การเตรียมตัวดูดจับชนิดใหม่ที่มีหมู่ไฮดรอกซามิกแอซิด โดยใช้ลำอิเล็กตรอนเหนี่ยวนำให้เกิดปฏิกิริยากราฟต์สำหรับดูดจับโลหะอิออน

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บทคัดย่อ

สังเคราะห์ตัวดูดจับชนิดใหม่ โดยใช้ลำอิเล็กตรอนเหนี่ยวนำให้เกิด ปฏิกิริยากราฟต์โคพอลิเมอร์ไรเซชันของเมททิลอะคริเลทบนแผ่น Nonwoven ซึ่งประกอบด้วยพอลิเอทิลีนเคลือบบนเส้นใยพอลิพอพิลีน จากนั้นจึงทำการเปลี่ยนหมู่เอสเตอร์ของกราฟต์โคพอลิเมอร์ ให้เป็นหมู่ไฮดรอกซามิค โดยทำปฏิกิริยากับสารละลายอัลคาไลต์ของไฮดรอกซิลเอไมด์ ตัวดูดจับที่มีหมู่ไฮดรอกซามิคแอซิดสามารถดูดจับ UO_2^{+2}, V^{+5}, Pb^{2+}, และ Al^{3+} ในปริมาณร้อยละ 99, 98, 97 และ 96 ที่ pH 5, 4, 6, และ 4 ตามลำดับเมื่อ สัมผัสกับสารละลายโลหะเข้มข้น 100 ส่วนในพันล้านส่วน เป็นเวลา 24 ชั่วโมง

คำสำคัญ: ตัวดูดจับ กราฟต์ ลำอิเล็กตรอน ไฮดรอกซามิคแอซิด โลหะอิออน

Preparation of New Adsorbent Containing Hydroxamic Acid Groups by Electron Beam-Induced Grafting for Metal Ion Adsorption

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Abstract

A new adsorbent containing hydroxamic acid groups was synthesized by electron beam-induced graft copolymerization of methyl acrylate (MA) onto nonwoven fabric composed of polyethylene-coated polypropylene fiber. Conversion of ester groups of the grafted copolymer into the hydroxamic groups was performed by treatment with an alkaline solution of hydroxylamine (HA). Adsorbent containing hydroxamic acid groups can adsorb 99% of UO_2^{2+}, 98% of V^{5+}, 97% of Pb^{2+} and 96% of Al^{3+} at pH, 5, 4, 6, and 4, respectively, after coming into contact with 100 ppb metal solution for 24 h.

Keywords: Adsorbent, Electron Beam, Hydroxamic Acid, Metal Ion

Introduction

Polymeric Chelating resins bearing hydroxamic acid group have been used for extraction and separation of metal ions, since the hydroxamic acid groups can form complexes with various metal ions such as Cd^{2+}, V^{5+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Hg^{2+}, Au^{3+}, Ag^{+}, Cu^{2+}, Co^{2+}, Cr^{3+} and UO^{2+}_2 [1-5]. A considerable number of poly(hydroxamic acid) chelating resins derived from poly(styrene-*co*-maleic acid)[2], poly(amidoximes) [6], poly(acrylonitrile) [7], and poly(methacrylate) [8] have been synthesized.

Radiation-induced graft polymerization has been used for preparation of metal adsorbents. Fabric adsorbent having amidoxime functional group was synthesized by radiation-induced graft-polymerization. It was applied to the removal of Cd from the scallop waste [9]. Adsorbent containing phosphoric acid was directly prepared by radiation-induced grafting of methacrylate monomer having phosphoric acid onto polyethylene nonwoven fabric. The adsorbent of 160% degree of grafting revealed that the total capacities were 2.8 and 3.0 mmol/g-adsorbent for Pb and Cd, respectively [10].

So far no work has been done for preparation of adsorbent containing hydroxamic acid groups by radiation-induced grafting for metal ion adsorption. This may be the first attempt for the preparation of poly(hydroxamic acid) chelating resin from poly(methyl acrylate) (PMA)-grafted nonwoven fabric by radiation-induced grafting. In the present work, a new adsorbent containing hydroxamic acid groups was synthesized by radiation-induced graft copolymerization of methyl acrylate (MA) onto nonwoven fabric composed of polyethylene-coated polypropylene fiber. Graft copolymerization was carried out in MA emulsion containing sodium dodecyl sulfate (SDS) as an emulsifier in the presence of water. Grafting polymerizations were studied with regard to various parameters of importance: dose, concentration of MA, reaction time, reaction temperature, and concentration of SDS. Conversion of the ester groups of the grafted copolymer into the hydroxamic groups was performed by treatment with an alkaline solution of hydroxylamine (HA). In addition, the adsorption behavior of chelating resin toward metal ions was investigated.

Experimental

2.1 Radiation-induced graft polymerization

The trunk polymer fabrics were cut into rectangle of 3cm x 6cm and were packed in a polyethylene bag under nitrogen atmosphere. Then, samples were irradiated with an electron accelerator (Dynamitron, Model IEA 3000-25-2, Radiation Dynamics Co.) operating at a beam energy of 1.9 Mev and a current of 3.0 mA at room temperature. After irradiation, fabrics were placed into a glass ampoule and were evacuated. The deaerated MA solution containing SDS was transferred into the ampoule. The reaction temperature was maintained in water bath. The residual MA and homopolymer were removed by washing with dimethylformamide (DMF), followed by methanol. The degree of grafting (Dg) was determined by the following equation:

$$Dg\ (\%) = 100[(W_g - W_0)/W_0]$$

where W_0 and W_g are the weights of trunk polymer and graft polymer, respectively.

2.2 Preparation of adsorbent containing hydroxamic acid groups

60g of hydroxylamine hydrochloride ($NH_2OH.HCl$) was dissolved in a 300ml methanolic solution ($MeOH:H_2O = 5:1$) The HCl was neutralized by the NaOH pellet. The precipitated NaCl was separated by filtration. The pH of the reagent was adjusted to pH 13 by addition of the NaOH pellet. One gram of graft copolymer was placed in the glass ampoule and the hydroxylamine solution was added. The reaction was carried at 75^{o}C for 2 hours. After completion of the reaction, the modified graft copolymer was washed several times with a methanolic solution ($MeOH:H_2O = 4:1$). Then, it was dried in vacuum oven at 30^{o}C overnight. Finally, the modified graft copolymer was treated with 100 ml of methanolic HCl solution (0.2 M) for 10 minutes, washed several times with the methanolic solution ($MeOH:H_2O = 4:1$) and then dried in vacuum oven at 30^{o}C overnight.

2.3 Particle size analysis

Micelle particle size was determined by using a FPAR-1000 fiber-optics particle size analyzer. The measurements were done at a temperature of 30^{o}C.

2.4 Metal adsorption

The adsorbent was cut into the square of the 1cm x 1cm (approximately 0.01 g). Then, it was soaked into 100 ppb metal solution and stirred at room temperature for 24 h. The concentration of the adsorbed metal was measured by an inductively coupled plasma mass spectroscopy (ICP-MS, 4500 Series, Hewlett Packard).

Results and Discussion

3.1 Effect of absorbed dose on degree of grafting

Figure 1 represents the effect of absorbed dose on degree of grafting. The degree of grafting increased with increasing adsorbed dose. An increase in absorbed dose enhances the formation of radicals, resulting in high degree of grafting. The degree of grafting reached about 200% at absorbed 40 kGy. Absorbed dose 20 kGy gave the percentage grafting about 140 which satisfied the requirements for preparing adsorbent for metal adsorption.

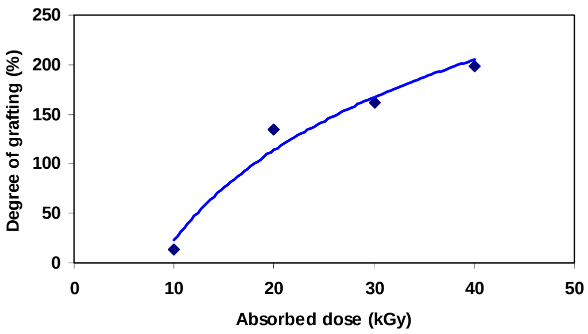

Figure 1: Effect of absorbed dose on degree of grafting of PMA onto nonwoven fabric: 2% MA, 0.5% w/v SDS in H2O, reaction temperature 50^{o}C, and reaction time 1h.

3.2 Effect of MA concentration and reaction temperature on degree of grafting

Figure 2 shows the effect of MA concentration and reaction temperature on degree of grafting of MA onto trunk polymer in emulsion. As the monomer concentration and reaction temperature increased, the degree of grafting was found to be increased. At higher monomer concentration, radicals generated on the trunk polymer are able to interact with more monomer molecules. An increase in temperature may increase the diffusion of monomer to the grafting sites.

The 115% of grafting was obtained at MA concentration of 2% w/v , and reaction temperature of 40°C which is enough for preparing metal adsorbents. Therefore, for further studies, concentration monomer, and reaction temperature were fixed at 2% w/v and 40°C, respectively.

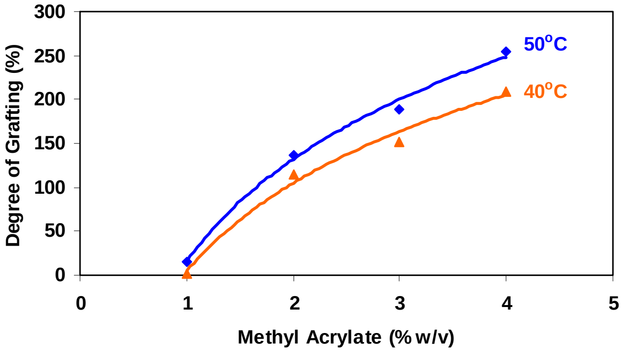

Figure 2: Effect of MA concentration and reaction temperature on degree of grafting: 0.5% w/v SDS in H_2O, reaction time 1 h, and absorbed dose 20 kGy.

3.3 Effect of SDS concentration on degree of grafting

Figure 3 illustrates the effect of SDS concentration on degree of grafting. The degree of grafting decreased with an increasing SDS concentration.

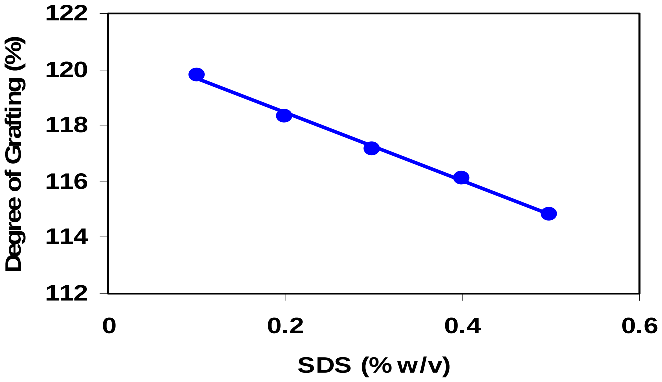

Figure 3: Effect of surfactant (SDS) concentration on degree of grafting: 2% MA, reaction time 1 h, reaction temperature 40°C, and absorbed dose 20 kGy.

In order to clarify the effect of surfactant on the degree of grafting, the micellae particle sizes were determined by light scattering technique. The results of this study have been summarized in Figure 4.

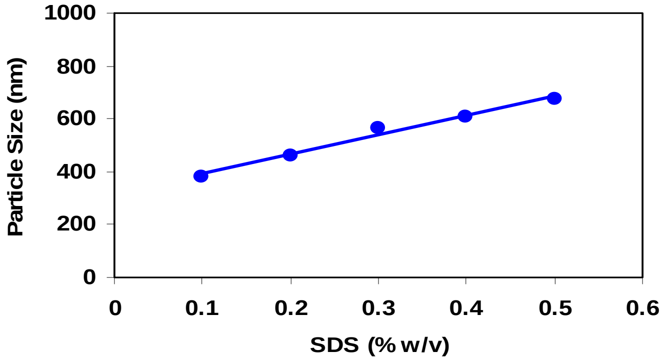

Figure 4: Effect of surfactant (SDS) concentration on particle size: 2% MA.

It was found that the higher the SDS concentration was, the bigger the diameter of micellae. The big micellae has low rate of diffusion, and small surface area. This results in decreasing of degree of grafting. The 120% (6.33 mmol/g MA) of grafting was obtained at SDS concentration of 0.1% w/v. No phase separation was observed after left MA/SDS mixture solution for one month.

3.4 Effect of reaction time on degree of grafting

The effect of the reaction time on the percentage of grafting is shown in Figure 5. The degree of grafting increased with increment of the reaction time. After 1 h reaction, the degree of grafting reached 120% (6.33 mmol/g of MA).

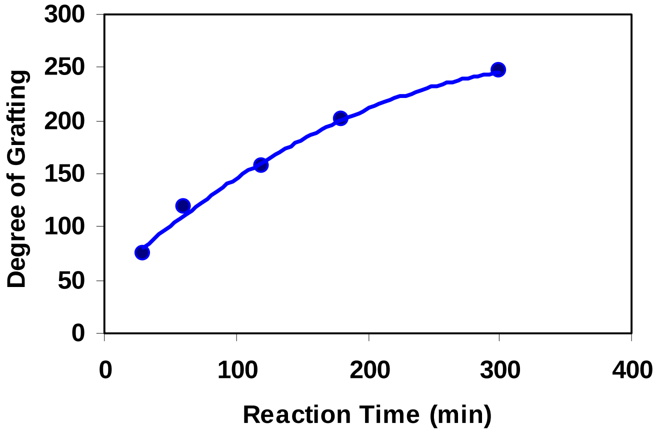

Figure 5: Effect of reaction time on degree of grafting: 2%MA, 0.1% w/v SDS in H_2O, reaction temperature 40°C, and absorbed dose 20 kGy.

3.1 FTIR analysis

FTIR spectra of trunk polymer, graft copolymer, and modified graft copolymer are presented in Figure 6.

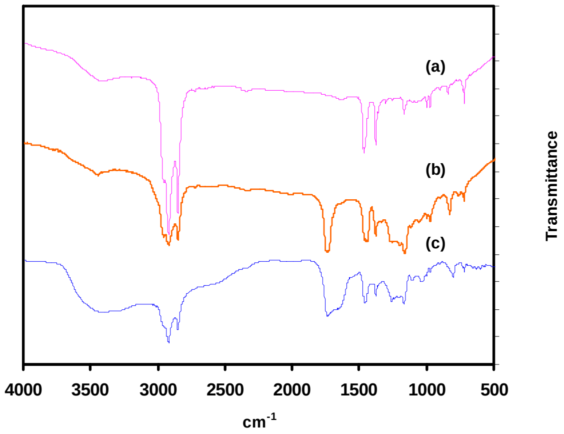

Figure 6: FTIR spectra of (a) trunk polymer, (b) graft copolymer and (c) modified graft copolymer.

The FTIR spectrum of trunk polymer in Figure 1 (a) showed the characteristic absorption bands at 2850 and 2917 cm^{-1} due to C-H stretching of aliphatic carbon and CH_2 and other absorption bands at 1377 and 1464 cm^{-1} for CH_3 deformation, respectively. While, the FTIR spectrum of grafted copolymer shows a new characteristic absorption band of an ester at 1725 cm^{-1} due to C=O stretching mode in addition to the same adsorption bands of trunk polymer. The FTIR spectrum of modified copolymer shows the characteristic adsorption bands of hydroxamic acid (C=O at 1711 cm^{-1}) and amide (N-H at 1629 cm^{-1}). These evidences confirm the presence of hydroxamic acid group in the modified copolymer.

3.4 Metal adsorption

The presence of electron donating groups in adsorbent containing hydroxamic acid groups gives it the ability to form polycomplexes with metal ions. The ability of the adsorbent to adsorb various metals was carried out in order to evaluate the possibility of their uses in metal adsorption. A diagram showing the percentage adsorption of adsorbents for various metals is shown in Figure 7. It was found that adsorbent containing hydroxamic acid groups can adsorb various metal ions. Each metal ion has its own pH at which it shows maximum percentage adsorption.

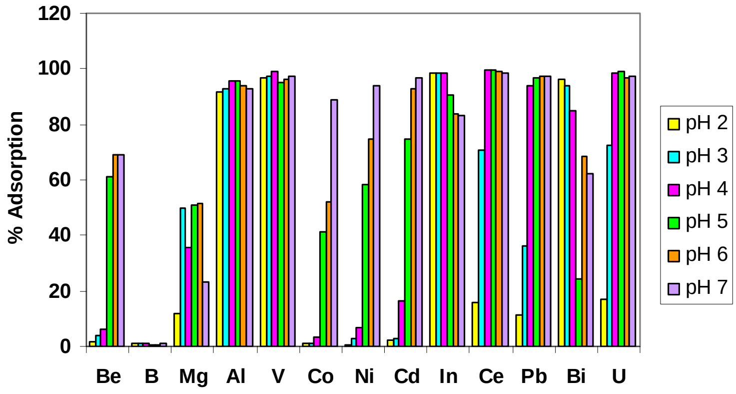

Figure 7: Adsorption of different metals by the adsorbent containing hydroxamic acid groups.

Adsorbent containing hydroxamic acid groups can adsorb 99% of UO_2^{2+}, 99% of V^{5+}, 97% of Pb^{2+}, 96%of Al^{3+}, and 97% of Cd^{2+} at pH, 5, 4, 6, 4, and 7 respectively after coming into contact with 100 ppb metal solution for 24 h (Figure 8). Increasing pH did not have significant effect on % adsorption of vanadium and aluminium.

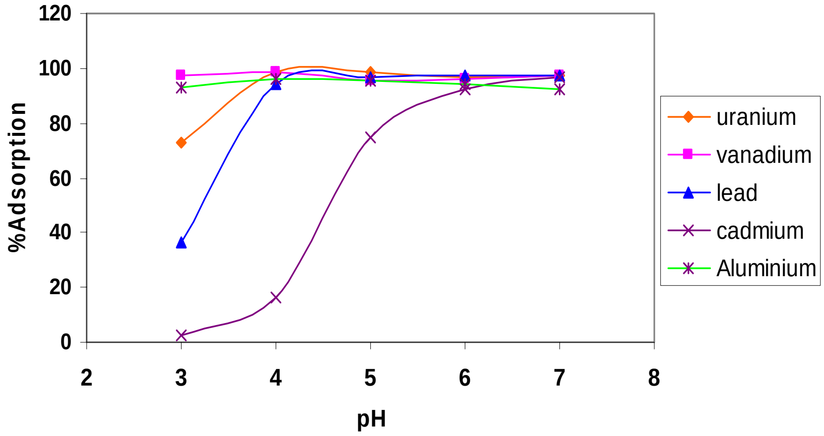

Figure 8: Effect of pH on aluminium, cadmium, lead, vanadium, and uranium adsorption.

Conclusion

New adsorbent containing hydroxamic acid groups was successfully prepared by electron beam-induced graft copolymerization of methylacrylate onto nonwoven fabric composed of polyethylene-coated polypropylene fiber followed by treatment with hydroxylamine. The graft copolymer produced with 2%MA, 0.1% w/v SDS in H_2O, reaction temperature 40^oC, reaction time 1 hr, and absorbed dose 20 kGy gave 120% (6.33 mmol/g MA) degree of grafting. This method used very low MA, and SDS concentration. The prepared graft copolymer showed a good affinity towards chelation with different metals.

References

[1] H. L. Yale, Chem Rev, **33**, 209 (1943).

[2] R. M. Mendez, V.N. Sivasankara Pillai, Talanta, **37**, 591 (1990).

[3] Y. K. Agrawal, H. Kaur, S.K. Menon, Reaactive & Functional Polymers, **39**, 155 (1999).

[4] M.R. Lutfor, S. Sidik, W.M.Z. Wan Yunus, M.Z.A. Rahman, A. Mansor, M.J. Haron, Journal of Applied Polymer Science, 79, 1256 (2001).

[5] R.J. Phillips, J.S. Fritz, Analytica Chemica Acta, 121, 225 (1980).

[6] F.Vernon, T. Shah, Reactive Polymers, 1, 301 (1983).

[7] A. Shah, S. Devi, Talanta, 34, 547 (1987).

[8] M.J. Haron, W.M. Z. W. Yunus, M.Z. Desa, A. Kassim, Talanta, 4, 805 (1994).

[9] T. Shiraishi, M. Tamada, K. Saito, T. Sugo, Radiation Physics and Chemistry, 66, 43 (2003).

[10] F. Basuki, N. Seko, M. Tamada, T. Sugo, T. Kume, J.Ion Exchange, 14, 209 (2003).