

Adsorption of Phosphate and Nitrate Ions on Surface Modified Polypropylene Nonwoven

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The fabrication of adsorbent textile fiber materials is of great scientific and industrial interests. In this work a new procedure for fabrication of an anionic compounds adsorbent based on polypropylene nonwoven has been described. Because of using atmospheric pressure plasma as a surface specific pretreatment, the described procedure can be considered as a convenient method without affecting the bulk properties of the fibers. Atmospheric pressure air plasma was used to produce peroxide groups on the surface of polypropylene fibers. Grafting of acrylic acid (AA) was followed to create carboxyl groups on the fibers surfaces and finally the grafted polypropylene fiber samples were aminated using diethylene triamine (DETA) to convert carboxyl groups to amine groups. The effects of various experimental conditions: such as the time for plasma treatment, monomer concentration, temperature and reaction time were investigated. The surface morphology of the fibers was evaluated by SEM. To determine the nitrate and phosphate adsorption on the modified fibers, UV-VIS spectrophotometer was used. Fiber samples modified under optimized conditions showed a high ability to adsorb nitrate and phosphate ions from aqueous media.

Keywords: polypropylene, Ion adsorption, Plasma treatment, nitrate, phosphate, acrylic acid

Nowadays pollution of water resources due to the excessive presence of nutrients, i.e., nitrogen and phosphorus species is a very important concern over the world. Nitrate and phosphate contaminations that have been caused by industrial uses (detergent manufacturing, mineral processing), agriculture activities (natural and synthetic fertilizers) and municipal wastewaters is a critical biological environment problem [1-4].

Drinking water containing excess nitrate may cause various health problems. Higher concentration of nitrate causes severe methemoglobinemia especially in the age group less than 1 year which is also called as "infant cyanosis" [3-6]. Nitrate converted to nitrite in the stomach leads to the formation of nitroso compound which is carcinogenic. Higher concentrations of nitrate not only affect the human being but also affect the marine life [7].

Graft polymerization on polymeric matrixes followed by functionalization is widely used for the surface modification of adsorbent materials and preparing polymeric adsorbents (hollow fiber, nonwoven fabric, film) of the desired forms with varied concentration of ion-exchange groups usually enhancing adsorption efficiency of the adsorbents [8, 9]. Graft polymerization can be initiated by using gamma rays, electron beams, ultraviolet (UV), plasma treatment and chemical initiators [10]. Among these methods plasma-induced graft polymerization is expected to be the most convenient method because the grafting location can be restricted to the surface of the polymer matrix without affecting any bulk properties.

In this work, a multi steps modification procedure for fabrication of anion-adsorbent polypropylene nonwoven fibers has been described. The presented modification procedure due to applying plasma treatment technique is expected to be one of the most convenient methods because the grafting can be restricted to the surface of the

polymer matrix without affecting any bulk properties. To produce PP adsorbent, first polypropylene nonwoven fiber samples were exposed to atmospheric pressure plasma treatment and then grafted by acrylic acid (AA) to create carboxyl groups and finally the grafted PP fiber samples were aminated by diethylene triamine (DETA) to convert carboxyl groups to new functional groups mainly amine (Am) groups.

Experimental part

Materials and methods

PP nonwoven with thickness of 109 μ m and density of 20 g/m² was used. Acetone, Acrylic Acid, Diethylene Triamine (DETA) Aluminum Chloride, Potassium Nitrate and dihydrogen potassium phosphate were analytical grade reagents obtained from Merck.

Before plasma treatment, to remove the spin finish, all samples (1 \times 10 cm²) were washed in acetone for 30 min at ambient temperature, rinsed with distilled water and finally dried at 50 °C.

Atmospheric pressure plasma was produced in a laboratory scale reactor designed in Textile Engineering Department, Amirkabir University of Technology-IRAN. Plasma treatments were done under frequency of 40 kHz and voltage of 10 kV and power of 300 W at different times. There was 2 mm space between electrodes and atmospheric air was used as plasma gas. Samples were grafted after plasma treatment, with different concentrations of acrylic acid in water. Prior to enter the plasma treated samples in the grafting solution, the solution was deaerated with nitrogen bubbling through it. The grafting process was carried out at different temperatures and times. After grafting, the residual monomers and homopolymers were removed from the surface of the fibers by washing in methanol and distilled water for 30 min respectively.

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The grafted PP nonwoven samples were dried in air and kept in dessicator for 24 h and then weighted. The grafting yield was calculated using the following equation:

$$\text{Degree of grafting (\%)} = 100(W_1 - W_0)/W_0 \quad (1)$$

where,

W_0 and W_1 are the dry weight of each sample before and after grafting respectively.

To convert the hydroxyl groups of acrylic acid to amine groups, AA grafted PP nonwoven fibers were immersed in DETA solution containing 4% (w/v) of AlCl_3 at 90 °C. The effect of reaction time (1,2,3,4,5 and 6 hr) on the efficiency of amination was investigation. After the amination reaction, modified PP nonwoven was immersed in 1N HCl solution and stirred at room temperature for one minute and then repeatedly washed with distilled water and dried.

The degree of amination was calculated as follows:

$$\text{Degree of amination (\%)} = 100(W_2 - W_1)/103.17/(W_1 - W_0)/72.06 \quad (2)$$

where:

W_2 is the weight after amination reaction, and the factors 103.17 and 72.06 corresponds to the molecular weight of DETA and AA respectively.

The surface morphology of samples was studied using a scanning electron microscope model AIS2100.

Adsorption studies

PP nonwoven samples with different degrees of amination were used for anion adsorption studies. Each sample was put in 100 mL of nitrate and phosphate solution (200 mg/L) and stirred for 2h at room temperature (200 rpm). The concentration of nitrate ion was determined using a Lovibond UV-Vis spectrophotometer. The amount of ions adsorption was calculated using the following equation:

$$Q_e \text{ (mg/g)} = V(C_0 - C_e)/W \quad (3)$$

where:

Q_e is the amount of adsorbed nitrate ion, C_0 and C_e are initial and equilibrium concentrations of nitrate and phosphate ion respectively and W is the dry mass of the adsorbent.

Results and discussions

Atmospheric air plasma treatment leads to the formation of hydro peroxides and peroxides on the surface of PP nonwoven. These species are stable at room temperature for a long time; however they are decomposed upon heating higher than 60–70 °C to generate hydroxyl and the peroxide radicals. The peroxide radicals offer a site for grafting, while the hydroxyl radical initiates the polymerization of a monomer [11].

Figure 1, shows the effect of plasma treatment time on the grafting yield. The degree of grafting increased with increasing the plasma treatment. The optimum time of plasma treatment was 180 s after which the grafting yield decreased.

The graft polymerization was carried out in aqueous solutions of acrylic acid (AA). The nitrogen was purged into the reactant mixtures in the glass flask for 10 min to remove air trapped inside the reaction mixture. Figure 2 shows changes of degree of grafting with increasing the acrylic acid concentration at 60 °C for 2 h. The degree of grafting increased with increase in the monomer concentration up to 40 % and subsequently tended to decrease. This result is due to the sudden increases in the homopolymerization [12, 13].

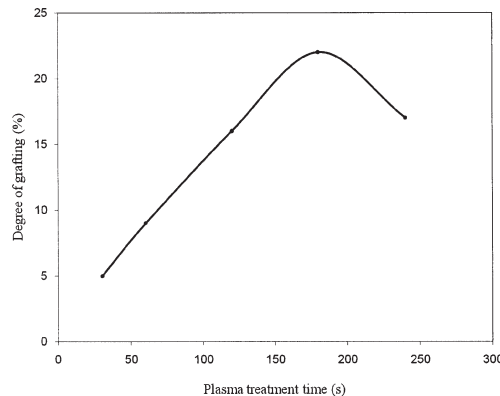


Fig.1. Effect of plasma treatment time on grafting yield of AA

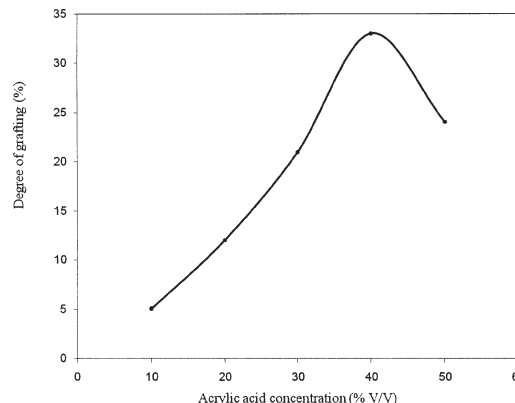


Fig. 2. Effect of AA concentration on grafting yield

Figure 3 shows the effect of reaction time on the degree of amination. As shown in figure 3 the degree of amination increased with increase in the reaction time.

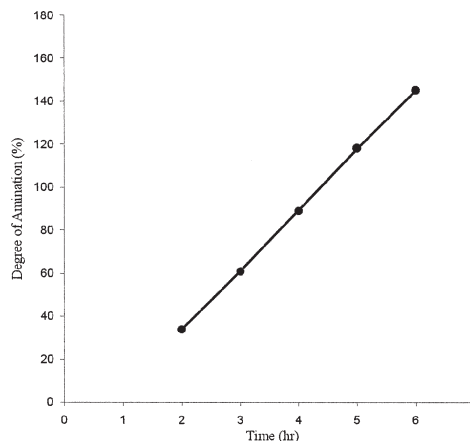


Fig. 3. Effect of amination time on the degree of amination

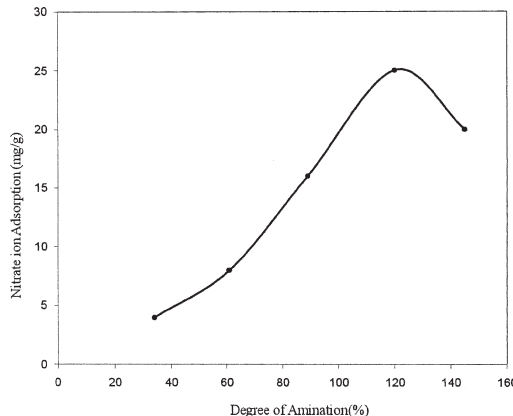


Fig. 4. Effect of degree of amination on the nitrate adsorption of the aminated sample

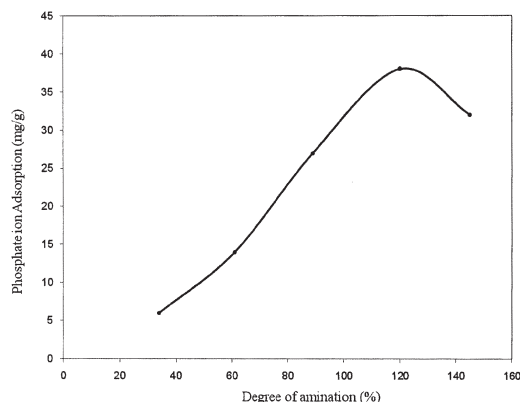


Fig. 5. Effect of degree of amination on the phosphate adsorption of the aminated sample

To evaluate the adsorption capacity of modified PP fiber depending on the degree of amination, adsorption tests were conducted on modified PP fiber with degree of amination in range of 30-150 %. The initial concentration of nitrate and phosphate was 200 mg/L. Figures 4 and 5 show the nitrate and phosphate adsorption capacity of the modified PP fiber depending on the degree of amination. As shown in both figures adsorption capacities increased as the degree of amination increased up to 120 % and then decreased with further increase in the degree of amination. The decreasing trend in high degree of amination may be because with the increase in degree of amination, the fiber became thicker and thereby reduced the effective surface with adsorption functionality on the modified fiber and probably required the longer contact time to reach adsorption equilibrium.

The morphology of the fiber was studied by SEM (fig. 6). The presence of grafted polyacrylic acid on the surface of the grafted and aminated fibers is evident. The raw PP fiber has a smooth surface which has been changed to a rough surface after grafting of AA on it.

Conclusions

In this study, an anion absorbent nonwoven was prepared. Acrylic acid was grafted to PP nonwoven after plasma treatment for 180 s. The degree of grafting depended on the monomer concentration and the time of plasma treatment. The carboxylic acid groups were converted to amide groups by reaction with DETA. The nitrate and phosphate adsorption capacity of the prepared nonwoven increased with increasing the degree of

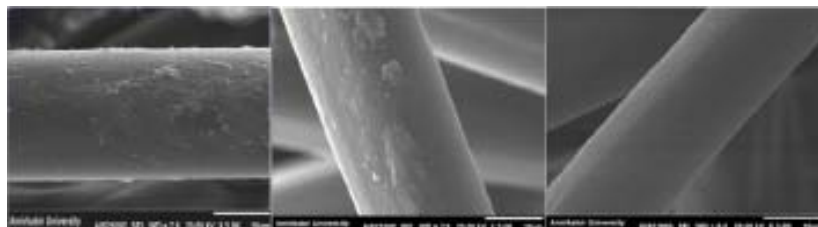


Fig. 6. SEM image of raw, AA grafted and aminated PP fibers (right to left)

amination and was at maximum at 120% amination. The modified fiber samples obtained under optimized conditions, showed the ability to adsorb up to 25 mg nitrate and 37 mg phosphate anions per gram of adsorbent from the aqueous solutions.

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