

## A kinetic study of metal ion binding by biomass immobilized in polymers

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### Abstract

A kinetic study of metal binding by various types of nonliving, immobilized biomass was carried out. Biomaterial studied included lichens, water hyacinth root, and some marine algae. All of these organisms have previously been shown to be strong sorbers of metal ions. Biomass was immobilized in polymeric matrix such as polysulfone, polyphenylene sulfide, and styrene-divinylbenzene copolymers.

The ability of nonliving biomass to sorb metal ions when immobilized in a polymeric matrix was evaluated. First-order rate constants indicate that copper and lead ion uptake on polysulfone-biomass systems are ten times larger than on the polysulfone only. The activation energy of copper ion sorption at pH 5.5 is lower than the activation energy at pH 4.7, an indication that copper is activated more easily and sorbs greater at pH 5.5. The activation energies of each metal-biomass interaction were calculated by using the Langmuir adsorption model; it was found that the activation energy is three times higher for copper sorption on the polysulfone matrix only without incorporation of algal biomass as compared to the sorption on polymer-biomass matrix. This shows that the sorption process is less efficient without algae.

Kinetic plots for both copper and lead sorption demonstrate that single sorption sites are responsible for binding. The equilibrium constants for the sorptions at different temperatures were evaluated as well as the rate constants for metal binding processes. As temperature increases, the equilibrium constant decreases for all sorptions. The most suitable conditions for polymer-biomass matrix for the maximum sorption of each metal ion were evaluated. This study indicates that algal biomass can be immobilized in a polymer matrix and packed into columns for a very efficient use as an ion exchanger.

*Keywords:* Polymer; Kinetics; Biomass; Langmuir adsorption

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## 1. Introduction

Researchers have recognized that immobilizing nonliving biomass in a granular or polymeric matrix may improve biomass performance and facilitate separation of biomass from solution [1–4]. Previous studies demonstrated that porous polysulfone beads containing thermally killed biomass removed metal contaminants from a variety of mining and mineral processing wastewater [5, 6]. For the evaluation of polymeric supports for immobilizing biomass to prepare sorbent materials for metal ions, polysulfone resin was used with biomass [7].

Several different configurations have been proposed for using beads in chemical processing. For continuous operation the most convenient configuration is that of a packed column, such as that used for ion exchange. The removal of metal ions by biomass is similar to that of ion exchange. There are several publications describing ion exchange from dilute multi-component mixtures [8, 9].

The kinetics of metal sorption on cell walls can be studied by using the Langmuir adsorption equation which can be obtained by assuming that  $\theta$  = fraction occupied by sorbed molecules,  $1 - \theta$  = fraction not occupied,  $k_a P(1 - \theta)$  = rate of sorption, and  $k_d$  = rate constant for desorption. At steady state, the equilibrium rate of sorption = rate of desorption; thus,  $k_a P(1 - \theta) = k_d \theta$ , which leads to  $\theta = k_a P / k_d + k_a P = bP / 1 + bP$ , where  $k_d$  is the rate of desorption. By rearrangement, the equation

$$1/\theta = 1 + 1/bP \quad (1)$$

is obtained, where  $b$  is the sorption coefficient and is equal to  $k_a/k_d$ .

For the sorption of each metal ion,  $1/\theta$  will be plotted against  $1/P$ , after replacing  $\theta$  with  $V$ , which is mg of metal sorbed per gram of dry biomass; and replacing  $P$  with  $c$ , which is the concentration of metal available (mg/l). The slope will be  $1/b$ , according to the above equation which gives the sorption coefficient. Since the sorption coefficient is directly proportional to the sorption rate constant,  $k_a$ , when  $\ln b$  is plotted against  $1/T$ , where  $T$  is the temperature, the slope of each line for each metal sorption must allow a calculation of the activation energy,  $E_a$ , of sorption. The activation energy of metal binding can be calculated also by another method. If the concentration  $A$  (mg of metal sorbed per gram of dry biomass) is plotted against time ( $t$ ), each curve reaches a steady value ( $A_\infty$ ) at saturation points. When  $\ln A$  values are plotted against time ( $t$ ), the first-order rate constants can be calculated from the initial slopes. After calculating the rate constants at different temperatures,  $\ln k$  vs.  $1/T$  will be plotted, and activation energies can be calculated from the slopes.

These calculations will be applied to different solid sorbents such as silica, polysulfone, polyphenylene sulfide resins, and styrene divinylbenzene copolymer, prepared with various types of biomass. These can also be extended to include other materials such as polyamide and phenoxy resins to obtain the most ideal substrate for immobilizing biomass.

Langmuir adsorption assumes that the sorption sites are equivalent and that the binding of a particular species is independent of occupied neighboring sites [10]. Consequently, the binding reaction may be represented as a single equilibrium

expression with the transposed Langmuir isotherm expressed by [10, 11].

$$1/a = (1/a_m K) (1/c) + 1/a_m, \quad (2)$$

where  $a$  is milligrams of metal adsorbed per gram of dry biomass,  $K$  is the equilibrium constant,  $c$  is the equilibrium concentration of available metal (mg/l), and  $a_m$  is milligrams of metal sorbed at saturation. If a single sorption site is responsible for binding, a plot of  $1/a$  vs.  $1/c$  should yield a straight line with a slope of  $1/a_m K$  and an intercept of  $1/a_m$  since  $a_m$  can easily be evaluated from the  $y$  intercept. From the slopes of these plots the equilibrium constant values can be calculated for each isotherm. The change of equilibrium constant values with temperatures and pH for all the metals sorbed can be plotted.

Langmuir plots can be drawn for some elements such as copper and lead, including both pH-dependent and pH-independent metals. If the plots are not linear, with two different slopes, it will indicate that at least two different sorption mechanisms are involved, and that a single formation constant cannot describe the biomass/metal binding over the concentration range of these studies.

## 2. Experimental

### 2.1. Materials and instruments

*Polysulfone*: It was a product of Aldrich Chemical Co., Milwaukee, WI (catalog no. 18244-3) with an average molecular weight of 30 000.

*Sargassum (S. fluitans)*: A large quantity of *S. fluitans* was collected along the Louisiana Gulf Coast near Cameron, Louisiana. The seaweed was washed thoroughly in the laboratory, first with tap water to remove dirt and debris, then with doubly deionized water. The seaweed was allowed to air dry and then was ground to a fine powder which was sieved through a set of standard testing sieves into different mesh sizes. For the preparation of biosorbents the finest sized powder (smaller than 250 mesh) was used.

*Styrene*: Styrene monomer (Aldrich Chemical Co.) was inhibited with 10–15 ppm 4-*t*-butylcatechol. It was removed from inhibitor by washing the monomer with 10% aqueous NaOH. The monomer was then washed with distilled water until litmus paper showed that all the base had been removed. A drying agent such as Na<sub>2</sub>SO<sub>4</sub> (100 g/l) was added. After adding about 1 g/l CuCl stabilizer, the monomer was distilled under dry nitrogen at 20–30 °C in vacuum (20 torr).

*Divinylbenzene*: It was a product of Aldrich Chemical Co. and was inhibited with less than 1500 ppm *p-t*-butylcatechol. To remove the inhibitor it was distilled in vacuum at 20 torr between 40 °C and 55 °C.

*Standard Pb solution* (1000 mg/l): It was a product of Baker Chemical Co., Baker Instra-Analyzed Atomic Spectral Standard, Lot 133118.

*Standard Cu solution* (1000 mg/l): It was a product of Fisher Scientific Co., Certified Atomic Absorption Standard.

*Peristaltic pump:* It was a microprocessor pump drive (Cole-Parmer Instrument Co., Chicago, IL, model 7524-10) with a Masterflex pump head.

*Atomic absorption spectrophotometer:* A Perkin-Elmer Model 372 flame atomic absorption spectrophotometer was used for all metal analyses.

*Constant temperature water bath:* A constant temperature water bath was used with a thermoregulator/circulator combination (Fisher Scientific, Model 70 Biotemp immersion circulator).

## 2.2. Procedures

A seaweed alga (*S. fluitans*) was immobilized as nonliving biomass in polysulfone polymer. Biomass powder (10% by weight) was blended into a chloroform solution containing 0.1 kg polysulfone per liter. The solution was then added to an aqueous methanol solution to precipitate the polymer containing encapsulated biomass. After filtering and drying the polymer in a vacuum oven at room temperature, it was ground to a fine powder and screened into selected mesh sizes. A light and porous polymer was obtained when *S. fluitans* biomass was trapped in the polymer matrix. Biomass can be immobilized in polysulfone by applying the procedure of Trujillo et al. [12]: *S. fluitans* blended into a solution containing 0.1 kg polysulfone per liter of *N, N'*-dimethylformamide. Biomass solution was then sprayed into an aqueous solution of precipitating polymer. The obtained polymer beads are stable in strong acid and base solutions.

Styrene-divinylbenzene is another porous polymer that is useful for immobilizing biomass. Styrene-divinylbenzene copolymer is prepared by an emulsion polymerization technique [13]. Biomass is immobilized in the polymer by adding biomaterial to the reaction vessel during the polymerization process. After completion of the reaction, the mixture is poured slowly into a hot aluminum sulfate solution. The precipitated polymer is filtered and washed with hot water to remove emulsifier. The polymer containing biomass is then dried in a vacuum oven, pulverized to a fine powder and sieved into various mesh size ranges.

The binding of metal ions by immobilized biomass can be studied in either the batch or the column mode. In the column mode the sorbent is packed into a small glass or plastic tube, stoppered at each end with glass wool, and kept in a vertical position into a constant temperature bath. The standard metal solution is then pumped through the column to bind metal to sorbent. About 1 m long glass tubing of similar diameter to plastic tubing was fabricated as heating and cooling column and connected to plastic tubing to ensure that the running solution was at the same temperature as the constant temperature bath. After each standard solution was run through, the column was stripped with 1 M nitric acid and 0.05 M ammonium acetate solution at pH 5.5.

The metal solution pumped through the column with a flow rate of 5 ml/min was collected at 2 min intervals in separate plastic bottles. For each 10 ml solution collected the amount of eluted metal ion was determined by flame atomic absorption spectrophotometry.

In the batch mode the particles of biosorbent were mixed with standard metal solutions for selected periods of time; subsequently the samples were filtered or centrifuged to separate the solid and liquid phases. The sorbed metal ions were then extracted from the solid sorbent by mixing with a stripping agent, usually 1 M nitric acid [12–14].

In this study the kinetics of metal binding by biomass was studied only in the column mode using treated and untreated biomaterials.

### 3. Results

The total amount sorbed ( $A$ ) was calculated each time after running copper and lead standard solutions (100 mg/l) at 10 min intervals with a flow rate of 5 ml/min. Total sorption was calculated by the difference between the total introduced and eluted amounts. Table 1 shows these data for copper sorption on polysulfone at 55 °C and pH 5.5. Table 2 shows copper sorption on polysulfone and alga combination at 25 °C and pH 4.7.

Tables 1 and 2 are given at different temperatures to show that even at much lower temperature (25 °C) the polysulfone/alga system sorbed more Cu (4500 µg) than polysulfone alone sorbed (790 µg) at a higher temperature (55 °C). Table 3 shows the Pb sorption results with polysulfone alone at pH 5.5 and a temperature of 50 °C. Table 4 shows the Pb sorption results with polysulfone/alga matrix at the same pH and temperature.

Table 1  
Copper adsorption on polysulfone at pH: 5.5, Cu: 100 mg/l (flow rate: 5 ml/min) at: 55 °C

Time (min)	Total µg introduced (c)	$(1/c) \times 10^{-5}$	Eluted (d) µg (in 10 ml solution)	Adsorbed mg 1000 – (d)	Total adsorbed (A) µg	$\ln A$	$(1/A) \times 10^{-3}$
2	1000	100	727.6	272.4	272.4	5.607	3.671
4	2000	50	949.2	50.8	323.2	5.778	3.094
6	3000	33.4	951.8	48.2	371.4	5.917	2.692
8	4000	25.0	957.6	42.4	413.8	6.025	2.416
10	5000	20.0	955.4	44.6	458.4	6.127	2.182
12	6000	16.7	960.2	39.8	498.2	6.211	2.007
14	7000	14.3	969.9	30.1	528.3	6.269	1.893
16	8000	12.5	968.8	31.2	559.5	6.327	1.787
18	9000	11.1	968.9	31.1	590.6	6.381	1.693
20	10 000	10.1	961.2	38.8	629.4	6.445	1.588
22	11 000	9.1	968.6	31.4	660.8	6.493	1.513
24	12 000	8.3	971.8	28.2	689.0	6.535	1.451
26	13 000	7.7	968.7	31.3	720.3	6.579	1.388
28	14 000	7.1	967.0	33.0	753.3	6.624	1.327
30	15 000	6.7	962.6	37.4	790.7	6.673	1.265

5 ml/min  $\times$  2 min = 10 ml solution (72.76 µg/ml  $\times$  10 ml = 727.6 µg).

Table 2  
Copper adsorption on polysulfone and algae at pH: 4.7, Cu: 100 mg/l (flowrate: 5 ml/min) at: 25 °C

Time (min)	Total $\mu\text{g}$ introduced (c)	$(1/c) \times 10^{-5}$	Eluted (d) $\mu\text{g}$ (in 10 ml solution)	Adsorbed $\mu\text{g}$ 1000-(d)	Total adsorbed (A) $\mu\text{g}$	$\ln A$	$(1/A) \times 10^{-4}$
2	1000	100	0	1000	1000	6.907	10.0
4	2000	50	37	963	1963	7.582	5.09
6	3000	33.4	226	774	2737	7.914	3.65
8	4000	25.0	468	532	3269	8.092	3.06
10	5000	20.0	568	432	3701	8.216	2.70
12	6000	16.7	594	406	4107	8.320	2.43
14	7000	14.3	897	103	4210	8.345	2.36
16	8000	12.5	921	79	4289	8.364	2.33
18	9000	11.1	942	58	4347	8.377	2.30
20	10 000	10.1	961	39	4386	8.386	2.28
22	11 000	9.1	962	38	4424	8.395	2.26
24	12 000	8.3	964	36	4460	8.403	2.24
26	13 000	7.7	988	12	4472	8.405	2.24
28	14 000	7.1	986	14	4486	8.408	2.23
30	15 000	6.7	986	14	4500	8.412	2.22

5 ml/min  $\times$  2 min = 10 ml solution (3.7  $\mu\text{g}/\text{ml} \times 10 \text{ ml} = 37 \mu\text{g}$ ).

Table 3  
Lead adsorption on polysulfone at pH: 5.5, Pb: 100 mg/l (flow rate: 5 ml/min) at: 50 °C

Time (min)	Total $\mu\text{g}$ introduced (c)	$(1/c) \times 10^{-5}$	Eluted (d) $\mu\text{g}$ (in 10 ml solution)	Adsorbed $\mu\text{g}$ 1000-(d)	Total adsorbed (A) $\mu\text{g}$	$\ln A$	$(1/A) \times 10^{-4}$
2	1000	100	280	720	720	6.579	13.88
4	2000	50	690	310	1030	6.937	9.708
6	3000	33.4	770	230	1260	7.138	7.936
8	4000	25.0	860	140	1400	7.244	7.142
10	5000	20.0	950	50	1400	7.279	6.896
12	6000	16.7	980	20	1470	7.293	6.802
14	7000	14.3	990	10	1480	7.249	6.756
16	8000	12.5	990	10	1490	7.206	6.711
18	9000	11.1	990	10	1500	7.313	6.666
20	10 000	10.1	990	10	1510	7.319	6.622
22	11 000	9.1	990	10	1520	7.326	6.578
24	12 000	8.3	990	10	1530	7.333	6.536
26	13 000	7.7	990	10	1540	7.339	6.493
28	14 000	7.1	990	10	1550	7.346	6.451
30	15 000	6.7	990	10	1560	7.352	6.410

5 ml/min  $\times$  2 min = 10 ml solution (28.0  $\mu\text{g}/\text{ml} \times 10 \text{ ml} = 280 \mu\text{g}$ ).

For lead sorption on polysulfone,  $A$  is the total adsorbed amount in micrograms and  $(c)$  is the total micrograms introduced. The plots of  $1/A$  vs.  $1/c$  for the polysulfone matrix incorporated with algae at two different pH values, 4.7 and 5.5, are shown in Fig. 1. Sorptions were carried out at 45 °C. Here, the  $y$  intercept gives  $1/a_m$

Table 4

Lead adsorption on polysulfone and algae at pH: 5.5, Pb: 100 mg/l (flow rate: 5 ml/min) at: 50 °C

Time (min)	Total $\mu\text{g}$ introduced (c)	$(1/c) \times 10^{-5}$	Eluted (d) $\mu\text{g}$ (in 10 ml solution)	Adsorbed $\mu\text{g}$ 1000 – (d)	Total absorbed (A) $\mu\text{g}$	$\ln A$	$(1/A) \times 10^{-4}$
2	1000	100	230	770	770	6.646	12.98
4	2000	50	310	690	1460	7.286	6.85
6	3000	33.4	390	610	2070	7.635	4.83
8	4000	25.0	490	510	2580	7.855	3.87
10	5000	20.0	520	480	3010	8.009	3.32
12	6000	16.7	630	370	3380	8.125	2.96
14	7000	14.3	750	250	3630	8.197	2.75
16	8000	12.5	800	200	3830	8.251	2.61
18	9000	11.1	850	150	3980	8.289	2.51
20	10 000	10.1	870	130	4110	8.321	2.48
22	11 000	9.0	930	70	4180	8.338	2.39
24	12 000	8.3	950	50	4230	8.349	2.36
26	13 000	7.7	980	20	4250	8.355	2.35
28	14 000	7.1	990	10	4260	8.357	2.34
30	15 000	6.7	1000	0	4260	8.357	2.34

values and from the slopes ( $1/a_m \cdot K_{eq}$ ), the equilibrium constants ( $K_{eq}$ ) were calculated. The straight lines obtained indicate that there are single sorption sites responsible for binding. Fig. 2 shows a plot of  $1/A$  vs.  $1/c$  values for polysulfone matrix only. When it was used in the column as a sorber at 25 °C and pH 5.5.

The initial rate constants ( $k$ ) are calculated by taking the initial slopes of the plots drawn between  $\ln A$  and time (Figs. 3–5). Activation energy ( $E_a$ ) is calculated from  $\ln k$  vs.  $1/T$  graphs which are drawn both for polysulfone matrix alone and for polysulfone incorporated with algae. Figs. 6 and 7 show these corresponding plots.

Results are tabulated in Tables 5 and 6 for copper adsorption and in Table 7 for lead sorption. First-order rate plots for copper uptake on lichen was reported with a rate constant  $k = 4.7 \times 10^{-2} \text{ min}^{-1}$  [15, 16]. This is close to the rate constant values obtained in the present work sorption on polysulfone alone (Table 6). In both cases as temperature increased rate constant values ( $k$ ) increased and equilibrium constant values decreased for the sorption of copper ions on polysulfone/alga matrix. This indicates that copper ions were sorbed more easily at pH 5.5. However, the sorption of ions on the polysulfone matrix when was not incorporated with algae gave much higher activation energies, both for copper and lead ion sorptions compared to the areas when it was not incorporated with algae. Table 6 shows the results of copper ion sorption on polysulfone at pH 5.5. This indicates that the sorption without incorporation of biomass with polysulfone matrix is about three times more difficult. Fig. 8 shows the change of equilibrium constants of sorption with temperature for the adsorption of copper ions on polysulfone/alga matrix, both for pH's 4.7 and 5.5. In both cases as temperature increased equilibrium constant values decreased. Fig. 9 shows the same plot when copper was sorbed on polysulfone only.

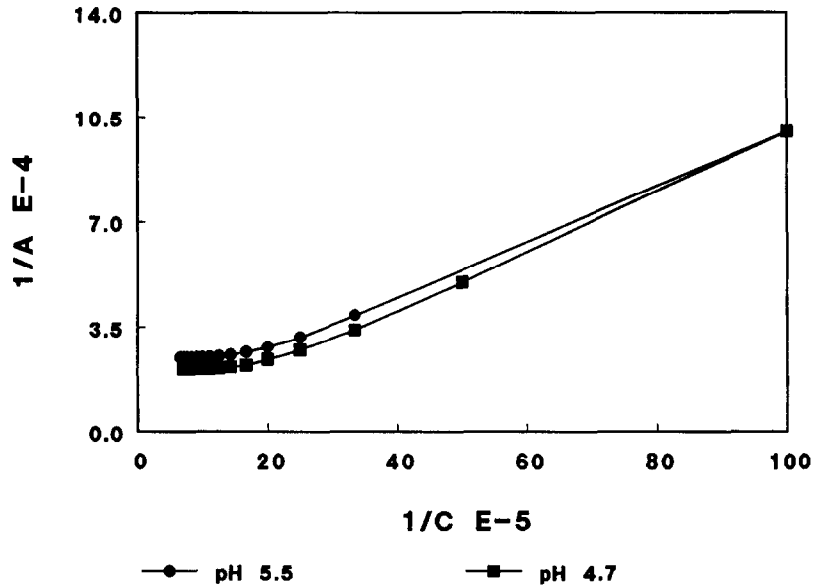


Fig. 1. Langmuir adsorption isotherms for  $1/A$  ( $A = \text{mg of metal sorbed/g dry algae}$ ) versus  $1/c$  ( $c = \text{concentration of available metal in mg/l}$ ) values for copper sorption on polysulfone + algae. Conditions: 100 mg/l Cu; 45 °C; (a) pH 5.5; (b) pH 4.7.

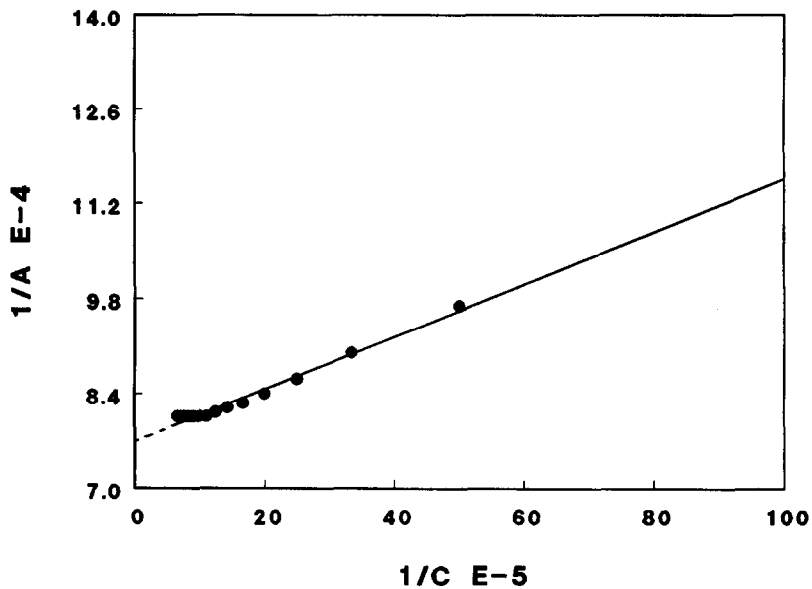


Fig. 2. Langmuir adsorption isotherms for  $1/A$  ( $A = \text{mg metal sorbed/g dry algae}$ ) versus  $1/c$  ( $c = \text{concentration of available metal in mg/l}$ ) values for copper sorption on polysulfone. Conditions: 100 mg/l Cu; 25 °C; pH 5.5.



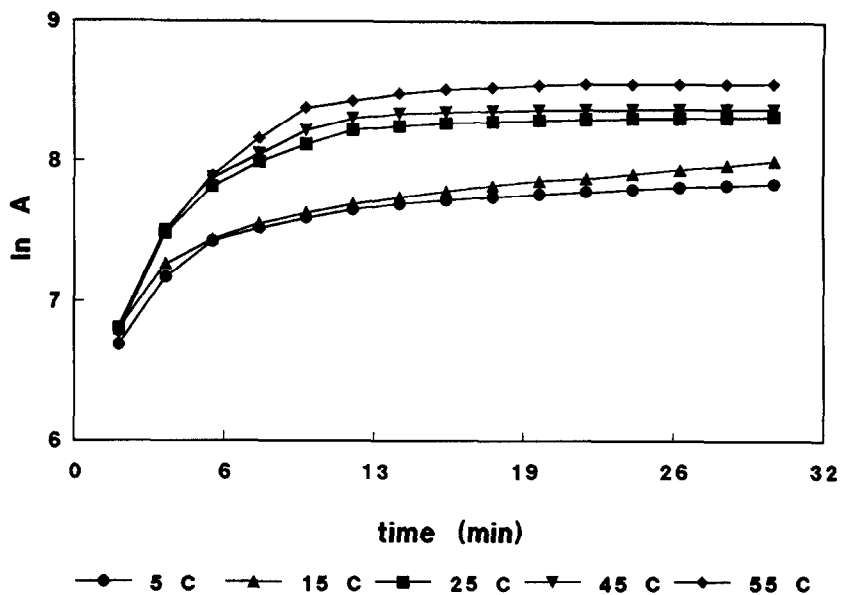


Fig. 3. Kinetics of copper ion sorption on polysulfone + algae at different temperatures. Conditions: 100 mg/l Cu; pH 4.7.

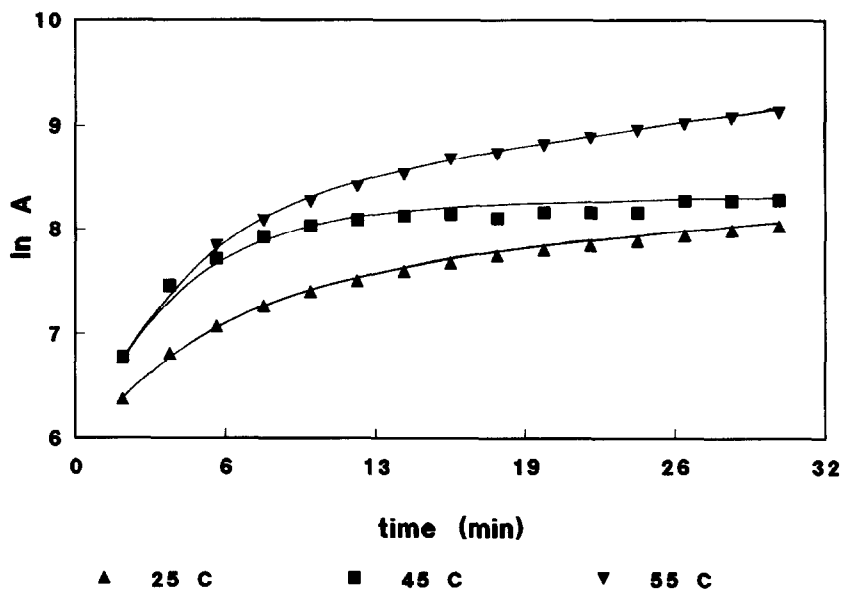


Fig. 4. Kinetics of copper ion sorption on polysulfone + algae at different temperatures. Conditions: 100 mg/l Cu; pH 5.5.

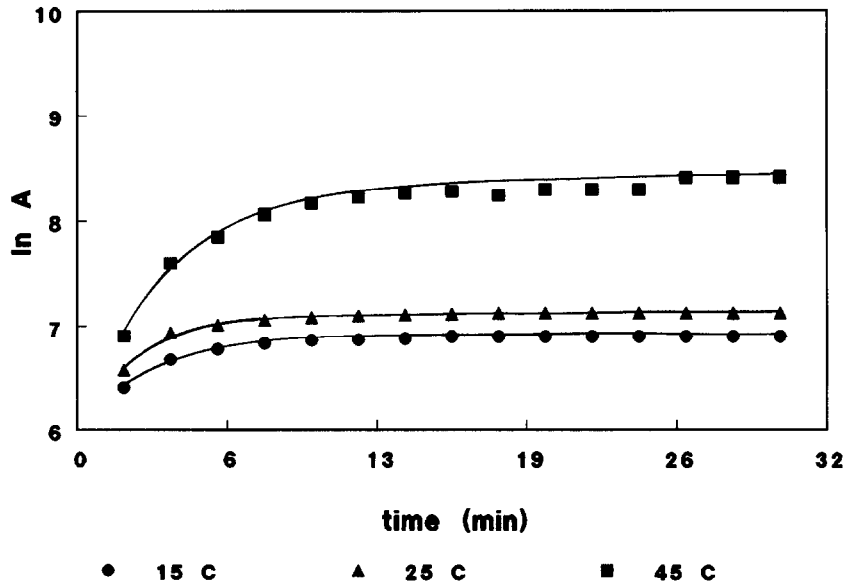


Fig. 5. Kinetics of copper ion sorption on polysulfone at different temperatures. Conditions: 100 mg/l Cu; pH 5.5.

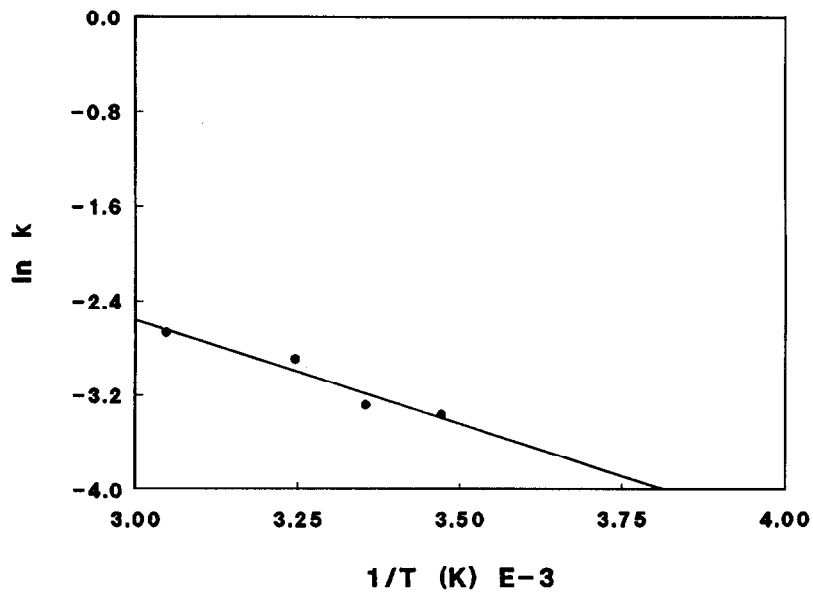


Fig. 6. Activation energy determination for copper ion sorption on polysulfone only. Conditions: 100 mg/l Cu; pH 5.5.

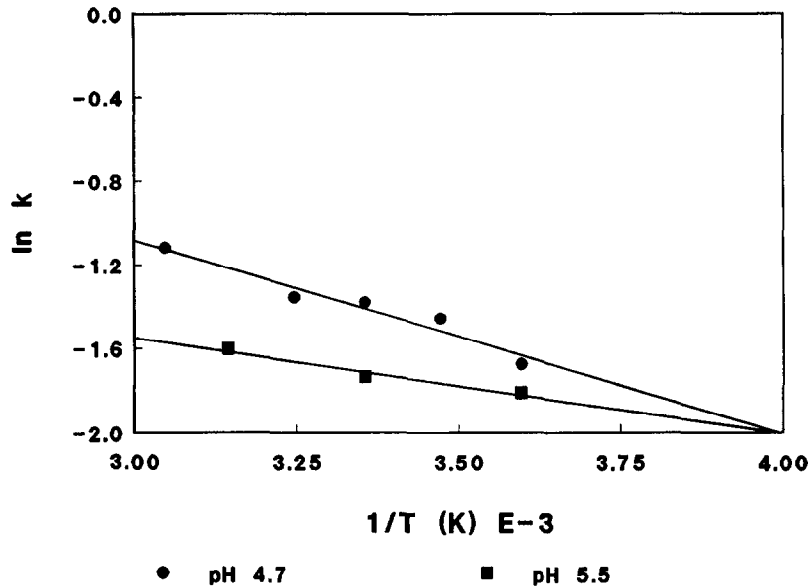


Fig. 7. Activation energy determination for copper ion sorption on polysulfone + algae. Conditions: 100 mg/l Cu; (a) pH 4.7, (b) pH 5.5.

Table 5  
Adsorption kinetics of copper on (polysulfone and algae)

$T(^{\circ}\text{C})$	$(k) \times 10^{-1} \text{ min}^{-1}$	$(K_{\text{eq}}) \times 10^{-4}$	$\ln k$	$T(\text{K})$	$(1/T)$ $(\text{K}^{-1} \times 10^{-3})$	$E_a$ (kcal/mol)
Cu: 100 mg/l, pH: 4.7						
5	1.875	4.660	-1.6739	278	3.597	1.936
15	2.330	4.086	-1.4567	288	3.472	
25	2.517	0.7518	-1.3795	298	3.355	
35	2.580	—	-1.3545	308	3.246	
45	2.660	0.3115	-1.3245	318	3.144	
55	3.276	0.0956	-1.1159	328	3.048	
Cu: 100 mg/l, pH: 5.5						
5	1.639	1.695	-1.8084	278	3.597	0.8456
15	—	—	—	—	—	
25	1.769	1.659	-1.7321	298	3.355	
35	—	—	—	—	—	
45	2.016	1.036	-1.6014	318	3.144	
55	2.733	0.300	-1.2970	328	3.048	

Here  $K_{\text{eq}}$  values are almost ten times larger than polysulfone/algae compositions and also decreased with increasing temperature.

By increasing temperature, binding rate increased, the system saturated faster, and the concentrations of metal bound to algae (A) became constant much sooner; then

Table 6  
Adsorption kinetics of copper on polysulfone Cu: 100 mg/l, pH: 5.5

$T$ ( $^{\circ}\text{C}$ )	$(k) \times 10^{-2} \text{ min}^{-1}$	$(K_{\text{eq}}) \times 10^{-4}$	$\ln k$	$T$ (K)	$(1/T)$ ( $\text{K}^{-1} \times 10^{-3}$ )	$E_a$ (kcal/mol)
5	—	52.2	—	278	3.597	
15	3.50	—	-3.3524	288	3.470	
25	3.75	—	-3.2741	298	3.355	3.202
35	5.57	37.7	-2.8875	308	3.246	
45	6.41	—	—	318	3.144	
55	6.95	19.4	-2.666	328	3.048	

Table 7  
Adsorption kinetics of Pb on polysulfone and algae

$T$ ( $^{\circ}\text{C}$ )	$(k) \times 10^{-1} \text{ min}^{-1}$	$(K_{\text{eq}}) \times 10^{-4}$	$\ln k$	$T$ (K)	$(1/T)$ ( $\text{K}^{-1} \times 10^{-3}$ )	$E_a$ (kcal/mol)
Pb: 100 mg/l, pH: 5.5						
0	1.60	—	-1.832	273	3.66	
5	—	1.685	—	288	—	
25	2.36	0.617	-1.444	298	3.35	2.414
30	2.41	0.604	-1.423	303	3.30	
35	—	0.548	—	308	3.25	
45	2.63	0.387	-1.335	318	3.14	
55	3.36	—	-1.091	328	3.05	
Pb: 100 mg/l, pH: 5.5						
15	0.840	6.489	-2.470	288	3.47	
25	0.976	5.660	-2.326	298	3.35	
35	1.300	3.642	-2.040	308	3.25	4.284
40	1.509	—	-1.891	313	3.19	
50	2.125	0.771	-1.548	323	3.09	

the concentration of metal unbound (**B**) in solution started to increase. Since the equilibrium constants can be considered as the ratio of metal bound to algae (**A**) to metal unbound in solution (**B**), by time (**A**) becomes constant and (**B**) starts to increase and consequently equilibrium constant decreases.

The same trend is obtained for the equilibrium constant values obtained for lead sorption at different temperatures. Fig. 10(a) shows the change of equilibrium constant values for the sorption of lead ions on polysulfone only. Larger equilibrium constant values and a sharp drop is obtained compared to the one obtained for lead sorption on polysulfone/algae combination (Fig. 10(b)).

Lead uptake on polysulfone/algae matrix was examined with the same procedure. When  $\ln A$  vs. time was drawn for such a system, the sorption isotherms shown in Fig. 11 were obtained at different temperatures. In these plots the slope became sharper with increasing temperatures and the first-order initial rate constants increased.

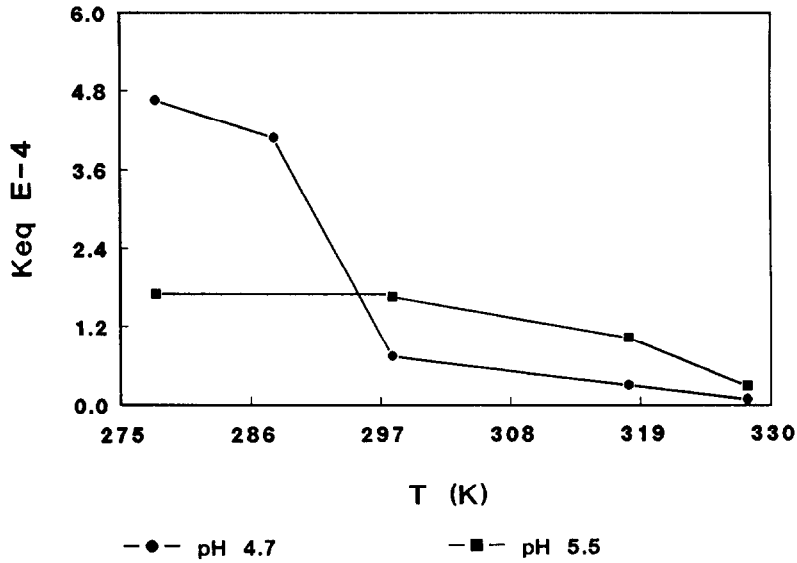


Fig. 8. Adsorption kinetics (change of equilibrium constant values with temperature) of copper ion sorption on polysulfone + algae. Conditions: (a) pH 4.7, (b) pH 5.5.

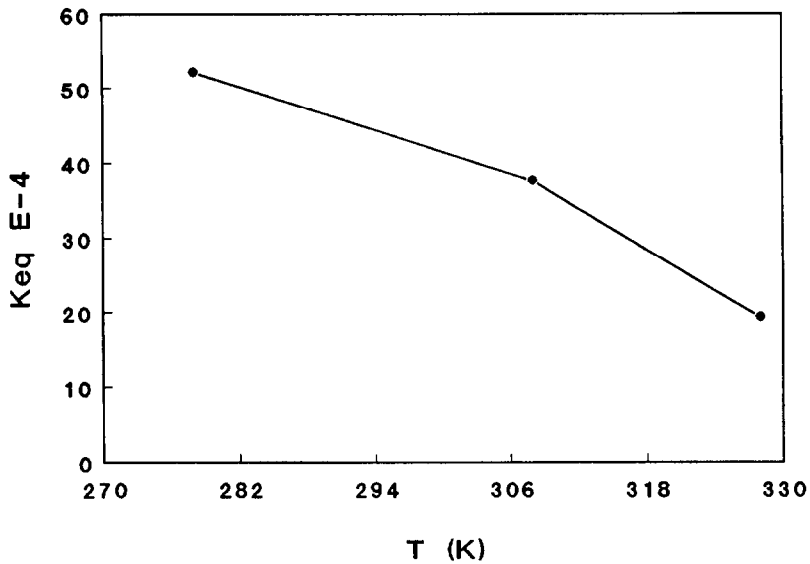


Fig. 9. Adsorption kinetics (change of equilibrium constant values with temperature) of copper ion on polysulfone at pH 5.5.

Fig. 12 shows the Langmuir sorption isotherms when  $1/A$  values are plotted vs.  $1/c$ . Obtained straight lines at different temperatures with the same  $1/a_m$  intercept also indicates a single sorption site responsible for each case.

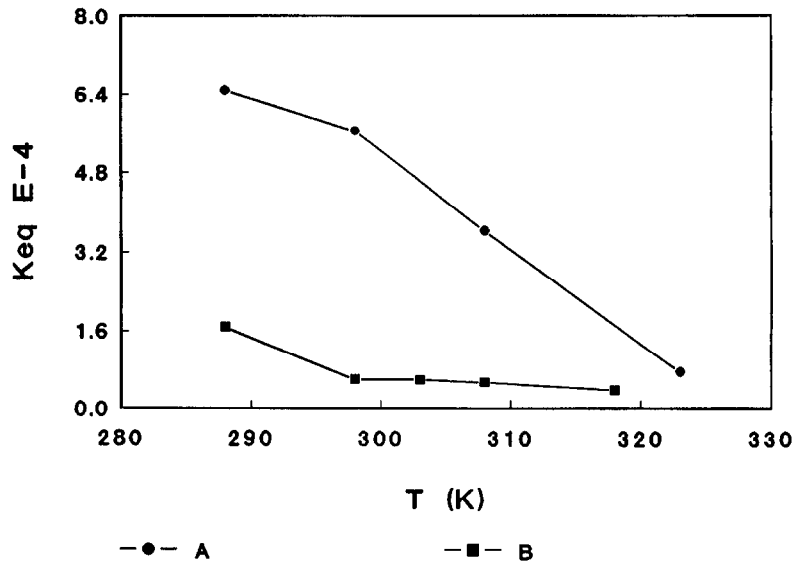


Fig. 10. Change of equilibrium constant values for lead ion sorption. (a) lead ion sorption on polysulfone only, (b) lead sorption on polysulfone + algae.

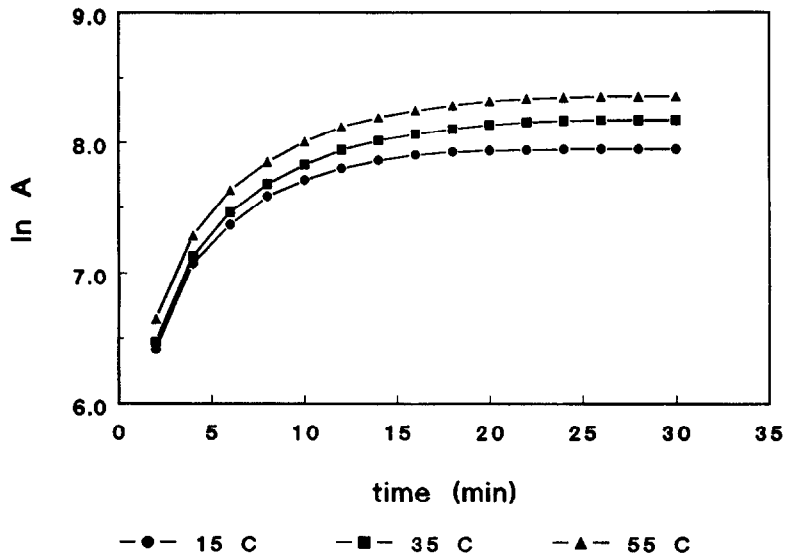


Fig. 11. Lead ion adsorption isotherms on polysulfone + algae at: (a) 15 °C, (b) 35 °C, (c) 55 °C.

The activation energies were calculated for lead uptake on polysulfone only as 4.284 kcal/mol from the slope of the plot shown in Fig. 13(a), and on polysulfone/alga combination as 2.446 kcal/mol from the slope of the plot shown in Fig. 13(b). This also indicates that lead sorption on polysulfone matrix alone is about two times more difficult than the system when polysulfone was incorporated with seaweed algae.

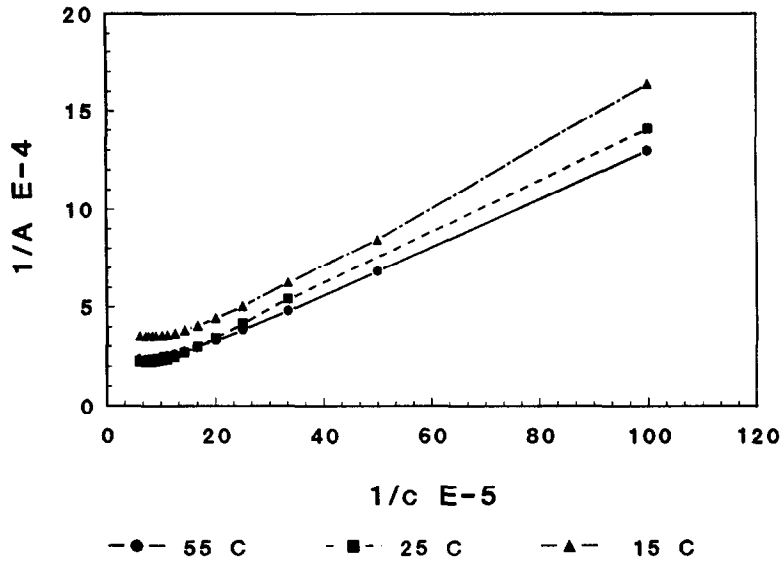


Fig. 12. Langmuir adsorption isotherms of  $1/A$  ( $A = \text{mg metal sorbed/g dry algae}$ ) versus  $1/c$  ( $c = \text{concentration of available metal in mg/l}$ ) values for lead sorption on polysulfone + algae at: (a) 55°C, (b) 25°C, (c) 15°C.

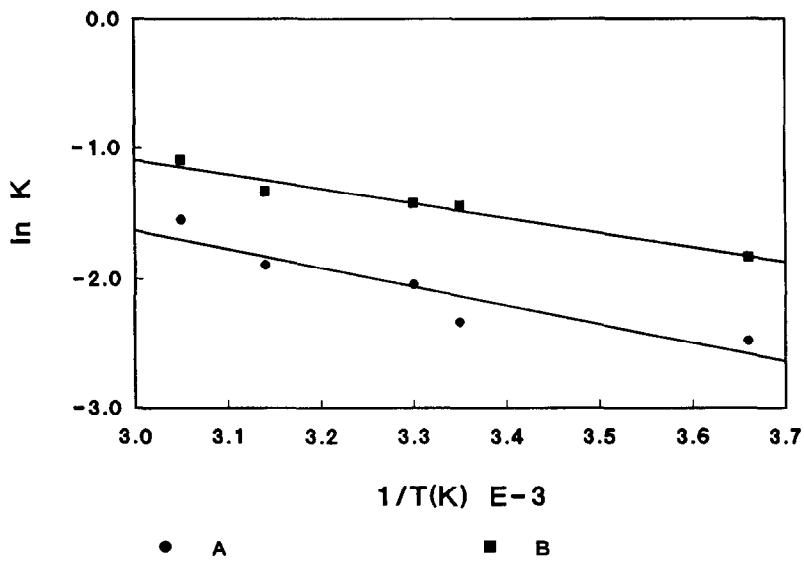


Fig. 13. Activation energy determination for the sorption of lead ion on: (a) polysulfone only, (b) polysulfone + algae.

#### 4. Discussion

Isotherms are frequently used to describe sorption behavior (anti-Langmuirian and Langmuirian shape). From the shape of the isotherms it can be determined whether the species that first sorb facilitate sorption of additional species (sorption mechanism). If the curves exhibit anomalous curvature, it might indicate the accumulation of another metal (which can be determined by electron microscopic X-ray analysis) on the cell wall surfaces of microorganisms. Langmuir adsorption assumes that the binding sites are equivalent and that binding is independent of neighboring sites. For example, the existence of two slopes in Langmuir adsorption isotherms would describe a different biphasic system and would indicate at least two sorption mechanisms or multi-layer sorption, and consequently a single formation constant would not describe the metal-binding process.

The study of the sorption of polymer beads with and without biomass may indicate the contribution of the polymer matrix and the importance of polymer/biomass interaction. Table 1 illustrates that the polysulfone polymer alone is capable of binding about 800  $\mu\text{g}$  of Cu. In Table 2 it is seen that the polymer/algae combination can sorb about 4500  $\mu\text{g}$  of Cu. One should not conclude that 800  $\mu\text{g}$  must reside on the polymer and about 3700  $\mu\text{g}$  must be attached to the algae. Algae and polymer in combination form a porous matrix. Even though the sorption mechanism is not known, most probably the point defects of this matrix are the sorption sites, and this increases the sorption ability.

From the time and rate of breakthrough for metal ions from biosorbent columns, the significance of the mass transfer characteristics of the biomass beads can be determined. This can be done by modifying the polymer bead fabrication procedures to improve the surface properties. Surface areas and porosities of the polymer particles can be monitored since it has been previously observed that biomass is completely and uniformly incorporated into silica gel [17].

Cell wall modifications of functionalities such as sulfhydryl and amino groups in microorganisms may cause a decrease in the sorption of some metals [2]. Binding of metal ions to cell walls represents complex reactions that are dependent on many factors such as the particular matrix constituents, concentrations, solution pH, and sorbate equilibrium concentrations. The ionic form of the metal ionic species that exist in solution, and the variety of sorption sites available (single or multi-layer sorption), where a single mechanism cannot explain a multi-component system sorption.

By determining the order of the sorption reaction, a reaction mechanism can be suggested. The rate of the surface reaction may be limited by several steps, including: (1) the rate at which the reactant reaches the surface by diffusion, (2) the rate of sorption, (3) the rate of reaction on the surface, (4) the rate of product desorption, and (5) the possibility of oxidation at elevated temperatures. All of these factors affect the rate of sorption; as a result, a single parameter cannot explain the rate constant values.

A bimolecular reaction on a surface may happen in two ways: (1) one reactant sorbs on the surface and the other reacts with it on the surface without being



itself sorbed or (2) both reactants are sorbed and subsequently come into contact and react on the surface, and their movements can be treated as a two-dimensional diffusion process. For a unimolecular reaction products not sorbed will appear to be zero order. This will be reflected in initial linearity of  $c$  vs. time plots. Thus, a first-order sorption that occurs on the surface by the reactant sorbing and obeying the Langmuir equation can be recognized by a deviation from linearity.

In this work initial rate constants, equilibrium constants, and activation energies of the sorption processes have been tabulated for polysulfone/biomass preparations. Although styrene-divinylbenzene copolymer was prepared and the copolymer matrix was incorporated with biomass, in this work its adsorption mechanism was not studied. In the future other polymeric systems such as phenylene sulfide resins and styrene-divinylbenzene copolymers will also be studied and the best sorbing medium will be evaluated. This will provide information about the functionalities involved in metal binding by cell wall components, and will suggest mechanisms for the observed differences in metal uptake behavior among organisms. This will contribute to the development of new sorbent materials for removing heavy and precious metals from solutions.

## 5. Conclusions

The sorption results obtained in this work show:

- (1) Biomass/polymer matrices can rapidly remove metal ions from aqueous solutions.
- (2) The first-order rate constant values calculated for copper and lead ion uptake on polysulfone alone are ten times smaller than the polysulfone/biomass systems, as indicated in Tables 1 and 2.
- (3) Activation energy of sorption at pH 5.5 is lower than the energy at pH 4.7 for copper ion adsorption. This indicates that copper is activated more easily and sorbs more at pH 5.5.
- (4) Activation energy is three times higher for copper sorption on polymer matrix only (polysulfone) without incorporation of algal biomass. This indicates that the sorption process is less efficient without algae.
- (5) Algal biomass can be immobilized in a polymer matrix and packed into columns for use as an ion exchanger.
- (6) As temperature increases, the equilibrium constant value decreases. Since equilibrium constant is given as a ratio of A (metal bound to algae)/B (metal not bound), as temperature increases, binding rate increases and the system reaches saturation more quickly; (A) becomes constant faster and (B) starts to increase; consequently, the equilibrium constant decreases.
- (7) The plots  $1/A$  vs.  $1/c$  give straight lines for both copper and lead sorptions, indicating that single sorption sites are responsible for binding.
- (8) The rate of surface sorption may be limited by several steps including: (a) the rate at which the reactant reaches the surface by diffusion, (b) the rate of sorption,

(c) the rate of reactions on the surface, (d) the rate of product desorption, and (e) possible oxidation reactions on the surface.

(9) This work can be extended to other polymer-algae matrices by changing both the type of polymer and algae to find out the maximum sorption conditions for each metal.

(10) One of the difficulties in describing the sorption of metal ions from waste streams is that waste waters contain many metal ions. Several isotherms have been proposed to describe equilibrium and competitive sorption for such a system [18]. These isotherms range from a simple Freundlich equation to the complicated isotherms as proposed by Suwanayuen and Danner [19].

(11) For the sorption of metal ions on biomass we have chosen to use the multi-component Langmuir isotherm, which assumes a monolayer sorption. This type of isotherm has also been shown to describe sorption quite well for dilute solutions.

(12) This work shows only copper and lead ion sorption on polysulfone and polysulfone/algae matrices. Further study will be the extension of this work to other polymeric systems such as styrene-divinylbenzene copolymer and phenylene sulfide resins, after incorporating them with algae, to test ions other than copper and lead and to find the optimum adsorption conditions and systems for each ion.

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