

Recovery of Gold(III) Ions by a Chitosan-coated Magnetic Nano-adsorbent

Yang-Chuang Chang and Dong-Hwang Chen*

Department of Chemical Engineering
National Cheng Kung University
Tainan, Taiwan 701, R.O.C.
Tel: 886-6-2757575 Ext.62680
Fax: 886-6-2344496
E-mail: chendh@mail.ncku.edu.tw

* All correspondence should be addressed to Dong-Hwang Chen

Abstract

The monodisperse chitosan-coated Fe_3O_4 nanoparticles with a mean diameter of 13.5 nm and 4.92 wt% chitosan were used as an anionic magnetic nano-adsorbent for the recovery of Au(III) ions from aqueous solutions. It was found that Au(III) ions could be fast and efficiently adsorbed, and the adsorption capacity increased with the decrease in pH due to the protonation of the amino groups of chitosan. The adsorption data obeyed the Langmuir equation with a maximum adsorption capacity of 59.52 mg/g (1210 mg/g based on the weight of chitosan) and a Langmuir adsorption equilibrium constant of 0.066 l/mg. From the studies on the adsorption kinetics and thermodynamics of Au(III) ions, it was found that the adsorption process obeyed the pseudo-second-order kinetic model. Furthermore, the time required to reach the equilibrium was significantly shorter than those using the micro-sized adsorbents due to the large available surface area.

Keywords

gold(III); adsorption; chitosan; magnetic

Introduction

The recovery of precious metals such as silver, gold and platinum group metals is always attracting considerable attention due to the increasing industrial need and limiting sources. Besides the traditional precipitation method, solvent extraction and ion exchange techniques are usually used [1-5]. Although the former usually has relatively high efficiency and selectivity, the latter is sometime preferred because of the advantages that the mixing and settling requirements are usually more easily achieved as well as the utilization and loss of solvent can be eliminated.

The natural polysaccharide chitosan and its derivatives have great potential applications in the areas of biotechnology, biomedicine, food ingredients and cosmetics [6-11]. Owing to the abundant amino groups, chitosan and its derivatives also have good capability for the uptake of metal ions via the chelation or ion exchange mechanisms, depending on the kind of metal ions and the pH of solution [12-17]. Chitosan beads and chitosan-inorganic composites for the adsorption of metal ions were usually prepared by crosslinking the amino groups on chitosan with dialdehyde such as glutaraldehyde via a Schiff's reaction [18-21]. They were submicron to micron-sized and needed large internal porosities to ensure adequate surface area for adsorption. However, the diffusion limitation within the particles led to the decreases in the adsorption rate and available capacity.

Recently, we developed a novel magnetic nano-adsorbent with Fe_3O_4 nanoparticles as cores and chitosan as ionic exchange groups. It could be easily manipulated by an external magnetic field, and has been shown to be quite fast and efficient for the adsorption of Cu(II) ions and acid dyes due to high specific surface area and the absence of internal diffusion resistance [22-23]. Also, it could be used as a magnetic nano-carrier for targeted cancer therapy [24]. In this work, we further demonstrate the feasibility of the chitosan-coated magnetic nano-adsorbent in the recovery of metal anions using the valuable Au(III) ions as the model compound. The corresponding adsorption kinetics and thermodynamics were studied.

Experimental

Chitosan (low-viscous) and ferrous chloride tetrahydrate were purchased from Fluka (Buchs). Carbodiimide (cyanamide, CH_2N_2) was supplied by Sigma Chemical Co. (St. Louis, MO). Ferric chlorides, 6-hydrate was purchased from J. T. Baker (Phillipsburg). Ammonium hydroxide (29.6%) was supplied by TEDIA (Fairfield). Hydrogen tetrachloroaurate was supplied by Alfa (Ward Hill, MA). All other chemicals were the guaranteed or analytic grade reagents and used as received.

Chitosan-coated magnetic nano-adsorbent was prepared according to our previous work [22]. Fe_3O_4 nanoparticles were prepared by co-precipitation method and chitosan was carboxymethylated. For the binding of carboxymethyl chitosan, 100 mg of Fe_3O_4 nanoparticles were first added to 2

Table 1

Langmuir and Freundlich isotherm constants for the adsorption of Au(III) ions on the chitosan-coated magnetic nano-adsorbent

q_m (mg/g)	Langmuir		Freundlich		
	$K_L \times 100$ (l/mg)	R^2	n	K_F (l/mg)	R^2
59.52	6.589	1.000	4.14	13.14	0.756

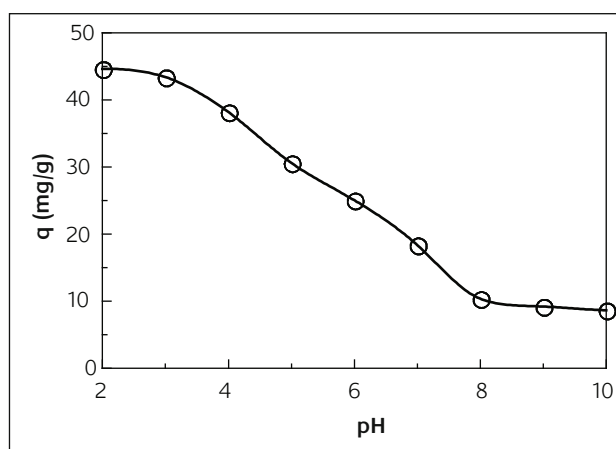
ml of buffer A (0.003M phosphate, pH 6, 0.1M NaCl). Then, the reaction mixture was sonicated for 10 min after adding 0.5 ml of carbodiimide solution (0.025 g/ml in buffer A). Finally, 2.5 ml of carboxymethyl chitosan solution (50 mg/ml in buffer A) was added and the reaction mixture was sonicated for 60 min. The product was recovered from the reaction mixture by a permanent magnet, and then washed with water and ethanol. The resultant chitosan-coated magnetic nano-adsorbent was monodisperse, with a mean diameter of 13.5 nm, 4.92 wt% chitosan, and an isoelectric point of 5.95. The characterization methods and other properties could be obtained in our previous works [22-24].

The adsorption of Au(III) ions by the chitosan-coated magnetic nano-adsorbent was investigated in aqueous solutions at pH 2-10. In general, 105.17 mg magnetic nano-adsorbent (i.e., 5.17 mg chitosan on 100 mg Fe_3O_4) was added to 5 ml of hydrogen tetrachloroaurate solution. The adsorption isotherms were investigated at 25°C, a contact time of 12h, and various Au(III) ion concentrations (200-3000 mg/l). The magnetic nano-adsorbent was removed magnetically from the solution and the concentrations of Au(III) ions were determined using a GBC Avanta atomic absorption spectrometer. The adsorption kinetics was studied at pH 2, 15-35°C, and various Au(III) ion concentrations (644-1539 mg/l). At various time intervals, the magnetic nano-adsorbent was removed magnetically and the concentrations of Au(III) ions in solutions were determined.

Results and discussion

Effect of pH on adsorption capacity

The effect of pH on the adsorption of Au(III) ions by the chitosan-coated magnetic nano-adsorbent at 25°C and an initial Au(III) ion concentration of 1039 mg/l was illustrated in Fig. 1. It was found that the adsorption capacity of Au(III) ions increased with the decrease in pH. This phenomenon was consistent with the pH-dependence of zeta potential as observed in our previous work [22], and could be attributed to the increased electrostatic attractions between the negatively charged Au(III) anions and the positively charged adsorption sites of chitosan at lower pH values although mixed gold chloride-hydroxide complexes might be present [16]. Because the isoelectric point of chitosan-coated magnetic nano-adsorbent was 5.95, the low adsorption capacity in alkaline solutions might be referred to the fact that chitosan-coated magnetic nano-adsorbent was not positively charged. Since the maximum adsorption capacity occurred at pH 2 in the examined pH range, the following adsorption studies were carried out at pH 2.

**Figure 1**

Effect of pH on the adsorption of Au(III) ions by the chitosan-coated magnetic nano-adsorbent at 25°C and an initial Au(III) ion concentration of 1039 mg/l

Adsorption isotherms

The equilibrium isotherm for the adsorption of Au(III) ions by the chitosan-coated magnetic nano-adsorbent at pH 2 and 25°C was shown in Fig. 2. The equilibrium data were fitted by Langmuir and Freundlich isotherm equations. The Langmuir equation can be expressed as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (1)$$

where q_e is the equilibrium Au(III) ion concentration on the adsorbent (mg/g), C_e is the equilibrium Au(III) ion concentration in solution (mg/l), q_m is the maximum capacity of adsorbent (mg/g), and K_L is the Langmuir adsorption constant (l/mg). The linear form of Freundlich equation, which is an empirical equation used to describe heterogeneous adsorption systems, can be represented as follows:

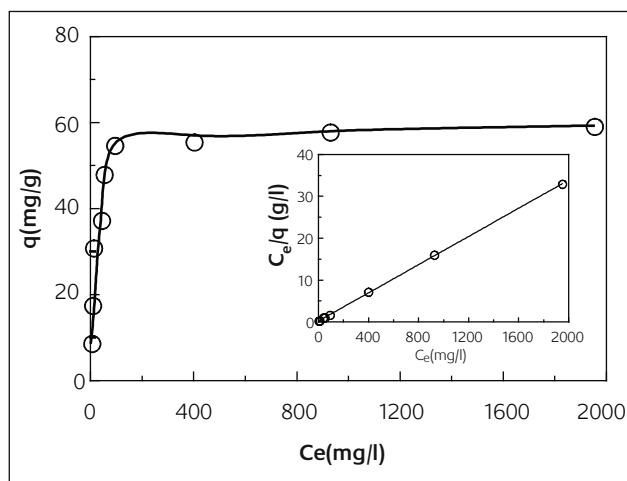
$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

where q_e is the equilibrium Au(III) ion concentration on the adsorbent (mg/g), C_e is the equilibrium Au(III) ion concentration in solution (mg/l), K_F is Freundlich constant (l/mg), and n is the heterogeneity factor. The equilibrium isotherm for the adsorption of Au(III) ions was shown in Fig. 2 and the corresponding Langmuir and Freundlich constants and correlation coefficients (R) were listed in Table 1. From the comparison of correlation coefficients, it was found that the data were fitted better by Langmuir equation than by Freundlich equation, revealing the adsorption of Au(III) ions on the chitosan-coated magnetic nano-adsorbent obeyed the Langmuir adsorption isotherm. From the slope and intercept in the inset of Fig. 2, the values of q_m and K might

Table 2

Kinetic parameters for the adsorption of Au(III) ions by the chitosan-coated magnetic nano-adsorbent at various initial Au(III) ion concentrations and temperatures

C_0 (mg/l)	T (°C)	$k_1 \times 10^3$ (min ⁻¹)	R_1^2	$k_2 \times 10^3$ (g/mg/min)	q_2 (mg/g)	R_2^2	k_p (mg/g/min ^{1/2})	C (mg/g)	R_p^2
644	25	5.68	0.935	28.83	31.04	1.000	0.31	26.57	0.618
1039	25	7.58	0.938	8.09	44.76	0.999	0.71	34.35	0.885
1283	25	2.81	0.903	5.93	48.73	0.999	0.61	38.26	0.936
1539	25	4.30	0.963	1.05	52.74	0.983	1.27	28.38	0.954
1039	15	5.30	0.893	6.57	46.21	0.999	0.49	37.48	0.931
1039	35	4.54	0.887	8.91	46.06	1.000	0.49	38.16	0.841

**Figure 2**

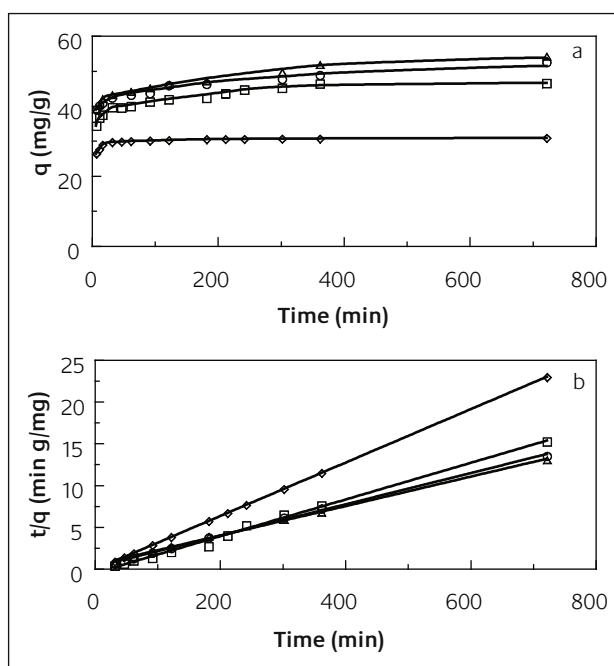
Equilibrium isotherm for the adsorption of Au(III) ions on the chitosan-coated magnetic nano-adsorbent at pH 2 and 25°C. The inset illustrates the linear dependence of C_e/q on C_e

be estimated as 59.52 mg/g and 0.066 l/mg, respectively. Based on the weight of coated chitosan, the maximum adsorption capacity could be calculated to be 1210 mg/g. This was significantly higher than the values 33.9 and 591 mg/g observed for the adsorption of Au(III) ions on microbeads of chitosan derivatives by Ngah et al. [25] and Arrascue et al. [16], respectively. This might be reasonably referred to the high specific surface area because the coated chitosan might be spread on the surface of Fe_3O_4 cores, leading to that almost all amino groups were available.

In addition, it was noteworthy that the equilibrium Au(III) ion concentration was almost undetectable (< 1 mg/l) when the initial Au(III) ion concentration was less than 100 mg/l. This revealed the chitosan-coated magnetic nano-adsorbent was quite efficient for the adsorption of Au(III) ions and could reduce the Au(III) ions to a concentration level less than 1 mg/l.

Adsorption kinetics

The kinetics for the adsorption of Au(III) ions on the chitosan-coated magnetic nano-adsorbent at pH 2 was investigated. The effect of initial Au(III) ion concentration was shown in Fig. 3(a). It was obvious that about 90% of the equilibrium adsorption capacity could be achieved after 30 min and the adsorption equilibrium was completely achieved after 6-12 h, increasing with the increase of initial Au(III) ion concentration. Since the chitosan with smaller particle size had a higher

**Figure 3**

(a) Effect of initial Au(III) ion concentration on the adsorption kinetics of Au(III) ions by the chitosan-coated magnetic nano-adsorbent at pH 2 and 25°C: 644 (\diamond), 1039 (\square), 1283 (\circ), and 1539 (\triangle) mg/l. (b) The linear dependence of t/q on t

adsorption rate due to the availability of larger specific surface area on the adsorbent [12], the contact time required to reach the equilibrium was shorter for the magnetic nano-adsorbent in this study than those for the micro-sized adsorbents reported in the literatures [5,16,25].

Three kinetic models were tested to find out the appropriate adsorption rate expression: the pseudo-first-order equation [26], pseudo-second-order equation [27], and intraparticle diffusion model [28] as expressed below

$$\ln \frac{(q_e - q_t)}{q_e} = -k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \quad (4)$$

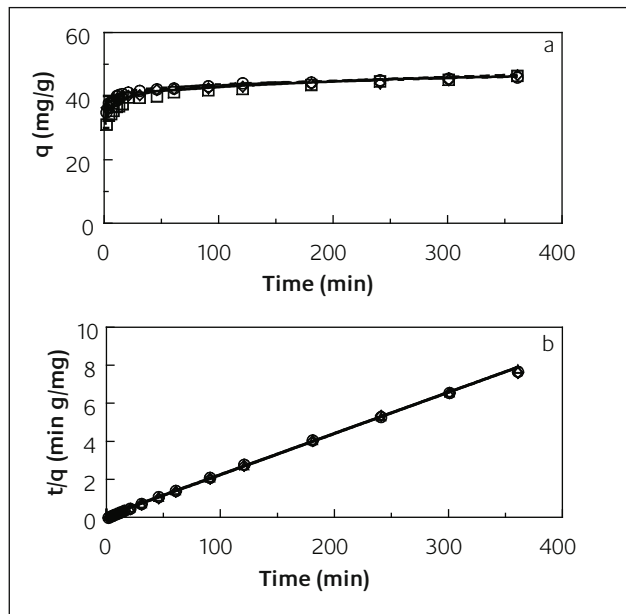
$$q_t = k_p t^{1/2} + C \quad (5)$$

where q_t is the amount of dye adsorbed (mg/g) at time t , q_e is the maximum adsorption capacity (mg/g) for pseudo-first-order adsorption, k_1 is the pseudo-first-order rate constant

Table 3

Thermodynamic parameters for the adsorption of Au(III) ions by the chitosan-coated magnetic nano-adsorbent at various temperatures calculated from the second-order rate constants

T(°C)	E_a (kJ/mol)	K^* (g/mg) $\times 10^{-17}$	ΔG^* (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J/mol)
15		18.25	86.77	8.88	-270.4
25	11.28	21.72	89.36	8.80	-270.3
35		23.14	119.13	8.72	-358.5

**Figure 4**

(a) Effect of temperature on the adsorption kinetics of Au(III) ions by the chitosan-coated magnetic nano-adsorbent at pH 2 and an initial Au(III) ion concentration of 1039 mg/l: 15 (○), 25 (◇), and 35 (□) °C. (b) The linear dependence of t/q on t

(min), q_2 is the maximum adsorption capacity (mg/g) for pseudo-second-order adsorption, k_2 is the pseudo-second-order rate constant (g/mg/min), C is the intercept, and k_p is the intraparticle diffusion rate constant (mg/g/min^{1/2}).

The kinetic parameters (k_1 , k_2 , k_p , q_1 , q_2 , C) and correlation coefficients (R_1^2 , R_2^2 , R_p^2) of Au(III) ions were calculated and listed in Table 2. The correlation coefficients revealed the adsorption data were best fitted by the pseudo-second-order kinetic model, revealing the rate limiting step may be chemical sorption involving valency forces through sharing or exchange of electrons between chitosan and Au(III) ions [27]. As shown in Fig. 3(b), all the plots of t/q_t vs t at various initial concentrations yield straight lines. In addition, it was notable that the correlation coefficients for intraparticle diffusion model were much below 1, indicating the adsorption process significantly deviated from the intraparticle diffusion kinetic model. This is reasonable because the adsorption of Au(III) ions occurred only on the surface of chitosan-coated Fe₃O₄ nanoparticles and the intraparticle diffusion resistance was absent.

Thermodynamic parameters

The effect of temperature on the adsorption of Au(III) ions by the chitosan-coated magnetic nano-adsorbent was not obvious as shown in Fig. 4(a). By fitting the adsorption data with the above three kinetic models, it revealed that the

pseudo-second-order kinetic model was still the best one for the adsorption of Au(III) ions at different temperatures. The kinetic parameters (k_1 , k_2 , k_p , q_1 , q_2 , C) and correlation coefficients (R_1^2 , R_2^2 , R_p^2) were given in Table 2, and the plots of t/q_t vs t at different temperatures also yield straight lines as shown in Fig. 4(b).

In spite of the weak temperature-dependence, from the rate constants (k_2) at different temperatures, the thermodynamic parameters for the adsorption process could be evaluated. The activation energy (E_a) was obtained from the Arrhenius plot. The other activation parameters such as activation free energy change (ΔG^*), activation enthalpy change (ΔH^*), and activation entropy change (ΔS^*), were calculated by the following equations [29-30]

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad (6)$$

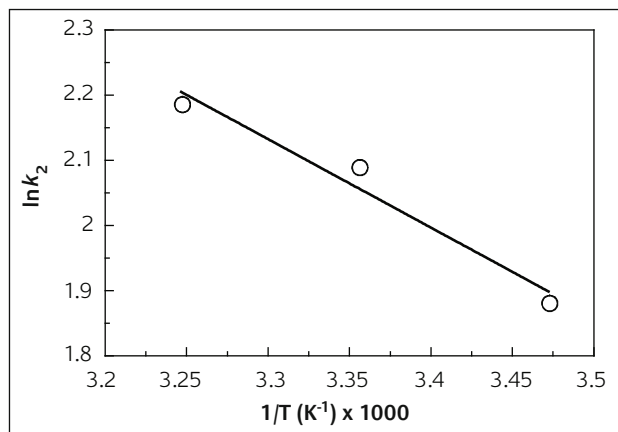
$$k_2 = \frac{k_b T}{h} K^* \quad (7)$$

$$\Delta G^* = -RT \ln K^* \quad (8)$$

$$\Delta H^* = -E_a - RT \quad (9)$$

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T} \quad (10)$$

where E_a is the Arrhenius activation energy, A is the Arrhenius factor, k_b and h are Boltzmann's and Planck's constants, respectively, R is the gas constant, and K^* is the equilibrium constant at temperature T . From the slope of the linear plot of $\ln k_2$ vs $1/T$ (shown in Fig. 5), the activation energy was obtained as 11.28 kJ mol⁻¹. Usually the activation energy of

**Figure 5**

Effect of temperature on the rate constant for the adsorption of Au(III) ions by the chitosan-coated magnetic nano-adsorbent at pH 2 and an initial Au(III) ion concentration of 1039 mg/l

physical adsorption is 5-40 kJ/mol while that of chemical adsorption is (40-800 kJ/mol) [31], so the adsorption of Au(III) ions on the chitosan-coated magnetic nano-adsorbent should be physical adsorption. This was reasonable because Au(III) ions were adsorbed on the chitosan via the ion-ion interaction.

The activation energy and other thermodynamic parameters were listed in Table 3. The positive values of E_a , ΔG^* , ΔH^* indicate the presence of an energy barrier in the adsorption process. This is quite common and reasonable because the activated complex in the transition state is an excited form. Furthermore, the negative value of ΔS^* was resulted from the decreased randomness due to the adsorption of Au(III) ions.

Conclusion

The adsorption of Au(III) ions by the chitosan-coated Fe_3O_4 nanoparticles via the anion exchange in aqueous solutions was studied. The adsorption capacity increased with the decrease in pH owing to the protonation of the amino groups of chitosan. The equilibrium isotherm could be described by the Langmuir equation, and the adsorption process obeyed the pseudo-second-order kinetic model with a shorter time required for reaching the equilibrium than those using the micro-sized adsorbents. Such a magnetic nano-adsorbent is useful for the efficient removal of Au(III) ions or other valuable metal anions from the aqueous solutions.

The authors thank the National Science Council of the Republic of China for support (NSC 93-2214-E006-023).

About the authors

Dr. Yang-Chuang Chang received his PhD in Chemical Engineering at National Cheng Kung University (Taiwan), focusing on the fabrication and applications of multi-functional magnetic nano-carriers. He currently is a researcher at Institute of Nuclear Energy Research (Taiwan), working on the development of fuel cells.

Dr. Dong-Hwang Chen is a professor of Chemical Engineering Department at National Cheng Kung University (Taiwan). His research works include the synthesis of nanoparticles, the fabrication of functional composite nanoparticles and thin films, the applications of surface-modified magnetic nanoparticles in separation, catalysis, and biomedicine, as well as the development of composite nanomaterials for electromagnetic wave absorption.

References

- 1 I. Villaescusa, V. Salvadó, J. de Pablo, *Hydrometallurgy*, 1996, **41**, 303
- 2 M.A. Barroso, F.A. López, A.M. Saatre, F.J. Alguacil, *Hydrometallurgy*, 1996, **45**, 199
- 3 C.P. Gomes, M.F. Almeida, J.M. Loureiro, *Sep. Purif. Technol.*, 2001, **24**, 35
- 4 E. Anticó, A. Masana, V. Salvadó, M. Hidalgo, M. Valiente, *Anal. Chim. Acta*, 1984, **296**, 325
- 5 M. Iglesias, E. Anticó, V. Salvadó, *Anal. Chim. Acta*, 1999, **381**, 61
- 6 M.J. Alonso, *Biomed. & Pharmacother.*, 2004, **58**, 168
- 7 A. Bozkir, O.M. Saka, *Drug Deliv.*, 2004, **11**, 107
- 8 A.K. Singla, M. Chawla, *J. Pharm. Pharmacol.*, 2001, **53**, 1047
- 9 J.L. Chew, C.B. Wolfowicz, H.Q. Mao, K.W. Leong, K.Y. Chua, *Vaccine*, 2003, **21**, 2720
- 10 X.G. Chen, C.M. Lee, H.J. Park, *J. Agr. Food Chem.*, 2003, **51**, 3135
- 11 M. Kabbaj, N.C. Phillips, *J. Drug Target.*, 2001, **9**, 317
- 12 G. Karthikeyan, K. Anbalagan, N.M. Andal, *J. Chem. Sci.*, 2004, **116**, 119
- 13 R.S. Juang, H.J. Shao, *Water Res.*, 2002, **36**, 2999
- 14 J.C.Y. Ng, W.H. Cheung, G. McKay, *J. Colloid Interface Sci.*, 2002, **255**, 64
- 15 K. Inoue, K. Yoshizuka, K. Ohto, *Anal. Chem. Acta*, 1999, **388**, 209
- 16 M.L. Arrascue, H.M. Garcia, O. Horna, E. Guibal, *Hydrometallurgy*, 2003, **71**, 191
- 17 M. Ruiz, A.M. Sastre, E. Guibal, *React. Funct. Polym.*, 2000, **45**, 155
- 18 T.Y. Hsien, G.L. Rorrer, *Sep. Sci. Technol.*, 1995, **30**, 2455
- 19 T.Y. Hsien, G.L. Rorrer, *Ind. Eng. Chem. Res.*, 1997, **36**, 3631
- 20 A.L. Debbaudt, M.L. Ferreira, M.E. Gschaider, *Carbohydr. Polym.*, 2004, **56**, 321
- 21 M.W. Wan, I.G. Petrisor, H.T. Lai, D. Kim, T.F. Yen, *Carbohydr. Polym.*, 2004, **55**, 249
- 22 Y.C. Chang, D.H. Chen, *J. Colloid Interface Sci.*, 2005, **283**, 446
- 23 Y.C. Chang, D.H. Chen, *Macromol. Biosci.*, 2005, **5**, 254
- 24 Y.C. Chang, D.B. Shieh, C.H. Chang, D.H. Chen, *J. Biomed. Nanotechnol.*, 2005, **1**, 196
- 25 W.S.W. Ngah, K.H. Liang, *Ind. Eng. Chem. Res.*, 1999, **38**, 1411
- 26 E. Tutem, R. Apak, G.F. Unal, *Water Res.*, 1998, **32**, 2315
- 27 Y.S. Ho, G. McKay, *Process Biochem.*, 1999, **34**, 451
- 28 W.J. Weber Jr., J.C. Morriss, J. Sanitary, *Eng. Div. Am. Soc. Civ. Eng.*, 1963, **89**, 31
- 29 R.S. Juang, F.C. Wu, R.L. Tseng, *Environ. Technol.*, 1997, **18**, 525
- 30 W. Stumm, J.J. Morgan, *Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*, 2nd edn, J. Wiley & Sons, New York, 1981
- 31 H. Nolle, M. Roels, P. Lutgen, P. Van der Meeren, W. Verstrate, *Chemosphere*, 2003, **53**, 655