

## ***Sargassum latifolium* as eco-friendly materials for treatment of toxic nickel (II) and lead (II) ions from aqueous solution**

**Ahmed E. Al prol\*, Mohamed E. A. El-Metwally and Adel Amer**

National Institute of Oceanography and Fisheries, Egypt

\* Corresponding author : [ah831992@gmail.com](mailto:ah831992@gmail.com)

### **ARTICLE INFO**

#### **Article History:**

Received: Oct. 28, 2019

Accepted: Nov. 29, 2019

Online: Dec. 2019

#### **Keywords:**

*Sargassum latifolium*

Heavy metals

Adsorption

Isotherm model

Kinetics equation

### **ABSTRACT**

The current study was undertaken to estimate the effectiveness of the brown algae *Sargassum latifolium* in removal of Ni<sup>2+</sup> and Pb<sup>2+</sup> ions from metal solution by adsorption as alternative low-cost adsorbents. Laboratory batch examination was conducted to estimate the influence of contact time, pH, initial Ni<sup>2+</sup> and Pb<sup>2+</sup> ions concentration, temperature and adsorbent dose on adsorption efficiency. The highest metal removal was obtained under condition of pH 7&6, temperature 25 & 30 °C, contact time of 5 & 60 min for Ni<sup>2+</sup> and Pb<sup>2+</sup> ions respectively, and optimum amount of 2.5 g with initial metal ions concentration of 10 mg L<sup>-1</sup>. Different isotherm models, namely Langmuir, Freundlich, Temkin and Dubinin–Radushkevich were used to analyze the investigational data, and the models parameters were evaluated. The maximum removal capacities ( $Q_{max}$ ) estimated by Langmuir isotherm were 0.276 and 0.171 mg g<sup>-1</sup> for Ni<sup>2+</sup> and Pb<sup>2+</sup>, respectively. Furthermore, the kinetic studies proved that alga has poor fit by pseudo first-order model while they have a good fitting with pseudo second-order model. In addition, the applications of alga to remove pb<sup>2+</sup> ions from seawater and wastewater were investigated under optimization conditions.

### **INTRODUCTION**

The accelerated urbanization, industrialization and human activities have resulted in serious pollution hazards in aquatic environment (Barquilha *et al.*, 2019). Heavy metals contamination received global concern in the last decades due to their toxicity, non-biodegradable nature and bioaccumulation properties (Yang *et al.*, 2015; Al Prol 2019). Heavy metals are constituents of earth's rocks and are utilized in many manufacturing operations (El-Metwally *et al.*, 2019). They are introduced to aquatic system through maritime, soil, weathering of rocks, industrial and municipal wastewaters (Valdman *et al.*, 2001). Discharge of industrial wastes usually contains large amounts of toxic metallic ions like Cd<sup>2+</sup>, Zn<sup>2+</sup>, Cr<sup>3+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and Pb<sup>2+</sup>; most of these wastes ultimately reach marine environment (Ajmal *et al.*, 1998). Wastewater from mining, metal processing, printing, electroplating, textile, photographic materials, petroleum refining in addition to battery manufacturing are the highest sources of heavy metal pollution (Al Prol 2019).

Removal of heavy metals from industrial effluents is essential before discharge into the environment. Many methods are adopted for wastewater treatment such as electrochemical processes, chemical precipitation, ion exchange, reverse osmosis in addition to membrane filtration. But these techniques are often costly and present poor

efficiency (Rao *et al.*, 2007). A number of studies concluded that adsorption technology is a promising low cost alternative for heavy metals elimination. The efficiency of this technique is directly related to the adsorbent materials (adsorbents), which should be derived from a suitable biomass, available, and have high removal capacity.

Among studied adsorbents, the brown macroalgae were proposed as suitable materials for metal removal due to their characteristic with great metal binding capacities, a renewable biological resource and availability in excess amounts (Schiewer and Volesky 2000; Romera *et al.*, 2007). The cell wall of the brown algae contains considerable amounts of polysaccharides such as alginates, fucoidans in addition to acid functional groups as acetamido, hydroxyl, amino, carbonyl, amido, and amino (Vieira and Volesky 2000). Both chemical functional groups and organic substances have great role in metal ion complexations. It has been assumed that one function of these polysaccharides compounds is to selectively absorb metal ions in a saltwater environment by ion exchange (Stewart 1974), and it is the main component responsible for metal sorption in treatment process (Barquilha *et al.*, 2019). The mechanisms underlying adsorption process are essentially explained by physical sorption (electrostatic affinity–vanderwaal power of affinity) or chemical sorption (covalent binding reaction among negative charge and cationic ions of cell surface) (Vijayaraghavan and Yun 2008). The aim of this paper was to estimate the feasibility of the raw biomass of brown alga *Sargassum latifolium* for the removal of nickel (II) and lead (II) from aqueous solution. The sorption studies have been examined by batch investigates with regard to the effect of contact time, pH, initial ions concentrations, temperature and adsorbent dosage. Furthermore, both isotherm and kinetics models were studied to investigate and predict the adsorption behaviour. Finally, the adsorption capacity of *S. latifolium* for  $Pb^{2+}$  was investigated in synthetic seawater compared to industrial effluent.

## MATERIALS AND METHODS

### **Adsorbent**

Brown alga (*S. latifolium*) was collected from the intertidal zone of Suez Bay, Egypt. The alga was first washed with sea water, then it was transported to laboratory and cleaned with tap water and deionized water to remove salts and particulate materials adhere to the surface. After that, the algae were sun-dried. The obtained biomass was powdered using a centrifugal grinder and sieved to gain a uniform particle sizes (about 500  $\mu\text{m}$ ).

### **Preparation of synthetic solution (Adsorbate)**

Stock solutions of 1000  $\text{mg L}^{-1}$  of metal ions were prepared in deionized water using  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (Carlo Erba, 99%) and  $\text{Pb}(\text{NO}_3)_2$  (Riedel-de Haën, 99%).  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$  standard solutions were prepared by acceptable diluting of stock solution (1000  $\text{mg L}^{-1}$ ) by deionized water. pH adjustment of all solutions was achieved using 1 Mole of HCl or 1 Mole of NaOH.

### **Batch adsorption studies**

Batch adsorption investigation was conducted in 250 mL conical flask (Erlenmeyer flasks) containing the dry mass of *S. latifolium* and constant volume (100 mL) of  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$  solution. Serial concentrations of metal ions (10 - 200  $\text{mg L}^{-1}$ ) were mixed with series of adsorbent doses (1 – 3.5 g), and different pH range (3 – 8) was adjusted to examine the function of pH. The suspensions were shaken using orbital shaker (Protech, model 720) with agitation speed of 110 rpm. The experiment

was repeated at different temperature values (20 – 50 °C), and solution samples were withdrawn at different time intervals (1min – 24h). Then, the mixture was separated from the adsorbent using membrane filter paper (whatman No.1, 0.47 µm Millipore) and measured by using Perkin Elmer Atomic Absorption Spectrometer (AAAnalyst 400). The metal removal efficiency was calculated from the Eqs:

$$\text{Metal removal (\%)} = 100 (C_i - C_e)/C_i \quad (1)$$

The adsorption capability for metals can be investigated based on the mass balance according to the Eq.:  $q_e = (C_i - C_e) V/m$  (2)

Where:  $C_i$  refers to initial of metal concentration in the mixture ( $\text{mg L}^{-1}$ ),  $C_e$  refers the equilibrium of metal concentration in the liquid phase ( $\text{mg L}^{-1}$ ),  $V$  is the volume of mixture (in liters) and  $m$  is the mass of alga applied in grams (Al Prol *et al.*, 2017).

### ***Isotherm studies***

Adsorption equilibrium isotherms were investigated using 1g of adsorbent that was suspended with 100 mL of metal solutions at different initial  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$  ions concentrations (varying range from 10 to 200  $\text{mg L}^{-1}$ ). The mixture was controlled at pH 7&6 and temperature 25 & 30 °C for  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$ , respectively. For these investigates, the flasks were shaken at a speed of 110 rpm for 240 min. Then, the mixture was filtered and measured.

### ***Kinetic studies***

Batch experiments were carried out in 250 ml conical flasks containing mixture of 1g adsorbent with 100 ml of metal solution ( $100 \text{ mg L}^{-1}$ ). The condition was adjusted to pH 7&6 and temp. 25 & 30 °C for  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$  respectively. The samples were shaken at time intervals (1, 5, 10, 15, 30, 45, 60, 120, 240, 1440 min) and centrifuged for 5 min. The clear mixture was analysed for residual  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$  concentration in the solution.

## **RESULTS AND DISCUSSION**

### ***Parameters affecting removal of $\text{Ni}^{2+}$ and $\text{Pb}^{2+}$ ions***

#### ***Effect of contact time***

The practical efficiency of adsorption process in solution largely depends on the immersion time in the medium (i.e., contact time) (Ibrahim *et al.*, 2016). Adsorption of nickel and lead ions was determined at given contact time for four initial metals concentrations of 10, 25, 50 and 100  $\text{mg L}^{-1}$ . Fig. (1) summarizes the effect of contact time on the removal of  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$  ions at different concentration levels.

The adsorption behavior over time varied between the studied metal ions. The rate of  $\text{Ni}^{2+}$  ion removal was fast, and basic adsorption processes completed within 5 min. On the other hand, Adsorption of  $\text{Pb}^{2+}$  increased steadily in the first 60 min, followed by slower increase until equilibrium at 240 min. The effect of contact time was not essential at high concentration ( $100 \text{ mg L}^{-1}$ ). During the initial stage larger surface area of algae is available; therefore the adsorption quickly occurs at the active binding sites (El-Moselhy *et al.*, 2017). But, normally, the adsorbate form one-molecule thick layer over the surface, and the biosorption process decreased with the time (Baia and Venkteswarlub, 2018).

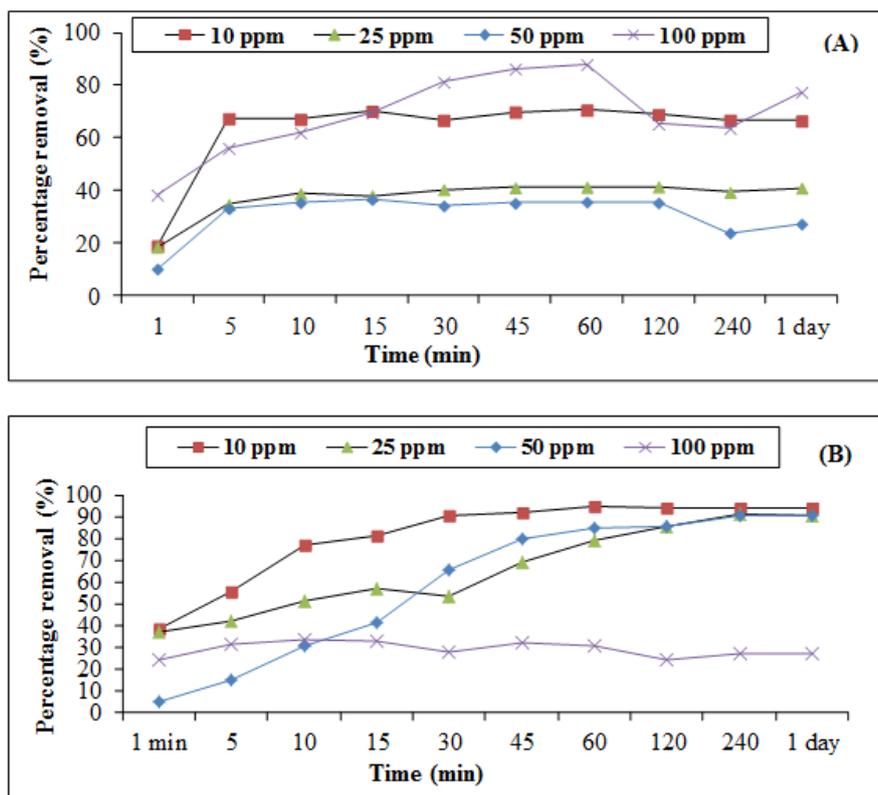


Fig. 1: Influence of contact time on elimination of (A) Ni<sup>2+</sup> and (B) Pb<sup>2+</sup> ions at various initial concentrations.

### Effect of pH

The pH value is a crucial factor for metal adsorption from aqueous medium. The external properties of alga and the functional groups in algal cell wall are greatly affected by the variations of pH values (Ibrahim *et al.*, 2016). The results for Ni<sup>2+</sup> and Pb<sup>2+</sup> are displayed in Fig. (2). The percentage removal of Ni<sup>2+</sup> metal was gradually raised up to pH 7 and then it was decreased. While, Pb<sup>2+</sup> adsorption showed peak values at pH 6 with maximum removal of 78.91 %. Adsorption is usually restrained at low pH, since excess positive charge (H<sup>+</sup>) on the surface inhibits the metal cations due to repulsive force. While at higher pH (than the optimum condition), the decline in percentage removal is attributed to the inactivity of binding site in basic condition (Ghoneim *et al.*, 2014).

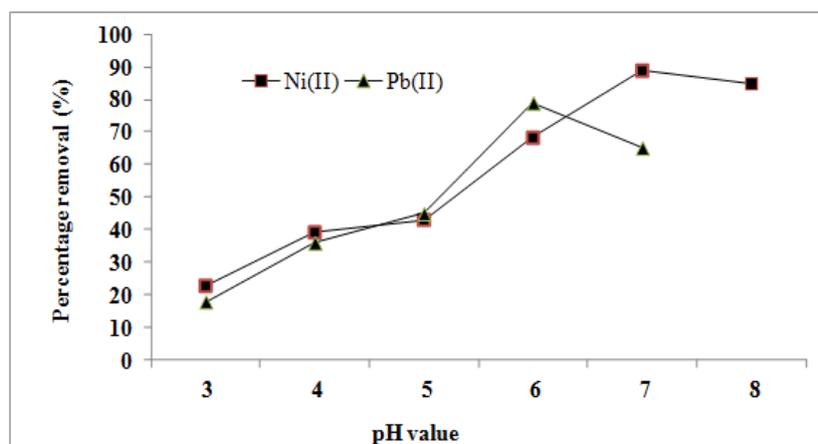


Fig. 2: Effect of pH parameter on adsorption of Ni<sup>2+</sup> and Pb<sup>2+</sup> onto *S. latifolium*.

The slow rate of  $Pb^{2+}$  adsorption after pH value 6 could be also explained by the possibility precipitation of  $Pb(OH)_2$  hydroxides (Das *et al.*, 2008). These results support the role of the chemical connections among the ions; since the olifinic double bond, sulphonic, amine groups and carbonyl of the *S. latifolium* alga are responsible for the adsorption of metal ions (Baia and Venkateswarlub 2018).

#### **Effect of initial ions concentration**

In this section, five initial  $Ni^{2+}$  and  $Pb^{2+}$  concentrations of (10, 25, 50, 100 and 200  $mg L^{-1}$ ) were examined with 1g of the dry alga dosage for 120 min. The results, in Fig. (3), indicate that the highest removal was found at initial concentration of 10  $mg L^{-1}$  with 68.9 and 94.6 % for both  $Ni^{2+}$  and  $Pb^{2+}$  ions respectively. After that, the percentage was decreased in both metal ions, however the removal of  $Pb^{2+}$  remained at high values (83%) until initial concentrations of 50  $mg L^{-1}$  before it was declined drastically afterward. It is obvious that adsorption process is more effective at low metal concentrations because all active sites on the algal surface are vacant (Ibrahim *et al.*, 2016). On the other hand, at higher metal levels the binding sites become consumed and finally the biosorbent surface becomes saturated and uptake rate decreased (Al-Qodah 2006).

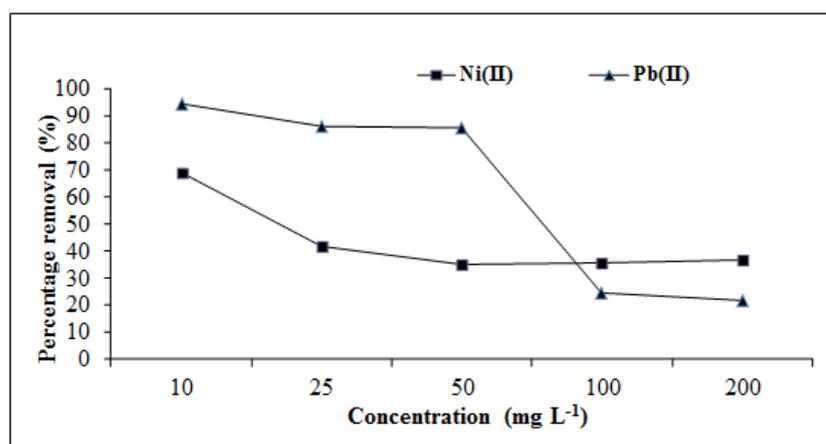


Fig. 3: Effect of initial metal concentration parameter on  $Ni^{2+}$  and  $Pb^{2+}$  removal using *S. latifolium*.

#### **Effect of temperature**

Nickel and lead ions adsorption on *S. latifolium* was examined as a function of temperature at several degrees of 20, 25, 30, 40 and 50 °C utilizing 10  $mg L^{-1}$  of metal ions with pH 6 and constant biomass dosage of 1 g. The highest percentage removal was found at 25 and 30 °C for  $Ni^{2+}$  and  $Pb^{2+}$  ions respectively. Further increase in temperature values led to the lessening in removal percentage as displayed in Fig. (4). This decrease is attributed to lower surface activity on *S. latifolium* alga at higher temperature and subsequent lower adsorption of metal ions. It is well-identified that adsorption process is an exothermic reaction (AjayKumar *et al.*, 2009). The temperature in the adsorption process has double main effects. Firstly, increasing the temperature values will raise the rate of metals diffusion outside the boundary layer, in addition to the internal holes of the adsorbent as a result of temperature constant increases with liquid viscosity decreases. Secondly, the equilibrium capacity of the heavy metal ions determines which process is endothermic or exothermic (Al-Qodah 2006).

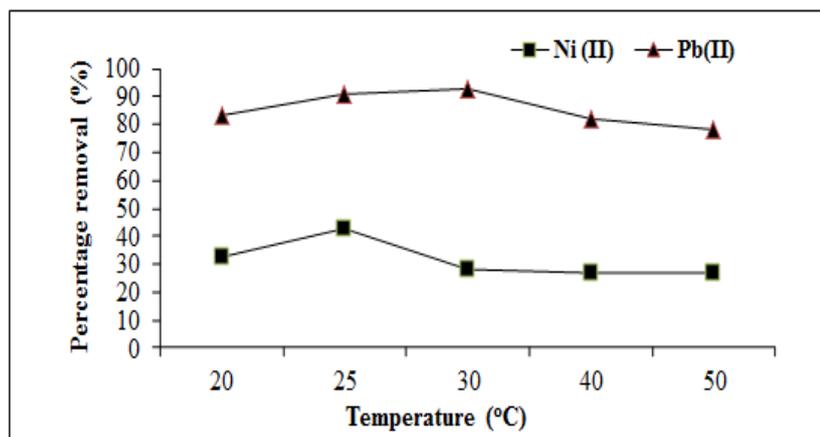


Fig. 4: Effect of temperature parameter on Ni<sup>2+</sup> and Pb<sup>2+</sup> removal by *S. latifolium*.

### Effect of adsorbent dose

The influence of the biomass dose was investigated at temperature (25 °C) by varying the sorbent amounts of dry *S. latifolium* from 1 to 3.5 g, while the initial metal ions concentration was fixed at 25 mg L<sup>-1</sup> with pH 6. The elimination of Ni<sup>2+</sup> and Pb<sup>2+</sup> ions by different doses of *S. latifolium* is presented in Fig. (5). The metal removal (i.e. adsorption process) for both Ni<sup>2+</sup> and Pb<sup>2+</sup> ions increased with increase in quantity of algae from 1 to 2.5 g. Any additional biomass beyond this did not change in the adsorption rate. Higher doses of the biomass means greater availability of the external area and more pore volume that will be available for the adsorption (Mall *et al.*, 2006). However at saturation point, further doses will not influence the removal efficiency since high biosorbent quantities can cause agglomeration in the biomass, in addition a consequent reduction in intercellular distance usually prevent binding sites from metal ions interaction (El-Sikaily *et al.*, 2011).

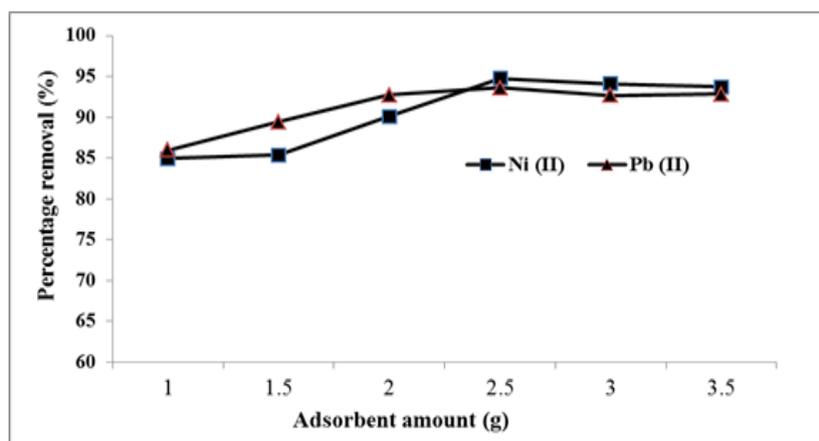


Fig. 5: Effect of adsorbent dose parameter on Ni<sup>2+</sup> and Pb<sup>2+</sup> removal by *S. latifolium*.

### Adsorption isotherms data analysis

Adsorption isotherms explain the equilibrium relations among adsorbate and adsorbent. Adsorption isotherms models were used to meet the equilibrium data known as Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models due to their simplicity and reliability (Langmuir, 1918, Freundlich, 1906, Tempkin and Pyozhev, 1940, Dubinin, 1960). Their applicability was judged by linear correlation coefficients ( $R^2$ ).

**Langmuir isotherm**

The Langmuir equations is the earliest theoretic treatments of non-linear adsorption, and assume that the uptake occurs on a homogeneous surface via monolayer adsorption without contact among adsorbed particles. The model suggests uniform energies of sorption onto the surface and no transmigration of the metal ions. Langmuir model can be linearized by the following Eq. (3):

$$1/q_e = 1/(b q_{max} C_e) + 1/q_{max} \tag{3}$$

Where;  $q_{max}$  represents the monolayer sorption capacity ( $mg L^{-1}$ ) and  $b$  is the Langmuir constant for free adsorption energy ( $L mg^{-1}$ ). The values of  $b$  and  $q_{max}$  are estimated from slope and intercept respectively.

Linear plot of Langmuir isotherm for nickel and lead ions adsorption, the calculated parameters and regression coefficients are presented in Fig. (6) and Table (1).

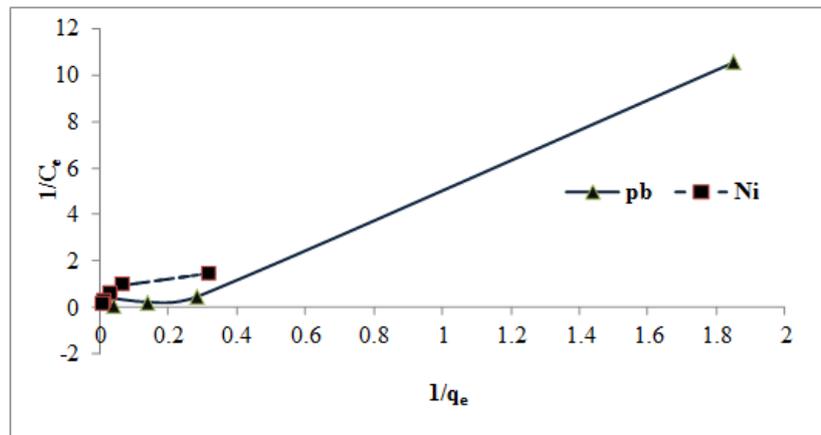


Fig. 6: Langmuir isotherm for Ni<sup>2+</sup> and Pb<sup>2+</sup> adsorption onto *S. latifolium*.

Fig. (6) shows the Langmuir plot of Ni<sup>2+</sup> and Pb<sup>2+</sup> sorption by *S. latifolium* with linear correlation coefficient of 0.804 and 0.984 respectively, where it was close to unity. Therefore, the results conform well-fit toward the Langmuir isotherm model for lead ions.

Maximum adsorption capacities,  $q_{max}$  related to complete monolayer coverage of Ni<sup>2+</sup> and Pb<sup>2+</sup> was found to be 0.276 and 0.171  $mg g^{-1}$ . While ‘b’ value was 10 and 15.58  $l/g$  (for Ni<sup>2+</sup> and Pb<sup>2+</sup> ions, respectively). The Langmuir equation were used to expect the affinity of *S. latifolium* surfaces to Ni<sup>2+</sup> and Pb<sup>2+</sup> ions via dimensionless separation factor ( $R_L$ ), where it was calculated in following Eq.(4).

$$R_L = 1 / (1 + b * C_i) \tag{4}$$

The average  $R_L$  values was 0.004 and 0.002 for Ni<sup>2+</sup> and Pb<sup>2+</sup> ions respectively, which mean that adsorption on *S. latifolium* was favorable since the values of  $R_L$  lies among 0 and 1 (Langmuir 1918).

**Freundlich isotherm**

The Freundlich model describes adsorption process on a heterogeneous surface with active sites possessing interactions among adsorbed molecules. Also, it assumes that a logarithmic lessening in the enthalpy of adsorption with the rise in the fraction of occupied sites.

Freundlich equation can be expressed by the following Eq. (5):

$$q_e = K_f C_e^{1/n} \tag{5}$$

Where:  $K_f$  indicates relative adsorption capacity of adsorbent and  $n$  is an intensity of the sorbent.

The linear plot of Freundlich equation for removal of  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$  ions and the calculated parameters are presented in Fig.(7) and Table (1). The linear correlation coefficient for *S. latifolium* is ranged between 0.837 and 0.989 for both  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$  ions, respectively, which shows that the investigated data fitted well for Freundlich model for lead ions.

Freundlich constant ( $K_f$ ) and  $n$  value could give a sign on the favorability of adsorption. The calculated  $n$  value, as represented in Table (1), proves that the adsorption onto *S. latifolium* is considered moderately for  $\text{Ni}^{2+}$  ions. It is suggested that values of  $n$  in the range of two to ten is perfect, one to two as ordinary difficult and below than one as poor adsorption specific (Chen *et al.*, 2010).

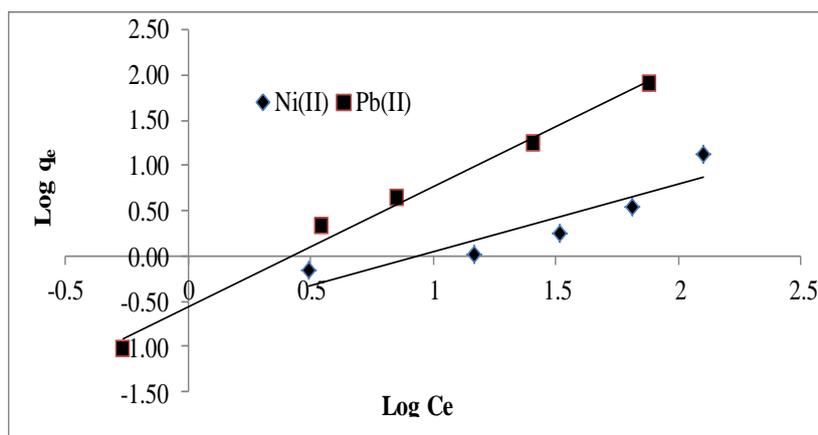


Fig. 7: Freundlich isotherm for  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$  ions adsorption onto *S. latifolium*.

### Temkin isotherm

Temkin model gives description for the behavior of adsorption process on the heterogeneous surface. This equation explains the effects of indirect adsorbate–adsorbate interface isotherms. This model assumes that the molecular heat of adsorption on the adsorbent surface layer would decline linearly when coverage increase.

The adsorption possibilities of the alga for metal ions can be calculated by using Temkin isotherm equation, which supposes that the fall in the heat of metal adsorption is linear rather than logarithmic “as assumed in the Freundlich model”. The Temkin isotherm is given by the following Eq. (6).

$$q_e = B \ln K_T + B \ln C_e \quad (6)$$

$B = RT/b$ , where:  $K_T$  represent Temkin isotherm constant ( $\text{Lg}^{-1}$ ),  $b$  represent a constant related to heat of sorption ( $\text{Jmol}^{-1}$ ) ( $\text{Lg}^{-1}$ ),  $R$  indicates the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) while  $T$  is the absolute temperature (K).

According to Temkin Eq. (6), we can estimate the values of constants  $A$  and  $B$  by plotting the relation of  $q_e$  versus  $\ln C_e$  (Fig. 8). The results showed low correlation coefficient for both metal ions (Table 1); therefore, the Temkin equation can not explain the removal of  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$  ions onto *S. latifolium*.

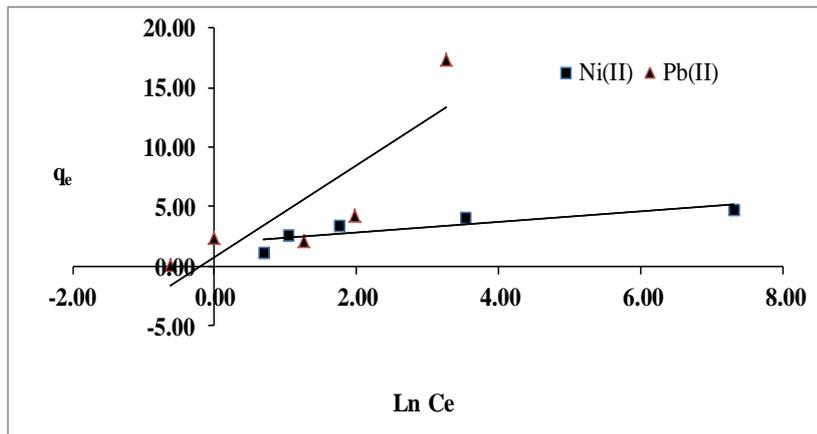


Fig. 8: Temkin isotherm for Ni<sup>+2</sup> and Pb<sup>+2</sup> ions adsorption onto *S. latifolium*.

**Dubinin–Radushkevich(D-R) isotherm**

This isotherm is used to evaluate adsorption mechanisms on a heterogenous surface. This model was selected to determine the characteristic porosity besides the apparent free energy of sorption (Gemeay *et al.*, 2002). The linear equation of the isotherm can be given by the Eq. (7):

$$\ln q_e = \ln Q_m - K \varepsilon^2 \tag{7}$$

Where: *K* and *Q<sub>m</sub>* are a constant relates with the sorption energy and the extreme adsorption capacity, respectively and  $\varepsilon$  can be calculated from Eq. (8).

$$\varepsilon = R T \ln (1+ (1/C_e)) \tag{8}$$

*E* represent the mean free energy of sorption (kJ mol<sup>-1</sup>). which expressed as the free energy variation when one mole of solution ions is transferred from infinity in solute solution to the surface of the solid, *E* value was expressed by the next Eq. (9):

$$E = 1/\sqrt{2k} \tag{9}$$

The slope of  $\ln q_e$  vs.  $\varepsilon^2$  was plotted for *S. latifolium* as presented in Fig. (9). The calculated D–R parameter, in addition to mean free energy for treatment process is expressed in Table (1).

The linear correlation coefficients found from this isotherm are in the same range or higher than those obtained from both Langmuir and Freundlich isotherm equations (Table 1), which indicates the applicability of D–R isotherm model for Ni<sup>+2</sup> and Pb<sup>2+</sup> ions. The parameter of *E* determined using Eq. (9) recorded 13.13 and 31.62 kJ mol<sup>-1</sup> for both Ni<sup>2+</sup> and Pb<sup>2+</sup> ions respectively. This result indicates that the adsorption process for both ions is of chemical nature (by ion-exchange mechanism) rather than physical adsorption.

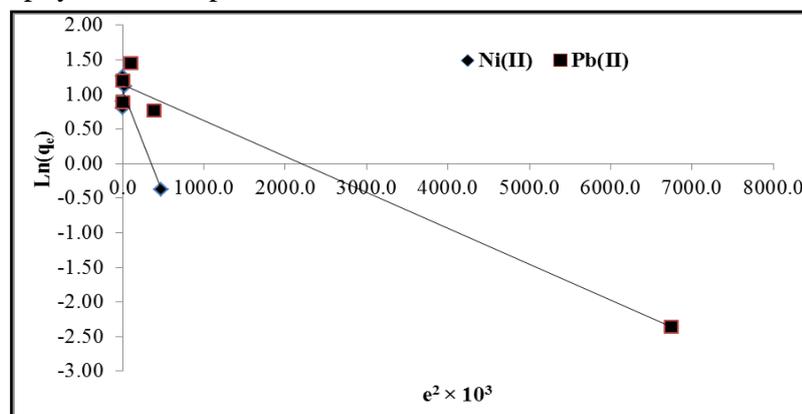


Fig. 9: Dubinin–Radushkevich isotherm for Ni<sup>+2</sup> and Pb<sup>+2</sup> ions adsorption onto *S. latifolium*.

Table 1: Isotherm parameters and linear correlation coefficients for the elimination of Ni<sup>2+</sup> and Pb<sup>2+</sup> ions onto *S. latifolium*.

Isotherm Model	Metal ions	
	Ni <sup>2+</sup>	Pb <sup>2+</sup>
<b>Langmuir</b>		
$Q_{max}$ (mg g <sup>-1</sup> )	0.276	0.171
$B$	10	5.58
$R^2$	0.804	0.984
$R_L$	0.004	0.002
<b>Freundlich</b>		
$N$	1.33	0.754
$K_F$	5.06	3.58
$R^2$	0.837	0.989
<b>Temkin</b>		
$A_T$	91.66	1.215
$B_T$	0.44	3.867
$R^2$	0.702	0.736
<b>Dubinin-Radushkevich</b>		
$Q_m$ (mol kg <sup>-1</sup> )	2.832	3.138
$K$ (mol kJ <sup>-1</sup> ) <sup>2</sup>	0.002	0.0005
$E$ (Kj mol <sup>-1</sup> )	13.13	31.62
$R^2$	0.913	0.975

### Adsorption kinetics

In the kinetic adsorption models, it's postulated that the total rate of the adsorption is controlled through the removal rate of the solute on the external layer of the adsorbent biomass. The kinetics are usually modeled by the pseudo-first-order, pseudo-second-order kinetics in addition to intraparticle diffusion models. The compatibility among investigational results and the model-predicted values was determined by values of linear correlation coefficients ( $R^2$ ) close or equal to unity.

#### The pseudo-first order model

This model was suggested by Lagergren's equation which describes adsorption in liquid-solid systems that depend on the adsorption capacity of solids. The pseudo-first order model represented by the following Eq. (10) (Ho *et al.*, 2000).

$$\text{Log}(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (10)$$

Where:  $q_e$  and  $q_t$  (mg g<sup>-1</sup>) are the adsorption capacity at equilibrium and time (t), respectively.  $K_1$  (min<sup>-1</sup>) represent the rate constant of pseudo-first-order adsorption. Parameters of  $\log(q_e - q_t)$  are correlated by  $t$  as shown in Fig. (10) in which the values of  $k_1$  and  $q_e$  are estimated from the slope and intercept of the kinetic equation, respectively.

Parameters of  $k_1$ , experimental  $q_e$  and calculated data of  $q_e$ , in addition to the  $R^2$  for the pseudo-first kinetic plots were observed in Table (2). As can be seen from data, the  $R^2$  parameter found from the plots were low, and the theoretical data of  $q_e$  were less than the corresponding experimental values. This proved a poor fitting between the kinetics data and the pseudo-first order isotherm.

#### The pseudo-second order model

The pseudo-second-order model depend on the assumption of chemisorption of the adsorbate on the biomass. This model as described by Ho (2000) is expressed as:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (11)$$

Where: the rate constant of the second-order equation is  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>). The values of  $k_2$  and  $q_e$  were estimated from the slope and intercept of the linear figure of  $t/q_t$  against (t) as presented in Fig. (11). Experimental data agreed with the second-order equation since correlation coefficients are close to or equal 1 for both metal ions

“unlike those resulting from pseudo first-order model”. Therefore, The pseudo-second order model better describes the mechanisms of adsorption of Ni<sup>+2</sup> and Pb<sup>+2</sup> onto *S. latifolium*. Similar results were found on brown and green algae by Nessim *et al.* (2011) and Bai *et al.* (2018).

**The intraparticle diffusion model**

In this model the adsorption method occurs in numerous steps including the transport of solute particles from the aqueous part to the solid particles surface followed by diffusion of the dissolved ions to the interior of the cavities (Weber and Morris 1963). The equation of the intraparticle diffusion model is expressed in Eq. (12) as follow:

$$q_t = K_{dif} t^{1/2} + C \tag{12}$$

Where: *C* mean the intercept in addition *K<sub>dif</sub>* (mg g<sup>-1</sup> min<sup>-0.5</sup>) mean the intraparticle diffusion rate constant. The figures of *q<sub>t</sub>* inverse *t<sup>0.5</sup>* may present a numerous-linearity correlation, which shows that two or more stages happen through adsorption process as showing in Fig. (12).

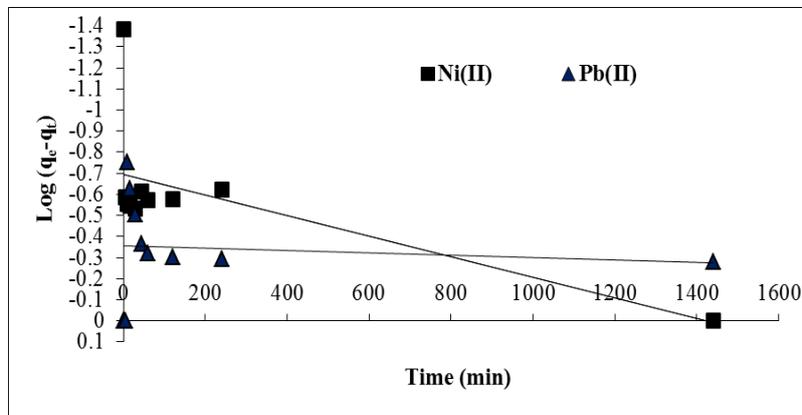


Fig. 10: Pseudo-first order plot for the sorption of Ni<sup>2+</sup> and Pb<sup>2+</sup> ions.

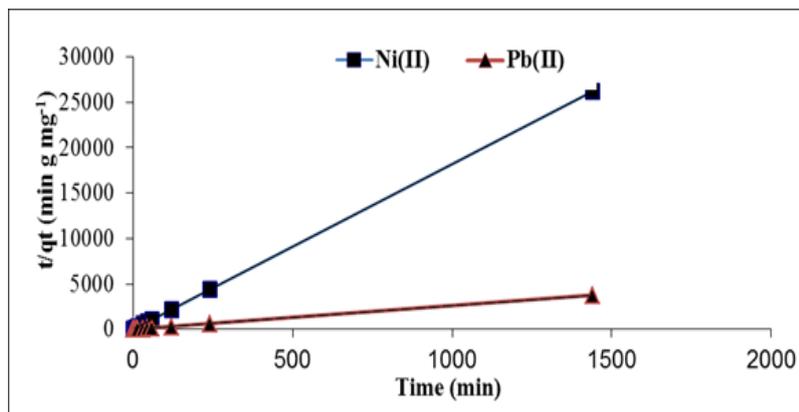


Fig. 11: Pseudo-second order plot for the sorption of Ni<sup>2+</sup> and Pb<sup>2+</sup> ions.

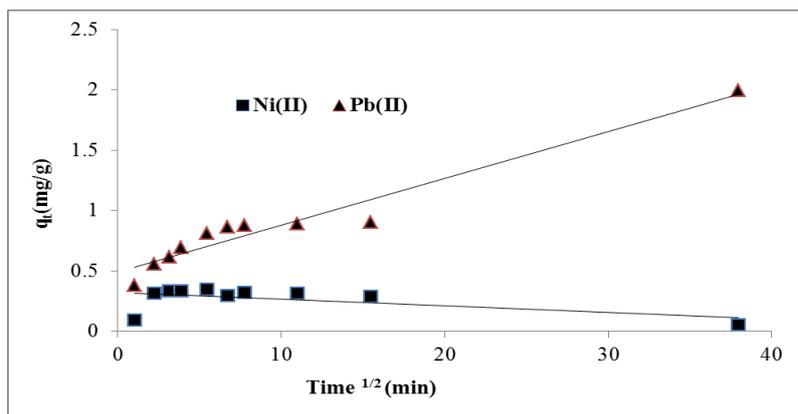


Fig. 12: Intraparticle diffusion model plot for the adsorption of  $\text{Ni}^{2+}$  and  $\text{Pb}^{2+}$  ions.

$K_{\text{dif}}$  directly calculated from the slope and the intercept is  $C$  as recorded in Table (2). The values of  $C$  offer information around the thickness of the border layer, where the resistance to the surface-mass transfer raises as the intercept increases. The linear relationship of the plots confirmed that intra-particle diffusion have a significant part in the uptake of the lead ions by sorbent where the  $R^2$  values become close to 0.945, while it showed low linearity for the adsorption of nickel ions ( $R^2$  value was 0.340).

Table 2: The adsorption rate constants with Pseudo-first-order model, the Pseudo-second-order model and intraparticle diffusion model.

Kinetic model	Metal ions	
	$\text{Ni}^{+2}$	$\text{Pb}^{+2}$
<b>Pseudo-first-order kinetic model</b>		
$q_e - \text{exp. (mg g}^{-1}\text{)}$	0.271	0.748
$q_e \text{ (mg g}^{-1}\text{)}$	4.95	2.454
$K_1 \text{ (min}^{-1}\text{)}$	$2.17 \times 10^{-4}$	0
$R^2$	0.43	0.0106
<b>Pseudo-second-order kinetic model</b>		
$K_2 \text{ (g mg}^{-1} \text{min}^{-1}\text{)}$	9.09	6.817
$q_e \text{ cal. (mg g}^{-1}\text{)}$	0.055	0.383
$R^2$	1	1
<b>Intraparticle diffusion model</b>		
$K_{\text{dif}} \text{ (mg g}^{-1} \text{min}^{-0.5}\text{)}$	0.324	0.495
$C$	0.005	0.038
$R^2$	0.34	0.945

### Application to wastewater and seawater

Due to the interferences of industrial wastewater with the environment, the evaluation of adsorption capacity of biomass in different solutions is principal to develop bioprocess to remove and recover metal from industrial effluents. So, the adsorption mechanism of *S. latifolium* in treatment of  $\text{Pb}^{2+}$  ions in distilled water, industrial effluent as well as synthetic seawater samples was studied here. The application of biomass of algae to remove  $\text{pb}^{2+}$  ions was achieved under optimization conditions (pH 6 at  $30^\circ\text{C}$  and 0.1 g of adsorbents in 10 mL of solution). The obtained results are illustrated in Table (3). The highest percentage of  $\text{pb}^{2+}$  removal was in distilled water (87.05 %), followed by wastewater (67.37 %) and finally synthetic sea water (57.48 %). It is obvious that seawater has concentration of cation metals such as ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) higher than of wastewater and deionized water. Therefore, lower  $\text{Pb}^{2+}$  ions removal may be owing to the inhibition effect of salts on the active

site on the biomass (Al Prol 2015). In addition, the concentration of the salts is directly proportional with the ionic strength of the solution.

Table 3: Removal percentage of lead ions by using raw *S. latifolium* in different water samples.

Solution of lead ions used	Removal (%)
Distilled water	87.05 %
Wastewater	67.37 %
synthetic sea water	57.48 %

## CONCLUSION

Adsorption as an effective technique for heavy metal removal has gained imperative credibility due to its good performance and low cost. This study provides important data about the adsorption behaviour of nickel and lead ions onto the brown marine alga *S. latifolium* in aqueous solution using batch system. The adsorption process depended on the influences of operational conditions as contact time, pH, temperature, initial metals concentration and biomass dose. The maximum removal of Ni<sup>2+</sup> (78.91 %) and Pb<sup>2+</sup> (88.78 %) ions was obtained within 60 min from the start of the experiment, at pH 7 & 6 and temp. of 25 & 30 °C, respectively. The isotherm equilibrium studies showed that Langmuir, Freundlich and Dubinin–Radushkevich models are the best fitted models for the adsorption process. Experimental results were tested in terms of adsorption kinetics, where the adsorption process in this study followed the pseudosecond-order model. Furthermore, the applications of biomass to remove Pb<sup>2+</sup> ions from distilled water, seawater and wastewater were carried out under optimization conditions. Removal efficiency from sea water was lower than other solutions, probably due to the inhibition of the adsorption by the cations in salt water. The present study concludes that *S. latifolium* algae can be employed as an effective, low cost, and environmentally friendly adsorbent for elimination of Ni<sup>2+</sup> and Pb<sup>2+</sup> ions from aqueous solution and wastewater.

## REFERENCES

- AjayKumar, V. A.; Darwish, N. A. and Hilal, N. (2009). Study of various parameters in the biosorption of heavy metals on activated sludge. W. Appl .Sci J., 5: 32-40.
- Ajmal, M. A.; Mohammad, R. and Yousuf, A. A. (1998). Adsorption behavior of Cadmium, Zinc, Nickel and Lead from aqueous solution by Mangifera India Seed Shell. Ind. J. Environ. Health., 40:15-26.
- Al Prol, A. E. (2015). Biosorption of some toxic heavy metal ions from industrial wastewater by some marine macro algae. M.SC Thesis, Tanta University. Egypt., P 76-77.
- Al Prol, A. E. (2019). Study of environmental concerns of dyes and recent textile effluents treatment technology: A Review. Asia. J. Fish & Aqua. Res., 3(2): 1-18.
- Al Prol, A. E.; Abd El Azzem, M.; Amer, A.; El-Metwally, M. E. A.; Abd El-Hamid, H.T. and El-Moselhy, K. M. (2017). Adsorption of cadmium (II) ions from aqueous solution onto mango leaves. Asi. J. Phy. Chem. Sci., 3:1-11.
- Al-Qodah, Z. (2006). Biosorption of heavy metal ions from aqueous solutions by activated sludge. Desalination., 196 :164-176.

- Baia, M. and Venkateswarlub, P. (2018). Fixed bed and batch studies on biosorption of lead using *Sargassum Tenerrimum* powder: characterization, kinetics and thermodynamics. *Materials Today: Proceedings.*, 5:18024–18037.
- Barquilha, C. E. R.; Cossich, E. S.; Tavares, C. R. G. and Silva, E.A. (2019). Biosorption of nickel (II) and copper (II) ions by *Sargassum sp* in nature and alginate extraction products. *Bioresource Technology Reports.*, 5: 43–50.
- Chen, H.; Zhao, J.; Dai, G.; Wu, J. and Yan, H. (2010). Adsorption characteristics of Pb (II) from aqueous solution onto a natural biosorbent fallen *Cinnamomum camphora* leaves. *Desalination.*, 262: 174-182.
- Das, N.; Vimala, R. and Karthika, P. (2008). Biosorption of heavy metals-An overview. *Ind. J. Biotech.*, 7: 159 - 69.
- Dubin, M. M. (1960). The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface. *Chem. Rev.*, 60:235–266.
- El-Metwally, M. E. A.; Othman, A. I. and El-Moselhy, K. M. (2019). Distribution and assessment of heavy metals in the coastal area of the Red Sea, Egypt. *Egy. J. Aqua. Bio& Fish.*, 23(2), 1 – 13.
- El-Moselhy, K. M.; Abdel Azzem, M.; Amer, A. and Al-Prol, A. E. (2017). Adsorption of Cu(II) and Cd(II) from aqueous solution by using rice husk adsorbent. *Phys. Chem. Ind. J.*, 2:109.1-14.
- El-Sikaily, A.; El Nemer, A. and Khaled, A. (2011). Copper sorption onto dried red alga *Pterocladia capillacea* and its activated carbon. *Chem. Eng. J.*, 14: 168-707.
- Freundlich, H. (1906). Adsorption in solution. *Phys Chem.*, 57:384-410.
- Gemeay, A. H.; El-Sherbiny, A. S. and Zaki, A. B. (2002). Adsorption and kinetic studies of the intercalation of some organic compounds onto Na<sup>+</sup> - montmorillonite. *J. Coll. Interf. Sci.*, 24:116–125.
- Ghoneim, M. M.; El-Desoky, H. S.; El-Moselhy, K. M.; Amer, A.; Abou El-Naga, E. H.; Mohamedein, L. and Al-Prol, A. E. (2014). Removal of cadmium from aqueous solution using marine green algae *Ulva lactuca*. *Egy. J. Aqu. Res.*, 40: 235–242.
- Nessim, R. B.; Bassiouny, A.; Zakia, H. R.; Moawada, M. N. and Kandeelb, K. M. (2011). Biosorption of lead and cadmium using marine algae. *Chem. Ecol.*, 1–16.
- Mall, D. I.; Srivastava, V. C. and Agarwal, N. K. (2006). Removal of Orange-G and methyl violet dyes by adsorption onto bagasse fly ash kinetic study and equilibrium isotherm analyses. *Dye. Pigment.*, 69: 210–223.
- Ho, Y. S.; Ng, J. C. Y. and McKay, G. (2000). Kinetics of pollutant sorption by biosorbents: Review. *Sep. Purif. Method.*, 29:189–232.
- Ibrahim, W. M.; Hassan, A. F. and Azab, Y. A. (2016). Biosorption of toxic heavy metals from aqueous solution by *Ulva lactuca* activated carbon. *Egypt. J. Basic Appl. Sci.*, 3: 241–249.
- Langmuir, I. (1918). The adsorption of gases on plane surface of glass, mica and platinum. *J. Am. Chem. Soc.*, 40:1361-1403.
- Rao, P. S.; Reddy, K. V. N. S. and Krishnaiah, S. K. A. (2007). Comparative sorption of copper and nickel from aqueous solutions by natural neem (*Azadirachta indica*) sawdust and acid treated sawdust. *Wood. Sci. Technol.*, 41: 427-442.
- Romera, E.; González, F.; Ballester, A.; Blázquez, M. L. and Muñoz, J. A. (2007). Comparative study of biosorption of heavy metals using different types of algae. *Biores. Techn.*, 98: 3344-3353.

- Schiewer, S. and Volesky, B. (2000). Biosorption processes for heavy metal removal. In: Lovley D R, editor. Environmental microbe - metal interactions. Washington, DC: ASM Press. 329– 357.
- Stewart, W. D. P. (1974). Algal physiology and biochemistry. Berkeley, CA: University of California Press. 40–76.
- Tempkin, M. J. and Pyozhev, V. (1940). Acta Physicochim. USSR., 12: 327–352.
- Valdman, E. L.; Erijman, F. and Pessoa, S. G. F. (2001). Continuous biosorption of Cu and Zn by immobilized waste biomass *Sargassum sp.* Proc. Biochem., 36: 869-873.
- Vieira, R. H. S. F. and Volesky, B. (2000). Biosorption: A Solution to pollution. Int Microbiol., 3: 17-24.
- Vijayaraghavan, V. and Yun, Y. S. (2008). Bacterial biosorbent and biosorption. Biotechnol. Adv., 26: 266–291.
- Weber, W. J. and Morris, J. C. (1963). Kinetics of adsorption on carbon from solution. J. Sanit. Eng. Div. Am. Soc. Civ. Eng., 89: 31–60.
- Yang, L.; Wang, L.; Wang, Y. and Zhang, W. (2015). Geochemical speciation and pollution assessment of heavy metals in surface sediments from Nansi Lake. China. Environ. Monit. Assess., 5:187-261.

## ARABIC SUMMARY

الطحلب البحري *Sargassum latifolium* كمادة صديقة للبيئة لمعالجة أيونات عناصر النيكل والرصاص السامة من المحاليل المائية

أحمد عيد البرل - محمد المتولى - عادل عامر  
المعهد القومي لعلوم البحار والمصايد، مصر.

تهدف الدراسة إلى تقدير كفاءة الطحالب البحرية كمواد قليلة التكلفة على إزالة أيونات العناصر من المحاليل المائية وذلك باستخدام الطحلب البني *Sargassum latifolium* ، حيث استخدم لتقليل مستوى النيكل والرصاص من المحاليل المائية. وتم دراسة بعض العوامل المؤثرة على كفاءة عملية الإدمصاص كالأس الهيدروجيني ودرجة الإتصال والتركيز الأولى لأيونات النيكل والرصاص ودرجة الحرارة بالإضافة الى جرعة المدمص (الطحلب). وقد أوضحت النتائج أن أفضل الظروف لعملية الامتصاص كانت عند الأس الهيدروجيني 6.7 وكانت كمية الكتلة الحيوية للطحلب 2.5 جم كافية لإزالة 94.15 % من 10 مجم/لتر من التركيز الأولى لأيونات النيكل والرصاص عند درجة حرارة 25 و 30 °م للمحاليل المائية بعد ساعة من وقت الاتصال. وقد طبق على نتائج الاتزان لعملية الامتصاص معادلات أيزوثرمات الامتصاص وهي (معادلة لانجمير وفروندليتش وتمكن ودوبين)، وأوضحت النتائج أن قيمة السعة القصوى للامتصاص بلغت حوالى 0.276 و 0.171 ملجم/جم لكل من عنصري النيكل والرصاص على الترتيب. ولقد أكدت النتائج أن الدراسة الحركية مناسبة لنموذج الدرجة الثانية ولم تكن مناسبة مع نموذج الدرجة الأولى. بالإضافة إلى تطبيق الظروف القياسية على مياه البحر ومياه الصرف للتحقق من كفاءة تلك الكتل الحيوية لعزل أيونات عنصر الرصاص منها.