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COMPARATIVE STUDY ON THE BIOSORPTION AND DESORPTION OF THREE SELECTED TOXIC HEAVY METALS BY SOME MICROALGAE

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Abstract

Biosorption has emerged as a cost-effective and efficient alternative technology for removal of heavy metals which produce adverse health effects on humans and living organisms. In the present study the biosorption and desorption of cadmium, lead and zinc by *Chlamydomonas variabilis*, *Anabaena constricta* and *Nitzschia linearis* were evaluated. Algal species were isolated and cultivated on a large scale to get an intensive biomass sufficient for metal binding experiments. The experimental adsorption data were fitted to the Langmuir and Freundlich adsorption model. Characterization of the metal-loaded biosorbent by FTIR spectrum, TEM and EDX analysis confirmed that the metal ions can bind to anionic groups due to electrostatic attraction and sorption capacity is strongly influenced from the type and number of functional groups of the biosorbent. The maximum efficiencies of Cd, Pb and Zn removal using *C. variabilis* were 97.9%, 96.1% and 96.1% for oven dried biomass and 96.3%, 94.2% and 94.1% for activated biomass. For dried and activated biomass prepared of *A. constricta* the maximum percentage of removal of heavy metals were 95.1%, 93.7%, and 93.1% and 94.3%, 96.1% and 94.1%. The maximum removals by *N. linearis* were 95.5%, 96.6%, 94.8% for oven dried biomass and 93%, 94.5% and 93.8% for activated one respectively. There are no clear variations in biosorption of cadmium, lead and zinc by sun dried, oven dried and activated biomass of *C. variabilis, A. constricta* and *N. linearis*. It is better to use sun dried algae as low cost biosorbent for metals removal.

Keywords: Biosorption, Cadmium, Lead, Zinc, *Chlamydomonas variabilis*, *Anabaena constricta* and *Nitzschia linearis*.

Introduction

Heavy metal pollution is a world-wide environmental problem especially in developing countries. The heavy metal contamination arising from the discharge of untreated aqueous streams, arising from the discharge of untreated metal containing effluent into water bodies is one of the most important environmental issues (**Hawari and Mulligan, 2006).** Their presence in aquatic ecosystem cause

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harmful effects to living organisms **(Wang *et al*., 2006).** Various industries discharge heavy metals into environment such as mining, leaching, surface finishing industry, energy and fuel production, fertilizer and pesticide industry, electroplating, leatherworking, electrical appliance manufacturing. Presence of heavy metals and their compounds, even in small amounts, in industrial wastewater is very dangerous and must be removed **(Sari and Tuzen, 2008)**. Cadmium, Lead and Zinc are kinds of heavy metals of concern as they are toxic metals **(Wang and Chen, 2009).**

Numerous studies have been carried out to find the most effective and low cost methods for the removal of heavy metals **(Babel and Kurniawan, 2003; Yadanaparthi *et al*., 2009)**. Biosorption has emerged as a cost-effective and efficient alternative treatment technology for removal of heavy metals. It has been employed as an alternative method for removal of toxic metal ions from dilute aqueous solutions and industrial effluents **(Sethunathan *et al*., 2005; Karthikeyan *et al*., 2007; Vieira *et al*., 2007; Anyurt *et al*., 2009; Atolaiye *et al*., 2009).**

Different types of biomass in non-living form have been studied for their heavy metal uptake capacities (**Gupta *et al*., 2006; Gupta and Rastogi, 2008**). Microorganisms are in fact considered intrinsically more efficient in the bioaccumulation of heavy metals when exposed to low concentrations in their surrounding aqueous environment **(Barange *et al*., 2014).** Of the many types of biosorbents recently investigated for their ability to sequester heavy metals, microalgal biomass has proven to be highly effective as well as reliable and predictable in the removal of heavy metals from aqueous solutions (**Priyadarshani *et al*., 2011)**.

The mechanism of binding metal ions by algal biomass may depend on the species and ionic charges of metal ion, the algal organism and the chemical composition of the metal ion solution. The identification of functional groups of algae is very important for understanding the mechanism. Cell walls of algae consist of functional groups, such as amino, carboxyl, thiol, phosphoric, and sulphydryl, which are responsible for binding of metal ions **(Yalçin *et al*., 2010; Yang *et al*., 2010; Christobel and Lipton, 2015)**. Algal cell wall has very high metal-binding capacities as proteins, carbohydrates and lipids present in cell walls and membranes could react with metallic species **(Monteiro *et al*., 2012**). Their intensity depends largely on the kind, number, affinity, and distribution on the cell wall. Therefore, to use algal biomass effectively for water purification, it is important to understand the chemical nature of the metal binding process **(Duygu and Bikem, 2013).** Metal biosorption may be enhanced by heat or chemical sterilization or by degradation of cell wall and theses would offer a larger available surface area and expose the intracellular components and more surface binding sites because of the destruction of the cell membranes (**Wang and Chen, 2009**).

The aim of this study is to carry out a comparative biosorption and desorption of cadmium, lead and zinc by *Chlamydomonas variabilis*, *Anabaena constricta* and *Nitzschia linearis* in order to evaluate the most efficient one in removal of these heavy metals.

Materials and Methods

A) Preparation of Biosorbent:

Three algal species (*Chlamydomonas variabilis* Dangeard, *Anabaena constricta* (Szafer) Geitler and *Nitzschia linearis* W. Smith) were isolated from the Nile River. Algal identification has been done according to the keys of identification **(Geitler, 1932; Hustedt, 1976; Komárek and Fott, 1983)**. Algal species were cultivated using BG11 medium and modified BG11 for green alga and blue green one respectively **(Stanier *et al*., 1971)** and diatom medium for diatom species **(Cohn *et al*., 2003).** The cultivation was performed on a large scale to get an intensive biomass production sufficient for metal binding experiments.

B) Structural elucidation of Biosorbent using FTIR, TEM and EDX analysis:

The characterizations of algal biosorbents were investigated by using: Fourier Transform Infra-Red Spectroscopy (FT-IR) **(Guibaud *et al*., 2003)**, Transmission Electron Microscope (TEM) (Jeol Electron microscope JEM-2100) and Energy Dispersive X-ray microanalysis (EDX) **(Figueira *et al*., 1999)**.

C) Sorption experiment:

The yielded biomasses of the three microalgae were sun dried and others were oven dried, the biomasses were grinded on an igate stone pestle mortar to obtain a homogeneous and a powdered dried algal biomass. The oven dried biomasses were then treated by $CaCl_2$, Na_2CO_3, Na_2SO_4 and H_2SO_4 to get activated algal biosorbents. These biosorbents subjected to patch removal experiments under controlled optimum conditions of pH range 4-5, 150 min contact time, and 2g/L biosorbents. The biosorbents dose were conducted in metal solutions with different concentrations of (10, 20, 30, 40, 50 and 60) mg/L.

D) Sorption isotherm experiment:

The relationship between metal biosorption capacity and metal concentration at equilibrium has been described by two-parameter sorption isotherm models:

i) Langmuir isotherm:

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

Where q_e is the amount of metal ions sorbed per unit mass onto dried algae (mg/g), q_{max} is maximum adsorption capacity at complete monolayer coverage (mg/g); b is a Langmuir constant that relates to the heat of adsorption (L/mg).

ii) Freundlich isotherm:

$$\text{Log } q_e = \log k_F + 1/n \log C_e$$

Where q_e is the equilibrium adsorption capacity, (mg/g), C_e is the equilibrium concentration of metal ions in the solution (mg/L). k_F represents the adsorption capacity when metal ion equilibrium concentration equals to 1 (mg/g), n is the degree of dependence of adsorption with equilibrium concentration.

E) Desorption Experiments:

After the biosorption cycle the biosorbents were centrifuged 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 biosorbents with eluent were left on the shaker at 150 rpm for 150 min., then the eluent was removed and the final ions concentration measured. Adsorption and desorption cycles are repeated to evaluate adsorption and desorption potential of the biosorbents to determine the availability of its reuse.

Results and Discussion

A) Characterizations of algal biosorbents

1- FT-IR Spectroscopy

The FT-IR spectroscopy method was used to obtain information on the nature of possible interactions between several functional groups of different microalgae biomasses and the metal ions. The FT-IR spectra display number of absorption peaks, indicating the nature of oven dried and activated biomasses of isolated algae (Figs. 1, 2, and 3). The bands located at 3553 and 3409 cm^{-1} in both oven dried and activated biosorbents of the three isolated algae represent bonded –OH of carboxylic groups on their surface. The bands at 3240 cm^{-1} representing stretching of –NH groups, while the band at 1541-1387 cm^{-1} representing stretching amide (C–N and N–H) from proteins for the three isolates. Also the peaks located at 1637-1617 cm^{-1}are representing carbonyl group (–HC =O, R_2 C=O) stretching for the three isolates. Aliphatic C–H group is represented by the bands at 2960-2920 and 2850 cm^{-1} for *Chlamydomonas* and by the bands at 2960 and 2850 for *Anabaena* and *Nitzschia* .The bands between 2366 and 2310 cm^{-1} could be assigned to the S-H stretching group for *Anabaena* and 2366-2028 S-H stretching group for *Chlamydomonas*. The bands between 2366-2317 cm^{-1} could be assigned to the Si-H stretching of Silicon group for *Nitzschia*. Alkyne C≡C group for *Anabaena* was represented by the bands between 2150-2028 cm^{-1}. Bands between 2028 cm^{-1} , 1755 cm^{-1} correspond to the free C=O for *Nitzschia* and *Chlamydomonas* respectively. These groups can be conjugated or non-conjugated to aromatic rings **(Cesar and Marco, 2004).** The vibrations observed at 466 and 1100 cm^{-1} correspond to asymmetric stretching modes of Si–O–Si bonds whilst the M–O–Si stretching vibration is indicated at 800 cm^{-1} for *Nitzschia,* **Huang *et al*., (2007) and Sheng *et al*., (2009)** found that, the peaks at 472 and 1095 cm−1 may be attributed to the asymmetric stretching modes of Si O–Si bonds, the peak at 800 cm−1 may correspond to the stretching vibration of Al–O–Si. The band at 615 cm^{-1} representing $H_2PO_4^{1-}$ or PO_4^{3-} for the three isolated algae, also band at 466 cm^{-1} representing metal compounds for the three algae. **Monteiro *et al*., (2012)** stated that the microalgal cell wall consisted mainly of polysaccharides, proteins, and lipids, which offer several functional groups

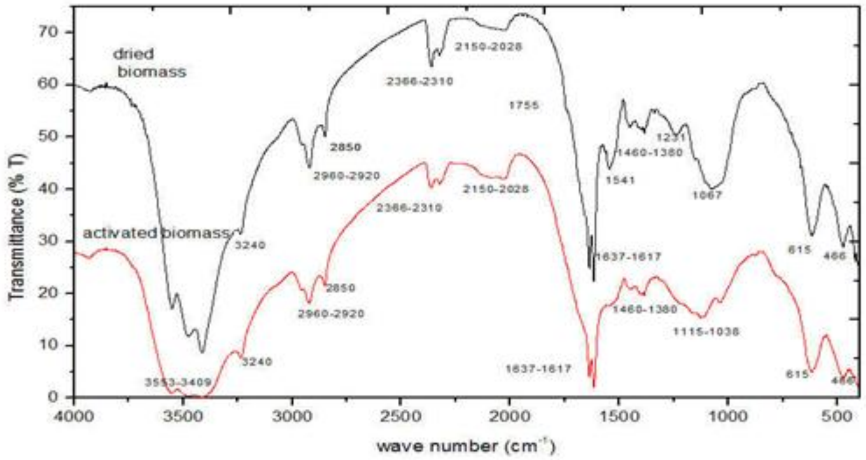

Fig. (1) FT-IR spectra of oven dried *Chlamydomonas variabilis* and its activated biomass

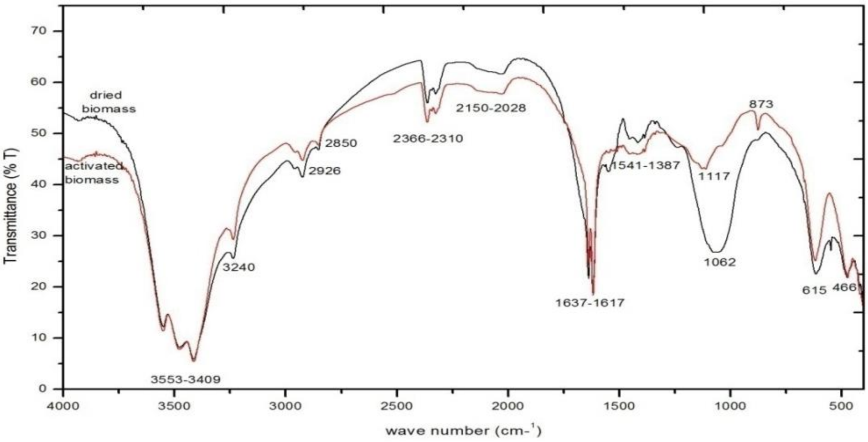

Fig. (2) FT-IR spectra of oven dried *Anabaena constricta* and its activated biomass

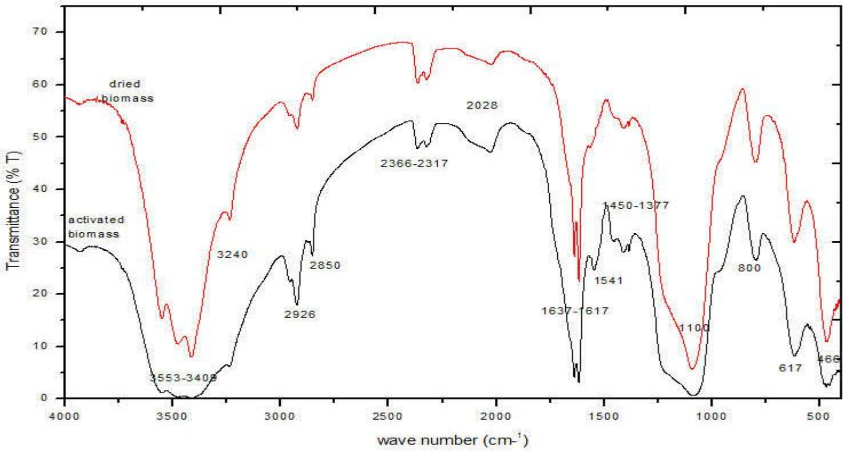

Fig. (3) FT-IR spectra of oven dried *Nitzschia linearis* and its activated biomass

(e.g., carboxyl,–COOH; hydroxyl, – OH; phosphate, – PO_3 ; amino,– NH2 ; and sulfhydryl, – SH) that confirm a net overall negative charge to the cell surface, and concomitantly a high binding affinity for metal cations via counter ion interactions. Also **Duygu and Bikem (2013)** stated that in *Nitzschia closterium* biomass carboxylate groups were mainly involved in coordination of bivalent ions, but also electron donors groups, such as amino, amide and hydroxyl groups, were likely to play a role in the sorption process. It has been well documented that these function groups located at cell wall could react with metallic species facilitating metal binding processes **(Sharma *et al*., 2011; Chinedu *et al*., 2012; Bakatula *et al*., 2014; Bulgariu and Bulgariu, 2014; Kumar *et al*., 2015).**

2- Transmission Electron Microscope (TEM)

The examination of the oven dried biomasses of isolated algae by (TEM) show the morphologic nature of the biomasses material of *Chlamydomonas*, *Anabaena*, and *Nitzschia*. The isolated algal biomasses can facilitate the sorption of metals by their irregular surfaces that contain fractions of nanopores and nanoparticles which have nanoscale measure ranged between 1-100 nm. It has been monitoring the nanoscale structures in *Chlamydomonas* biomass ranged between 36-47 nm (Fig. 4), while in *Anabaena* were ranged between 23-51 nm (Fig. 5), and in *Nitzschia* were ranged between 4.7-120 nm (Fig. 6). The sheath or projection in *Chlamydomonas* might be one of the defense mechanism against metal ion toxicity and may not allow the metal ions to enter the algal cell since the functional chemical groups on the sheath would complex or chelate the metal ions **(Staley, 1989)**. In the biomass of *Nitzschia* nanopores are distributed along the frustules shell wall in symmetric manner through the two silica valves and they will allow the free passage of molecules and ions in aqueous solutions.

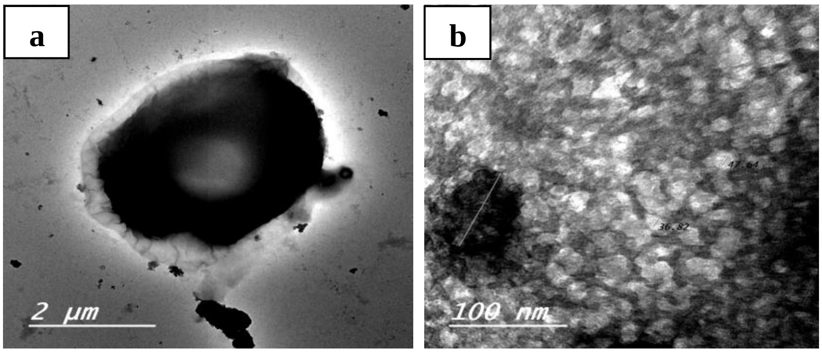

Fig. (4) TEM micrographs of oven dried biomass of *Chlamydomonas variabilis* showing: a- the cell with outer sheath, b- nonporous and nanoparticles at nanoscale measure ranged between (36-47 nm).

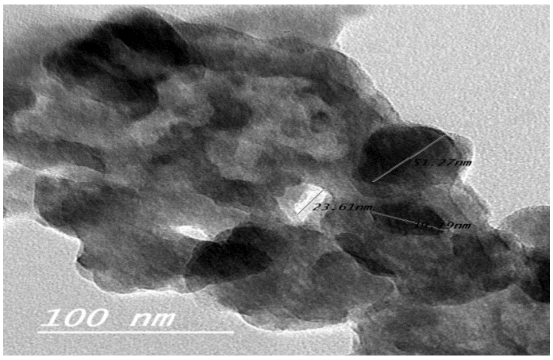

Fig. (5) TEM micrographs of oven dried biomass of *Anabaena constricta* showing irregular surface of the algal biomass, as well as nonporous and nanoparticles at nanoscale measure ranged between (23 -51 nm)

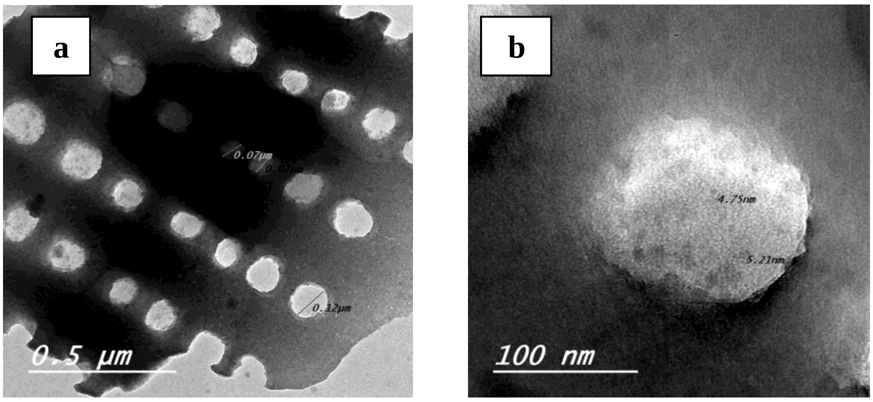

Fig. (6) TEM micrographs of oven dried biomass of *Nitzschia linearis* showing: - a- symmetric form of nonporous, b- nanoscale measure of nanopores and nanoparticles ranged between (4.7-120 nm).

This finding was in agreements with **Poulsen *et al*., (2007)**; **Yu *et al*., 2012; Jeyakumar and Chandrasekaran, 2014**. On the other hand **Eggen (2012)** reported that diatoms are known to have a high affinity towards a variety of dissolved trace elements and they will therefore exert a strong control on the transfer of heavy metals along the water column to the sediments. So, it can be concluded that the biomass material of the isolated algae has a morphological profile enable it to adsorb metal ions and these were similarly reported by **El-Sikaily *et al*., 2011.** Grinding the algal cells offers a larger available surface area and exposes the intracellular components and more surface binding sites because of the destruction of the cell membranes **(Errasquin and Vazquez, 2003).**

3- Energy Dispersive X-ray spectroscopy (EDX)

The oven dried and activated biomasses of the three isolated algae were characterized and examined by using (EDX) to find out chemical composition. Carbon and oxygen were abundance components of oven dried and activated biomass of *Chlamydomonas* with percentages weight of 54.8% C and 33.5% O for dried biomass and 62.1% C and 31.2% O for activated biomass. Oxygen, carbon and nitrogen were the abundance components for *Anabaena* with percentage weight of 37.2% O, 31.3% C and 21.2% N for oven dried biomass and 37% O, 47.7% C for activated biomass. But in case of *Nitzschia* oxygen, carbon and silica were the abundance components with percentages weight of 43% O, 29% C and 21% Si for oven dried biomass and 48% O, 29.3% C, 24% Si for activated biomass. The presences of these abundance components as the major groups in isolated algal biomasses are compatible with FT-IR data in which many functional groups have a role in metals uptake.

B) Metal removal

1. Determination the optimum initial metals concentrations

For sun dried biomass, in *Chlamydomonas variabilis*, it was found that the maximum percentages of removals for Cd, Pb, and Zn were 96.8%, 95.8%, and 98.6% respectively. *Anabaena constricta* show maximum removals 95.1%, 93.7%, and 93.1% for Cd, Pb, and Zn respectively. The highest percentages of removals in *Nitzschia linearis* were 92.0 %, 89.6%, and 88.6% for Cd, Pb, and Zn respectively (Fig.7). These percentages of removals were obtained at initial metal concentrations 9.4, 9.6 and 8.8 mg/L, for Cd, Pb and Zn, respectively. **Romera *et al*., (2007)** recorded that the optimum pH value for recovery of Cd, Ni and Zn was 6 and the optimum sorption pH for Cu ranged from 4 to 5 and for Pb from 3 to 5.

For the oven dried biomass (Fig.8), the maximum removals of Cd, Pb and Zn by *Chlamydomonas* were 97.9%, 96.1% and 96.1% respectively. These percentages were reached at 9.8, 9 and 8.9 mg/L of Cd, Pb and Zn respectively. For *Anabaena* Cd, Pb and Zn the maximum removals accomplished at 97.5%, 94.1% and 96.7% respectively; these removals were correlated with 9.5, 8.5 and 8.7 mg/L of Cd, Pb and Zn ions respectively. **Abdel-Aty *et al*., (2013)** found that the biosorption of Cd and Pb by oven dried biomass of *Anabaena sphaerica* was achieved at 94.3% and 88.6% respectively. The maximum removals of Cd, Pb and Zn by *Nitzschia* were 95.5%, 96.6% and 94.8% respectively, these removals were obtained at initial concentrations 9.3, 9 and 8.6 mg/L for Cd, Pb and Zn ions respectively. Also the data show that percentage adsorption decreased with increase in initial concentration of the adsorbate (**Abdel-Aty *et al*., 2013)**.

For activated biomass, in *Chlamydomonas* the maximum removals of Cd, Pb and Zn ions were 96.3%, 94.2% and 94.1% respectively, with initial metal concentrations 9.6,9 and 9.3 mg/L for Cd, Pb and Zn respectively. In *Anabaena* the maximum removals for Cd, Pb and Zn were 94.6%, 96.1% and 94.2% respectively.

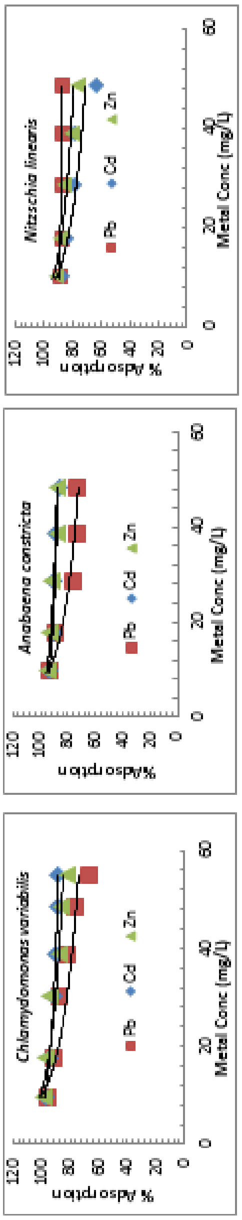

Fig. (7) Effect of Cadmium, Lead and Zinc concentration on the percent adsorption (%) using sun dried of *Chlamydomonas variabilis*, *Anabaena constricta*, and *Nitzschia linearis*.

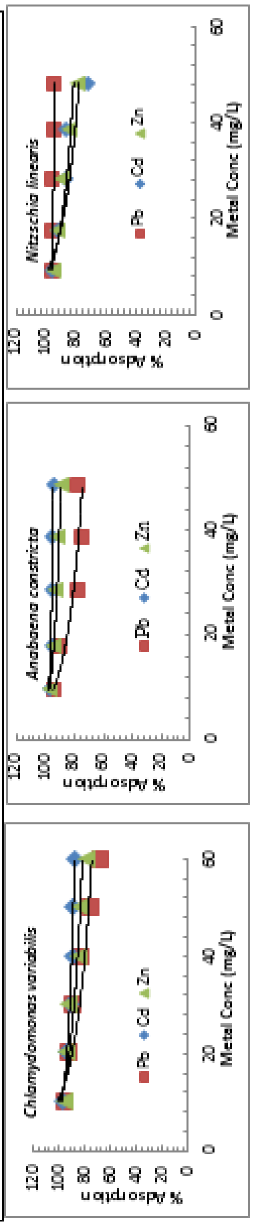

Fig. (8) Effect of Cadmium, Lead and Zinc concentration on the percent adsorption (%) using oven dried of *Chlamydomonas variabilis*, *Anabaena constricta* and *Nitzschia linearis*.

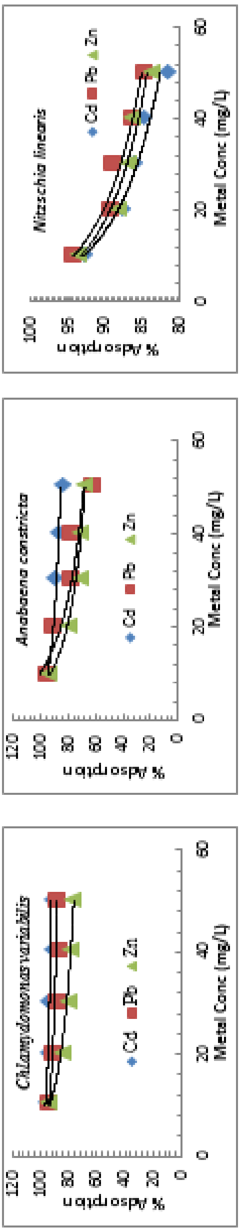

Fig. (9) Effect of Cadmium, Lead and Zinc concentration on the percent adsorption (%) using activated biomass of *Chlamydomonas variabilis*, *Anabaena constricta* and *Nitzschia linearis*.

In *Nitzschia* the percentage removals for Cd, Pb and Zn ions were 93.0%, 94.5% and 93.8% respectively. These removals were obtained at 9.3, 9 and 8.6 mg/L for Cd, Pb and Zn ions respectively (Fig. 9). Also the data show percentages adsorption decreased with increase in initial concentrations of the adsorbate which in agreement with **Arıca *et al*., (2005)** when used the *Chlamydomonas reinhardtii* activated with acid for chromium ion biosorption, they found that the biosorption decrease as the initial concentration of chromium ions increased.

Barange *et al*., (2014) recorded that maximum biosorption of Pb with green algal species corresponding to contact time was 131.6 mg/g (3 h) and minimum was 28.72 mg/g (3 h), while maximum for Zn was 43.43 mg/g (1 h) and minimum was 1.37 mg/g (0.3 h).

2. Application of biosorption isotherms for different biomasses of isolated algae

The experimental data of Cd, Pb, and Zn for different biomasses of the three isolated algae could better be described by the two isotherms where R^2 is more than 0.9.

Concerning the sun dried biomass, in *Chlamydomonas* the Langmuir maximum sorption capacity of algal biomass (q_{max}) was found to be 31.25 mg/g for Cd, 24.15 mg/g for Pb and 24.4 mg/g for Zn, and Freundlich constants (K_f) were found to be 8.24 for Cd, 7.03 for Pb and 10.11 for Zn. **Tüzün *et al*., (2005)** reported that the (q_{max}) for removal of Cd using *Chlamydomonas reinhardtii* was 42.7 mg/g at pH 6 and equilibrium time 1h. The (q_{max}) for *Anabaena* was found to be 34.7 mg/g for Cd, 14.9 mg/g for Pb and 31 mg/g for Zn, and Freundlich constants (K_f) were found to be 6.15 for Cd, 5.57 for Pb and 7.29 for Zn. In *Nitzschia* it was found that (q_{max}) 20.8 mg/g for Cd, 74.6 mg/g for Pb and 25.6 mg/g for Zn and Freundlich constants (**K_f**) were found to be 7.1 for Cd, 4.2 for Pb and 5.7 for Zn (Table 1).

Table (1) Isotherm model parameters for sun dried algal biomass of *Chlamydomonas variabilis, Anabaena constricta* and *Nitzschia linearis*

Algal isolates	*Chlamydomonas variabilis*			*Anabaena constricta*			*Nitzschia linearis*		
Langmuir constants	**Cd**	**Pb**	**Zn**	**Cd**	**Pb**	**Zn**	**Cd**	**Pb**	**Zn**
$1/q_{max}$ (g/mg)	0.032	0.0414	0.041	0.028	0.067	0.0323	0.048	0.0134	0.039
q_{max} (mg / g)	31.25	24.15	24.4	34.7	14.9	31	20.8	74.6	25.6
$1/ bq_{max}$	0.086	0.117	0.076	0.132	0.116	0.095	0.085	0.227	0.141
1/b	2.68	2.82	1.85	4.58	1.73	2.9	1.7	16.9	3.6
b l/mg	0.37	0.354	0.54	0.218	0.577	0.34	0.56	0.059	0.27
R^2	0.949	0.988	0.971	0.990	0.969	0.978	0.995	0.927	0.915
Freundlich constants									
K_f	8.24	7.03	10.11	6.15	5.57	7.29	7.1	4.2	5.7
N	1.9	2.525	2.81	1.48	2.4	1.62	2.38	1.13	1.72
R^2	0.994	0.984	0.981	0.984	0.961	0.985	0.942	0.998	0.992

For oven dried biomass, the Langmuir maximum sorption capacity (q_{max}) of *Chlamydomonas* was found to be 27.7 mg/g for Cd, 25 mg/g for Pb and 24.4 mg/g for Zn, while (K_f) was found to be 9.66 for Cd, 8.37 for Pb and 5.99 mg/g for Zn. In *Anabaena* (q_{max}) of algal biomass was found to be 38.4 mg/g for Cd, 15.4 mg/g for Pb and 29.4 mg/g for Zn whereas the (K_f) was found to be 11.64 for Cd, 5.5 for Pb and 8.61 mg/g for Zn. In *Nitzschia* (q_{max}) of algal biomass was found to be 20.8 mg/g for Cd, 50 mg/g for Pb and 18.8 mg/g for Zn, where (K_f) was found to be 7.1 for Cd, 10.4 for Pb and 6.6 mg/g for Zn (Table 2). **Matei *et al*., (2014)** found that the adsorption capacity (q_{max}) of dried biomass of green alga *Spirogyra* sp. with Cd ion was 22.5 mg/g. Also **Kumar *et al*., (2009)** observed that, the adsorption capacity (q_{max}) of the oven dried biomass of green algae, for Pb biosorbtion were 31.2, 29.4, 37.0 and 21.2 mg/g respectively. **Arıca *et al*., (2005)** investigated the biosorption of Cr (VI) by heat treated *Chlamydomonas reinhardtii*. They found that (q_{max}) equal to 30.2 mg/g. **Aksu and Dönmez (2006),** used dried *Chlorella vulgaris* to achieve Cd removal as they found (q_{max}) equal to 86 mg/g at pH 4 in 24h, while **Ferreira *et al*., (2011),** used it to remove Pb and Zn and the (q_{max}) equal 131.4 and 43.3 mg/g respectively. **Gaur and Dhankhar (2009)**, when examined the removal of Zn ions from aqueous solution using oven dried biomass of *Anabaena variabilis*, they found that (q_{max}) was 44.4 mg/g. Also **Abdel-Aty *et al.*, (2013)** found that, by using *Anabaena sphaerica* biomass (K_f) were 15.3 for Cd and 28.28 for Pb. Similarly, **Duygu and Bikem (2013)** demonstrated that the oven dried biomass of *Nitzschia closterium* offers interesting possibility as a cation biosorbent with equilibrium sorption capacity (q_{max} = 81.45, 81.73, 86.04, 87.94, 116.72 and 130.08 mg/g for Fe^{3+}, Cr^{6+}, Zn^{2+}, Ni^{2+}, Cd^{2+} and Pb^{2+}, respectively) and removal efficiency (28.2, 23.3, 16.9, 15.8, 16.6, 16.2%, respectively).

Table (2) Isotherm model parameters for oven dried algal biomass of *Chlamydomonas variabilis, Anabaena constricta* and *Nitzschia linearis*

Algal isolates	***Chlamydomonas variabilis***			***Anabaena constricta***			***Nitzschia linearis***		
Langmuir constants	**Cd**	**Pb**	**Zn**	**Cd**	**Pb**	**Zn**	**Cd**	**Pb**	**Zn**
$1/q_{max}$ (g/mg)	0.036	0.040	0.041	0.026	0.65	0.034	0.048	0.02	0.053
q_{max} (mg / g)	27.7	25	24.4	38.4	15.4	29.4	20.8	50	18.8
$1/ bq_{max}$	0.207	0.106	0.076	0.053	0.110	0.071	0.085	0.072	0.087
1/b	5.75	2.65	1.85	2.04	1.7	2.08	1.77	3.6	1.64
b l/mg	0.173	0.377	0.540	0.5	0.6	0.48	0.56	0.27	0.61
R^2	0.918	0.987	0.980	0.924	0.972	0.974	0.996	0.852	0.999
Freundlich constants									
$\mathbf{K_f}$	9.66	8.37	5.99	11.64	5.5	8.61	7.1	10.4	6.6
N	2.14	1.74	4.29	1.55	2.3	1.77	2.4	1.33	2.16
$\mathbf{R^2}$	0.987	0.973	0.970	0.984	0.964	0.989	0.947	0.995	0.961

Regarding the activated biomass (Table 3), In *Chlamydomonas* (q_{max}) was found to be 38.5 mg/g for Cd, 33.3 mg/g for Pb, and 17.5 mg/g for Zn whereas (K_f) and (n) were found to be 9.1 and 1.51 for Cd, 6.45 and 1.45 for Pb; and 5.41 and 2.1 for Zn respectively. In *Anabaena* (q_{max}) was found to be 32.2 mg/g for Cd, 14.9 mg/g for Pb and 15.6 mg/g for Zn, while (K_f) was found to be 6.5 for Cd, 6.33 for Pb and 5.0 for Zn. In *Nitzschia* (q_{max}) was found to be 33.3 mg/g for Cd, 28.6 mg/g for Pb and 25.6 mg/g for Zn and (K_f) 8.7 mg/g for Cd, 6.12 mg/g for Pb and 5.7 mg/g for Zn. **Arıca *et al.*, (2005)** found that (q_{max}) and

(n) were 25.6 mg/g and 2.18 respectively for *Chlamydomonas reinhardtii* activated by acid.

Table (3) Isotherm model parameters for activated algal biomass of *Chlamydomonas variabilis, Anabaena constricta* and *Nitzschia linearis*

Algal isolates	***Chlamydomonas variabilis***			***Anabaena constricta***			***Nitzschia linearis***		
Langmuir constants	**Cd**	**Pb**	**Zn**	**Cd**	**Pb**	**Zn**	**Cd**	**Pb**	**Zn**
1/q_{max} (g/mg)	0.026	0.03	0.057	0.031	0.067	0.064	0.030	0.035	0.039
q_{max} (mg / g)	38.5	33.3	17.5	32.2	14.9	15.6	33.3	28.6	25.6
1/ bq_{max}	0.077	0.120	0.140	0.127	0.09	0.185	0.172	0.135	0.141
1/b	2.96	4	2.45	4.1	1.3	2.9	5.7	3.8	3.6
b l/mg	0.337	0.250	0.407	0.24	0.74	0.34	1.74	2.6	0.27
R^2	0.944	0.955	0.922	0.944	0.988	0.910	0.918	0.905	0.915
Freundlich constants									
K_f	9.1	6.45	5.41	6.5	6.33	5.0	8.7	6.12	5.7
N	1.51	1.45	2.1	1.7	3.2	2.7	1.52	1.73	1.72
R^2	0.994	0.994	0.971	0.966	0.961	0.970	0.988	0.986	0.992

C) Metal recovery

Regarding sun dried biomasses of algae species**,** it was found that the percentages recovery by *Chlamydomonas* were at the first run Zn (85.8%) = Pb (85.8%) > Cd (83.3%) but at the second run decrease to Cd (43.5%) > Zn (41.8%) > Pb (40%). In *Anabaena* the percentages of recovery were Cd (52.6%) > Pb (40 %) > Zn (39.42%) and at the second run the percentages were Cd (53.7%) > Zn (45.8 %) >Pb (38.4%). In *Nitzschia* according to the percentages recovery at the heavy metal can arranged in descending manner at first run as Cd (54.1%) > Pb (45.3%) > Zn (44.4%) but at the second run the order was Pb (54.5 %) > Zn (50.9%) > Cd (48.8%).

In oven dried biomasses, the percentages recovery by *Chlamydomonas* biomass at the first run were Zn (88.4%) > Cd (87.3%) > Pb (84.3%) and at the second run decreased to be Cd (43.9%) > Zn (42.8%) > Pb (41.5%). In *Anabaena* the percentages of recovery at the first run were Zn (51.9%) > Cd (46.3%) >Pb (43.3%) and decreased at the second run to be Zn (50.7%) > Cd (49.09%) > Pb

(40%). The three metals can be arranged according to percentages recovery in *Nitzschia* at the first run as Cd (56.3%) >Pb (46%) > Zn (44.8%) and at the second run the order was Pb (63.7%) > Zn (61.9%) > Cd (50.7%).

In case of activated biomasses, the percentages of recovery in *Chlamydomonas* at the first run were arranged as Cd (76.6%) > Zn (69.7%) > Pb (65.4%) and at the second run the order was Zn (44.1%) > Cd (43.6%) >Pb (40.8%). Regarding the percentages of recovery in *A. constricta* while the percentages of recovery were arranged as Cd (58.6%) > Zn (47.03%) > Pb (46.2%) at the first run and Zn (56.7%) >Pb (56.6%) > Cd (52.9%) at the second run. Similarly in *Nitzschia linearis* the percentages of recovery were Cd (57.8%) > Pb (46.1%) > Zn (44.8%) at the first run and Cd (69.3%) >Pb (52%) > Zn (47.3%) at the second run. **Gupta and Rastogi (2009)**, found that acid-treated green alga *Oedogonium hatei* could be regenerated from metal, with up to 75% recovery. **Deng *et al*., (2007)** investigate the desorption of lead from waste water by green algae *Cladophora fascicularis*, they found that recovery with 0.1 mol/L HNO_3 was 85%. **Gupta and Rastogi (2009)**, found that acid-treated green alga *Oedogonium hatei* could be regenerated from metal, with up to 75% recovery.

By comparing the efficiency of the different biosorbents for metal removal and recovery experiments, it is evident from data predicted that: no clear differences between sun dried, oven dried, and activated biosorbents (Table 4, 5).

Conclusion

The results of this investigation conclude that, there are no clear variations in biosorption of cadmium, lead and zinc by *C. variabilis*, *A. constricta* and *N. linearis;* also there are obvious similarities between sun dried, oven dried and activated biosorbents of different algal isolates in metal removal. Subsequently, it was recommended using sun dried algae as low cost biosorbent for metals removal.

Table (4) Comparison between the efficiency of metal removal by sun dried, oven dried and activated for different algal biosorbents

Algal biosorbents	Sun dried			Oven dried			Activated		
	Cd	**Pb**	**Zn**	**Cd**	**Pb**	**Zn**	**Cd**	**Pb**	**Zn**
Chlamydomonas variabilis	98.6	95.8	96.8	97.9	96.1	96.1	96.3	94.2	94.1
Anabaena constricta	95.1	93.7	93.1	97.5	94.1	96.7	94.3	96.1	94.1
Nitzschia linearis	92.0	89.6	88.3	95.5	96.6	94.8	93.0	94.5	93.8

Table (5) Comparison between the efficiency of metal recovery by sun, oven dried and activated biomass of different algal biosorbents

Algal biosorbents	Sun dried						Oven dried						Activated					
	Cd		**Pb**		**Zn**		**Cd**		**Pb**		**Zn**		**Cd**		**Pb**		**Zn**	
	Run1	**Run2**	**Run1**	**Run2**	**Run1**	**Run2**	**Run1**	**Run2**	**Run1**	**Run2**	**Run1**	**Run2**	**Run1**	**Run2**	**Run1**	**Run2**	**Run1**	**Run2**
Chlamydomonas variabilis	83.3	43.5	85.8	40	85.8	41.8	87.3	43.9	84.3	41.5	88.4	42.8	76.6	43.6	65.4	40.8	69.7	44.1
Anabaena constricta	52.6	53.7	40	38.4	39.42	45.8	46.3	49.09	43.5	40	51.9	50.7	58.6	52.9	46.2	56.6	47.03	56.7
Nitzschia linearis	54.1	48.8	45.3	54.5	44.4	50.90	56.3	50.7	46	63.7	44.8	61.9	57.8	69.3	46.1	52	44.8	47.3

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دراسة مقارنة عن الادمصاص الحيوي والامتزاز لثلاث معادن ثقيلة سامة منتخبة باستخدام بعض أنواع من الطحالب الدقيقة

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ظهرت عملية الادمصاص الحيوي بوصفها تكنولوجيا بديلة قليلة التكلفة وفاعلة لإزالة المعادن الثقيلة التي تؤدى إلى الآثار الصحية الضارة على البشر والكائنات الحية. في الدراسة الحالية تم تقييم عملية الادمصاص الحيوي والامتزاز للكادميوم والرصاص والزنك من قبل أنواع من الطحالب المعزولة كطحلب *Chlamydomonas variabilis* وطحلب *Anabaena constricta* وطحلب *Nitzschia linearis* . تم عزل أنواع الطحالب وزراعتها على نطاق واسع للحصول على كمية كثيفة من الكتلة الحيوية كافية لإجراء التجارب على إزالة هذه المعادن. تم مطابقة نتائج تجارب الادمصاص والامتزاز على نموذجى Langmuir و Freundlich . أظهرت النتائج المتحصل عليها من اختبارات FTIR ، TEM و EDX أن أيونات المعادن يمكن أن ترتبط بالمجموعات الأيونية على الطحالب بقوة الجذب الكهربائي كما أن القدرة على الادمصاص قد ترجع إلى وجود نوع أوعدد من المجموعات الوظيفية الموجودة على سطح الكتلة الحيوية للطحالب. كانت الكفاءة القصوى لإزالة كلا من الكادميوم والرصاص والزنك باستخدام طحلب *C. variabilis* 97.9٪، 96.1٪ و 96.1٪ للكتلة الحيوية المجففة بالفرن و96.3٪، 94.2٪ و 94.1٪ للكتلة الحيوية المنشطة. أما بالنسبة للكتلة الحيوية المجففة بالفرن والمنشطة لطحلب *A. constricta* فكان الحد الأقصى لإزالة تلك المعادن الثقيلة 95.1٪، 93.7٪، 93.1٪ و 94.3٪ ، 96.1٪ ، 94.1٪. وأيضا كانت أفضل إزالة لتلك المعادن في طحلب *N. linearis* بنسبة 95.5 ٪، 96.6٪،

94.8٪ للكتلة الحيوية المجففة بالفرن و 93٪، 94.5٪ ، 93.8٪ للكتلة الحيوية المنشطة على التوالي. أثبتت النتائج أنه لا توجد اختلافات جوهرية لادمصاص الكادميوم والرصاص والزنك باستخدام الكتلة المجففة بحرارة الشمس أو المجففة بالفرن أو الكتلة الحيوية المنشطة لجميع أنواع الطحالب المستخدمة فى الدراسة لذا يفضل استخدام الكتلة المجففة بحرارة الشمس لانخفاض تكلفتها فى عملية إزالة المعادن.