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Adsorption and desorption of phosphate and nitrate ions using quaternary (polypropylene-g-N,N-dimethylamino ethylmethacrylate) graft copolymer

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ABSTRACT

Study has been made on the preparation of functionalized copolymer by grafting *N*,*N*-(dimethylaminoethyl) methacrylate (DMAEMA) onto polypropylene (PP) films using γ -irradiation technique. The effect of monomer concentration and irradiation dose on the grafting yield was studied. It was found that grafting yield increases with increasing the monomer concentration and irradiation dose. Subsequent quaternization of the amine group of PDMAEMA graft chain using different reagents, 1-bromo octadecane, methyl iodide and benzyl chloride, to improve their ionic character was carried out. The grafted PP films were characterized by IR spectroscopy, and mechanical and thermal properties. During the adsorption of phosphate (PO₄³⁻) and nitrate (NO₃⁻) ions, the rate of adsorption, pH effect, desorbability and initial feed concentration effect were investigated. It was found that the adsorption of PO₄³⁻ and NO₃⁻ ions increases with increasing from 18 to 30%, and it is relatively difficult to desorb PO₄³⁻ and NO₃⁻ ions from the functionalized grafted copolymers. Results showed good possibility for the use of such functionalized grafted film in the field of removal of some anions such as PO₄³⁻ and NO₃⁻ from their media.

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1. Introduction

Recent recognition of the risk of very dilute contaminants in water makes it important to produce a new kind of adsorbents and to avoid any risk that may be produced such as contamination by agents through their dissolution [1,2].

Because of industrial and agronomical interests, most investigations about the adsorption of anionic polyelectrolytes on minerals have focused their attention on the influence of the polymer on the dispersion state [3–5]. Wastewater discharges carrying nitrate, ammonium, or sulfate ions create serious and often unanticipated problem to water management experts [6]. Phosphate is interesting substance from a water treatment point of view. It is of value to collect the finally disposed phosphates from effluents and drain water before further dispersion and dilution of them in the water environment. The extent of adsorption depends on the affinity of the anions for the surface, the relative concentration of anions, and the pH. Phosphorus is of central concern to a wide variety of biological and chemical processes in natural waters. The excess release of phosphorus into surface water may cause eutrophication, and hence deteriorate the water quality. Phosphorus is released to aquatic environments through the weathering of rocks and by various human activities such as mining and industrial and agricultural uses. Water pollution by phosphorus is increasing, and therefore, there is an increasing demand for the removal of phosphorus.

The need for selective removal of toxic anions at trace concentration levels has been well recognized. Anion exchange has attracted interest as a treatment process for the removal of anions [7–9].

The extensive use of chemical fertilizers and improper treatment of wastewater has led to several environmental problems such as increased concentration of nitrate in underground and surface water. A high concentration of nitrate in drinking water leads to the production of nitrosamine, which is related to cancer [10].

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 enhancing adsorption efficiency of the adsorbents [11–13]. Graft polymerization can be initiated by using gamma 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 [14] is a convenient method for

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the modification of physical and chemical properties of polymeric materials [15,16]. Radiation grafted adsorbents have been used usually for separation and wastewater treatment [17–20].

Poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA) may be used as a flocculant [21] and it can also be used as an ionexchange resin and a dye mordant [22]. Cho et al. [23] reported the thermo-sensitive properties of PDMAEMA hydrogels, and they explained that hydrogen bonds between amide and *N*,*N*dimethylamino groups might result in a hydrophobic contribution to the lower critical solution temperature (LCST).

In the case of the adsorption mechanism, there is less agreement about the nature of the forces involved. However, recent studies show the importance of pH, ionic strength, and the surface charge density for the adsorption of polyelectrolytes [24,25]. The objectives of this study were to create anion adsorbent PP film by chemical modification of grafted PP based on *N*,*N*-(dimethylaminoethyl)methacrylate (DMAEMA) copolymer followed by quaternization with different alkyl halides and applying the resulting anion adsorbent for the removal of various anions of environmental concern (e.g., phosphate (PO_4^{3-}) and nitrate (NO_3^{-})).

2. Experimental

2.1. Materials

PP films of thickness 30 µm were produced by El–Nasr Co. for medical supplies, Egypt. Reagent grade DMAEMA of purity 99% (Merck, Germany) was used as received. 1-Bromo octadecane, methyl iodide and benzyl chloride supplied from (Aldrich), which were used as received. Other chemicals were of reagent grade and used without further purification.

2.2. Graft copolymerization

The graft copolymers were prepared by radiation grafting of DMAEMA binary monomer solution onto PP films using Co-60 γ -rays at a dose rate of 2.86 Gy/s. Film of PP weighted and then immersed in different concentrations of DMAEMA solutions ranging from 10 to 60% (w/w) in water. The direct radiation grafting method was used as a technique in N₂ atmosphere. Water was used as solvent. The grafted films were removed and washed thoroughly with water to extract the residual monomer and the homopolymer, which may be accumulated in the film. The films were then dried in a vacuum oven at 40 °C for 24 h and weighed.

The degree of grafting was determined by the percentage increase in weight as follows:

Grafting yield (%) =
$$\frac{Wg - W0}{W0} \times 100$$

where W_0 and W_g represent the weight of initial and grafted film (g), respectively.

2.3. Quaternization of the grafted films

Definite weight 5 g of PP-g-DMAEMA film was immersed in 34.49 mmole with different alkyl halides; methyl iodide, 1-bromo octadecane and benzyl chloride. The mixture was heated in thermostat at 50 °C under vacuum with stirring. The reaction was allowed to proceed for 12 h at this temperature. The film was withdrawn and then washed with dry ether several times and dried under vacuum at room temperature, according to literature [26–28].

2.4. FTIR spectroscopy

Mattson 1000 FTIR spectrophotometer product of Unicam Ltd., England, was used for analysis by IR spectroscopy. IR was recorded by passing the IR radiation through the transparent film.

2.5. Thermogravimetric analysis (TGA)

TGA for the investigated samples were performed under nitrogen atmosphere at a flow rate of 50 ml/min of pure nitrogen gas and the heating rate was 10 °C/min from ambient temperature up to 600 °C using Shimadzu TGA-50 (Japan) thermal analysis system of type TGA-50 thermal analysis system.

2.6. Mechanical properties

Dumbell shaped specimens of 50 mm long and 4 mm neck width were used for the measurement of tensile strength and elongation at break using a H10KS instrument (Houns.eld Test Equipment, Ltd., England).

2.7. Adsorption study

About 0.1 g of the grafted and quaternized film was immersed in the phosphate and nitrate feed solution of definite concentration (100 ppm) and the concentration of the anion solution was measured according to American Society for Testing and Materials (ASTM, 2000) [29]. The effect of pH of phosphate and nitrate solutions was studied at different pH values with the same initial phosphate concentration (100 mg P/L). The pH of the solution was adjusted by addition of 1 M HCl or 1 M NaOH solution.

2.8. Desorption studies

The phosphate and nitrate loaded adsorbent easily desorbed under suitable conditions and was reusable. Desorption of the adsorbed phosphate and nitrate ions from the film was done by immersing it in 200 ml of 0.1 M NaOH for 24 hours. The quantity of desorbed phosphate and nitrate was determined by the amount of phosphate and nitrate in solution after the desorption experiment.

The total uncertainly for all experiments ranged from 3 to 5%

3. Result and discussion

3.1. Preparation of the grafted film

Radiation grafting is a well-known method for modification of the chemical and physical properties of polymeric materials. When the DMAEMA monomer and PP are irradiated together with γ -rays, the double bond of C=C of DMAEMA is broken by ionizing radiation and free radicals are generated which react with each other to form graft copolymer film. Quaternization of the grafted film with different alkyl halides to improve their ionic character, the possible mechanism, is shown in Scheme 1.

The parameters which affected the preparation process and grafting yield; namely monomer concentration and irradiation dose, have been investigated here to obtain DMAEMA-g-PP film with reasonable grafting yield.

The effect of monomer concentration on the grafting yield is investigated in Fig. 1. As follows from figure, the grafting yield increases with increasing of the monomer content within the studied concentration range of 10–60 wt%. From the above results, the increase in the grafting yield with monomer concentration may be due to increase in diffusion rate of the monomer into the bulk polymer. Also the high monomer concentration at the grafting sites



Scheme 1. Possible copolymerization of DMAEMA-g-PP and its quaternization with methyl, octadecane and benzyl groups.

favors propagation of growing chains, consequently increasing the grafting yield.

The influence of irradiation dose on the extent of the grafting process is shown in Fig. 2. It can seen that under the chosen reaction



Fig. 1. Effect of DMAEMA concentration on the grafting yield onto PP films at irradiation dose, 10 kGy.

conditions, the grafting yield within the studied range of irradiation dose ranging from 5 to 15 kGy increases with increasing irradiation dose This trend can be explained to the fact that the increase in the irradiation dose leads to more free radical formation in the grafting site which leads to an increase in the grafting yield. At irradiation



Fig. 2. Effect of irradiation dose on the grafting yield at DMAEMA concentration, $50\,\rm wt\%$ in solvent.

Table 1
FTIR spectra for PDMAEMA-g-PP film and quaternization

Polymer	Characteristic band	Wave number (cm ⁻¹
DMAEMA-g-PP	C=0 C-O-C Tertiary amino groups	1730 1300–1100 1270
Methyl iodide quaternized film	CH3 asym.	2950
	CH₃ sym. C–I	2860 ~500
1-Bromooctadecane quaternized film	-CH3	2940
-	-CH ₂	2914
	C–Br	750–500
Benzyl chloride quaternized film	The strong stretching band of aromatic CH	3000
•	C-Cl	950
	C=C ring stretching	1660
	C-H out of plan bending	788

doses above 15 kGy, a very rigid homopolymer was formed and was difficult to extract.

3.2. Characterization of the grafted film

3.2.1. FTIR spectroscopy

Table 1 shows the FTIR of DMAEMA-g-PP film and its quaternized form. The IR spectrum of the DMAEMA-g-PP shows the absorption bands at 1730 cm^{-1} and $1300-1100 \text{ cm}^{-1}$, arising from C=O and C-O-C stretching of acrylate group as well as tertiary amino groups at 1270 cm^{-1} . The IR-spectrum for quaternized DMAEMA-g-PP was focused on the addition of different alkyl halides on nitrogen atom resulting in quaternization structure.

Quaternized film by adding methyl iodide showed the absorption bands –CH₃, respectively. In 1-bromooctadecane quaternized film, the absorption bands appeared at 2940 cm⁻¹ and 2914 cm⁻¹ attributed to –CH₃ and CH₂ stretching with more increase in the intensity of both CH₃ and CH₂ bands, respectively.

Quaternized film by adding benzyl chloride showed a new strong stretching vibration band around $3000 \,\mathrm{cm}^{-1}$ was appeared as characteristic C–H bond in benzene ring of benzyl chloride. Other absorption band at 950 cm⁻¹ characterizes to C–Cl. Also, new absorption bands appeared around 1660 cm⁻¹ and 788 cm⁻¹ which correspond to C=C in benzene ring and C–H out of plan bending, respectively. All the above data recorded in the table confirm the structure of the new product.

3.2.2. The mechanical properties

Because of the importance of physical properties in practical applications, mechanical properties (tensile strength (T_b) and elongation percent (E_b)) were measured at break point. As summarized in Table 2, there was a clear tendency that the tensile strength increases and elongation decreases with an increase in the

Table 2

The mechanical properties of DMAEMA-g-PP at different DMAEMA concentration and irradiation dose, $10\,kGy$

Monomer concentration (wt%)	Elongation (%)	Tensile strength (MPa)
0	23.47	500
10	21.29	557
20	13.57	687
30	11.36	709
40	8.00	762
50	7.00	822.5
60	6.47	880



Fig. 3. Effect of initial concentration (mg/L) on the durable adsorption time and the amount of adsorption of phosphate ion onto 1-bromooctadecane quaternized film at pH 7.2.

DMAEMA content. It can be noted that the T_b of the PP was 500 MPa addition of 10 wt% of DMAEMA, the T_b increased to 557 MPa, which is 11.4% higher than that of PP. The increase in T_b was accompanied with 9% decrease in the E_b . Addition of 20 wt% DMAEMA further increased the T_b to 37.4% higher than PP. Generally, the rigidity of PP film increases as a result of grafting and radiation, consequently, a decrease in E_b and an increase in T_b are expected for such grafted film [30,31]. The rigidity of the graft film increases with increasing degree of grafting due to two reasons; the first one is the incorporation of the polar groups and their interactions. The second reason is the crosslinking formation due to grafting and irradiation, which leads to restriction in chain mobility.

3.2.3. Adsorption of PO_4^{3-} and NO_3^{-} ions

The anion adsorbent was synthesized as a result of radiationinduced graft copolymerization of DMAEMA onto PP film with subsequent quaternization of amine group of PDMAEMA grafted chain. Among the factors affecting on the adsorption of PO_4^{3-} and NO_3^{-} were studied as the follows:

3.2.4. Effect of time and initial anion concentration

Figs. 3 and 4 show the effect of adsorption time on the adsorption of PO_4^{3-} and NO_3^{-} ions, respectively, at various initial feed concentrations. The result showed that the amount of adsorbed



Fig. 4. Effect of initial concentration (mg/L) on the durable adsorption time and the amount of adsorption of nitrate ion onto 1-bromooctadecane quaternized film at pH 7.2.



Fig. 5. Effect of different treatment films on the durable adsorption time and the amount of adsorption of phosphate ion onto 1-bromooctadecane quaternized film at pH 7.2, at conc. 200 mg/L.

PO₄³⁻ and NO₃⁻ ions increases with increasing the adsorption time within the first 10 h and then tends to level off towards the equilibrium adsorption capacity. It was evident that, for all anions, the adsorption efficiency increases with increasing sorbate concentration [32,33]. In general, increasing concentration of the salt solution causes the decrease in water content of the adsorbent material. Therefore, the hydrophilicity of the adsorbent decreases with increasing concentration of the salt solution, which increases their permeation [34]. It can also be seen that the adsorption of PO4³⁻ and NO3⁻ ions increases with increasing the initial feed concentration due to increase in the concentration of ions on the adsorbed sites. On the other hand the adsorption of NO₃⁻ ions is higher than PO_4^{3-} ions at the same adsorption time which is mainly dependent on the nature of interaction with the functional groups of the films. These results were explained by many researchers who suggested that there are two mechanisms for anion exchange: electrostatic attraction and ligand exchange. Simple anions such as chloride, nitrate, sulfate, and carbonate ions are adsorbed on the surface through the electrostatic attraction. Phosphate adsorption takes place only on the surface of the adsorbents and therefore the rate of adsorption is fast. Phosphate ions cannot enter into pore of the adsorbents, because the sizes of pore sites are too small to accommodate larger ions such as phosphate ions [35].

Figs. 5 and 6 show the effect of quaternization type on the adsorption of $PO_4{}^{3-}$ and $NO_3{}^{-}$ ions, respectively. In general, the adsorption of quaternized film was higher than unquaternized one due to increase in the polarity of the film as a result of quaternization. It can be noted that the highest film of $PO_4{}^{3-}$ ion adsorption was 1-bromo octadecane quaternized film but for $NO_3{}^{-}$ ion adsorption it was benzyl chloride the quaternized one.

The IR spectra for PO_4^{3-} and NO_3^{-} ion adsorption film are shown in Fig. 7. IR spectrum confirmed the expected uptake of both anions PO_4^{3-} and NO_3^{-} . The IR representation provided the possible interaction of anion groups with nitrogen quaternary position by appearing new bands at 1080 cm^{-1} corresponding to the PO_4^{3-} as shown in spectrum (a). The other side the spectrum (b) showed the absorption band at 1384 cm^{-1} and 1766 cm^{-1} characteristic for the NO_3^{-} as well as the stretching vibration of N–O and N=O bands.

3.3. Effect of pH of medium

The pH of the aqueous solution is an important variable that influences the adsorption process. Figs. 8 and 9 show the effect of



Fig. 6. Effect of different treatment films on the durable adsorption time and the amount of adsorption of nitrate ion onto 1-bromooctadecane quaternized film at pH 7.2, at conc. 200 mg/L.

pH of the medium on the adsorption of PO_4^{3-} and NO_3^- ion, respectively, for all investigated films. The PO_4^{3-} and NO_3^- ion adsorption tends to decrease with increasing the pH for all investigated films, similar trends were also observed for PO_4^{3-} ion adsorption on different adsorbents [36–38]. This is attributed when the pH of the solution decreases; the positive charge on the adsorbent



Fig. 7. FTIR spectra for PDMAEMA-g-PP film and quaternization with 1-bromooctadecane adsorbed of (a) phosphate ion (b) nitrate ion.



Fig. 8. Effect of pH of medium on PO_4^{-3} ion adsorption at initial feed concentration 100 mg/L, treatment time 24 h.

surface favors the adsorption of PO_4^{3-} and NO_3^{-} ions due to the electrostatic attraction. As the pH of solution is increased, the concentration of the OH⁻ in solution, which competes with the PO_4^{3-} and NO_3^{-} species, becomes higher. The highly negatively charged adsorbed surface sites do not favor the adsorption of oxanion due to the electrostatic repulsion [39,40].

3.4. Adsorption isotherm

The adsorption isotherms of phosphate and nitrate ions on all investigated films are shown in Fig. 10a and b. The adsorption isotherms indicate that the uptake of the investigated anions increases with increasing equilibrium concentration anions. The isotherm data were analyzed by Freundlich equation. The equilibrium isotherm results were found to be best fitted by Freundlich isotherm model:

$\log q_{\rm e} = \log k_{\rm F} + 1/n \log C_{\rm e}$

where q_e is mg adsorbate per gram of dry adsorbent, C_e is the equilibrium anion concentration (mg/L), and the Freundlish empirical constants k_F and n referred to the ability of polymer adsorbent and affinity of adsorbat solution, respectively. The intercept and the slope of the linear plot of $\log q_e$ versus $\log C_e$ at given experimental conditions provide the values of k_F and 1/n, respectively. The Freundlich isotherm constants and R^2 values for different solutions are given in Table 3. The constant n refers to the interaction between



Fig. 9. Effect of pH of medium on NO_3^- ion adsorption at initial feed concentration 100 mg/L, treatment time 24 h.



Fig. 10. Adsorption isotherm of phosphate (a) and nitrate (b) by quaternized and unquaternized films at 24 h.

exchange sites in the adsorbent and phosphate and nitrate ions. A high value for n > 1 indicates favorable adsorption [35].

The isotherms from anion solution also indicate that phosphate uptake on 1-bromo octadecan films is considerably higher than that on another films and the maximum uptake of nitrate on benzyl chloride.

3.5. Thermal gravimetric analysis (TGA)

TGA thermograms for the ungrafted, grafted PP and anions adsorbed films are shown in Fig. 11. Ungrafted PP showed stable thermograms up to \sim 400 °C, beyond which a smooth decrease in the weight is observed. There is only one decomposition peak in the TGA curve of the ungrafted PP and complete depolymerization of the sample to monomer at \sim 470 °C. The result shows that the thermal stability of PP film has been changed by grafting of DMAEMA

Table 3

Freundlich isotherm constants and correlation coefficient for the adsorption of phosphate and nitrate by quaternized and unquaternized films

Polymer	Freundlich constants						
	Phosphate		Nitrate				
	k _F	п	R ²	k _F	n	R ²	
Unquaternized	0.0450	1.001	0.9999	0.0752	1.0042	0.9989	
Methyl iodide	0.2026	1.004	0.998	0.2144	1.0197	0.9919	
1-Bromo octadecane	0.23	1.042	0.9999	0.2338	1.0324	0.9978	
Benzyl chloride	0.2173	1.021	0.9990	0.24	1.0370	0.9984	

All experiments were done at 35 °C and pH 7.5.

Table 4

The desorbabilit	v of the PO	$^{3-}$ and NO ₃	ions with	1-bromoctadecane	uaternized film
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Initial feed concentration (mg/L)	Adsorbed (mg/g)		Desorbed (mg/g)		Desorbability (%)	
	PO4 ³⁻	NO ₃ -	PO4 ³⁻	NO ₃ -	PO4 ³⁻	NO ₃ -
25	2.85	3.4	0.57	0.765	20	22.5
50	5.7	6	1.03	1.5	18.1	25
75	8.5	9.24	1.913	2.587	22.5	28
100	11.4	12.5	3.01	3.8125	26.46	30.5

onto it; the grafted films exhibited two decomposition peaks, i.e., the first decomposition occuring at 400 °C may be attributed to elimination of the grafted side chains. The first decomposition peak is very similar to that of PDMAEMA, so the first decomposition peak should be attributed to the decomposition of the grafted film. The second decomposition stage was observed in the temperature range of 400-500 °C. This is the region of major weight loss due to extensive degradation of the polymer backbone chain. Also, in Fig. 11 it can be seen that the thermal stability PDMAEMA-g-PP film was higher than that of ungrafted one; the introduction of DMAEMA into PP film would improve the thermal stability of the PP film. TGA curve of the modified PDMAEMA-g-PP with benzyl chloride is shown in Fig. 11. It is observed that there are three stages of decomposition appearing in TGA curves. The first stage at decomposition temperature 230 °C is attributed to elimination of water molecule in the side groups. The second stage of weight loss in the temperature range 230-400 °C is attributed to quaternized graft chain degradation and the last stage of decomposition of the backbone polymer. It can also be noted from the figure that at the same decomposition temperature the weight percent of the modified PDMAEMA-g-PP with benzyl chloride is higher than both PDMAEMA-g-PP and PP films. Thus, introduction of benzyl group into the grafted film increases its thermal stability, this may result from the resonance of the benzyl ring. The TGA curves of the modified PDMAEMA-g-PP with benzyl chloride and adsorbed PO₄³⁻ and NO₃⁻ ions also have three decomposition beaks but introduction of PO₄^{3–} and NO₃[–] ions reduces the thermal stability of the films than the modified PDMAEMA-g-PP with benzyl chloride.

3.6. Desorption studies

The desorption of the PO_4^{3-} and NO_3^{-} ions from the film is done by socking it in 0.1 M NaOH for 1 day. The quantity of desorbed PO_4^{3-} and NO_3^{-} was determined by the amount of PO_4^{3-} and NO_3^{-} in solution after the desorption experiment. The desorbability was



Fig. 11. TGA of blank PP grafted, quaternized with benzyl chloride and after uptake of phosphate and nitrate.

calculated by the following equation:

The desorbability (P)

- Amount of ion desorbed to the elution medium
- Amount of ion sorbed on the on the adsorbant

The desorbability (*P*) can be used to indicate the degree of desorption from the adsorptive materials [41]. Table 4 shows the desorbability of different initial feed concentrations of PO_4^{3-} and NO_3^{-} ions, the amount of the desorbed is slightly increased with increasing the PO_4^{3-} and NO_3^{-} ion adsorption. The *P* in Table 4 is ranging from 18 to 30% for all samples, regardless the initial feed ions concentrations used for the batch adsorption experiments. These results indicate that the adsorption on the adsorbent quaternized with 1-bromoctadecane is not completely reversible and the bonding between it and adsorbed PO_4^{3-} and NO_3^{-} is likely to be strong. Thus, it is relatively difficult to desorb PO_4^{3-} and NO_3^{-} ions from the films.

4. Conclusions

The γ -radiation induced grafting of *N*,*N*-(dimethyl amino ethyl) methacrylate (DMAEMA) onto polypropylene (PP) film was investigated by simultaneous irradiation technique. The grafting yield was affected by the monomer concentration and irradiation dose. The adsorption properties of the grafted film were improved by quaternization of amine group with different alkyl halides. The grafted film has acceptable mechanical and thermal properties which make it useful in application. The modified grafted film was used as adsorbent to PO₄³⁻ and NO₃⁻ ions. In the adsorption test, the effect of adsorption time, initial feed concentration and pH was examined. It was found that the equilibrium adsorption capacity was 10 h and the adsorption decreases with increasing pH of the medium. The desorbability of the films ranged from 18 to 30% for adsorbent material. It can be concluded that the prepared film can be used as adsorbent to reduce PO₄³⁻ and NO₃⁻ ions in wastewater.

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