto CA; q_t (mg/g) sorbet amount from the metal at time t; and K_1 and K_2 represent pseudo-first-order equilibrium rate biosorption constant (1/min) and rate constant of the pseudo-second-order biosorption. (g/mg·min), respectively.

According to the correlation coefficient (R^2) values in Table 2, the pseudo-second-order kinetic model effectively characterizes the empirical data of the adsorption of Cd(II) onto AC.

3.5. Lipids extraction

The results of oil extracted from the Cd(II)-loaded algae experiments were quite encouraging results as compared with other studies as can be seen from Table 3. The physical

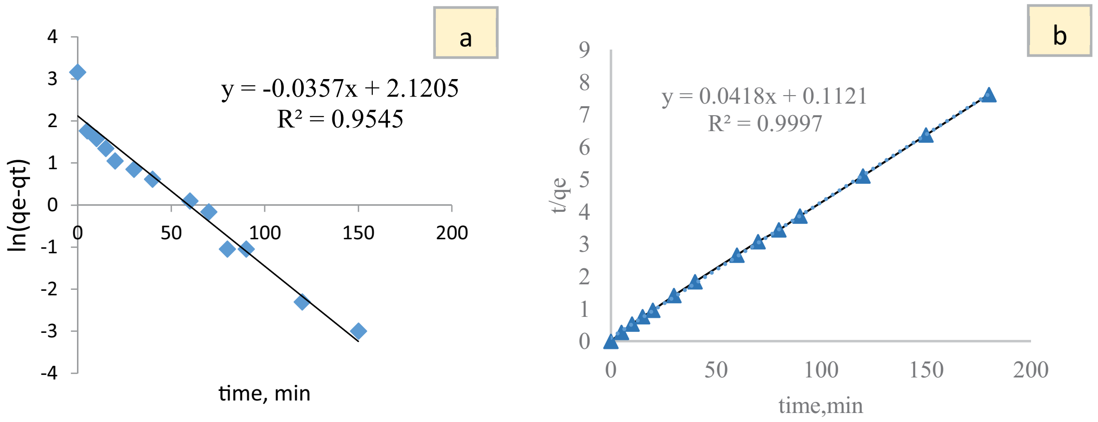

Fig. 7. Kinetic models for Cd(II) ion biosorption in *Chlorophyceae* algae biomass (a) pseudo-first-order and (b) pseudo-second-order.

Table 2
Kinetics models parameters for Cd(II) ions biosorption onto Chlorophyceae algae

$q_{e,\text{exp}}$	Pseudo-first-order			Pseudo-second-order		
23.6	q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g/mg·min)	R^2
	8.335	0.0357	0.9545	23.923	0.015586	0.9997

Table 3
Yields of oil and of biodiesel obtained in different microalgae species

Algae species	Oil extracted (w/w)	References
Spirogyra	14.82	[42]
Cladophora	11.76	[42]
Mixed culture (*Chlorophyceae* sp., *Cyanophyceae* sp., *Euglenophyceae* sp. and *Bacillariophyceae* sp.)	13.3	[43]
Nannochloropsis salina	46	[44]
Nannochloropsis sp.	18.8	[45]
Chlorella vulgaris	6.1	[46]
Mixed culture from a raceway pond	14.4	[47]
Chlorophyceae	10.5	Current study

properties of extracted oil was 0.95 g/cm^3 and 57 mPa·s for density and viscosity, respectively. Academically, this method is considered as a starting point for other studies that include, 'how to increase oil production in algae?' especially through genetic engineering research. On the industrial level, it is possible to create fields of algae on the wastewater and extract oil from them for the purpose of producing biofuels.

3.6. Biodiesel production

The experimental result of using 5 mL of oil extracted from the Cd(II)-loaded algae, by the transesterification process, resulted in 4 mL of biofuel, this corresponded with the theoretical value in the chemical equation. The resulting physicochemical properties of the biodiesel are shown in Table 4. They met the requirements of international standards for biofuels ASTM D 6751 and EN 14214. All characterizations have been performed in the laboratory of the Ministry of Oil/Dora Refinery. Biodiesel that has resulted from transesterification must have properties very similar to those of fossil diesel, to enable its direct use in combustion engines. The biofuel must have a low viscosity to allow better atomization during combustion, improving the efficiency of its burning. Therefore, it cannot be used directly as a diesel fuel in engines. The resulting chromatogram of the methyl ester peaks typically seen in the biodiesel sample production from algae feedstock, before the contaminant is present, is equal to 81.43%.

Furthermore, the GC-mass analysis results for the composition of biodiesel produced from Cd(II) ion-loaded algae are illustrated in Table 5. There are eight main components present, namely butyl propyl ester, followed by pentadecanoic acid, nitrous acid, butyl ester. Acetonitrile, 2-butenoic acid-ethenyl ester-ethyl tridecanoate, tridecanoic acid and 1-hexyl-2-nitrocyclohexane peaks. Also, it can be noticed that the presence of nitrogen compounds in the product may be due to the effect of cadmium salt [$Cd(NO_3)_2·2H_2O$]. In addition, as the methylation process converts fatty acids to FAME, it can be concluded that four fatty acids

Table 4
Physico-chemical properties of biodiesel and method used

Property	Method	ASTM D 6751	EN 14214	Algal biodiesel
Density at 15°C, (kg/m^3)	EN ISO12185	–	860–900	888
Kin. viscosity at 40°C, (mm^2/s)	EN ISO 3104	1.9–6.0	3.5–5.0	4.15
Flash point, °C	EN ISO 3679	130 min	120 min	139
Acid value, (mg·KOH/g)	EN 14104	0.5 max	0.8 max	0.1
Calorific value, (kJ/kg)	ASTM D 240	–	–	39.685
Fire point	–	–	–	149
Pour point	ASTM D97	−5 to −16	–	–5
Cloud point	EN 23015	3 max	–4	1.1
Cetane number	EN ISO 5165	47 min	51 min	68
Specific gravity at 15.5°C	ASTM D-941	0.86–0.89	–	0.869
Boiling point, (°C)	ASTM-7398	100–615	–	270
Water, (ppm by wt.)	EN ISO12937	<300	<500	44
Sulphur content, (mg/kg)	ASTM D5453	150 max		Nil
Ash content, (wt.%)	ASTM D482	100 max	–	Nil
Iodine number, (mg·I^2/100 g oil)	EN 14111	–	<120	98
Carbon residue, (%)	ASTM D975	–	–	0.008

Table 5
Peaks of biodiesel by gas chromatography-mass analysis

Peak#	R. Time (min)	I. Time	F. Time	Area	Area%	Height	Height%	A/H	Mark
1	14.993	14.958	15.017	19,122	4.2	8,379	5.38	2.28	MI
2	16.055	16	16.083	35,263	7.74	16,621	10.67	2.11	MI
3	16.171	16.1	16.2	28,694	6.3	9,569	6.14	3	MI
4	16.604	16.575	16.625	10,539	2.31	5,998	3.85	1.76	MI
5	18.015	17.975	18.042	17,477	3.84	7,696	4.94	2.27	MI
6	18.232	18.183	18.258	105,975	23.26	48,603	31.2	2.17	MI
7	18.456	18.317	18.5	218,291	47.9	47,350	30.39	4.63	MI
8	19.976	19.942	20	20,342	4.46	11,573	7.43	1.7	MI
	–	–	–	455,703	100	155,789	100	–	MI

are converted to FAME. Algae-based biodiesel may also perform as petroleum diesel, because it has reduced emissions of particulate matter, CO, hydrocarbons, and So_x, and does not contain sulfur, but may have an increase in NO_x, depending on the type of engine [48]

4. Conclusion

The results indicated that *Chlorophyceae* algae was a sustainable and cost-effective adsorbent for the removal of Cd(II) ions from aqueous solutions. The maximum removal percentage of 93% was achieved at 1 g/L of CA adsorbent dose, pH 5, shaking speed of 300 rpm, and an optimum contact time of 90 min for a 20 mg/L initial Cd(II) ion concentration. Both Langmuir and Freundlich isotherm models described the biosorption data in better form, where the coefficient of determination (R^2) was more than 0.991; while the modeling of kinetics data showed the biosorption of Cd(II) ions on CA followed pseudo-second-order kinetics with regression coefficients more than 0.999. The characterization experiment was carried out using the SEM technique, which indicated that the used algal biomass had good biosorption features related to the surface morphology. The tests of biodiesel production from CA loaded with Cd(II) ions proved that the fuel specifications of FAMEs compounds closely coincided with the biodiesel standards prescribed by EN 14103, even in the presence of nitrogen compounds, and could meet the requirements of clean construction. Therefore, it was proven that algae were a renewable source of energy, even though it was loaded with toxic contaminants.

Acknowledgements

We like to express our gratitude to the Department of Environmental Engineering. We're grateful to the folks at the Biochemical Engineering lab at Al-Khwarizmi College of Engineering for their assistance with our experiments.

Financial and ethical disclosures

No specific grant was given to this research by funding organizations in the public, private, or not-for-profit sectors.

Data availability

The data that has been used is confidential.

References

[1] X. Liu, Microbial technology for the sustainable development of energy and environment, Biotechnol. Rep., 27 (2020) e00486, doi: 10.1016/J.BTRE.2020.E00486.

[2] S.D. Salman, I.M. Rashid, Production and characterization of composite activated carbon from potato peel waste for cyanide removal from aqueous solution, Environ. Prog. Sustainable Energy, (2023) e14260, doi: 10.1002/EP.14260.

[3] A.K. Mohammed, H.F. Hameed, I.M. Rashid, Wastewater remediation using activated carbon derived from Alhagi plant, Desal. Water Treat., 300 (2023) 36–43.

[4] S.D. Salman, I.M. Rasheed, A.K. Mohammed, Adsorption of heavy metal ions using activated carbon derived from Eichhornia (water hyacinth), IOP Conf. Ser.: Earth Environ. Sci., 779 (2021) 012074, doi: 10.1088/1755-1315/779/1/012074.

[5] M. Plöhn, C. Escudero-Oñate, C. Funk, Biosorption of Cd(II) by Nordic microalgae: tolerance, kinetics and equilibrium studies, Algal Res., 59 (2021) 102471, doi: 10.1016/j.algal.2021.102471.

[6] S.D. Salman, I.M. Rasheed, M.M. Ismaeel, Removal of diclofenac from aqueous solution on apricot seeds activated carbon synthesized by pyro carbonic acid microwave, Chem. Data Collect., 43 (2023) 100982, doi: 10.1016/J.CDC.2022.100982.

[7] F.I.A. Al-Obaidi, Removal of copper ion from wastewater by flotation, J. Eng., 17 (2011) 1483–1491.

[8] T.K. Hussein, Comparative study for removal of Zn^{+2} ions from aqueous solutions by adsorption and forward osmosis, Iraqi J. Chem. Pet. Eng., 18 (2017) 125–138.

[9] N.A.A. Qasem, R.H. Mohammed, D.U. Lawal, Removal of heavy metal ions from wastewater: a comprehensive and critical review, 4 (2021), doi: 10.1038/s41545-021-00127-0.

[10] I.S. Bădescu, D. Bulgariu, I. Ahmad, L. Bulgariu, Valorisation possibilities of exhausted biosorbents loaded with metal ions – a review, J. Environ. Manage., 224 (2018) 288–297.

[11] I.M. Rashid, S.D. Salman, A.K. Mohammed, Removal of pathogenic bacteria from synthetic contaminated water using packed bed silver nanoparticle-coated substrates, Energy Ecol. Environ., 6 (2021) 462–468.

[12] I.N. Abd, M.J. Mohammed-Ridha, Simultaneous adsorption of tetracycline and amoxicillin by *Cladophora* and *Spirulina* algae biomass, Iraqi J. Agric. Sci., 52 (2021) 1290–1303.

[13] A. Petrovič, M. Simonič, Removal of heavy metal ions from drinking water by alginate-immobilised *Chlorella sorokiniana*, Int. J. Environ. Sci. Technol., 13 (2016) 1761–1780.

[14] D.S. Alobaidi, A.I. Alwared, Role of immobilised *Chlorophyta* algae in form of calcium alginate beads for the removal of phenol: isotherm, kinetic and thermodynamic study, Heliyon, 9 (2023) e14851, doi: 10.1016/j.heliyon.2023.e14851.

[15] S.M. Monica Sharma, Nitin Thukral, Microalgae as future fuel: real opportunities and challenges, J. Thermodyn. Catal., 6 (2015), doi: 10.4172/2157-7544.1000139.

[16] K. Chojnacka, Biosorption and bioaccumulation - the prospects for practical applications, Environ. Int., 36 (2010) 299–307.

[17] A.H. Sulaymon, A.A. Mohammed, T.J. Al-musawi, Competitive biosorption of lead, cadmium, copper, and arsenic ions using algae, Environ. Sci. Pollut. Res., (2013) 3011–3023, doi: 10.1007/s11356-012-1208-2.

[18] N. Khanjani, P. Molazadeh, M.R. Rahimi, A. Nasiri, Adsorption of lead by microalgae *Chaetoceros* sp. and *Chlorella* sp. from aqueous solution, J. Community Health Res., 4 (2015) 114–127.

[19] H.N. Abdulkareem, A.I. Alwared, Performance of immobilized *Chlorella* algae for removing Pb(II) ions from aqueous solution, Iraqi J. Chem. Pet. Eng., 20 (2019) 1–6.

[20] H. Abdelkareem, A. Alwared, T.J. Al-Musawi, F. Brouers, A comparative study for the identification of superior biomass facilitating biosorption of copper and lead ions: a single alga or a mixture of algae, Int. J. Environ. Res., 13 (2019) 533–546.

[21] A.R. Lucaci, D. Bulgariu, M.C. Popescu, L. Bulgariu, Adsorption of Cu(II) ions on adsorbent materials obtained from marine red algae *Callithamnion corymbosum* sp., Water (Switzerland), 12 (2020), doi: 10.3390/w12020372.

[22] A.A. Mohammed, A.A. Najim, T.J. Al-Musawi, A.I. Alwared, Adsorptive performance of a mixture of three non-living algae classes for nickel remediation in synthesized wastewater, J. Environ. Health Sci. Eng., 17 (2019) 529–538.

[23] S. Khan, R. Siddique, W. Sajjad, G. Nabi, K.M. Hayat, P. Duan, L. Yao, Biodiesel production from algae to overcome the energy crisis, Hayati J. Biosci., 24 (2017) 163–167.

[24] S. Zhang, L. Zhang, G. Xu, F. Li, X. Li, A review on biodiesel production from microalgae: influencing parameters and recent advanced technologies, Front. Microbiol., 13 (2022) 1–20.

[25] A.K. Mohammed, Z.A. Alkhafaje, I.M. Rashid, Heterogeneously catalyzed transesterification reaction using waste snail shell for biodiesel production, Heliyon, 9 (2023) e17094, doi: 10.1016/j.heliyon.2023.e17094.

[26] E. Uçkun Kiran, K. Stamatelatou, G. Antonopoulou, G. Lyberatos, Production of Biogas *via* Anaerobic Digestion, Handbook of Biofuels Production (2nd ed.), Processes and

Technologies, Elsevier Ltd., 2016. Available at: https://doi.org/10.1016/B978-0-08-100455-5.00010-2

[27] S.A. El-Mekkawi, S.M. Abdo, F.A. Samhan, G.H. Ali, Optimization of some fermentation conditions for bioethanol production from microalgae using response surface method, Bull. Natl. Res. Cent., 43 (2019), doi: 10.1186/s42269-019-0205-8.

[28] D.T. Zewdie, A.Y. Ali, Cultivation of microalgae for biofuel production: coupling with sugarcane-processing factories, Energy J. Sustain. Soc., 10 (2020) 1–16.

[29] I.M. Rashid, Y.D. Abdulwahab, A.K. Mohammed, W.N.R. Wan Isahak, B.A. Jassam, Modeling and optimization of biodiesel from high free-fatty-acid chicken fat by non-catalytic esterification and mussel shell catalyzed transesterification, J. Chem. Technol. Biotechnol., (2023), doi: 10.1002/jctb.7488.

[30] Z.A. Alkhafaje, A.K. Mohammed, I.M. Rashid, Development of two-step noncatalytic esterification of waste cooking oil for biodiesel preparation, React. Kinet. Mech. Catal., 131 (2020) 645–659.

[31] M.A. Islam, M. Magnusson, R.J. Brown, G.A. Ayoko, M.N. Nabi, K. Heimann, Microalgal species selection for biodiesel production based on fuel properties derived from fatty acid profiles, Energies, 6 (2013) 5676–5702.

[32] A.B.M. Sharif Hossain, A. Salleh, Biodiesel fuel production from algae as renewable energy, Am. J. Biochem. Biotechnol., 4 (2008) 250–254.

[33] I.M. Rashid, M.A. Atiya, B.H. Hameed, Production of biodiesel from waste cooking oil using CaO-egg shell waste derived heterogeneous catalyst, Int. J. Sci. Res., 6 (2017) 94–103.

[34] F.O. Olal, Biosorption and biomonitoring studies of selected heavy metals using green algae, *Spirogyra* species, J. Nat. Sci., 6 (2012) 22–34.

[35] J. Ren, L. Zheng, Y. Su, P. Meng, Q. Zhou, H. Zeng, T. Zhang, H. Yu, Competitive adsorption of Cd(II), Pb(II) and Cu(II) ions from acid mine drainage with zero-valent iron/phosphoric titanium dioxide: XPS qualitative analyses and DFT quantitative calculations, J. Chem. Eng., 445 (2022) 136778, doi: 10.1016/J.CEJ.2022.136778.

[36] A.A. Najim, A.A. Mohammed, Biosorption of methylene blue from aqueous solution using mixed algae, Iraqi J. Chem. Pet. Eng., 19 (2018) 1–11.

[37] R.K. Gautam, A. Mudhoo, M.C. Chattopadhyaya, Kinetic, equilibrium, thermodynamic studies and spectroscopic analysis of Alizarin Red S removal by mustard husk, J. Environ. Chem. Eng., 1 (2013) 1283–1291.

[38] O.A. Mohamad, X. Hao, P. Xie, S. Hatab, Y. Lin, G. Wei, Biosorption of copper(II) from aqueous solution using non-living *Mesorhizobium amorphae* strain CCNWGS0123, Microbes Environ., 27 (2012) 234–241.

[39] M.R. Samarghandi, A. Poormohammadi, N. Fatemeh, M. Ahmadian, Removal of Acid Orange 7 from aqueous solution using activated carbon and graphene as adsorbents, Fresenius Environ. Bull., 24 (2015) 1841–1851.

[40] L. Khodadadi, Q. Cheng, A. Radbruch, F. Hiepe, The maintenance of memory plasma cells, Front. Immunol., 10 (2019), doi: 10.3389/fimmu.2019.00721.

[41] A.I. Alwared, T.J. Al-Musawi, L.F. Muhaisn, A.A. Mohammed, The biosorption of reactive red dye onto orange peel waste: a study on the isotherm and kinetic processes and sensitivity analysis using the artificial neural network approach, Environ. Sci. Pollut. Res., 28 (2020) 2848–2859.

[42] A.S. Japar, M.S. Takriff, N.H.M. Yasin, Harvesting microalgal biomass and lipid extraction for potential biofuel production: a review, J. Environ. Chem. Eng., 5 (2017) 555–563.

[43] A.P. Florentino de Souza Silva, M.C. Costa, A. Colzi Lopes, E. Fares Abdala Neto, R. Carrhá Leitão, C.R. Mota, A. Bezerra dos Santos, Comparison of pretreatment methods for total lipids extraction from mixed microalgae, Renewable Energy, 63 (2014) 762–766.

[44] L. Bulgariu, M. Lupea, D. Bulgariu, C. Rusu, M. Macoveanu, Equilibrium study of Pb(II) and Cd(II) biosorption from aqueous solution on marine green algae biomass, Environ. Eng. Manage. J., 12 (2013) 183–190.

[45] M. Imran, K. Anwar, M. Akram, G.M. Shah, I. Ahmad, N. Samad Shah, Z.U.H. Khan, M.I. Rashid, M.N. Akhtar, S. Ahmad, M. Nawaz, R.J. Schotting, Biosorption of Pb(II) from contaminated water onto *Moringa oleifera* biomass: kinetics and equilibrium studies, Int. J. Phytorem., 21 (2019) 777–789.

[46] F. Yaşar, Ş. Altun, Biodiesel properties of microalgae (*Chlorella protothecoides*) oil for use in diesel engines, Int. J. Green Energy, 15 (2018) 941–946.

[47] T. Liu, J.H. Hou, J.B. Wang, W. Wang, X.Y. Wang, J.L. Wu, Biosorption of heavy metals from aqueous solution by the novel biosorbent *Pectobacterium* sp. ND2, Environ. Prog. Sustainable Energy, 37 (2018) 968–974.

[48] T.M. Mata, A.A. Martins, N.S. Caetano, Microalgae for biodiesel production and other applications: a review, Renewable Sustainable Energy Rev., 14 (2010) 217–232.