Article

Direct Synthesis of Adsorbent Having Phosphoric Acid with Radiation Induced Graftpolymerization

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Abstract

Radiation induced graftpolymerization is a sophisticated tool for introducing the aiming functional group into the conventional polymer. Adsorbent having phosphoric acid was directly synthesized by grafting methacrylate monomer having phosphoric acid onto polyethylene nonwoven fabric. Degree of grafting (D_g), which was estimated by increment weight after grafting, reached 185 % when the 10% monomer in the mixture of 10% methanol and 90% water was reacted with 200 kGy-irradiated nonwoven fabric. The adsorbent of 160% D_g revealed that adsorption capacity was 3 mmol/g-adsorbent for Pb and Cd ions in column mode. The removal of these metals could be performed with space velocity of 250 h⁻¹.

1 Introduction

Removal of toxic metal from the industrial waste water and mine water is important to preserve clean environment. A chelate adsorbent has been researched extensively since this is a promising material to remove such toxic metal ions effectively. On the point of view of adsorbent synthesis, radiation-induced graftpolymerization is an excellent method to introduce the chelate function into variety shapes of conventional polymers such as fiber, membrane, particle, and hollow fiber. Especially, fibrous adsorbent prepared by this method realized 100 times higher space velocity than that of commercialized particle-adsorbent in the removal column of the toxic metals.[1] Such chelate adsorbent is synthesized by grafting the precursor monomer and the following chemical reaction. In the case of phosphoric acid adsorbent having high selectivity to hard Lewis acids cations,[2] the monomer having the functional group of epoxy[3] was grafted on the trunk polymer at first and then the resulting material was phosphorylated by chemical reagents. The direct synthesis of phosphoric acid adsorbent was attempted by chemical grafting. However, enough high grafting yield for adsorbent was not obtained.[4] The present paper dealt with the direct synthesis of phosphoric acid adsorbent by radiation-induced graft polymerization and the evaluation of the obtained adsorbent for the removal of toxic metals. In the direct synthesis of adsorbent, the production process is quite simplified and the density of functional group can be controlled only by condition of grafting reaction. These points will become big merit in the industrial production of the adsorbent.

2 Experimental

2.1 Materials

A phosphoric acid monomer (2-hydroxyethyl methacrylate phosphoric acid (HMPA); Kyoeisha Co. Osaka, Japan,) was used for grafting monomer which was composed of the mixture of mono (50%) and diester (50%) as shown in Fig. 1. Nonwoven fabric composed of polyethylene-coated polypropylene fiber (Fig. 2; Kurashiki Textile MFG Co. Ltd., Osaka, Japan) was used as a trunk polymer.

2.2 Radiation induced graftpolymerization

The nonwoven fabrics were cut into the rectangle of 3 cm x 5 cm and were irradiated with electron beam up to 200 kGy in nitrogen gas. Then, the methanol-water (10/90 wt%) solution of HMPA was contacted with these irradiated nonwoven fabrics in a deaerated glass reactor. The reaction temperature was maintained by dipping the glass reactors into a warm bath. After the grafting reaction, the degree of grafting (D_g) was calculated by the following equation:

$$D_g [\%] = (W_g - W_o) \times 100 / W_o$$

where W_o and W_g are the weights of nonwoven fabrics before and after graftpolymerization, respectively.

2.2 Metal adsorption

In the batch adsorption, the adsorbent of 150 % D_g was cut into the squares of 1 cm x 1 cm (approximately 0.01 g). The square adsorbent was soaked in the 50 ml of 10 ppm metal solution for 48 h. The metal solutions were obtained by dissolving $Pb(NO_3)_2$ and $CdCl_2$. After adsorption in the pH range from 1 to 6, the concentrations of remaining metals in the solutions were measured by an inductively coupled plasma mass spectroscopy (ICP-MS). In the column mode, 0.05g of adsorbent was packed into the column, 7 mm in inner diameter. The height of the adsorbent was 1.0 cm in the column. Then, 10 mM ($M = \text{mol dm}^{-3}$) of metal solution (pH 5) was pumped into the column with a peristaltic pump. The metal concentration in the outflow solution was monitored by ICP-MS, also.

3 Results and Discussion

3.1 Effect of solvent and reaction time

The effect of solvent compositions on D_g was investigated in the mixture of methanol and water. First, the grafting was carried out for 24 hours at 50°C in 20 % HMPA aqua solution. Many nodules of homopolymer were observed on the trunk polymer though the D_g reached 190%. Fig. 3 shows the effect of methanol component in water on D_g . The addition of 10 % methanol to water was effective on prohibition of nodule production and the D_g was still 186%. Further increase of methanol composition monotonously reduced the D_g . In the methanol composition of 50% and 90%, the

Fig. 1 Components of phosphoric acid monomer and their chemical structures

Fig. 2 SEM observation of trunk polymer (nonwoven fabric)

Fig. 3 Effect of solvent composition on degree of grafting; (○) 12 h grafting and (●) 24 h grafting

Fig. 4 Effect of reaction time on D_g ; (●) 20% monomer and (○) 10 % monomer.

Fig. 5 IR spectra of trunk polymer and grafted polymers; (a) trunk polymer (b) 56 % D_g and (c) 106 % D_g

degrees of grafting became 105% and 40%, respectively.

Figure 4 shows the effect of grafting time on D_g at reaction temperature of 60°C by using 10 and 20% of HMPA in the mixture of 10% methanol and 90% water. The D_g increased with increment of the reaction time. After 24 h reaction, the D_g reached 185 and 354 % for 10 and 20% of HMPA concentration. As a result, the increase of the monomer concentration from 10 to 20% gave 2 times higher D_g . The rise of reaction temperature is effective on the increase of D_g . The rise from 50 to 60°C doubled the D_g .

3.2 Characterization of adsorbent

The introduction of HMPA on the trunk polymer was evaluated by IR spectroscopy. Fig. 5 shows the spectra of KBr compressed disk containing the milled nonwoven fabric and the grafted one. In the spectrum of 56% D_g , the absorption peaks appeared at 1732, 1262, and 1151 cm^{-1} on the spectrum of the trunk polymer. The peaks of 1732, 1262, and 1151 cm^{-1} were attributed to C=O, P=O, and O-P-O bonds of HMPA, respectively. When the D_g was 106 %, the corresponding three peaks to HMPA increased proportionally.

The trunk polymer and grafted one were observed with scanning electron microscope to compare their fiber diameter. The average diameters of fiber in the trunk polymer, D_g of 100, 200, and 300 % were 13, 15, 16 and 17 μm , respectively. Fig. 6 shows the observation of the enlarged trunk polymer and 300 % D_g polymer. The both fiber surfaces were smooth and there were little considerable damages by grafting. These results imply the grafting HPMA up to around 300% D_g were possible without any physical damages on the nonwoven fabric. Fig.7 shows the cross-section areas which were calculated from their diameter were plotted against the D_g . There is a linear relationship between the cross-section area and D_g .

Fig. 6 SEM photographs of (a) trunk polymer and (b) grafted polymer of 300% D_g .

Fig. 7 Relationship between D_g and cross-section area

Fig. 8 Effect of pH on distribution coefficients; (○) Pb and (□) Cd

3.3 Batch adsorption

Effect of pH on metal adsorption was investigated at pH range from 1 to 6 by using 10 ppm of Pb and Cd solutions. The highest performance on the adsorption was obtained at pH 6 for these two metals. After contact with 10 ppm metal solution for 48 h, 99.6% of Pb and 99.0 % of Cd were caught on the phosphoric adsorbents. The distribution coefficient of each metal was calculated by dividing the concentration in the solution with that on the adsorbent as shown in Fig. 8. The obtained distribution coefficients for Pb and Cd were 1.2×10^6 and 4.9×10^5 at pH 6. The adsorbent had excellent ability without any significant loss of adsorption capacity after the adsorption-desorption was repeated 5 times.

3.4 Column adsorption

Column mode adsorption was carried out by using the 10 mM solutions of Pb and Cd with the space velocity of 250 h^{-1} . The characteristic of breakthrough was observed by plotting C/C_0 which was the value of outflow concentration divided by the injecting concentration against bed volume as shown in Fig. 9. When the breakthrough points were determined at C/C_0 of 0.1, the breakthrough capacities were 23 and 25 bed volume for Pb and Cd, respectively. These values correspond to 1.8 and 2.0 mmol/g-adsorbent. After breakthrough point, the value of C/C_0 went up 0.9 quickly. The total capacities of adsorption were 2.8 and 3.0 mmol/g-adsorbent for Pb and Cd, respectively.

Fig. 9 Column mode of adsorption; (○) Pb and (□) Cd

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