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Research Article

Adsorption Studies of Lead by *Enteromorpha* Algae and Its Silicates Bonded Material

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Lead adsorption by green *Enteromorpha* algae was studied. Adsorption capacity was 83.8 mg/g at pH 3.0 with algae (E) and 1433.5 mg/g for silicates modified algae (EM). FTIR and thermal analysis of algae materials were studied. Thomas and Yoon-Nelson column model were best for adsorbent (E) and algae after reflux (ER) and Yan model for (EM) with capacity 76.2, 71.1, and 982.5 mg/g, respectively. (ER) and (EM) show less swelling and better flow rate control than (E). Nonlinear methods are more appropriate technique. Error function calculations proved valuable for predicting the best adsorption isotherms, kinetics, and column models.

1. Introduction

The contamination of wastewater and soil with heavy metal ions is a complex problem, since these metals are toxic in both their elemental and chemically combined forms. Natural water is contaminated with several heavy metals due to their widespread use in industry and agriculture arising mostly from mining wastes and industrial discharges. From an environmental protection point of view, heavy metal ions should be removed at the source in order to avoid pollution of natural waters and subsequent metal accumulation in the food chain. In fact, removal of this contamination has received much attention in recent years [1, 2].

Lead being one of the "big three" toxic heavy metals, it is of profound concern as a toxic waste and contaminant of surface waters as it becomes concentrated throughout the food chain to humans [3]. Lead damages different body organs (central and peripheral nervous systems and kidney); also, lead has a teratogenic effect, causing stillbirth in women and affecting the fetus [4].

Conventional methods for removal are chemical precipitation, chemical oxidation, chemical reduction, ion exchange, filtration, electrochemical treatment, and evaporation [5, 6]. These methods often are very expensive.

Alternative method for heavy metal removal was developed in the last past decade and known as biosorption. Marine algae, an abundant renewable natural biomass, have been used as dead nonliving materials for removal of heavy metals [7, 8]. In addition, algae were found accumulating heavy metal in their habitat and are thus used as heavy metal pollution monitors in fresh and salty water such as river, sea, and ocean. They have been also used in on-site bioremediation of polluted natural water [9, 10].

Furthermore, the search for a low-cost and easily available adsorbent has led to the investigation of materials of agricultural and biological origin (bacteria, fungi, yeast, and algae can remove heavy metals from a solution in considerable quantities), along with industrial byproducts, as potential metal sorbents. These low-cost and nonconventional adsorbents include agricultural wastes like natural compost, Irish peanut, peanut shell, coconut shell, bone, and biomass such as *Aspergillus terreus* and *Mucus remanianus*, polymerized onion skin with formaldehyde and EDTA, modified cellulosic material, and natural materials such as hair and cattails

(*Typha* plant), waste wool, peanut skin, modified barks, barely straw, low rank coal, soils, human hair, peat moss, fertilizer waste slurry, waste tire rubber, and tea leaves [11–22].

Biosorption process for metal removal has a performance comparable to a commercial competitor, ion exchange treatment. While commercial ion exchange resins are rather costly, the price tag of biosorbents can be an order of magnitude cheaper (1/10 of the ion exchange resin cost) [23, 24].

Some of the key features of biosorption compared to conventional processes include competitive performance, heavy metal selectivity, cost-effectiveness, regenerative, process equipment known, no sludge generation, and metal recovery possible [25].

In the literature, there are divergent mechanisms explaining the metal uptake by marine algae. A semispeculative model of the structure of the cell walls of the algae has been proposed recently. This could suggest that there are two common moieties to which the uptake ability of taxonomically different algal biomass was attributed: sulfated ester polysaccharides (fucoidans, carrageenans, and galatians and xylans) and polyuronides (galacturonic, glucuronic, guluronic, and mannuronic acids). The sulfate and carboxylic acid groups could be considered as responsible for the bulk of metal uptake sorption [26]. In general, the algae are very soft, with the tendency to disintegrate which prevents the follow-up experiments even in laboratory column [27]. Also, the small size of algae particles with low density, mechanical strength, and rigidity affects the performance of algae. Immobilization of algae within a matrix (e.g., silicates) through chemical pretreatment can overcome these problems and allow industrial application [28–30].

The present work is focused on the ability of green algae *Enteromorpha* collected from Lebanese coast to adsorb Pb^{2+} from aqueous medium at 25°C. Comparative studies are made between nonmodified *Enteromorpha* algae (E), algae residue after reflux (ER), and algae modified with silicates (EM).

Optimum conditions for adsorption (mass, pH, concentration, and residence time) are considered in batch experiments. Also column application for algae materials was studied for maximum capacity per one gram.

Infrared spectra and thermogravimetric analysis of *Enteromorpha* algae were detected before and after adsorption.

2. Theoretical

2.1. Isotherm and Column Models. The equations and parameters of the isotherms adsorption models (Langmuir, Freundlich, Redlich-Peterson, Temkin, Elovich, and Dubinin-Radushkevich), column kinetic models (Thomas, Yoon-Nelson, and Yan model) are described in detail in our previous work [31–34] and references therein, Tables 1 and 2.

In general all calculations are based on the following two terms: q_e (mg/g), the equilibrium metal uptake (mass of adsorbed pollutant (mg) per mass of adsorbent (g)) and C_e (mg/L) or (ppm), the equilibrium ion concentration of pollutant remaining in solution.

Table 1: Nonlinear equations of different adsorption isotherms.

Isotherm model	Equation
Langmuir	$Q_e = \dfrac{Q^o K_L C_e}{1 + K_L C_e}$
Freundlich	$Q_e = K_F (C_e)^{1/n}$
Redlich-Peterson	$Q_e = \dfrac{A_{\mathrm{RP}} C_e}{1 + K_{\mathrm{RP}} C_e^{\beta}}$
Temkin	$Q_e = B_T \ln\left(K_T\right) + B_T \ln\left(C_e\right)$
Elovich	$\dfrac{Q_e}{Q_E} = K_E C_e e^{-(Q_e/Q_E)}$
Dubinin-Radushkevich	$Q_e = Q_m \exp^{\beta[RT \ln(1+(1/C_e))]^2}$

2.2. Error Analysis. The computational part of the obtained experimental measurements is introduced. To obtain the curve which best fits the data in least-squares sense, the following minimization problem is solved by calculating error parameters R^2, χ^2, and SSE. Error calculations were used for the fitting quality of the isotherm and column models to the experimental data, Table 3 [31–34], where $x\mathrm{data}_i$ and $y\mathrm{data}_i$ are the experimental measurements and $f(x, x\mathrm{data}_i)$ is a function of the linear or nonlinear curve proposed to fit the given data. The $x\mathrm{data}_i$ is the equilibrium concentration C_e and $y\mathrm{data}_i$ is dependent on q_e.

The squared correlation coefficient R^2 is defined in Table 3, R being the correlation between the experimental data and the used model, where $X = y\mathrm{data}_i = y_{e,\exp}$ and $Y = f\left(x, x\mathrm{data}_i\right) = y_{e,\mathrm{cal}}$.

The sum of squares of errors SSE and chi-square test χ^2 depend on the total deviation of the calculated values from the fit to the experimental values in Table 3.

If data from the model are similar to the experimental data, χ^2 and SSE will be a small number. On the other hand, the closer R^2 value to 1.00 the better is the fitting and the more suitable is the model. Thus, the best model chosen in each case is the one giving highest R^2 and lowest SSE and χ^2.

3. Experimental

3.1. Chemicals. All reagents are from Fluka: lead nitrate $Pb(NO_3)_2$, sodium silicates for chemical modification of algae, sodium acetate, and acetic acid for preparation of acetate buffer.

3.2. Algae Collection. The raw algae *Enteromorpha intestinalis* was harvested from the Lebanese coast, washed with tap and deionized water in order to remove extra salts, sun dried, and grounded to particle size (0.5 mesh). Finally, the fine powder is oven dried at 60°C for 24 hours to give algae material (E) for further use in metal uptake study.

3.3. Preparation of Algae Residue (ER), Modified Algae (EM), and Swedish Wood Sawdust (SWS)

3.3.1. Preparation of Algae Residue Material (ER). Enteromorpha algae (*J*) powder 10 gm was refluxed in deionised

Table 2: Nonlinear and linear equations of different kinetic column models.

Kinetic models	Nonlinear equations	Linear equations
Thomas model	$\frac{C_e}{C_o} = \frac{1}{1 + \exp\left(\left(K_{\mathrm{Th}}/Q\right)\left(q_T m - C_o V_{\mathrm{eff}}\right)\right)}$	$\ln\left[\left(\frac{C_o}{C_e}\right) - 1\right] = \left(\frac{K_{\mathrm{Th}} q_T M}{Q}\right) - \left(K_{\mathrm{Th}} C_o t\right)$
Yoon-Nelson model	$\frac{C_e}{C_o} = \frac{1}{1 + e^{K_{\mathrm{YN}}(\tau - t)}}$	$\ln\left(\frac{C_e}{C_o - C_e}\right) = K_{\mathrm{YN}} t - \tau K_{\mathrm{YN}}$
Yan et al. model [42]	$\frac{C_e}{C_o} = 1 - \frac{1}{1 + \left(Q^2 t / K_y q_y m\right)^{K_y C_o / Q}}$	$\ln\left[\left(\frac{C_e}{C_o - C_e}\right)\right] = \left(\frac{K_y C_o}{Q}\right) \ln\left(\frac{Q^2}{K_y q_y m}\right) + \left(\frac{K_y C_o}{Q}\right) \ln t$

Table 3: Error function and squared correlation coefficient for best-fitting model estimation.

$R^2 = \frac{\left(\sum\left(X - \overline{X}\right)\left(Y - \overline{Y}\right)\right)^2}{\sum\left(X - \overline{X}\right)^2\left(Y - \overline{Y}\right)^2}$	$\text{Chi-square} = \chi^2 = \sum \frac{\left(y_{e,\exp} - y_{e,\mathrm{cal}}\right)^2}{y_{e,\mathrm{cal}}}$	$\mathrm{SSE} = \sum\left(y_{e,\exp} - y_{e,\mathrm{cal}}\right)^2$

water 100 mL for 15 min giving green suspension; the residue material was separated from the green solution by filtration and then dried to give *Enteromorpha* algae after reflux (ER) in 80% yield.

3.3.2. Preparation of Swedish Wood Sawdust (SWS). Swedish wood sawdust was ground to 0.5 mesh particle size washed with deionized water and dried similar to algae.

3.3.3. Preparation of Sodium Silicate Algae Material (EM). Enteromorpha powder (E) was washed with HCl (0.1 M) and water, respectively. The material was then separated by centrifuging. Sulfuric acid (120 mL, 5%) was mixed with enough sodium silicate (Na_2SiO_3) (6%) to raise the pH of the solution to 2.0. At pH 2.0, the washed biomass was added to the solution and stirred for 10 minutes. Additional amount of sodium silicate (6%) was then slowly added to raise the pH of the solution to 7.0. The resulting polymer gel was washed with water and oven dried at 60°C for one week. The dried polymer was ground by mortar and pestle and sieved to be ready for further application [34].

3.4. Equipment and Instruments. The potentiometric measurements were carried out using Denver Instrument Model 225 pH-ion selective electrode meter fitted with a combined glass electrode (reading to ±0.01 pH unit). The reaction flask was kept constant at 25°C (±0.1°C) by using a thermostat Model Heto HMT 200. The shaker (Wiggen Hauser OS-150, Germany) and centrifuge (Sigma 203) were used for agitation experiment. Lead content was analyzed using Buck Scientific Atomic absorption spectrometer. Infrared data were collected on a Shimadzu 8300 FTIR spectrophotometer using KBr pellet method. Thermogravimetric-differential scanning calorimetry (TG-DSC) curve was recorded on SETARAM LABSYS thermal analyzer in the flow of N_2 within the 25–900°C temperature range, with a heating rate of 3°C/min [31–33].

3.5. Effect of Mass of Algae. The effect of mass of algae (E) on metal uptake was studied in batch system. 25 mL solution of 300 ppm lead (at pH 4.00) in 50 mL Erlenmeyer flask was shaken with different masses of algae for 2 min at 200 r.p.m and left to stand for 24 hrs in water bath at 25°C and then analyzed for the remaining lead [35].

3.6. pH Effect. The mass of algae (E) used in this experiment is the optimum mass 0.3 g done in batch system using 50 mL Erlenmeyer flasks with a reaction volume of 25 mL lead solution (300 mg/L) at 25°C. The mixture was shaken for 2 min (at 200 r.p.m) and left to stand for 24 hrs, at different pH using hydrochloric acid, sodium acetate buffer, and sodium hydroxide to cover the pH range 3.0–7.5 (3, 3.6, 4, 5, 6.08, 7.08, and 7.50). In this experiment the pH value does not exceed 7.50 due to the precipitation of lead as lead hydroxide [36].

3.7. Effect of Lead Concentration. This experiment was done as above at only pH 3.0 (optimum value) using sodium acetate buffer but with different lead concentrations (10, 25, 50, 100, 150, 200, 250, 300, 400, 500, and 1000 ppm).

3.8. Effect of Residence Time. This experiment was done at 25°C with 25 mL lead (200 ppm) and 0.3 g algae (E) in 50 mL Erlenmeyer flasks at pH 3.0 (using sodium acetate buffer) and shaken at 200 r.p.m for 2 minutes with variable standing time (2, 5, 10, 15, 20, 30, 45, 60, 90, and 120 minutes) [36].

3.9. Swelling Characteristics. Swelling characteristics (distention index, swelling ratio, and volume of absorbed solvent) were obtained from the weights and volumes of dry and swollen particles for algae alone (E), algae residue after reflux (ER), algae modified with silicates (EM), and Swedish wood sawdust (SWS). Dry particles were swollen in cylinders with deionized water and degassed under lower pressure. The volume was measured after periodically till two hours [27].

The distention index (DI) was calculated from the ratio V_s/W_D, where V_s is the volume of the particles after swelling and W_D is the weight of the dry particles. The swelling ratio is W_s/W_D, where W_s is the weight of swollen particles. The volume of absorbed solvent (V_{AS}) was calculated from the ratio $(W_s - W_D)/W_D$.

3.10. Procedure for Column Utilization (Breakthrough Curve). The column used has a diameter of 2 cm and a length of

Table 4: Thermal analysis of algae materials: *Enteromorpha* algae (E), *Enteromorpha* algae with adsorbed Lead (E-Pb), and *Enteromorpha* algae modified with sodium silicates (EM).

Sample	Peak (°C) (temperature range)	% Experimental mass loss	Enthalpy (J/g)
(E)	84.10	12.77	238.50
	174.82	3.34	8.22
	215.12	33.88	−17.31
	231.41	—	23.98
	442.21	16.22	541.42
	726.16	20.91	254.63
(E-Pb)	73.61	17.83	234.55
	169.58	—	19.72
	221.14	39.14	−30.03
	428.15	15.57	−7.14
	656.85	21.91	161.65
(EM)	(25–180)	4.0	—
	(180.0–750.0)	13.0	41.59
	290.56	—	—
	756.85	2.0	13.43

44 cm. It was packed uniformly with 1.0 g of green *Enteromorpha* algae powder (E) or *Enteromorpha* algae powder after reflux (ER) or modified *Enteromorpha* algae with sodium silicates (EM). The column dead volume was 30 mL. The lead solution (200 ppm) at pH 3.0 was drained through the column at a constant rate 2.5 mL/min in the case of (E) and (ER). The lead solution (1000 ppm) was eluted at a rate of 2.0 mL/min in the case of column packed with (EM). Collected aliquots of similar volume were collected from the column and analyzed for lead [37].

4. Result and Discussion

4.1. Infrared Spectroscopy. FTIR spectra of *Enteromorpha* algae (E) show strong stretch at 3395 $\mathrm{cm^{-1}}$ due to –NH of amino group, strong stretch at 1646.5 $\mathrm{cm^{-1}}$ and a weaker ones at 1436 $\mathrm{cm^{-1}}$ due to carboxylate group, and strong bending vibration at 1105 and 1158 $\mathrm{cm^{-1}}$ due to C–O of ether and alcoholic group, respectively [38]. FTIR spectra of *Enteromorpha* algae with adsorbed lead also show many peaks similar to free algae spectra. However the peak due to –NH stretch has been shifted to lower wave number 3291 $\mathrm{cm^{-1}}$ indicating involvement of binding of lead to –NH group. The bands due to carboxylate group show a little shift to higher wave number (1651 $\mathrm{cm^{-1}}$) compared to free algae peak, indicating the involvement of carboxylate and ester groups in the binding with lead.

FTIR of (EM) is similar to that of (E) but with increasing peak strength at 1100 $\mathrm{cm^{-1}}$ and at 3437 $\mathrm{cm^{-1}}$ due to Si–O–Si and SiO–H stretching vibrations, while FTIR of (ER) has no noticeable difference from that of (E).

4.2. Thermal Analysis. Thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) curves were recorded for algae materials, which were heated to 800°C under N_2, where all relevant weight loss was complete. The results of thermal analysis (% mass loss at each temperature and associated enthalpy) of free *Enteromorpha* algae (E) and algae with adsorbed lead (E-Pb) and modified algae with sodium silicates (EM) are listed in Table 4. The two TGA and dTG curves reveal difference between loss in weight with temperatures for both materials (E) and (E-Pb), with greatest difference occurring about 220°C where free algae show a loss of 33.88% at 215.12°C (exothermic) and 231.41°C (endothermic) while algae with biosorbed lead show a loss of 39.14% at 221.14°C (exothermic). The 5.26% difference in mass loss between the two could be attributed to the adsorbed amount of lead. This peak is shifted to higher temperature (290.56°C) in the case of (EM) with endothermic peak, indicating chemical binding of algae to sodium silicates. The amount of bonded algae is about 19.0%.

The sharp decrease at 726.16°C (20.91%) for (E), 656.85°C (21.91%) for (E-Pb), and 756.85°C for (EM), respectively, is associated with high endothermic heat energy attributed to the conversion of $CaCO_3$(s) to CaO(s) and CO_2(g). The weight loss occurring before this step (50 to 600°C) is due to organic materials volatilization and decomposition.

4.3. Batch Studies

4.3.1. Effect of Mass of Algae. The effect of mass of algae on metal uptake was studied in batch system for initial lead concentration (300 ppm) and contact time (24 h) in water bath at 25°C. There was a steep increase in % extraction of lead as the mass of algae increased from 0.05 g to 0.30 g (from 53% to 82%). For biomass weight greater than 0.30 g there were no significant increases in the metal uptake. Thus the optimum mass of algae (E) and (ER) was 0.30 g corresponding to a maximum % metal uptake for a volume reaction of 25 mL

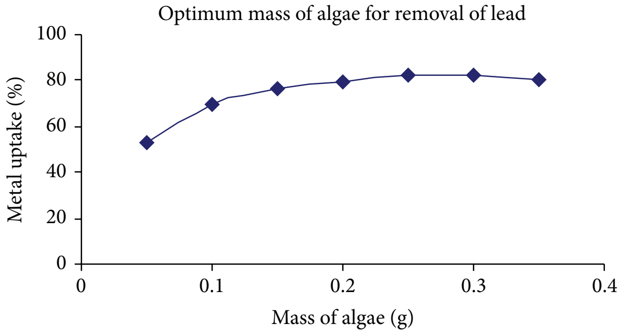

FIGURE 1: Effect of mass of *Enteromorpha* algae on metal uptake for a 25 mL lead solution (300 ppm).

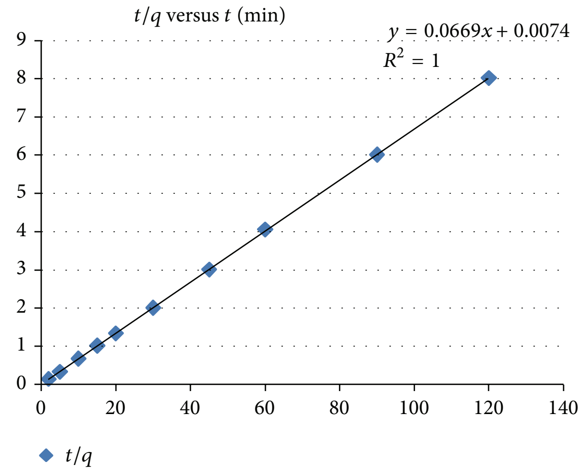

FIGURE 2: Pseudosecond order kinetics for adsorption of lead onto *Enteromorpha* algae (E) at 25°C.

lead (300 ppm), Figure 1, while the optimum mass and reaction volume are 0.1 g and 100 mL for (EM).

4.3.2. pH Effect. Experiments concerning the effect of pH on the sorption were carried out within a pH range that avoids the metal precipitation as hydroxide. The standard lead solution (300 ppm) was prepared in acetate buffer to cover a pH range 3.0–7.5. The data of metal uptake by 0.30 g algae in a 25 mL standard lead solution was studied for different pH values. It was found that lead shows maximum binding to the biomass at an optimum pH 3.0 with a metal uptake of 86.62% and capacity of 21.55 mg/g. There is no change in metal uptake for pH values between 3.6 and 7.5.

4.3.3. Effect of Lead Concentration. The experimental effect of lead concentration on metal uptake was done in batch system concentrations of 0.3 gm at optimum pH 3.0 (using sodium acetate buffer) for a residence time of 24 hrs and different lead concentrations in the range (10–1000 ppm). There was a sharp increase in adsorption as lead concentration increases from 10 to 150 ppm and reaches a maximum at 200 ppm lead with a % metal uptake of 95.50% and a metal uptake capacity q of 15.29 mg/g algae. For lead solution greater than 200 ppm, the algae become saturated and a decrease in % uptake was noticed. Thus the optimum concentration was found to be 200 ppm.

4.3.4. Effect of Residence Time. Previous work showed that sorption of heavy metal ions by lived algae followed a two-step mechanism where the metal ion was physico/chemically uptaken onto the surface of the algae before being taken up biologically into the cell. The first step, known as a passive transport, took place quite rapidly, that is, within 20–30 min, whilst the second biological step or active transport could take much longer time to complete. In this case, since the algae were dried and biological functions were no longer active, the sorption could only take place on the surface of the cell. Therefore the sorption equilibrium took place quickly within 20 min and no further sorption was observed thereafter [39, 40].

The effect of residence time on metal uptake was studied with 0.30 g algae in 25 mL lead solution 200 (ppm) at optimum pH 3.0 using sodium acetate buffer and variable residence time (2–120 min), in which each flask was periodically shaken at 200 r.p.m for 2 min. This experiment shows that algae have bound most of the metal after 20 min and that equilibrium was reached after maximum metal uptake 88.94% (capacity 14.49 mg/g). This result is in parallel with those previously obtained with different algae and fungi for heavy metal uptake [37].

The linear equation for pseudosecond order model [41] is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 (q_e)^2} + \frac{t}{q_e}, \qquad (1)$$

where q_e and q_t in mg/g are the amount of lead adsorbed at equilibrium and at time t, respectively. k_2 (g·mg^{-1}·min^{-1}) is the rate constant of pseudosecond order adsorption. The plot of t/q_t versus t (min) gave a linear relationship from which q_e was determined from the slope and k_2 from the intercept of the plot, Figure 2. The values of k_2, q_e, and R^2 are 0.605, 14.95, and 1.0, respectively. $R^2 = 1.0$ for the plot clearly indicates that adsorption kinetics is best described as pseudosecond order.

4.3.5. Swelling Behavior. The volume of swollen particles increased during the first 20 minutes and then it remained constant during 2 hours. The values of DI, Q, and V_{AS} of the biomass particles are presented in Table 5. The values for algae modified with silicates (EM) and algae after reflux (ER) indicate an improvement of stability and mechanical properties of the biomass and better flow rate [27].

4.3.6. Adsorption Isotherm Calculations. Adsorption is usually modeled by isotherms which relate the relative concentrations of solute adsorbed to the solid (Q_e) and in solution (C_e). The equilibrium data were analyzed using most commonly used nonlinear isotherms equations: Langmuir, Freundlich, Redlich-Peterson, Temkin, Elovich, and Dubinin-Radushkevich models, Table 1, Figure 3 [31–33].

Table 5: Swelling characteristics of different algae biomass.

Type of biomass	Particle size (mesh)	W_D (g)	W_s (g)	Q	V_s cm^3	DI cm^3/g	V_{AS}
Enteromorpha algae (E)	0.5	1.442	10.41	7.219	10	6.934	6.219
Enteromorpha algae after reflux (ER)	0.5	1.442	6.876	4.775	7	4.166	3.775
Enteromorpha algae modified with silicates (EM)	0.5	4.320	11.54	3.687	10.5	2.430	1.671
Swedish wood sawdust (SWS)	0.5	1.442	8.92	6.185	10	6.935	5.185

Table 6: Results of nonlinear approach of Langmuir, Freundlich, Temkin, Elovich, Redlich-Peterson, and Dubinin-Radushkevich isotherm constants for the adsorption of lead at 25°C onto (a) raw *Enteromorpha* (E); (b) *Enteromorpha* modified with sodium silicates (EM).

(a)

Sorbent (E)								
Langmuir			Freundlich			Temkin		
Q^0 calc (mg/g)	K_L (L/mg)	R^2	K_F (L/g)	n	R^2	B_T (J/mol)	K_T (L/mg)	R^2
83.82	0.0105	0.879	0.3411	0.8576	0.9593	14.342	0.143	0.8562
χ^2	SSE		χ^2	SSE		χ^2	SSE	
20.66	165.29		6.970	55.76		24.651	197.21	
Elovich			Redlich-Peterson			Dubinin-Radushkevich		
Q_E (mg/g)	K_E (L/mg)	R^2	A_{RP} $(\text{L/mg})^{\beta}$	β_{RP}	K_{RP} (L/g)	Q_m (mg/g)	β $(\text{mol}^2/\text{J}^2)$	E (J/mol)
42.8513	−0.00786	0.52311	1.3644	0.5525	0.1754	37.92	-8×10^{-5}	79.06
χ^2	SSE		R^2	χ^2	SSE	R^2	χ^2	SSE
0.02838	0.2270		0.8160	36.16	253.14	0.9532	8.0182	64.15

(b)

Sorbent (EM)								
Langmuir			Freundlich			Temkin		
Q^0 calc (mg/g)	K_L (L/mg)	R^2	K_F (L/mg)	n	R^2	B_T (J/mol)	K_T (L/mg)	R^2
1433.46	0.00157	0.9872	6.7298	1.3555	0.9925	186.746	0.0373	0.9260
χ^2	SSE		χ^2	SSE		χ^2	SSE	
415.336	3322.7		241.09	1928.74		2392	19136	
Elovich			Redlich-Peterson			Dubinin-Radushkevich		
Q_E (mg/g)	K_E (L/mg)	R^2	A_{RP} $(\text{L/mg})^{\beta}$	β_{RP}	K_{RP} (L/g)	Q_m (mg/L)	β $(\text{mol}^2/\text{kj}^2)$	E (J/mol)
754.41	0.00366	0.7515	10.4550	0.313	0.9915	557.44	−0.00244	14.32
χ^2	SSE		R^2	χ^2	SSE	χ^2	SSE	R^2
0.0607	0.4853		0.9924	282.1	1974.5	5440.24	43522	0.8317

The data is well fitted with *Langmuir model* indicating the presence of chemical monolayer adsorption onto a surface with a finite number of similar active sites. The calculated maximum sorbate uptake Q^0 (mg/g) is 83.82 for nonmodified algae (E) and 1433.46 mg/g for algae modified with sodium silicates (EM). The K_L and R_L values are also calculated where $R_L = 1/(1 + K_L C_0)$ and K_L is a coefficient related to the affinity between the sorbent and sorbate. C_0 is the maximum initial concentration. The R_L value implies that adsorption to be unfavorable for ($R_L > 1$), linear for ($R_L = 1$), and favorable for ($O < R_L < 1$), or irreversible ($R_L = 0$). Adsorption of lead is favorable since the obtained value of R_L for the materials (E) is (0.0872) and for (EM) is (0.389), Table 6. The ability of *Freundlich model* was examined. It is the best suited model in our study indicating that sorption occurs onto a heterogeneous surface. It was also reported that Freundlich model was applicable in adsorption studies of lead with *Enteromorpha* algae [37]. It is of importance to realize that the values of $1/n$ greater than unity in the case of (E) algae indicate formation of multilayer of metal on the surface of biomass, Table 6.

Redlich-Peterson model is also suitable model, where A_{RP}, K_{RP}, and β are parameters to be estimated, Table 1. The obtained β values lie in the middle between 0 and 1 indicating that adsorption includes both Freundlich and Langmuir features, Table 6. *Temkin* model explains sorbent/sorbate interactions in relation to heat of adsorption, where B_T is a factor related to the heat of adsorption and K_T is Temkin equilibrium constant (L/mg). The B_T for (EM) 186.75 J/mol is much greater than 14.34 J/mol for (E), Tables 1 and 6.

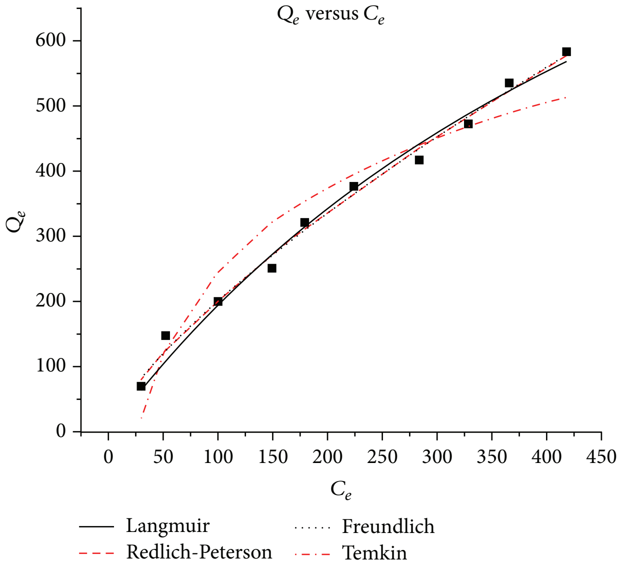

FIGURE 3: The curves of the four nonlinear isotherm models with the experimental data at $t = 25^{\circ}$C, for adsorption of lead onto *Enteromorpha* modified with sodium silicates (EM).

Elovich model deals with multilayer adsorption, based on a kinetic principle that adsorption site increase exponentially with adsorption, where K_E is Elovich equilibrium constant and Q_E is Elovich maximum adsorption capacity. The low R^2 value indicates than Elovich model is not applicable to lead adsorption onto (E) and (EM) in Tables 1 and 6.

Dubinin-Radushkevich isotherm, where Q_m is the maximum amount of ions sorbed onto algae (mg/g), β (mol^2/kJ^2) is a constant related to the sorption energy $E = 1/\sqrt{-2\beta}$ in kJ/mol, Table 1. The obtained values of E 14.32 kJ/mol for modified algae (EM) and 79.06 kJ/mol for nonmodified algae (E) are greater than 8 kJ/mol, indicating that the adsorption process is chemical in nature, Table 6.

4.3.7. Comparative with Literatures. However, the results obtained for metal uptake (q) of lead cations using dead algae *E. intestinalis* (E) in agitation experiments at optimum conditions show a medium uptake of *E. intestinalis* for these cations in comparison to the other published data, Table 7 [43–47, 49–52]. However, the highest adsorption capacity 1433 mg/g was obtained for *Enteromorpha* algae modified with sodium silicates (EM) indicating the presence of strong electrostatic force of attraction between lead ions and binding-sites on the surface of the silicates-algae modified material. This indicates that silicates support greatly improves the adsorption capacity compared to nonmodified algae.

4.4. Column Studies. The batch experiments have demonstrated the ability of green algae *Enteromorpha* to bind lead ions from solution. A practical approach to decontaminate metal-polluted water with the biomass would be to pass the contaminated water through a column contain the biomass. This experiment was performed using different biomass in which the biomass was packed in the column by rewetting it in deionized water.

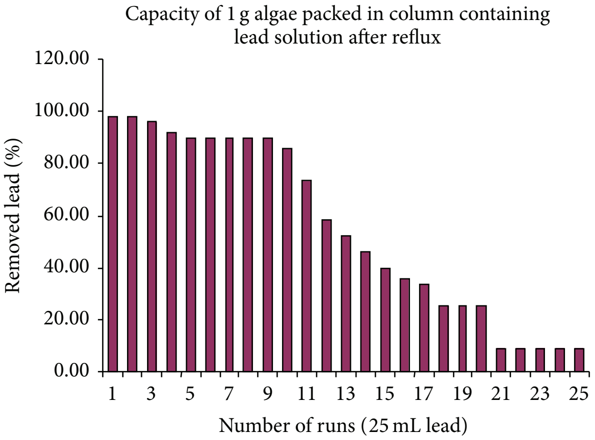

FIGURE 4: Saturation of the column after passage of 25 aliquots of 25 mL lead (200 ppm) for a column filled with 1 g *Enteromorpha* algae residue after reflux (ER).

4.4.1. Column Capacity. The breakthrough curve of lead was determined using column packed uniformly with 1.0 g of *Enteromorpha* algae materials (E), (ER), or (EM). Aliquots were collected from the column and analyzed for lead till reaching saturation, Figure 4. The column capacity q_e was calculated from the area A under the breakthrough curve (Figure 5) according to the equations presented in Table 8.

(i) The experiment using column filled with (E) showed that 67.4 mg/g of lead was removed after passage of 525 mL solutions of lead (200 ppm) and that the percent removal is 64.2%. This result is in parallel with those recently obtained with different microalgae *Chlamydomonas reinhardtii* for heavy metal uptake [45].

(ii) In the case of column filled with (ER), saturation occurs after passage of 625 mL of lead (200 ppm). The column capacity and percent removal are 66.3 mg/g and 53.04%, respectively.

(iii) Column studies using sodium silicates modified algae (EM) indicate higher adsorption capacity and % removal (230.20 mg/g and 60.6%, resp.). Saturation occurred after passage of 380 mL of lead (1000 ppm).

4.4.2. Column Models. Three kinetic coulmn models (Thomas, Yoon-nelson, and Yan and Clark) (Table 2) were used to analyze column performance using the data for the adsorption of lead (1000 ppm) with 1 gm (EM) materials.

Thomas model assumes negligible axial dispersion in the column adsorption since the rate driving force obeys the second order reversible reaction kinetics. K_{Th} (mL/mg·min) is Thomas rate constant, q_T (mg/g) is the equilibrium adsorption capacity, m (g) is the amount of adsorbent in the column, Q (mL/min) is the volumetric flow rate, and C_o (mg/L) is the initial concentration of the adsorbate in the feed solution [48].

Yoon-Nelson developed a model based on the assumption that the rate of decrease in the probability of adsorption for

TABLE 7: Lead uptake: optimum results obtained from batch experiments, comparison with literature.

Name of algae—color	pH	Contact time (min)	Metal uptake (q) mg/g	Reference
E. intestinalis (E)—green	3.0	5–20	83.82	Present work
E. intestinalis modified with sodium silicates (EM)—green	7.0	60	1433.46	Present work
Caulerpa lentillifera—green	5.0	10–20	28.71	[43]
Cystoseira baccata—brown	4.5	—	186	[44]
Chlamydomonas reinhardtii—green	5.0	60	96.30	[45]
Sargassum sp.—brown	5.0	60	183.37	[46]
Ulva lactuca—green	4-5	5–30	126.5	[47]
Enteromorpha spp. (living)—green	—	0–5	20.72	[28]
Anabaena sphaerica—blue green	3.0	90	121.95	[52]
Mixture of Ulva lactuca, Jania Rubens, and Sargassum (green, red, and brown)	4.0	120	281.80	[36]
Ecklonia radiata—brown	5.0	10	282	[49]
Codiumtaylori—green	3.5	—	130.00	[50]
Sargassum natans—brown	3.5	—	220.00	[51]

TABLE 8: Column adsorption capacity and parameters calculation of a column loaded with (a) 1 gm of (E), (b) 1 gm of (ER), eluted with MG 200 ppm at a flow rate Q of 2.5 mL/min, and (c) with 1 gm (EM) eluted with MG 1000 ppm at Q = 2.0 mL/min.

Parameter	$A =$	$q_{\text{total}} =$	$m_{\text{total}} =$	% total removal =	$q_e =$	$C_e =$
Equation	$\int_{t=o}^{t=t_{\text{total}}} C_{\text{ads}}dt$	$\frac{QA}{1000}$	$\frac{C_oQt_{\text{total}}}{1000}$	$\frac{q_{\text{total}}}{m_{\text{total}}} \times 100$	$\frac{q_{\text{tot}}}{m}$	$C_o - \frac{A}{t_{\text{total}}}$
Unit	mg·min/L	mg	mg	%	mg/g	mg/L
(a) (E)	26948	67.37	105	64.16	67.37	71.68
(b) (ER)	26520	66.30	125	53.04	66.30	93.92
(c) (EM)	115095	230.20	380	60.58	230.19	394.24

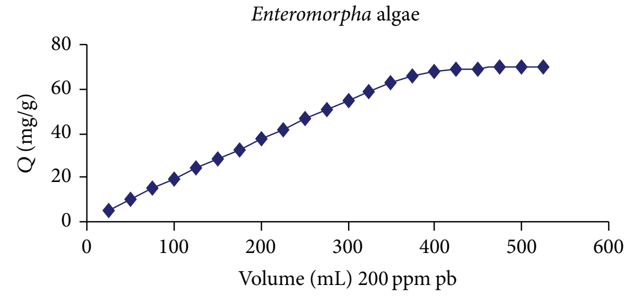

FIGURE 5: Breakthrough curve: capacity of 1 gram of *Enteromorpha* algae (E) at pH 3 and flow rate 2.5 mL/min with 200 ppm lead solution (particle size 0.5 mesh).

each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. K_{YN} (min^{-1}) is the rate constant and τ_{YN} (min) is the time required for 50% adsorbate breakthrough [53].

Yan et al. model is described in Table 2, where K_Y (L/min·mg) is the kinetic rate constant for Yan et al. model and q_Y (mg/g) is the maximum adsorption capacity of adsorbent estimated by Yan model [42].

Thomas, Yoon-Nelson, and Yan and Clark models were applied using linear and nonlinear regression statistical techniques according to the equations listed in Table 2. The values of the maximum capacity q, the rate constant K, and error functions for each model are presented in Table 9. The nonlinear methods having higher R^2 values would be more appropriate techniques in predicting the adsorption column models, for nonlinear methods.

Comparing the values of χ^2, SSE, and R^2, we find that Thomas and Yoon-Nelson models describe better the adsorption behavior than Yan model for column packed with (E) and (ER). However, Yan model was found the best for column packed with (EM). The predicted capacity value is $q_T = q_{\text{YN}} = 76.2$ mg/g for column (E) and =71.1 mg/g in the case of column (ER), while the capacity q_Y is equal to 982.5 for column (EM). Again algae anchoring onto silicates improved the performance capacity of column more than 10 times compared to nonmodified algae materials. Application of Yoon-Nelson model indicated that τ the half-life of adsorbate breakthrough is equal to 152.35 min and 142.10 min for column (E) and (ER), respectively using nonlinear approach, Table 9.

5. Conclusion

(i) The amount of lead uptake increased steeply by increasing the weight of *Enteromorpha intestinalis* algae and reached equilibrium state after 20 minutes in batch experiment with g at 25°C. The algae show also high adsorption of lead at optimum conditions

Table 9: Statistical evaluation of parameters of a column loaded with 1 gm (EM) and eluted with 1000 ppm lead using linear and nonlinear fit of breakthrough data to Thomas, Yoon-nelson, and Yan and Clark kinetic models.

	Adsorbent	Linear approach				Nonlinear approach				
		K_{Th} mL·(mg·min)$^{-1}$	q_T (mg·g^{-1})	R^2	SD	K_{Th} mL·(mg·min)$^{-1}$	q_T (mg·g^{-1})	R^2	SSE	χ^2
Thomas model	(E)	1.72×10^{-4}	69.25	0.8305	0.8988	3.1×10^{-4}	76.18	0.9720	0.07145	3.8×10^{-3}
	(ER)	1.32×10^{-4}	72.14	0.9677	0.3529	1.4×10^{-4}	71.08	0.9827	0.0496	0.0022
	(EM)	7.15×10^{-6}	375.9	0.6994	0.2715	6.0×10^{-6}	396.78	0.7422	0.0397	0.0023
		K_{YN} (min^{-1})	τ_{YN} (min) q_{YN} (mg·g^{-1})	R^2	SD	K_{YN} (min^{-1})	τ_{YN} (min) q_{YN} (mg·g^{-1})	R^2	SSE	χ^2
Yoon-Nelson model	(E)	0.0344	138.50 69.26	0.8305	0.8988	0.0615	152.35 76.18	0.9720	0.07145	0.0038
	(ER)	0.0264	144.18 72.10	0.9651	0.3529	0.0280	142.10 71.05	0.9819	0.04839	0.0022
	(EM)	0.0072	187.96 375.92	0.6994	0.2715	0.0061	198.40 396.80	0.7422	0.03969	0.0023
		K_Y L·(mg·min)$^{-1}$	q_Y (mg·g^{-1})	R^2	χ^2	K_Y L·(mg·min)$^{-1}$	q_Y (mg·g^{-1})	R^2	SSE	χ^2
Yan's model	(E)	4.0×10^{-5}	21.83	0.6412	1.709	1.2×10^{-4}	7.58	0.9658	0.0874	0.0046
	(ER)	3.3×10^{-5}	23.73	0.8525	0.0526	5.0×10^{-5}	17.16	0.9818	0.0484	0.0022
	(EM)	1.5×10^{-6}	817.34	0.9365	0.0156	1.0×10^{-6}	982.46	0.9387	0.0094	5.5×10^{-4}

adsorbent (0.3 g), pH (3.0), and lead concentration (200 ppm) and followed Freundlich model adsorption isotherm. The Langmuir adsorption capacity of lead was 83.8 mg/g using nonmodified algae (E) and 1433.5 mg/g using algae modified with silicates (EM). Comparative study of thermal analysis and FTIR of algae materials clearly proves the presence of adsorbed lead in the algae materials.

(ii) Breakthrough area method indicated that 64.2% and 53.0% of lead can be removed from 200 ppm eluting solution using column filled with (E) and algae after reflux (ER), respectively, while, for column filled with sodium silicates modified algae (EM), the % removal was 60.6% of lead from 1000 ppm. Thomas and Yoon-Nelson models describe better the adsorption behavior than Yan model for column packed with (E) and (ER). The predicted capacity value was 76.2 mg/g for column (E) and 71.1 mg/g in the case of column (ER). However, Yan model was the best for column packed with (EM), with a capacity 982.5 mg/g, indicating that sodium silicates modification of algae improved the performance capacity of column. Moreover, (ER) and (EM) show less swelling and better flow rate control than (E).

(iii) The calculation of various error functions proved to be valuable for predicting the best adsorption isotherms, kinetics, and column models. The nonlinear methods would be more appropriate techniques in predicting the best adsorption models.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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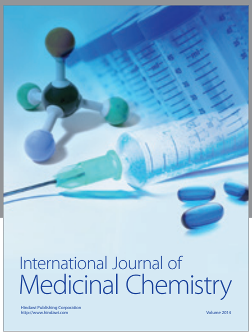
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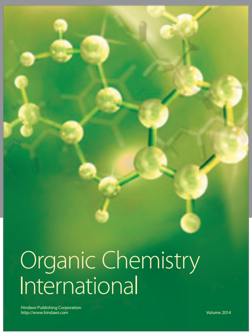
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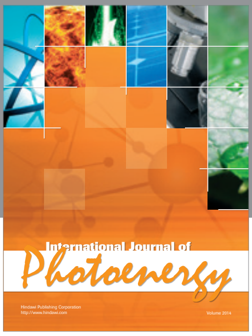
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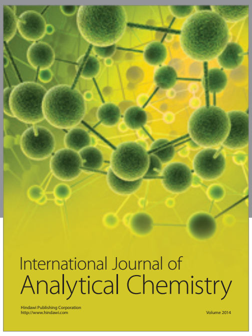
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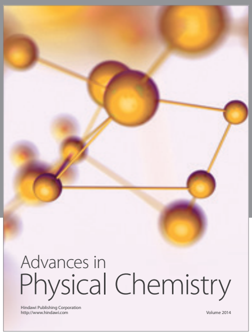
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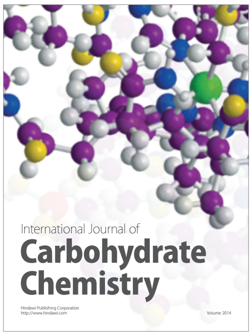
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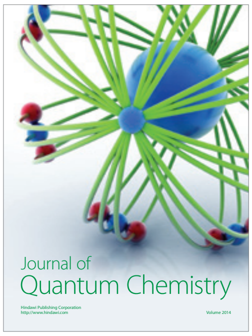
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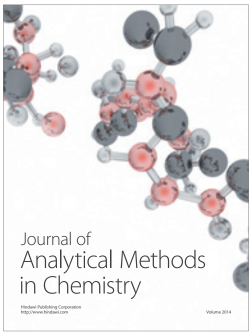
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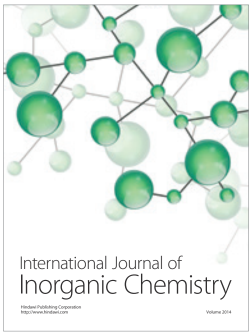
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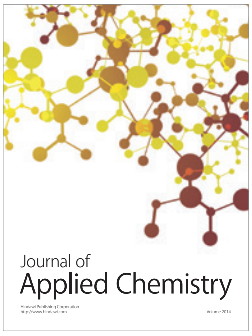
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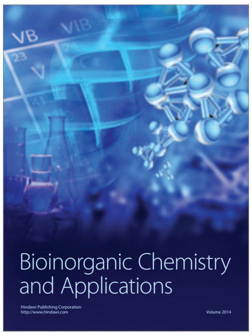
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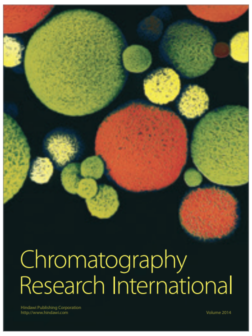
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