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Removal of Heavy Metals from Contaminated Water Using Local Algal Species

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ABSTRACT

Heavy metal contamination of water resources has become a major environmental challenge due to the persistence, toxicity, and bioaccumulation of these pollutants in aquatic ecosystems and living organisms. The present study evaluated the biosorption potential of two locally algal species, Oedogonium (filamentous green alga) and Chlorella (unicellular microalga), for the removal of lead (Pb), cadmium (Cd), and copper (Cu) from contaminated water. Batch biosorption experiments were conducted to investigate the effects of pH, contact time, and algal biomass concentration on metal removal efficiency. Residual metal concentrations were determined using Atomic Absorption Spectroscopy (AAS), and removal efficiencies were calculated under different experimental conditions.

The results showed that both species were capable of removing heavy metals from aqueous solutions, but Oedogonium had a consistently higher biosorption capacity than Chlorella. The optimal pH and algal biomass concentration with maximum removal efficiencies were recorded at pH 7 and 100 mg/L, respectively. The maximum removal efficiencies were 91.03% for Cd, 74.63% for Pb, and 53.50% for Cu using Oedogonium, compared with 84.33%, 73.13%, and 49.79%, respectively, using Chlorella. As stated in the even better performance of Oedogonium can be explained by its morphology filamentous, therefore larger surface area and more actives sites for binding with maximum metal adsorption. These findings indicate that locally isolated algal biomass represents an environmentally friendly, sustainable, and cost-effective biosorbent for the remediation of heavy metal-contaminated water. The study highlights the potential application of Oedogonium, in particular, as an efficient biological material for wastewater treatment.

KEYWORDS: Biosorption, Heavy metals, Oedogonium, Chlorella, Wastewater treatment, Freshwater, algae.

1. Introduction

Levels of heavy metals in water pose one of the greatest environmental threats globally because of rapid industrialization, urban expansion, mining activities, agricultural runoff and discharge of untreated industrial wastewater to aquatic systems (du Plessis, 2023; Machado *et al.,* 2024; Mahlangu *et al.,* 2024). Heavy metals are not biodegradable, highly persistent, and can enter the food chain and cause massive ecological disturbances and pose great risks to human health unlike many organic pollutants (Carreira *et al.,* 2023).

Long-term exposure to toxic metals like lead (Pb), cadmium (Cd), and copper (Cu) can cause many disease-like neurological disorders, kidney dysfunction, liver damage, reproductive toxicity and various forms of cancer have been linked together. So, heavy metal removal from the contaminated water has emerged as a significant focus area of environmental protection and sustainable management of water resources (Mahmoud *et al.,* 2023).

Leaded is known to be one of the most harmful toxic metals among these pollutants as it has adverse effect on nervous, haematological, and cardiovascular system even at low concentrations. Cadmium (Cd) is a metal that is highly toxic and has a long biological half-life, and is mainly deposited in the liver and kidneys causing permanent damage.

Copper (Cu) is a required trace element in biological systems, but is highly toxic when present in excess. Hence, effective removal of these metals from effluents is crucial prior to releasing into environment or its reuse in agriculture or industries. Although several traditional technologies are available for the removal of heavy metals, such as chemical precipitation, ion exchange, membrane filtration, electrochemical treatment, and activated carbon adsorption, these techniques have been reported to have certain drawbacks (Ordóñez *et al.,* 2023).

Most of the conventional methods are high operating and maintenance costs, high energy consumption, and produce secondary sludge which need more treatment, and are not efficient in low concentration of heavy metals. In recent ten years, therefore, the quest for viable environment-friendly, economical and highly efficient alternatives has gained momentum. Environmentally friendly, economical, and effective biological treatment technologies, including microbial biomass biosorption, are promising alternatives as they do not generate harmful secondary pollutants (Mahlangu *et al.,* 2024; Carreira *et al.,* 2023).

Algae have been of great interest as highly effective biosorbents since they can be abundant, renewable, and contain various surface functional groups. Polysaccharides, proteins, lipids, and other biopolymers found in the cell walls of the macroalgae and microalgae are also rich in functional groups, such as hydroxyl (–OH), carboxyl (–COOH), amino ($–NH_2$), phosphate ($–PO_4^{3-}$), and sulfate ($–SO_4^{2-}$), which act as active binding sites for metal ions via mechanisms of ion exchange, complexation, chelation, electrostatic attraction, and surface adsorption (Salman ,2025).

Algal biomass has several merits as compared to conventional adsorptive materials such as production costs, adsorption performance, and biodegradability, ease of cultivation, and biomass regeneration and reuse. The recent research has shown that different types of freshwater and marine algae are found to be effective in the removal of toxic metals like lead (Pb), Cadmium (Cd), copper (Cu), nickel (Ni), chromium (Cr) and zinc (Zn) from contaminated water, which also signifies their great potential in wastewater treatment and environmental remediation process.

In freshwater algae, the *Oedogonium* and *Chlorella* are more and more being studied and observed as potential biosorbent for the remediation of heavy metals, due to their structural and biochemical properties. *Oedogonium* is a filamentous green alga with high surface area and a strong cell-wall structure with polysaccharides and negative functional groups which are able to bind metal ions in solution. As a filamentous species, *Oedogonium* can be easily harvested from water and has shown great potential to be used in the remediation of trace metal contaminated wastewater (Salman *et al.,* 2024).

Likewise, *Chlorella* is one of the most widely studied freshwater microalgae because of its fast growth rate, high biomass productivity, adaptability to the environment and unique ability to accumulate and/or adsorb toxic metals. *Chlorella* is considered an attractive biosorbent for wastewater treatment because of its rich hydroxyl, carboxyl, amino and phosphate groups that are present on the cell surface of *Chlorella*, which increases its affinity toward various metal ions (Kyratzopoulou *et al.,* 2025)

The removal efficiency of algal biosorption is very high for toxic metals under optimal conditions, which is evidence to the increasing significance of algal biosorption as a sustainable remediation technology, and has been confirmed by recent studies on both freshwater and marine species (Asaad & Amer, 2024).

In spite of many studies on heavy metal biosorption by various algal species, most of studies reported are on marine algae or the commercially available microalgae while limited information has been reported on the ability of locally isolated freshwater algae such as *Oedogonium* and *Chlorella* to biosorb heavy metals under the environmental conditions found in Iraq.

Furthermore, comparative evaluations of these two locally isolated species under the same experimental conditions are few. In this regard, the present work was aimed at evaluating and comparing the biosorption efficiency of *Oedogonium* and *Chlorella,* being local isolates, to remove the lead (Pb), cadmium (Cd) and copper (Cu) from contaminated water. The effects of pH, contact time and algal biomass concentration on the removal of heavy metals were systematically examined, and the maximum operating conditions for the removal of the heavy metals were determined. The feasibility of using algal biomass as biosorbent in wastewater treatment was also examined by using indigenous algal biomass as an environmentally friendly and cost-effective biosorbent in wastewater treatment.

2. Materials and Methods

2.1 Collection and Identification of Algal Species

The samples of fresh water algae were taken from the Tourist Island area, Baghdad, Iraq. Samples were collected and then stored in sterile polyethylene containers and were immediately examined under a light microscope. Algal species were morphologically identified by following standard taxonomic keys as unicellular green microalga, *Chlorella* and filamentous green alga, *Oedogonium*.

2.2 Preparation of Algal Biomass

Algal biomass collected was washed thoroughly several times with distilled water to wash off the suspended particles and impurities. The cleaned biomass was then placed in the oven at 60°C for 24 hours to achieve a constant weight. The dried algae were then ground into fine powder by using a laboratory grinder and stored in airtight containers at room temperature till further use in the biosorption experiments.

2.3 Preparation of Heavy Metal Solutions

Analytical grade metal salts were used to make stock solutions of lead (Pb), cadmium (Cd) and copper (Cu) with deionized water at 1000 mg/L. Working solutions of the desired concentrations were made up by serial dilutions just before the experiments. 2.4 Batch Biosorption Experiments the ability of *Oedogonium* and *Chlorella* to remove heavy metals was assessed by the batch biosorption experiments. Dried algal biomass of 0.5 g was added to each of the 100 mL of heavy metal solution in 250 mL Erlenmeyer flasks. Experiments were performed under continuous shaking at 150 rpm at a room temperature. The effects of the following operating parameters were studied separately:

- pH: 4, 7, and 8

-Contact time: 24, 48, and 72 h

-The initial concentrations of the metals were 10, 50 and 100 mg/L.

The mixtures after the predetermined contact time were filtered through Whatman No. 1 filter paper to separate algae biomass from aqueous phase. The filtrates were collected for metal analysis. To determines concentration of the heavy metals in water samples. Atomic Absorption Spectroscopy (AAS) was used for the determination of the residual concentrations of Pb, Cd and Cu. The calibration curves were derived from the certified standard solutions for each metal before samples were analyzed. All the measurements were made based on the operating instructions of the manufacturer (APHA 2017).

2.4 Calculation of Removal Efficiency

The efficiencies of the removal (%) for each metal were determined as shown in(Pham et al. 2021).

Removal Efficiency (%) = $[(C_0 - C_e) / C_0] \times 100$ where:

C_0 = initial concentration of the metal (mg/L) C_e = Concentration of metal ion remaining in solution after biosorption (mg/L).

2.5 Statistical Analysis

Each experiment was repeated 3 times and all the results were reported as Mean ± SD. One-way analysis of variance (ANOVA) was used to analyze the significant difference among the experimental conditions. Significance was defined as $P < 0.05$.

3. Results and Discussion

3.1 Effect of Algal Species on Heavy Metal Removal

The removal of lead (Pb), cadmium (Cd) and copper (Cu) from the aqueous solutions by the local algal species, *Oedogonium* and *Chlorella*, was tested and the efficiency of their biosorption was determined. The results indicated that both algal species had high potential for removal of heavy metals. The microphotographs presented below are the morphological features of *Oedogonium* and *Chlorella* before their use in the biosorption experiments under the light microscope.

Table (3.1): Effect of *Oedogonium* in heavy metal removal.

Heavy metals / Experimental conditions		Cadmium (Cd)	Lead (Pd)	Copper(Cu)
pH	4	0.0731	0.023	0.951
	7	0.0091	0.019	0.727
	8	0.0470	0.021	0.863
Time	24 h	0.0842	0.023	0.924
	48 h	0.0437	0.020	0.811
	72 h	0.0124	0.018	0.689
Concentration	10 mg/L	0.0658	0.022	0.901
	50 mg/L	0.0326	0.020	0.781
	100 mg/L	0.0087	0.017	0.651

Table (3.2): Effect of *Chlorella* in heavy metal removal.

Heavy metals / Experimental conditions		Cadmium (Cd)	Lead (Pb)	Copper (Cu)
pH	4	0.0812	0.024	0.972
	7	0.0178	0.020	0.768
	8	0.0528	0.022	0.887
Time	24 h	0.0931	0.024	0.949
	48 h	0.0568	0.021	0.842
	72 h	0.0198	0.019	0.721
Concentration	10 mg/L	0.0741	0.023	0.921
	50 mg/L	0.0417	0.021	0.819
	100 mg/L	0.0152	0.018	0.703

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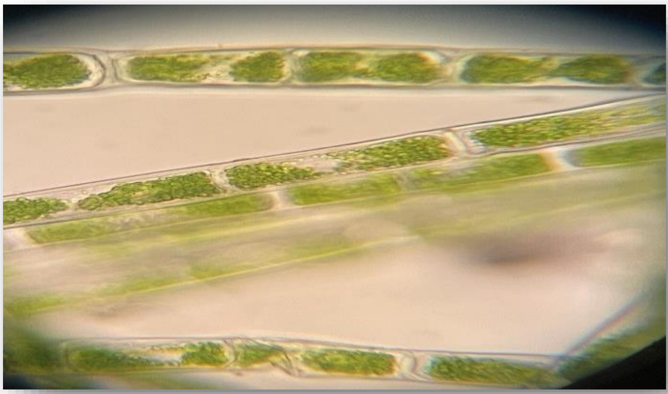

Figure 3.1: ***Oedogonium*** **under alight microscope 40x**

Table 3.3: Removal efficiency (%) of heavy metals by *Oedogonium*

Experimental conditions	**Cd (%)**	**Pb (%)**	**Cu (%)**
pH 4	24.64	65.67	32.07
pH 7	90.62	71.64	48.07
pH 8	51.55	68.66	38.36
24 h	87.22	73.13	50.79
48 h	54.95	70.15	42.07
72 h	13.20	65.67	34.00
10 mg/L	32.16	67.16	35.64
50 mg/L	66.39	70.15	44.21
100 mg/L	**91.03**	**74.63**	**53.50**

Figure 3.2: ***Chlorella*** **under alight microscope 40x**

Table 3.4: Removal efficiency (%) of heavy metals by *Chlorella*

Experimental conditions	**Cd (%)**	**Pb (%)**	**Cu (%)**
pH 4	**16.29**	**64.18**	**30.57**
pH 7	**81.65**	**70.15**	**45.14**
pH 8	**45.57**	**67.16**	**36.64**

24 h	**4.02**	**64.18**	**32.21**
48 h	**41.44**	**68.66**	**39.86**
72 h	**79.59**	**71.64**	**48.50**
10 mg/L	**23.61**	**65.67**	**34.21**
50 mg/L	**57.01**	**68.66**	**41.50**
100 mg/L	**84.33**	**73.13**	**49.79**

3.2 Effect of pH on Heavy Metal Biosorption

The pH of the solution is considered as one of the important parameters that influences the biosorption of heavy metals as it directly controls the surface charge of the biosorbent and the chemical speciation of metal ions in the aqueous solution. The effect of pH on biosorption efficiency of *Oedogonium sp.* and *Chlorella sp.* for the removal of Cd, Pb and Cu has been presented in tables (3.1) and (3.2).

The results showed that both algal species had the best biosorption efficiency at pH 7. In this case, *Oedogonium* lowered the levels of Cd, Pb and Cu to 0.0091 mg/L, 0.019 mg/L and 0.727 mg/L, respectively, with removal efficiencies of 90.62%, 71.64% and 48.07%. As for *Chlorella*, the removal efficiencies were 81.65%, 70.15% and 45.14%, respectively. The results obtained suggest that the ability of *Oedogonium* to bind heavy metal ions is higher than that of the *Chlorella* under neutral conditions. The lower removal efficiency at pH 4 is possibly due to the high level of hydrogen ions (H^+) in the solution which compete with the metal ions for the binding sites on the algal cell surface leading to a decrease in biosorption efficiency and this result agree with Abbrar *et al*,. 2017 . The extent of protonation decreased as the pH of the solution approached neutrality, and the hydroxyl (–OH), carboxyl (–COOH) groups became more electro-negative and were able to interact with the positive charge of metal ions through electrostatic attraction and ion exchange. For both algal species, a slight decrease of biosorption efficiency was noticed at pH 8. This decrease can be explained by the precipitation of metal hydroxides and metal speciation that decreases the amount of available free metal ions for biosorption. The highest removal efficiency observed at near neutral pH aligns with previous studies showing that algal biomass performs better in terms of adsorption at neutral pH because of the increased availability of active binding sites, and the decreased competition from hydrogen ions (Wang and Chen, 2009; *Bilal et al.,* 2018).

3.3 Effect of Contact Time on Heavy Metal Biosorption

Contact time is one of the most important parameters of biosorption process as it can affect the biosorption process duration, as it affects the time of interaction between metal ions and active binding sites available on algal biomass. The biosorption efficiency of *Oedogonium* and *Chlorella* for the removal of Pb, Cd and Cu from wastewater for three different contact times (24 h, 48 h & 72 h) is presented in Table 3.1 and 3.2 respectively.

The results showed that the biosorption efficacy of both algal species was increased with increase in contact time. The maximum removal efficiencies occurred after 72 h, suggesting that there was a need for adequate contact time for reaching equilibrium between the dissolved metal ions and the adsorption sites on the algal cell surface. *Oedogonium* showed higher removal efficiencies for all the metals under the same experimental conditions compared to *Chlorella* among the tested biosorbents. The gradual removal of metals as contact time increases can be explained by the slow diffusion of metal ions towards the algal surface, after which they attach to the functional groups that are available on the algal surface such as hydroxyl (–OH), carboxyl (–COOH), amino ($–NH_2$) and phosphate groups. In the first phase of biosorption, there are plenty of empty binding sites which allow the metal to be taken up quickly. With increasing contact time, more of the metal ions migrate into less accessible binding sites until finally, equilibrium is reached. The superiority of biosorption ability of *Oedogonium* when compared to *Chlorella* might be explained by the filamentous structure of *Oedogonium*, which has a larger surface area, and a higher number of adsorption sites that are accessible to the target ions, than *Chlorella* unicellular structure.This study was in line with the reports of increased biosorption efficiency with the increase of contact time. Pham *et al.* (2021) demonstrated a gradual increase in the levels of heavy metals up to adsorption equilibrium. Likewise, Mahmoud *et al.* (2023), and Machado *et al.* (2024) explained the better removal efficiency as being due to the increased contact time between metal ions and the active binding sites of the algal biomass.

3.4 The effect of initial metal concentration

The initial level of metal ion solution concentration is one of the factors that influence the biosorption process since it controls the concentration gradient between the solution and the biosorbent surface. The biosorption capacity of *Oedogonium* and *Chlorell*a with respect to Pb, Cd and Cu at various metal concentrations (10, 50 and 100 mg/l) is presented in Tables 3.1 and 3.2.Under all experimental conditions, the biosorption efficiency for both algal species increased with the increase of the initial metal concentration, and the maximum efficiency of removal of heavy metals was achieved at the initial concentration of 100 mg/L, thus proving the capability of *Oedogonium* to remove the heavy metals more efficiently than *Chlorella*. The increased probability of collision of metal ions with active binding sites on the algal biomass could be responsible for the improved biosorption of the metal ions at higher metal concentrations. The mass transfer between the bulk solution and the biosorbent surface increases with a higher concentration gradient until equilibrium is reached, and the mass transfer gets higher the adsorption rate gets higher. Furthermore, the presence of numerous negatively charged functional groups in algal cell wall leads to the presence of more binding sites for positively charged metal ions, which could be through ion exchange and complexation. The filamentous form of *Oedogonium* that possesses a larger effective surface area and more adsorption sites compared with the unicellular form of *Chlorella* may account for the superior performance. In addition, the variation in cell wall composition, such as the amount of polysaccharides and functional groups, may have been a factor for the greater affinity of *Oedogonium* for the ions of Pb, Cd and Cu. This has been observed in earlier studies. The greater driving force for mass transfer also enabled for enhanced biosorption when the metal concentrations were increased as shown by Pham *et al.* (2021). Similarly, and Abdel-Raouf *et al.* (2012) showed that the higher the metal concentration, the higher the capability of algal biomass to adsorb metals because of increased interaction between the dissolved metal ions and functional groups on the active surface. The optimum concentrations found in the present study, however, varied slightly from previous studies which could be explained by a change in algal species, experimental conditions, initial biomass dosage, and the physicochemical properties of the metals investigated.

4. Conclusion

It was concluded in the present study that the locally isolated freshwater algae *Oedogonium* and *Chlorella* are effective biosorbents to remove the lead (Pb), cadmium (Cd), copper (Cu) from contaminated water. Both algae species had a highly significant effect on biosorption efficiencies with changes in pH, contact time and initial metal concentrations. The best biosorption conditions were obtained at pH 7, initial metal concentration 100 mg/L and contact time 72 h. In all the experimental conditions, *Oedogonium* showed consistently higher removal efficiency than *Chlorella*, among the biosorbents investigated. This enhanced performance is due to filamentous shape, a high surface area and increased number of groups that can interact with metal ions via electrostatic attraction, ion exchange and complication interactions. The result obtained in this study indicated that algal biomass of local origin is a low cost, eco-friendly and sustainable option to the traditional physicochemical treatment for the removal of heavy metals from water in contaminated areas. Using indigenous freshwater algae could be an important feature in the progress of environmentally friendly wastewater treatment technologies, lower operational expenses and environmental impacts. Future work should be focused on testing the biosorption performance of these algal species in real industrial effluents, regeneration and reusability of algal biomass and the application of adsorption isotherm, kinetic and thermodynamic models to understand the biosorption mechanism and support the large scale applications. The present study was successful in showing that biosorption efficiencies can be achieved under laboratory conditions, but there are some limitations that should be mentioned. The experiments were carried out in the laboratory with synthetic contaminated water, which could be different in complexity from the actual industrial wastewater. In addition, the effect of the operational parameters (pH, contact time and initial metal concentration) was only tested, and the effect of the biomass regeneration and the effect of competing ions were not investigated. The factors mentioned should be explored in future studies to adequately assess the feasibility of the explored algal species in real environmental conditions.

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