

# Thermodynamic studies of the interaction at the solid/liquid interface between metal ions and cellulose modified with ethylenediamine

Jocilene D. Torres, Elaine A. Faria, Alexandre G.S. Prado\*

*Instituto de Química, Universidade de Brasília, Caixa Postal 4478, 70904-970 Brasília, Distrito Federal, Brazil*

Received 6 May 2005; received in revised form 26 August 2005; accepted 27 August 2005

Available online 10 October 2005

## Abstract

The chelate molecule, ethylenediamine, has been incorporated onto the surface of cellulose by sequential reaction of cellulose fibres with phosphorous oxychloride followed by the chelating agent. The modified material (CeINN) retained its fibrous nature and was shown to be efficient at adsorbing divalent metal cations from water by complexation. Adsorption isotherms were determined for suspensions of CeINN in metal ion solutions of different concentrations, and the data were adjusted to fit the modified Langmuir equation. The maximum numbers of moles of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  adsorbed per gram of modified cellulose were  $1.64 \times 10^{-3}$ ,  $5.25 \times 10^{-4}$  and  $1.06 \times 10^{-3}$ , respectively. The thermodynamic effects related to the adsorption of metal ion onto the cellulose surface were determined by calorimetric titration. Gibbs free energy was spontaneous for all interactions. The adsorption processes all exhibited endothermic enthalpy values and were accompanied by increases in entropy. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Cellulose fibre; Metal ion adsorption; Calorimetry

## 1. Introduction

Heavy metal contaminants are often present in the wastewater effluents produced by industries involved in, for example, metal processing (particularly finishing and plating), mining and tanning. In general, heavy metals are not biodegradable and tend to accumulate in living organisms [1–3]. In natural water supplies, even low concentrations of such contaminants may be harmful to wildlife and can be the cause of various diseases in human beings [3,4]. For this reason, the monitoring of local water sources for heavy metal content is of paramount importance in ensuring the well-being of a given community [5]. However, in order accurately to determine concentrations of metal cations at trace levels, it is often necessary to carry out a pre-concentration step, typically involving specific adsorption of analyte onto a solid substrate [6]. In this respect, cellulose is a particularly attractive support since it is available at low cost as a renewable feedstock, and presents excellent mechanical and thermal resistance, and thermal and dimensional stability [7,8].

Furthermore, the active hydroxyl group present on C6 of each monomeric unit of cellulose (Fig. 1) has the ability to react with appropriate groups of organic ligands. In this manner, the surface of cellulose may readily be modified, through low-cost chemical processes, to produce materials with considerable ion exchange capacity [9,10].

The aim of the present study was to examine the adsorption from aqueous solution of divalent metal ions ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ ) by a novel form of cellulose fibre, the surface of which had been modified with ethylenediamine. An understanding of the thermochemical characteristics of the adsorption interaction was developed by determination of the calorimetric adsorption data at the solid/liquid interface.

## 2. Experimental

### 2.1. Chemicals

Reagent grade cellulose fibre and phosphorus oxychloride were purchased from Merck, and ethylenediamine and xylene were from Aldrich: reagents were used without prior purification.

\* Corresponding author. Tel.: +55 61 307 2166; fax: +55 61 32734149.  
E-mail address: agsprado@unb.br (A.G.S. Prado).

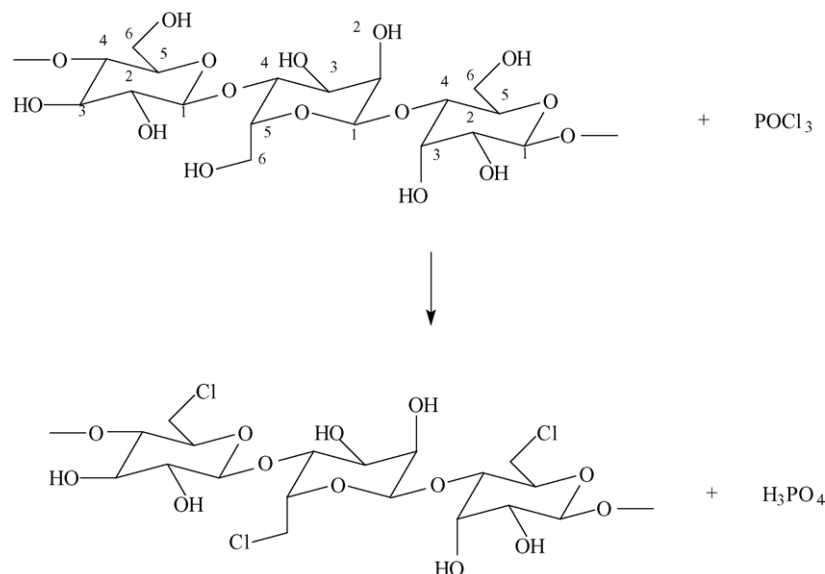


Fig. 1. The modification of cellulose by reaction with phosphorous oxychloride to give the precursor cellulose (CelCl).

## 2.2. Synthesis of modified cellulose

Cellulose fibre (6.0 g) was suspended in xylene (50.0 ml) and stirred mechanically for 1 h at  $70^\circ\text{C}$  under an atmosphere of dry nitrogen. Phosphorus oxychloride (10.0 ml) was added dropwise to the resulting suspension, and the reaction mixture maintained under the same conditions for 24 h in order to obtain the precursor cellulose, CelCl (Fig. 1) [11]. Subsequently, ethylenediamine (5.0 ml) was added to the reaction mixture and the whole maintained under the same conditions for a further 24 h in order to yield the final product, CelINN (Fig. 2). The resulting solid mate-

rial was washed with ethanol and water, and dried under vacuum at room temperature.

## 2.3. Characterisation of modified cellulose

The amount of ethylenediamine incorporated into the cellulose was determined by Kjeldahl analysis. In order to study the morphology of CelINN, samples were coated with carbon using a Balzer model MED 020 metalliser and subsequently examined by scanning electron microscopy performed on a JEOL model JSM-6360 LV instrument [12].

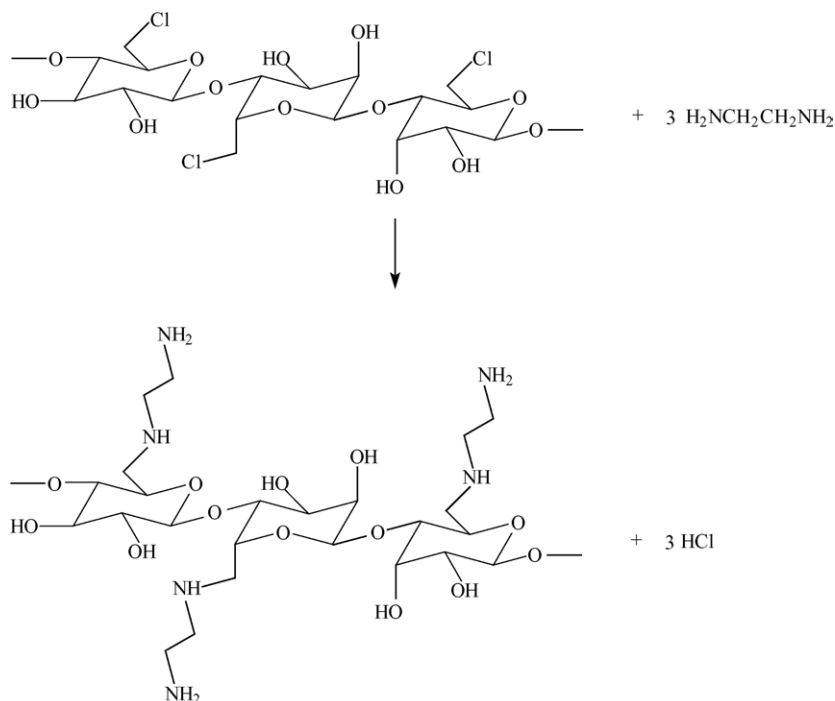


Fig. 2. Reaction between precursor cellulose (CelCl) and ethylenediamine to produce the modified cellulose CelINN.

#### 2.4. Determination of adsorption isotherms

The process of adsorption by CeINN of the metal ions  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  was followed in a series of batchwise experiments. Samples (25.0 mg) of CeINN were suspended at 25 °C in 50.0 ml aliquots of aqueous solutions of  $\text{CuCl}_2$ ,  $\text{ZnCl}_2$  or  $\text{NiCl}_2$  with concentrations in the range  $0\text{--}15.0 \times 10^{-3} \text{ mol l}^{-1}$ , pH was controlled at 5 by using  $\text{Na}_3\text{PO}_4/\text{H}_3\text{PO}_4$  buffer [13]. The amount of metal ion adsorbed was determined from the difference in metal ion concentration (measured by atomic adsorption spectrometry using a Buck model A-200 instrument) in the aqueous sample before and after treatment with CeINN. All experiments were carried out in triplicate.

#### 2.5. Calorimetric analyses

The adsorption of metal ion by CeINN was monitored calorimetrically by titration using an Isoperibol CSC model ISC 4300 calorimeter. In a typical experiment, a sample (0.50 g) of modified cellulose was suspended in 50.0 ml of water, equilibrated at  $25 \pm 0.02$  °C (thermostatically controlled), and titrated with metal ion solution ( $0.50 \text{ mol l}^{-1}$ ) under continuous stirring. The metal ion solution was added in increments of 0.40 ml, via a syringe coupled to the calorimetric vessel, up to saturation of the active surface sites of the modified cellulose. Following each addition, the constant heat flux ( $\Delta_{\text{tit}}Q$ ) was recorded at the end of the operation, and the mixture allowed to re-equilibrate. A similar procedure was employed to monitor the heat flux associated with the dilution of the cationic solution ( $\Delta_{\text{dil}}Q$ ) in the absence of CeINN, and also the heat flux of solvation of the suspended modified cellulose ( $\Delta_{\text{sol}}Q$ ) [12].

### 3. Results and discussion

The modification of cellulose fibre with ethylenediamine formed a new material (CeINN) that exhibited the ability to complex with metal ions. The amount of ethylenediamine incorporated onto the cellulose was determined by Kjeldahl analysis [14], which gave  $8.13 \times 10^{-4} \text{ mol g}^{-1}$  CeINN. The modified material retained its fibre morphology, as indicated by scanning electron microscopy (Fig. 3), hence the material was readily recoverable from the reaction medium. Retention of the fibrous nature of the material is an important characteristic of the modified cellulose and contrasts with the situation typical of silica, derivatives of which become difficult to recover following modification.

The number of moles of cation adsorbed per gram of cellulose fibre ( $N_f$ ) was obtained from the initial number of moles of cation added to the adsorbent system ( $n_i$ ) and the number of moles of cation remaining in solution at equilibrium ( $n_s$ ) for a given mass ( $m$ ) of CeINN by application of the expression:  $N_f = (n_i - n_s)/m$ . These experimental data were applied to the general equation for the modified Langmuir model [15,16]

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s K}$$

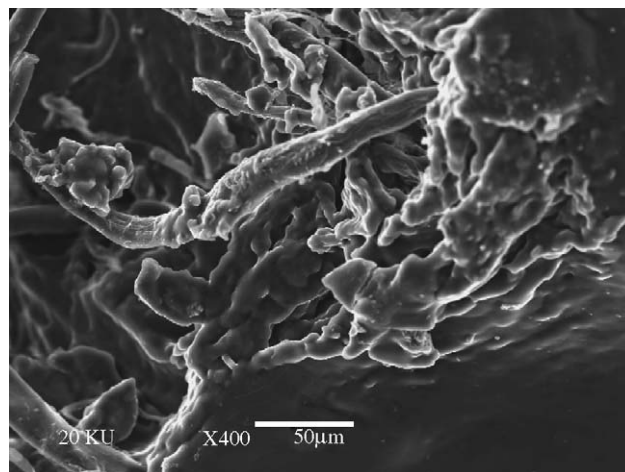


Fig. 3. Scanning electron micrograph of the modified cellulose CeINN showing fibre morphology.

where  $C_s$  is the concentration of cation in solution at equilibrium ( $\text{mol dm}^{-3}$ ),  $N_s$  the maximum amount of cation adsorbed per gram of CeINN ( $\text{mol g}^{-1}$ ), which depends on the number of adsorption sites, and  $K$  is an equilibrium constant ( $\text{mol dm}^{-3}$ ). All further data were derived from the linearised form of the adsorption isotherm, i.e. from plots of  $C_s/N_f$  as a function of  $C_s$ ; values of  $N_s$  and  $K$  were obtained from the slope and intercept as shown in (Fig. 4). Table 1 presents the values of  $N_s$ , from which it can be seen that  $\text{Zn}^{2+}$  was more efficiently adsorbed than  $\text{Ni}^{2+}$ , which in turn was adsorbed more efficiently than  $\text{Cu}^{2+}$ .

The CeINN material adsorbs at around 100 times more than unmodified cellulosic material as described before [17,18]. Indeed, the modification of cellulose with ethylenediamine improve the adsorption ability of the cellulose. Furthermore, the amount of metal ions adsorbed by CeINN was similar to cations amount adsorbed by chitosan as reported before [19–21], this fact proves the quality of this new modified cellulose material.

The thermodynamic effects related to the adsorption of a compound onto a material surface at a solid/liquid interface may be derived from theoretical consideration [22,23], adsorption studies at different temperatures [24,25], or calorimetric titration [26–28]. In the present study, a suspension of CeINN was calorimetrically titrated with divalent metal ion in order to obtain more information about the interactions between cation and the basic centre on the CeINN surface. The thermal effects associated with each interaction were determined from a series of calorimetric experiments and the complete thermodynamic cycle obtained by summation. Three independent titration experiments were carried out to measure: (a) the heat evolved by the

Table 1  
Maximum adsorbed amounts ( $N_s$ ) of the cations  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  per gram of CeINN and thermodynamic data for these interactions at  $298.15 \pm 0.02$  K

	$N_s$ ( $\text{mol g}^{-1}$ )	$\Delta H$ ( $\text{kJ mol}^{-1}$ )	$\Delta G$ ( $\text{kJ mol}^{-1}$ )	$\Delta S$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )
Cu	$1.64 \times 10^{-3}$	7.91	−2.59	35
Ni	$5.25 \times 10^{-4}$	16.31	−2.82	64
Zn	$1.06 \times 10^{-3}$	6.70	−1.90	29

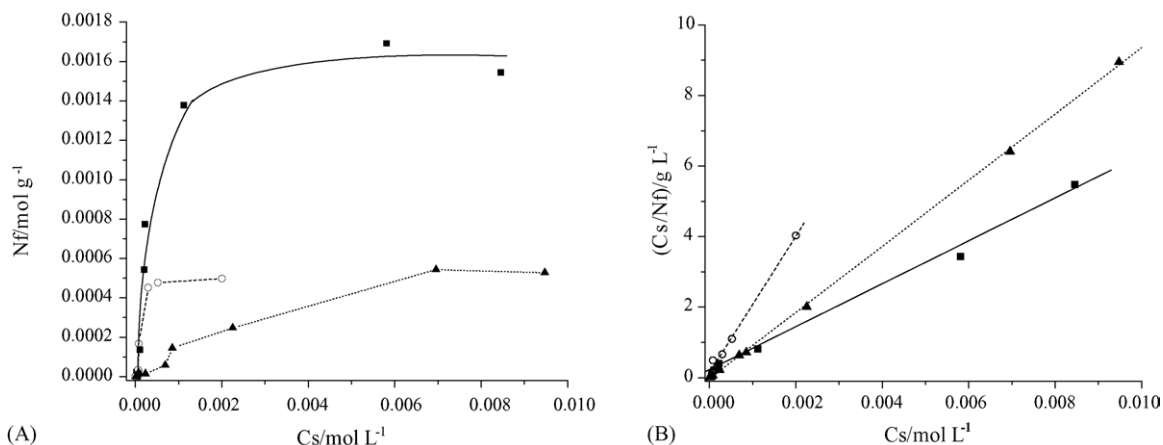


Fig. 4. Adsorption isotherms (A), and the corresponding linearised forms (B), for the interaction between CeINN fibre and aqueous solutions of  $\text{CuCl}_2$  (■),  $\text{NiCl}_2$  (○) and  $\text{ZnCl}_2$  (▲) at  $298 \pm 1$  K.

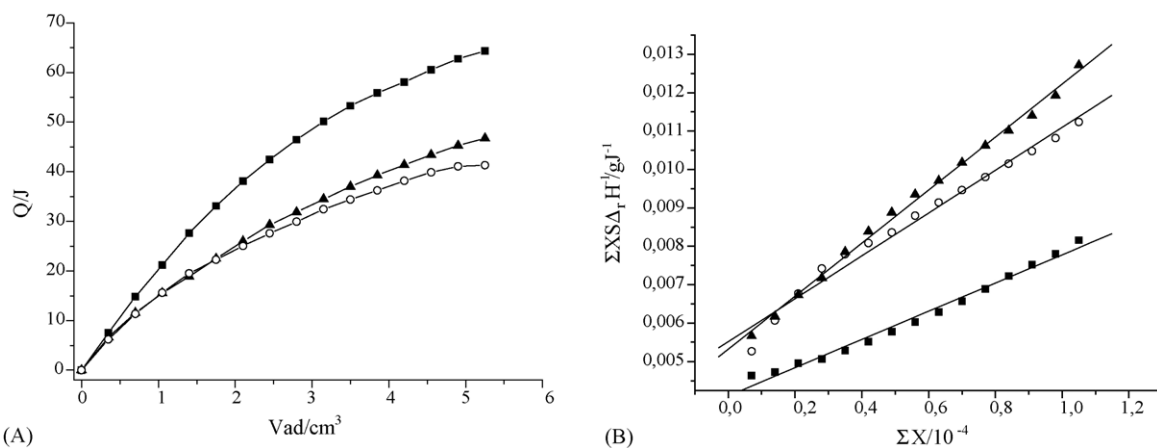


Fig. 5. (A) Heat output ( $\sum_r Q$ ) obtained by calorimetric titration of a suspension of CeINN fibre (50.0 mg in 50.0 ml of water) with  $0.50 \text{ mol l}^{-1}$  of  $\text{CuCl}_2$  (■),  $\text{NiCl}_2$  (○) and  $\text{ZnCl}_2$  (▲) at  $298.15 \pm 0.02$  K. (B) The linearised form of the isotherm showing integral enthalpy of adsorption vs. the molar fraction.

host/metal ion interaction ( $Q_{\text{tit}}$ ), (b) the heat of solvation of the solid ( $Q_{\text{sol}}$ ), and (c) the heat of dilution of the metal ion solution ( $Q_{\text{dil}}$ ). (d) The net heat change ( $Q_{\text{tot}}$ ) is given by the equation  $\sum Q_{\text{tot}} = \sum Q_{\text{tit}} - \sum Q_{\text{dil}} - \sum Q_{\text{sol}}$ . Since the heat of solvation of the aqueous, suspended modified material was zero, the expression reduced to  $\sum Q_{\text{tot}} = \sum Q_{\text{tit}} - \sum Q_{\text{dil}}$ , the results of which are shown in Fig. 5A [12,29].

The enthalpy of interaction,  $\Delta_{\text{R}}H$ , was obtained from an expression fitted to the modified Langmuir equation (Fig. 5B), viz.,

$$\frac{\sum X}{\sum \Delta_{\text{R}}H} = \frac{1}{(K-1)\Delta_{\text{imono}}H} + \frac{\sum X}{\Delta_{\text{mono}}H}$$

where  $\sum X$  is the sum of the molar fractions of the metal ion remaining in solution after adsorption and  $\sum \Delta_{\text{R}}H$  is the enthalpy of interaction per gram of adsorbent. Based on the Langmuir equation, it is possible to calculate the reaction enthalpy of the monolayer formed,  $\Delta_{\text{mono}}H$ , from plots of  $\sum X/\sum \Delta_{\text{R}}H$  versus  $\sum X$ . The molar enthalpy,  $\Delta H$ , of the interaction process was calculated from  $\Delta_{\text{mono}}H$  and the maximum number of moles inserted,  $N_s$ , using the expression

$\Delta H = \Delta_{\text{mono}}H/N_s$ . The Gibbs free energy changes were calculated [29,30] from  $\Delta G = -RT \ln K_{\text{eq}}$ . All thermodynamic values obtained are presented in Table 1.

Consideration of the set of thermodynamic data obtained for the adsorption processes indicated that the reactions between divalent metal ions and CeINN were spontaneous. However, all of the interactions presented endothermic enthalpy values

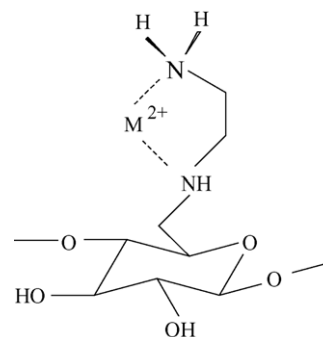


Fig. 6. The adsorption of divalent metal cations by CeINN with the formation of a chelate.

produced by chelating effect of metal ion complexation by ethylenediamine (Fig. 6). Hence, the spontaneity of adsorption was a consequence of the increase in entropy [31].

#### 4. Conclusion

Cellulose modified with ethylenediamine (CeINN) is a low-cost material that is readily synthesised in a form that retains the fibre morphology ensuring facile recovery from the reaction mixture. The modification of the cellulose improved the adsorption capacity of this material, as result, the modified cellulose (CeINN) presented adsorption ability similar to chitosan biopolymer. The modified material is efficient at adsorbing cations from water by complexation in which chelates between CeINN and metal ions are formed. Such interactions are accompanied by an increase in entropy and exhibit endothermic enthalpy values. CeINN represents a promising new material for the adsorption of metal ion contaminants from aqueous systems.

#### Acknowledgments

The authors acknowledge CNPq/Universal (478012/2003-9) and Finatec for support of this research, and CNPq for fellowships to JDT and EAF. Thanks are due to Professor C. Airoldi for SEM analysis.

#### References

- [1] N. Chiron, R. Guilet, E. Deydier, *Water Res.* 37 (2003) 3079–3086.
- [2] E. Deydier, R. Guilet, P.J. Sharrock, *J. Hazard. Mater.* 101 (2003) 55–64.
- [3] S. Samal, S. Acharya, R.K. Dey, A.R. Ray, *Talanta* 57 (2002) 1075–1083.
- [4] J.W. Moore, S. Ramamoorthy, *Heavy Metals in Natural Waters*, Springer Verlag, New York, 1984.
- [5] A.G.S. Prado, L.N.H. Arakaki, C. Airoldi, *J. Chem. Soc., Dalton Trans.* (2001) 2206–2209.
- [6] P.K. Jal, S. Patel, B.K. Mishra, *Talanta* 62 (2004) 1005–1028.
- [7] R.A. Zoppi, M.C. Gonçalves, *J. Appl. Polym. Sci.* 84 (2002) 2196–2205.
- [8] G. Bayramoglu, *J. Appl. Polym. Sci.* 88 (2003) 1843–1853.
- [9] R.R. Navarro, K. Sumi, M. Matsumura, *Water Sci. Technol.* 38 (1998) 195–201.
- [10] S.R. Shukla, R.S. Pai, *Sep. Purif. Technol.* 43 (2005) 1–8.
- [11] G.R. Castro, I.L. Alcantara, P.S. Roldan, D.F. Bolzano, P.M. Padilha, A.O. Florentino, J.C. Rocha, *Mater. Res.* 7 (2004) 329–333.
- [12] A.G.S. Prado, J.D. Torres, E.A. Faria, S.C.L. Dias, *J. Colloid Interf. Sci.* 277 (2004) 43–47.
- [13] A.G.S. Prado, C. Airoldi, *Anal. Chim. Acta* 432 (2001) 201–211.
- [14] A.G.S. Prado, C. Airoldi, *Pest Manage. Sci.* 56 (2000) 419–424.
- [15] P.S. Roldan, I.L. Alcantara, C.R. Castro, J.C. Rocha, C.C.F. Padilha, P.M. Padilha, *Anal. Bioanal. Chem.* 375 (2003) 574–577.
- [16] P.M. Padilha, C.C.F. Padilha, J.C. Rocha, *Quim. Anal.* 18 (1999) 299–303.
- [17] R.A. Jorge, A.P. Chagas, *Quim. Nova* 11 (1988) 489–490.
- [18] F.E. Okieimen, C.E. Sogbaiké, J.E. Ebhoaye, *Sep. Purif. Technol.* 44 (2005) 85–89.
- [19] S. Babel, T.A. Kurniawan, *J. Hazard. Mater.* 97 (2003) 219–243.
- [20] E. Guibal, A. Larkin, T. Vincent, J.M. Tobin, *Ind. Eng. Chem. Res.* 38 (1999) 4011–4022.
- [21] A.J. Varma, S.V. Deshpande, J.F. Kennedy, *Carbohydrate Polym.* 54 (2004) 77–93.
- [22] Y. Okuno, T. Yokoyama, S. Yokoyama, S. Kamikado, S. Mashiko, *J. Am. Chem. Soc.* 124 (2002) 7218–7225.
- [23] W. Rudzinski, R. Charmas, W. Piasecki, F. Thomas, F. Villieras, B. Prelot, *J.M. Cases, Langmuir* 14 (1998) 5210–5225.
- [24] F.S.C. Anjos, E.F.S. Vieira, A.R. Cestari, *J. Colloid Interf. Sci.* 253 (2002) 243–246.
- [25] P. Trivedi, L. Axe, *Environ. Sci. Technol.* 34 (2000) 2215–2223.
- [26] R. Lehrmann, J. Seelig, *Biochim. Biophys. Acta* 1189 (1994) 89–95.
- [27] M.N. Dimitrova, H. Matsumura, A. Dimitrova, V.Z. Neitchev, *Int. J. Biol. Macromol.* 27 (2000) 187–194.
- [28] W. Rudzinski, R. Charmas, W. Piasecki, J.M. Cases, M. Francois, F. Villieras, L.J. Michot, *Colloids Surf. A* 137 (1998) 57–68.
- [29] A.G.S. Prado, B.S. Miranda, G.V.M. Jacintho, *Surf. Sci.* 542 (2003) 276–282.
- [30] A.G.S. Prado, A.H. Tosta, C. Airoldi, *J. Colloid Interf. Sci.* 269 (2004) 259–264.
- [31] A.G.S. Prado, B.S. Miranda, L.F. Zara, *J. Hazard. Mater.* 120 (2005) 243–247.