

Radiation Synthesis of Adsorbents for Phosphate Removal from Aqueous Systems

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Abstract

Nonwoven fabrics made of PE coated PP fibres were irradiated by accelerated electrons in inert atmospheres for grafting of two different monomers, glycidyl methacrylate and dimethylaminoethyl methacrylate. Grafting conditions were optimized by a systematic investigation of the effects of absorbed dose, monomer concentration, reaction temperature and duration. 150% grafted copolymers were later modified by protonation and quaternization of poly(dimethylaminoethyl methacrylate) chains and by Cu(II) loading of dipyrindyl amine modified poly(glycidyl methacrylate) graft chains. The PE/PP based adsorbents thus prepared were used for their suitability of removing phosphate ions from aqueous systems. Adsorption/removal studies were carried out in both batch and continuous flow type systems. The selectivity of adsorption of phosphate ions in the presence of other competing anions were also checked showing the enhanced selectivity for phosphate ions.

Introduction

The rapid increase in the world population together with the increased development in industry and utilization of a variety of chemicals in agriculture have led to generation of large quantities of polluted industrial and municipal waste waters both in developed and developing countries.

Water resources have been and continue to be contaminated with biologically and environmentally resistant pollutants from industrial, municipal and agricultural discharges. Pollution coming from these resources include untreated sewage, chemical discharges, petroleum leaks and spills and agricultural chemicals that are washed off from farm fields.

The short and long term consequences of these polluted waters causing a serious threat to mankind has led the scientists and technologists to look for developing new technologies for treatment of wastewaters. A variety of methods based on biological, chemical, photochemical and electrochemical processes are being explored for treating the chemical and biological contaminants present in wastewaters.

The number and kind of chemical and biological species causing pollution in especially drinking water sources are enormous mainly consisting of ionic and molecular products. Among the ionic pollutants phosphorous containing anionic species require special attention.

Phosphates are not toxic to people or animals unless they are present in very high levels. Digestive problems could occur from extremely high levels of phosphate. It is very well known that phosphorus can provide an additional nutrient for growth of photosynthetic macro- and microorganisms in aquatic bodies, but also leading to the eutrophication problem especially in enclosed water bodies. The removal of phosphate from waters can be an effective method for the control of eutrophication in natural waters. Phosphorus concentrations in excess of 0.03-0.05 mg/L have been associated with algae blooms, which lead to the eutrophication of lakes and rivers [1-3]. In order to decrease eutrophication in lakes and other water sources, concentration of phosphorus must be limited to 0.01 mg/L or less [4]. Extensive studies on the effective treatment of phosphates in water systems have been previously conducted [5-8]. The major methods for the removal of phosphate include precipitation and coagulation, as well as adsorption or ion exchange process. The precipitation and co-

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agulation processes with iron (III) [9], aluminum [10], calcium [11], and lanthanum salts [12], which convert anions into insoluble form, have been widely used. Although the precipitation and coagulation method is simple and economical, this process will result in a wet bulky sludge disposal problem and requires final filtration for secondary treatment. Moreover, the ion-exchange process using ion exchangers has also been identified as a treatment method for phosphate removal [8]. The process development for the removal and recovery of phosphorus from wastewater using enhanced activated alumina has been published in a series by Urano and Tachikawa [13]. They reported that the enhanced activated alumina can adsorb various inorganic phosphorus species in a pH range from 4-7. Recently, a new class ion-exchange sorbent after treatment of commercial DOW 3N polymer with copper solution which is designated as DOW 3N-Cu or PLE (polymeric ligand exchanger) used for the selective removal of phosphates from contaminated water [7]. A PLE consists of a polymer with chelating functional groups that can bind tightly to a transition metal, which can remove anions from water by complex formation. PLE used in the above mentioned work is basically a copper-loaded chelating ion exchanger with styrene-divinylbenzene polymer matrix designed to effectively remove divalent phosphate ion (HPO_4^{2-}) at above neutral pH. The results were appeared technically feasible. However, in actual municipal and industrial wastewater, where the pH widely varies, the existence of other forms of phosphate ions such or other species is inevitable due to nature of phosphate originating from a polyprotic acid. In such H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} a case, PLE sorbent becomes technically ineffective unless those phosphate species are first converted into divalent form and then the pH of the solution is adjusted to above the neutral range for adsorption. Therefore, it is very important to use an adsorbent that can adsorb various species of phosphates and that can work effectively in a wide range of pH.

Graft polymerization on polymeric matrixes followed by functionalization is widely used for the surface modification of adsorbent materials. The polymeric adsorbents prepared in different forms (hollow fiber, nonwoven fabric, film) with varied concentration of ion-exchange groups usually enhance adsorption efficiency of the adsorbents [14-17]. 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 [18] is a convenient method for the modification of physical and chemical properties of polymeric materials [19-21]. Radiation grafted adsorbents have been used usually for separation and wastewater treatment processes [22-26]. 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 [27-29].

Experimental

Radiation-induced Grafting of Functional Monomers onto PE/PP Non-woven Fabric

Grafting of Glycidyl Methacrylate (GMA)

The preparation of nonwoven fabric adsorbents based on GMA grafting and further functionalization requires two steps: (1) grafting of an epoxide group containing monomer, glycidyl methacrylate (GMA) by preirradiation grafting technique and (2) modification of epoxy group with a proper ligand.

First GMA was grafted onto PE coated PP nonwoven fibers by preirradiation technique as described above. The concentration of GMA solution was set at 10 (w/w) % in methanol as the solvent. The degree of grafting was calculated as described above. GMA grafted fabrics with 150% graft ratio was used for the further characterizations and modifications as this graft ratio was found to be the optimum in one of our previous publications [30].

Functionalization of GMA Grafted Fabrics

Following the grafting of GMA, epoxide groups in grafted nonwoven fabric were reacted with different chemicals such as triazol, bipyridyl, dipyrindylamine (DPA). In this second step, effect of solvent choice, ligand concentration and the reaction time were investigated to achieve an optimized reaction condition. Modifications were performed in four solvents; methanol, ethanol, DMSO and Dioxane. In a typical modification reaction, approximately 0.5 g of GMA grafted nonwoven fabric was immersed in 25 ml of DPA containing solutions. Three different

DPA concentrations were examined: 5%, 10% and 15% w/v. The reaction was performed at 80°C for different time periods to construct the conversion curve. After binding of DPA onto the epoxide group of GMA grafted polymer, the remaining unreacted epoxy groups were hydrolyzed with acid solution for 2 hrs at 80°C. Subsequently nonwoven fabric was washed with methanol and then was dried at room temperature and in a vacuum oven at 40°C. The percent replacement of the epoxide groups with DPA was calculated as follows:

$$\text{Conversion (\%)} = (\text{mmol DPA})/(\text{mmol GMA}) \quad (1)$$

Preparation of Cu-loaded Polymeric Ligand Exchangers

Preparation of polymeric ligand exchanger (PLE) was conducted by loading Cu(II) onto DPA modified PP/PE fabric. For this purpose approximately 0.5 g of DPA immobilized fabric was placed into 200 mL of 1500 ppm Cu(II) ion solution at pH ~ 4 in a bottle stirred magnetically at moderate rpm for a given time period. The time needed was predetermined in a separate adsorption kinetics study. In order to determine the amount of Cu(II) ions loaded onto the fabric, Cu(II) ion concentration remaining in the solutions was determined by using an UV-vis. spectroscopic technique [31]. The amount of Cu(II) ion adsorbed per unit mass of PP/PE fabric was evaluated using the following expression,

$$q_e = \frac{(C_e - C_0) \times V}{W} \quad (2)$$

where, q_e is the amount of Cu(II) ions adsorbed onto unit dry mass of PP/PE fabric (mg/g); C_0 and C_e are the concentrations of Cu(II) ion solutions (mg/L) prior and after the treatment for a certain period of time, respectively; V is the volume of aqueous phase (L) and W is the amount of dry fabric used (g).

Grafting of Dimethylaminoethyl Methacrylate (DMAEMA)

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 an electron beam (2 MeV, 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 (Dg) was determined by using the following expression:

$$Dg = [(W_1 - W_0)/W_0] \times 100\% \quad (3)$$

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

Protonation of the DMAEMA Grafted Fabrics

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

Continuous Flow Adsorption Tests

100 ppb phosphate (as P) solution was prepared by dissolving analytical grade sodium dihydrogen phosphate (NaH_2PO_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).

Batch Adsorption Experiments

Batch adsorption experiments with quaternized DMAEMA grafted fabrics for phosphate removal were conducted by using low phosphate concentrations (0.5-25 ppm) and high phosphate concentrations (50-1000 ppm). The effect of pH on phosphate

adsorption was studied at different pH values with the same initial phosphate concentration (100 mg phosphate/L). Competitive adsorption experiments were also carried out with two concentration levels (low concentration: 1 ppm phosphate, 1 ppm bromide, 1 ppm nitrite, 10 ppm sulphate and 10 ppm nitrate mixture and high concentration: 50 ppm phosphate, 50 ppm bromide, 50 ppm nitrite, 500 ppm sulphate and 500 ppm nitrate mixture). The pH of the solution was adjusted by either HCl or NaOH solution. The phosphate ion concentrations in the equilibrated solutions were measured with the UV-Visible Spectrophotometer (Carry 100, Varian) according to ISO standard [31]. Phosphate, bromide, nitrite, sulphate and nitrate analyses were carried out by using a Dionex ion chromatograph (DIONEX ICS 3000, USA).

Results and Discussion

Grafting of GMA and Functionalization of GMA Grafted Fabrics

DPA was immobilized onto GMA grafted nonwoven fabric with 150% graft ratio by a reaction between the epoxy rings of GMA grafts and the amine group of DPA (the details of the preparation of GMA grafted fabric can be found in our previous publication) [16]. The percent replacement of the epoxide groups by DPA was calculated by *eq. (1)* and the modifications were tested in four different solvents; methanol, ethanol, dioxane and DMSO. Modifications in methanol and ethanol resulted in similar DPA replacement ratios which were lower than those obtained in other two solvents. The conversion (*i.e.* replacement) ratio obtained in DMSO was slightly lower than that observed in dioxane (both were around 70% at 80 hrs). As the boiling point of dioxane is lower than DMSO, we preferred this solvent as it offers an easier removal after the modification. The effect of DPA concentration on the conversions was also investigated in three solvents having different amounts of DPA (*i.e.*, 5%, 10% and 15% DPA (w/v)) in dioxane (Fig. 1). Figure 1 shows that the conversion of epoxides has not been fully completed (most probably due to inactivation of some epoxy rings during the grafting process and difficulty in access to sterically hindered ones) and a maximum of ~70% conversion has been achieved for all concentrations examined at the end of 80 hrs reaction time. Figure 1 indicates that the effect of DPA amount is more distinct at lower reaction times, *e.g.* the con-

version is around 8%, 44% and 49% for the solutions having 5%, 10% and 15% DPA, respectively at 40 hrs. This shows that the replacement of epoxy groups by DPA is quicker at high concentrations. However, the difference becomes indistinct in longer time, and the maximum conversion reaches to ~70% at 80 hrs for all the concentrations studied. Functionalization of GMA grafted nonwoven fabrics was therefore achieved in 5% DPA (w/v) containing solutions for monomer saving and these adsorbents (the exact conversion value is 76%) were used in all experimental characterizations and further metal ion uptake studies. The detail preparation condition and results were given in our previous paper [34].

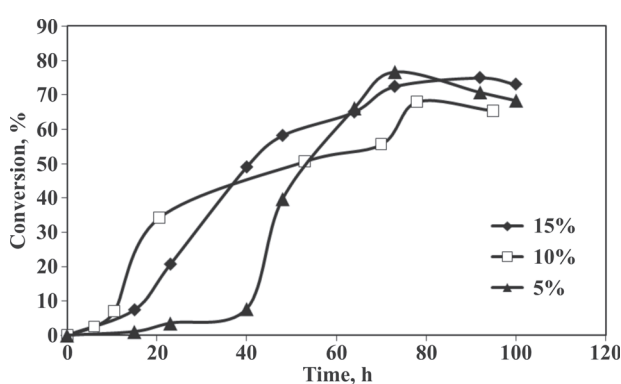
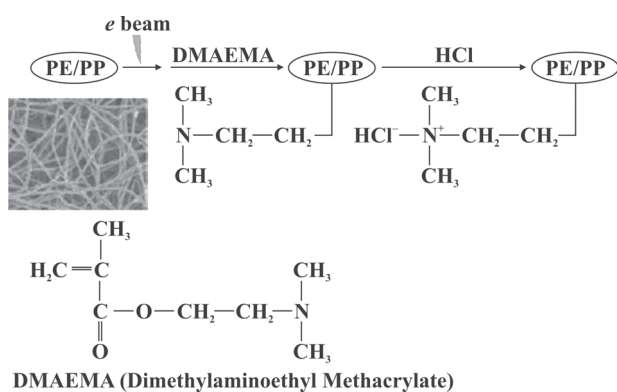


Fig. 1. Effect of DPA concentration (w/v) on the conversion of epoxide groups of GMA: GMA grafted nonwoven fabric with 150% graft ratio, dioxane used as the solvent, reaction temperature: 80°C.

Preparation of the Protonated and Quaternized DMAEMA Grafted Nonwoven Fabric

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.

The effect of irradiation dose and initial monomer concentration on degree of grafting (*Dg*) of DMAEMA were investigated. For this purpose, PE/PP nonwoven fabric was irradiated at four different irradiation doses (30, 50, 100 and 200 kGy) by an electron accelerator in nitrogen atmosphere at dry ice temperature (-20°C). Irradiated nonwoven fabrics were then reacted with three different monomer concentrations (5%, 10% and 15%). The results shown in Figure 2 indicate that the maximum grafting was achieved at 200 kGy irradiation dose and 15% monomer concentration at 4 hours reaction time. These



Scheme 1. Schematic preparation of DMAEMA grafted nonwoven fabric adsorbent

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% monomer concentration and 4 hrs reaction time were selected as optimum conditions for the preparation of DMAEMA grafted nonwoven fabrics. The detail preparation conditions of DMAEMA grafted fibers were given in our previous paper [30]. Recently, DMAEMA grafting onto polypropylene films by using radiation induced graft polymerization has been reported by Chen *et al.* [17]. 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 hrs reaction times in EtOH/H₂O.

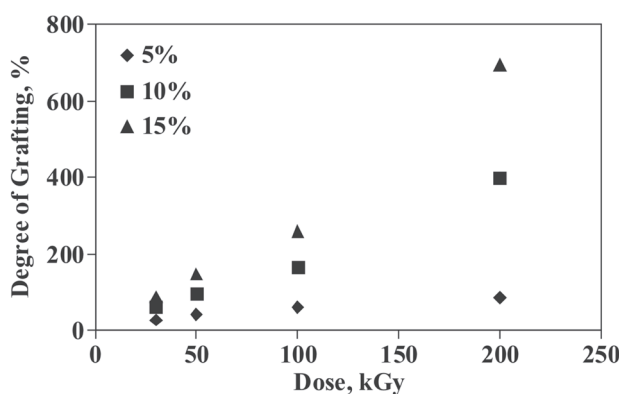


Fig. 2. Change in degree of grafting with different pre-irradiation doses for fabrics at indicated DMAEMA concentrations

After grafting of DMAEA, the tertiary amine group of DMAEMA graft chain was then protonated by using acid solution and chemically treated with dimethyl sulphate to obtain quaternized DMAEMA grafted nonwoven fiber having ion exchange properties. Approximately 90% quaternization was obtained in 24 hours.

Adsorption of Phosphate

Adsorption of Phosphate by Using DPA Modified GMA Grafted Nonwoven Fabric

The performance of polymeric ligand exchanger (PLE) was investigated with respect to adsorption kinetics, adsorption and desorption behavior and pH effects toward the target phosphate anion. The pH of the aqueous solution is an important variable influencing the adsorption process especially in ion exchangers. Phosphate species present in water include H₃PO₄, H₂PO₄⁻, HPO₄²⁻ and PO₄³⁻, and their relative amounts depend on the pH of the medium. pH experiment was performed for five different pH values ranging from 5 to 9 and it was observed that phosphate adsorption did not change virtually within the studied pH range. This shows that adsorbent material can effectively remove different forms of phosphate ions, namely H₃PO₄, H₂PO₄⁻, HPO₄²⁻ and PO₄³⁻ from aqueous solution at each pH value where these species exist.

The effect of initial concentration of phosphate on the adsorption behavior of PLE was determined in 8 hrs contact time for five solutions (50 ml) with different phosphate concentrations (10, 50, 100, 250, and 500 ppm) at pH 7 and the adsorption amounts were given in Fig. 3. Figure 3 shows that, the new PLE exhibited a very high affinity for phosphate at low concentration levels reaching a value of 16 mg of phosphate/g dry PLE from 10 ppm phosphate solution. It was found that adsorption of phosphate by Cu-loaded fabrics increased with increasing phosphate concentration and 101 mg/g dry PLE phosphate adsorption was obtained from 500 ppm phosphate solution.

Anion selectivity studies were also achieved using ion chromatography and the quantitative determination of anions was presented in Fig. 4. For the solution with low concentrations, phosphate adsorption is the significantly highest one among the others with a removal of around 82%. The adsorption order for this solution is phosphate >> nitrate ≈ bro-

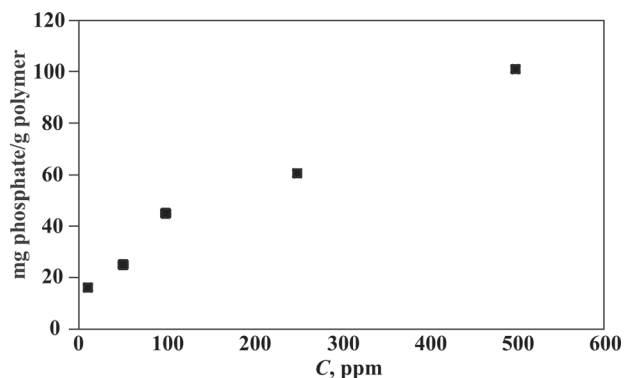


Fig. 3. Effect of initial concentration of phosphate on the adsorption behavior of the PLE

mid > nitrite \approx sulphate. However for the solution with high concentration the selectivity among the anions disappears; all the anions present a removal ratio ranging between 38% and 26%. This shows that although the adsorbent is selective to phosphate at lower concentrations, it also adsorb competing ions along with phosphate ion at high concentrations. Therefore we believe that the prepared PLE is suitable for the specific removal of trace amounts of phosphate from aqueous solution.

The PLEs should be suitable for efficient regeneration so that they can be used for multiple cycles of operations. Sodium chloride is an ideal regenerant as it is easily available, inexpensive and nontoxic. Therefore, 6% of NaCl solution was used for regeneration of phosphate adsorbed by the PLEs. Ion chromatography was used for the determination of regeneration amount. PLEs easily desorbed the loaded phosphate under given conditions and were reusable. High regeneration efficiencies were achieved with a phosphate recovery of nearly 100%.

Adsorption of Phosphate by Using Protonated DMAEMA Grafted Nonwoven Fabric

Adsorption experiments were performed in column mode for removal of phosphate ions by using protonated DMAEMA grafted nonwoven fabric. Figure 5 shows the adsorption characteristics of phosphate ions on protonated DMAEMA grafted nonwoven fabric by plotting C/C_0 vs. bed volumes. Here C and C_0 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) [35]. Approxi-

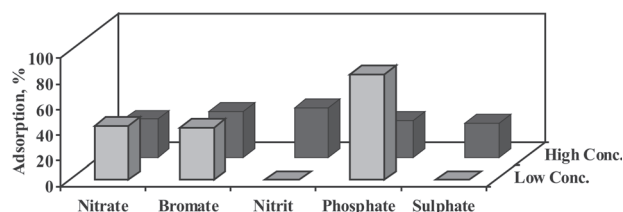


Fig. 4. Adsorption selectivity of the PLE; Low concentration: 1 ppm phosphate, 1 ppm bromide, 1 ppm nitrite, 10 ppm sulphate and 10 ppm nitrate. High concentration: 50 ppm phosphate, 50 ppm bromide, 50 ppm nitrite, 500 ppm sulphate and 500 ppm nitrate.

mately 2000 bed volumes (BV) of phosphate-free water can be produced from 10 ppb phosphate solution at low (250 SV) and high (1000 SV) space velocities. After 2000 BV, phosphate adsorption showed breakthrough gradually.

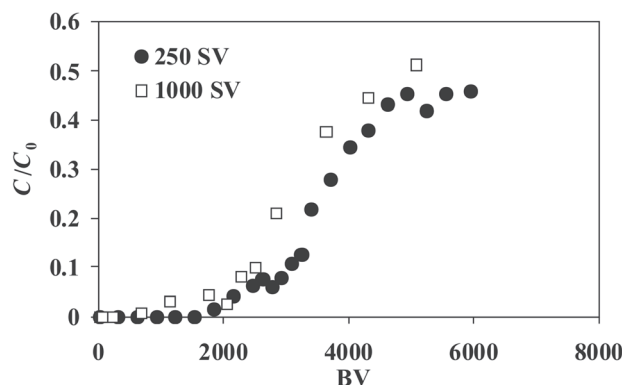


Fig. 5. Breakthrough curves for phosphate removal at indicated space velocities (SV)

Adsorption of Phosphate by Using Quaternized DMAEMA Grafted Nonwoven Fabric

Figure 6 and Figure 7 show adsorption of phosphate ions at low phosphate concentrations (0.5-25 ppm) and high phosphate concentrations (50-1000 ppm) at pH 7.00 on quaternized DMAEMA grafted fabrics, respectively. Both results showed that the adsorption of phosphate ions increases linearly with increasing the initial feed concentration both at low and high phosphate concentrations due to density of ion exchange sites on the adsorbent. Adsorbed phosphate amounts were found to be 63 mg phosphate/g polymer and 512 mg phosphate/g polymer for low phosphate concentration (25 ppm) and high phosphate concentration (1000 ppm), respectively. This result shows that the adsorbent material quite effective in removing phosphate in wide concentration

range. Detail adsorption results are given in our previous paper [36].

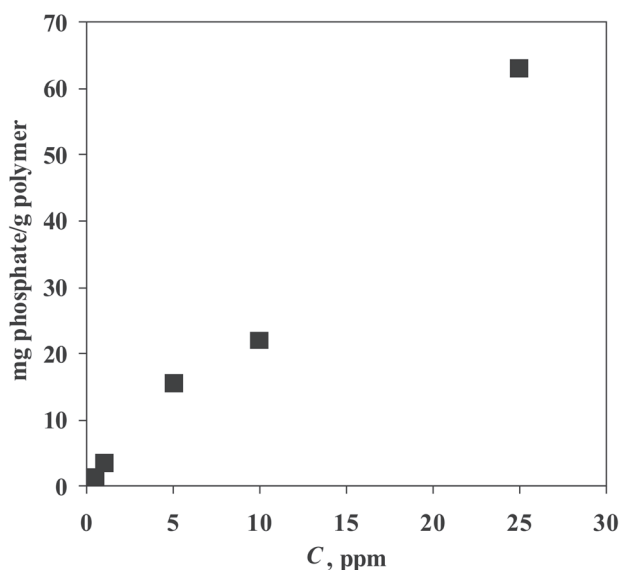


Fig. 6. Phosphate uptake onto quaternized DMAEMA grafted nonwoven fabric at low phosphate concentrations at pH 7.

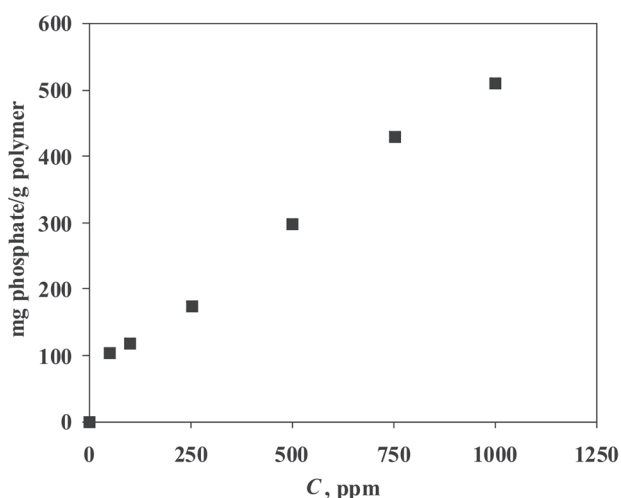


Fig. 7. Phosphate uptake onto quaternized DMAEMA grafted nonwoven fabric at high phosphate concentrations at pH 7.

Effect of Competing Anions on Phosphate Adsorption

Figure 8 shows the effect of competing ions at two concentration levels at pH 7. Phosphate adsorption on quaternized DMAEMA grafted nonwoven fabric was higher than the other competing ions at two concentration levels. At high concentration level, the adsorption order was phosphate > nitrite > bro-

midate > sulphate > nitrate and at low concentration level, the adsorption order was phosphate \equiv sulphate > bromide > nitrite > nitrate, respectively. These results indicate that adsorbent can also adsorb competing ions beside phosphate ion which is a normal (expected result) effect due to relative affinities of anions toward adsorbent. 6% of NaCl solution was used for regeneration of phosphate adsorbed quaternized DMAEMA grafted nonwoven fabric. High regeneration efficiencies were achieved with a phosphate recovery of nearly 100%.

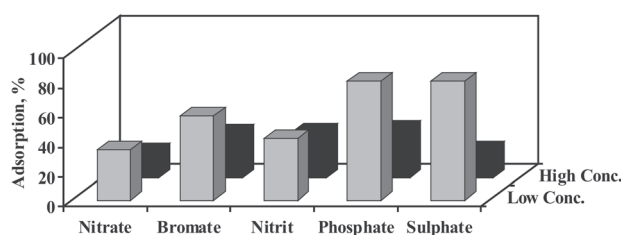


Fig. 8. Adsorption selectivity of quaternized DMAEMA grafted nonwoven fabric for indicated anions: 50 ppm and 1 ppm of phosphate, bromide, nitrite and 500 ppm and 10 ppm of sulphate and nitrate.

It was concluded that the protonated and quaternized DMAEMA grafted nonwoven fabric have higher adsorption capacity for phosphate ions than the DPA modified GMA grafted nonwoven fabric. The explanation can be given as follows; DMAEMA grafted nonwoven fabric was obtained as a homopolymer directly from dimethylaminoethylmethacrylate monomer but the DPA modified GMA grafted nonwoven fabric was firstly grafted with GMA (glycidyl methacrylate) and then modified with 2,2'-dipyridylamine (DPA) with a maximum of ~70% conversion.

Conclusions

Radiation-induced graft polymerization is an easy and highly efficient surface modification procedure for functionalization of base polymeric materials. Environmentally stable PE/PP nonwoven fibers were used as base material for the synthesis of a new adsorbent for anions. To introduce specific functional groups to the trunk polymer, GMA and DMAEMA were grafted onto preirradiated fabrics. Following the grafting of GMA and DMAEMA, epoxide groups in GMA grafted nonwoven fabric were reacted with DPA and the tertiary amine group of DMAEMA graft chains were protonated by using acid solution and quaternized by using dimethyl sulphate for removal

of phosphate ions in aqueous solutions. The protonated and quaternized DMAEMA grafted nonwoven fabrics were found to have higher adsorption capacity for phosphate ions than the DPA modified GMA grafted nonwoven fabric.

Acknowledgements

The authors are grateful to Dr. Cengiz Kavakli, Dr. Noriaki Seko, Dr. Masao Tamada and Murat Barsbay for their help. One of the authors (O.G.) appreciates the support of Academy of Sciences of Turkey.

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Received 12 October 2008.