Adsorption Removal of Cu^{2+} and Ni^{2+} from Waste Water Using Nano-Cellulose Hybrids Containing Reactive Polyhedral Oligomeric Silsesquioxanes

Kongliang Xie, Lixia Jing, Weiguo Zhao, Yanli Zhang

Department of Chemistry and Chemical Engineering, College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai, 200051, People's Republic of China

Received 17 May 2010; accepted 20 February 2011
DOI 10.1002/app.34411
Published online 29 June 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Cellulose is an important biomass in natural material fields. Reactive polyhedral oligomeric silsesquioxane (*R*-POSS) bearing multi-*N*-methylol groups is novel high reactive POSS monomer. The nano-cellulose hybrids containing *R*-POSS were synthesized by crosslinking reaction. It was interesting to investigate properties and applications of hybrids containing *R*-POSS. In this work, nano-cellulose hybrids as novel biosorbent were used for adsorpting copper and nickel ions in aqueous solution. Adsorption kinetics and equilibrium isotherm of Cu^{2+} and Ni^{2+} on the nano-cellulose hybrids were investigated. The results showed that *R*-POSS had been grafted to cellulose macromolecule. The nano-cellulose hybrids could form new adsorptive position for heavy metal ions. The adsorption capacities of hybrid materials were obviously higher than that of control cellulose. The adsorption of heavy metal ions on nano-cellulose hybrids followed the second-order model. The equilibrium isotherms for adsorpting copper and nickel ions on the hybrids followed Langmuir isotherm model. Nano-cellulose materials containing POSS as biosorbents or ultrafiltration membranes would be used in separation of toxic heavy metal ions. J Appl Polym Sci 122: 2864–2868, 2011

Key words: cellulose; hybrid; nano-technology; heavy metal, adsorption

INTRODUCTION

In recent years, the pollution of heavy metal ions in the environment has received extensive attention due to increased discharge and toxicity in the environment.[1,2] Waste streams from industrial process, such as metal cleaning, plating facilities, mining, corrosion, and electric devise manufactures, may contain considerable amount of heavy metal ions. Heavy metals can accumulate in living organisms, causing several disorder and diseases. They have highly toxic and other adverse effects at low concentrations.[3,4] Many new methods such as membrane separation, chemical precipitation, electrodeposition, ion exchange, and adsorption have been used to remove and recover metal ions from wastewater.[5–8] Adsorption is one of important methods for removing heavy metal.[9] However, some adsorptive materials used are either ineffective or expensive, when heavy metals are present in the wastewater at low concentrations. New biomasses and their composites from natural polymers should be developed because of their nature and reproduction.[10–12]

In natural polymers, cellulose and chitosan polymers are two important biomasses. A lot of attempts have been made to modify chitosan as biosorbents for removing heavy ions from aqueous solutions.[9–12] However, reports of modified cellulose as biosorbents for removing heavy ions are scarce. The cellulose fiber is one of the excellent natural biomaterials and easy to be reused.[13] Cellulose has been explored as a substrate for composite materials because of the presence of functional groups that may be employed in various activation processes. Chemical modification of cellulose can change itself chemical and morphological structures for different purpose.[14,15] The incorporation of nanoscale particles into cellulose matrix leads to a strong interfacial interaction.[16,17]

Nanofibers and nanocomposite materials have gained much interest due to the remarkable change in properties.[18] Hybrid organic–inorganic molecules like polyhedral oligomeric silsesquioxanes (POSS) can serve as model nanofillers. POSS can be effectively incorporated into polymers by copolymerization, grafting, or even blending through traditional processing methods.[19–22] Typical advantages of cellulose-based hybrids are flexibility, low density, reusability, adsorbability, and formability; moreover,

Correspondence to: K. Xie (klxie@dhu.edu.cn).

nano-sized POSS has excellent mechanical, optical, and thermal properties. Novel high-reactive polyhedral oligomeric silsesquioxane may be utilized for preparing nano-cellulose materials.[23,24] *R*-POSS has a nanometer-sized structure with a cubic silica core and can be functionalized with a variety of organic compounds. These composite materials from nature are biocompatible, biodegradable, and possess low toxicity in biomaterial field.

In this article, nano-cellulose hybrids containing *R*-POSS were synthesized by crosslinking graft reaction. Nano-cellulose hybrids as biosorbents were used for adsorpting copper and nickel ions in aqueous solution. The adsorption characteristic of Cu^{2+} and Ni^{2+} on the hybrids was discussed. Adsorption kinetics and equilibrium isotherm of Cu^{2+} and Ni^{2+} on the nano-cellulose hybrids were investigated.

EXPERIMENTAL

Materials

Scoured and bleached cellulose fabrics (cotton fiber) were obtained from Jinqiu Textile Company, Shaoxing, China. *R*-POSS was obtained from National Research Center of Dying and Finishing, Shanghai, China. Analytical grade nickel sulfate and copper sulfate were obtained from Shanghai Chemical Reagent Plant, Shanghai, China. Highly pure water was prepared in the laboratory by double distillation. Other chemicals were obtained from Shanghai Chemical Reagent Plant, Shanghai, China.

Preparation of nano-cellulose hybrids containing *R*-POSS

R-POSS was diluted with distilled water to certain concentration solution according to two recipes. Two solution ingredients were *R*-POSS 1.6%, $MgCl_2$ 1.5%, Citric acid 0.5%, and alcohol 2%; *R*-POSS 2.0%, $MgCl_2$ 1.5%, Citric acid 1%, alcohol 2%, respectively. Citric acid and $MgCl_2$ as catalysts were used in the crosslinking reaction. The mixtures were sufficiently mixed by stirring at room temperature.

Cellulose fabrics were padded with *R*-POSS solutions to give 80% wet pick-up, respectively. The dry temperature and time were 95°C and 3 min, respectively. After drying, the fabrics were cured for 1.5 min at 160°C. After crosslinking, the samples were rinsed in hot water at 65°C for 15 min at liquor ratio 1 : 15. Then the samples were removed and air-dried. The *R*-POSS crosslinking nano-cellulose hybrids were obtained. The modified hybrids according to the above two recipe were named as H-1 and H-2. FTIR spectra of the samples were measure by a OMNI Sampler of the Nexus-670 FTIR-Raman spectrometer (Nicolet Analytical Instruments, Madison, WI) using a single attenuated total reflection method. Compared with control sample (the unmodified cellulose), the characteristic absorption band of the —OH near 3470 cm^{-1} on the hybrids, H-1, H-2, became weak. The typical absorption bands for Si—O— were located at 1650 and 810 cm^{-1}. The percentage silicon content was determined by Leeman Prodigy (USA). Si element contents of samples, H-1, H-2, and control sample, were 1.92 mg/g, 1.99 mg/g and 0.64 mg/g, respectively.

Absorption experiments

The nano-cellulose hybrids were cut into a piece of square sample (0.2 g). Batch experimental studies were carried out with the adsorbents (0.2 g) and metal ion solution of desired concentration (20 mL) at certain pH. In the experiment of pH and agitation time effects, the initial concentration of Cu^{2+} and Ni^{2+} were 25.4 mg/L, and 22.3 mg/L, respectively. The solutions were adjusted to pH 3–7 with hydrochloric acid solution, 1.0 mol/L, and then stirred for desired time at 30°C, respectively. The adsorbents were removed and metal ion concentrations of solutions were measured on Leeman Prodigy (USA) atomic absorption spectrophotometer. The adsorption ratio (E%) was calculated by Eq. (1).

$$E(\%) = \left(\frac{C_0 - C_1}{C_0}\right) \times 100\% \quad (1)$$

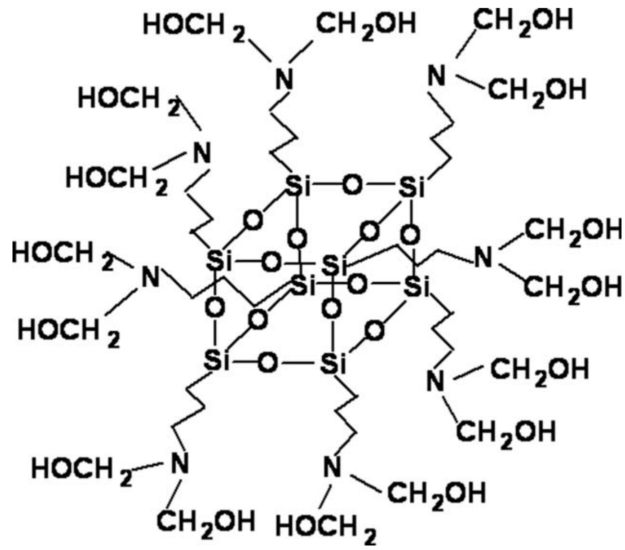
where C_0 was the initial concentration of metal ion, C_1 was the final concentration of metal ion.

Equilibrium isotherm and adsorption kinetic

Metal solutions were diluted to required concentrations. The initial concentrations of Cu^{2+} were 12.7 mg/L, 25.4 mg/L, 50.9 mg/L, and 76.3 mg/L, respectively. The initial concentrations of Ni^{2+} were 11.2 mg/L, 22.3 mg/L, 44.7 mg/L, and 67.0 mg/L, respectively. Batch experimental studies were carried out at pH 6 condition for 4 h. After attaining equilibrium, the adsorbents were removed and metal ion concentrations of the solutions were measured by atomic absorption spectrophotometer. The equilibrium uptake capacity of the biosorbents for each metal ion was calculated by Eq. (2):

$$q_e = \frac{(C_0 - C_e) \times v}{m} \quad (2)$$

where q_e was the adsorbed amount per unit mass of adsorbent (mg/g). C_0 was the initial concentration of metal ion. C_e was the equilibrium concentration of



Scheme 1 Chemical structure of *R*-POSS.

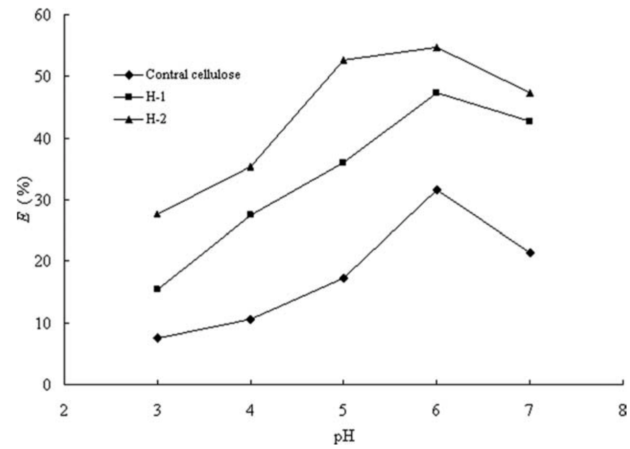


Figure 2 Effect of pH on Ni^{2+} adsorption on the nano-cellulose hybrids.

metal ion; *m* was the mass of adsorbent (*g*) and *v* was volume of solutions in liters. Each experiment was repeated three times independently and the means were taken. Kinetic was carried out at 30°C. The initial concentration of Cu^{2+} and Ni^{2+} were 25.4 mg/L, and 22.3 mg/L, respectively.

RESULTS AND DISCUSSION

Effect of pH and contact time on adsorption properties of nano-cellulose hybrids

R-POSS had nano-sized core and high-reactive multi-*N*-methylol groups.[23] The high-reactive multi-*N*-methylol of *R*-POSS could be used to modify polymer materials and form network structure containing nano-sized inorganic particles. The structure of reactive polyhedral oligomeric silsesquioxane containing multi-*N*-methylol groups (*R*-POSS) is shown in Scheme 1.

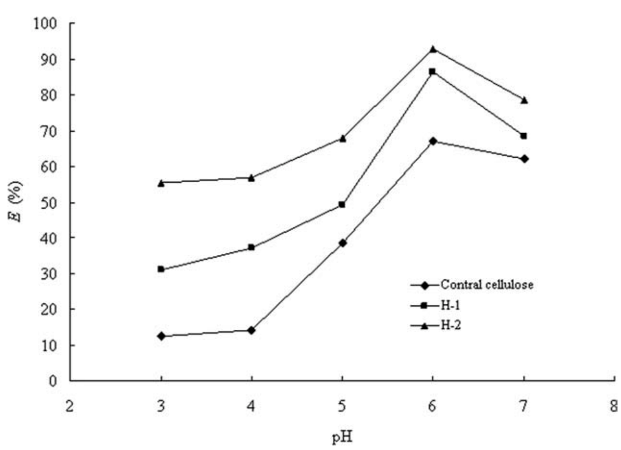


Figure 1 Effect of pH on Cu^{2+} adsorption on the nano-cellulose hybrids.

The cellulose macromolecule had numerous hydroxyl groups (-OH). The cellulose fibers could be crosslinked by *R*-POSS with citric acid and $MgCl_2$ as catalyst. Nano-cellulose hybrid macromolecules formed have nano-sized cores and numerous amino (—C—N—) and hydroxyl groups (—OH). They would form numerous new adsorptive positions for heavy metal ions. The effect of pH on the adsorption of Cu^{2+} and Ni^{2+} were investigated at 30°C. The solutions were adjusted to pH 3–7 with hydrochloric acid solution (1.0 mol/L) and stirred for 4 h, respectively. The results are shown in Figures 1 and 2. It can be seen that the maximum uptake of heavy ions, both Cu^{2+} and Ni^{2+}, took place at pH 6. The uptake of heavy ions became decrease at pH 7. At low pH values the adsorption of the metal ions significantly reduced due to the protonation of the active groups at this acidic medium, and this could lead to reduction of the metal chelation by the modified polymer. Meantime, the adsorption ratio of hybrid materials (H-1 and H-2) was obviously higher than that of control cellulose at the experimental pH. It indicates that the amino (—C—N—) and hydroxyl groups (—OH) of nano-cellulose hybrids were easy to adsorb heavy ions.

Effect of time on Cu^{2+} and Ni^{2+} adsorption on the nano-cellulose hybrids were also studied. The results are shown in Figures 3 and 4 for Cu^{2+} and Ni^{2+}, respectively. Figure 3 shows that the adsorption of Cu^{2+} mainly took place at the beginning. The adsorption ratio of hybrids significantly increased with time at beginning stage. After the equilibrium time (120 min), the adsorbed amount of Cu^{2+} did not obviously change with time. The similar trend was observed for Ni^{2+}. After 120 min, the adsorption of Ni^{2+} on the hybrids had

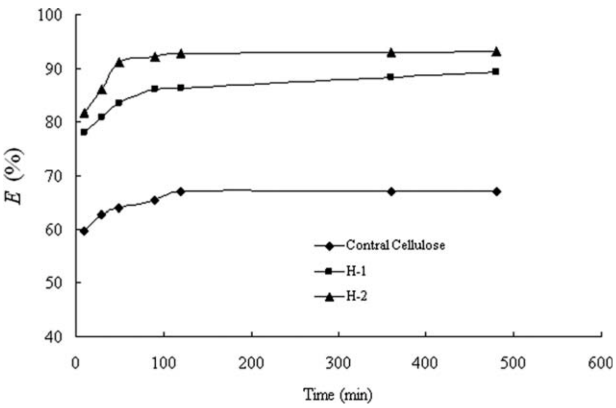


Figure 3 Effect of time on Cu^{2+} adsorption on nano-cellulose hybrids ($C_0 = 25.4$ mg/L, $T = 30°C$).

reached equilibrium. Comparing Figures 3 and 4, the adsorption capacity of the hybrids for Cu^{2+} was obviously higher than that of the hybrids for Ni^{2+}. The nano-cellulose hybrids imparted selective adsorption of heavy metal ions. According to Figures 3 and 4, the modified cellulose showed a higher selectivity toward Cu^{2+} than Ni^{2+}. This selectivity could be attributed to the increase of the nitrogen content after the modification, regarding the high stability of the copper amino complexes. Also, high selective could be attributed to the Jahn-Teller effect, which is predominant with copper complexes.[25,26]

Adsorption kinetics of metal ions on the nano-cellulose hybrids

The kinetics for the adsorptions of copper and nickel ions on the nano-cellulose hybrid H-2 were studied at pH 6 and 30°C. Adsorption curves of Cu^{2+}, Ni^{2+} on the nano-cellulose hybrids with time are shown in Figure 5, respectively.

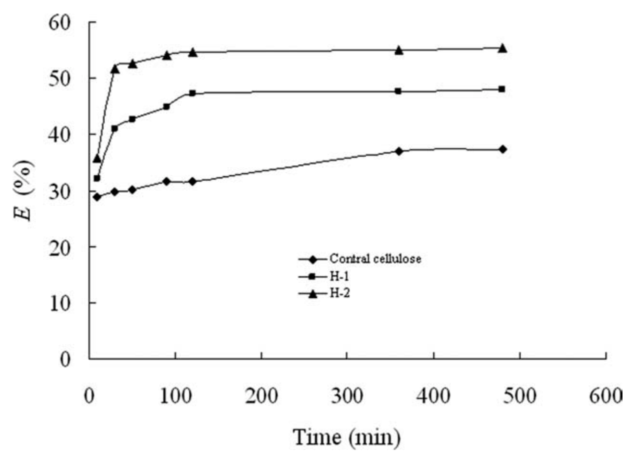


Figure 4 Effect of time on Ni^{2+} adsorption on nano-cellulose hybrids ($C_0 = 22.3$ mg/L, $T = 30°C$).

The dynamical experimental data were treated according to the second-order equation model (eq. 3).

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

where q_e and q_t refered to the amount of heavy metal ions at equilibrium (mg/g) and at t time (min), k_2 was the overall rate constant of the pseudo-second order of adsorption (g mg^{-1} min^{-1}). The kinetic parameters obtained from the straight-line plots between t/q_t versus t. The kinetic equations of Cu^{2+} and Ni^{2+} are shown by Eq. (4) and (5), respectively.

$$t/q_t = 0.4211t + 0.0112 \quad (4)$$

$$t/q_t = 0.8039t + 0.0469 \quad (5)$$

Kinetic parameters (k_2) for Cu^{2+} and Ni^{2+} were 503.50 [g· (mg min)$^{-1}$] and 32.99 [g· (mg min)$^{-1}$], respectively. It can be seen that the adsorption of heavy metal ions on nano-cellulose hybrids were good fit with the second-order models. The correlation coefficients of Cu^{2+} and Ni^{2+} were 1 and 0.9999, respectively. They follow chemical adsorption theory and practice. Meantime, absorption rate of Cu^{2+} on the hybrids was obviously higher than that of Ni^{2+} ($k_{Cu2+} > k_{Ni2+}$).

Adsorption equilibrium model

The equilibrium adsorption data were subjected to Langmuir adsorption isotherm and Freundlich adsorption isotherm. The Langmuir isotherm equation, which was the most commonly used for monolayer adsorption onto a surface with a finite number of identical sites, was represented by Eq. (6)

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \quad (6)$$

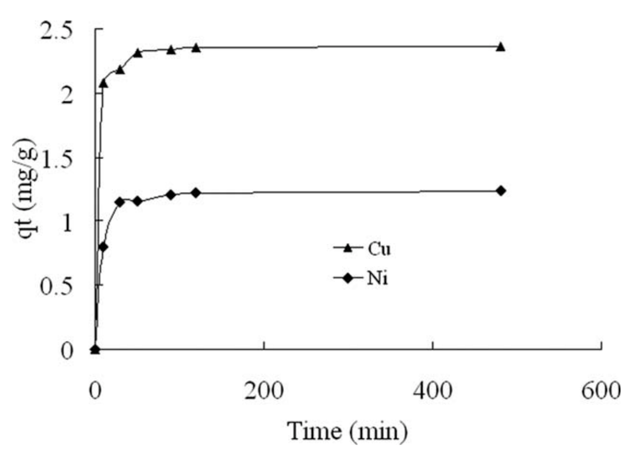


Figure 5 Adsorption curves of Cu^{2+}, Ni^{2+} on nano-cellulose hybrids.

TABLE I
Langmuir and Freundlich Isotherm Constants for Cu^{2+} and Ni^{2+} on the Hybrid H-2

Metal ions	Langmuir equation			Freundlich equation		
	q_m (mg g^{-1})	b (L mg^{-1})	R^2	K	n	R^2
Cu^{2+}	24.5098	0.0437	0.9911	0.9061	1.0765	0.9707
Ni^{2+}	8.1833	0.0872	0.9898	0.6820	1.3273	0.9777

where C_e was the equilibrium concentration of metal ions. q_e was the amount of metal ions adsorbed (mg/g) on the hybrids. q_m was the maximum adsorption of metal ions (mg/g). b was the Langmuir adsorption equilibrium constant (ml/mg). Therefore, the plot of $1/q_e$ against $1/C_e$ gave a straight line with a slope of $1/(q_m b)$ and an intercept of $1/(q_m)$.

The Freundlich isotherm equation, the most important multilayer adsorption isotherm for heterogeneous surfaces, was described by Eq. (7).

$$q_e = k_f C_e^{1/n} \tag{7}$$

where C_e was the equilibrium concentration of metal ions. q_e was the amount of metal ions adsorbed (mg/g) on the hybrids. k_f and n were the adsorption constant, respectively. k_f and n could be determined from a linear plot of $\ln q_e$ versus $\ln C_e$.

The experimental equilibrium isotherms for adsorption copper ion and nickel ion on the hybrid H-2 were carried out. The experimental data for adsorption on the hybrid H-2 were treated according to Langmuir model and Freundlich model. Their isotherm constants are summarized in Table I. Comparing their linear correlation coefficients in Table I, it can be seen that the adsorptions of two ions on the nano-cellulose hybrid were good fit with Langmuir isotherm equation under the studied concentration. The order of the adsorption capacities (q_m, mg/g) from the Langmuir isotherm equation for two ions were as follows: $Cu^{2+} > Ni^{2+}$.

CONCLUSIONS

The nano-cellulose hybrids containing *R*-POSS were synthesized by crosslinking reaction. Nano-cellulose hybrids could form new adsorptive position for heavy metal ions. The adsorption capacities of hybrids materials were obviously higher than that of control cellulose. The maximum uptakes of Cu^{2+} and Ni^{2+} took place at pH 6. The adsorption of Cu^{2+} and Ni^{2+} ions on nano-cellulose hybrids were good fit with the second-order model. Adsorption rate of Cu^{2+} on the hybrids was obviously higher than that of Ni^{2+}. The equilibrium isotherms for adsorption copper and nickel ions on the hybrid were good fit with Langmuir isotherm equation under the studied concentration. The order of the adsorption capacities from the Langmuir isotherm model for two ions was $Cu^{2+} > Ni^{2+}$.

References

1. Ngah, W. S. W.; Hanafiah, M. A. K. M. Biores Technol 2008, 99, 3935.
2. Sud, D.; Mahajan, G.; Kaur, M. P. Biores Technol 2008, 99, 6017.
3. Chen, A. H.; Liu, S. C.; Chen, C. Y.; Chen, C. Y. J Hazard Mater 2008, 154, 184.
4. Srinivasa, R. P.; Vijaya, Y.; Veera, M. B.; Krishnaiah, A. Biores Technol 2009, 100, 194.
5. Harazono, K.; Nakamura, K. Chemosphere 2005, 59, 63.
6. Ngah, W. S. W.; Fatinathan, S. Chem Eng J 2008, 143, 62.
7. Verma, V. K.; Tewari, S.; Rai, J. P. N. Biores Technol 2008, 99 1932.
8. Vijayalakshmi, A.; Arockasamy, D. L.; Nagendran, A.; Mohan, D. Sep Purif Technol 2008, 62, 32.
9. Kobya, M.; Demirbas, E.; Senturk, E.; Ince, M. Biores Technol 2005, 96, 1528.
10. Gurgel, L. V. A.; Gil, L. F. Carbohydr Polym 2009, 77, 142.
11. Haider, S.; Park, S. Y. J Membr Sci 2009, 328, 90.
12. Zhou, L.; Wang, Y.; Liu, Z.; Huang, Q. J Hazard Mater 2009, 161, 995.
13. Hou, A.; Zhou, M.; Wang, X. Carbohydr Polym 2009, 75, 328.
14. Xie, K.; Liu, H.; Wang, X. Carbohydr Polym 2009, 78, 538.
15. Hou, A.; Sun, Y. J Dispersion Sci Technol 2009, 30, 643.
16. Jeon, H. G.; Mather, P. T.; Haddad, T. S. Polym Int 2000, 49, 453.
17. Xie, K.; Hou, A.; Sun, Y. J Dispersion Sci Technol 2008, 29, 1385.
18. He, J.; Wan, Y.; Xu, L. Chaos Solitons Fract 2007, 33, 26.
19. Janowski, B.; Pielichowski, K. J Organomet Chem 2008, 693, 905.
20. Liu, H.; Kondo, S.; Tanaka, R.; Oku, H.; Unno, M. J Organomet Chem 2008, 693, 1301.
21. Hou, A.; Wang, X.; Yu, Y. Carbohydr Polym 2009, 77, 201.
22. Wu, G.; Chen, Y.; Xu, D.; Liu, J.; Sun, W.; Shen, Z. J Organomet Chem 2009, 694, 1571.
23. Xie, K.; Zhang, Y.; Chen, S. J Organometal Chem 2010, 695, 687.
24. Xie, K.; Gao, X.; Zhao, W. Carbohydr Polym 2010, 81, 300.
25. Monier, M.; Ayad, D. M.; Sharhan, A. A. J Hazard Mater 2010, 176, 348.
26. Monier, M.; Ayad, D. M.; Wei, Y.; Sharhan, A. A. J Hazard Mater 2010, 177, 962.