Radiation-induced grafting of dimethylaminoethylmethacrylate onto PE/PP nonwoven fabric

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Abstract

A new adsorbent was prepared by radiation-induced graft polymerization of dimethylaminoethylmethacrylate (DMAEMA) onto polyethylene/polypropylene (PE/PP) nonwoven fabric. The trunk polymer was irradiated by electron beam at a voltage of 2 MeV and a current of 3 mA in nitrogen atmosphere at dry-ice temperature to different doses. The degree of grafting was determined as a function of irradiation dose, monomer concentration, temperature and reaction time. Grafting conditions were optimized and about 150% grafted samples were used for further experiments. DMAEMA grafted polymer was later protonated in acid solution to prepare specialty adsorbent for the removal of phosphate. Adsorption experiments were performed in column mode for removal of phosphate. It was shown that 2000 bed volumes of phosphate-free water can be produced from 100 ppb phosphate (as P) solution at high space velocity.

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1. Introduction

Graft polymerization on polymeric matrixes followed by functionalization is widely used for the surface modification of adsorbent materials and prepared polymeric adsorbents (hollow fiber, nonwoven fabric, film) of the desired forms with varied concentration of ion-exchange groups usually enhance adsorption efficiency of the adsorbents [1–4]. Graft polymerization can be initiated by using γ rays, electron beams, ultraviolet (UV), plasma treatment and chemical initiators. Among these methods, ionizing radiation is one of the most promising methods, because of ease of creation of active sites for initiating grafting through the matrix of a polymeric substrate and moderate reaction conditions. Radiation-induced graft polymerization being both economical and environmentally clean technique [5] is a convenient method for the modification of physical and chemical properties of polymeric materials [6–8]. Radiation grafted adsorbents have been used usually for separation and wastewater treatment [9–13]. Several types of ion-exchange matrices have been prepared by grafting monomers like acrylic acid, methacrylic acids, acrylonitrile on trunk materials like polyethylene and polypropylene [14–16].

The main objective of this study is to develop special polymeric adsorbent to remove phosphate ions from aqueous systems. For this purpose, a novel adsorbent was prepared by radiation-induced graft polymerization of dimethylaminoethylmethacrylate (DMAEMA) onto PE/PP nonwoven fabric. The different parameters including irradiation dose, monomer concentration, reaction time and temperature that effect grafting reaction were studied.
2. Experimental

2.1. Materials

PE/PP nonwoven fabric was supplied by Kurashiki Sen-I Kako Co. Okayama, Japan. Dimethylaminoethylmethacrylate (DMAEMA) was purchased from Kanto Chemical, Tokyo, Japan and used without purification. Other reagents were of analytical or higher grade and used as received.

2.2. Preparation of DMAEMA grafted nonwoven fabric

A new adsorbent was prepared by radiation-induced graft polymerization of DMAEMA onto polyethylene/polypropylene (PE/PP) nonwoven fabric. The PE/PP nonwoven fabrics cut into pieces of 10 cm by 5 cm were sealed in polyethylene bags purged with nitrogen gas. The trunk polymer was irradiated by electron beam at a voltage of 2 MeV and a current of 3 mA at dry-ice temperature to different doses. The irradiated fabrics were immersed in different concentrations of DMAEMA solutions ranging from 5% (w/w) to 20% in water at different temperatures. After a pre-determined period, the DMAEMA grafted nonwoven fabrics were removed from the grafting solution, washed several times with distilled water and methanol to remove the homopolymer and residual monomer and dried under reduced pressure. The degree of grafting was determined gravimetrically as a function of the irradiation dose, monomer concentration, temperature and reaction time.

The degree of DMAEMA grafting ($D_g$) was determined as follows:

$$D_g (\%) = \left( \frac{W_1 - W_0}{W_0} \right) \times 100,$$

where $W_0$ and $W_1$ are the weights of the trunk and DMAEMA grafted nonwoven fabrics in dry state.

Grafting conditions were optimized and DMAEMA grafted polymer was later protonated by using acid solution to prepare an adsorbent for the removal of phosphate. DMAEMA grafted nonwoven fabric was placed into 1 M HCl solution for 24 h at room temperature. The protonated DMAEMA grafted nonwoven fabric was removed from the solution and washed with distilled water to remove unreacted acid and keep it wet for the adsorption tests.

2.3. Adsorption test

100 ppb phosphate (as P) solution was prepared by dissolving analytical grade sodium dihydrogen phosphate (NaH$_2$PO$_4$) in water. 100 ppb phosphate solution was passed through protonated DMAEMA grafted nonwoven fabric adsorbent-packed in 7 mm inner diameter column. The phosphate solution was fed into fabric adsorbent-packed column at two flow rates (space velocities, SV) 250 h$^{-1}$ and 1000 h$^{-1}$. Column effluents were collected by a fraction collector (Advantec SF2100). The concentration in each fraction was measured by an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, Perkin Elmer, Optima 5200).

3. Results and discussion

The preparation of DMAEMA grafted nonwoven fabric requires two steps as shown in Scheme 1. (1) Grafting of DMAEMA monomer by pre-irradiation grafting technique and (2) Protonation of amine groups by using acid solution.

PE/PP nonwoven fabric was previously irradiated to a total dose of 200 kGy by an electron accelerator in nitrogen atmosphere at dry-ice temperature (~20 °C). DMAEMA solution (5%) in water was used for grafting of DMAEMA onto pre-irradiated PE/PP nonwoven fabrics in nitrogen atmosphere at three different temperatures (40 °C, 50 °C and 60 °C). The degree of DMAEMA grafting ($D_g$) on nonwoven fabric at different reaction temperatures as a function of time is given in Fig. 1. As seen from this Figure, the degree of grafting increases with increasing reaction time and temperature. The degree of grafting reached to 150%, 120% and 85% at 60 °C, 50 °C and 40 °C within 4 h, respectively. The increasing grafting degrees related to increasing reaction temperature may be explained by the increase of interaction between free radicals and DMA-
EMA monomer. Grafting of DMAEMA was also carried out by decreasing irradiation dose to 100 kGy and increasing DMAEMA concentration to 10% at two different reaction temperatures and different reaction times. Fig. 2 shows that degree of grafting increases almost linearly with increasing reaction time and temperature. At 10% DMAEMA solution, 165% and 199% degree of grafting was observed for 40°C and 50°C reaction temperatures at 4 h reaction time, respectively.

Effect of initial monomer concentration on \( D_g \) was investigated at 100 kGy irradiation dose. Irradiated fibers (100 kGy) were reacted with three different DMAEMA concentrations (5%, 10% and 15%) and different reaction times at 40°C. As can be seen from Fig. 3, the degree of grafting increased proportionally with increasing monomer concentration and reaction time. Degree of grafting (60%, 165% and 258%) were observed for 5%, 10%, 15% initial monomer concentrations at 4 h reaction time, respectively. This effect is simply due to higher concentrations of monomer available to react with the active sites on irradiated PE/PP nonwoven fabric [17].

The effect of irradiation dose and initial monomer concentration on \( D_g \) were also investigated. For this purpose, PE/PP nonwoven fibers were irradiated at four different irradiation doses (30, 50, 100 and 200 kGy) and irradiated nonwoven fabrics were reacted with three different monomer concentrations (5%, 10% and 15%). The results shown in Fig. 4 indicate that the maximum grafting was achieved at 200 kGy irradiation dose and 15% monomer concentration at 4 h reaction time. These results show that the grafting yield of DMAEMA increases with the increasing irradiation dose due to the formation of more free radicals at higher irradiation doses. But this reaction medium was not chosen as the optimum grafting condition due to reduced flexibility of the nonwoven fabric at this dose. It was also observed that at higher degrees of grafting (>200%), the cloth became even brittle. Considering these unwanted properties, 50 kGy irradiation dose, 15% mono-
mer concentration and 4 h reaction time were selected as optimum conditions for the preparation of DMAEMA grafted nonwoven fabrics. Recently, DMAEMA grafting onto polypropylene films by using radiation-induced graft polymerization has been reported by Chen et al. [4]. It was found that 170% degree of grafting was obtained as an optimum DMAEMA grafting condition at 200 kGy irradiation dose, 20% DMAEMA concentration and 4 h reaction times in EtOH/H₂O.

All above results show that the optimum conditions to prepare DMAEMA grafted polymeric adsorbent have been achieved by using relatively low irradiation dose, low monomer concentration and water as the reaction medium. Adsorption experiments were performed in column mode for removal of phosphate ions. Fig. 5 shows the adsorption characteristics of phosphate ions on protonated DMAEMA grafted nonwoven fabric by plotting C/C₀ versus bed volumes. Here C and C₀ are effluent and feed solution concentrations of anion and bed volume is defined as the ratio of feed solution volume to the fixed polymer bed volume (mL feed solution/mL polymer). Flow rate is calculated as the bed volumes of feed solution hourly provided (h⁻¹ in space velocity) [18]. Approximately 2000 bed volumes (BV) of phosphate-free water can be produced from 100 ppb phosphate solution at low (250 SV) and high (1000 SV) space velocities. After 2000 BV, phosphate adsorption showed breakthrough gradually.

4. Conclusions

In order to introduce specific functional groups to the trunk PE/PP polymer, DMAEMA was grafted onto pre-irradiated fibers. Changing the experimental variables like irradiation dose, temperature of grafting and composition of initial monomer solution affects the grafting extent considerably. The optimum degree of grafting was found to be 150% at 50 kGy irradiation dose, 15% DMAEMA concentration and 4 h reaction time in water. Using water as a solvent is economical as well as environmentally advantageous for the grafting process. The DMAEMA grafted nonwoven fabric can be used for the removal of phosphate ion very efficiently at low and high space velocities. It was concluded that DMAEMA grafted nonwoven fabric can be considered as a promising adsorbent for phosphate removal from aqueous media.

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References


Fig. 5. Breakthrough curves for phosphate removal at indicated SV from 100 ppb phosphate solution.