

Adsorption of heavy metal ions from aqueous solution by crosslinked carboxymethyl konjac glucomannan

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Abstract

Crosslinked carboxymethyl konjac glucomannan (CMKGM) with degrees of substitution (DS) 0.265 and 0.550 were prepared through reaction of monochloroacetic acid (MCA), konjac glucomannan (KGM) and epichlorohydrin and used to adsorb Cu^{2+} , Pb^{2+} and Cd^{2+} ions from the aqueous solutions. Regardless of the metal ion species, the adsorption capacity rapidly reached equilibrium within 20 min and adsorption followed second-order kinetic equation. The effect of pH on adsorption was apparent, the appropriate range was 5–6. The adsorptions of three metal ions are well followed as the Langmuir adsorption isotherm. The maximum adsorption capacity (Q_m) and Langmuir constant (b) of CMKGM (DS = 0.550) for Pb^{2+} were 41.7 mg/g and 0.305 mg/L. These values were higher than those for Cu^{2+} and Cd^{2+} . Among the tested ions, the order of adsorption capacity was $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$ in mass basis. The regeneration study indicates that CMKGM could be used repeatedly without significantly changing their adsorption capacities and desorption percentage.

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1. Introduction

Environmental pollution caused by toxic heavy metal in industrial effluents is one of the most pressing problems in the world. Strict legislation on the discharge of these toxic products makes it necessary to develop various efficient technologies for the removal of pollutants from wastewater [1]. Different technologies and processes are currently used. Biological treatments [2], membrane processes [3], advanced oxidation processes [4], chemical and electrochemical techniques [5,6] and adsorption procedures [7–9] are the most widely used for removing metals from industrial effluents. Among all the treatments proposed, adsorption using sorbents is one of the most popular methods. It is now recognized as an effective, efficient and economic method for water decontamination applications and for separation to analytical purpose.

Recently, numerous approaches have been studied for the development of cheaper and more effective adsorbents containing natural polymers. Polysaccharides which are abundant, renewable and biodegradable resources, have the capacity to associate by physical and chemical interaction with a wide variety of molecules [10,11]. But much attention was focused on chitin [12,13], starch and cyclodextrin [14].

Konjac glucomannan (KGM) is a high molecular weight water-soluble non-ionic polysaccharide found in tubers of the amorphophallus konjac. KGM is a linear random copolymer of β -(1 \rightarrow 4) linked D-glucose and D-mannose in the molar ratio of 1:1.6 with a low degree of acetyl groups [15,16]. It is more attractive for industrial use because of its renewability, biodegradability and low cost. At present, many investigation related to KGM are focused on isolating and characterizing properties of solution and solid, it is mainly used in biochemical, medical and food fields [17–20]. The investigation of konjac glucomannan used to adsorb metal ions have not been reported so far.

The objective of the present study is focused on the development of konjac glucomannan modified by monochloroacetic

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acid and epichlorohydrin for removal of heavy metal ions. The three metal ions selected in this study were copper, lead and cadmium ions because of their environmental significance. The effects of pH, adsorbent dose, initial concentration of Cu^{2+} , Pb^{2+} and Cd^{2+} , adsorption time and temperature on adsorption capacity were investigated. The characterization of isothermal adsorption and adsorption kinetics were also studied in order to provide a new method and theoretical evidences for wastewater treatment.

2. Materials and methods

2.1. Reagents

Konjac glucomannan, refined powder was dried at 60°C in vacuum oven before used; epichlorohydrin, monochloroacetic acid and sodium hydroxide (analytical reagent-grade) were used as received; $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (ultra pure grade) were also used as received.

2.2. Preparation of crosslinked carboxymethyl konjac glucomannan (CMKGM)

Fifteen grams konjac glucomannan was dispersed in 60 mL isopropyl alcohol, 15 g NaOH solution (45 wt.% in mass basis) was added dropwise over 20 min while stirring at 50°C . After 1.5 h, the required amount of 80 wt.% monochloroacetic acid was then added gradually. Mechanical stirring was continued for 4 h at 50°C . At this point, the mixture was adjusted to pH 11.0 with 1 mol/L NaOH and crosslinking agent, epichlorohydrin was added and crosslinking reaction was kept for 2 h at 40°C . The mixture was then allowed to cool, neutralized with hydrochloric acid, washed with 50 wt.% alcohol to remove impurities, filtered and dried. The degree of substitution (DS) of carboxymethyl group was determined as Ref. [21].

2.3. Measurement of heavy-metal ions

Stock solution (1000 mg/L) of Cu^{2+} , Pb^{2+} and Cd^{2+} ions were prepared by using ultra pure grade $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. The stock solution was then diluted to give standard solutions of appropriate concentration. The designated crosslinked carboxymethyl konjac glucomannan (0.0625–0.5 g) was added to the copper nitrate, lead nitrate and cadmium nitrate solution (50 mL), respectively, and stirred continuously. To avoid metal precipitation at high pH and the competition by hydrogen ions at low pH, the pH value of the solution was maintained at 5 by adding nitric acid (69.5%, ultra pure) except for those experiments for studying the pH effect before the addition of CMKGM. Sixty minutes was selected as the optimum contact time for konjac glucomannan to form a complex with the metal ions, centrifuged for 5 min at 1500 rpm, the supernatant (dilute it if necessary) was used for the residual metal analysis. The residual metal ion content in the supernatant was measured by atom adsorption spectrophotometer (a model WFX-IE2 made in China) at the maximum adsorption wavelength (324.2, 283.3 and 228.8 nm for Cu^{2+} , Pb^{2+} and Cd^{2+} , respectively). The adsorption

capacity Q (mg/g) of CMKGM was calculated as follows

$$Q = \frac{(C_0 - C_t)V}{m} \quad (1)$$

where C_0 and C_t are the concentrations of Cu^{2+} , Pb^{2+} and Cd^{2+} ions before and after adsorption, respectively (mg/L), V the total volume of the aqueous solution (L), and m is the dry weight of CMKGM (g).

2.4. Adsorption kinetics

For kinetic measurements, 0.5 g CMKGM was added into 50 mL solution containing heavy metal ions with the initial concentrations 200 mg/L under the condition of pH 5. Then 0.5 mL of the supernatant was withdrawn at a given time interval by using a 1 mL pipette and used for the residual metal analysis and the pH was measured. In order to examine the controlling mechanism of adsorption process such as mass transfer and chemical reaction, the first- and second-order equations were used to fit the experiment data. The first-order kinetic equation and second-order kinetic equation are expressed as (2) and (3), respectively [22]:

$$\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303}t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_e and q_t are the amounts of metal ions adsorbed on adsorbent (mg/g) at equilibrium and at time t , respectively, and k_1 is the rate constant of first-order adsorption (min^{-1}). The straight-line plots of $\ln(q_e - q_t)$ against t were used to determine the rate constant k_1 ; k_2 is the rate constant of second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$), it can be obtained from the straight-line plots of t/q_t against t .

2.5. Adsorption isothermals

Keeping the other conditions constant and changing the Cu^{2+} , Pb^{2+} and Cd^{2+} initial concentration, adsorption behavior of metal ions onto CMKGM surface was described by Langmuir isotherm plots and Freundlich isotherm plots. The equations are shown as Eqs. (4) and (5) [23,24]:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m^b} \quad (4)$$

$$\ln Q_e = \ln k_f + \left(\frac{1}{n}\right) \ln C_e \quad (5)$$

where C_e is the equilibrium concentration of the metal ion in solution (mg/L), Q_e the equilibrium adsorption capacity (mg/g), Q_m the monolayer saturated adsorption capacity (mg/g), and b , k_f , n are the constants.

2.6. Desorption of heavy metal ions

In order to determine the reusability of the CMKGM, consecutive adsorption–desorption cycles were repeated three times.

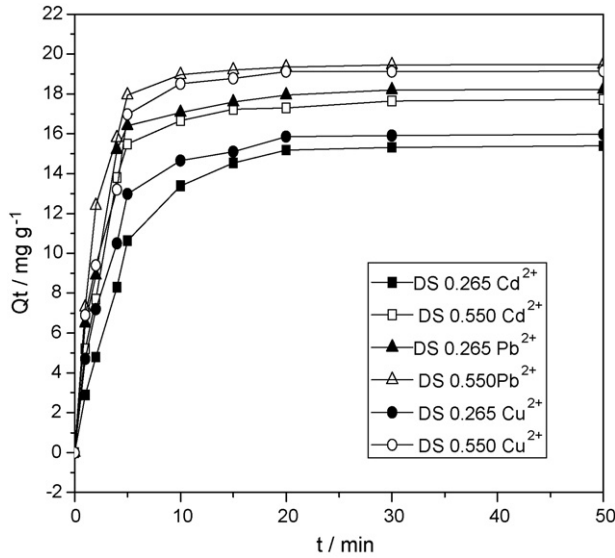


Fig. 1. Kinetics of the adsorption of Cu^{2+} , Pb^{2+} and Cd^{2+} ions.

Desorption of heavy metal ions were performed by using 0.1 mol/L HCl solution. The CMKGM loaded heavy metal ions were placed in this desorption medium and stirred at 600 rpm for 30 min at room temperature. The final metal ion concentration in the aqueous phase were determined and the desorption percentages of metal ions were calculated by the following expressions:

$$\text{percentage of desorption} = \frac{m_r}{m_0} \times 100\% \quad (6)$$

where m_r is the amount of metal ions desorbed (mg) and m_0 is the amount of metal ions adsorbed (mg).

3. Results and discussion

3.1. Adsorption kinetics

Fig. 1 shows the time profiles of metal ions adsorption onto crosslinked CMKGM with the initial concentration of 200 mg/L. Adsorption equilibrium of Cu^{2+} , Pb^{2+} and Cd^{2+} ions onto CMKGM can be obtained in about 20 min, the equilibrium time is independent on DS of carboxymethyl group and metal ion species. The adsorption capacity of CMKGM (DS = 0.550) is bigger than that of CMKGM (DS = 0.265). The order of adsorption capacity of metal ions onto CMKGM is $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$.

In process application, the rapid adsorption phenomenon is an advantage because short adsorption time can directly affect operation cost.

The first- and second-order equations were used to test the experiment data. The validity of both kinetic models is checked and shown in Table 1. From the correlation coefficient of R_1 and R_2 , we can see a good agreement of dynamical data with second-order kinetic equation, while the first-order kinetic model fits the experimental data poorly. It is more likely to predict that the rate-limiting step may be chemical adsorption [22] and the adsorption behavior may involve valency forces through sharing of electrons between transition metal cations and adsorbent [25].

During the course of metal ion removal by CMKGM, it was observed that the pH of the solution increased with increasing of adsorption capacity. At equilibrium, the pH of solutions containing Cu^{2+} , Pb^{2+} and Cd^{2+} ions is 5.5, 6.8 and 7.5, which is lower than the corresponding precipitation pH (5.9, 7.2 and 8.2). This indicates that there no precipitation appeared, reduced concentration of metal ions at equilibrium is only a result of adsorption process.

3.2. Effect of adsorbent dose

Fig. 2 shows the effect of adsorbent dose on adsorption capacity under the condition of pH 5 and $C_0 = 200$ mg/L. The adsorption capacity of metal ions adsorbed by different CMKGM followed the same trend, that is, adsorption capacity increased with increasing of CMKGM dose. But when the CMKGM weight fraction was beyond 1%, the adsorption capacity changed little. As far as improving Q is concerned, increasing the DS of the absorbents is more effective and economical than increasing the absorbents dose.

3.3. Effect of pH on the adsorption

Metal-ion adsorption is known to be dependent on the pH of solution (see Fig. 3). The amount of adsorption increased significantly as the pH increased from 2 to 5 and then leveled off at pH 5–7, pH over 7 was not taken into account to avoid precipitation [26]. Metal ion uptake capacities at lower pH were more dependent than those at higher pH. At the same pH, adsorption capacity of CMKGM with DS equal to 0.550 was higher than that of CMKGM with DS equal to 0.265. At low pH, carboxymethyl groups existed in the form of $-\text{COOH}$, and they prevented the

Table 1
Kinetic parameters for heavy metal ions on crosslinked carboxymethyl konjac glucomannan

Sample	Metal ion	First-order kinetics		Second-order kinetics	
		k_1 (min^{-1})	R_1	k_2 ($\times 10^{-2}$ $\text{g mg}^{-1} \text{min}^{-1}$)	R_2
CMKGM (DS = 0.265)	Cu^{2+}	0.492	0.9806	2.43	0.9990
	Pb^{2+}	0.391	0.9438	3.38	0.9989
	Cd^{2+}	0.465	0.9950	1.23	0.9961
CMKGM (DS = 0.550)	Cu^{2+}	0.632	0.9845	2.78	0.9986
	Pb^{2+}	0.457	0.9472	4.26	0.9994
	Cd^{2+}	0.394	0.9409	2.66	0.9980

Note: R_1 and R_2 are the correlation coefficients of first- and second-order kinetic equation plots.

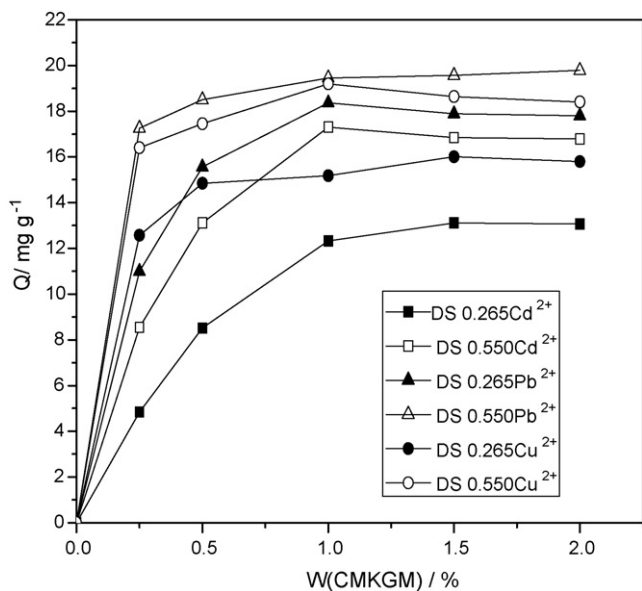


Fig. 2. Effect of CMKGM mass fraction on adsorption capacity for Cu²⁺, Pb²⁺ and Cd²⁺.

adsorption of metal ions onto CMKGM. The chelation between CMKGM and metal ions was stronger at higher pH. Moreover, the carboxymethyl groups in CMKGM were responsible for the interaction; the adsorption was more effective when the DS of carboxymethyl groups was higher.

It is worth mentioning that the increased metal ion uptake at pH 5.0 is not caused by metal hydroxide precipitation. From the initial metal ion concentration in solution and the solubility (*pK*s) of Cu(OH)₂ (18.8), Pb(OH)₂ (16.7) Cd(OH)₂ (14.4), the pH values which would cause precipitation of metal ions were calculated as 5.9, 7.2, 8.2, respectively [27]. Therefore, the optimum pH for Cu²⁺, Pb²⁺ and Cd²⁺ was graphically determined as 5 and used in all experiments (very close to the original pH of the solutions).

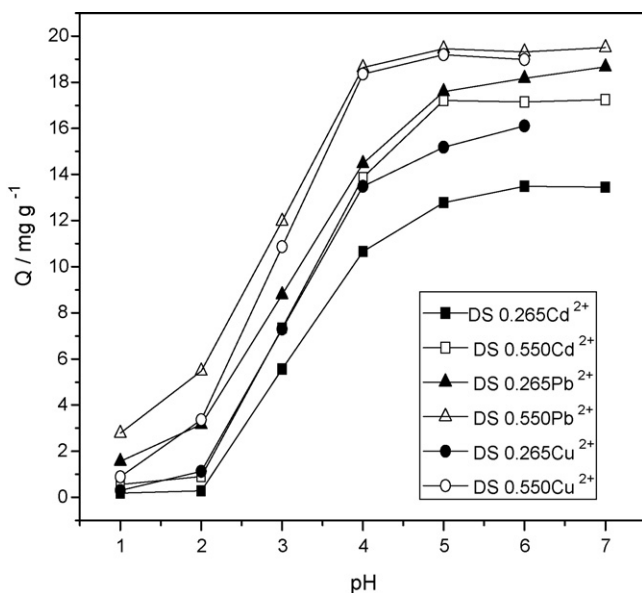


Fig. 3. Effect of solution pH on adsorption capacity for Cu²⁺, Pb²⁺ and Cd²⁺.

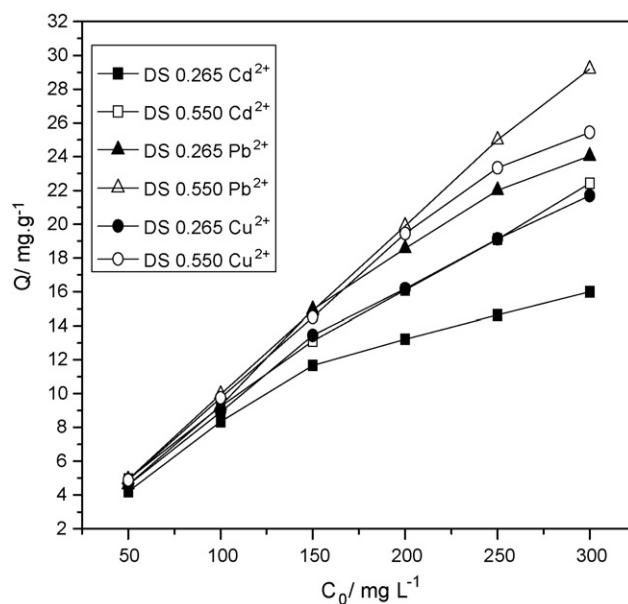


Fig. 4. Effect of the initial concentration of Cu²⁺, Pb²⁺ and Cd²⁺.

3.4. Effect of the initial concentration of metal ions

Fig. 4 showed the relationship between the metal ions initial concentration and the adsorption capacity. The six curves of the adsorption capacity of metal ions versus the initial concentration of metal ions shared the same trend, that is, adsorption capacity increased with increasing of initial concentration of metal ions and the higher DS of carboxymethyl group benefit adsorption of metal ions. The maximum adsorption capacities in the studied range for lead, copper and cadmium ions were 29.2, 25.5 and 22.4 mg/g for CMKGM (DS = 0.550) and 24.0, 21.7 and 16.0 mg/g for CMKGM (DS = 0.265).

3.5. Isothermal adsorption

The Langmuir isotherm data together with the Freundlich data for the investigated heavy metal ions on CMKGM were summarized in Table 2. Comparing the correlation coefficients listed in Table 2, we can draw the conclusion that the adsorption of three kinds of metal ions onto CMKGM is well followed as Langmuir isotherm equation under the concentration range studied. It indicated the monolayer coverage of CMKGM by the ions, all the adsorption sites supplied nearly same action to metal ions. This could reflect indirectly that ligand ion exchange was predominant in the adsorption process. A higher DS value of the carboxymethyl group led to a higher Q_m and k_f , it corresponded to the above-mentioned conclusion that a higher DS resulted in a higher adsorption capacity. The order of Q_m and k_f of the three kinds of metal ions is as follows

$$Q_{mPb^{2+}} > Q_{mCu^{2+}} > Q_{mCd^{2+}}, \quad k_{fPb^{2+}} > k_{fCu^{2+}} > k_{fCd^{2+}}$$

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L that is used to predict if an adsorption system is “favorable” or “unfavorable”. The separa-

Table 2
Langmuir and Freundlich isotherm parameters for Cu²⁺, Pb²⁺ and Cd²⁺ with CMKGM

Sample	Metal ion	Langmuir equation parameters			Freundlich equation parameters		
		<i>b</i> (L/g)	<i>Q_m</i> (mg/g)	<i>R₁</i>	<i>n</i> (g/L)	<i>k_f</i> (mg/g)	<i>R₂</i>
CMKGM (DS = 0.265)	Cu ²⁺	0.062	24.1	0.9984	2.07	2.739	0.9688
	Pb ²⁺	0.070	30.7	0.9758	1.79	3.160	0.8975
	Cd ²⁺	0.043	18.4	0.9975	2.34	2.145	0.9487
CMKGM (DS = 0.550)	Cu ²⁺	0.244	27.8	0.9980	2.32	6.430	0.9074
	Pb ²⁺	0.305	41.7	0.9872	2.36	9.607	0.9140
	Cd ²⁺	0.092	23.6	0.9784	3.18	5.294	0.9641

Note: *R₁* and *R₂* are the correlation coefficient of Langmuir and Freundlich isothermal adsorption plots.

Table 3
Adsorption/desorption cycles for heavy metal ions

Sample	Cycle no.	Cu ²⁺		Pb ²⁺		Cd ²⁺	
		<i>A</i> (mg/g)	<i>D</i> (%)	<i>A</i> (mg/g)	<i>D</i> (%)	<i>A</i> (mg/g)	<i>D</i> (%)
CMKGM (DS = 0.550)	1	25.5	91.0	29.2	94.1	22.4	86.9
	2	24.9	93.1	29.4	89.7	20.1	88.7
	3	25.1	90.7	28.9	91.8	21.7	76.9
CMKGM (DS = 0.265)	1	21.7	88.7	24.0	92.4	16.0	88.9
	2	20.4	92.7	23.7	93.0	16.2	86.1
	3	21.0	91.4	23.0	89.9	15.5	84.7

Note: *A* and *D* represent adsorption capacity (mg/g) and desorption percentage (%), respectively.

tion factor, *R_L* is defined by

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

where *C₀* is the initial concentration of metal ions (mg/L), and *b* is the Langmuir adsorption equilibrium constant (mL/mg). Because *b* values are all beyond zero, *R_L* values are in the range 0 < *R_L* < 1, which indicates that the adsorption of metal ions of CMKGM are favorable. Thus, CMKGM are favorable adsorbents for Pb²⁺, Cu²⁺ and Cd²⁺ ions.

3.6. Regeneration of CMKGM

The adsorption–desorption data of heavy metal ions after three cycles of consecutive adsorption and desorption procedure were listed in Table 3. When HCl was used as a desorption agent, the chelated metal ions is disrupted and subsequently metal ions release from the solid adsorbents into the desorption medium. Table 3 clearly shows that the CMKGM can be used repeatedly without changing significantly their adsorption capacities, and there are high desorption percentages for all metal ions studied here.

4. Conclusion

Carboxymethyl konjac glucomannan can effectively remove Cu²⁺, Pb²⁺ and Cd²⁺ ions from their solutions. Adsorption capacity is affected by solution pH, initial concentration of metal ions, adsorbent dose and DS of carboxymethyl group. The adsorption capacity of CMKGM (DS = 0.550) is bigger than that of CMKGM (DS = 0.265). The order of adsorption capacity of

metal ions onto CMKGM is Pb²⁺ > Cu²⁺ > Cd²⁺ in mass basis. Metal ion uptake capacities at lower pH were more dependent than those at higher pH. Adsorption follows the second-order kinetic model and Langmuir isotherm adsorption under the concentration range studied. The regeneration study indicates that CMKGM can be used repeatedly without changing significantly their adsorption capacities and with high desorption percentage.

References

- [1] S.K. Shany, J. Reedijk, Coordination chemistry of chelating resins and ion exchangers, *Coord. Chem. Rev.* 59 (1984) 1–11.
- [2] G. McMullan, C. Meehan, A. Conneely, N. Kirby, T. Robinson, P. Nigam, Microbial decolourisation and degradation of textile dyes, *Appl. Microbiol. Biotechnol.* 56 (2001) 81–87.
- [3] R.Y. Ning, Arsenic removal by reverse osmosis, *Desalination* 143 (2002) 237–241.
- [4] J.M. Lee, M.S. Kim, B. Hwang, W. Bae, B.W. Kim, Photo-degradation of acid red 114 dissolved using a photo-Fenton process with TiO₂, *Dyes Pigments* 58 (2003) 171–178.
- [5] G.U. Von, Part 1 Oxidation kinetics and product formation, *Water Res.* 37 (2003) 1443–1467.
- [6] X. Chen, G. Chen, P.L. Yue, Novel electrode system for electroflotation of wastewater, *Environ. Sci. Technol.* 36 (2002) 778–783.
- [7] Z. Hu, L. Lei, Y. Li, Y. Ni, Chromium adsorption on high-performance activated carbons from aqueous solution, *Sep. Purif. Technol.* 31 (2003) 13–18.
- [8] Z. Reddad, C. Gerente, Y. Andres, J.F. Thibault, P. Le Cloirec, Cadmium and lead adsorption by natural polysaccharide in MF membrane reactor: experimental analysis and modeling, *Water Res.* 37 (2003) 3983–3991.
- [9] A.J. Varma, S.V. Deshpande, J.F. Kennedy, Metal complexation by chitosan and its derivatives: a review, *Carbohydr. Polym.* 55 (2004) 77–93.
- [10] W. Ciesielski, C.Y. Lii, M.T. Yen, P. Tomasik, Interaction of starch with salts of metals from the transition groups, *Carbohydr. Polym.* 51 (2003) 47–56.

- [11] E. Polaczek, F. Starzyk, K. Malenki, P. Tomasik, Inclusion complexes of starches with hydrocarbons, *Carbohydr. Polym.* 43 (2000) 291–297.
- [12] M.N.V. Ravi Kumar, A review of chitin and chitosan applications, *React. Funct. Polym.* 46 (2000) 1–27.
- [13] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water a review, *J. Hazard. Mater. B* 97 (2003) 219–243.
- [14] E.M.M. Del Valle, Cyclodextrins and their uses: a review, *Proc. Biochem.* 39 (2004) 1033–1046.
- [15] M. Maeda, H. Shimahara, N. Sugiyama, Detailed examination of the branched structure of konjac glucomannan, *Agric. Biol. Chem.* 38 (1980) 315–323.
- [16] F. Smith, H.C. Srivastava, Constitution studies on the glucomannan of konjac flower, *J. Am. Chem. Soc.* 39 (1959) 1715–1718.
- [17] C. Huang, Effect of konjac food on the blood glucose level in diabetics, *Acta Nutritional Sinica* 2 (1990) 360–366.
- [18] K. Hannigan, This food helps control weight, *Food Eng. Int.* 5 (1980) 21–25.
- [19] Y. Gu, J. Shi, Z. Hu, Fight against senium action of konjac polysaccharides, *Chin. Trad. Herb. Drugs* 30 (1999) 78–81.
- [20] C. Mao, N. Yu, Z. Gu, Hypoglycemic effects of amorphophallus konjac in alloxan diabetic rats, *Chin. Mod. Appl. Pharm.* 18 (2001) 12–17.
- [21] Mitchell, Wijnberg, Standardization of methodology for chemical functions in starch derivatives, *Starch/Starke* 47 (1995) 46–51.
- [22] M.S. Chiou, H.Y. Li, Adsorption behavior of reactive dye in aqueous solution of chemical cross-linked chitosan beads, *Chemosphere* 50 (2003) 1095–1102.
- [23] Y. Yanchao, S. Guang, C. Bingnian, Study on adsorption mechanism of Cu(II) onto crosslinked chitosan, *Ion Exchange Adsorp.* 20 (2004) 223–230.
- [24] S. Cay, A. Uyanik, A. Ozasil, Single and binary component adsorption of copper and cadmium from aqueous solutions using tea-industry waste, *Sep. Purif. Technol.* 38 (2004) 273–280.
- [25] M.S. Chiou, H.Y. Li, Equilibrium and kinetic modeling of adsorption of reactive dye of cross-linked chitosan beads, *J. Hazard. Mater.* 93 (2002) 233–248.
- [26] A. Denizli, G. Ozkan, M. Yakup Arica, Preparation and characterization of magnetic polymethylmethacrylate microbeads carrying ethylene diamine for removal of Cu(II), Pb(II), Cd(II) and Hg(II) from aqueous solutions, *J. Appl. Polym. Sci.* 78 (2000) 81–89.
- [27] D.R. Lide, *CRC Handbook of Chemistry and Physics*, 79th ed., CRC Press, Boca Raton, 1998.