Research Journal of Pharmaceutical, Biological and Chemical Sciences

Non-Conventional Low-Cost Biosorbents for Adsorption and Desorption Of Heavy Metals.

Sabah A. Badr, Azza A. Ashmawy, Iman Y. El-Sherif, and Reda M. Moghazy*.

Water Pollution Department ,National Research Centre, Dokki, Giza, Egypt.

ABSTRACT

Metals adsorption and desorption were investigated on different types of non-conventional low-cost bisorbents, including sun, oven dried and activated Nile water algae. The optimum adsorption condition obtained at pH 4, 150 min contact time, and 2 g/l adsorbent dose. The optimum initial concentrations for Cadmium, Lead and Zinc ions of the sun, oven dried and activated algal biomass was about 10 mg/l. The maximum efficiencies of Cadmium removal were 99.28 % in case activated biosorbent with H_2SO_4. The results show that there are no clear variations between the percentages removal of metals from the sun, oven dried, and activated biosorbents, where the maximum percentages removal of metals were 97.9%, 97.2% and 99.3% for the sun, oven dried, and activated biosorbents respectively. On the other hand, the Langmuir maximum sorption capacity (q_{max}) of sun dried biomass was found to be 16 mg/g for Cd, 31.3 mg/g for Pb and 12.2 mg/g for Zn, q_{max} of oven-dried biomass was found to be 20 mg/g for Cd, 10.8 mg/g for Pb and 9.1 mg/g for Zn. Also, q_{max} of activated biomass was found to be 11.36 mg/g for Cd, 11.76 mg/g for Pb and 12.65 mg/g for Zn. the recovery of metals by using 0.1 M HNO_3 from dried and activated biomass was more effective at 1st run with the maximum recovery 99.8% for sun dried biosorbent, 99.3% for oven dried biosorbent and 96.3% for activated biosorbent, but at 2nd run the effectiveness of the recovery was decreased to be 64.3% for sun dried biomass, 69.4% for oven-dried biomass and 85.7% for activated biomass. No clear variations in efficiency of removals and recovery between the three biosorbents.
Keywords: Adsorbtion, Desorption, Cadmium, Lead, Zinc, Low-cost biosorbents.

*Corresponding author

INTRODUCTION

A serious problems have been created by Industrial development that emitting wastewater containing many different kinds of pollutants including heavy metals, dyes, pesticides, phenols, organic compounds, etc. [1]. Heavy metals are recognized as one of the most toxic groups, which reach in the food chain through the disposal of wastes to water receptors or land [2]. Heavy metals are taxed in causing toxic effects on human being through some toxic metals accumulation like mercury, nickel, copper, cadmium, chromium and zinc as several bad consequences such as developmental and growth abnormalities, carcinogenesis, neuromuscular control defects, mental retardation, renal malfunction and a wide range of other kinds of illnesses [3]. There are several chemical and physical conventional processes for heavy metals removal, such as adsorption, sedimentation, electrochemical processes, ion exchange, cementation, coagulation flocculation, filtration and membrane processes, chemical precipitation etc. The major disadvantage that we come across these conventional processes is expensive and not eco-friendly; other disadvantages include an incomplete high reagent, metal removal, and energy requirements, generation of toxic sludge or other waste products that require careful disposal. [3]. In view of these problems and legal constraints being imposed on the discharge of effluents a need for an alternative and cost effective technology is essential [3]. The bioremediation technology has also a good prospect. As the wastewater from different industries is deposited in the rivers nearby so the more studies for aquatic flora are needed to be used to remove all these heavy metals. Fresh- water microalgae are one of the potential organisms, that can be used in safe without any hazard to the environment [4]. The search for novel technologies that involves the complete removal of the toxic heavy metals from wastewater has led to finding the process of biosorption that relies on the metal binding capacities of various biological materials. The microbial biomass has proved to be a boon for developing economic and eco- friendly waste water treatment process [5]. Moreover, algae have received a great deal of attention for decontamination of water by biosorption process. Algal biomass of algae can be used for live or dead form in a biosorption system. The biomass of the non-living algae is more favorable and practical due to the fact that living biomass cells needs minimum nutrients and environmental conditions, while non-living biomass does not. Moreover, dead biomass is not affected by the toxicity of metal ions, while they can undergo different physical and chemical pretreatments to increase their adsorption capacity [5], so that there are main factors influencing metals speciation in solution such as pH, heavy metal concentration in solution, and the presence of light anions and metals. It is known that almost all metals tend to precipitate at basic pH value, as carbonate or hydroxide forms. heavy metals Precipitation is a disadvantageous method for heavy metals removal because can generate toxic chemical sludge [6].

One of the most popular of these technologies is activated carbon adsorption which is widely used but it is expensive. Therefore, there is a growing interest in using low-cost, and most available materials for the metal ions adsorption. A low-cost adsorbent is defined as one which is abundant in nature, a by-product or waste material from another industry [7]. More recently, great effort has been contributed to developing new adsorbents and improve existing adsorbents like granular activated carbon, other adsorbents such as iron oxide coated sand, porous cellulose carrier modified with polyethyleneimine etc. [8].

The main goal of this study is investigation of possible applications of low-cost absorbents from non-living freshwater algae for removal and recovery of heavy metals.

MATERIALS AND METHODS

Biosorbents preparation

Drying of algal biomass

Nile water algae were collected from the river Nile at the intake of El-Giza water work using phytoplankton net (80 µmesh). The biomass was washed several times with deionized water to remove dirt, and/or other impurities present in the raw materials. The sample was dried:

- In an oven at 60°C for 24h or until constant weight then ground with a mortar.
- Sun dried by exposing to sunlight for 3 days and covering it during night.

Activation of dried algal biomass

Activation with Calcium chloride (PAC₁), Sodium carbonates (PAC₂) and Sodium sulphate (PAC₃).

The oven-dried algae to be activated are impregnated with 10 % calcium chloride, sodium carbonate and sodium sulphate solutions. The solution gets well adsorbed for 24 h, the excess solution was decanted off and air dried. The dried algae treated with (Calcium chloride, Sodium carbonate and Sodium sulphate) were placed in muffle furnace carbonized at 400 °C for 10 min. The dried materials were powdered and activated in a muffle furnace kept at 800 °C for 10 min. After activation, the carbon washed sufficiently with 4 N HCl to remove the cations. Then, the materials were washed with plenty of water to remove excess acid, then dried and powdered [9].

Activation with Sulphuric acid (PAC₄)

500 g of the dried algae was added in small portion to 400 mL of 98% H_2SO_4 and the resulting mixture was kept for 24 h at room temperature followed by refluxing in fume hood for 5 h. After cooling, the reaction mixture was poured onto ice water (2 L) and filtered. The filtrate was washed repeatedly with distilled water and soaked in 1% $NaHCO_3$ solution to remove any remaining acid. The sample was then washed with distilled water until pH of the activated carbon reached 6, dried in an oven at 160 °C for 48 h and kept in a glass bottle until used [10].

Biosorbents characterizations

FT-IR analysis of dried and activated algae

FT-IR analysis of dried and activated algae was determined as follows: KBr pellet was prepared. The infra-red spectra were collected by FT-IR within the range 400 to 4000 cm-1 .the spectrum analysis was realized according to [11].

High resolution Transmission Electron Microscope (HRTEM]

Biomass specimen examined under High resolution transmission electron microscope according to [12] using (Jeol Electron microscope JEM-2100).HRTEM allows to evaluate morphological characteristics of the algal biomass surface and to measure the fractions of pores and particle size if they will be in nanoscale measure (1-100 nm) or not.

Energy Dispersive X-ray microanalysis (EDX)

Energy dispersive X-ray microanalysis techniques it can provide valuable inputs in determining the distribution of various elements inside the biomass [13]

Preparation of metal ion solutions

Cadmium, Lead and Zinc standard solutions were prepared by using analytical grade chemical of cadmium chloride ($CdCl_2$ 2.5 H_2O), Lead nitrate (Pb (NO_3)₂), and Zinc chloride ($ZnCl_2$).

Batch adsorption studies

Batch adsorption equilibrium experiments were conducted to determine the optimum adsorption conditions of Cadmium, Lead and Zinc on oven dried and activated biosorbents. For studying these optimum conditions, adsorbent dose, initial metal concentrations, and contact time the experiments were conducted at various adsorbent doses of (0.1, 0.15, 0.2, 0.25 and 0.3 g/100 ml), at different concentrations of metals (10, 20, 30, 40, 50, and 60) mg/L in 250 mL stoppered reagent bottles at a constant shaking speed (150 rpm) at different contact times of (0,5,15,30,50,60,90,120,150, 180, and 240 min.). All the experiments were carried out at room temperature (25°C ± 2°C). For studying the influence of pH on the adsorption of Cadmium, Lead and Zinc the experiments were conducted at various initial metal solution pH values of 2 to 7 for Cadmium, 1

to 7 for lead and zinc. The pH of each solution was adjusted to different values with either 0.1 N NaOH or 0.1 N HCl. The solutions were filtered through a 0.45 µm membrane filter; the concentrations of Cadmium, Lead and Zinc ions in solution before and after adsorption were determined using flame atomic adsorption spectrophotometer (Model Varian 220).

Batch desorption studies

After the biosorption cycle the biosorbents were centrifuged at 2000 rpm for 15 min and washed twice with distilled water and dried. The biosorbents were added to 50 mL of the desorption eluent 0.1 M HNO$_3$ (the solid to liquid ratio was kept constant for all experiments at 0.2g/ 100 mL (2g/L). The biosorbents with eluent were left on the shaker at 150 rpm for 150 min. the eluent was removed and the final ions concentration measured. The sorbent was then centrifuged and washed as previously described. Adsorption and desorption cycles are repeated to evaluate adsorption and desorption potential of the biosorbents to determine the availability of its reuse.

<div align="center">

RESULTS AND DISCUSSION

</div>

Characterizations of algal biosorbents

FT-IR Spectroscopy

The FT-IR spectra for sun, oven dried and activated algal biomass are shown in fig. (1) the spectra display number of absorption peaks, indicating the nature of sun, oven dried and activated algal biomass.
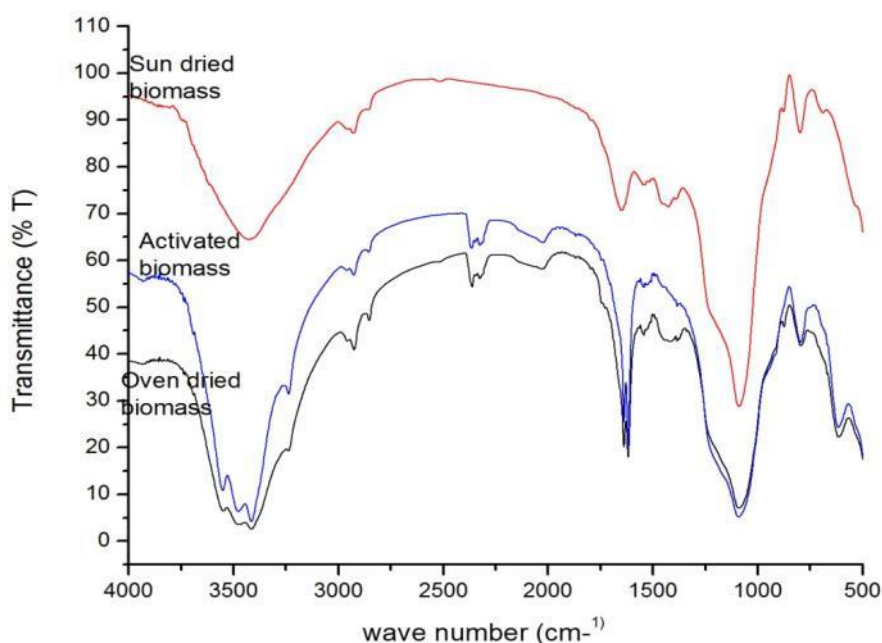

<div align="center">

Fig. (1) The FT-IR spectral characteristics of the three biosorbents of Nile water algae

</div>

The bands observed at 3553 and 3409 cm^{-1} in sun, oven dried and activated algal biomass represent bonded –OH of carboxylic groups on their surface. The band located on 3240 cm^{-1} in oven dried and activated algal biomass representing stretching of –NH group. Aliphatic C–H group in is represented by the bands at 2960-2920 and 2850 cm^{-1} in the sun, oven dried and activated algal biomass. The bands between 2366 - 2310 cm-1 in oven dried and activated algal biomass could be assigned to the Si-H stretching of silicon group. The bands between 1747 and 1710 cm^{-1} in the sun, oven dried and activated algal biomass correspond to the free C=O. The peaks located at 1637-1617 cm^{-1} in sun, oven dried and activated algal biomass are representing carbonyl group (–HC =O, R$_2$ C=O) stretching. **[14]** reported that these groups can be conjugated or non-

conjugated to aromatic rings. The bands between 1541-1415 cm^{-1} in sun, oven dried and activated algal biomass representing stretching amide (C–N and N–H) from proteins. [15-17] The band at 1090 cm^{-1} in the sun, oven dried and activated algal biomass was representing Si–O–Si or Si–O–C of silicon content [18- 20]. The bands between 873 - 795 cm^{-1} in the sun, oven dried and activated algal biomass could be assigned to be a silicate, the band at 615 cm^{-1} in sun, oven dried and activated algal biomass representing H$_2$PO$_4$– or PO$_4$- and band at 466 cm^{-1} in sun, oven dried and activated algal biomass representing metal compounds. It has been well documented that the composition of cell wall of algal biomass contains a large number of complex organic components such as proteins, lipids, carbohydrate polymers (xylane, cellulose, alginic acid, mannan) and inorganic ions (Ca $^{2+}$, Mg^{2+}) [21 & 22].

High resolution Transmission Electron Microscope (TEM)

High resolution Transmission Electron Microscope for sun, oven dried, and activated biomasses as shown in Fig (2). Prove that the morphology of the biomass material can facilitate the sorption of metals, due to presence of irregular surface of the algal biomass contain fractions of nanopores and nanoparticles have nanoscale measure ranged between (9-20 nm), these nanopores are distributed in a symmetric manner through the two silica valves of diatoms which represent the most abundant algal group in the Nile water [23]. So based on the morphology of the biomass material, as well as on the fact that high amounts of silicate which concentrated on the oven dried algal biomass it can be concluded that the biomass material presents an adequate morphological profile to adsorb metal ions [24].
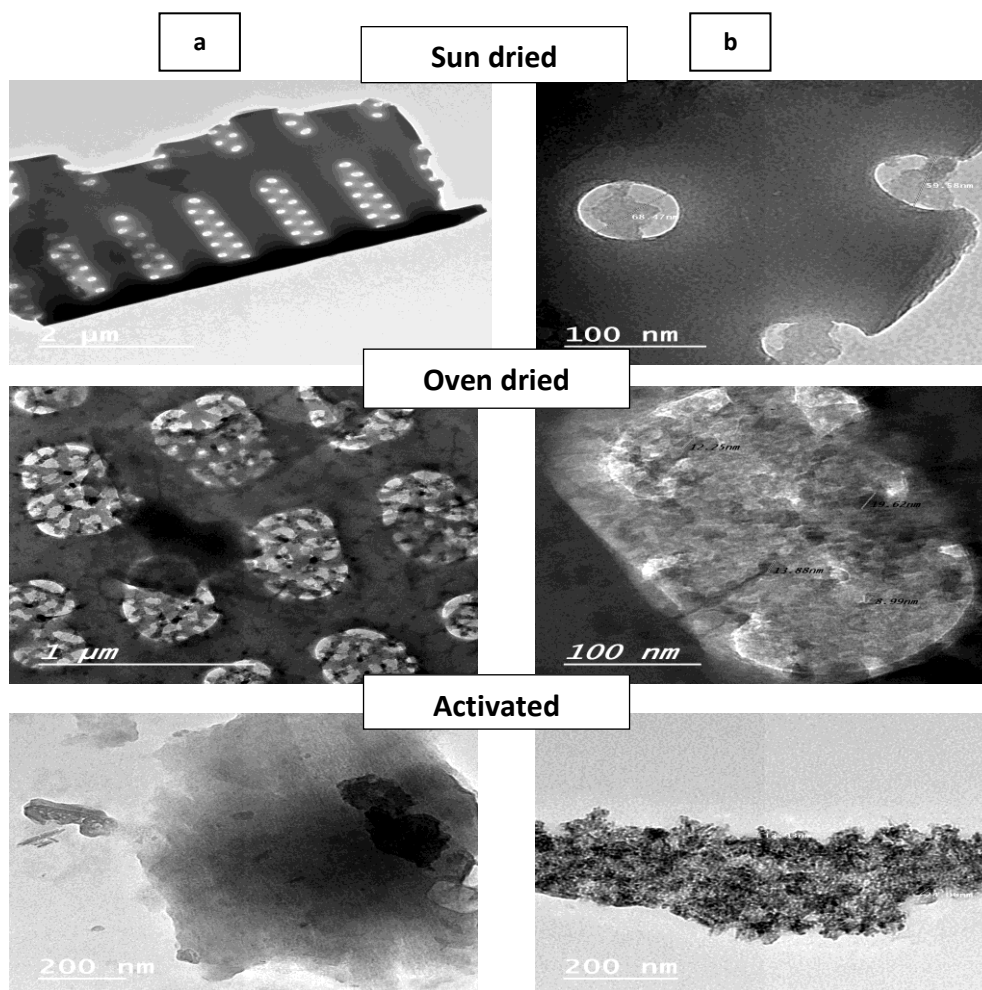
Fig. (2) TEM micrographs of sun, oven dried, and activated biomasses of Nile water algae showing:-

a-   Symmetric form of nanopores
b-   nanoscale measure of pores and particles ranged between (1-100 nm).

Energy Dispersive X-ray spectroscopy (EDX)

The chemical composition of sun, oven dried and activated biosorbents were characterized and examined by using (EDX) as shown in Table (1) which showed that oxygen and silica were abundant components of sun, oven dried and activated Nile water algae with percentage weight of 52% O and 35% Si for sun dried, 50% O and 37% Si for oven-dried biomass and 49% O and 33% Si for activated biomass. High amounts of silicate which concentrated on the oven dried and activated algae due to the diatoms with outer shells of silica component represented the most abundant algal group in the Nile water [25 & 26]. These data are in agreement with FT-IR data in the presence of oxygen and silica which are conjugated in many function groups that have a role in the absorption of metals, however, there are no clear differences between oven dried and activated biomass in the percentages weight of the major components as oxygen and silica.

Table (1) Energy dispersive X-ray microanalysis (EDX) of the three biosorbents of Nile water algae

Element	Weight%		
	Sun dried biomass	Oven dried biomass	Activated biomass
C	3.1	3.39	5.93
O	52	50	49.01
Mg	0.35	1.39	0.39
Al	2.2	5.58	3.26
Si	35	37	33
S	0.3	0.2	-
K	2.1	2.54	0.5
Ca	0.45	3.43	0.58
Ti	0.5	0.8	0.9
Mn	0.1	0.19	-
Fe	5	8	2.84

Metal removal

Determination of the optimum condition for metal removal

The results of the optimum adsorption conditions as pH, contact time, algal dose, and initial metal concentration for metal removal are shown in fig (3).

pH is considered as the most important parameter that could affect the biosorption of metal ions from solutions indicate that the best adsorption of Cd, Pb and Zn achieved at pH 4. However, the percentage removal of Cd, Pb and Zn were 88%, 98.7% and 86%, respectively. [27 & 28] found that the highest removal of Pb and Cd were achieved at pH 4. [29] show that maximum adsorption of Zn was obtained in the pH range 5.0–6.0 .

Contact time was studied in the range from 0 time to 240 min. the percentage removal of Cd by oven dried algae was about 93% at 0 time then increased gradually to reach maximum removal 99.1% at 150 min. [30] found that the adsorption time was rapid and approached maximum within 30 min but attained equilibrium after 120 min.

The maximum removal of Cadmium achieved at a dose of adsorbent (2 g/l). However, the percentage removal was 88%. [31] showed that the best removal of Pb at dose 2g/l by oven dried algae. Also [32] found that the biosorption of Cd and Pb ions was increased with subsequent increasing the biosorbent dose and almost became constant at dosage 2 g/l for Pb and Cd .

The results of optimum initial metal concentrations show that the maximum removal of Cd, Pb and Zn were 95.3%, 97.2% and 96.6%, respectively. These removals were achieved at 9.8, 10 and 9 mg/L, for Cd, Pb and Zn, respectively. The variations of percentage removal at different initial metal concentrations were not altered greatly from concentrations between 10-60 mg/l [27 & 28].

Evaluation the efficiency of different types of activated Nile water algae for metal removal

The efficiency of activated algae by CaCl$_2$, Na$_2$CO$_3$, Na$_2$SO$_4$, H$_2$SO$_4$ and commercially activated carbon were studied for Cadmium removal. The maximum removal of Cd achieved by using PAC$_4$ was 99.28%, the removal of cadmium were 96.5%, 94.62 and 98.96% by using PAC$_1$, PAC$_2$ and PAC$_3$ respectively, on the other hand, the less removal was achieved by PAC$_{com}$ where reached 74.6% (Fig.4).

The similar results, the green alga *Ulva fasciata* when activated by CaCl2, Na$_2$SO$_4$ and Na$_2$CO$_3$ give the maximum adsorption for lead 91.54%, 97.24% and 95.37% respectively, also, it gave less removal 74.8% with the commercial activated carbon PAC$_{com}$ [8], Also, [10] observed that the green alga *Ulva lactuca,* when activated by H$_2$SO$_4$, give the maximum adsorption to chromium by 98%.
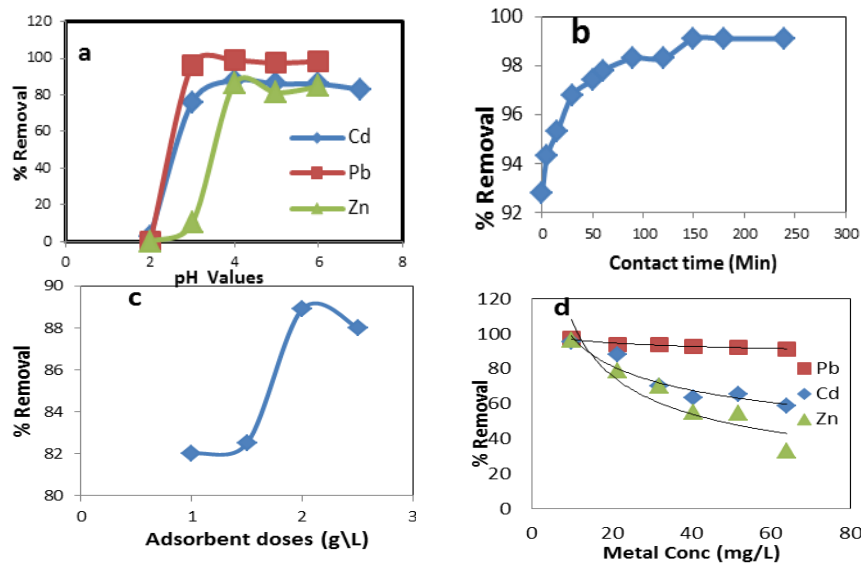

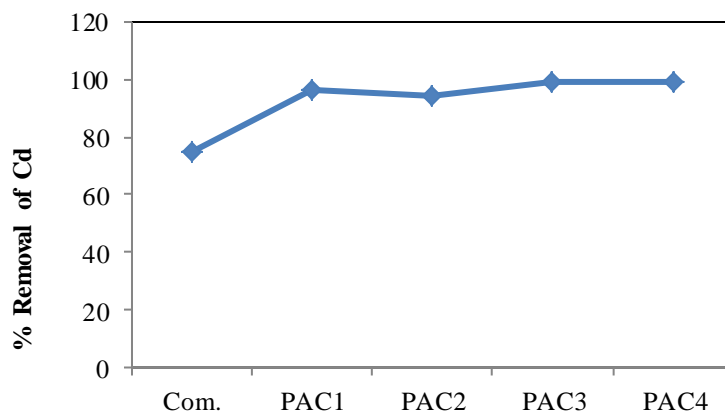**Fig. (3)Adsorption of metals by oven dried Nile water algae to determine the optimum conditions for metal removal**

Fig (4) Evaluation the efficiency of different types of activated oven dried Nile water algae for metal removal

Evaluation the sun dried, oven dried, and activated biosorbents of Nile water algae for metals removal

Determination the optimum initial metals concentrations

The results in Table (2) Predicted that the maximum removals of Cd, Pb and Zn were 91.5%, 97.9% and 93.3%, respectively for sun dried biosorbent, for oven dried biosorbents the maximum removals of Cd, Pb and Zn were 95.3%, 97.2% and 96.6%, respectively, and The maximum removal by using activated algae for Cd, Pb and Zn was 99.28%, 96.8% and 95.5%, respectively. These removals were achieved at 9.4, 9.6 and 8.8 mg/L, for Cd, Pb and Zn, respectively by using sun-dried bio sorbents, for oven dried bio sorbents the removals were achieved at 9.79, 10 and 9 mg/L, for Cd, Pb and Zn, respectively, and for activated bio sorbents were achieved at initial concentrations 9.78, 9 and 8.6 mg/L for Cd, Pb and Zn ions respectively. Analysis of percentage adsorption versus initial varying concentration of Cd, Pb and Zn ions showed that the percentage adsorption decreased with increase in initial concentration of the adsorbate, but the increase in uptake capacity takes place with the increase in initial concentration. This is due to an increase in the initial ion concentration providing a larger driving force to overcome all mass transfer resistances between the aqueous and the solid phase resulting in higher metal ion adsorption. Similar results have been reported [33-35].

Application of Biosorption isotherms

It is necessary to optimize the biosorption process design, the appropriate correlation for the equilibrium curve must be obtained. In this study, the relationship between metal biosorption capacity and metal concentration at equilibrium has been described by two-parameter sorption isotherm models: Langmuir [36], Freundlich [37]. The two isotherms were applied on the sun dried, oven dried and activated algal biomasses to indicate the surface properties and affinity of the bio sorbent and can also be used to compare the biosorptive capacities of the bio sorbent for different metal ions. These isotherms are represented by the following linearized equations:

Langmuir isotherm

The Langmuir isotherm is a theoretical model for monolayer adsorption, which assumes that the adsorption takes place at specific sites of homogeneous adsorbent, is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}}$$

Table (2) Adsorption of Cadmium, Lead and Zinc ions by sun dried, oven dried, and activated biomass as a function of initial concentration at the optimum removal conditions

pH Value = 4   Contact time = 150 min.   Adsorbent dose = 2g/L

Metals	Sun dried algae		Oven dried algae		Activated algae	
	C_i (mg/l)	% Removal	C_i (mg/l)	% Removal	C_i (mg/l)	% Removal
Cd	9.4	91.5	9.79	95.3	9.78	99.28
	19.5	84.3	21.43	88.3	19.7	83.2
	31	66.5	32	70.3	29.5	77.6
	40.55	60.3	40.55	63.6	39.25	64.9
	51.8	58.4	51.8	65.4	50	55.6
	64	55	64	59	55	38.3
Pb	9.6	97.9	10	97.2	9	96.8
	20	93.2	20	93.8	18	96.5
	30	92.5	30	93	32	83.3
	40	92.1	40	93	40	78.7
	50	91.8	50	92.2	50	71
	60	91.0	60	91.3	60	75.4
Zn	8.8	93.3	9	96.6	8.6	95.5
	19	75.9	19	78.9	19	63
	27.5	67	27.5	70	27.5	58.5
	37.5	52.3	37.5	55.3	37.5	51.3
	46.5	51.0	46.5	54.8	46.5	46.2
	50	30	50	33	50	46

C_i: Initial concentration

The two linearized isotherms acquired for Cd, Pb, and Zn, in sun, oven dried, and activated bio sorbents were presented in Fig. (5). The experimental data of Cd, Pb and Zn could better be described for Langmuir and Freundlich isotherms where R^2 is more than 0.9. The Langmuir maximum sorption capacity (q_{max}) of sun dried bio sorbent was found to be 20 mg/g for Cd, 10.8 mg/g for Pb and 9.1 mg/g for Zn, (q_{max}) of oven dried bio sorbent was found to be 16 mg/g for Cd, 31.3 mg/g for Pb and 12.2 mg/g for Zn, and (q_{max}) of activated bio sorbent was found to be 11.36 mg/g for Cd, 11.76 mg/g for Pb and 12.65 mg/g for Zn. [38] studied isotherm constants for heavy metal biosorption by oven dried biomasses of various green marine macroalgae, they found that the values of Freundlich model constants and isotherm indicated good biosorption, where Langmuir constant (q_{max}) ranged between 2.6 to 20.4 mg/g for Cd and 21.3 to 83.3 mg/g for Pb, also Freundlich constants (n) were ranged between 2.6 to 8.9 for Cd and 1.3 to 2.6 for Pb, while [8] found that adsorption process was better described by the Langmuir model, and q_{max} of lead adsorbed by activated biomass ranged between 15.62 mg/g to 24.15 mg/g, and (n) ranged between 2.83 to 4.2.

Comparison between the efficiency of sun dried, oven dried and activated Nile water algae for metal removal

It is evident from the data predicted from the optimum removal of the metals by sun dried, oven dried and activated algae in fig. (6), that no clear variations between the percentage removal of metals for sun dried, oven dried and activated Nile water algae, however, the percentages removal of metals were ranged between (91.2%-97.9%) for sun dried algae, (95.3%-97.2%) for Oven dried algae, and (95.5%-99.3%) for activated algae. [10] show that there are low differences between dried and activated, however, the maximum chromium removal were 92 and 98%, respectively for dried algae and its activated biomass by H_2SO_4.
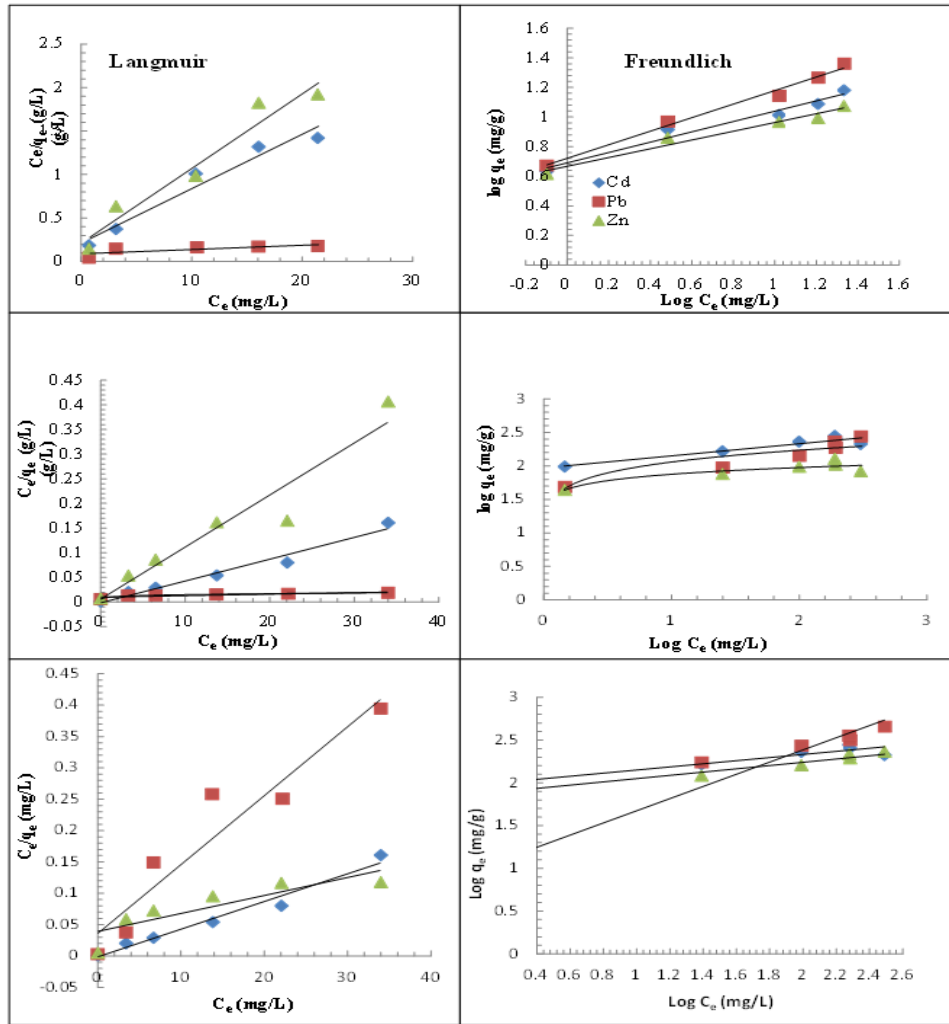
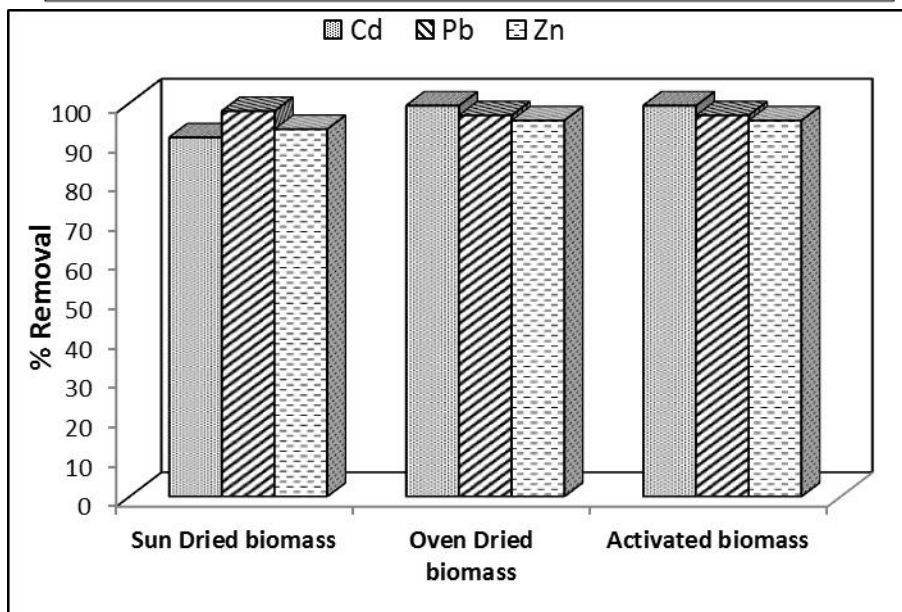Fig (5) isotherm model parameters for sun, oven dried and activated algal biosorbents

Fig. (6) Comparison between the efficiency of sun dried, oven dried and activated Nile water algae for metal removal.

Metal recovery

Metal removal and recovery for sun dried Nile water algae

The results of desorption experiments are shown in fig. (7) which clearly indicates that there are effective adsorption and desorption of Cd, Pb and Zn ions at the first run, where the percentages removal were 91.5%,97.9%, and 93.3% respectively and the percentages recovery were 98.8%,95.7%, and 99.8%, respectively. At the second run the effectiveness of adsorption and desorption of Cd, Pb and Zn were decreased, where the percentages removal were 75%, 81.7%and 78%, respectively and the percentages recovery were 64.3%, 61.7% and 56.3% respectively.

Metal recovery for oven dried Nile water algae

There are effective adsorption and desorption of Cd, Pb and Zn ions at the first run, however, the percentages removal were 95.8%,98.4% and 96.6% respectively, also the percentages recovery were 94.5%, 99.3% and 96.3% respectively. At the second run the effectiveness of adsorption and desorption of Cd, Pb and Zn were decreased, however, the percentages removal were 73%, 80% and 72% respectively and the percentages recovery were 61.5%, 69.4% and 58% respectively (Fig. 7).

Metal recovery for activated dried Nile water algae

There are no clear variations in effectiveness of adsorption and desorption of Cd, Pb and Zn ions at the first run between dried and activated biomass, whereas the percentages removal of Cd, Pb and Zn ions were 96.8%, 97.4% and 95.5% respectively and the percentages recovery were 92.5%, 91.2% and 96.3% respectively. This effectiveness was decreased in the second run, however, the percentages removal were 66.3%, 77.7% and 63% for Cd, Pb and Zn ions, the percentages recovery of Cd, Pb and Zn ions were 81.3%, 85.7% and 78.6% respectively (Fig. 7). **[39]** when investigated the recovery of lead from dried Sargassum biomass, found that a successful recovery achieved by eluting with 0.1 M HNO_3 for 15 min and a high degree of metal recovery was observed (95%).
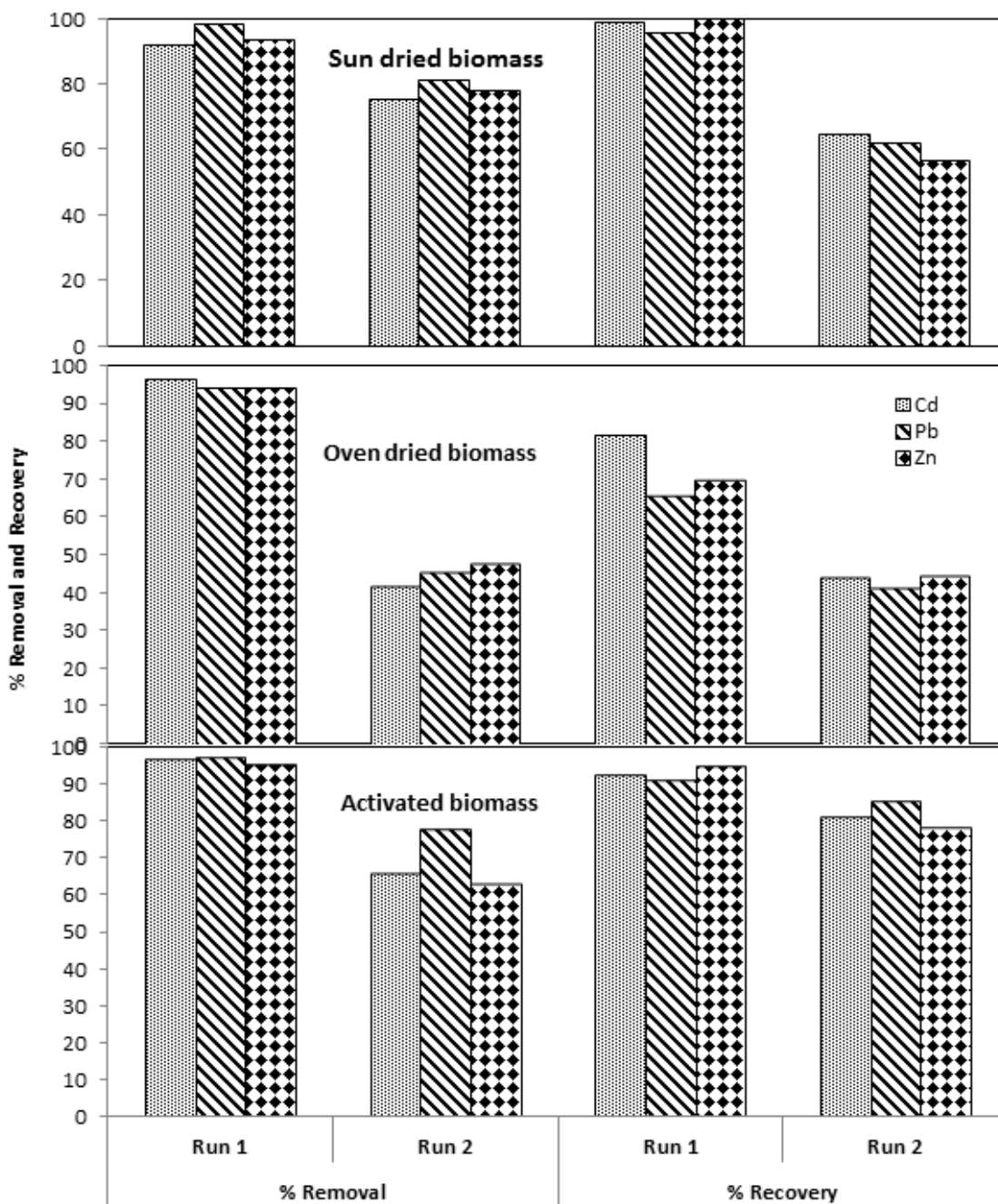
Fig (7) Removal and recovery of Cd, Pb and Zn by sun dried, oven dried, and activated biomass

REFERENCES

[1]   Kyzas GZ, Kostoglou M. J Materials 2014; 7: 333–364.
[2]   Anastopoulos IG, Kyzas Z. J Molecular Liquids 2015; 209: 77–86.
[3]   Thiele DJ. Metal detoxification in eukaryotic cells. Crisp. Data Base of national Institute of Health. Washington D.C,1995.
[4]   Soma H. A Review. Sch. Acad. J Biosci 2014; 2(11): 825-830.
[5]   Sabat S, Kavitha RV, Shantha SL, Nair G, Ganesh M, Chandroth N, Murthy VK. Indian J. of applied research 2012; 2 (3): ISSN - 2249-555X.
[6]   Brinza L, Dring MS, Garrilescu M. J Environment and Management 2007; 6(3): 237-251.
[7]   Akbar E, Samira G, and Abdolhossein R. J. Marine Sci. and Tec 2010; 18(4): 587-592.
[8]   Jeyakumar RPS. and Chandrasekaran AV. Adsorption of lead(II) ions by activated carbons prepared from marine green algae: Equilibrium and kinetics studies. Int. J Ind. Chem 2014; 5: 2.

[9]   Karthikeyan S, Sivakumar P, Palanisamy PN,. J Chem 2008; 5: 409–426.
[10]   El-Sikaily A, El Nemr A, Khaled A, and Abdelwehab O. J Hazard. Mater 2007; 148: 216-228.
[11]   Guibaud G, Tixier N, Bouju A, and Baudu M. J Chemosphere 2003; 52: 1701-1710.
[12]   Williams DB, and Carter CB. Plenum Press New York. 1996.
[13]   Figueira M, Volesky B, Azarian K, and Ciminelli VS,. Multimetal biosorption in a column using *Sargassum* biomass," Biohydrometallurgy and the environment toward the mining of the 21st century (part b): International biohydrometallurgy symposium - proceedings , R. Amils and A. Ballester (Editors), Elsevier Science, Amsterdam, the Netherlands 1999, 503 -512.
[14]   Cesar TTR., and Marco ZAA. J Chemosphere 2004; 54: 987–995.
[15]   Malik JD. Algal Biomass as Adsorbents for Heavy Metal Sorption from Aqueous Solutions. Ph.D (Loughborough University) 1999.
[16]   Davis TA, Volesky B, and Mucci A. J Wat. Res 2003; 37: 4311-4330.
[17]   Raize O, Argaman Y, and Yannai S,. (www.interscience.wiley.com). DOI:10.1002/bit. 20136.
[18]   Kleinübing SJ, Silveira VR, Marisa MB, Guibal E, and da Silva MGC. J Materials Research 2010; 13(4): 541-550.
[19]   Fenoradosoa AT, Ghina A, Delattre C, Laroche C, Petit E, Wadouachi A, and Michaud P. J Appl Phycol 2010; 22: 131–137.
[20]   Asbchin AS, and Mohammadi M,. J Biol. Environ. Sci. 2011; 5(15): 121-127.
[21]   Vilar VJP, Valle JAB, Bhatnaga AR, Santosa CJ, Selene MA, Guelli U, Augusto AU, Cidália MS, and Botelhoa RAR. 200–202: 140–148.
[22]   Jinsong H, and Chen JP. J Bioresource Technology 2014; 160: 67–78.
[23]   Eggen M. Department of Biotechnology ,Institutt for bioteknologi 2012.
[24]   El-Sikaily A, El Nemr A, and Khaled A. J Chemical Engineering Journal 2011; 168: 707–714.
[25]   Shehata SA, Lasheen MR, Bader SA, and Ali GH. Egypt J. Appl. Sci. 2000; 15 (7): 643-665.
[26]   Shehata SA, Badr SA, Ali GH, Ghazy MM, Moawad AK, and Wahba SZ. Applied Sciences Research 2009; 5(12): 2083-2095.
[27]   Abbas HS, Mohammed AA, and Al-Musawi TJ,. J Environ. Sci. Pollut. Res. 2013 a; 20:3011–3023.
[28]   Abbas HS, Mohammed AA, and Al-Musawi TJ. J Bioproces Biotechniq 2013 b; 3:1.
[29]   Bayramoglu GM, and Arıca Y. J Bioresource Technology 2009; 100: 186–193.
[30]   Lan CM. Biosorption of heavy metals (Cu, Zn, Cd and Pb) by marine algae biomass. M.Sc school of science and technology university Malaysia Sabah 2010.
[31]   Karaca M. Biosorption of aqueous Pb^{2+}, Cd^{2+}, and Ni^{2+} ions by *Dunaliella salina*, *Oocystis* sp., *Porphyridium cruentum* and *Scenedesmus protuberans* prior to atomic spectrometric determination. M.Sc of School of Engineering and Sciences of İzmir Institute of Technology 2008.
[32]   Abdel-Aty AM, Nabila SA, Hany HA, and Rizka KA. J Advanced Research 2013; 4: 367–374.
[33]   Chen Z, Ma W, and Han M. J Hazard Mater 2008; 155: 327-333.
[34]   Riaz M, Nadeem R, Hanif MA, Ansari TM, and Rehman KU. Pb (II) J. Hazard. Mater 2009; 161: 88-94.
[35]   Nasuha NH, and Mohd Din AT. J. Hazard. Mater 2010; 175: 126-132.
[36]   Langmuir I. J Am. Chem. Soc. 1918; 40: 1361-1403.
[37]   Freundlich H.. Phys. Chem. 1907; 57: 385-470.
[38]   Kumar R, Singh R, Kumar N, Bishnoi K, and Bishnoi NR.,. *Bacillus brevis*, J Chem. Eng 2009; 146: 401–407.
[39]   Jalali R, Ghafourian H, Asef Y, Davarpanah SJ, and Sepehr S. J Hazardous Materials 2002; 92 (3):253–262.