



Bioremediation of Fe, Zn and Cd ions from aqueous solution using died cells of cyanobacterial mats from extreme habitat, Siwa Oasis, Egypt.

Mohamed H. H. Ali¹; Mohamed S. Abd Elkarim¹; Samia A. Haroun² and
Khadija M. Attwa¹

1- National Institute of Oceanography & Fisheries, Cairo, Egypt.

2- Botany Department, Faculty of Science, El-Mansoura University. Egypt.

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ABSTRACT

The ability of microbial cyanobacterial mats naturally grown in the extreme habitat in western desert, for removing heavy metals from its aqueous solution were studied. SEM, EDX, FTIR and surface area examinations of well fine dry dead cell of two different mats were carried out to demonstrate the physical characterizations of the biosorbent surface. The results showed that the mats characterized by high surface area, porous diameter and cracks. The dry dead cells of two mats were used to remove Zn^{+2} , Fe^{+2} and Cd^{+2} ions from its aqueous solution under specific conditions; different pH, biosorbent dosage, contacts time and initial metals concentrations. The optimum removal efficiency of metals reached at pH = 6, 150 min contact time and 2.5 g/L biosorbent dose. Isotherms studies showed that Langmuir and Freundlich adsorption isotherm models were well fitted for the adsorption process. The removal of studied metals ions following the order of $Zn^{2+} > Fe^{2+} > Cd^{2+}$ according to values of maximum biosorption capacities (q_{max}), Langmuir constant (b), separation factor (R_L) and Freundlich intensity parameter (1/n).

INTRODUCTION

Nowadays, protection of our Environment becomes an important issue to ensure function and balance ecosystem. Several kinds of environmental pollutants influenced a serious level deterioration of ecosystem components. Trace elements especially which have toxic effects still exist in the ecosystem and inevitably appear at wide concentrations ranges. These metals tended to accumulate and its excess concentration results an environmental contamination problems (Emenike *et al*, 2018). The increasing of the anthropogenic activities leads to consequence release of these metals to the surrounding environment. In addition to, heavy industries have rapid expansion (metallurgy, mining, energy and fuel producing, finishing, painting, electroplating, etc.), wastewaters flowing into surface waters lead to severe environmental pollution then human life was threaten (Ali *et al.*, 2007). Some trace elements such as As, Cd, Pb, Hg, Cr and Ni, etc. are present in industrial wastes which have serious triggers in the aquatic ecosystem due to their toxicity, bioaccumulation, non-biodegradation nature and the long half-lives for their removal from the tissues (Gupta *et al.*, 2016).

Bioremediation considered as promising pathway to remove different pollutants from the aquatic environment. Plants play a significant role in concentrate some compounds and elements from surrounding environment and simultaneously induce molecular metabolism in their tissues (Garbisu and Alkorta 2003). This process includes usage of higher plants or different microorganisms (e.g. microbial mats) to treat either organic pollution which have break down difficulty (xenobiotics) or to remove toxic trace elements (Cunningham *et al.*, 1995; Davis *et al.*, 2003). Also, bioremediation considered as a simple procedure carried out with normal actions and without needs to major disruption or threats to human and ecosystem during transportation. In addition to, bioremediation own the lowest effluent than other used technologies for removal of dangerous waste (Gupta *et al.*, 2016; Fawzy, and Mohamed, 2017).

Several species of cyanobacteria such as *Aphanocapsa*, *Phormidium*, *Westiellopsis* and *Oscillatoria* showed high effectiveness adsorption capacity for removing toxic metal ions from wastewaters (Anjana *et al.* 2007; Boominathan, 2000; Blier, *et al.*, 1995; Cain *et al.*, 2008; Vijayakumar, 2005).

The main objectives of this work were to determine the metal removing efficiency from aqueous solution using two different microbial mats, also to describe its metal biosorption isotherm models through exploring different factors affecting bioremediation process i.e. pH, contact duration time, and adsorbent dosage.

MATERIALS AND METHODS

Collection of samples

Considerable amount of two cyanobacterial mats samples were collected from Zeiton Lake (biosorbent 1) and fresh water cold spring (biosorbent 2) located in Siwa City during summer 2018, the collected samples were kept in a clean dry polyethylene bags till reach to laboratory. The samples were washed very well several times with deionized water. Then the microbial biomass was dried at 105°C for 48 h, ground in an electric mill and passed through a 63 µm sieve.

Characterizations

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) observations were performed on a JEM-2100 (JEOL, Tokyo Japan) at an acceleration voltage of 200 kV. The Fourier transform infrared (FTIR) spectra were acquired using a spectrum spectrometer (6700FTIR, Nicolet, America). Samples were grounded with KBr (1:100) and confined into the sample's holder to record the measurements within the range of 4000–400 cm⁻¹. BET (Brunauer–Emmett–Teller) method was used for samples' surface area determination from nitrogen adsorption–desorption isotherms at liquid nitrogen temperature using a Coulter SA3100 instrument with outgas 15 min at 150 °C. (Brunauer *et al.*, 1938), the pore size distribution (pore diameter, pore volume and micropore surface area of the samples) was determined by the Barrett–Joyner–Halenda (BJH) method (Barrett *et al.*, 1951).

Biosorption study

Different serial standard solutions of Iron, zinc and cadmium were prepared from stock solution (1000mg/L) of each metal. The adsorption of different metals onto two microbial mats adsorbents were studied by adsorption batch method as a function of pH, duration times, adsorbent dose and initial metal concentration. The microbial mat was first placed in a 250-ml Erlenmeyer flask, and then 50 ml of a standard heavy metal solution was added to the flask. The mixtures were stirred

continuously for 2 hr, and then the samples were centrifuged for 5 minutes at 5000 rpm and the supernatant of each sample was analyzed using GBC atomic Absorption Spectroscopy; Australia. The adsorption capacity of heavy metal ions by different microbial mats could be expressed as follows (Horsfall *et al.*, 2006; Zulkali *et al.* 2006).

$$q_e = \frac{(C_0 - C_e) \times V}{M}$$

$$R \% = \frac{(C_0 - C_e) \times 100}{C_0}$$

Where; C_0 is the initial metal ions concentration, C_e is the concentration of metal ions in solution (mg/L) at equilibrium, C_t is the concentration of metal ions in solution (mg/L) at time, t in solution, V is volume of initial metal ions solution used (L) and M is mass of adsorbent used (g).

RESULTS AND DISCUSSION

SEM and EDX

The morphology and EDX spectra showed high similarity degree for the different two biosorbents as shown in Figure (1a & b) where the SEM micrographs at high magnification power showed highly porous surface, deep grooves and cracks structure for each biosorbent samples. EDX spectra showed slight variation between the two used mats consortia, the major elements are; C, O, K, Mg, Na, Al, Si, S, Cl, N in biosorbent 1, while in biosorbent 2 are; C, K, O, Mg, Al, Si, Ca, S within energy range of 0 – 9 keV (Figure 1a & b). Appearance of Na and Cl in first sample in low density (2.34 and 3.54 % respectively) indicated their interference with other phases (Shaltout *et al.*, 2017). Moreover, the low intensities of S-K α and Al-K α (0.79, 0.74, 0.25 and 0.12 % in both two samples respectively) reveal presence of S and Al in traces into biosorbent cells. On the other hand, the high intensity of O and K with a considerable Si and Ca percentages found in the two biosorbents indicate presence of silicates and calcite. Furthermore, the considerable content of C (16.52 and 19.71 % in both biosorbent respectively) indicate existence of organic matter with a considerable amount (Mafra *et al.*, 2013).

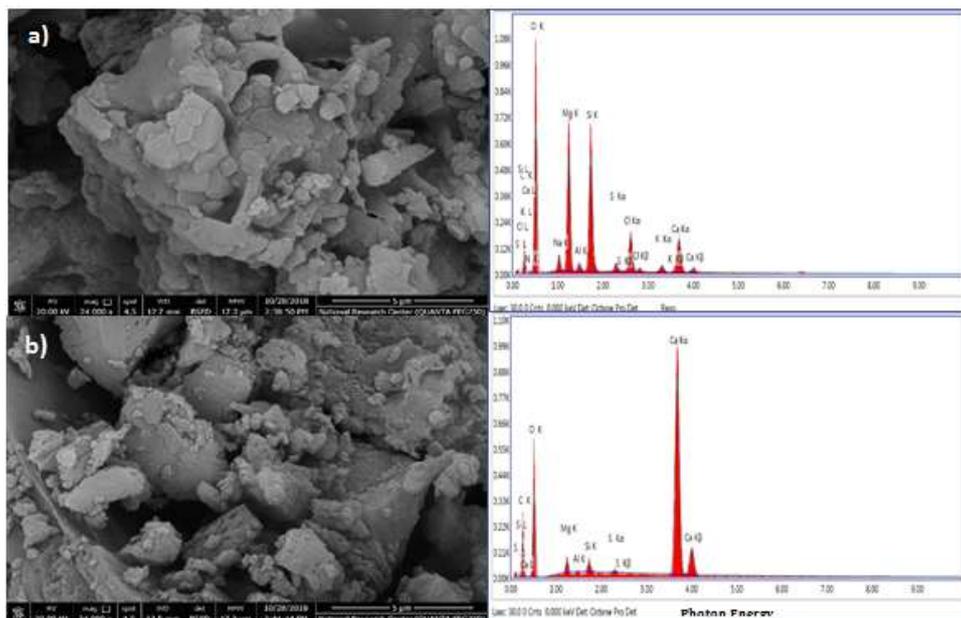


Fig.1: Scanning electron microscope (SEM) and related X-Ray spectra (EDX); a) biosorbent 1 and b) biosorbent 2 samples collected from Siwa Oasis

FTIR

FTIR spectrum have been widely used to determine the functional groups which were responsible for metals uptake, FTIR spectrum curve of both two microbial biosorbents before and after metal adsorption were recorded in the range of 4000-400 cm^{-1} . FTIR spectrum of two microbial biosorbents showed slight variation in the range of 4000 – 1750 cm^{-1} while a remarkable variation could be observed in the range of 1750 – 400 cm^{-1} (Fig. 2a &b). The spectra of FTIR showed several peaks; a broad peak at 3431 and 3433 cm^{-1} for biosorbent 1 and biosorbent 2 respectively, which indicate to the O-H stretching mode of hydroxyl group characterize hemicellulose, cellulose, pectin, and lignin components (Mandina *et al.*, 2013). Another highly intensive band appeared at 2925 and 2926 cm^{-1} for two used biosorbents, respectively which is corresponding to -C-H and =C-H stretch vibration of methyl and methylene groups. An observed peak appeared at 1630 and 1631 cm^{-1} for two biosorbents corresponding to C=C stretching that can be attributed to the aromatic C-C bond and may be indicate asymmetric and symmetric vibration of C=O amide group. Weak peaks appeared between 1400 and 1200 cm^{-1} for two biosorbents may be resulting from the symmetric stretching of -COO- of pectin, while peaks at 1024 and 1022 cm^{-1} attributed to stretching vibration of C-OH groups of alcohols and carboxylic acids (Liang *et al.*, 2009). After the biosorption process the spectrum of FTIR spectra showed some differences in the position of the absorbance peaks appeared (red lines in Fig 2a & b). Slight shifting of the stretching vibration from 3433 and 3431 cm^{-1} to 3445 and 3447 cm^{-1} for two biosorbents respectively after the biosorption of studied metals postulating that a chemical reaction was occurred between the ions of metal and the OH groups on the biosorbents' surface (Figure 2a &b).

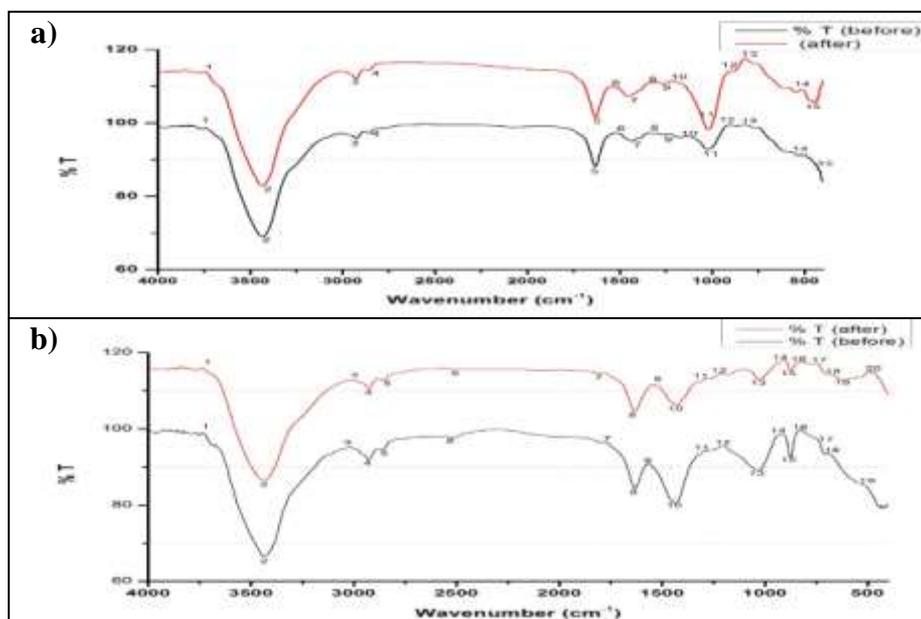


Fig. 2. FTIR spectrum for; a) biosorbent 1 and b) biosorbent 2 samples collected from Siwa Oasis before and after adsorption process.

Surface Area

It is notable that, biosorbent 1 has a lower surface area, micropore volume and micropore area in comparison with the corresponding results of biosorbent 2 (Table 1).

Table 1: The specific surface area, radius and pore volume of microbial biosorbents.

Samples	S_{BET} ($m^2 g^{-1}$)	r (nm)	V_p^{total} ($cm^3 g^{-1}$)
Biosorbent 1	1.28	356	0.114
Biosorbent 2	2.54	198	0.125

Batch biosorption experiments

Effect of pH:

The pH considered as a key factor in adsorption of heavy metals onto the surface of different biosorbents whereas pH of a solution impacts the functional groups protonation on the biosorbent surfaces as well as affects behavior of metal chemistry (Rafique and Nazir, 2013). Figure 3 demonstrates the removal efficiency of Zn^{+2} , Fe^{+2} and Cd^{+2} at different pH values range (3- 9) applying a precise condition (30 mg/l initial metal concentration, 2.5 g/L biosorbent dose and 150 min duration time).

Both the microbial mats have great adsorption efficiency achieving at least 85 % and sometimes reached to 100 %. In addition, there is slight narrow difference of removal percentage between two used biosorbents. Furthermore, the removal of zinc ions attained the highest removal percent more than other two ions in both two biosorbents with insignificant pH effect (Figure 3a& b).

Removal ratio of Cd^{+2} and Fe^{+2} ions increased gradually reaching maximum of 90 and 89% with increase pH values on the surface of microbial biosorbent 1 and 88 and 91% for biosorbent 2 at pH = 6 (Fig 3a &b). Annadurai *et al* (2003) reported that the maximum adsorption ratio occurs at pH ranged between 6–8 for banana and orange peels. But at low pH (< 2), adsorption decreases which may be attributed to the competition of high H^+ content in the solution with metal ions on the binding sites of biosorbent surface making difficulty of metals' sorption (Hema and Srinivasan, 2010). Edris *et al.* (2012) indicated that lead and cadmium maintained highest removal biosorption using *C. vulgairs* at pH value around 7.

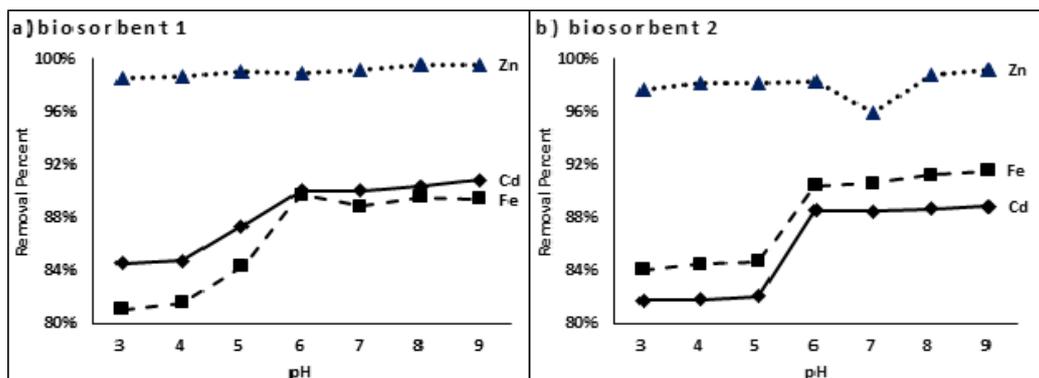


Fig. 3: Effect of pH on the biosorption of Zn^{+2} , Fe^{+2} and Cd^{+2}

Effect of retention time

Fig. 4 (a&b) shows the impacts of retention time (15 – 150 min) on adsorption efficiency of the studied metal ions using 2.5 g/L of each of the two microbial biosorbents. In general, the results revealed that the adsorption efficiency of studied metals increased with increasing duration time (Goher *et al.*, 2016). High removal efficiency was observed for Zn^{+2} ions reached up to 99 % in both two biosorbents after 150 min and the rate of reaction still at steady state. Furthermore, the removal percentage of Fe^{+2} and Cd^{+2} have lower values in comparison with Zn^{+2} reached to 89

and 88% for biosorbent 1 and 92 and 85 % for biosorbent 2 after 150 min, respectively. Lo *et al* (2012) reported that the removal efficiency of Pb^{2+} was 71.6 and 86.4% after 120 min using Ma bamboo activated carbon reached to 98.8–99.9% and 100% after 24 h soaking (Figs. 4a&b).

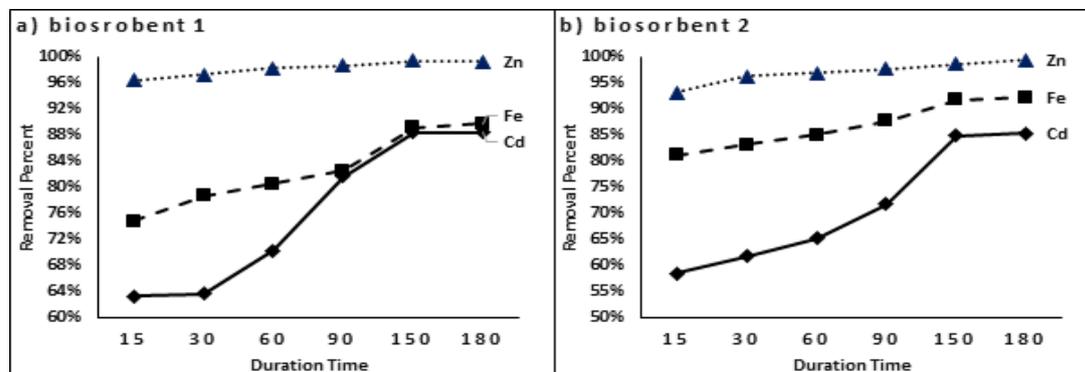


Fig. 4: Effect of contact time on the biosorption of Zn^{+2} , Fe^{+2} and Cd^{+2} .

Effect of biosorbent Dosage:

Biosorbent dose is considered as one of the most parameter that has strong effect on the adsorption capacity (Moghadam *et al.*, 2013). Different biosorbent doses (0.25, 0.5, 1, 1.5, 2, 2.5 and 3 g/L) were used for both microbial biosorbents to determine the biosorption efficiency on removal of studied metal ions. Notable increasing of biosorption capacity were observed by increasing the biosorbent dose due to the greater availability of the surficial exchange sites on both biosorbent.

The removal percentage of Zn^{+2} still attained maximum values reached 99.8 % and 99.6 % of each two biosorbents with insignificant variation by differing either dose or biosorbent. On the other hand, removal efficiency of Fe^{+2} and Cd^{+2} exhibited considerable variation with increasing of biosorbent dosage at 2.5 g/L with maximum removal percent of 90, 84 % and 92, 81 % for biosorbent 1 and 2 respectively. Ali and Abdel-Satar (2017) indicated that 2 g/L was an optimum adsorbent dosage of orange peel activated carbon for removing Cd^{+2} from its aqueous solution . (Figs. 5a&b).

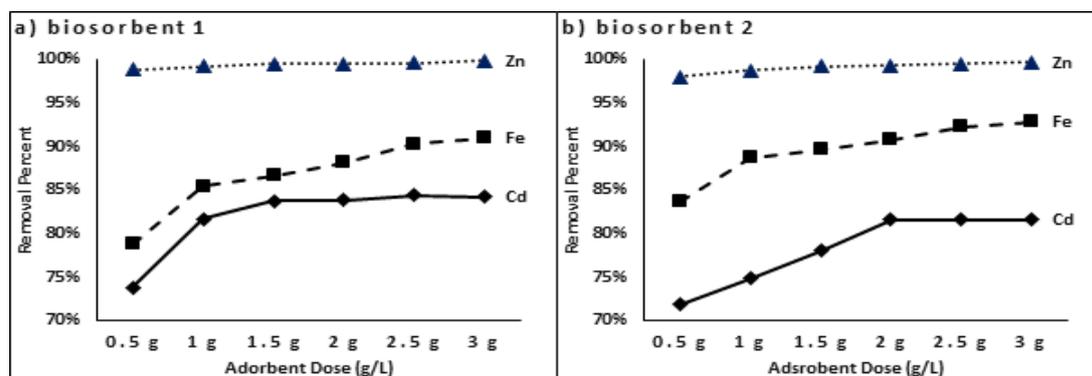


Fig. 5: Effect of biosorbent dose on the biosorption of Zn^{+2} , Fe^{+2} and Cd^{+2} .

Effect of Initial metal Concentration

The effect of initial metal concentration (5, 10, 15, 20 and 25 mg/l) on the removal capacity at biosorbent dose of 2.5 g/L, duration time of 150 min was studied

for both two microbial biosorbents (Figs. 6a & b). The results showed a gradual decrease in removal percentage by increasing the metal's concentration which explained on basis of at low metals' concentrations, metals tend to be adsorbed to specific sites onto biosorbent surface, while with the increase of metals' concentration, the specific sites are saturated and the exchange sites were occupied and equilibrium was attained (Moghadam *et al.*, 2013).

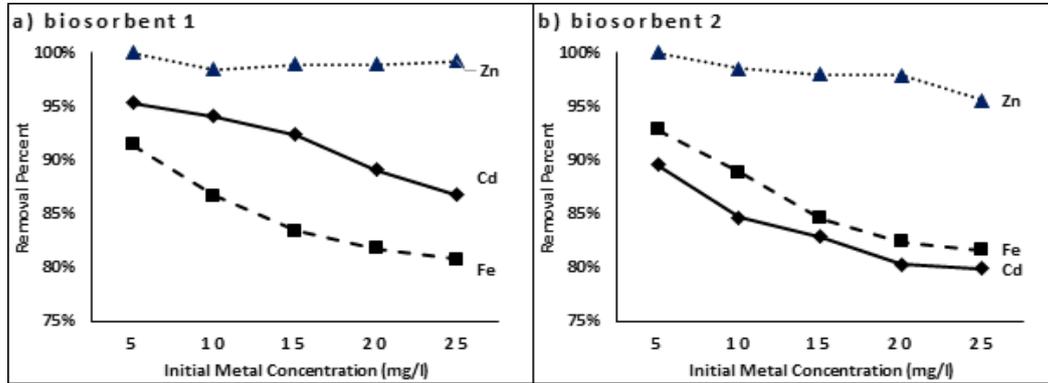


Fig. 6: Effect of initial metal concentration on the biosorption of Zn^{+2} , Fe^{+2} and Cd^{+2} .

Adsorption isotherms

The biosorption equilibrium of Zn, Fe and Cd ions were studied at different metals' concentrations ranging from 5 to 25 mg/l and 2.5 g/L for biosorbents. Different isotherms i.e. Langmuir and Freundlich isotherms usually describe the adsorption process which is functions between the amount of adsorbate on the adsorbent (Moreno-Piraján and Giraldo, 2012). Both Langmuir and Freundlich constants and isotherms graphs were showed in Table 2 and Figures 7 and 8.

Langmuir isotherm was used in many monolayer biosorption processes (Moghadam *et al.*, 2013), is given by the equation:

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

While, the linear form of isotherm equation is:

$$1/q_e = 1/q_{max} + (1)/(b q_{max}) (1)/C_e$$

Where: q_{max} ($mg\ g^{-1}$) maximum sorbate uptake

b ($L\ mg^{-1}$), Langmuir isotherm constant

q_e ($mg\ g^{-1}$), amount of metal adsorbed; and C_e $g\ L^{-1}$ the equilibrium metal ion concentration

Freundlich isotherm model is based on sorption of heterogeneous energetic active sites distribution accompanied by interactions between adsorbed molecules. The model is described by the following equation

$$q_e = K_f C_e^{1/n}$$

The linear logarithmic form for the Freundlich equation gives a linear plot with relation between $\log q_e$ versus $\log C_e$:

$$\log q_e = \log K_f + 1/n \log C_e$$

Where: q_e is the amount of metal adsorbed by biosorbent (mg/g), C_e is the equilibrium adsorbate concentration in mg/L , K_f is the adsorbent capacity and n

is the adsorption intensity determined from the linear plot.

The obtained results showed high R^2 values (> 0.9 in most cases) indicate that biosorption of the studied metals ions obeyed Langmuir and Freundlich isotherm models. Furthermore, it was clearly observed that the biosorbent biosorbent 2 showed

high q_{\max} and R^2 values than microbial biosorbent 1 (Table 2; Fig. 7), so Langmuir model provides a better fit in biosorbent 2 than biosorbent 1. The values of b , which indicate the metals affinity to the surface of the biosorbent, revealed that the sorbent had higher affinity with the metal in the order $Zn^{2+} > Fe^{2+} > Cd^{2+}$. In addition, the prediction of the affinity between the sorbate and sorbent could be used as essential features of Langmuir adsorption isotherm using a dimensionless constant (R_L) which called separation factor or equilibrium parameter (Malik, 2004). R_L factor expressed by the following relationship.

$$R_L = \frac{1}{1 + bC_i}$$

Where C_i is initial concentration and b is the Langmuir constant. R_L values detected the Langmuir isotherm type, if ($R_L = 0$) irreversible, ($R_L = 1$), linear, ($R_L > 1$), unfavorable or ($0 < R_L < 1$) mean favorable adsorption (McKay *et al.*, 1982). The obtained R_L value in the present study ranged from 0.003 to 0.15 (Table, 2), indicating favorable adsorption of studied metal ions onto both used microbial biosorbents. These data agreement with that obtained Ali *et al* (2016) they obtained R_L value within 0 – 1 for adsorption of Cd, Cu and Pb on dead cells of *C. vulgaris*.

Table 2: Constants of Langmuir and Freundlich isotherm for Zn, Cd and Fe biosorption by different two biosorbents

metal	Langmuir Isotherm								Freundlich Isotherm					
	Biosorbent 1				Biosorbent 2				Biosorbent 1			Biosorbent 2		
	b	q_{\max}	R_L	R^2	b	q_{\max}	R_L	R^2	K_f	n	R^2	K_f	n	R^2
Zn	13.2	4.30	0.003	0.891	2.89	8.84	0.014	0.972	8.99	1.68	0.788	687	0.56	0.930
Cd	0.34	4.25	0.105	0.953	0.772	5.79	0.049	0.999	2.28	1.75	0.973	1.30	1.50	0.996
Fe	0.78	4.20	0.048	0.983	0.57	4.42	0.066	0.981	1.62	1.77	0.997	1.45	1.64	0.998

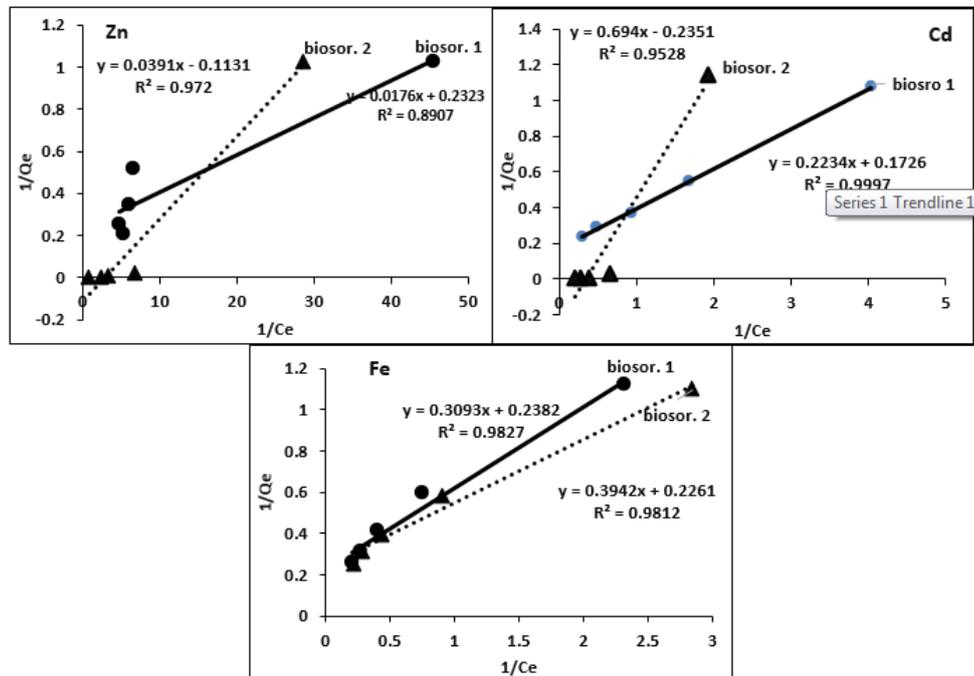


Fig. 7: Langmuir isotherm plot for adsorption of Zinc, Iron and cadmium ions by two different biosorbents.

On the other hand, the experimental equilibrium coefficients data revealed that Freundlich model well fitted to iron ions biosorption on both used biosorbents

microbial mats ($R^2 > 0.99$) and biosorption of Cd on the surface of biosorbent 1 (Table 2 and Fig. 8).

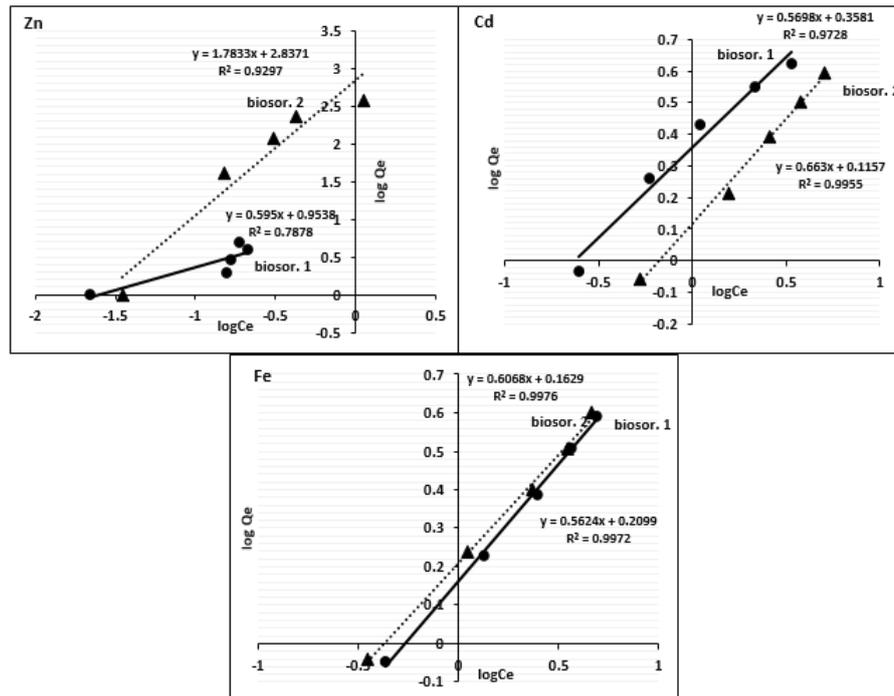


Fig. 8: Freundlich isotherm plot for adsorption of Zinc, Iron and cadmium ions by two different biosorbents.

Intensity parameter of Freundlich ($1/n$) is a function of the adsorption strength in the adsorption process (Voudrias *et al.* 2002), so n value demonstrates the nonlinearity degree between adsorption and the concentration of solution; adsorption is linear in case of $n = 1$, adsorption is a chemical process if $n < 1$ and adsorption is a physical process if $n > 1$ (Desta, 2013). The present study showed that n value almost > 1 (Table 2) which represent good adsorption of studied metals and physical biosorption of metal ions onto the surface of two mats were occurred.

CONCLUSION

Bioremediation process is considered to be a highly simply, safe and obliging technology since it depends on naturally microbes which could be carried out without any normal action disruption or threats to human and environment. In our recent study we use two different microbial mats collected from an extreme habitat in western desert Siwa Oasis, the dry cells of these mats are an environment friendly, low cost, and available in local environment were used as biosorbent for biosorption of Zn^{+2} , Fe^{+2} and Cd^{+2} ions their aqueous solutions. The obtained results proved that these mats have great ability to remove the metals efficiently. the biosorbent, revealed that the studied biosorbents had high removal affinity in the order $Zn^{2+} > Fe^{2+} > Cd^{2+}$. Furthermore, the studies of isotherm equilibrium indicated that both Langmuir and Freundlich models were the highest fitted models for the adsorption process.

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ARABIC SUMMARY

الإزالة الحيوية لأيونات الحديد والزنك والكاديوم من المحاليل المائية باستخدام الخلايا الميتة من تجمعات الطحالب الخضراء المزرقمة النامية في البيئات القاسية، واحة سيوة ، مصر

محمد حمدي حسن علي^١ ، محمد سعد عبد الكريم^١ ، سامية علي هارون^٢ ، خديجة محمد عطوة^١

١- المعهد القومي لعلوم البحار والمصايد - مصر.

٢- قسم النبات - كلية العلوم - جامعة المنصورة - مصر

تمت دراسة قدرة التجمعات الكثيفة من الطحالب الخضراء المزرقمة والتي تنمو بشكل طبيعي في البيئات القاسية في الصحراء الغربية لإزالة أيونات بعض المعادن الثقيلة من محلولها المائي. تم تعيين الخصائص الفيزيائية لنوعين من هذه التجمعات الكثيفة من خلال إجراء بعض القياسات والفحوصات الفيزيائية مثل SEM و EDX و FTIR ومساحة السطح للخلايا الميتة الجافة. وأظهرت النتائج أن هذه التجمعات من الطحالب تتميز بمساحة سطح كبيرة وذات مسام وشقوق على السطح الخارجي لها. تم استخدام الخلايا الميتة الجافة من تجمعات الطحالب الخضراء المزرقمة في إزالة أيونات Zn^{+2} و Fe^{+2} و Cd^{+2} من محلولها المائي تحت ظروف محددة مثل اختلاف قيم الأس الهيدروجيني، اختلاف جرعات المادة الممتزة (biosorbent)، اختلاف أوقات التلامس والتركيزات الأولية للمعادن. تم الوصول إلى أعلى كفاءة لإزالة أيونات المعادن عند الظروف المثلى (قيمة الأس الهيدروجيني = 6 و 150 دقيقة من وقت التلامس و 2.5 جم/لتر من المادة الممتزة الحيوية). وأظهرت دراسات الامتصاص لنماذج لانجمير وفريندليش تطابقها بشكل كبير لعملية الامتزاز. وطبقاً لقيم السعة القصوى للإمتصاص (q_{max})، ثابت لانجمير (b) ، عامل الفصل (R_L) ومعامل الشدة لفريندليش ($1/n$) فإن إزالة أيونات المعادن التي تم دراستها كانت مرتبة كالتالي: الزنك < الحديد < الكاديوم.