Biosorption of Heavy Metals from Aqueous Industrial Effluent by Non-living Biomass of Two Marine Green Algae *Ulva lactuca* and *Dunaliella salina* as Biosorpents

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ABSTRACT

The growing industries in Suez Gulf lead to two serious environmental problems, heavy metals pollution, and eutrophication. The present work focused on, how those two problems can solve each other. Therefore, non-living dried biomass of the most blooming algae, "*Ulva lactuca* and *Dunaliella salina*" in Suez Gulf were used as biosorpents to remove heavy metals (Zn, Cu, Cd, Fe, Mn, Pb, Ni and Cr) from two types of aqueous industrial effluents, belonging to petrochemicals (E.1) and fertilizers (E.2) production. The results clarify that Biosorption capacity of *D. salina* was more powerful for Cd, Zn and Pb within E.1, especially in case of lead (22.34 mg.g^{-1}) showing distinct gap with E.2 (7.63 mg.g^{-1}). However, *U. lactuca* was more efficient for Fe (4.07- 15.86 mg.g^{-1}) and Cu (0.83- 11.49 mg.g^{-1}) within E.1, meanwhile it gave its maximum (2.75- 10.9 mg.g^{-1}) within E.2 with significant capacity in case of Mn. On the other hand, anent the removal efficiencies, Cu, Fe and Mn had maximum removal efficiencies by *U. lactuca* within both effluents (91.8, 87.2 and 84.8% respectively) with a superiority of E.2. However, in case of Zn (87.4%), Pb (86.2%) and Cd (81.5%), *D. salina* was most efficiency. In conclusion, this work confirms the potential use of *U. lactuca* for removal of Cu, Fe, and Mn, however, *D. salina* was more powerful in removing Cd, Zn, and Pb from industrial wastewater.

Keywords: Biosorption, heavy metals, industrial waste, *Ulva lactuca Dunaliella salina*.

INTRODUCTION

Modern industry plays the key role in the scenario of environmental pollution. Aquatic bodies are being overwhelmed with microbes and waste matter. Among toxic substances, heavy metal cause threatening to human health and ecosystem and may lead to a serious groundwater pollution problem Since, heavy metals are among the conservative pollutants Kaparapu *et al.* (2015). Walter *et al.* (2011) reported that, three kinds of heavy metals are of concern, including precious metals (such as: Pd, Ag, Pt, Ru, Au etc.), toxic metals (such as: Hg, Cr, Pb, Zn, Cu, Ni, As, Cd, Sn, Co, etc.) and radionuclides (such as: U, Ra, Th, Am, etc.). That are bio-accumulative and non-biodegradable toxins (Walter *et al.*, 2011 and Prabha *et al.*, 2016), the presence of such metals in aquatic environments cause severe damage to aquatic life, hence they find their way to the food chain (Hassan *et al.*, 2013 and 2014; Brouersa *et al.*, 2016) and as a result profoundly disrupting the biological processes. Moreover, heavy metals enter our bodies through eating, drinking, skin and inhaling (Renge *et al.*, 2012), once in the body these metals have serious consequences on human such as nervous system deteriorations, reproductive failures, brain damage, irritability, kidney damage, anaemia, tumour formation, muscles weakness, etc (Bhatnagar and Kumari, 2013). Moreover, they also accumulate in the sediments and slowly released into the water body (Hassan *et al.,* 2013 and 2014; Prabha *et al.,* 2016).

Therefore, removal of heavy metals from discharged effluents has become important to maintain water quality that is suitable for human health and environment. Concerning remediation of harmful industrial effluent, various conventional methods have been employed in removal of heavy metals from aqueous industrial effluents such as; membrane filtration, ion exchange, chemical precipitation, reverse osmosis, solvent extraction, electrodialysis, oxidation, evaporation, activated carbon adsorption (Pappalardo *et al.*, 2010 and Brouersa *et al.,* 2016). Nevertheless, those methods have extremely high potential in the removing of heavy metals, but often with high operational costs (Prabha *et al.*, 2016) and difficult to maintain due insufficient to meet strict regulatory requirements, in addition to, extra cost for treating the resulting sludge. Hence, there is the insistence on innovative technologies with low cost, and high efficiency, for the removal of metal from contaminated industrial wastewater (Oilgae, 2010 and Brouersa *et al.,* 2016).

Biosorption has been shown to be a feasible economically favourable alternative with high adsorptive capacities for the removing of heavy metals from wastewater (Bhatnagar and Kumari, 2013). Besides, it enhanced selectivity for specific metals of interest, reduced operation time, improved the removal effici-ency from diluted solutions, and minimization of chem-ical or biological sludge, so, no production of secondary compounds which might be toxic (Kaparapu *et al.*, 2015). Simply, biosorption is an effective technology using living or dead biomasses to remove toxic metals from aqueous solutions (Davis *et al.*, 2003 and Nirmal and Cini, 2012).

The mechanism of biosorption is mainly based on physical adsorption (electrostatic attraction-Vanderwaal forces of attraction) and/or chemical adsorption (covalent binding between negative charge of cell surface and cationic ions). Various biomasses such as bacteria, yea-

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st, fungi, plants and alga for biosorption of metal ions have been extensively studied in the last two decades (Vieira and Volesky, 2000). Among all the biological materials, marine algae have many features to be considered as an ideal candidates as biosorpent, including rich source in the oceanic environment, relatively cheap to process, able to accumulate high metal content and have high metal binding capacities due to the presence of hetero-polysaccharides, proteins or lipid in its cell wall structure for sequestration of heavy metal ions (Davis *et al*., 2003), high tolerance to heavy metals, and large surface area/volume ratios (Davis *et al.,* 2003 and Bhatnagar and Kumari, 2013), beside all of that it is ecologically safer way. The commercial use of algal cultures spans about 75 years with application to wastewater treatment and mass production of different strains such as *Chlorella* and *Dunaliella* (Abdel-Raouf *et al*., 2012).

Algae are significantly effective in treating more than one problem at a time, which is not possible by a conventional process of chemical treatment (Bhatnagar and Kumari, 2013). Qari and Hassan (2014) reported that *Dunaliella* sp. has removed 95% of Zn and Cd after 108 hours, and 90% of Cu after 60 hours of incubation. Moreover, 93% of Pb, Ni and Cr were removed after 36 hours of incubation. However, concerning *Ulva lactuca* Ghoneim *et al.* (2014) mentioned that the dead biomass of the green alga *Ulva lactuca* could be used as an efficient biosorpent material for the removal of heavy metals ions from aqueous solutions. Further, green algal species like *Scenedesmus quadricauda, Chlorella vulgaris* (Awasthi and Rai, 2004) and *Chlorella homosphaera* (Nirmal *et al.,* 2010) have also been tested for their biosorption capacities.

Suez Gulf has a unique geographic location, where it is ended with Suez Canal. This canal is a vital navigational passage way linking between the Mediterranean and the Red Sea and then connects between east and west. In this area, a large number of industries were created and discharged wastes containing different compound including heavy metals (Ghoneim *et al.,* 2014) leading to serious environmental and public health problems. On the other hand, the discharged effluent contains high loads of organic pollutants which enhance flourishing of green seaweed causing another coastal environmental problem of eutrophication along shorelines. When the coast becomes covered with algae especially *Ulva* making a green mat called ''Green Tide'', the landscape becomes bad with a disgusting odour generated from rotten algae. The green tide is a serious environmental problem in coastal areas. Currently, the enormous amount of algal biomass presents a significant problem in waste disposal. Therefore, the development of a technology which effectively utilizes algae biomass is desired. Kaparapu *et al*. (2015) have noted the applicability of algal biomass as a biosorpents

The present work focused on, how one of those problems can solve the other. In this context, two of the most dominant and commonly blooming marine green algae

in Suez Gulf are used as biosorpent for heavy metals in the industrial effluent. Hence, to be a applicable, the present study investigated the biosorption performance and efficiency of non-living dried biomass obtained from the local blooming of the green unicellular microalgae; *Dunaliella salina* and the green seaweed; *Ulva lactuca* to remove heavy metals (Zn, Cu, Cd, Fe, Mn, Pb, Cr and Ni) from two different types of aqueous industrial effluents, one for petrochemicals and the other for fertilizers production. Beside of that, the choice of this species was based on its availability and cost.

MATERIALS AND METHODS

Preparation of Adsorpents Biomass
Two species of the most frequent and common green alga inhabiting Suez Gulf, a northern part of the Red Sea, were selected to use as adsorbents agent. One of them, *Ulva lactuca*, is macro-green alga and the other *Dunaliella salina* is unicellular green phytoplankton.

Preparation of *Ulva lactuca*
The marine macroalgae *Ulva lactuca* was collected from the intertidal zone Suez Gulf at Suez governorate, Egypt in the beginning of spring season (at the end of March 2016). Where *Ulva lactuca* was always flourished and give a blooming growth during that period of the year at Suez Gulf (Fig. 1). The collected algal biomass which used in its natural forms was washed several times with excess tap water and finally with distilled water in order to remove sand, impurities, and salt from the surface. The washed algal biomass air-dried for four days and then was oven dried for 48 h at 60°C.
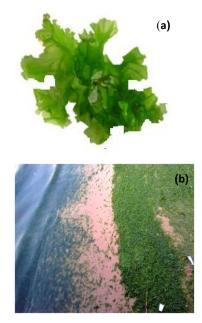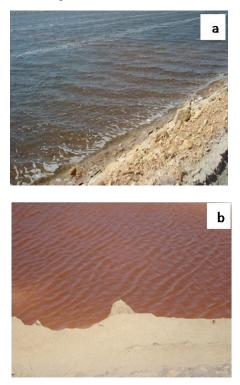

Figure (1): (a) *Ulva lactuca* (b) blooming growth at the intertidal zone Suez Gulf.

Preparation of *Dunaliella salina*
The marine unicellular green microalgae *Dunaliella*

Salina was collected from Suez Gulf and from two small saline lakes near the Gulf in Egypt (Fig. 2) during summer season (at the mid of July 2016). The alga was harvested and rinsed several times with deionized water by centrifugation (5000rpm for 20min) to remove impurities and salts. Algal biomass pellets were then dried at 60°C until a constant weight was achieved (Vijayaraghan *et al*., 2005). The dry weight of the algal biomass was estimated from the average of at least three representative samples.

Figure (2): *Dunaliella salina* blooming at the intertidal zone of Suez Gulf (a) and saline lake (b).

Industrial wastewater

Two aqueous industrial effluents belonging to different industries; one from petrochemical (E.1) and the other from fertilizer industries (E.2) discharged their wastewater in Suez Gulf were collected in polyethylene containers. The collected samples were filtered through GF/C glass filter paper and stored in dark at 4°C. The Initial heavy metal concentration within each effluent was determined. The pH was adjusted at 5 by using 0.1M NaOH and 0.1M HCl solutions; where pH 5 reported being the optimum pH for heavy metal removal (Sweetly *et al*., 2014).

Adsorption Experiment

The adsorption experiments were carried out in batch mode, in a 250 ml conical flask containing; 100 ml of wastewater; 1 g of the adsorbent was added. The mixture was agitated on mechanical shaker (at 250 rpm) for 180 min, with designed intervals period of 30, 60, 90, 120, 150 and 180 min. The pH adjusted at 5 and temperature at 25°C before adding adsorbent. After that, 5 ml of each mixture was centrifuged for 15 minutes at a speed of 5400 rpm to separate the supernatants from the adsorbent. Control for heavy metals without addition of adsorbent was also maintained. The residual concentration of the tested heavy metals (Cd, Zn, Cu, Mn, Pb, Fe, Cr and Ni) in the supernatant was determined using atomic absorption (Hashim and Chu, 2004; Ajaykumar *et al*., 2008). The percentage removal and metal uptake efficiencies (Biosorption, %) of all adsorbents were determined with following expressions (Zhang *et al.,* 1998; Hashim and Chu, 2004):

$$Biosorption (\%) = (C_i - C_f)/ C_i \times 100$$

The amount of metal adsorbed, Q (mg metal/gram absorbent) was computed using the following equation (Chen, 2005):

$$Q = (C_i - C_f) V/m$$

Where,
Q = Amount of metal adsorbed (mg/g)
C_i= Initial metal concentration in solution (mg/l)
C_f = Final metal concentration in supernatant after adsorption (mg/l)
V = Volume of solution (ml)
m = Mass of the adsorbent (g).

Statistical analysis

All the biosorption experiments were conducted in triplicates to substantiate the results. The data shown are the mean values of three replicate determinations. One - way ANOVA was applied to log-obtained data (Anonymous, 1993). Cluster analysis was performed using the MVSP program, where it is a multi-dimensional analysis classify the data into partition or division of a set and then into subsets (Legendre and Legendre, 1998) to clarify the similarity between heavy metals, algal species and effluents. Multivarate analysis of Canonical correspondence analysis (CCA) and Detrended Correspondence Analysis (DCA) Ordinations were performed using the CANOCO program version 2.1, according to Ter-Braak (1988) to elucidate the relations between the heavy metals and algal species, where the axes are constrained to optimize their relationship them.

RESULTS

The heavy metals (Cd, Pb, Zn, Ni, Cr, Cu, Fe and Mn) concentrations (mg.l^{-1}) in the two industrial effluent of petrochemicals (E.1) and fertilizers (E.2) industry were cited in table (1). As it was illustrated in figure (3) it is clear that, the biosorption capacity of *D. salina* for Cd, Zn and Pb was at its maximum level, especially in case of lead (22.34 mg.g^{-1}) within petrochemical effluent during the entire period of the investigation showing a distinct gap, where it gave 7.63 mg.g^{-1} after the same period within the fertilizer effluent. Zinc occupies the second position after lead (12.1 mg.g^{-1}) within the same effluent. In this context, the biosorption capacity of *D.*

salina for Cd was fluctuated in narrow range (0.81 to 6.73 mg.g^{-1} and from 0.79 to 6.32 mg.g^{-1} within petrochemical and fertilizer effluent respectively).

Figure (3): The amount of metal adsorbed (mg.g^{-1}) by *Ulva lactuca* and *Dunalliela salina* in the two industrial wastewater containing heavy metals. (Where E1: petrochemical effluent and E2: fertilizer effluent).

Figure (4): The biosorption efficiency (%) of *Ulva lactuca* and *Dunalliela salina* in the two industrial wastewater containing heavy metals. (Where E1: petrochemical effluent and E2: fertilizer effluent).

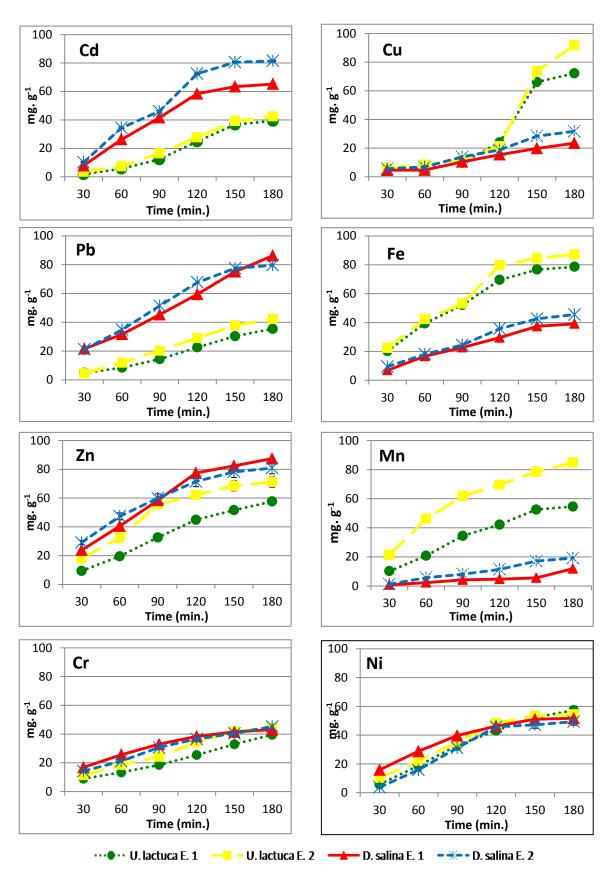**Table (1):** Heavy metals concentrations (mg L^{-1}) in the two industrial effluents. (Where E1: Petrochemical effluent and E2: Fertilizer effluent).

	Heavy metals							
Effluent	**Cd**	**Pb**	**Zn**	**Ni**	**Cr**	**Cu**	**Fe**	**Mn**
E. 1	10.33	25.91	14.04	12.41	6.2	18.48	20.18	7.32
E. 2	7.76	9.58	10.41	8.26	2.9	12.31	11.59	12.86

Mean (+SD) heavy metal concentration (mg L^{-1}) in wastewater. (n = 10)

On the other hand, *U. lactuca* was the most efficient absorbent in case of Cu, Fe and Mn. Among this, it gave the maximum biosorption capacity within petrochemical effluent (E.1) for *Fe* (4.07 - 15.86 mg.g^{-1}) and *Cu* (0.83 -11.49 mg.g^{-1}) during the entire period of investigation. However it gave its maximum (2.75 - 10.9 mg.g^{-1}) within the fertilizer effluent with significant capacity in case of Mn. It is of interest to mention that, talking about Cr and Ni will take another direction, where the controlling factor appear not to be the biosorbent species or the heavy metal itself, but it was the type of industrial effluent. Where, for both heavy metals (Ni and Cr) the biosorption capacity of the two tested species gave its maximum with in fertilizer effluent (E2) during the entire period of the investigation with superiority of *D. salina* in case of Chromium.

Anent the percentage of removal efficiencies of all adsorbents "Biosorption (%)", the recorded results (Fig. 4) reveal that Cadmium by *Ulva lactuca* and *Dunalliela salina* reach its maximum (10.2% after 30 min. - 81.5 % after 180 min.) by *D. salina* within E2 followed by the E.1. While the biosorption of cadmium by *U. lactuca* had lower rang within both petrochemicals (1.8 % after 30 min. - 39.3 % after 180 min.) and fertilizer (3.58 % after 30 min. - 42.5 % after 180 min.) effluents. Again, the ability of *U. lactuca* to remove Pb was lower than that of *D. salina*, where its maximum efficiencies did not exceed 42.3 % and 35.4 % in the fertilizer and petrochemicals effluents respectively after 180 min.

It is noticeable that, there was a large gap between the biosorption efficiency of *D. salina* and that of *U. lactuca*, with superiority of *D. salina* over *U. lactuca*. In this context, again *D. salina* was more effective in bioremoval of *Zinc* from both petrochemicals (87.4 % after 180 min.) and fertilizer (80.9 % after 180 min.) effluent than *U. lactuca*, however, the minimum Zinc biosorption efficiency was recorded in case of *U. lactuca* within petrochemicals effluent (57.6 % after 180 min).

Compared to the previous results, *U. lactuca* had the superiority in the uptake efficiencies of Mn, Fe and Cu over *D. salina* As shown in figure (4), the maximum Manganese (Mn) biosorption efficiency (84.8% within fertilizer effluent and 54.6% within petrochemical effluent) was recorded by using *U. lactuca*. However, low range of Mn biosorption efficiency (19.2% within fertilizer effluent and 11.9% within petrochemicals effluent) was recorded by using *D. salina*. At the same time and by the same trend, *U. lactuca* had the sovereignty over *D. salina* in their biosorbtion ability of

ferric (Fe) from both fertilizers effluent (87.2%) and petrochemicals effluent (78.6%). A glance on figure (4) reveled that, the biosorption of copper (Cu) from the two types of effluent and by using the two algal species showed compatible efficiency during the first 120 minutes (15.4 -18.7%). While the results reflect a great jump in the copper biosorption ability by using *U. lactuca* after infect the 120 minutes barrier, where it reaches its maximum (91.8% in fertilizer effluent and 72.2% in petrochemicals effluent) after 180 minutes.

It is worth mentioning that, the uptake efficiencies of both Nickel (Ni) and Chromium (Cr) by the two tested species within both types of industrial effluents was tight and uneven without fixed trend giving its maximum (57.3 - 49.4 %) for Nickel after 180 minutes. The same phenomenon was recorded to Chromium (Cr), which fluctuated from 39.5 % (by using *U. lactuca*) and 46.1% (by using *D. salina* as biosorping agent) within the fertilizer effluent; however petrochemical effluent was more or less affected.

Regarding cluster analysis (Fig. 5) reflect the similarity between the biosorption of tested heavy metals, where Mn, Fe and Cu were grouped in one group with noticeable higher similarity between Fe and Mn, which grouped in minor subgroup. On the other hand Pb and Cd were grouped in minor subgroup which related *with* less similarity with Zn. However Ni and Cr were grouped together but with high dissimilarity. Beside the mentioned, inspection of ordination diagram produced by the Canonical Correspondence Analysis (CCA) showed the relation between biosorption of tested heavy metals and the tested species. A glance of (Fig. 6) described a noticeable relation between *Ulva lactuca* and Mn, Fe and Cu uptake. Meanwhile, Zn, Pb and Cd uptake were closely related with *D. salina.* It is of interest to mention that, Ni and Cr were grouped in separate intermediate group.
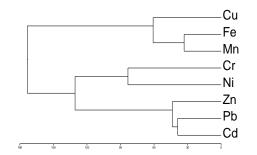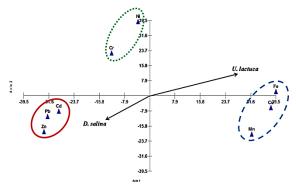

Figure (5): Dendrogram produced by the Cluster analysis of the tested heavy metals.

Figure (6): Canonical Correspondence Analysis (CCA) joint plot ordination diagram for correlation between algal species (arrow) and heavy metal ions.

DISCUSION

In developing countries, weak supervisions and inefficient implementation of laws for industry have caused rising pollution of water bodies. Hence, environmental pollution is currently one of the most important issues facing humanity, whether it is organic pollutants or containing heavy metals. Since, Suez Gulf suffer from troublesome bloom of *Ulvala lactuca* and *Dunaliella salina* beside the accumulation of heavy metals and there consequences problems, the effective utilization of this enormous algal biomass due to blooms become desired and very effective to solve the two serious coastal environmental and wastewater problems. The algal biomass considered as potential effective and cheap metal adsorbents for heavy metals removal. Biosorption of heavy metals from aqueous solutions is a relatively alternative technology for the treatment of industrial wastewater, which utilized naturally occurring materials derived from biomass (Kaparapu *et al*., 2015). Micro-algae have a remarkable ability to take up and accumulate heavy metals from their surrounding environment (Mishra *et al*., 2011). (Abdel-Raouf *et al*., 2012) also reviewed that, numerous species of algae (living and non-living cells) are capable of sequestering significant quantities of toxic heavy metal ions from aqueous solu-tions. Algal metal sequestering processes occur by diff-errent mechanisms. This can be dependent on the alga, the metal ion species, the solution conditions and whether the algal cells are living or nonliving**.**

Anent the cited results, it is clear that, the biosorption capacity of *D. salina* for Cd, Zn and Pb was at its maximum level, especially in case of lead during the entire period of the investigation. Zinc occupies the second position after lead within the petrochemical effluent. While, the biosorption capacity of *D.salina* for Cd was fluctuated in narrow range within petrochemical and fertilizer effluent respectively. The results which agrees with Puranik and Paknikar (1997) who recorded that, the biosorption capacity of *Dunalliela* towards Cd, Pb, Zn and Cu is higher than other elements. Renge *et al*. (2012) also reported that *Dunaliella salina* cells have

high tendency for zinc, Pb and Cd accumulation, the lowest tendency was for Ni. It is noticeable that, in case of *U. lactuca* there is no significant difference between the amount of metal adsorbed from the two types of effluents in case of Zn and Cd. In this context, *U. lactuca* was the most efficient absorbent in case of Cu, Fe and Mn. where, it gives the maximum biosorption capacity within petrochemical effluent for Fe and Cu during the entire period of investigation. However, it gave its maximum within the fertilizer effluent in case of Mn.

On the other hand, in case of Cr and Ni the contr-olling factor was the type of industrial effluent, was the biosorption capacity of the two tested species gave its maximum within fertilizer effluent during the entire period of the investigation with superiority of *D.salina* in case of Chromium Chopra and Pathak (2010) report-ed that, removal of Ni from single metal solutions by *Chlorella vulgaris* was more efficient than in mixture. The decrease in biosorption efficiency could be due to the interference between compounds and metals in mixture. Bulgariu and Bulgariu (2014) noted that, the biosorptive characteristics of marine Green algae (*Ulva lactuca*) have been investigated for the removal of Cu, Mn and Co ions from an aqueous solution.

The uptake of Cadmium by *Ulva lactuca* and *Dunalliela salina* it reached its maximum by *D. salina* within fertilizer effluent followed by the petrochemical effluent, while the biosorption of cadmium by *U. lactuca* had lower range within both effluents. However, (Ghoneim *et al*., 2014) concluded that *U. lactuca* can be used as an effective, low cost, and environmentally friendly biosorbent for removal of Cd ions from aqueous solution. A more or less the same phenomenon was recorded in the uptake efficiencies of Lead (Pb), where *D. salina* gave the maximum uptake of Pb from both types of tested effluents (86.2% and 79.6% in fertilizers and petrochemical effluent respectively after 180 min.). Puranik and Paknikar (1997) recorded that, biosorption efficiency of *Dunaliella* towards Zn and Cd (95%), Pb (93%) and Cu (90%) is higher than other elements (Cr and Ni). In another study, Mendoza-Cozatl *et al*. (2006) recorded that, *Euglena gracilis* has high efficiency (80%) for Cd removal by however, it was found to be less than the efficient for Pb by 15%. The result which agree with our results where, the ability of *U. lactuca* to uptake Pb was lower than that of *D. salina*, where it's maximum uptake efficiencies did not exceed 42.3 % and 35.4 % in both effluents after 180 mins.

Dunaliella salina was more effective in bioremoval of *Zinc* from both effluents than *U. lactuca*. However, the minimum Zinc biosorption efficiency was recorded in case of *U. lactuca* within petrochemicals effluent. *D. salina* cells have high tendency for zinc accumulation, while the lowest tendency was for cadmium, this may be due to the importance of zinc as hydrogen transf-erring in photosynthesis. Generally, it has been report-ed that, *Dunaliella* sp. can tolerate high concentrations

of toxic metabolites than most of the other phyto-plankton (Shafik, 2008).

Ulvala lactuca had the superiority in the remove efficiencies for Mn, Fe and Cu over *D. salina*. The results which supported by Ibrahim *et al.* (2016) who noted that, *Ulva* seaweed is a good biosorbent material for removing heavy metals. It is worth mentioning that, the uptake efficiencies of both Nickel (Ni) and Chromium (Cr) by the two tested species within both types of industrial effluents was tight and uneven without fixed trend (Liu *et al.*, 2014) indicated that, the algal biomass had a highly selective biosorption capacity for heavy metals, where the order of biosorption for heavy metals was Fe > Cr > Ni.

Cluster analysis reflects a high similarity between the biosorption of Mn, Fe and Cu and also between Pb, Cd and Zn. On the other hand Ni and Cr were grouped together but with high dissimilarity.

However, the ordination diagram produced by the Canonical Correspondence Analysis (CCA) showed noticeable relation between *Ulva lactuca* and Mn, Fe and Cu removal. Meanwhile, Zn, Pb and Cd removal were closely related with *D. salina.* While, Ni and Cr were grouped in separate intermediate group. Shanab *et al.* (2012) mentioned that, algae isolated from polluted water were found to be more tolerant to metal toxicity. Moreover, tolerance of algae to heavy metals differed among algal species. The difference in biosorption ability between algal species attributed to the cell surf-ace has several kinds of functional groups with varying affinity for an ionic species. Both low and high affinity functional groups are responsible for the sorption of metal ions at high and low concentrations of metal ions (Mehta and Gaur, 2001).

CONCLUSION

In conclusion, the most dominant and commonly blooming marine green algae" *Ulva lactuca* and *Dunalliela salina* in Suez Gulf can be utilized as biosorpent for heavy metals in the industrial effluent to solve both problems of eutrophication and heavy metals pollution. Both the green seaweed *Ulva lactuca* and the micro-algae *Dunalliela salina* reflected a strong capability for selective biosorption of heavy metals from aqueous wastewater. This advanced technology is not only cheaper and more effective but also quick and easy to operate.

However, the comparison of the two algal genera revealed that they differed somewhat in their abilities to adsorb Cd, Pb, Zn, Ni, Cr, Cu, Fe and Mn. Based on the obtained results, it can be concluded that the dried biomass of *Dunaliella salina* and *Ulva lactuca* has a relatively high affinity towards the heavy metal, particularly Pb, Zn and Cd for *Dunaliella salina* and Cu, Fe and Mn for *Ulva lactuca*. Moreover, the biosorbtion of heavy metals by algal species from aqueous solutions is a complex process, depending upon the algal species,

the heavy metal ion, and the contributing source. So, deeper studies should be done in the future to determine the most efficient biosorpent species for every type of industrial waste. Actually, during solving the problem of heavy metals using blooming biomass of the local algae got rid of the problem of eutrophication. Therefore, biosorption of heavy metals by algal biomass is being strongly recommended as a powerful technique for the removal of heavy metals from various industrial polluted effluents.

REFFERENCES

ABDEL-RAOUF, N., A.A.AL-HOMAIDAN AND I.B. M. IBRAHEEM. 2012. Review: Microalgae and wastewater treatment. Saudi Journal of Biological Sciences, 19: 257-275.

AJAYKUMAR, A.V., S. AL HASHIMI, AND N. HILAL. 2008. Investigation of kinetics and mechanism involved in the biosorption of heavy metals on activated sludge. Int. J. Green Energy 5: 313-321.

ANONYMOUS. 1993. SPSS program for Windows. Base system user's Guide Release 5.0 SPSS INC.

AWASTHI, M. AND L.C. RAI. 2004. Adsorption of nickel, zinc and cadmium by immobilized green algae and cyanobacteria: A comparative study. Annals Microbiol., 54: 257-267.

BHATNAGAR, S., AND R. KUMARI. 2013. Bioremediation: A Sustainable Tool for Environmental Management. A Review. Annual Review and Research in Biology. 3(4): 974-993.

BROUERSA, F., J. TARIQ, AND M. AL-MUSAWIB. 2016. On the optimal use of isotherm models for the characterization of biosorption of lead onto algae. bioRxiv (In press).

BULGARIU, L., AND D. BULGARIU. 2014. Enhancing Biosorption Characteristics of Marine Green Algae (*Ulva lactuca*) for Heavy Metals Removal by Alkaline Treatment. J Bioprocess Biotech 4: 1-8.

CHEN, S. 2005. Bioremediation potential of spirulina: toxicity and biosorption studies of lead. J Zhejiang Univ. SCI, Biology. 6B (3): 171-174.

CHOPRA, A.K., AND C. PATHAK. 2010. Biosorption technology for removal of metallic pollutants-An overview .Journal of Applied and Natural Science 2 (2): 318-329.

DAVIS, A.T., B. VOLESKY, AND, A. MUCCI. 2003. A review of the biochemistry of heavy metal biosorption by brown algae. Water research 37: 4311-4330.

GHONEIM, M., S.H. EL-DESOKY, K. EL-MOSELHY, A. ADEL, E.H. ABOU.ELNAGA, AND L. MOHAMEDEIN. 2014. Removal of cadmium from aqueous solution using marinegreen algae, *Ulva lactuca*. Egyptian Journal of Aquatic Research, 40: 235-242

HASHIM, M.A., AND K.H. CHU. 2004. Biosorption of cadmium by brown, green, and red seaweeds. Chem. Eng. J. 97: 249-255.

HASSAN, I., J. BASAHI, I. ISMAIL, AND A. ZAHRAN. 2014. Effects of airborne heavy metal pollution on physiological and biochemical proce-sses in lettuce (Lactuca sativa L. Romaine) Plants. Advances in Env. Biology), 25(3): 85-97.

HASSAN, I.A., J.M. BASAHI, AND I.M. ISMAIL. 2013. Gas exchange, chlorophyll fluorescence and antioxidants as bioindicators of airborne heavy metal pollution in Jeddah, Saudi Arabia. Current World Environment, 8(2): 203 -213.

IBRAHIM, W.M., A.F. HASSAN, AND A.Y. AZAB. 2016. Biosorption of toxic heavy metals from aqueous solution by *Ulva lactuca* activated carbon. Egyptian journal of basic and applied sciences 3: 241-249.

KAPARAPU, J., R.G. NARASIMHA, AND P. KRISHNA. 2015. Marine algae as biosorbents. J. Algal Biomass Utln. 6 (3): 16- 19.

LEGENDRE, P., AND L. LEGENDRE. 1998. Numerical ecology. Elsevier. Developments in environ-mental modelling,3. Elsevier Scientific Publ. Co., Amsterdam Netherlands 9: 419 p

LIU, X., D. BEYREND, G. DUR, S. BAN. 2014: Effects of temperature on life history traits of Eodiaptomus japonicus (Copepoda: Calanoida) from Lake Biwa (Japan). Limnology, 15: 85-97

MEHTA, S. K., AND P.G. JAI. 2001. Removal of Ni and Cu forms ingle and binary metal solutions by free and immobilized Chlorella vulgaris. European J. Protistology, 37: 261-271.

MENDOZA-CÓZATL, D.G., E. RANGEL GON-ZALEZ, AND R. MORENO AND SÁNCHEZ. 2006. MSimultaneous $Cd^{2+,}$ Zn^{2+} and Pb^{2+} uptake and accumulation by photosynthetic Euglena gra-cilis. Arch. Environ. Contam. Toxicol., 51: 521-528.

MISHRA, S.P., J. THIRREE, A.S. MANENT, B. CHABOT, AND C. DANEAULT. 2011. Ultrasound-catalyzed TEMPO-mediated oxidation of native cellulose for the production of nano-cellulose: Effect of process variables. Bio Reso-urces, 6(1): 121-143.

NIRMAL K.J.I., RITA, N. KUMAR AND O. CINI. 2010. Removal of heavy metals by biosorption using freshwater alga. Journal of Pure and Applied Sciences, 17: 028-034.

NIRMAL, K.J.I., AND O. CINI, 2012. Removal of heavy metals by biosorption using freshwater alga Spirogyra hyalina. J. Environ. Biol. 33: 27-31.

OILGAE, R. 2010. The definitive guide for algae fuel researchers Academic Edition Tamilnadu India.

PAPPALARDO, L., JUMEANF.AND N. ABDO. 2010. Removal of Cadmium, Copper, Lead and Nickel from aqueous Solution by White, Yellow and Red United Arab Emirates Sand America Journal of Environmental Sciences. 6(1): pp 41-4.

PRABHA, Y., S.K. SONI, G. SHARMITA, AND SONALB. 2016. Potential of Algae in Bio-remediation of Wastewater Current Research Int J Curr.Microbiol. App. Sci, 5(2): 693-700

PURANIK, P.R., AND K.M. PAKNIKAR. 1997. Biosorptionof lead and zinc from solutions .using strep to verticillium cinnamoneum wastebiomass J Biotechnol. 55: 113-124.

QARI, H.A., AND I.A. HASSAN. 2014. Removal of pollutants from waste water .using Dunaliella algae. Biomed. Pharmacol. J., 7(1): 147 151.

RENGE, V.C., S.V. KHEDKAR, AND S.V. PANDE. 2012. Removal of heavy metals from wastewater using low cost adsorbents: a review. Scientific Revi-ews and Chemical Communications, 2 (4): 580-584.

SHAFIK, M.A. 2008. Phytoremediation of Some Heavy Metals by *Dunaliella salina*. Global Journal of Environmental Research 2 (1): 01-11.

SHANAB, S., E. ASHRAF, AND E. SHALABY. 2012. Bio removal capacity of three heavy metals by some microalgae species (Egyptian Isolates). Plant Signaling and Behavior, 7(3): 1-8.

SWEETLY, D.J., K. SANGEETHA, AND B. SUGA-NTHI. 2014. Biosorption of Heavy Metal Lead from Aqueous Solution by Non-living Biomass of Sarga-ssum myriocystum. International Journal of Applica-tion or Innovationin Engineering and Management, Volume 3(4): 39-45.

TER BRAAK, C.J.F. 1988. CANOCO-A FORTRAN program version 2 1 for. [Partial]. [Canonical] Correspondence Analysis Principal Component Analysis and Redundancy Analysis Agricultural Mathematics Group Report LWA-88-02, Wageningen 95 pp.

VIEIRA, R.H.S.F., AND .B. VOLESKY. 2000. Bio-sorptio: a solution to pollution? Int. Microbiol. 3 (1): 17-24.

VIJAYARAGHAVAN, K., J.R. JEGAN, K. PALANIVELU, AND M. VELAN. 2005. Copper removal from aqueous solution by marine green alga *ulva reticula* Electronic J. Biotecnol. 7(1): 22 -23.

WALTER, H.A., P.C. KANGAS, AND M. WALTER. 2011. Algalturf scrubbing cleaning surface water swit solar energy while producing a biofuel. Bio-Science 61 (6): 434-44.

ZHANG, W.X., Y.C. SHEN, L.I. SR. 1998. Epidemi-ological investigation on mental disorders in 7 areas of China. Chinese J Psychiatry, 31:69–77.

الامتزار الحيوي للمعادن الثقيلة من المخلفات الصناعية السائلة بإستخدام الكتلة الحيوية الجافة لإثنين من الطحالب الخضراء البحرية "*Ulva lactuca*" و "*Dunaliella salina*"

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إن النهضة الصناعية المتزايدة في منطقة خليج السويس تؤدي إلى مشكلتين بيئيتين خطيرتين، الاولي هي تلوث المياة بالمعادن الثقيلة و الثانية التخثث. لذا فقد إستهدف البحث دراسة كيف يمكن لهاتين المشكلتين حل بعضهما البعض. و بالتالي فقد تم إستخدام الكتلة الحيوية الجافة من الطحالب الأكثر ازدهارًا، "*Ulva lactuca*" و "*Dunaliella salina*" في خليج السويس في تنقية مياة إثنين من النفايات الصناعية السائلة، أحدهما ينتمي إلى الصناعات البتروكيماوية (E.1) و الأخري لمخلفات صناعة الأسمدة(E.2) من المعادن الثقيلة (Zn و Cu و Cd و Fe و Mn و Pb و Cr و Ni. أوضحت النتائج أن D.salina كانت أكثر كفائة في التخلص من Cd و Zn و Pb من المخلفات البترولية E1، خاصة في حالة الرصاص (٢٢.٣٤ ملي جرام /لتر) كما سجل ٧.٦٣ ملي جرام /لتر في مخلفات مصنع السماد E.2. و كانت U. lactuca هي الأكثر فعالية في التخلص من الحديد (٤.٠٧ - ١٥.٨٦ ملي جرام /لتر) و النحاس (٠.٨٣ - ١١.٤٩ ملي جرام /لتر) في المخلفات البترولية، في حين كانت أقدر علي إمتزاز المنجنيز من مخلفات مصنع السماد. من ناحية أخري أظهرت النتائج أن كفائة الإمتزاز لكل من النحاس و الحديد و المنجنيز كانت أعلي بإستخدام U. lactuca في كلا النوعين من المخلفات (٩١.٨ و٨٧.٨ و ٨٤.٨ % علي التوالي) مع الأخذ في الإعتبار تفوقها في تنقية مخلفات مصنع السماد. في الوقت ذاتة كانت D.salina أكثر فاعلية في التخلص من الزنك (٨٧.٤%) و الرصاص (٨٦.٢%) و الكادميوم (٨١.٥%). ختاما فقد ساهمت الدراسة في إبراز أفضلية إستخدام U. lactuca للتخلص من النحاس و الحديد و المنجنيز في حين أن D.salina أكثر كفائة للتخلص من الرصاص و الزنك و كذلك الكادميوم من مياة الصرف الصناعي.