Available online at www.sciencedirect.com
ScienceDirect
Carbohydrate Research 343 (2008) 267–273
Carbohydrate RESEARCH

Preparation and metal-binding behaviour of chitosan functionalized by ester- and amino-terminated hyperbranched polyamidoamine polymers

Rongjun Qu,* Changmei Sun, Chunnuan Ji, Chunhua Wang, Hou Chen, Yuzhong Niu, Chengju Liang and Qiyi Song

School of Chemistry and Materials Science, Ludong University, Yantai, Shangdong, PR China

Received 12 June 2007; received in revised form 26 October 2007; accepted 30 October 2007
Available online 5 November 2007

Abstract—A series of insoluble chitosan (CTS) derivatives were prepared by grafting ester- and amino-terminated dendrimer-like polyamidoamine (PAMAM) into CTS using a divergent method by repeating two processes: (1) Michael addition of methyl acrylate (MA) to surface amino groups, and (2) amidation of the resulting esters with ethylenediamine (EDA). Their structures were characterized by infrared spectra (IR) and wide-angle X-ray diffraction (WAXD). The adsorption capabilities of the products for Au^{3+}, Pd^{2+}, Pt^{4+}, Ag^{+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Ni^{2+}, and Cd^{2+} were studied. The results showed that the products exhibited better adsorption capabilities for Au^{3+} and Hg^{2+} than for other metal ions, and the adsorption capabilities of amino-terminated products were higher than those of ester-terminated ones. Also it was observed that a high percentage of grafting of PAMAM into CTS does not ensure a high adsorption capacity.

Keywords: Chitosan; Polyamidoamine-typed hyperbranched polymer; Preparation; Adsorption; Metal ion

1. Introduction

Chitosan (CTS), poly-((1→4)-β-D-glucopyranosamine), is a linear biopolymer obtained by N-deacetylation of chitin [poly-(*N*-acetyl-(1→4)-β-D-glucopyranosamine)], which is a naturally occurring polymer found in the exoskeleton of marine crustaceans and is the second-most abundant biopolymer next to cellulose.[1] CTS has gained more and more attention because of its particular structure, physicochemical characteristics, chemical stability, high reactivity, and excellent selectivity toward metals.[2,3] The excellent adsorption behaviour of CTS is mainly attributed to (1) high hydrophilicity of the polymer due to the hydroxyl groups of the glucosamine units; (2) the presence of a large number of functional groups (acetamido, primary amino, and/or hydroxyl groups); (3) high chemical reactivity of some of these groups; (4) flexible structure of the polymer chain. Moreover, it is well known that CTS is an abundant, renewable, modifiable, and biodegradable resource, has a capacity to associate by physical and chemical interactions with a wide variety of molecules such as phenolic compounds and dyes.[4,5] In spite of these properties and advantages, some problems can occur. For example, CTS is soluble in acidic media, and, therefore, cannot be used as an insoluble sorbent under these conditions, except after physical and chemical modifications. For this purpose, many research projects are underway to modify crosslinking methods of CTS. The most common crosslinking agents include epichlorohydrin (EPI),[6–8] ethylene glycol diglycidyl ether,[9–15] diethylene glycol bisglycidyl ether,[16] PEG bisglycidyl ether,[17] glutaraldehyde,[18,19] and benzoquinone.[20]

In recent years, hyperbranched polymers represented by 'dendrimers' have received considerable attention because of their multifunctional properties such as medical

* Corresponding author. Tel.: +86 535 6673982; e-mail addresses: rongjunqu@sohu.com; qurongjun@eyou.com

0008-6215/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carres.2007.10.032

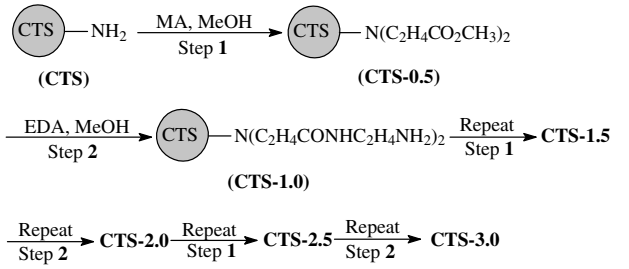
applications, host–guest chemistry, and dendritic catalysts.[21] Introduction of hyperbranched polymers into CTS will introduce many kinds of novel functional materials.[22–24]

Tsubokawa and his co-workers reported the preparation and characterization of CTS modified by 0–9 generations amino-terminated hyperbranched polyamidoamine polymer via a divergent method.[25] The experimental results showed that the solubilities of hyperbranched dendritic polyamidoamine-grafted CTS in 10% HCl decreased with increasing percentage of dendrimer grafting. Insolubilities in acidic media are just a prerequisite to metal adsorbents. Accordingly, we tried to prepare insoluble CTS derivatives by the above-mentioned method. Their adsorption capacities for several noble and base metal ions were also investigated in this study.

2. Results and discussion

CTS is a type of biopolymer that is soluble in aqueous acidic solution. Ref. 25 demonstrated that the solubility of CTS derivatives decreased with the increase of grafting percentage of dendrimer onto the surface of CTS. Therefore, the content of the grafting polymer was the critical factor in being able to obtain insoluble CTS derivatives. To introduce more functional groups to the skeleton of CTS, in this study the Michael addition and amidation reaction times were prolonged from 24 h (reported by Ref. 25) to 4 and 3 days, respectively. The ideal synthetic routes of ester- and amino-terminated hyperbranched polyamidoamine polymers-grafted CTS are illustrated in Scheme 1.

The data in Table 1 reveal that the grafting percentage of dendrimer onto the surface of CTS prepared by this method increased significantly compared to that by the method described in Ref. 25. It should be noted that when the grafting percentage of dendrimer was 20.3% (that is CTS-1.0), the sample was only swollen but not dissolved in 2% hydrochloric acid; and when the grafting percentage of dendrimer was 37.1% (that is CTS-1.5), the sample dissolved in neither 2% acetic acid nor 2% hydrochloric acid. Considering that the samples of



Scheme 1. The ideal synthetic routes of ester- and amino-terminated hyperbranched polyamidoamine polymers-grafted CTS.

Table 1. Observed and expected grafting percentage of dendrimer onto CTS and their solubility in aqueous acidic solution

Generation	Grafting (%)		Soluble part (%)	
	Observed	Expected	2% CH_3CO_2H	2% HCl
0	0	0	100	100
0.5	15.10	15.10	15.2	12.5
1.0	18.31	20.3	2.4 (Swollen)	0 (Swollen)
1.5	37.12	50.2	0 (Swollen)	0
2.0	46.70	60.8	0	0
2.5	76.61	120.7	0	0
3.0	97.32	142.0	0	0

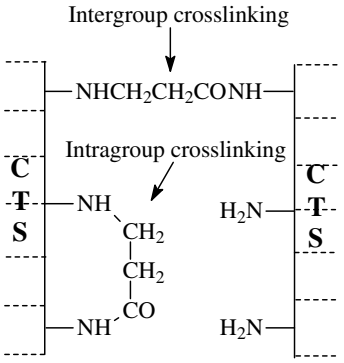
CTS-2.0, CTS-2.5, and CTS-3.0 were absolutely insoluble in the two kinds of aqueous acidic solutions, they were considered suitable for use as sorbents for metal ions.

Table 2 showed main absorption peaks of FTIR spectra of CTS and its derivatives.

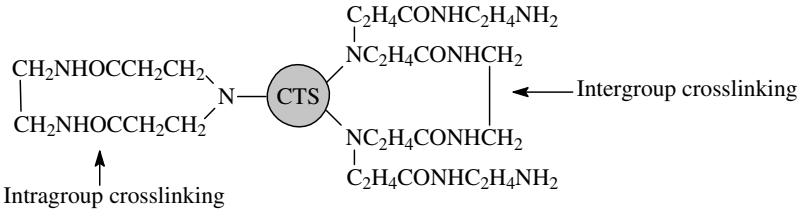
In ester-terminated dendrimer polymer grafting samples CTS-0.5, CTS-1.5, and CTS-2.5, the absorption at 1733 cm^{-1} suggested the presence of ester bonds (–CO_2CH_3). The characteristic absorption peaks of ester bonds disappeared in the corresponding amino-terminated samples CTS-1.0 and CTS-2.0, indicating that the ester bonds were almost inverted into amino-terminated products. However, different from the above-mentioned samples, the characteristic absorption peaks of ester bonds in the sample CTS-3.0 did not disappear completely even though the reaction time was prolonged from 3 to 5 days at 50 °C. These experimental results could be explained by the formation of intra- and inter-group crosslinking products as shown in Scheme 2: (1) in the Step 1 reaction process, except for the routine Michael addition reaction, the side reaction of the ester group with an amine group would lead to the formation of crosslinking product **I**, which would drastically decrease the amount of $–NH_2$; (2) in the Step 2 reaction process, the side reaction of one molecular equivalent of EDA with each ester group of two molecules would lead to the formation of crosslinking product **II**, which would drastically decrease the number of ester groups. The fact that the observed grafting percentage of dendrimer at every generation was much less than that of the expected value supports this deduction. These grafted dendrimers were called 'dendrimer-like highly branched

Table 2. The main absorption peaks of FTIR spectra of CTS and its derivatives

Samples	Main absorption peak of FTIR (cm^{-1})
CTS	3423, 2921, 2880, 1654, 1420, 1382, 1077
CTS-0.5	3436, 2952, 2876, 1731, 1631, 1483, 1375, 1074
CTS-1.0	3423, 2921, 2875, 1637, 1458, 1384, 1070
CTS-1.5	3431, 2951, 2876, 1733, 1646, 1438, 1384, 1070
CTS-2.0	3431, 2925, 2873, 1735, 1647, 1437, 1383, 1069
CTS-2.5	3421, 2923, 2853, 1735, 1647, 1438, 1382, 1069
CTS-3.0	3422, 2926, 2876, 1733, 1646, 1438, 1383, 1070



Crosslinking Product **I**



Crosslinking Product **II**

Scheme 2. The illustrations of intra- and intergroup crosslinking products.

polymers' in Ref. 26. The formation of crosslinking products blocked the diffusion of EDA into the matrix of hyperbranched polymer to react with $-CO_2CH_3$ distributed in the inside of polymer, and the blockage increased with the increase of generations of dendrimers.

Based on the above analysis, it was concluded that ester- and amino-terminated hyperbranched polymer was grafted successfully on the CTS surface via the Step 1 and Step 2 repeating reactions.

As representatives, CTS-0.5, CTS-1.0, and CTS-1.5 were chosen to investigate the effect of grafting dendrimer on the crystallinity of CTS. Their X-ray powder diffraction patterns are shown in Figure 1.

Compared with CTS, the intensity and position of the maximum peak at $2\theta = 20.4°$ in the diffractogram of the sample CTS-0.5 had not evidently changed, but the peak at $2\theta = 11°$ disappeared, which means that the introduction of grafted groups (ester groups here) affected the crystallinity of the main chain of CTS. The novel peak at $2\theta = 6.5°$ appearing in the diffractogram of the sample CTS-0.5 could be attributed to the conjugation between the grafted groups and main chain of CTS. From the diffractogram of the sample CTS-1.0, it could be seen that the intensity of the peak at $2\theta = 6.5°$ increased compared with that of CTS-0.5, indicating that the conjugation between the grafted groups and main chain of CTS increased when the ester-terminated groups were converted into the amino-terminated groups. This fact could be interpreted as that amino groups were more easily available than ester groups to form hydrogen-bonds with the main chain of CTS. The intensity of the peak at $2\theta = 20.4°$ in the diffractogram of sample CTS-1.0 apparently increased compared with CTS and CTS-0.5, demonstrating that the introduction of polar amino groups increased the crystallinity of CTS. It should be noted that the intensity of the peak at $2\theta = 20.4°$ of CTS-1.5 evidently decreased, and the peak at $2\theta = 6.5°$ moved to $2\theta = 4.9°$. Its intensity also decreased compared with CTS-1.0, which demonstrates that the crystallinity of CTS-1.0 decreased when the polar amino groups were reconverted into weakly polar ester groups.

The above-mentioned fact revealed that introducing weakly polar groups (e.g., ester groups) into CTS would result in a decrease in the crystallinity of derivatives of CTS, and introducing strongly polar groups (e.g., amino groups) would result in an increase in the crystallinity of the derivatives of CTS.

The saturated adsorption capacities of CTS and its derivatives for base metal ions and novel metal ions are shown in Figure 2a and b, respectively. From Figure 2a, it can be seen that (1) The products had higher adsorption capability for Hg^{2+} than for the four other metal ions, which could be interpreted in that the amide groups also participated in coordination with Hg^{2+} besides $-NH_2$, and the amide groups were not capable of forming coordinate bonds with other transition metal ions.[27] This fact demonstrated that these products could

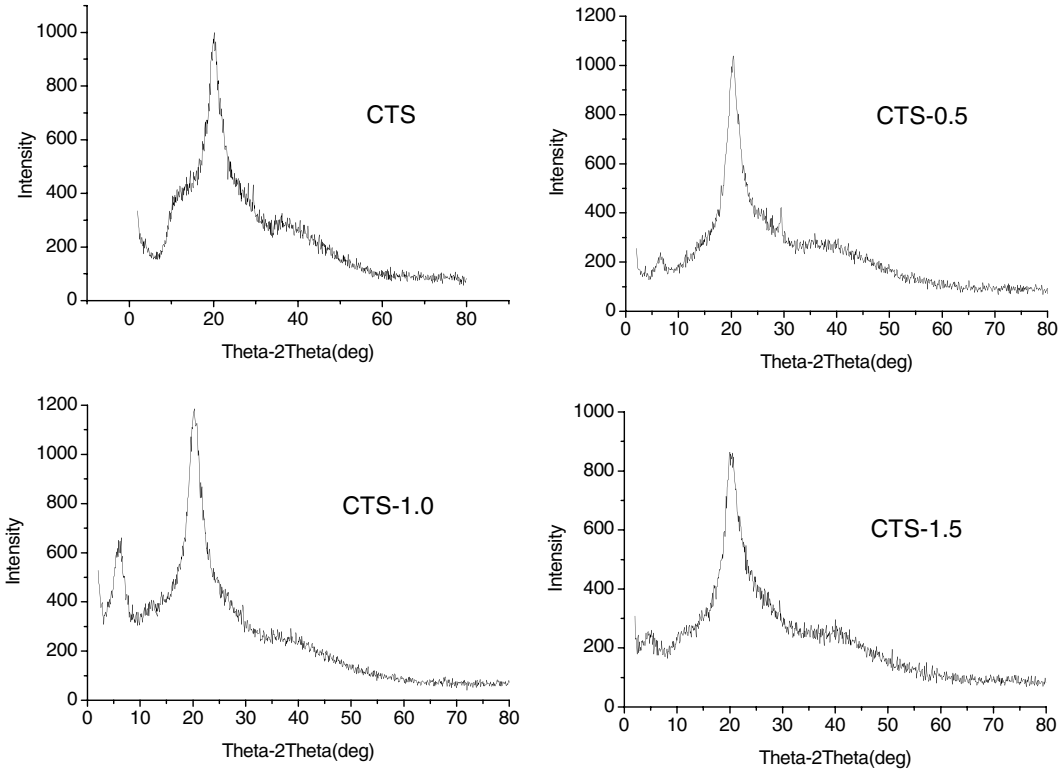


Figure 1. X-ray diffraction of CTS, CTS-0.5, CTS-1.0, and CTS-1.5.

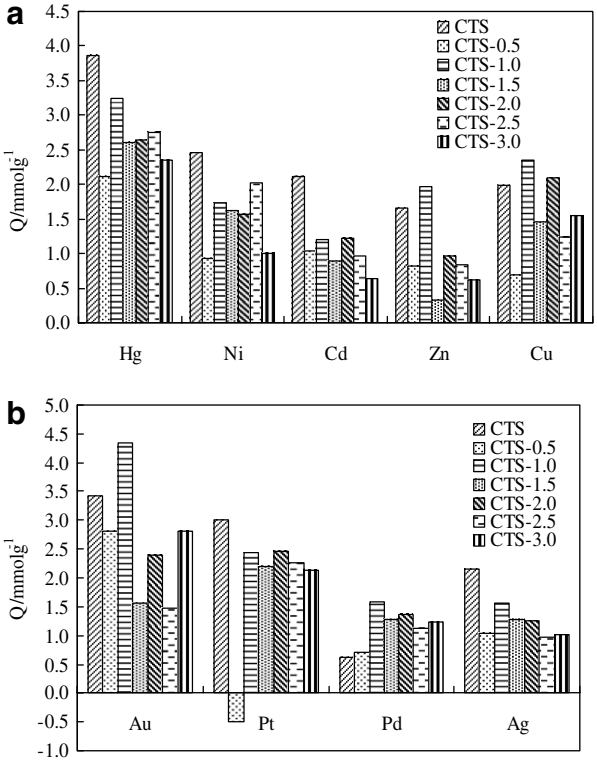


Figure 2. The saturated adsorption capacities of CTS and its derivatives for (a) base metal ions and (b) for novel metal ions.

probably be used to separate Hg^{2+} from other metal ions. (2) When the generation of grafted dendrimer was smaller than 2.0, amino-terminated products exhibited better adsorption than their corresponding counterparts (e.g., CTS-0.5 compared with CTS-1.0 or CTS-1.5 compared with CTS-2.0), implying that the amino group was the main contributor to the complexation with metal ions. When the generation of grafted dendrimer was more than 2.0, the adsorption capabilities of the products decreased with increasing generation of the grafted dendrimer. A reasonable explanation for this is as follows: in the adsorption process of lower generation products, the lower steric hindrance and the lower crosslinking made metal ions easy to diffuse into the interior of the dendrimer-like polymer matrix and to be adsorbed. In contrast, although CTS-3.0 possessed the highest percentage of grafting among all the products, the strong steric hindrance and crosslinking structures made metal ions difficult to diffuse into the interior of the dendrimer-like polymer matrix, which resulted in a decrease of adsorption capacity. (3) In general, the adsorption capacity of CTS was higher than its derivatives. However, CTS was not a suitable adsorbent because it was soluble in aqueous acidic solution and could not be recovered. Considering the solubility in aqueous acidic solution as well as its adsorption capability, CTS-2.0 may be the most suitable adsorbent.

From Figure 2b, we can see that the adsorption for noble metal ions was similar to that for base metal ions. A phenomenon that should be noticed was that the adsorption capacity of CTS-1.0 for Au^{3+} was much higher than for other three metal ions, demonstrating that ester groups participated in the complexation with Au^{3+}.[28]

3. Experimental

3.1. Materials

CTS with a degree of deacetylation 81.69%, (5.07 mmol NH_2 g^{-1}), was purchased from Yuhuan Halobios Company (Zhejiang province, China); methyl acrylate (MA) and ethylenediamine (EDA) were redistilled just before use. All of the other reagents used were of analytical-reagent grade.

3.2. General methods

Fourier transform infrared (FTIR) spectra of the CTS and its derivatives were measured in the 4000–400 cm^{-1} region using a Nicolet MAGNA-IR 550 (series II) spectrophotometer, Nicolet Co., the US; test conditions: KBr pellets, scanning 32 times, resolution is 4 cm^{-1}. The data were treated with Thermo Nicolet Corporation OMNIC 32 software v. 6.0a. Crystalline structures of the CTS and its derivatives were analyzed on a wide-angle X-ray diffraction on a Rigaku-D/max-2500VPC (Japan). These samples prepared as powders were laid on the glass sample holder ($20 \times 15 \times 2$ mm) and analyzed under plateau conditions. Ni-filtered Cu Kα radiation ($k = 1.54$ Å) generated at a voltage of 40 kV and a current of 40 mA was utilized, and a scan speed of 0.1°/s from 2° to 80° was used. The measured temperature was 25 °C.

The concentration of metal ions was determined using a 932B-model atomic adsorption spectrometer (AAS), GBC, Australia.

3.3. Preparation of CTS-0.5

CTS-0.5 was prepared via the Michael addition of MA to amino groups on the surface of CTS. The typical procedure was as follows: under a nitrogen atmosphere, 51 mL of redistilled MA were added to a 500-mL flask that contained 10 g of CTS powder, which was swollen for 4 h by 80 mL of MeOH. The flask was sealed, and the mixture was stirred with a magnetic stirrer at 50 °C. After 4 days, the solid product was filtered off and washed twice with MeOH, then transferred to a Soxhlet extraction apparatus and extracted with refluxing EtOH for 12 h. After extraction, the product was dried under vacuum at 50 °C over 48 h.

3.4. Preparation of CTS-1.0

CTS-1.0 was prepared via the amidation reaction of CTS-0.5 with EDA. The typical procedure was carried out as follows: under an N_2 atmosphere, 14.4 mL of EDA were added to a 500-mL flask that contained 7.5 g of CTS-0.5, which was swollen for 4 h by the addition of 60 mL of MeOH. The mixture was stirred with a magnetic stirrer at room temperature for 5 days and at 50 °C for 3 days. The solid product was filtered off and washed with a little MeOH, then transferred to a Soxhlet extraction apparatus for reflux-extraction in EtOH for 12 h. After extraction, the product was dried under vacuum at 50 °C over 48 h.

3.5. Preparation of CTS-1.5

Under an N_2 atmosphere, the reaction was carried out with 3.6 g of CTS-1.0 and 40 mL of MA in MeOH. The reactant mixture was stirred for 4 days at 50 °C, and then the product CTS-1.5 was filtered off. The purification procedure was the same as that for CTS-0.5.

3.6. Preparation of CTS-2.0

Under an N_2 atmosphere, the reaction was carried out with 3.6 g of CTS-1.5 and 12.5 mL of EDA in 40 mL of MeOH. The mixture was stirred with a magnetic stirrer at room temperature for 5 days and 50 °C for 3 days. The purification procedure was similar to that for CTS-1.0.

3.7. Preparation of CTS-2.5

Under an N_2 atmosphere, the reaction was carried out with 2.0 g of CTS-2.0 and 40 mL of MA in MeOH. The reactant mixture was stirred for 4 days at 50 °C, and then the solid product was filtered off. The purification procedure was the same as that for CTS-0.5.

3.8. Preparation of CTS-3.0

Under an N_2 atmosphere, the reaction was carried out with 1.5 g of CTS-2.5 and 12.5 mL of EDA in 40 mL of MeOH. The mixture was stirred with a magnetic stirrer at room temperature for 5 days and 50 °C for 5 days. The purification procedure was similar to that of CTS-1.0.

3.9. Determination of grafting percentage

The percentage of grafting polymer onto the surface of CTS was determined by the following equation:

$$\text{Grafting } (\%) = (A - B/B) \times 100\%$$

where A is the weight of grafted polymer and B is the weight of CTS charged.

3.10. Adsorption properties of CTS and its derivatives

A static adsorption experiment was employed to determine the adsorption capability of CTS and its derivatives for different kinds of metal ions. A typical way was that a dose of desired amount of the metal ions solution was added to a 50-mL Pyrex glass tube, and then the glass tube was placed in a thermostated shaking assembly. A known amount of sample (0.03–0.05 g) was charged, and the mixture was mechanically shaken at room temperature for 24 h. The solution in the tube was then separated from the adsorbent, and the concentration of metal ion was detected by means of AAS. The adsorbed amount was calculated according to the equation as follows:

$$Q = \frac{(C_0 - C)V}{W}$$

where Q is the adsorption amount (mmol/g); C_0, the initial concentrations of metal ions (mmol/mL); C, the final concentrations of metal ions (mmol/mL); V, volume (mL); W, the dry weight of CTS or its derivatives (g).

3.11. Solubilities of CTS and its derivatives

CTS (0.1 g) and its derivatives were dispersed in 15 mL of 2% CH_3CO_2H (or 2% HCl), respectively. The mixtures were mechanically shaken at room temperature for 3 h in a thermostated shaking assembly, and the insoluble materials were filtered off through a sintered-glass filter. The solid materials were washed with 10 mL of distilled water to remove the soluble matter, 5 mL of 0.5% NaOH to remove the CH_3CO_2H reacted with amine, 10 mL of distilled water and 10 mL of EtOH. The product was dried in vacuum at 50 °C and weighed.

4. Conclusions

A series of chitosan (CTS) derivatives were prepared by grafting ester- and amino-terminated dendrimer-like polyamidoamine (PAMAM) into CTS using a divergent method. Their structures were characterized by infrared spectra (IR) and wide-angle X-ray diffraction (WAXD). Their solubility in diluted acidic solutions was investigated. The results showed that the CTS derivatives were completely insoluble in dilute acid solutions when the generations of grafted dendrimers were greater than or equal to 2. The adsorption capabilities of the products for Au^{3+}, Pd^{2+}, Pt^{4+}, Ag^{+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, Ni^{2+}, and Cd^{2+} were studied. The results showed that the products exhibited better adsorption capabilities for Au^{3+} and Hg^{2+} than for other metal ions, and the adsorption capabilities of amino-terminated products were higher than those of ester-terminated ones. The CTS derivative with a high percentage of grafting of PAMAM did not exhibit a high adsorption capacity as expected because of the existence of strong steric hindrance and crosslinked structures.

Acknowledgments

The authors are grateful for support from the Nature Science Foundation of Shandong Province (No. Y2005F11), the Nature Science Foundation of Yantai Normal University (Nos. 032912, 20052901, 042920), and the Educational Project for Postgraduate of Yantai Normal University (Nos. YD05001, Ycx0612).

References

1. Muzzarelli, R.; Jeuniaux, C.; Gooday, G. W. *Chitin in Nature and Technology*; Plenum Press: New York, 1986.
2. Sanhya, B.; Kurniawan, T. A. *J. Hazard. Mater.* **2003**, *B97*, 219–243.
3. Varma, A. J.; Deshpande, S. V.; Kennedy, J. F. *Carbohydr. Polym.* **2004**, *55*, 77–93.
4. Spagna, G.; Pifferi, P. G.; Rangoni, C.; Mattivi, F.; Nicolini, G.; Palmonari, R. *Food Res. Int.* **1996**, *29*, 241–248.
5. Cestari, A. R.; Vieira, E. F. S.; Santos, A. G. P.; Mota, J. A.; Almeida, V. P. *J. Colloid Interface Sci.* **2004**, *280*, 380–386.
6. Chiou, M. S.; Ho, P. Y.; Li, H. Y. *Dyes Pigments* **2004**, *60*, 69–84.
7. Wan Ngah, W. S.; Endud, C. S.; Mayanar, R. *React. Funct. Polym.* **2002**, *50*, 181–190.
8. Qu, R.; Wang, C. *Technol. Water Treat.* **1997**, *23*, 230–235.
9. Chiou, M. S.; Li, H. Y. *Chemosphere* **2003**, *50*, 1095–1105.
10. Mi, F. L.; Shyu, S. S.; Chen, C. T.; Lai, J. Y. *Polymer* **2002**, *43*, 757–765.
11. Zeng, X.; Ruckenstein, E. *J. Membr. Sci.* **1998**, *148*, 195–205.
12. Qu, R. *Chin. J. Appl. Chem.* **1996**, *13*, 22–25.
13. Qu, R.; Wang, C.; Tang, Q. *Technol. Water Treat.* **1996**, *22*, 173–176.
14. Qu, R.; Liu, Q. *Polym. Mater. Sci. Eng.* **1996**, *12*, 140–143.
15. Qu, R.; Liu, Z.; Wang, C.; Zhang, P.; Liu, Q. *Acta Sci. Circumstantiae* **1997**, *17*, 121–125.
16. Qu, R.; Xu, Y.; Wang, C.; Liu, Q. *Environ. Chem.* **1996**, *15*, 214–219.
17. Qu, R.; Liu, Q. *Environ. Chem.* **1996**, *15*, 41–46.
18. Arrascue, M. L.; Garcia, H. M.; Horna, O.; Guibal, E. *Hydrometallurgy* **2003**, *71*, 191–200.
19. Jeon, C.; Höll, W. H. *Water Res.* **2003**, *37*, 4770–4780.
20. McAfee, B. J.; Gould, W. D.; Nadeau, J. C.; da Costa, A. C. A. *Sep. Sci. Technol.* **2001**, *36*, 3207–3222.
21. Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665–1688.

22. Sashiwa, H.; Shigemasa, Y.; Roy, R. *Carbohydr. Polym.* **2002**, *47*, 201–208.
23. Sashiwa, H.; Shigemasa, Y.; Roy, R. *Carbohydr. Polym.* **2002**, *47*, 191–199.
24. Sashiwa, H.; Shigemasa, Y.; Roy, R. *Carbohydr. Polym.* **2002**, *49*, 195–205.
25. Tsubokawa, N.; Takayama, T. *React. Funct. Polym.* **2000**, *43*, 341–350.
26. Tsubokawa, N.; Ichioka, H.; Satoh, T.; Hayashi, S.; Fujiki, K. *React. Funct. Polym.* **1998**, *37*, 75–82.
27. Torigoe, K.; Suzuki, A.; Esumi, K. *J. Colloid Interface Sci.* **2001**, *241*, 346–356.
28. Sonmez, H. B.; Senkal, B. F.; Sherrington, D. C.; Bicak, N. *React. Funct. Polym.* **2003**, *55*, 1–8.