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Heavy Metals Removal from Industrial Wastewater Using Dry Green Macro Alga *Ulva lactuca* Linnaeus

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ABSTRACT

Marine green algae *Ulva lactuca* was used as an efficient, low cost and eco-friendly biosorbent for the removal of some heavy metal ions from an industrial drainage station of Petrochemicals Company. Temperature, pH, nitrates, orthophosphate, sulphates and heavy metals (Cd, Pb, Zn, Ni, Cr, Cu, Fe and Mn) were measured. The study revealed that the biosorption efficiency was 50% after 15min of water treatment by *Ulva lactuca*. While, after 60min, the efficiency reached a percentage of 95, and after 120 min, the efficiency rate remained stable or was slightly lower than that recorded for the 60min interval at a biomass weight of 1g/ L. In addition, the smallest size (0.063µm) was the most efficient to bind more metal ions by algal biomass with the best result, compared to the largest size (0.250µm) which showed the least efficiency for binding ions. It was deduced that 1g/ L of dry *U. lactuca* biomass at a size of 0.065 was found to successfully remove 90, 83.7, 98.1, and 93.1 for Cd, Fe, Pb and Ni, respectively, from aqueous solution.

INTRODUCTION

Since the beginning of creation, water has been the mainstay of life, hence cleaning water resources is essential to all living organisms for their growth, reproduction and even for survival. Domestic, agricultural and industrial wastewater, especially mining, manufacturing and power generation has a negative impact on water quality and consequently on biota and human health (**Gad *et al*., 2011; Mosleh *et al.,* 2012**). Heavy metals are elements with atomic weights ranging from 63.5 - 200.6, with a basic gravity greater than 5.0. Industrial wastewater is the main source of heavy metals contamination (**Shanab *et al*., 2012; Mofeed & Mosleh 2013**). In recent years, heavy metal pollution in wastewater has become a big concern. Heavy metals are not biodegradable but they have the ability to accumulate in living tissues, resulting in long-term sustainability, which affects the human health (**Deng *et al*., 2008; Ibrahim *et al*., 2016; Mosleh *et al*., 2021**).

Heavy metals (HM) are released into water environment mainly through agricultural (pesticides, fertilizers) and industrial activities (painting, petroleum refining, mining activities, smelting, car exhausts, battery manufacturing and pigments) (**Ahmed *et al*., 1998; Lesmana *et al*., 2009; Ardila *et al*., 2017**). They can endanger ecosystems and public health because of their high mobility, lack of degradation and high capacity to accumulate within all living

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beings. In addition, it can participate in biological reactions that ruin vital processes within cells, tissues and organs promoting disease even if present with its low concentration in the environment (**Topcuoglu *et al*., 2003; Mosleh *et al.*, 2006; Mosleh, 2013; Alkaladi *et al*., 2014; Jinsong & Paul Chen, 2014; Abraham *et al*., 2018**).

However, some of these metals are essential micronutrients for plant growth (e.g., zinc, copper, manganese, nickel, and cobalt), whereas others may have unknown biological functions and are poisonous such as Cd, Pb and Hg (**Gaur and Adholeya, 2005**). Mercury, cadmium, copper, zinc, lead, and nickel, among other harmful heavy metals, are the most common contaminants in freshwater and marine (**Travieso *et al*., 1999; Yu *et al*., 1999; Mehta & Gaur 2005; Singh *et al*., 2007, Mosleh *et al*., 2012**).

The conventional treatment methods for extracting biologically polluted heavy metals or wastewater effluents include ions exchange, membranes filtration, reduction of contaminants, chemical precipitation, adsorption of activated carbon, treatment of nanotechnology, electrochemical removal and advanced oxidation (**Nashwa, 2018**).

Additionally, there are biological processes that use live or dead, free or immobilized cells of bacteria, fungi and algae or plant tissues, as cells have carbohydrates and polypeptides in their walls with hydroxyl, aldehydes, ketones, amines, phosphates and carboxyl groups responsible for metal caption adsorption and chelation (**Wang, 2009**). Unfortunately, using these conventional processes is limited due to significant disadvantages, such as low selectivity, high cost, incomplete removal, high energy consumption or high toxic waste generation. Therefore, the world is constantly in need to find safe, low-cost and more effective alternative methods for extracting heavy metals from contaminated water

Adsorption is using the dried organisms as adsorbents (**Nashwa, 2018**). For the adsorption mechanism; there are many ways for metal uptake by microbial cells (**Ahalya *et al*., 2003; Mosleh & Almagrabi, 2013, 2014; He & Paul, 2014; Mosleh *et al*., 2014; Younis *et al*., 2015, 2016**). They can be classified according to different criteria, depending on the cell structure according to the location where metal is removed from the solution by extracellular accumulation. Whereas, biological material may have a physiochemical property that help in the removal of heavy metals from wastewater by ionic or covalent bonding (**He & Chen 2014; Zeraatkar *et al*., 2016; Salama *et al*., 2019**). Metal adsorption from aqueous solutions has the potential for being a useful wastewater treatment system. It focuses on the biological materials' ability to absorb heavy metals' ions from wastewater through metabolically mediated or physicochemical uptake pathways (including living or dead microorganisms and their components, seaweeds and others (**Chubar *et al*., 2003; Fard *et al*., 2011; Nashwa, 2018**).

Adsorption is an alternative powerful technique for extracting heavy metals from wastewater due to many advantages such as its low cost and high efficiency (**kumar *et al*., 2006; Handojo *et al*., 2016**). In addition, it can compensate for the drawbacks of commercial resins, which reduce sorption efficiency at lower metal concentrations in wastewaters (**Eccles, 1999**). Most studies have focused on the removal efficiency of metals by algal dry materials biomass, which indicates that dead cells may absorb more metals than living cells (**Mehta & Gaur, 2005**). Furthermore, algae are ideally suited for evaluating water quality and have been shown to be effective bio indicators because they have rapid reproduction rates, very sensitive responses to chemical changes, eutrophication and pollution, and receiving a wide variety of typically specific species (**Larson & Passy, 2012; Ghada, 2017**).

Macroalgae are considered a raw material for many applications because they contains various active substances with different properties. Since the 1970s, green algae species of the genus *Ulva* sp. have been utilized as biofilters in several nations, acting to remove nitrogen and phosphorus. Therefore, the study aimed to evaluate the efficiency of the dry green microalgae *U. lactuca* as a biofilter for the adsorption of six of the most prevalent heavy metals in the effluents of a petrochemical plant as an applied model.

MATERIALS AND METHODS

Green macro algae samples were collected from the Gulf of Suez (29*56/44* N32*29/27E), regularly collected (during the first half of the morning 10- 12 A.M.) monthly from October 2017 to December 2018. The collected algae were washed with tap water then twice with distilled water for removing the external sand and salts. Later, the algae were used in biosorption experiment and dried in an oven at 70°C for 48h, and then milled with a blender and sieved to get particle with the size pass through a laboratory test sieve, with mesh sizes of 250, 125 & 63µm. Two species of green microalgae were cultured on BBM medium. After algal growth, harvesting was performed via centrifuge (3500rpm), and finally pellets were dried at 70ºC for about 30 mintues.

The green macro algal *Ulva luctuca* (Ulvaceae, Chlorophyta) is the most frequent and common green algal inhabiting the Suez Gulf (29*56/44*N32*29/27E). It was collected during its bloom in September 2018 at 10-12 am. The collected macro algae were washed with tap water then washed twice with distilled water for removing the external sand and salts. Later, the algae samples were dried in oven at 70°C for 48h, and then milled with a blender and sieved to get particle with the size passing through a laboratory test sieve with mesh sizes of 0.250 and 0.062µm, then they were stored in dark bottle at 4^{o}C.

Industrial wastewater sample

Collection and preparation

Water samples were collected during the mornings in July 2018 and 2019 from industrial drainage of Petrochemicals Company; the samples were kept in the dark and transported to the laboratory, where the chemicals investigations were done. Industrial wastewater samples were mixed well and filtrated through millipore filtration system (Millipore Comp. 0.22) and stored at 4°C to be used for chemicals analysis.

Physico-chemical analysis

About 250ml of the filtered sample was taken in a polyethylene bottle in order to directly determine the physico-chemical analysis (temperature, pH, nitrite –N, nitrate-N, ammonia-N and total dissolved salts, chlorides, sulfate, reactive silica, hardness, total carbon, alkalinity and ortho-phosphate) for the collected industrial wastewater samples upon reaching the laboratory according to standard methods followed by American Public Health Association (**APHA, 1995)**. The concentration of heavy metal samples were determined using atomic absorption spectrophotometry (shimadzu). Standard operating parameters were set and the hollow lamps for Cd, Zn, Cu, Mn, Pb, Fe, Cr and Ni (shimadzu) were used as a radiation source and fuel was air acetylene. All the standard and samples were run in duplicate (**Kunkel, 1973**).

Adsorption Experiment

The scientific objective of this experiment was to evaluate the adsorption efficiency of dried algae biosorpent (*U. lactuca*) depending on three parameters, contact time, size of biomass and concentrations of *U. lactuca* as biosorpent. The adsorption experiments were carried out in batch mode in different concentrations (1, 0.8, 0.6, 0.4 and 0.2 g.L^{-1}) of the dried crushed (0.25 and 0.065 µm) algae biosorpent. They were added to a 100ml of the industrial wastewater in 250ml conical flask for designed interval period of 15, 30, 60 and 120min on an orbital shaker at 400 rpm. The temperature was adjusted at 25 ± 1°C, with a pH value of 6.5 before adding the adsorbent. The suspended solids were separated out with GF/C filter. Heavy metal ion concentrations were then measured in the filtrate water. Several sets of experiments were conducted to determine the effect of the size, the mass and contact time of dried algae to remove the heavy metals from the industrial effluent wastewater. The residual concentration of the tested heavy metals (Cd, Zn, Cu, Mn, Pb, Fe, Cr and Ni) in the filter was determined using an atomic absorption spectrophotometry (**Kunkel, 1973**). The percentage removal and metal uptake efficiencies (Biosorption%) of all adsorbents were determined with the following expressions **(Hashim & Chu, 2004)**:

$$\text{Biosorption (\%)} = (Ci - Cf)/ Ci \times 100$$

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

$$Q = (Ci - Cf)\, V/m$$

Where, Q = Amount of metal adsorbed (mg/g); Ci= Initial metal concentration in solution (mg/l); Cf = Final metal concentration in supernatant after adsorption (mg/l); V = Volume of solution (ml), and 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 means ± standard deviations. Data were analyzed by Student's T- test for independent samples. Analysis was performed using the SPSS 14.0 for Windows (SPSS, Michigan Avenue, Chicago, IL, USA), and the minimum significant level was set at 0.05.

RESULTS

Physical and chemical properties

Table (1) reveals that, total alkalinity values fluctuated between 6mg/ L in industrial effluent wastewater before treatment and 4.4mg/ L after treatment. While, the total hardness value after treatment was 3.86mg/ L higher than that recorded before treatment process (1.48mg/ L) (Table 1). The mean concentration of total dissolved solid (TDS) in the industrial effluent is presented in Table (1); the concentration of TDS is recorded as 180mg/ L for the industrial effluent wastewater before treatment and 112mg/ L after treatment. Moreover, the pH values of the samples varied from 6.2 to 7.8, and the values of the free dissolved carbon dioxide during the whole period of investigation showed a value up to 7.25mg/ L in the industrial effluent before discharge. However, the industrial effluent wastewater discharged total carbon level reached a value of 6.5mg/ L. While, chloride concentration fluctuated between two points of petrochemical industrial effluent wastewater; the one before the treatment with a value of 16.76mg/ L, and the other point after treatment recording a value of 17.11mg/ L, as shown in Table (1). Other parameters such as phosphate, sulphate, nitrite, nitrate, ammonia and silica were calculated and fluctuated within two points of industrial effluent wastewater before treatment/and after treating the industrial effluent wastewater, as shown in Table (1).

Table 1. Physico-chemical parameters of the discharged petrochemical industrial effluent wastewater before and after treatment

Parameter	**Industrial wastewater (mg.L^{-1})**	
	Before treatment	**After treatment**
pH (Unit)	6.20 ± 0.1	7.80 ± 0.89
Temperature ^{0}C	24.00 ± 1.00	24.4 ± 1.20
Sulphate mg.L $^{1-}$	1.40 ± 0.003	0.20 ± 0.16
O. Phosphate mg.L^{-1}	0.015 ± 0.002	0.022 ± 0.04
TDS (mg.L ($^{1-}$	180.5 ± 12.7	112.30 ± 4.8
Ammonia (mg.L^{-1})	5.50 ± 0.027	1.32 ± 0.08
Nitrate (mg.L^{-1})	3.80 ± 0.003	2.20 ± 0.01
Nitrite (mg.L^{-1})	0.20 ± 0.003	0.027 ± 0.01
Silica	1.30 ± 0.002	0.027 ± 0.0
Chloride (mg.L^{-1})	16.76 ± 0.81	7.11 ± 0.51
Total alkalinity (mg $CaCO_3$.L^{-1})	6.00 ± 0.12	4.00 ± 0.14
Total carbon (mg.L ($^{1-}$	7.25 ± 0.32	6.50 ± 0.11
Hardness (mg $CaCO_3$.L^{-1})	1.48 ± 0.07	3.86 ± 0.08

The efficiency removal of heavy metals by the dry algae *U. lactuca*

The experiment was conducted to study the effect of dry *U. lactuca* on the removal of some heavy metals (Cd, Pb, Zn, Ni, Cr, Cu, Fe and Mn (mg/L)) in the petrochemicals industrial effluent wastewater. Results of heavy metals removal% from the petrochemicals industrial effluent depended on the biomass amount, size and contact time.

Cu removal efficiency

Data presented in Fig. (2) show that, at size 0.063µm of dry *U. lactuca*, the Cu adsorption after 60min ranged from 63.5% to 83.4% at concentrations of 0.4 and 1g/ L of algal biomass, respectively. While, after 60 min and at size 0.25µm (largest size of dry algal biomass), the Cu adsorption ranged from 44.45% to 54.46% at concentrations of 0.4 and 1g/ L of algal biomass, respectively.

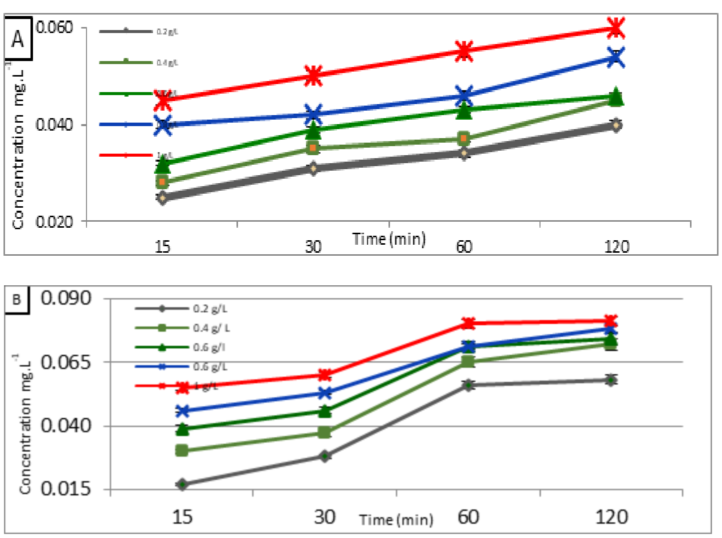

Fig. 1. The adsorbed amount of Cu (mg/L) by dry *U. lactuca* after different time and 2 mesh sizes of biomass (A, 0.25 µm and B, 0.063 µm).

Cd removal efficiency

Data presented in Fig. (3) show that, the best treatment for Cd metal ion by dry *U. lactuca* was 51.6% and 84.3% at the concentrations of 0.4 and 1g/ L of algal biomass within size 0.250µm of dry algae after 120min, respectively. However, by using the size 0.063µm, the percentage was 68% and 90% for the concentration of 0.4 and 1g/ L after 120min of treatment, respectively.

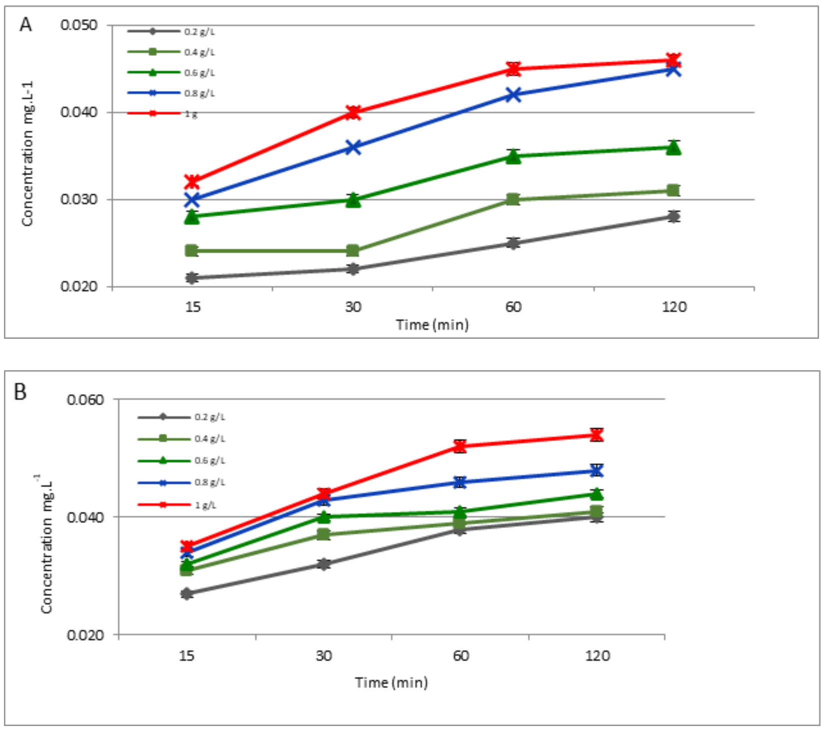

Fig. 2. The adsorbed amount of Cd (mg/L) by dry *U. lactuca* different time and 2 mesh sizes of biomass (A, 0.25 µm and B, 0.063 µm).

Mn removal efficiency

It is clear that the capacity of dry *U. lactuca* to remove Mn was 80.5% with the mesh size 0.063µm after 120min of water treatment with the concentration of 1g/ L, respectively (Fig. 4). While, after the same time using the concentration of 0.4g/ L, the adsorption ranged from 55.8% to 35.3% according to the algal mesh sizes (0.063 and 0.250µm), respectively.

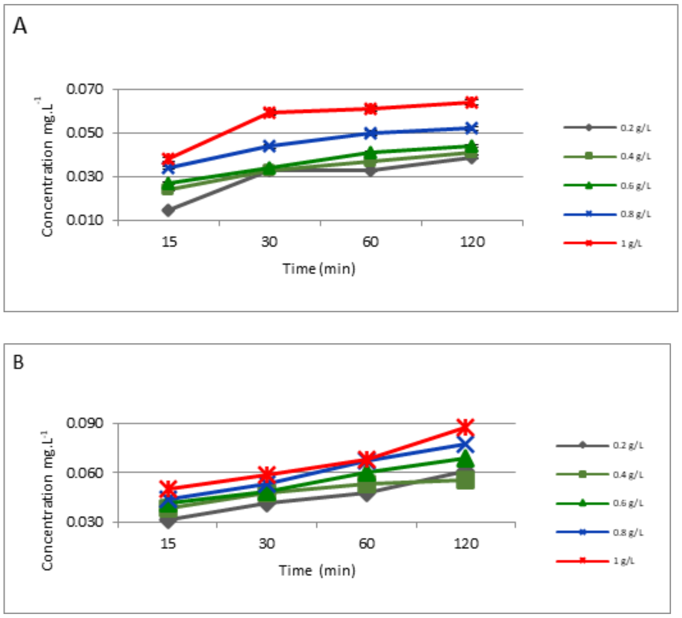

Fig. 3. The adsorbed amount of Mn (mg/L) by dry *U. lactuca* according to different time and 2 mesh sizes of biomass (A, 0.25 µm and B, 0.063 µm).

Fe removal efficiency

Data presented in Fig. (5) reveal that, the initial concentration of Fe in the petrochemicals industrial effluent detected was 0.472mg/ L. After 120min of treatment with a concentration of 0.2g/ L and size of 0.063µm, the adsorbed amount of Fe by dry *U. lactuca* reached to 66.32%. While after 120 min at concentration 0.8 g/L the adsorption ranged from 63.08 to 83.27%mg/ L, with the mesh sizes of 0.250 and 0.063µm, respectively.

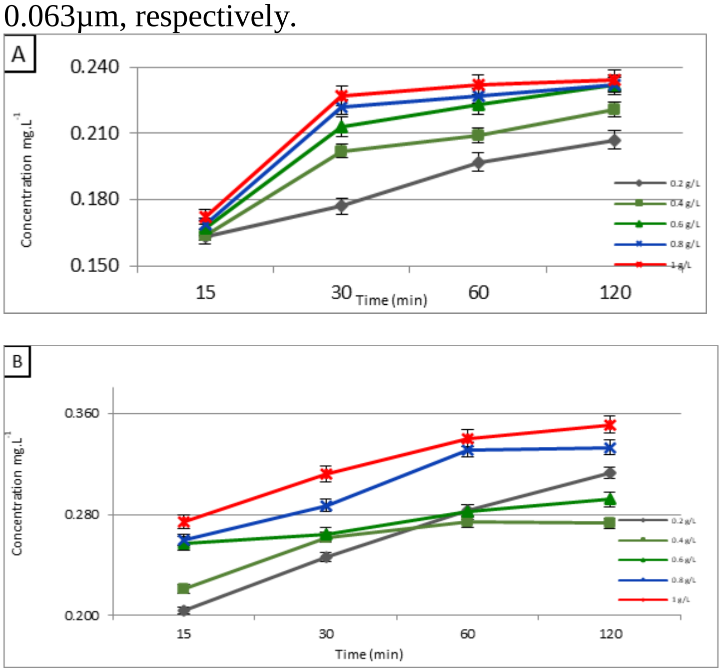

Fig. 4. The adsorbed amount of Fe (mg/L) by dry *U. lactuca* after different times and 2 mesh sizes of biomass (A, 0.25 µm and B, 0.063 µm)

Co removal efficiency

The ability to remove Co from the petrochemicals industrial effluent after treatment with different concentrations of dry *U. lactuca* was studied, and the results are displayed in Fig. (6). The results indicate that, the amount of Co metal ion adsorbed at the concentration of 0.2g/ L of *U. lactuca* after 120min within a mesh size of 0.063µm of dry biomass was 0.059mg/ L.

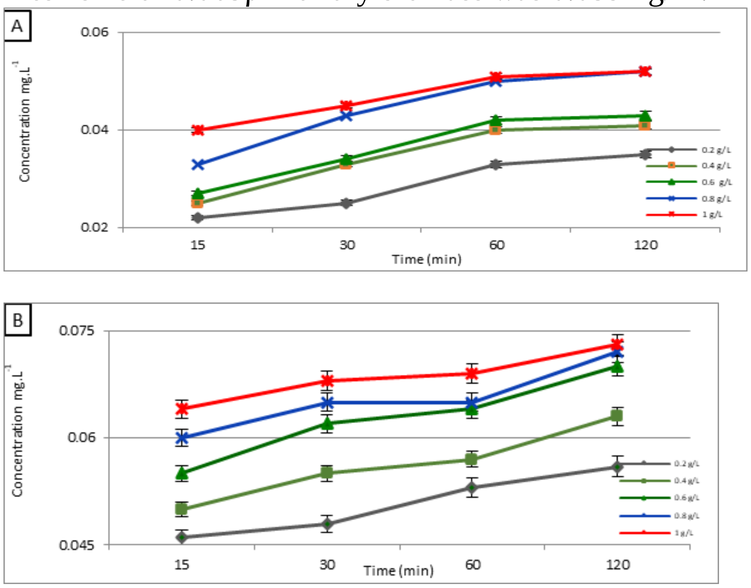

Fig. 5. The adsorbed amount of Co (mg/L) by dry *U. lactuca* after different times and 2 mesh sizes of biomass (A, 0.25 µm and B, 0.063 µm)

Pb removal efficiency

The removal percentage of Pb metal ion from aqueous solution with the dry *U. lactuca* at the concentration of 0.4g/ L and after 120min was 90.9% with the sizes of 0.063µm. While, at the concentration of 1g/ L, the %removal reached a value of 98.1% within the size of 0.063µm after 120min.

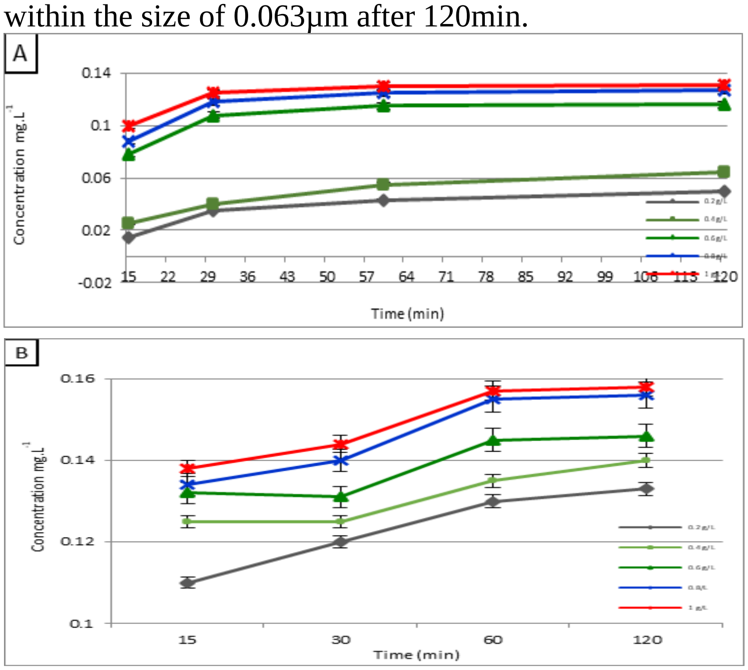

Fig. 6. The adsorbed amount of Pb (mg/L) by dry *U. lactuca* after different times and 2 mesh sizes of algae biomass (A, 0.25 µm and B, 0.063 µm).

Ni removal efficiency

The removal percentage of Ni by dry *U. lactuca* was 87.1% after 15min of treatment with the concentration of 1g/ L of algal biomass (Fig. 8), with the mesh size of 0.063µm of algal. While, after 60min of treatment with the same concentration, the Ni %removal reached a percentage of 92.1 according to the algae size of 0.063µm.

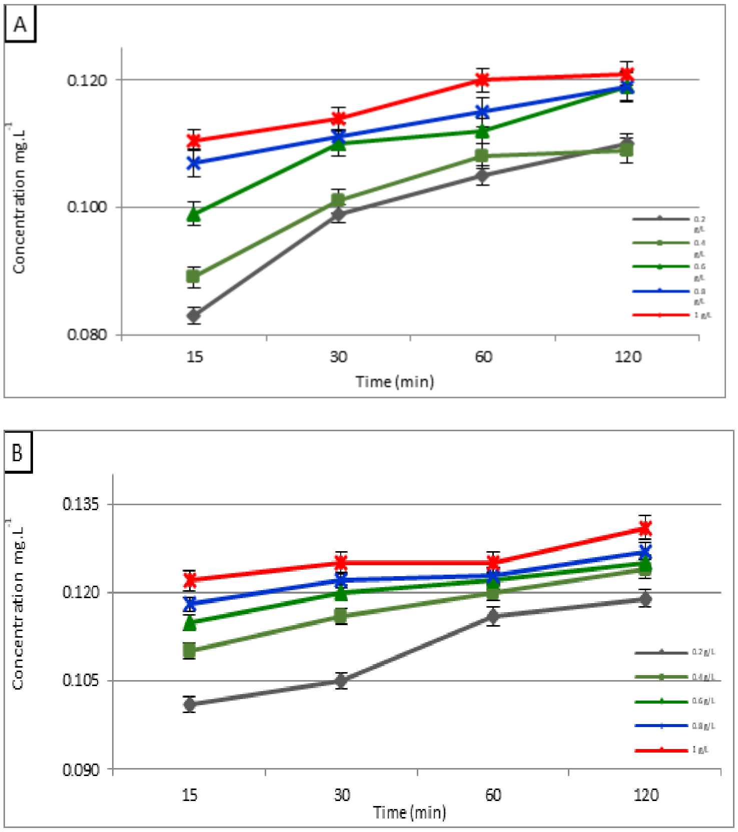

Fig. 7. The adsorbed amount of Ni (mg/L) by dry *U. lactuca* after different times and 2 mesh sizes of algae biomass (A, 0.25 µm and B, 0.063 µm)

Zn removal efficiency

The ability to remove Zn in the petrochemicals industrial effluent after treatment with different concentrations of dry *U. lactuca* was studied, and the results are presented in Fig. (9). The results indicate that, the amount of Zn metal ion adsorbed at concentration 0.8g/ L of *U. lactuca* after 60 min within mesh size 0.063µm of dry biomass reached a percentage of 93.1.

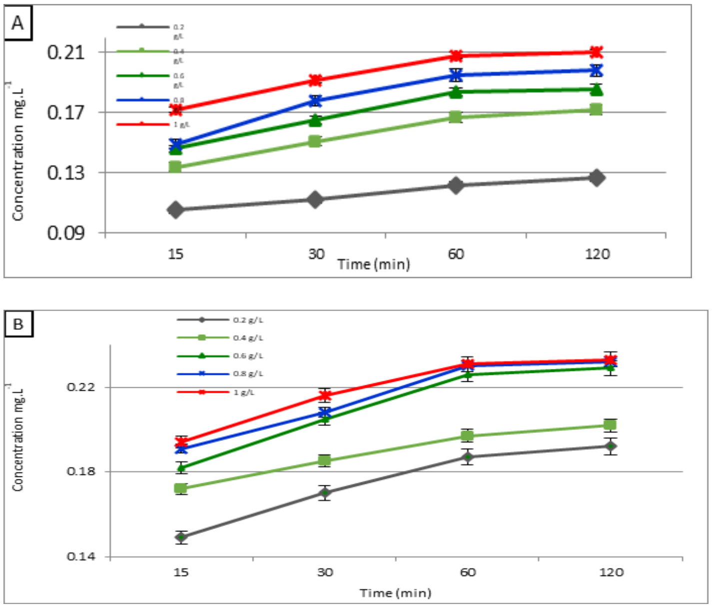

Fig. 8. The adsorbed amount of Zn (mg/L) by dry *U. lactuca* different times and 2 mesh sizes of algae biomass (A, 0.25 µm and B, 0.063 µm)

DISCUSSION

Increasing urbanization and industrialization have caused heavy metals to reach dangerously harmful levels in the environment, implying that heavy metals enrichment in many ecosystems is directly linked to human activity (**Lasat, 2000; Estrella and Garcia, 2009**). Mercury, cadmium, copper, zinc, lead, and nickel, and other harmful heavy metals, are well-known freshwater and marine contaminants (**Travieso *et al.*, 1999; Yu *et al.*, 1999; Mehta and Gaur 2005; Singh *et al*., 2007**). In an ecological way, however, any metal or metalloid that pollutes the environment or cannot be decomposed biologically is considered a pollutant (and is therefore bio accumulated) it's possible to classify it as heavy metals (**Estrella and Garcia, 2009**). Some of these metals are essential micronutrients for plant growth (e.g., zinc, copper, manganese, nickel, and cobalt), whereas others have unknown biological functions and are poisonous such as Cd, Pb and Hg (**Gaur and Adholeya, 2005**).

During our investigation the value of TDS in industrial effluent water before treatment was (180.5 ± 12.69 mg/L) higher than obtained value after treatment (112.3 ± 4.79 mg/L), in which explained that the water had previously been treated. On the other hand, TDS isn't usually thought of as a major pollutant, it is not deemed to be associated with health effects. It's used to determine the aesthetic qualities of drinking water as well as an overall measure of the existence of a wide range of chemical pollutants (**Ogemdi and Gold, 2018**).

While chloride levels have been shown to rise in direct proportion to pollution levels (**Drakare *et al.*, 2003; Gao and Song, 2005**).

Physico-chemical parameters of the discharged petrochemical industrial effluent wastewater before and after treatment (Table 1). Petrochemical industrial effluent water of company had high chlorosity values ranged from 16.76 mg/L in water before discharge while it was 17.11 mg/L in water after discharge. It's appeared that chloride value became higher after the treatment than before. That result had the compliance to (**WHO, 1990**) which reported that chloride in water may be considerably increased by treatment processes in which chlorine or chloride is used. In similar studies (**Aziz *et al.*, 1996**) investigated that Damietta estuary had a relatively high chlorosity values (9-20.5 g/L) higher sodium and chloride concentrations are known to cause plant toxicity.

While carbon dioxide levels are predicted to nearly double in the next century (**Muylaert *et al.*, 2005**) free and total carbon dioxide concentrations increased by increasing pollution (**Schippers *et al.*, 2004**). The result recorded for carbon dioxide within industrial effluent after water discharged into the sea was lower than in industrial effluent of factory before water discharge. It was reported by (**Aziz *et al.*, 1996 and Abd el-Baky, 2001**) that agricultural and urban effluents both cause CO_2 concentrations in water to rise, whereas industrial discharge affects total CO_2 concentrations depending on the chemicals used.

Total alkalinity values in present study was 6 mg/L in wastewater before treatment and reached to 4.4 mg/L in wastewater after treatment so the result in our investigation observed high level of eutrophic conditions, according to study by (**Campbell *et al*., 2015**) who reported total alkalinity values greater than 1.4 m equ.l indicate eutrophic conditions. The parameters that determine the amenability of waste water to biological treatment are alkalinity and pH (**Jingxi Ma *et al*., 2020**).

Nitrate, a nitric acid compound, is a photosynthetic autotroph and in some cases, a growth-limiting nutrient. Algae and other aquatic plants use it to make plant protein, which can then be used by animals to make animal protein. The nitrate levels in wastewater effluent were higher before treatment than after treatment. Nitrate is an important component of farm fertilizers because it is needed for plant uptake and development. Nitrate in the aquatic environment is the most heavily oxidized source of nitrogen (**Atul and Narang, 2018; Kumar *et al.*, 2018**).

Only inorganic forms of silica are used in the main cycle of silica, which includes the use of dissolved silicon and its degradation following the death of species (Raymont, 1980). Generally the dissolved reactive silica value in the present study area discharged from two points in the petrochemicals industrial effluent wastewater the first one was before treatment and it was higher than the second point which was after treatment. Agriculture activities such as mineral application, fertilizer application, extensive irrigation, and increased weathering were linked to an increase in silicate concentration (**Juttner *et al*., 1996**).

Efficiency removal of heavy metals by the dried algal biomass the experiment was conducted to study the effect of dry *U. lactuca* on removal of some heavy metals (Cd, Pb, Zn, Ni, Cr, Cu, Fe and Mn ($mg.L^{-1}$) from the petrochemicals industrial effluent wastewater. Results of heavy metals removal from the petrochemicals industrial effluent were depended up on, both biomass amount and contact time.

Algae are a wide category of eukaryotic organisms ranged from unicellular like *Chlorella* to multicellular like giant kelp and to huge brown algae that can grow up to 50 meters. Several reports had been demonstrated that algae can absorb nitrate, phosphorus and heavy metals leading to an enhancement of the water quality (**Davis *et al*., 2003; Li *et al*., 2010**). The benefits of algal biosorbents can compensate for the drawbacks of commercial resins, which have reduce sorption efficiency at lower metal concentrations in wastewaters (**Eccles, 1999**).

The majority of studies focus on the removal efficiency of metals by algal dry materials biomass, meaning that dead cells may absorb more metals than living cells (**Mehta and Gaur, 2005**). Bacteria or (bacterial exopolysaccharides), land plants or (their products), aquatic plants, algae, fungi, and peat moss have all gotten a lot of attention recently for their ability to remove heavy metals from the surrounding media (**Sandau *et al.*, 1996a; Iyer *et al*., 2004, 2005; Kumar *et al*., 2014**).

The discharge of unaffected tannery wastewater containing toxic substances of heavy metals in the ecosystem is one of the most important environmental and health challenges in our society. Therefore there is a rapidly need for the development of novel, efficient, eco-friendly and cost-effective approach for the remediation of inorganic metals (Cr, Hg, Cd and Pb) released into the environment and to safeguard the ecosystem. Biosorption is a physiochemical property of biological material that causes contaminants, primarily HMs, to be removed from wastewater by ionic or covalent bonding (**He and Chen 2014; Zeraatkar *et al*., 2016; Salama *et al*., 2019**). Metal biosorption from aqueous solutions has the potential to be a useful wastewater treatment system. It focuses on biological materials ability to absorb heavy metals ions from wastewater through metabolically mediated or physicochemical uptake pathways (which can include living or dead microorganisms and their components, seaweeds, and so on) (**Chubar *et al*., 2003; Fard *et al*., 2011; Nashwa, 2018**). Protons compete with metal cations for binding sites because ion exchange is the mechanism of biosorption, and PH is the most critical control parameter that influences the availability of the site to the sorbate (**Vijayaraghavan and Yun, 2008**). Two other important factors in biosorption are the presence of the biosorbent and the availability of binding sites type and the concentration of the biomass (**Li and Tao, 2015**).

The effect of contact time on bisorbtion of metal ions by *U. Luctuca* during investigation period was as evident, the rapid reduction of the concentration of metal ions in the solution was at the first 15 min (65%) and up to 60 min, where by the removal rate reached to its maximum up to 85% and 95% After 120 min, the metal removal was reduced or remained steady**.**

The effect of biomass amount of dry *U. Luctuca* was seemed that the amount of metal ions adsorbed changed according to algae biomass. The result recorded the maximum removal percentage it was by different algae specie at biomass weight 1 g/L of biomass weight of dried algal cells, while the minimum removal percentage was at weight 0.2 g/L of algae biomass.

During the entire investigation period of present study the biosorption performance affected by 3 factors (contact time, algal mesh size and biomass amount/weight) the following was evident from data presented within the study. According to the contact time especially in first 15 min the biosorption efficiency was 50 %, however after about 60 min the efficiency reached to 85 % or more, after 120 min, the efficiency rate remained stable or was slightly lower than 60 min at biomass weight 4 mg/L, the biosorption capacity reached to the maximum while at biomass weight 0.2 g/L the capacity of biomass for binding metal ions was the lowest. Also algae mesh size of present study ranged between 0.250 and 0.063, the largest and the smallest respectively. As the smallest size 0.063 µm was the most efficient to bind more metal ions by algal biomass and give the best result than other the largest size 0,250µm had the least efficiency for binding ions.

biosorption ability of *U. lactuca* for Cd, Pb and Co was at its peak during the entire investigation period our results agrees with (**Bulgariu and Dumitru, 2014**) who reported Cu, Mn, and Co ions have been removed from an aqueous solution using the biosorbent properties of marine green algae *U. lactuca*. While *U. lactuca* biosorption was the ability for Ni, Mn and Fe further down in petrochemical industrial effluent during investigation period in compare to other metal ions (Cd, Pb, Co Zn and Cu). Another study by (**Mofeed, 2017**) recorded that *U. lactuca* was the most efficient absorbent in case of Cu, Mn and Fe. While Cd metal ion was one of the highest adsorbed metal ions by *U. lactuca* during the period of investigation. The result that had the compliance with study of (**Ghouneim *et al*., 2014**) who verified that *U. lactuca* was enough to remove 99.2% of Cd^{+2} from aquoues solution and concluded that *U. lactuca* can be used as an effective, low cost, and environmentally friendly biosorbent for removal of Cd ions from aqueous solution.

Aroua *et al*., 2008, showed that there are two phases of biosorption: the first step includes the dissociation of the complexes formed between solution metals and water hydronium ions, followed by the interaction of metals with the functional groups of algae. The adsorption efficiency of *U. lactuca* was found to be significantly higher because of the differences in the composition of proteins, lipids or other carbohydrates that influence the number of adsorption sites. Also algal biomasses represent a rich source of biosorption material that is capable of accumulating a high metal content while being ecologically safer and needing relatively inexpensive processing. Due to the presence of proteins, hetero-polysaccharides or lipids in the algal cell-wall structure, as well as large surface-area-to-volume ratios, these biomasses have high metal-binding capacities (**Mofeed, 2017**). Marine macro-algae possess strong metal-biosorption capacities due to the presence of active functional groups on the surface of their cell walls. Using marine macroalgae-activated carbon provides a number of advantages, including low cost, wide availability, and high metal-binding capability (**Ibrahim *et al*., 2016; Mofeed *et al*., 2022**). The marine green alga Ulva lactuca officinali is the specie that was tested in this study for the removal some heavy metals from an aqueous solution. Furthermore, because of its high surface area, relatively simple structure, and modest and uniform distribution of binding sites, this material is very useful in heavy-metal processing (Mosleh *et al*., 2021; Mofeed *et al*., 2022), and it may be utilized directly for heavy-metal recovery as a biosorbent.

CONCLUSION

Dry biomass of *Ulva lactuca* was proven to be cost-effective and efficient to eliminate some heavy metals from in the petrochemicals industrial effluent wastewater and the process is feasible, reliable and eco-friendly. The contact time especially after 60 min of treatment of petrochemicals industrial effluent wastewater with the *U. lactuca,* the efficiency reached to 95% with the concentration 1 g/L of algal biomass. Also the smallest size 0.063µm was the most efficient to bind more metal ions than the largest size 0.250µm at the same time and concentration.

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