

Removal of organic compounds by alginate gel beads with entrapped activated carbon

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Abstract

The adsorption of alginate gel (AG) beads and AG with activated carbon entrapped (AG–AC) beads prepared using different types of metal ions were investigated by measuring the removal of several organic compounds with different charges and size. AG–AC beads prepared in a CaCl_2 solution adsorbed strongly positively charged compounds as well as electrically neutral and low molecular weight compounds such as *p*-chlorophenol. However, a high molecular weight humic acid was not adsorbed by AG–AC. The AG–AC selectively adsorbed *p*-chlorophenol from a humic acid solution. The adsorption capacity obtained from the adsorption isotherm of AC entrapped in AG was compared with that of AC. The AG–AC beads prepared in a solution of FeCl_3 were able to specifically adsorb negatively charged gallic acid. Thus, entrapping AC into AG resulted in the selective adsorption.

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1. Introduction

The large surface area of activated carbon (AC) enables it to efficiently adsorb many kinds of pollutants. As a result, AC is used widely to remove organic substances, which are evaluated as BOD (biochemical oxygen demand) or COD (chemical oxygen demand), and halogen from tap water and waste water, as well as dyes, phosphate and nitrogen from colored textile waste water and inorganic nutrient rich waste water [1–4]. AC can be used for the removal of both inorganic and organic materials, as well as low molecular weight and polymer substances. The above facts serve to indicate the lack of selectivity in adsorption by activated carbon. It is impossible to remove certain compounds from many substances in waste water selectively with AC. AC is not expensive, but its cost is not low enough to permit the consumption of adsorption sites by a large quantity of substances other than the intended compound to be removed. Management of treatment

plants for pollutants in which AC is used is not easy because of the dispersion of AC powder.

On the other hand, alginic acid is a heteropolysaccharide composed of β -D-mannuronic acid and α -L-guluronic acid and is widely distributed in organisms as diverse as seaweeds and bacteria. The molecular weight of alginic acid is several tens of thousands to hundreds of thousands and it is non-toxic and has a high viscosity. Because of these physical and chemical characteristics, alginic acid has been used widely as a phase stabilizer in foods and beverages, suspending and shear-thinning agents, tablet binders and enteric coatings in the pharmaceutical field. Alginic acid forms a stable gel with calcium ions and alginate gels are used in the immobilization of microbial and enzymes [5–8]. Alginate gel (AG) has been used as a new material for absorbable co-polymer pads and for an articular cartilage repair [9,10]. In the environmental field, AG has been used for the removal of heavy metal ions such as Cd^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Cr^{3+} and Hg^{2+} , and alginate complexes, with several types of adsorbents such as activated carbon [11], chitosan [12], polyvinyl alcohol [13] carboxylate [14] and humic acid [15] have been reported and their adsorption characteristics have been estimated.

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The behavior of *p*-chlorophenols in the environment has attracted considerable interest because of its potential to serve as a precursor of dioxins. *p*-Chlorophenol of 0.002 mg/L in water has an unpleasant smell and is toxic to fish and microbial organisms [16]. Consequently, the presence of *p*-chlorophenol affects microbial systems in the waste treatment facilities. On the other hand, humic substances, a soil organic material, is widely distributed in the aquasphere and plays important roles in supplying nutrients to plants and microbial organisms and in maintaining the structure of soil. Since humic substances are very important components in agricultural water, it is usually not necessary to remove it, except when it is used for tap water. Therefore, new materials which can selectively adsorb low molecular weight pollutants but do not adsorb high molecular weight polymers having negative charges, such as humic substances, are needed.

In this study, several types of alginate gel beads containing entrapped AC powders were prepared by reaction with calcium and ferric chloride and the adsorptive properties of these alginate gel beads were compared using negatively charged, neutral and positively charged model compounds, such as humic acid, gallic acid, methyl orange; *p*-chlorophenol; and methylene blue as adsorbates. AG–AC has been used for the removal of heavy metal ions from waste water, however, only a few applications of AG–AC to the removal of organic compounds have been reported. Jodra and Mijangos reported the adsorption of phenol on AG–AC, however, they did not investigate its selectivity [11]. The introduction of selectivity to AC by entrapping it within an alginate gel was examined in this study.

2. Material and methods

2.1. Material

Humic acid was prepared by extraction from peat soil at Bibai in Hokkaido followed by purification according to the protocol recommended by the IHHS (International Humic Substances Society). An elemental analysis of the purified humic acid indicated the following composition: 52.1% C, 5.5% H, 3.3% N and 0.7% S. Sodium alginate (300–400 cP), methyl orange, ferric chloride hexahydrate, *p*-chlorophenol and gallic acid were obtained from Wako Pure Chemicals Co. (Tokyo, Japan). Activated carbon powder (the surface area: 1000 m²/g) was also obtained from Wako Pure Chemical Co. Methylene blue was from Kanto Chemical Co. (Tokyo, Japan). The water used in this study was double distilled water.

2.1.1. Preparation of alginate gel beads (AG)

A 1% alginate solution was added dropwise from a 15 ml pipette to a solution of 0.9 M (10%) calcium chloride. The diameter of the AG beads was about 2 mm. These beads were filtered and washed with distilled water overnight and then used in the adsorption experiments.

2.1.2. Preparation of alginate gel beads entrapped with activated carbon (AG–AC)

After mixing 250 mg of AC with 15 ml of 1% alginate solution, the solution was added to a 0.9 M (10%) calcium solution in the same manner as used in the preparation of AG.

2.2. Procedure of adsorption experiment

AG or AG–AC gel beads prepared with 15 ml of alginate solution (about 250 beads) were added to 50 ml of a solution containing 100 ppm adsorbate. After mixing for a constant time, the solution was filtered through filter paper and the supernatant was used for the measurement of absorbance. The concentration of humic acid after adsorption was evaluated by measuring the absorbance at 400 nm by means of a UV/Vis spectrometer V-550 (Jasco Co., Tokyo, Japan). The concentration of other compounds such as *p*-chlorophenol, gallic acid, methyl orange and methylene blue were also determined by measurement of their absorbance at 280, 257, 455 and 665 nm, respectively.

3. Results and discussion

3.1. Adsorbing properties of AC, AG and AG–AC

Fig. 1 shows the removal ratio as the function of the time of adsorption when 0.25 g activated carbon powder (AC) was used as the adsorbent. A neutral compound, *p*-chlorophenol and positively charged methylene blue were adsorbed strongly and rapidly to the AC. Negatively charged gallic acid was also adsorbed to the AC although at a slower rate than for *p*-chlorophenol and methylene blue. The adsorption of humic acid, a negatively charged polymer, to AC was the slowest among of the compounds examined, but half of 100 ppm humic acid was adsorbed after 240 min. Thus AC

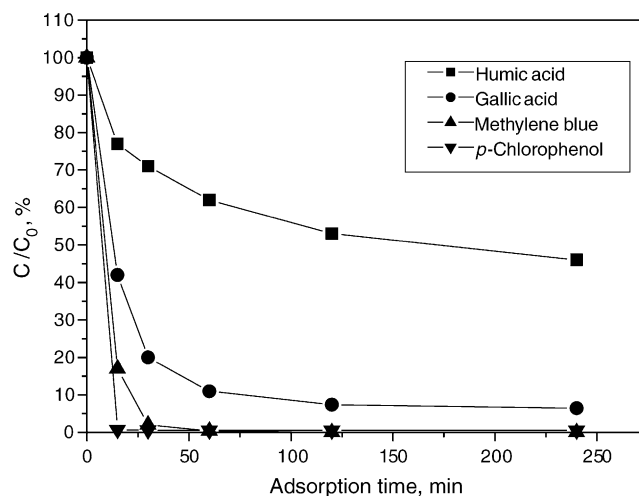


Fig. 1. Removal ratio as a function of adsorption time using activated carbon powder of 0.25 g, 100 ppm humic acid, gallic acid, methylene blue and *p*-chlorophenol, pH = 7.

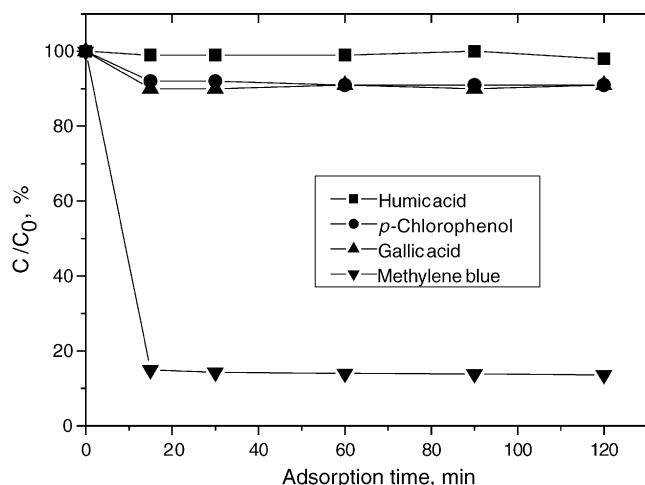


Fig. 2. Removal ratio as a function of adsorption time using AG beads, 100 ppm humic acid, gallic acid, methylene blue and *p*-chlorophenol, pH = 7.

can adsorb many types of substances regardless of charge or size, i.e., it is impossible to predict the selectivity of adsorption on AC.

Fig. 2 shows the removal ratio when AG beads were used as the adsorbent. Negatively charged gallic acid and humic acid were not adsorbed to AG because AG has many negative charges due to the dissociation of the carboxyl groups. *p*-Chlorophenol was also not adsorbed to AG because AG does not contain any hydrophobic parts. AG strongly adsorbed the positively charged methylene blue due to electrostatic interactions with the negatively charged AG.

The adsorption behavior of each adsorbates are shown in Fig. 3 for AG-AC as the adsorbents. The strong adsorption of methylene blue to AG-AC is the same as that for AG. The AC entrapped into AG resulted in the practically complete adsorption of neutral *p*-chlorophenol but only the partial adsorption of gallic acid. It is noteworthy that humic acid was

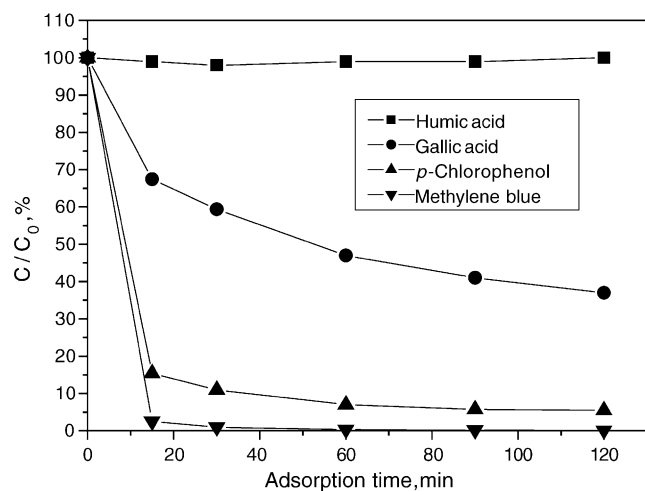


Fig. 3. Removal ratio as a function of adsorption time using AG-AC beads, 100 ppm humic acid, gallic acid, methylene blue and *p*-chlorophenol, pH = 7.

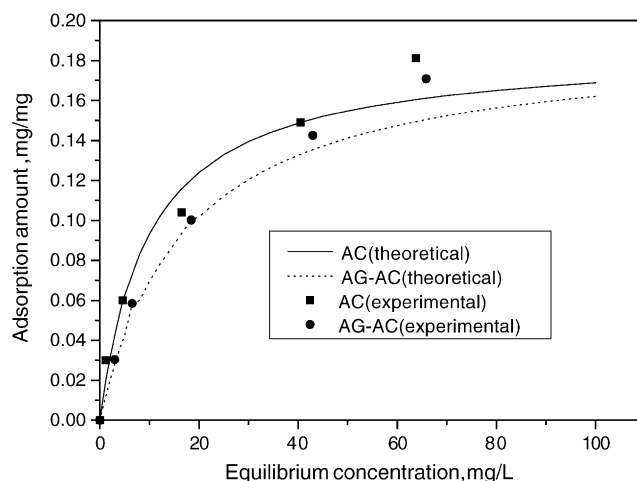


Fig. 4. Adsorption isotherm curves of *p*-chlorophenol on AG-AC and AC, 100 ppm *p*-chlorophenol solution (pH = 7), 15 ml of AG beads containing different amounts of AC. Adsorption time of 48 h.

not adsorbed at all to AG-AC. The gel structure of alginate around the AC might suppress the transport of humic acid to the AC entrapped within the AG and the negative charges of the alginate gel could become a barrier to the approach of negatively charged compounds to the AC in the AG. It was confirmed that when AC is entrapped into an alginate gel, the selective adsorption of several organic compounds to AC results.

3.2. Adsorption capacity of AC and AC in AG

The adsorption capacity of AC in AG for *p*-chlorophenol was evaluated from the measurement of the adsorption isotherm. The adsorption isotherm of AC was measured under the same conditions. As shown in Fig. 4, the adsorption isotherm of AC in AG was very similar to that of AC. Since both adsorption isotherms are of the Langmuir type, the adsorption equilibrium constant (α) and the saturation adsorption amount (W_s) as parameters for the Langmuir equation were estimated by curve fitting to the adsorption isotherm. As shown in Table 1, the α value of AC in AG was about half than that for AC. On the other hand, the saturated adsorption amount of AC in AG was similar to that of AC but slightly larger than that of AC. This is due to the distribution of *p*-chlorophenol in water in the gel beads. That is, the amount of AG-AC adsorbed in Fig. 4 contains the amount of *p*-chlorophenol distributed into water in the gel. Therefore, in order to precisely estimate the value of W_s for AC in AG, it is necessary to subtract the amount distributed into the water

Table 1
Parameters for Langmuir isotherm of AC and AG-AC

Parameters	AC	AG-AC
α	0.10	0.058
W_s (mg/mgAC)	0.19	0.20
R^2	0.997	0.998

in the gel from the value in Fig. 4. The W_s obtained from the adsorption isotherm, where the corrected values were plotted, was 0.19, this value was the same as that for AC. These results confirm that the adsorption constant of AC in AG was reduced by being surrounded by alginate gel, but the adsorption capacity of AC in AG does not change from the original AC. If a sufficient time to achieve equilibrium is involved AC in AG would have a similar ability to that of AC.

3.3. Selective adsorption of *p*-chlorophenol on AG–AC from a solution containing humic acid

The selectivity of AG–AC in adsorption was demonstrated using a mixed solution of 100 ppm *p*-chlorophenol and 50 ppm humic acid. The removal ratios for *p*-chlorophenol and humic acid were plotted as a function of adsorbing time, as shown in Fig. 5. The AG–AC beads almost completely remove *p*-chlorophenol due to hydrophobic interactions with AC in AG, while humic acid was not adsorbed to AG–AC. The peak for *p*-chlorophenol at 280 nm decreased rapidly and the UV/Vis spectra of the mixed solution after adsorption for 30 min corresponded to that of 50 ppm humic acid. These results show that AG–AC has the potential for the selective removal of agricultural chemicals without changing the fundamental water quality, that is, by maintaining useful components such as humic and fulvic acids in agricultural water.

3.4. Control of charge of AG–AC

The charge of the AG–AC is an important factor in terms of selective adsorption as well as the structure of the gel. If the charge of the AG–AC can be controlled, it would be possible to obtain the more selective adsorption of pollutants by AG–AC. Min and Hering succeeded in the efficient removal of arsenate using Fe-doped alginate gels but the mechanism for this is not clear [17]. In this study, the control of the charge

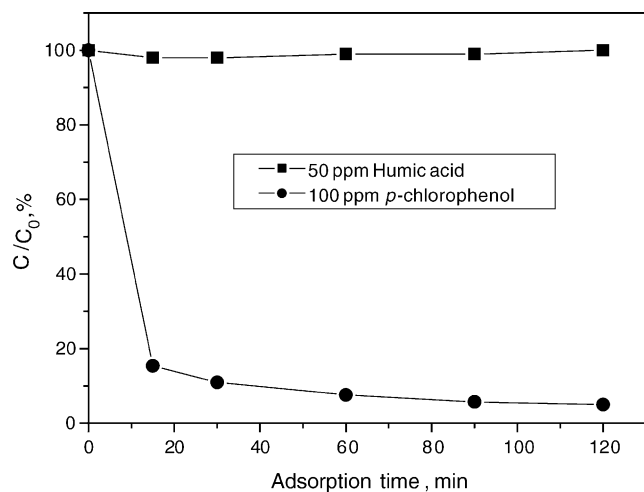


Fig. 5. Removal ratio of 50 ppm HA + 100 ppm *p*-chlorophenol from a mixed solution with AG–AC.

of the AG beads was attempted by the preparation of gels using different concentrations of calcium ion or by preparing gels using ferric ion. The adsorbing properties of the AG–AC were evaluated by measurement of the adsorption of some differently charged compounds.

The adsorption of negatively charged compounds, gallic acid and methyl orange on AG–AC increased with increasing concentration of calcium ion. The UV/Vis spectra of methyl orange before and after adsorbing on AG–AC samples that were prepared using different concentrations of calcium ion are shown in Fig. 6. This behavior can be explained by the decrease in the negative charges of the AG–AC by electrical neutralization due to the association of carboxyl groups with calcium cations. Consequently, the repulsion between the negative charges of methyl orange and the AG–AC decreased, thus enhancing the adsorbing ability for negatively charged compounds. On the other hand, positively charged compounds, such as methylene blue were adsorbed more strongly on the AG–AC prepared with lower concentrations of calcium as shown in Fig. 7. The adsorption of *p*-chlorophenol remained constant, irrespective of the concentration of calcium. These results show that the charge of the gel can be controlled to some extent from negative to almost neutral by changing the concentration of calcium ion used in the preparation process of the gel.

On the other hand, the AG–AC prepared with Fe(III) removed gallic acid in a highly efficient manner. The efficiency was better than that of activated carbon itself. After adsorbing gallic acid on AG–AC, the surface of the gel beads changed to a black color. The effect of Fe(III) concentration was also investigated by measuring the adsorption of gallic acid and methylene blue. The adsorption of gallic acid increased with increasing concentration of Fe(III) but become constant for concentrations over 0.1 M Fe(III). To the contrary, the adsorption of methylene blue decreased with increasing concentration of Fe(III). However, even gel beads prepared

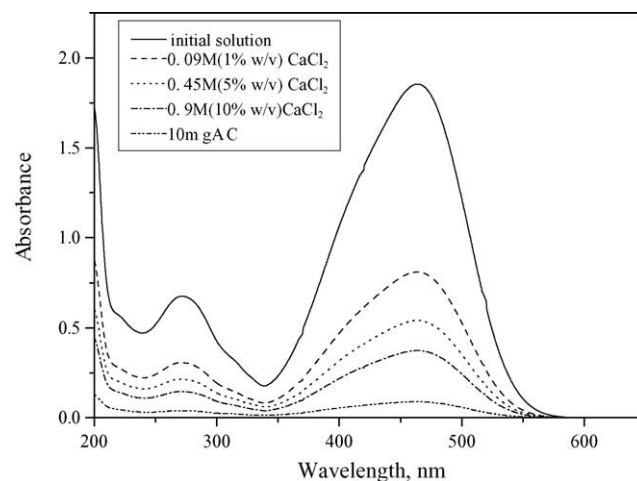


Fig. 6. UV/Vis spectra of 25 ppm methyl orange solution before and after adsorption with the AG–AC prepared with different concentrations of calcium ion. Stirring time for 2 h.

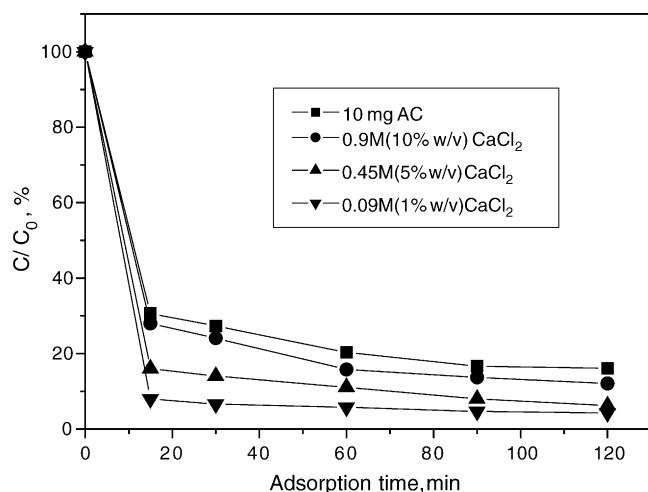


Fig. 7. Removal ratio of methylene blue on AG-AC prepared with different concentrations of calcium ion.

with high concentrations of Fe(III) adsorbed considerable amounts of methylene blue and the color changed to a pale blue. From these findings, we conclude that AG-AC prepared with Fe(III) has partially positive charges on the surface of the gel although overall the gel is charged negatively. The part that is charged positively of the gel can adsorb gallic acid strongly and produce Fe-gallic acid complex on the AG-AC. The introduction of Fe(III) in the gel beads can result in the specific adsorption of gallic acid to the gel beads on the basis of the specific reactivity between ferric ion and gallic acid. As shown in Fig. 8, other negatively charged compounds such as humic acid and methyl orange were not adsorbed but methylene blue could be adsorbed on AG-AC prepared with Fe(III). Therefore, the adsorption property of AG-AC is dependent on the types of metal ion used in the preparation, its concentration and its reactivity.

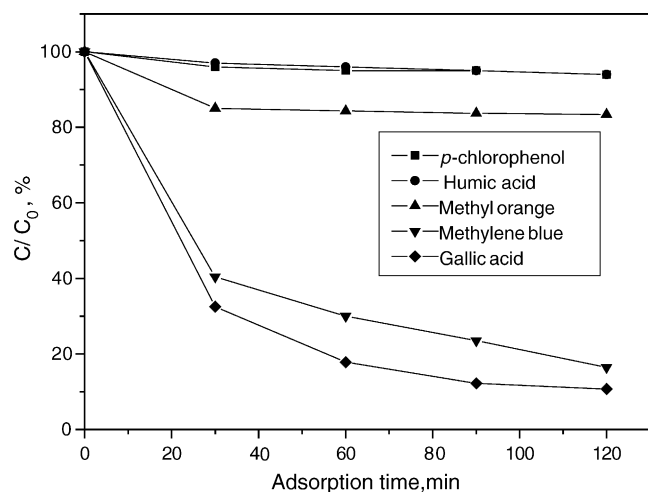


Fig. 8. Removal ratio as a function of adsorption time using Fe-AG beads; 100 ppm *p*-chlorophenol, methyl orange, humic acid, methylene blue and gallic acid, pH=7.

4. Conclusion

In this study, several types of alginate gels containing activated carbon (AG-AC) were prepared in an attempt to improve the selectivity of the gel beads and the property of these gel beads on the adsorption of some compounds with different charges and size, such as *p*-chlorophenol, humic acid, gallic acid, methyl orange and methylene blue. AG-AC prepared using calcium ion has negative charge and adsorbs positively charged compounds as well as neutral compounds. The extent of charge can be controlled by adjusting the concentration of calcium ion used in the preparation process. The alginate gel prepared using Fe(III) has a specific adsorption property for negative charge gallic acid. The AG-AC prepared using calcium ion selectively adsorbed *p*-chlorophenol from a mixture of *p*-chlorophenol and humic acid. The results in this study suggest that AG-AC has the potential for removing agricultural chemicals at low concentrations from large amount of dissolved organic matter such as humic substances in water and that AG-AC can lead to the success in the treatment of and the long life of activated carbon, thus lowering the overall cost.

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References

- [1] G. McKay, M.J. Bino, A.R. Altamemi, *Water Res.* 19 (1985) 491.
- [2] G. McKay, M.J. Bino, A. Altamemi, *Water Res.* 20 (1986) 435.
- [3] J. Jia, J. Yang, *Water Res.* 33 (1999) 881.
- [4] G. Bressa, L. Cima, F. Giunta, *Inorg. Chim. Acta* 79 (1983) 304.
- [5] C.A. Steginsky, J.M. Beale, H.G. Floss, *Carbohydr. Res.* 225 (1992) 11.
- [6] J.D. Carballeira, E. Alvarez, J.V. Sinisterra, *Mol. Catal. B: Enzym.* 28 (2004) 25.
- [7] N. Vassilev, M. Vassileva, R.A. Medina, *Biotechnology* 91 (2001) 237.
- [8] W. Jianlong, N. Horan, E. Stentiford, Q. Yi, *Process Biochem.* 35 (1999) 465.
- [9] S.B. Cohen, C.M. Meirisch, H.A. Wilson, D.R. Diduch, *Biomaterials* 24 (2003) 2653.
- [10] S. Sotome, T. Uemura, *Mater. Sci. Eng. C* 24 (2004) 341.
- [11] Y. Jodra, F. Mijangos, *Sep. Sci. Technol.* 38 (2003) 1851.
- [12] T. Gotoh, K. Matsushima, K. Kikuchi, *Chemosphere* 55 (2004) 135.
- [13] C. Jeon, J.Y. Park, Y.J. Yoo, *Biochem. Eng. J.* 11 (2002) 159.
- [14] C. Jeon, J.Y. Park, Y.J. Yoo, *Water Res.* 36 (2002) 1814.
- [15] A.K. Pandey, S.D. Pandey, V. Misra, S. Devi, *Hazard. Mater.* B98 (2003) 177.
- [16] G. McKay, M.J. Bion, *Environ. Pollut.* 66 (1990) 33.
- [17] J.H. Min, J.G. Hering, *Water Res.* 32 (1998) 1544.