Polish Journal of Environmental Studies Vol. 11, No. 4 (2002), 375-384

The Effect of Poly(vinyl Alcohol) on Cadmium Adsorption and Desorption from Alginate Adsorbents

E. Klimiuk, M. Kuczajowska-Zadrożna

Faculty of Environmental Sciences and Fisheries, Department of Environmental Protection Engineering,
Institute of Ecological Engineering University of Warmia and Mazury,
Prawochenskiego 10, 10-957 Olsztyn, Poland

Received: 22 October, 2002
Accepted: 5 March, 2002

Abstract

Cadmium adsorption onto and desorption from sodium alginate and sodium alginate with polyvinyl alcohol) (PVA) were studied. Intraparticular diffusion was demonstrated to limit adsorption kinetics during the first 20 min of process. The D_{eff} value was dependent on adsorbent chemical composition and ranged from 3.35 x 10^{10} m^2/s to 1.86 x 10^{10} m7s for the 1.5% alginate with 0.5% PVA and for the 2% alginate with 5% PVA, respectively.

At equilibrium the adsorption was more effective onto the 2% alginate and was lower for the alginate sorbent containing poly(vinyl alcohol). The dimensionless separation factor R_L increased from 0.26 to 0.68 for the 2% alginate and the 2% alginate + 5% PVA, respectively. The maximum adsorption capacities in Langmuir isotherm for both the 2% and 1.5% alginate with 0.5% PVA were similar and were 176 and 178 mg/g dry weight, respectively. However, the adsorption capacity decreased to 48 mg/g dry weight for the 2% alginate with the 5% PVA (in proportion to the polymer amount increase in the adsorbent).

Cadmium desorption was more effective for nitric acid than for sulfuric and hydrochloric acids (desorption pH 2.2). More cadmium was desorbed from 2% alginate with 5% PVA than from 2% alginate or 1.5% alginate with 0.5% PVA.

Keywords: cadmium, alginate, poly(vinyl alcohol), adsorption, desorption coefficient, diffusion, Langmuir equation, Langmuir constans

Introduction

Many industries such as metal plating facilities, mining operations and tanneries discharg waste containing heavy metal ions. Treatment processes for metals contaminated waste streams include classical physico-chemical processes. As an alternative to chemical precipitation, membrane filtration, or ion exchange, adsorption processes with a wide variety sorbents have been tested. Microorganisms, activated sludge and immobilized biomass were used as biosorbents [5, 21, 23, 26, 27, 29].

Correspondence to: Prof. E. Klimiuk

Metal adsorption was also studied using chemical sorbents such as activated carbon [25] and fly ash [2] as well as plant- and animal-origin sorbents, for example bark/tannin-rich materials, humus, peat moss, modified cotton and wool, chitin, chitosan, seaweed, and alginate [3, 7, 10].

A material derived from the processing of brown seaweed is algin, a high-molecular weight polymer. Alginate, a polysaccharide-based biosorbent, is formed from algin by replacing protons in carboxylic groups with metal ions. In the adsorption process, the heavy metal ions appear to exchange with calcium ions to form a metal alginate [3].

Alginate was found to effectively adsorb copper and

lead [7]. It has also been used as an immobilizing carrier for microbial cells. Wilkinson et al. [26] used the alginate immobilized *Chlorella emersonii* for mercury removal, while Wojnowska-Baryta et al. [28] investigated cadmium adsorption onto the immobilized *Klebsiella pneumoniae.* However, widespread utilization of alginate sorbents is limited as its mechanical strength and durability are relatively low. Kuczajowska-Zadrozna [14] improved the alginate mechanical properties by introducing polyvinyl alcohol) to the sorbent. The effect of polyvinyl alcohol) on metal adsorption has not yet been recognized.

The aim of this paper was to investigate cadmium adsorption onto sodium alginate and sodium alginate with poly(vinyl alcohol). Adsorption efficiency was evaluated based on diffusion coefficients and the Langmuir equation constants. Mineral acids were used for cadmium recovery from alginate sorbents.

Methods

Preparation of Alginate Adsorbents

2% sodium alginate and sodium alginate with polyvinyl alcohol) (PVA) (1.5% alginate with 0.5% PVA and 2% alginate with 5% PVA) were used.

Preparation of the 2% Sodium Alginate

2 g of sodium alginate (medium viscosity by Sigma) was dissolved in 98 g of water. A homogenous alginate solution was dropped into the 0.05 M $CaCl_2$ solution to from granules of 2.8 mm diameter. The granules were left for 24 h to gel and the chlorides were removed by washing with deionized water.

Preparation of Sodium Alginate with PVA

1.5 g of sodium alginate with 0.5 g PVA was dissolved in 98 g of distilled water. The combined polymer homogenous solution was dropped into the 0.05 M solution of $CaCl_2$ in the saturated solution of boric acid. The boric acid was necessary for the PVA to gel. The 2% alginate with the 5% PVA was prepared analogically by modifying the respective weighed amounts (2 g of alginate, 5 g of PVA, 93 g of distilled water).

Cadmium Adsorption

The adsorbate used in this study was Cd^{2+} in concentration of 5, 10, 50, 100, 200 mg Cd/dm^3 which were obtained from Cd $(SO_4)_2 \cdot 8H_2O$ (SIGMA). 500 cm^3 of respective cadmium solution was introduced into 1 dm^3 test tubes with 40 g of sorbent and stirred on a magnetic stirrer. After 0, 2, 4, 6, 8, 10, 15, 30, 45, 60, 90, 120, 1440 min. equal amounts of the liquid and the adsorbent were sampled for analysis.

Cadmium Desorption

Cadmium desorption from the alginate sorbents was analyzed after it was first adsorbed from the aqueous solution of cadmium sulfate.

The desorption efficiency was analyzed in dependence on pH, respectively with 1 M HNO_3, 1 M H_2SO_4 and 1 M HCl as eluants.

The analysis of the pH effect: 500 cm^3 of the 50 mg Cd/dm^3 aqueous solution was introduced into the 1 dm^3 test tubes with 40 g of sorbent and stirred on a magnetic stirrer. Both the pH and cadmium concentration in the solution were measured after 24 h. The pH was adjusted 5.0, 4.0, 3.0, 2.5, 2.2 by adding respective amounts of 1 M organic acid.

Analytical

Cadmium adsorption and desorption was analyzed by measuring the amount of cadmium residue in the aqueous solution using the atomic absorption method SpectrAA, Varian. The 10 cm^3 samples were centrifuged for 15 min. at 12 000 r.p.m. and the cadmium concentrations were read out from the standard curve.

Results

Cadmium Adsorption onto the Alginate Sorbents

Adsorption kinetics of cadmium from aqueous solutions is controlled by various steps including diffusion processes:

- cadmium transfer from the bulk solution to the boundary film covering the adsorbent surface (1),
- cadmium transport from the boundary film to the surface of the adsorbent, (external diffusion) (2),
- transfer of the cadmium from the surface to the intraparticular active sites, (internal diffusion) (3)
- metal ion uptake on the active sites of adsorbent (4).

Step 1 relates to batch agitation and may be omitted when the agitation rate provides sample homogeneity. Step 2 describes film mass transfer resistance. Step 3 is related to the intraparticular diffusion model. Step 4 is a rapid, non-limiting phase [12].

Several models such as the homogenous surface diffusion model, pore diffusion model and heterogeneous model have been applied in batch reactors to describe the transport of adsorbate inside the adsorbent particle. In order to primarily estimate the adsorption controlling mechanisms such as mass transfer or intraparticular diffusion, they could be formulated and analyzed as two independent processes. The results obtained from uncomplicated models are useful for further application in designing systems for the practical treatment of contaminated waste [31].

The adsorption rate was assumed to be limited by the external diffusion rate and then the C_t/C_0 = f(f) function is linear [19].

By analogy, when there is $(-\log(1 - (q_t/ q_m)^2)) = f(t)$ a straight line, the cadmium removal rate is limited by the internal diffusion rate [24].

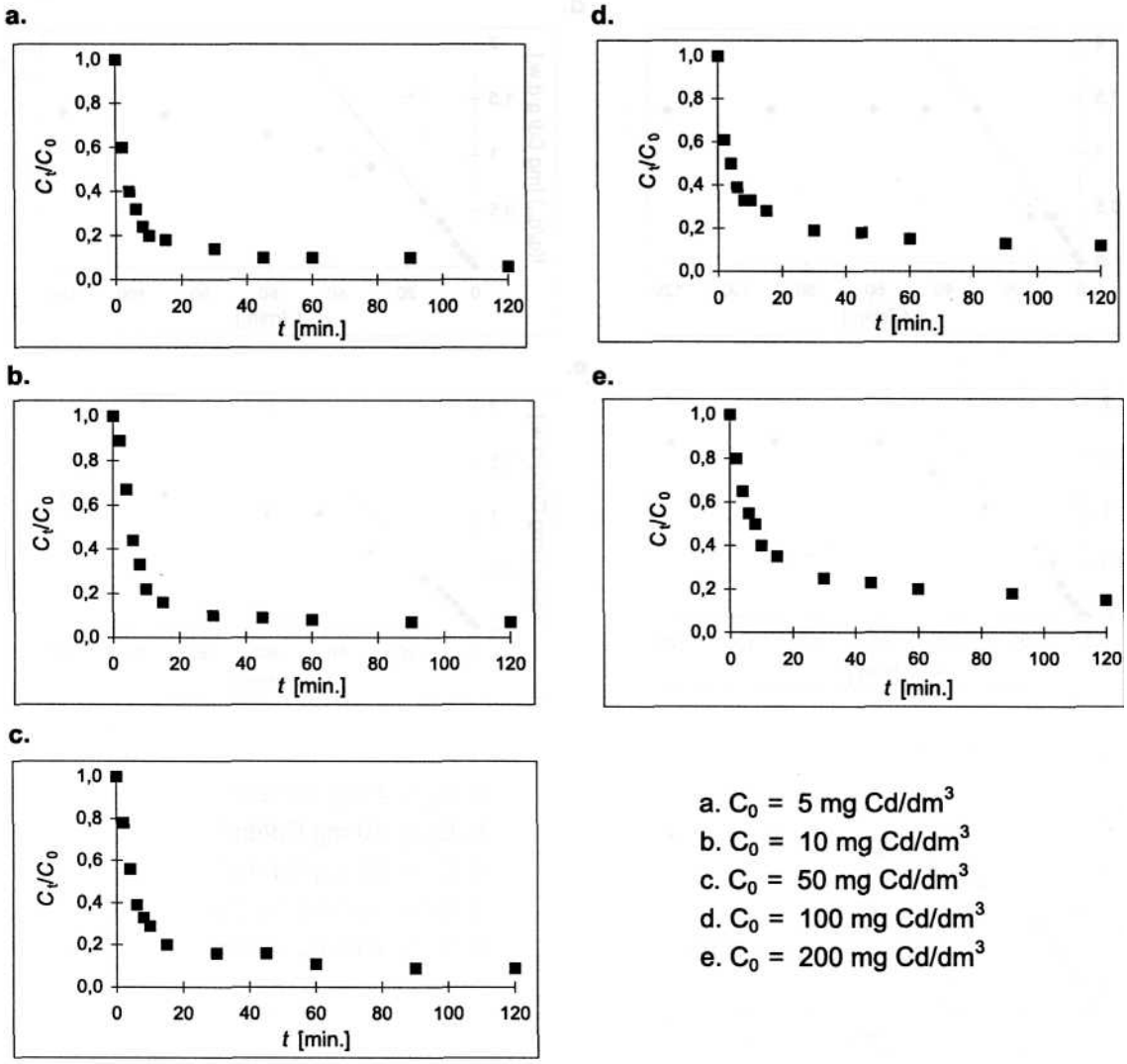

Fig. 1. Cadmium decrease (C_t/C_o) during sorption onto the 2% alginate.

The effect of five different cadmium initial concentrations on the changes of cadmium concentration in the time was used to determine if the external or internal diffusion limited the adsorption process.

Fig. 1 presents the experimental results of cadmium adsorption as the C_t/C_o — $f(t)$ function, where:

C_t - cadmium concentration in the solution in time t,(mg Cd/dm^3)

C_o - finitial cadmium concentration in the solution, (mg Cd/dm^3)

In the experimental results the C_t/C_o — $f(t)$function was not linear; thus, it was assumed that the external diffusion rate did not limit the rate of cadmium adsorption from aqueous solutions.

Figures 2, 3 and 4 present the results of cadmium adsorption by chemical sorbents as a $(-\log(1 - (q_t/ q_m)^2)) = f(t)$ function in time. Within the initial 20 min. of contact, the function was near-linear. Thus the $(t, (-\log(1 - (q_t/ q_m)^2)) = f(t)$ values were used to determine the linear, regression coefficients (a). Linearization was carried out using initial time of contact between 0 and 20 min. The regression coefficient values were used to calculate the internal diffusion coefficient D_{eff}.

The following equation was used to calculate the diffusion coefficients (D_{eff}):

$$f(q_t / q_m) = -[\log(1-(q_t / q_m)^2)] = \frac{4\pi^2 D_{\text{eff}}}{2.3d^2} \cdot t \qquad (1)$$

where:

q_t – solid phase cadmium concentration after time (t), (mg/g)

q_m – equilibrium solid phase cadmium concentration in $t \to \infty$, (mg/g)

d – diameter of alginate granule, (m)

D_{eff} – intraparticular diffusion coefficient, (m^2/s)

$$a = \frac{4\pi D_{\text{eff}}}{2.3d^2} \qquad (2)$$

$$D_{\text{eff}} = a \cdot 0.4576 \qquad (3)$$

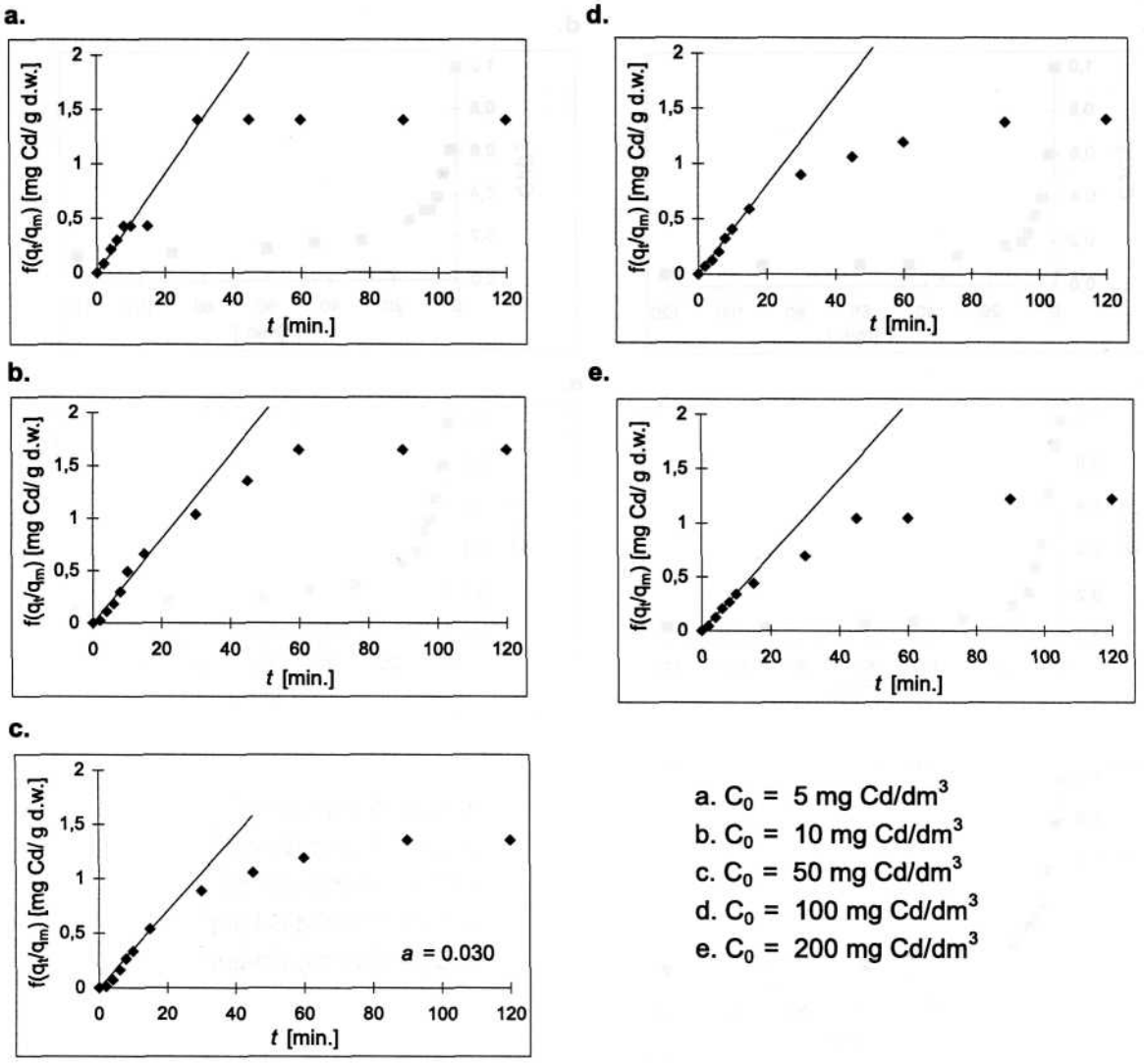

Fig. 2. Plotting the internal diffusion coefficient for 2% alginate in time $f(q_t/q_m)$.

The diffusion coefficient *(D_{eff})* was found to be determined by the adsorbent chemical composition (Table 1). D_{eff} was the highest for the 1.5% alginate with the 0.5% PVA and averaged 3.35 x 10^{-10} m^2/s. It was slightly lower (3.0 x 10^{-10} m^2/s) for the 2% alginate. When the percentage of PVA in the adsorbent reached 5%, D_{eff} greatly decreased to 1.86 x 10^{-10} m^2/s.

It was also found that D_{eff} values tended to decrease as the cadmium concentration in the solution increased regardless of the adsorbent tested.

Among the tested adsorbents, alginate with 5% polyvinyl alcohol) was characterized by the lowest internal diffusion coefficients within the analyzed concentration range.

The equilibrium of cadmium separation between the liquid and solid phases is described by Langmuir equation (4):

$$Q = q_{max} \cdot K_C \cdot \frac{C}{1 + K_C \cdot C} \qquad (4)$$

where:

Q - equilibrium solid phase cadmium concentration, (mg Cd/g)

C - equilibrium liquid phase cadmium concentration, (mg Cd/dm^3)

q_{max} - constant in Langmuir isotherm (maximum adsorption capacity), (mg /g)

Kc - constant in Lagmuir isotherm (adsorption affinity), (dm^3/mg)

The q_{max} and K_c constants in the Langmuir equation were determined based on $(C_i\ Q_i)$ values with the use of APNIELIN software. APNIELIN software is intended to approximate with the use of the least squares method by

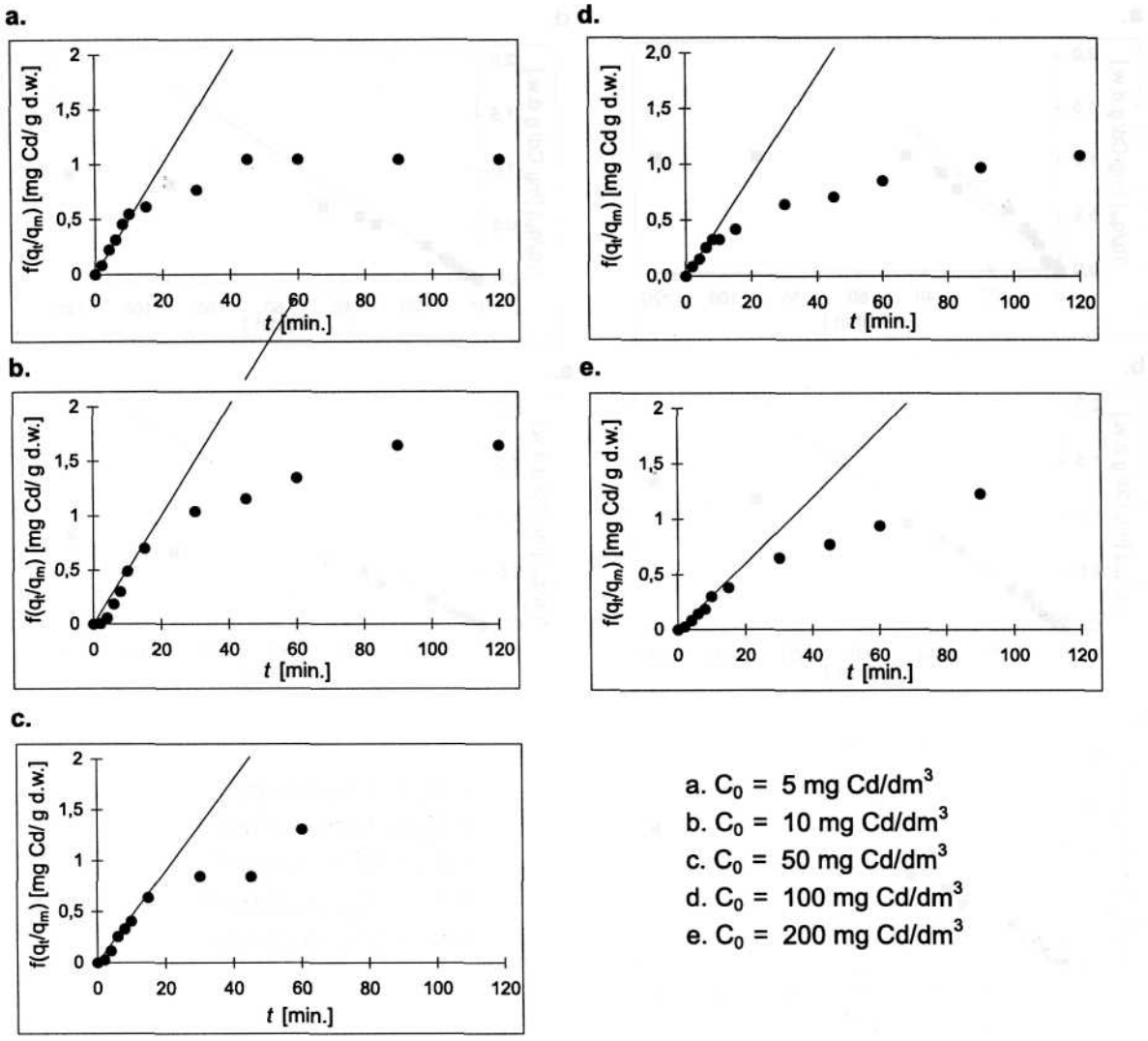

Fig. 3. Plotting the internal diffusion coefficient for 1.5% alginate with 0.5% PVA in time $f(q_t/q_m)$.

Table 1. Diffusion coefficient D_{eff} for the tested adsorbents calculated based on linear regression coefficient (a).

Cadmium concentration (mg/dm³)	Diffusion coefficient D_{eff} 10^{-10} [m²/s]					
	2% alginate		1.5% alginate with 0.5% PVA		2% alginate with 5% PVA	
	value	R^2	value	R^2	value	R^2
5	3.43	(0.98)	3.81	(0.99)	2.29	(0.98)
10	3.05	(0.96)	3.81	(0.95)	1.75	(0.97)
50	2.67	(0.98)	3.43	(0.99)	2.21	(0.99)
100	3.05	(0.98)	3.43	(0.98)	1.53	(0.99)
200	2.67	(0.99)	2.29	(0.98)	1.53	(0.92)

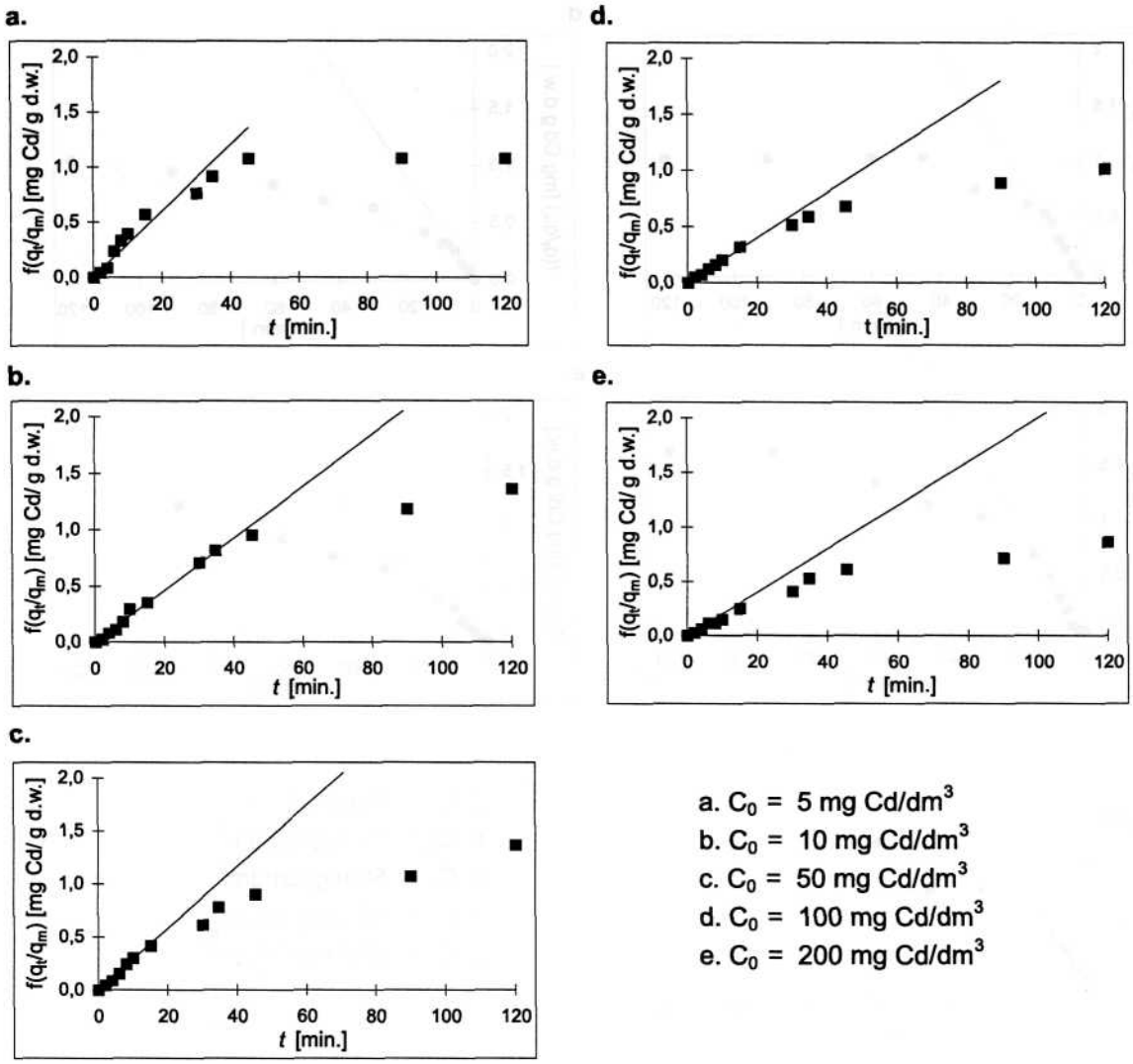

Fig. 4. Plotting the internal diffusion coefficient for 2% alginate with 5% PVA in time $f(q_t/q_m)$.

means of a non-linear function of the parameters. This is an iteration method and requires an initial approximation. Corrections to the determined parameters are calculated by replacing the increment of the function with its total differential, which allows a linear problem to be solved in each iteration. Additionally, the reduction of the step was applied to improve convergence, and the Marquardt method to expand the convergence range [4]. The initial approximation mentioned above can be obtained either by transforming (e.g. by logarithmical operation) the equation describing the model or by simplifying the model itself.

In order to evaluate the goodness of fit the φ^2 coefficient was used [13]. This coefficient is a quotient of the sum of squares of deviations between two experimental data (Q_i) and values *(Q(Ci))* to the sum of squares of deviations between the experimental data (Q_i) and their average value *Q*. If the coefficient φ^2 is closer to zero the goodness of fit is better.

At equilibrium, cadmium removal from aqueous solutions was determined by maximum adsorption capacities q_{max} and K of the tested adsorbents calculated with the Langmuir equation. The q_{max} values have a great importance for adsorbent evaluation and in mathematical modeling for adsorption process in kinetic and column studies.

The essential characteristic of the Langmuir equation can be expressed in terms of a dimensionless separation factor R_L, which is defined by McKay et al. [20] as:

$$R_L = \frac{1}{1 + a_L \cdot C_0} \tag{5}$$

where a_L is separation factor expressed as $Q_{max} \bullet Kc$ (dm^3/g)

$$a_L = Q_{max} \bullet K_c \tag{6}$$

The value R_L indicates the shape of the isotherm to be either linear $R_L = 1$, favorable $(0<R_L< 1)$ or irreversible $(R_L = 0)$.

Table 2. Langmuir equation constants.

Sorbent	Langmuir isotherm constants			
	q_{max} (mg/g)	K_C (dm³/mg)	R_L (–)	φ^2
2% alginate	176	0.08	0.26	0.015
1.5% alginate with 0.5% PVA	178	0.05	0.36	0.004
2% alginate with 5% PVA	48	0.05	0.67	0.065

The calculated adsorption capacities and the dimensionless separation factors values are given in Table 2. The 1.5% alginate with 0.5% PVA sorbent had identical maximum adsorption capacity as the 2% alginate, whereas its K_c value was about 37% lower than that of the latter. The maximum adsorption capacity decreased as the poly (vinyl alcohol) concentration increased to 5% in the alginate adsorbent (proportionally as the poly(vinyl alcohol) increased in the adsorbent).

The R_L values were higher for the PVA containing adsorbents than for the pure alginate. The R_L values in Table 2 show that cadmium adsorption for the three adsorbents were moderately favorable ($R_L < 1$) and tended to deteriorate when PVA was present.

Cadmium Desorption from the Alginate

Cadmium desorption from alginate and alginate with poly(vinyl alcohol) was analyzed using mineral acids such as sulfuric, nitric and hydrochloric. Cadmium was adsorbed from the C_o = 50 mg Cd/dm^3 solution prior to its desorption. The residual cadmium concentrations (C_s) after adsorption were about 4.5 mg/dm^3, 4.2 mg/dm^3 and 5.3 mg/dm^3 for the 2% alginate, the 1.5% alginate with the 0.5% PVA, and the 2% alginate with the 5% PVA, respectively. Figure 6 presents desorption efficiency calculated as a concentration of the recovered cadmium increase to the concentration of the initially adsorbed cadmium (C_o - C_s).

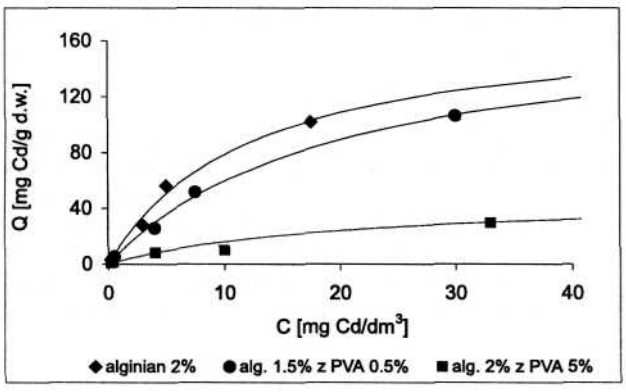

Fig. 5. Cadmium adsorption from aqueous solutions onto alginate adsorbents.

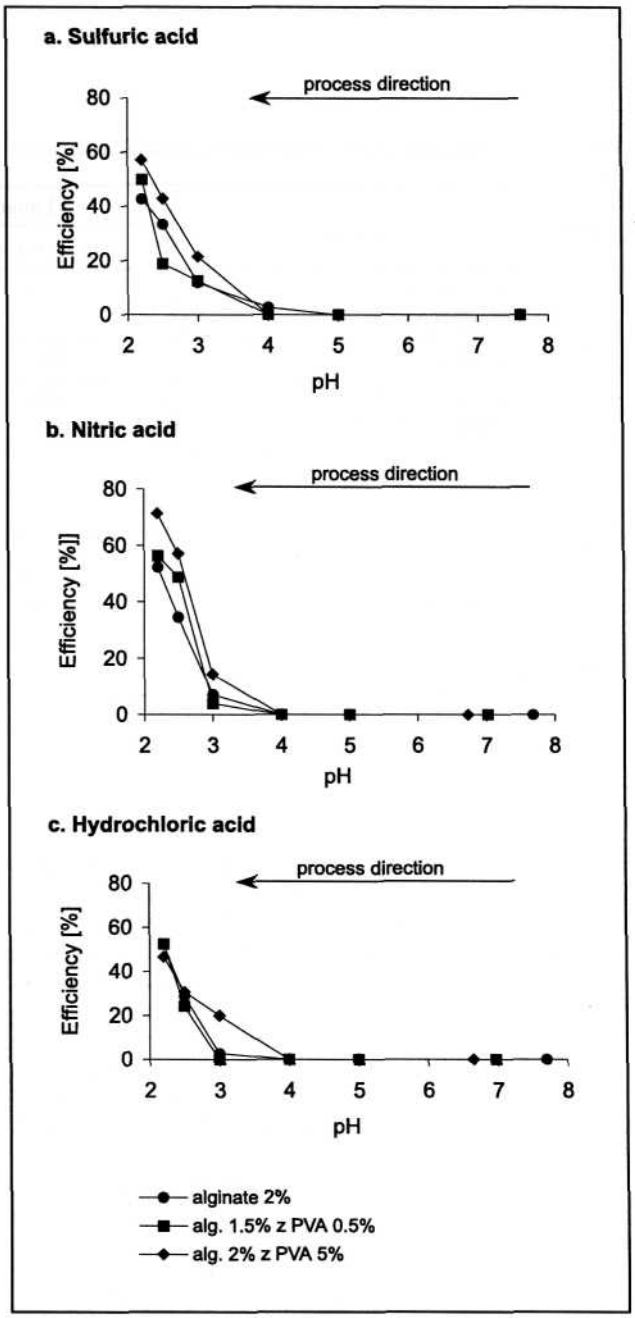

Fig. 6. Effect of pH and acid used on cadmium desorption efficiency.

Table 3. Internal diffusion coefficients determined for alginate.

Sorbent	Sorbate	Diffusion coefficient D_{eff} (m^2/s)	Reference
Alginate	blood serum albumin	$1.77 \cdot 10^{-10}$	Martinsen et al. [18]
Alginate	copper Cu^{2+}	$1.18 - 1.56 \cdot 10^{-10}$	Jang [9]
Alginate	copper Cu^{2+}	$1.86 \cdot 10^{-9}$	Lewandowski, Roe [15]
Alginate	lactose lactic acid glucose saccharose succinic acid	$6.1 \cdot 10^{-10}$ $10.1 \cdot 10^{-10}$ $6.4 \cdot 10^{-10}$ $4.6 \cdot 10^{-10}$ $7.8 \cdot 10^{-10}$	Øyaas et al. [22]

Table 4. The Langmuir isotherm constants in metal adsorption on biological and chemical sorbents.

Metal	Sorbent	Langmuir isotherm constants		Reference
		q_{max} (mg/g)	K_C (dm^3/mg)	
Cd Zn	extracellular polysaccharides	125 75	0.202 0.382	Löaec et al. [16]
Cu	alginate	108.5	0.083	Jang et al. [10]
Cd	carrageenan 1% carrageenan 0.25% + alginate 0.75% carrageenan 0.5% + alginate 1.5%	491 239 135	0.0026 0.029 0.050	Wojnowska-Baryła [28]
Pb Cu Cr Cd Zn	blast furnace sludge	64.17 16.07 9.55 6.74 4.26	0.017 0.041 0.05 0.03 0.05	Lopez-Delgado et al. [17]

Cadmium was not desorbed at pH over 4 regardless of either acid or adsorbent used (Fig. 6). Cadmium was desorbed from the alginate only at pH 3 and below. Desorption efficiency was determined by both the adsorbent type and mineral acid used. The greatest amounts of cadmium were recovered at pH 3 from 2% alginate using either sulfuric or nitric acid as well as from 2% alginate with 5% poly(vinyl alcohol) using either sulfuric or hydrochloric acid. A further decrease in pH to 2.2 caused further great increases in cadmium desorption to the solution.

Among all the tested sorbents, cadmium desorption (calculated as the cadmium percentage in the adsorbent and in the solution after desorption at pH 2.2) from 2% alginate with 5% PVA using nitric acid was the highest and was about 88%. The amounts of the recovered cadmium were lower for sulfuric acid, followed by hydrochloric acid, and were 77% and 65%, respectively. The 2% alginate was found to the least effective in cadmium recovery regardless of the acid used.

Discussion

The efficiency of cadmium adsorption by the alginate and alginate with poly(vinyl alcohol) (PVA) from aqueous solutions was evaluated based on the internal diffusion coefficient and the adsorption constants.

Intraparticular diffusion was found to limit adsorption during the initial 20 min. of contact. The adsorption onto the 1.5% alginate with 0.5% poly(vinyl alcohol) was limited by the internal diffusion to a smaller extent, whereas diffusion was a factor limiting the adsorption onto 2% alginate with 5% poly(vinyl alcohol) to the largest extent with the lowest D_{eff} within the analyzed range. Results of the D_{eff} of Cu^{+2} and some organic substances in alginate are presented in Table 3.

The diffusion coefficients D_{eff} in the experiment were lower than those obtained by Jang [9] (D_{eff} 1.18-1.56 $\cdot 10^{-9}$ m^2/s) or Lewandowski, Roe [15] (D_{eff} 1.86 $\cdot 10^{-9}$ m^2/s) when copper was adsorbed onto alginate (Tab. 3). These differences may result from different process con-

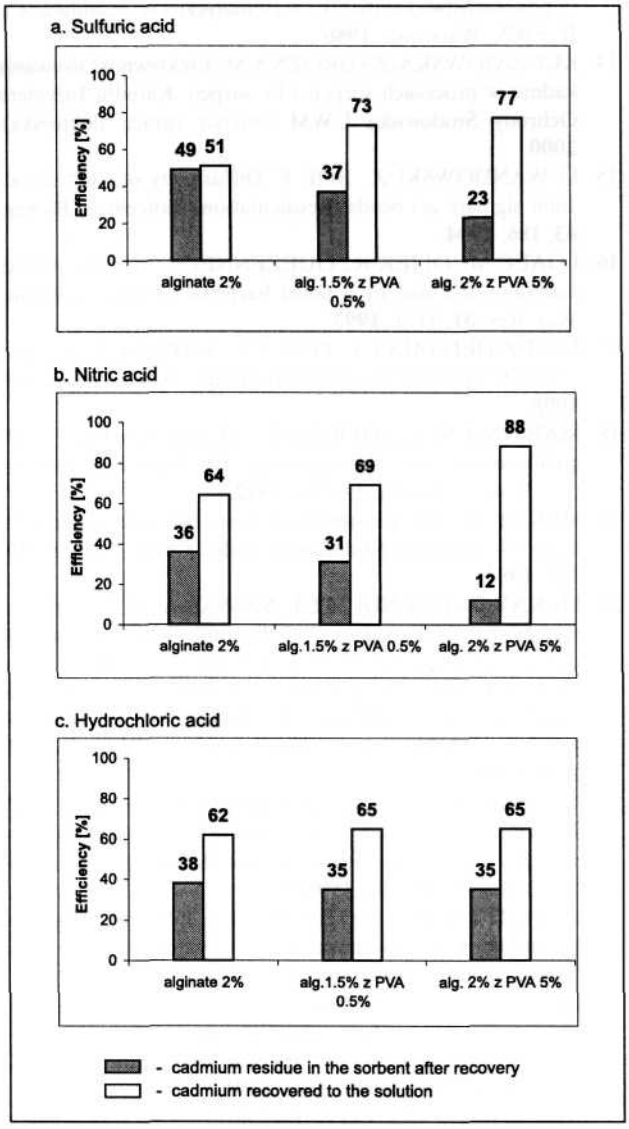

Fig. 7. Desorption efficiency for the tested alginate sorbents (pH 2.2).

ditions. Jang [10] used a gel-forming biopolymer directly dispensed into a loop fluidized bed reactor to recover dissolved copper.

According to the literature, the diffusion coefficients (D_{eff}) for the cadmium adsorbed on chitosan were lower and ranged from $0.43 \cdot 10^{-14}$ m^2/s to $16.5 \cdot 10^{-14}$ m^2/s in relation to granule size and from $0.43 \cdot 10^{-14}$ m^2/s to $1.66 \cdot 10^{-14}$ m^2/s in relation to C_o [12].

The effect of the tested adsorbents on their maximum adsorption capacity was studied. The 2% alginate and 1.5% alginate with 0.5% PVA were characterized by the same maximum adsorption capacities. However, the poly(vinyl alcohol) containing adsorbent had lower *Kc* value for cadmium adsorption.

Maximum adsorption capacity decreased when the alginate adsorbent contained 5% poly(vinyl alcohol), although the K_c was identical to the alginate adsorbent with 0.5% PVA.

Jang et al. [11] calculated that 1 g alginate can theoretically uptake 2.17 mole of Cu^{2+}. According to their experimental results, the amount of the uptaken copper was lower and was 77.3% of the theoretical value. Assuming that the same stoichiometry can be applied to cadmium, the theoretical maximum amount of uptake cadmium is 234.9 mg Cd/g. In our experiment, the maximum adsorption capacity for alginate was 176 mg Cd/g, which is 72.2% of the theoretical value.

A comparison of the results with literature (Tab. 4) shows that the *Kc* values for the alginate adsorbents were similar to the chemical adsorbents such as blast furnace sludge and carrageenan with alginate; however, it was one order lower than those offered by biosorbents (extra cellular polysaccharides). The maximum adsorption capacity was considerably lower only for 1% caragenian with low metal-sorbent affinity (K_c - 0.0026 dm^3/mg).

The efficiency of metals removal by natural and synthetic ionites has been investigated by many authors [1, 6]. The ion-exchange isotherms for lead and cadmium snowed that capacity of Clinoptilolit depended on metals and chemical composition of zeolite. Respectively, 0.38, 0.41, 0.44 mmol Pb^{2+} and 0.12, 0.16, 0.21 mmol Cd^{2+} were taken up by 1 g of zeolite sample. The efficiency of cadmium removal decreased drastically from 90, 96 and 99% at 1 mmol/dm^3 of Cd^{2+} to 27, 36 and 46 at 4.5 mmol Cd^{2+}/dm^3 [6].

According to Anielak and Cieslak [1] synthetic ionites (e.g. chelating selective cation exchanger Wofatit MC-50) also adsorb heavy metals, but do not adsorb calcium ions. Thus it can be used for heavy metals removal from waste neutralized with calcium hydroxide.

Excepting the direct application of ionites, adequate to heavy metal forms, it is possible to modify (before the ion exchange) the metals forms occurring in water, e.g. to anions. Next, the anions can be eliminated during the deanionization process. The investigations of cadmium and lead removal, occurring in the form of anion complexes with EDTA, confirmed the possibility of using this method. Both strongly and slightly alkaline anion exchangers, Amberlit IRA and SRW, respectively, to a large extent exchanged the anion complexes of cadmium and lead [8].

Our own research shows that nitric acid was found to be the most effective in recovering cadmium. Hydrochloric and sulfuric acids were less effective. There is scarce information about metal desorption efficiency in literature. Wong et al. [30] have reported that the type of acid used (hydrochloric or sulfuric) did not determine the recovery of cadmium, copper, lead or nickel from the activated sludge.

The sulfuric and nitric acid desorption efficiency is determined by the sorbent, and 2% alginate with 5% PVA was found to be most effective. Cadmium removal by rinsing with hydrochloric acid was similar regardless of the adsorbent used.

Conclusions

Sodium alginate and alginate with polyvinyl alcohol) are effective adsorbents of cadmium from aqueous solutions. The experimental results permitted us to formu-

late the following conclusions on how an adsorbent effects cadmium adsorption and desorption:

1. Initially, the adsorption was limited by the intraparticular diffusion rate. The D_{eff} values for the tested adsorbents decreased in the following order: 1.5% alginate with 0.5% PVA > 2% alginate » 2% alginate with 5% PVA
2. Under equilibrium conditions the 2% alginate was the most effective in adsorbing cadmium; when poly(vinyl alcohol) was introduced to harden the alginate carrier, it decreased adsorption capacity. Based on the dimensionless separation factor as the efficiency criterion, the R_L values for the tested adsorbents increased in the following order: 2% alginate > 1.5% alginate with 0.5% PVA > 2% alginate with 5% PVA
3. Nitric acid was found to be more effective in cadmium recovery (desorption at pH 2.2) than other tested acids. 2% alginate with 5% PVA provided the highest cadmium desorption among the tested adsorbents.

Reference

1. ANIELAK A., CIESLAK G. Analiza studialna metod oczyszczania sciekow potrawiennych i galwanicznych. Mat. II Ogolnopolskiej Konferencji Naukowej „Kompleksowe i szczegotowe problemy inzynierii srodowiska", **8,** 72, **1987.**
2. APAK R., TUTEM E, HUGUL M., HIZAL J. Heavy metal cation retention by unconventional sorbents (red muds and fly ashes). Wat. Res. **32,** 430, **1998.**
3. BAILEY S.E, OLIN T.J., BRICKA R.M, ADRIAN D.D. A review of potentially low-cost sorbents for heavy metals. Wat. Res. **33,** 2469, **1999.**
4. BRANDT S. Analiza danych. PWN. Warszawa. **1998.**
5. CHANG J., LAW R., CHANG C. Biosorption of lead, copper and cadmium by biomass of *Pseudomonas aeruginosa* PU 21. Wat. Res. **31,** 1651, **1997.**
6. CURKOVIC L., CEJRAN-STEFANOWIC S., FILIPAN T. Metal ion exchange by natural and modified zeolites. Wat. Res., **37,** 1379, **1997.**
7. DEANS J.R., DIXON B.G. Uptake of Pb^{2+} and Cu^{2+} by novel biopolymers. Wat. Res. **26,** 469, **1992.**
8. EJIFOR H. CH. Studies on ion exchange method for removal of lead and cadmium ions from potable water. Politechnika Lubelska, (praca doktorska), Lublin. **1990.**
9. JANG L.K. Diffusitivity of Cu^{2+} in calcium alginate gel beads. Biotechnol. Bioeng. **43,** 183, **1993.**
10. JANG L.K, GEESEY G.G, LOPEZ S.L, EASTMAN S.L., WICHLACZ P.L. Use of a gel-forming biopolymer directly dispensed into a loop fluidized bed reactor to recover dissolved cooper. Wat. Res. **24,** 889, **1990.**
11. JANG L.K., NGUYEN D, GEESEY G.G. Efect of pH on the adsorption of Cu(II) by alginate gel. Wat. Res. **29,** 315, **1995.**
12. JANSSON-CHARRIER, GUIBAL E., RUOSY J., DELANGHE B., CLOIREC P. Vanadium (IV) by chitosan kinetics and equilibrium. Wat. Res. **30,** 465, **1996.**
13. KRYSICKI W., BARTOS J., DYCZKA W., KROLIKOWSKA K., WASILEWSKI M. Rachunek prawdopodobienstwa i statystyka matematyczna w zadaniach: Cz. II. PWN, Warszawa. **1986.**
14. KUCZAJOWSKA-ZADROZNA M. Efektywnosc usuwania kadmu w procesach sorpcji i biosorpcji. Katedra Inzynierii Ochrony Srodowiska UWM Olsztyn (praca doktorska). **2000.**
15. LEWANDOWSKI Z., ROE F. Diffusitivity of Cu^{2+} in calcium alginate gel beads: Recalculation. Biotechnol. Bioeng. **43,** 186, **1994.**
16. LOAEC M., OLIER R., GUEZENNEC J.. Uptake of lead, cadmium and zinc by a novel bacterial exopolysaccharide. Wat. Res. **31,** 1171, **1997.**
17. LOPEZ-DELGADO A, PEREZ C, LOPEZ F.A. Sorption of heavy metals on blast furnace sludge. Wat. Res. **32,** 989, **1998.**
18. MARTINSEN A., STORRO I., SKJAK-BRAEK G. Alginate as immobilization material: III. Diffusional properties. Biotech. Bioeng. **39,** 186, **1992.**
19. MCKAY G. The adsorption of basic dye onto silica from aqueous solution-solid diffusion model. Chem. Eng. Sci. **39,** 129, **1984.**
20. MCKAY G., GEUNDI M.ET, NASSAR M.M. Equilibrium studies during the removal of dyestuffs from aqueous solutions using bagasse pith. Wat. Res. **21,** 1513, **1987.**
21. MULLEN M.D, WOLF D.C., FERRIS F.G., BEVERIDGE T.J., FLEMMING C.A., BAILEY G.W. Bacterial sorption of heavy metals. Appl. Environ. Microbiol. **55,** 3143, **1989.**
22. 0YAAS J, STORRE I, SVENDSEN H., LEVINE D.W. The effective diffusion coefficient and the distribution constant for small molecules in calcium-alginate gel beads. Biotech. Bioeng. **47,** 492, **1995.**
23. STERRITT R.M., LESTER J.N. The influence of sludge age on heavy metal removal in the activated sludge process. Wat. Res. **15,** 59, **1981.**
24. URANO K., TACHIKAWA H. Process development for removal and recovery of phosphorus from wastewater by a new adsorbent. 2. Adsorption rates and breakthrough curves. Ind. Eng. Chem. Res. 30, 1897, **1991.**
25. WILCZAK A, KEINATH T.M. Kinetics of sorption and desorption of copper (II) and lead (II) on activated carbon. Wat. Environ. Res. **65,** 238, **1993.**
26. WILKINSON S.C., GOULDING K.H., ROBINSON P.K Mercury accumulation and volatilization in immobilized algal cell system. Biotechnol. Letters. **11,** 861, **1989.**
27. WILLIAMS C.J., ADERHOLD D, EDYVEAN R.G.J. Comparison between biosorbents for the removal of metal ions from aqueous solutions. Wat. Res. 32, 216, **1998.**
28. WOJNOWSKA-BARYLA I., STOLARCZYK E., GRETJZINSKA A. Charakterystyka zdolnosci usuwania kadmu przez wolne i immobilizowane bakterie *Klebsiella pneumoniae.* Biotechnologia. **4,** 125, **1997.**
29. WOJNOWSKA-BARYLA I.. Charakterystyka zdolnosci usuwania kadmu z roztworow wodnych przez biosorbenty karagenianowe. Substancje Toksyczne w Srodowisku. **4/5,** 41, **1995.**
30. WONG L.T.K, HENRY J.G. Bacterial leaching of heavy metals from anaerobically digested sludge. In: Biotreatment systems, v II, CRC Press, Inc., Boca Raton, Florida. **1988.**
31. WU F-CH., TSENG R-L., JUANG R-S. Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan. Wat. Res. **35,** 613, **2001.**