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Algal Technology as Low Cost - effective Technique for Heavy Metal Ions bio-removal from Industrial Wastewater Effluents

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Abstract

The objective of this work is to study the effectiveness of two algal species; *Anabaena variabilis* and *oscillatoria sp.*, as bio-sorbent for removal of divalent ions of cadmium, copper, iron, lead and zinc, from industrial wastewater samples collected from different manufacturing processes located at Khartoum state.

The industrial wastewater samples were collected and composited well from Al-Asaad Steel factory, Saria Battery factories and Khartoum tannery. The results showed that: the two algal species used as dried biomass have great abilities to remove heavy metals from industrial wastewater samples, also the obtained results revealed that the removal ability of the two algal species depend upon treatment time. Therefore, the study concluded that the heavy metals removal followed the orders: $Zn^{2+} > Cd^{2+} > Pb^{2+} > Cu^{2+} > Fe^{3+}$ and $Cd^{2+} > Pb^{2+} > Fe^{3+} > Zn^{2+} > Cu^{2+}$ for *Osc.* and *Ana.* algal species, respectively.

Key words: Algal Technology; Heavy metals; phytoremediation

Introduction

Industry development has created an important number and volumes of wastewaters coming from the new manufacturing processes. Some of them contain pesticides, heavy metals and other toxic substances. In some cases, the toxic substances could be degraded by biological treatment, but in the case of heavy metals, they remain in the sediments and are slowly released into the water body (De la Noue, de Pawn 1988). Some authors have studying the pH influence on the toxicity of heavy metals

for microalgae growth (Darnall *et al.* 1986). Microalgae show certain attraction for polyvalent ions resulting on the removal of heavy metals from the environment. This aspect is very important from the environmental protection point of view. The aim of this work is to evaluate the usage of two algal species; *Anabaena variabilis* and *oscillatoria sp.*, as bio-sorbents, at semi-industrial scale, as a novel bioremediation system for steel industry wastewater. Moreover, this technique could help industry avoiding disabilities of traditional purification systems, along with synthesis value-added compounds (Serra, *et al.* 2020). Regarding the insistence to find innovative and green wastewater treatments, the use of algal species for effluent cleaning provides an alternative to conventional methods (bioremediation). The main advantages are the cost-efficiency rate, high public approval, and major results (Meng M. Zhao, *et al.* 2021).

Industrial development has created considerable values of wastewater containing environmentally harmful substances, such as heavy metals which are introduced into the environment by wide range of natural and anthropogenic sources (Pelgram *et al.* 1994). The wastewater mostly comes from chemical, tanning, automotive, paper, oil refining, dying, metallurgy and mining industries. Those industrial activities evacuate wastewater with high pollutants, such as heavy metals, that need to be removed before evacuating to natural water sources (Miao, *et al.* 2021; Sun, *et al.* 2020).

Heavy metals release into the environment can cause serious damage to the aquatic life, reduction in photosynthesis for plants and a lot of diseases for humans, exposure of heavy metals give rise to many diseases like *osteomalacia*, kidney, renal dysfunction and sometimes cancer (WHO, 1984).

The need to protect the environment gave rise to many methods for heavy metals removal from wastewater like, chemical precipitation, ion exchange, adsorption, electrochemical processes and reversed osmosis. The majority of those methods are expensive and they can generate hazardous waste (Meta *et al.* 2008). Therefore, solutions are sought which would be path for the environment and effective in the function of purifying waters polluted with heavy metals.

The trend now is focusing on biological methods, especially bio-sorption and bioaccumulation processes. These methods are cheap and with higher efficiency than the conventional methods. Many algae species can be used for this purpose. Algae are non – vascular plants that range in size from single – celled or colonial microalgae or “phytoplankton” such as diatoms and dinoflagellate, to large multicellular macro-algae such as seaweed or kelp. Every alga contains chlorophyll but the majority of them lack stems, vascular tissue, roots and leaves (Anbuezhian, 2015). Bioremediation by algae, called “phytoremediation”, has emerged as a viable method for removing HMs from wastewater (Poo *et al.* 2018; Ahmad *et al.* 2020; Koul *et al.* 2022). Advantages of phycoremediation include economic viability (Kotrba, 2011); algal biomass may be used over a period of years (Darda *et al.* 2019); algae

have the potential to sequester diverse contaminants (e.g., HMs, pesticides, inorganic and organic toxins) (Ajayan *et al.* 2011); in dilute effluents, they are quite effective, due to their high surface area-to-volume ratio (Yu *et al.* 1999); they are highly efficient at sequestering HMs (Ajayan *et al.* 2011); they are suitable even in wastewater containing higher metal concentrations (Yu, *et al.*, 1999); algae are appropriate for aerobic and anaerobic effluent treatment units (Salama *et al.* 2017); and cultures of microalgae may be cultivated in large-scale reservoirs, open ponds, and also in the laboratory (Salama *et al.* 2017).

The concept of using microorganisms as heavy metals bio-sorbents deserves special attention due to their biological origin and much lower costs of obtaining and use than in the case of membrane filtration. Moreover, heavy metals removal using microorganisms is a very quick process (Klimiuk, E.; Łebkowska, M., 2005).

To the best of our knowledge, this is the first study focused on industrial scale microalgae culturing for composite industrial wastewater process bioremediation.

Materials And Methods

Materials

This study was carried out in the facilities of Al-Assad steel factory, Saria battery complex and Khartoum tannery (Khartoum, Sudan). Industrial wastewater phytoremediation through microalgae culturing depends on tolerance and uptake capability. On this basis, experimental design was depended on tolerance and bioremediation. Established on their competence for metals removal as free living individuals, two living species of the tested algae namely *Anabaena variabilis* and *Oscillatoria algal* species were obtained from fresh water seasonal pods located at El- Salha district, Omdurman during April, 2021.

Methods

Algal preparation

Algal masses of filaments were collected in a glass beaker; the species were identified under the microscope with the aid of algae reference (Pham *et al.* 2021) and imaged using a Mega pixel digital camera for documentation. The algal species were washed two wise with tap water and thereafter with double distilled water to remove epiphytes and adhering dust and dirt particles. The washed biomass was first air dried for 24 hrs and then dried in an oven at 105 °C for 20 min to constant weight. The dried biomass was then ground, sieved through a 2 mm mesh size sieve and stored in polyethylene bottles (El Bestawy, 2019).

Collection and analysis of wastewater samples

Industrial wastewater samples were collected from the three selected sites. Al-Assad steel factory, Saria battery complex and Khartoum tannery. The wastewater samples were collected using 1L polyethylene sampling bottles. The three samples were composited perfectly and taken to laboratory using ice box at 4 °C. The sample after filtration was subjected to analysis by atomic absorption spectrophotometer for determination of heavy metals before treatment with algae. The analysis was replicated three times.

Treatment of industrial wastewater by algal species

Batch equilibrium experiments were performed in 250 mL Erlenmeyer glass flasks containing samples of industrial wastewater. An accurately weighed 250 mg portion of biomass were added to each flask and the mixtures were agitated on magnetic stirrer for different time intervals; 30, 60, 90 and 120min. After the respective agitation period, the solutions were separated from the biomass by filtration and subjected to further analysis by (AAS). All the bio-sorption experiments were done in triplicates, and the mean values were recorded.

Results And Discussion

The bio-sorption process was controlled by determining the concentration of studied metal ions in the algal biomass and industrial wastewater samples after a specified incubation time. Assessment of the process efficiency was achieved with reference to the control samples.

Analyzing of the composited industrial wastewater sample in this work revealed the presence of five heavy metals namely copper, iron, zinc, cadmium and lead with high concentrations. Their levels reported 0.18, 13.44, 4.88, 4.21 and 2.31mg/L for Cu^{2+} , Fe^{3+} , Zn^{2+} , Pb^{2+} and Cd^{2+} , respectively. Based on the experiments performed to study the ability of two selected algal species for removing the five selected metals, *Oscillatoria* and *Anabaena variabilis* represent the most promising species for remediation of metals-contaminated effluents. Therefore, *Oscillatoria* and *Anabaena* were chosen to study their capacity to remove Cu^{2+} , Fe^{3+} , Zn^{2+} , Pb^{2+} and Cd^{2+} ions from the contaminated industrial wastewater as individual cultures.

Residual concentrations and removal efficiencies of the five metals polluted industrial wastewater by *Oscillatoria* and *Anabaena variabilis* (**Table 1**) revealed that RE% is a function of the type of heavy metal, exposure time, and algal species. Removal efficiencies (REs) % of all the investigated metals are proportionally increased with exposure time regardless metal type, algal species or metal concentration. Consequently, the highest removal percentage was recorded at the end of the experiment (120min).

Table 1 and represented data in Figures (1-5) revealed that the maximum removal efficiency (RE) percentage ranges achieved by the tested individual *Oscillatoria* after two exposure hours are (30.53–

97.34), (39.83–96.10), (28.50–93.11), (35.56–90.56) and (65.69–86.24) %, for Zn^{2+} , Cd^{2+} , Pb^{2+} , Cu^{2+} and Fe^{3+} , respectively. Also, the ranges of RE (%) achieved by *Anabaena* are (21.65–95.67), (20.19–91.45), (67.65–81.77), (28.89–80.94) and (39.44–80.00) %, for Zn^{2+} , Cd^{2+} , Pb^{2+} , Cu^{2+} and Fe^{3+} , respectively. Removal efficiency efficiencies showed variations for the tested metals by different algal species even from the same group. This observation may attribute mainly to the selectivity and different tendencies of such algal species to different metals based on their metabolic capabilities and resistance and/or tolerance to such selected metals. The present study, is certainly proved this circumstance. Therefore, results explained that the free individual algal species of the two selected species could remove the tested metals with very high RE (%) in the following orders $Zn^{2+} > Cd^{2+} > Pb^{2+} > Cu^{2+} > Fe^{3+}$ and $Cd^{2+} > Pb^{2+} > Fe^{3+} > Zn^{2+} > Cu^{2+}$ for *Osc.* and *Ana.* algal species, respectively. Also high selectivity was observed among the tested algae. This was shown by the highest removal of Zn^{2+} and Cd^{2+} achieved by *Oscillatoria* while the highest removal of Cd^{2+} and Pb^{2+} was achieved by *Anabaena*.

Table 1 Residual concentration and removal efficiency percentage of the composite industrial wastewater sample after different treated periods by *Osc.* and *Ana.* algal species

Heavy metal	Treated period times (mins)	Osc.		Ana.	
		RC (ppm)	RE%	RC (ppm)	RE%
Cu	0	0.18	100	0.18	100
	30	0.103	35.56	0.109	39.44
	60	0.081	55	0.093	48.33
	90	0.052	71.11	0.071	60.56
	120	0.017	90.56	0.036	80.00
Fe	0	13.44	100	13.44	100
	30	4.61	65.69	4.36	67.65
	60	3.76	72.02	4.03	70.01
	90	3.09	77.01	3.65	72.84
	120	1.85	86.24	2.45	81.77
Zn	0	4.88	100	4.88	100
	30	3.39	30.53	3.47	28.89
	60	3.08	36.89	3.16	35.25
	90	2.15	55.94	2.56	47.54
	120	0.13	97.34	0.93	80.94
Pb	0	4.21	100	4.21	100
	30	3.01	28.50	3.36	20.19
	60	2.65	37.05	2.87	33.97
	90	1.07	74.58	1.19	71.73
	120	0.29	93.11	0.36	91.45
Cd	0	2.31	100	2.31	100
	30	1.39	39.83	1.81	21.65
	60	0.96	58.44	1.02	55.84
	90	0.41	82.25	0.61	73.59

120	0.09	96.10	0.1	95.67
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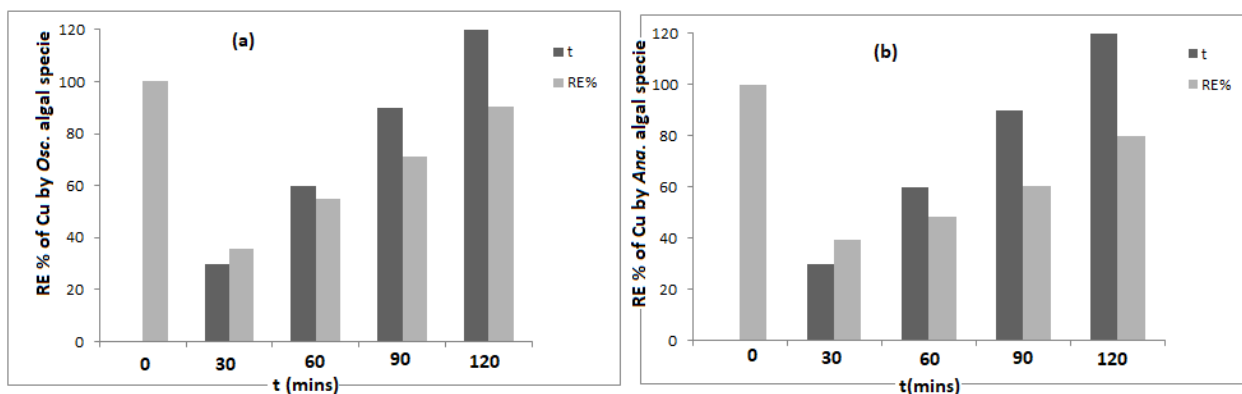


Figure 1 Removal efficiency (%) of Copper in the composite industrial wastewater sample after different treated periods by a: *Osc.* b: *Ana.* algal species

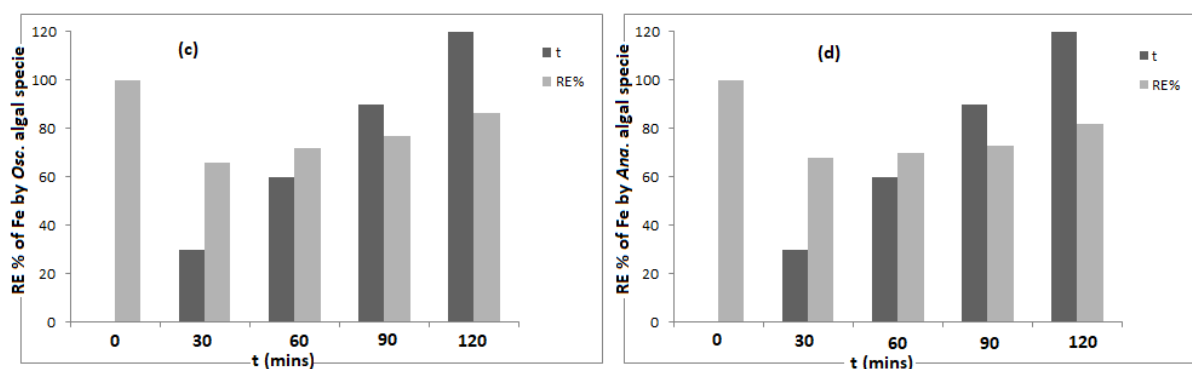


Figure 2 Removal efficiency (%) of Iron in the composite industrial wastewater sample after different treated periods by c: *Osc.* d: *Ana.* algal species

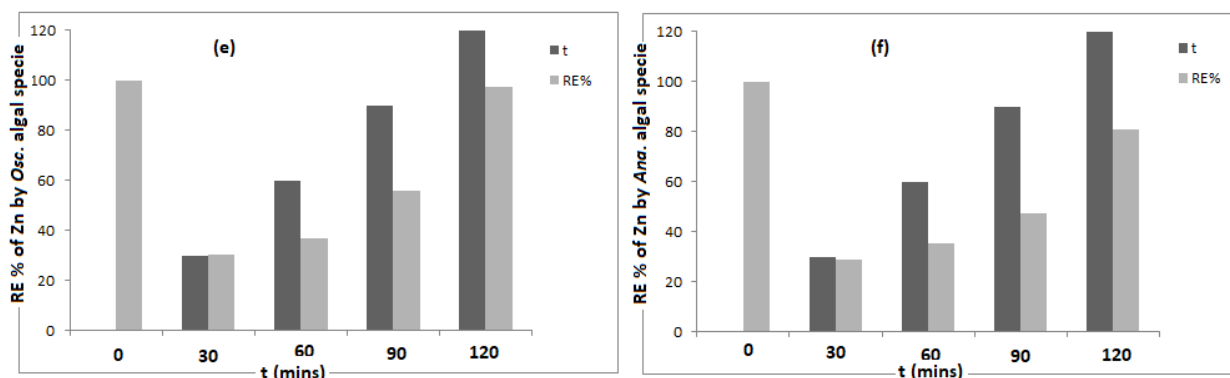


Figure 3 Removal efficiency (%) of Zinc in the composite industrial wastewater sample after different treated periods by e: *Osc.* f: *Ana.* algal species

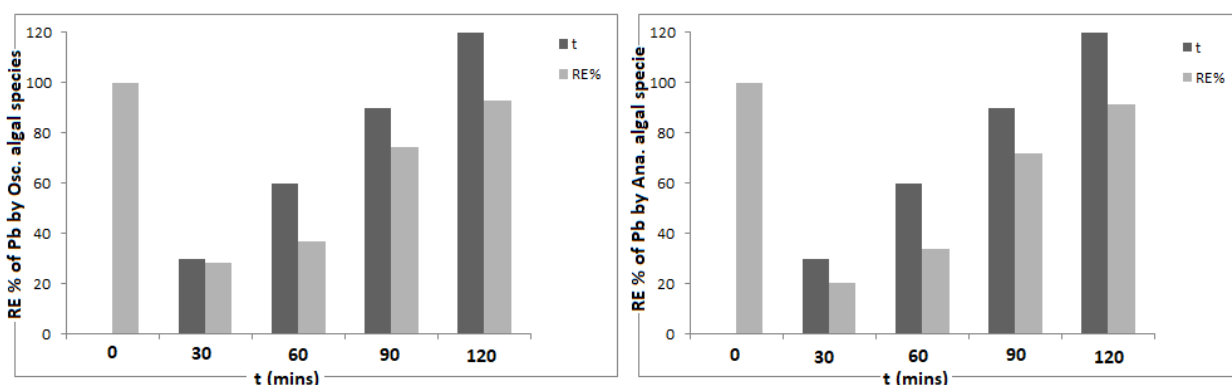


Figure 4 Removal efficiency (RE %) of Lead in the composite industrial wastewater sample after different treated periods by g: *Osc.* h: *Ana.* algal species

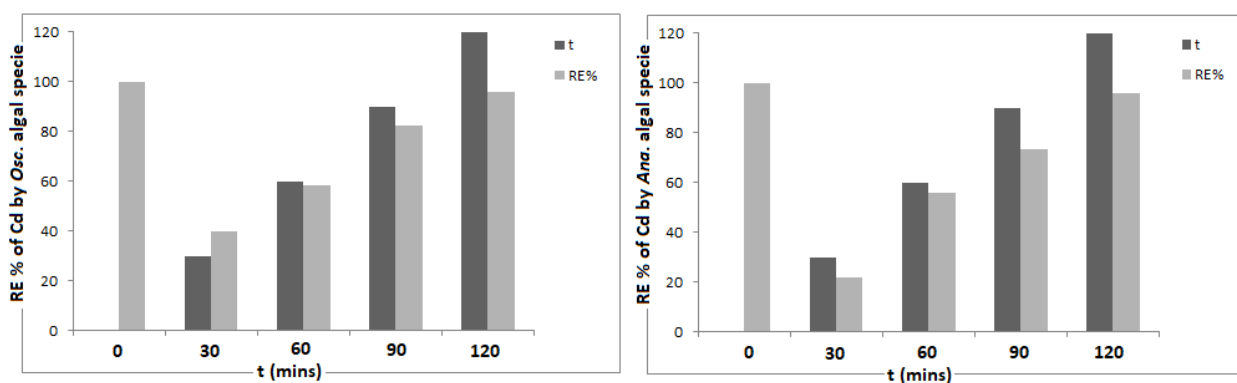


Figure 5 Removal efficiency (RE %) of Cadmium in the composite industrial wastewater sample after different treated periods by i: *Osc.* j: *Ana.* algal species

Conclusion

Industrial wastewater remediation through traditional systems are difficult, mainly due to the high concentrations of heavy metals present in these types of residues. Though, this study has been proven the successful adaptation to composite industrial wastewater by *Osc.* and *Ana.* algal species, along with the bioremediation of contaminants of concern. This result proves the possibilities of microalgae culturing as a novel way for compounds recovery from residues, approaching future industry to a circular economy system.

Heavy metals polluted of aquatic ecosystems are a serious concern because of its toxicity towards human health and all biota. Several species of algae have been identified as promising candidates for removal or detoxification of HMs and are potential economical substitutes to physico-chemical techniques of remediation.

Study findings revealed that the two selected algal species free characterize by excellent bio-removal abilities toward metals polluted water or wastewater even at their high concentrations with selective preferences among them. This advantage could be efficiently used for decontaminating wastewater

effluents as well as natural aquatic ecosystems. It also provides an economic and excellent tool not only for the protection of the received environments but also to recover and reuse the treated compatible wastewater in any purpose such as irrigation of agricultural non edible crops.

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