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Surface adsorption of cationic surfactant from aqueous solution by modified poly (ethylene terephthalate) fibers

***F. Azizinezhad*[1*]*, N. YAahyazadeh*[2]*, E. Moniri*[3]

[1,2,3]*Department of Chemistry and Chemical Engineering, College of Science,*
Varamin-Pishva Branch, Islamic Azad University, Varamin, Iran

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ABSTRACT: The purpose of this study is to investigate the graft copolymerization of 2-hydroxy propyl methacrylate (2HPMA)-Acrylic Acid (AA) compound within poly (Ethylene terephthalate) fibers in the presence of Benzoyl Peroxide Bz_2O_2 initiator. The modified fibers have been used as a new adsorbent to eliminate Cethyl Pyridinium Bromide (CPB) for the aqueous solution. Fibers characterizations have been done using CEC, BET, TGA, FTIR, and SEM methods. The impacts of different parameters such as pH, adsorbate concentration, adsorbent quantity, and time have been investigated. pH=6.0, t=90 min, and q_m=14.2 mg/g have been declared as favorable adsorption conditions. It is acceptable due to the high stability of the PET fibers in acidic and alkaline environments.

Keywords: *Acrylic acid, Cethyl pyridinium bromide, 2-Hydroxy propyl methacrylate*

INTRODUCTION

Adsorption is an important method which has noticed by many researchers. Different adsorbents have been introduced so far for purification of industrial sewages from environmental hazards such as active carbon, carbon nanotubes, peanut shells, charcoal, perlite, zeolite, bentonite, montmorillonite, sepiolite, etc. [1-5]. Azizinezhad *et al.*, investigated the adsorption of cationic brill red X-5 GN in poly (ethylene terephthalate) grafted by 2-hydroxy propyl methacrylate. Then, the impact of pH on adsorption, adsorbent concentration, temperature, contact duration, and grafting performance has been investigated. The adsorbent concentration, grafting parentage, contact duration, and optimum pH were recorded as 200 mg/l, (%53), 60 min, and 10.0, respectively. The results have been compared with freundlich's isotherm and intra- particle diffusion kinetic and it has been found that the results obtained from the adsorption process are mainly the results of a physical and spontaneous process [6]. In Taghizade *et al.*'s study, concerning of the grafting of acrylic acid, ethyl methacrylate and ammonium nitrate on to starch were investigated, kinetically. They study the graft copolymerization of acrylic acid and ethyl methacrylate on starch in an aqueous solution using ammonium nitrate as the

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(*) Corresponding Author - e-mail: fazizinejad@iauvaramin.ac.ir red-ox system and a medium to reduce N_2 atmosphere. The impacts of pH, reaction time, temperature, cation concentration, and monomer on graft performance have been investigated. The grafted copolymers have been studies through FT-IR spectrometry. The total activation energy of AA graft co polymerization to starch was 36.25 kJ/mol, its temperature was 20-40 ºC and the same energy for EMA graft copolymerization to starch was 11.88 kJ/mol and the temperature was 25-45 ºC [7]. Nayak *et al.*, study on the graft of vinyl's monomers on wool fibers against methyl methacrylate's copolymerization graft to wood using proxy di-phosphate as the catalyzer, the copolymerization graft f methyl methacrylate on the wood and in aqueous solutions using peroxy di-phosphate as the initiator has been investigated. The grafting rate using various monomers, peroxy di-phosphate ion, temperature, solvent, and the type of wood have been defined. The product will increase upon any increase in monomer concentration. The graft product will insignificantly increase upon increasing peroxy diphosphate ion to 8×10^{-3}mol/L. With increasing more peroxy diphosphate ion, the graft product will decrease. The grafting rate will increase by increasing the temperature. The impact of acid and aqueous soluble solutions on the bonding quality has been investigated and an equation for rate resulted [8]. In another study by Tonali *et al.* about synthetic and equilibrium investigation of Acid Red 57 aqueous solutions' adsorption using calcined-alunite, it has been shown that adsorption is related to pH, time, and temperature. The reaction's synthetic has been investigated based on three models including pseudo-first order, pseudo-second order, and intra-particle diffusion. Then, the best model introduced was pseudo-second order, and Langmuir and freundlich isotherm models have been investigated to evaluate the equilibrium data. Then, the variations in gibb's free energy, and adsorption's enthalpy and entropy have been calculated. The results illustrated that this adsorbent can be used in the textile industry as a cheap adsorbent in removing acid paints from industrial sewages [9]. In another study, Alkan et al, regarding AR57 and AB294 acid colors using modified sepiolite in aqueous solutions through batch technique. It has been found out that color adsorption depends upon various parameters including temperature, time, and environment's pH. On the other hand, freundlich isotherm and second-order kinetic models were compatible with results and color adsorption activation energy has been computed and reported later [10]. Celic and Sacak studied the grafting copolymerization of PET fibers using a mixture of acrylamide and methacrylic acid monomers using azobis izobutiro nitrile and they defined the optimal copolymerization conditions from the viewpoint of monomer concentration, initiator concentration, temperature and reaction time [11].

Azizinezhad *et al.*, was reported the graft copolymerization of PE fibers using a mixture of acrylic acid and methyl methacrylate monomers by using benzoyl peroxide as initiator. They studied the important properties, such as water absorption capacity, dyeability, and kinetic of reaction [12]. It's noteworthy that there are different studies regarding adsorption and defining adsorbent isotherms, kinetic models, and thermodynamic parameters of active carbon, mineral adsorbents, and mineral-polymer composites. Besides, the researchers were looking for to research for more efficient and cheaper adsorbents [13].

EXPERIMENTAL SECTION

Materials and Methods

In this study, Poly (Ethylene Terephthalate) fibers (30 filament) have been purchased from Amirkabir Textile University and after washing them with acetone in the soxhlet system for six hours to remove of any probable impurities, and drying it up in 50 degrees centigrade, have been put inside the autoclave. 2-hydroxy propyl methacrylate (2-HPMA) and acrylic acid (AA) have been purchased from Merk Company (Germany) and were used after purification. To this aim, for 2-HPMA the vacuum distillation process has been finalized under a temperature of 99 °C and 23 mmHg and for AA's distillation also occurred in vacuum conditions. Bz_2O_2 has been purchased from Merk Company as the initiator and it has been used after two times of repeated crystallization in the presence of methanol-chloroform and it has been kept in darkness till the end of the experiments. All the solvents including toluene, acetone, methanol, chloroform and cationic surfactant (cetyl pyridinum bromide) (CPB) have been purchased from

Merk Company and the grafting and adsorption experiments have been done using twice distilled water.

Grafting Procedure

The monomers' grafting operation has been done inside PET fibers in a water bath and inside 100 ml Pyrex tubes. To this end, 0.4 g fibers, 0.006 molar benzoyl peroxide (Bz_2O_2) solved in 5 ml of acetone, 0.1 molar from %80 2-hydroxy propyl methacrylate monomer mixtures, %20 acrylic acid, and 45 ml distilled water in a total volume of 50 ml and constant temperature of 85 °C, have been used [14]. To yield a product with high grafting efficiency, the reaction has been conducted in 60 minute and then the fibers have been diligently taken out of the tubes. The grafting percentage has been computed based on the weighing method by repeated washing with distilled water for removing acrylic acid homopolymers for 24 hours and washing for the second time with a mixture of toluene, acetone for 6 hours and dimethylformamide for eight hours to remove 2-hydroxy propyl methacrylate homopolymers by soxhlet system.By the following equation the grafting percentage was determined:

$$G(\%) = (W_g - W_0) / W_0 \times 100 \qquad (1)$$

W_0 and W_g in this equation are primary fiber's and grafted fibers' weights, respectively.

Adsorption Studies

Surfactant (CPB) adsorption experiments have been done in the presence of 0.1g of the adsorbent (the copolymerized fibers), in a total volume of 20 ml and cetyl pyridinium bromide solution with a concentration of 100 mg/l in 250 ml Erlenmeyer in the shaker. They have been stirred with a constant speed of shaker (150 rpm) and the adsorption value has been obtained as a function of pH, adsorbate concentration, absorbent quantity, and percentage of graft product. CPB concentration in the solution has been calculated after fiber infiltration using Wattman 40's filtration sheet and ultracentrifuge in 3000 rpm using UV spectrometry device (Shimadzu 1208 UV-Vis) in λ_{max}= 260 nm and based on CPB calibration curve (Fig. 1). The calculations were based on the following equation:

$$q = (C_0 - C).V / m \qquad (2)$$

Where C_0 and C were CPB (mg/l) primary and equilibrium concentrations respectively, V is solution's total volume (L), m is the adsorbent weight (g), and q is obtained based on mg/g of the CPB adsorbed in a definite time.

RESULTS AND DISCUSION

Characterization of adsorbent

In order to determine the properties of the modified fibers, (pH_{ZPC}) has been computed in a pH range of 3-10 according to Milonjic *et al.*, [15] in the presence of 0.1 adsorbent, 20 ml of cetyl pyridinium bromide solution in one hour and the stirring speed of 150 rpm and upon plotting the variations in pH_i-pH_f (pH_{ZPC}=3.1) (Fig. 2). Cation Exchange Capacity (CEC) based on saturation with sodium acetate 1N and its consequent extraction

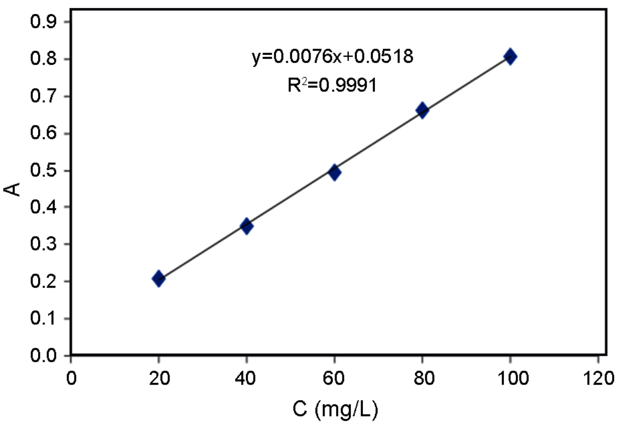


Fig. 1. Calibration curve of CPB.

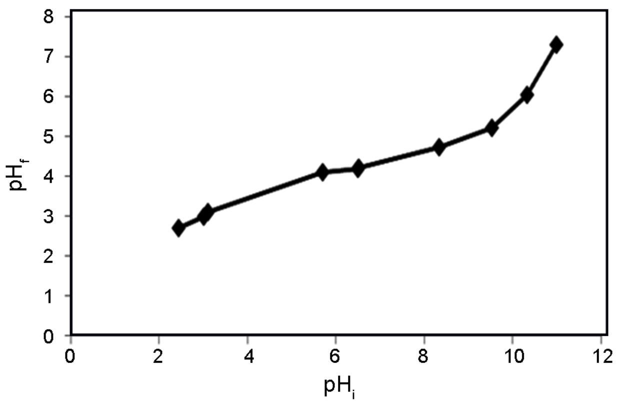


Fig. 2. Determination of pH(ZPC).

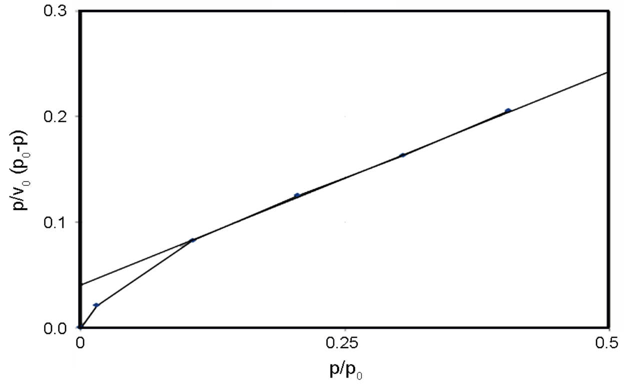
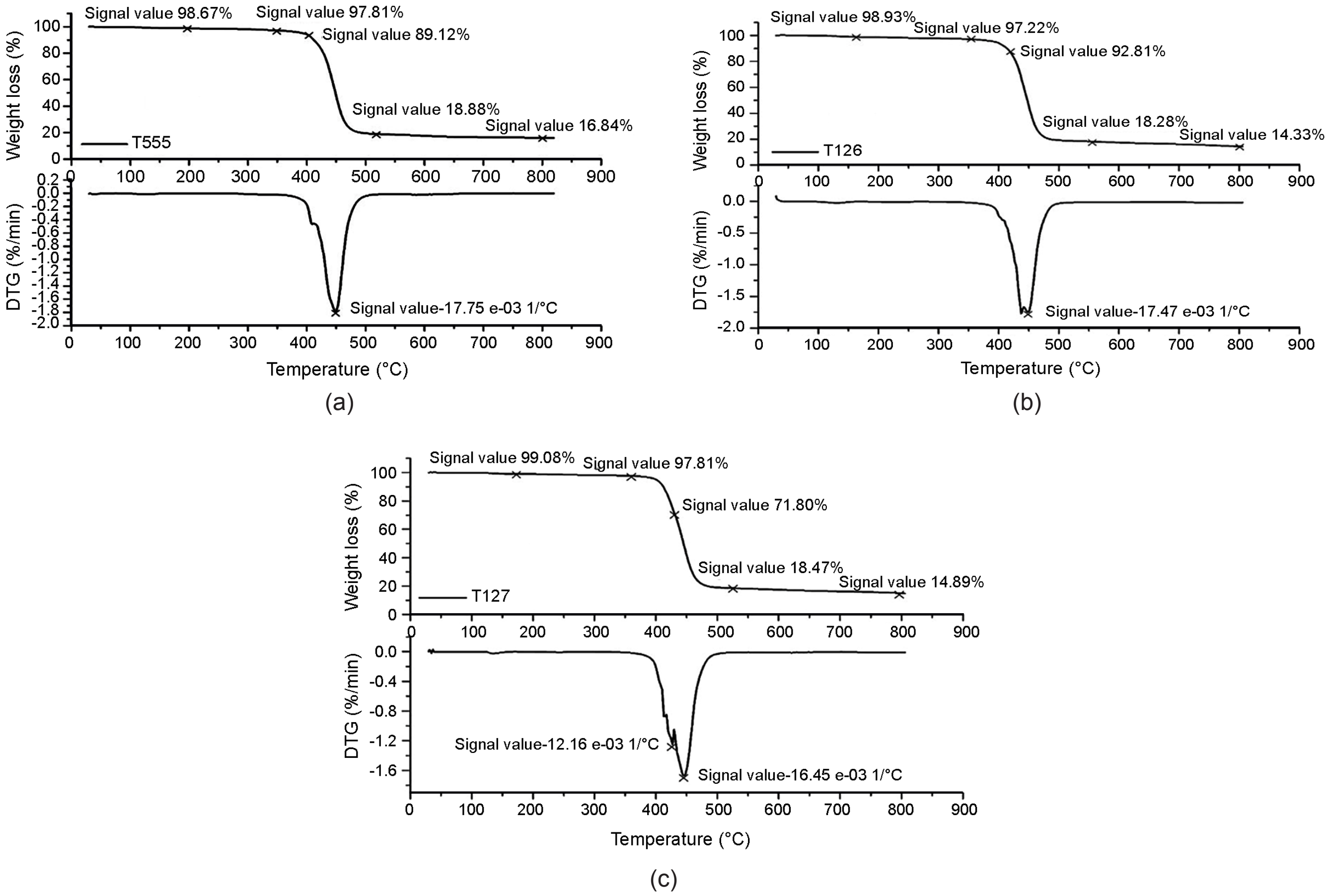


Fig. 3. BET plot of modified fibers.

with ammonium acetate using a flame photometry device (Jenway Clinical PFP7 model) and the resulting value obtained was 83 mg/l [16]. The specific surface area using nitrogen gas' adsorption and desorption (BET) in 77 K, was 9.8 m2/g (Fig. 3). This value isn't high compared with mineral adsorbents such as Montmorillonite, nebtunite, nano-compounds and the main reason behind adsorption must be related to the functional groups connected to PET fibers which are capable of forming a complex and grafting with CPB cation surfactant [17]. The thermo gravimetric analysis (TGA) figures show that upon adsorption of cetylpyridinium bromide by grafted fibers, there will be a decrease in fiber's thermal stability. The fracture decreased from 400 degrees centigrade to 370 degrees centigrade in raw fibers after adsorbing CPB. This issue is related to the crystallization reduction of the fibers and confirms the optimized adsorption of cetylpyridinium bromide (Fig. 4 a,b,c). On the other hand, the figures for scanning electron microscopy (SEM) show that fibers' diameter increased after adsorption which confirms the adsorption of CPB surfactant on the surface of the modified fibers (Fig. 5 a,b). FT-IR spectrums related to the raw and modified fibers and post-adsorption shows that the cyclic C-N of the stretching vibration is evident in 1254 cm^{-1} and confirms the CPB adsorption by the modified adsorbent. The other peaks for the raw and grafted fibers in 3400

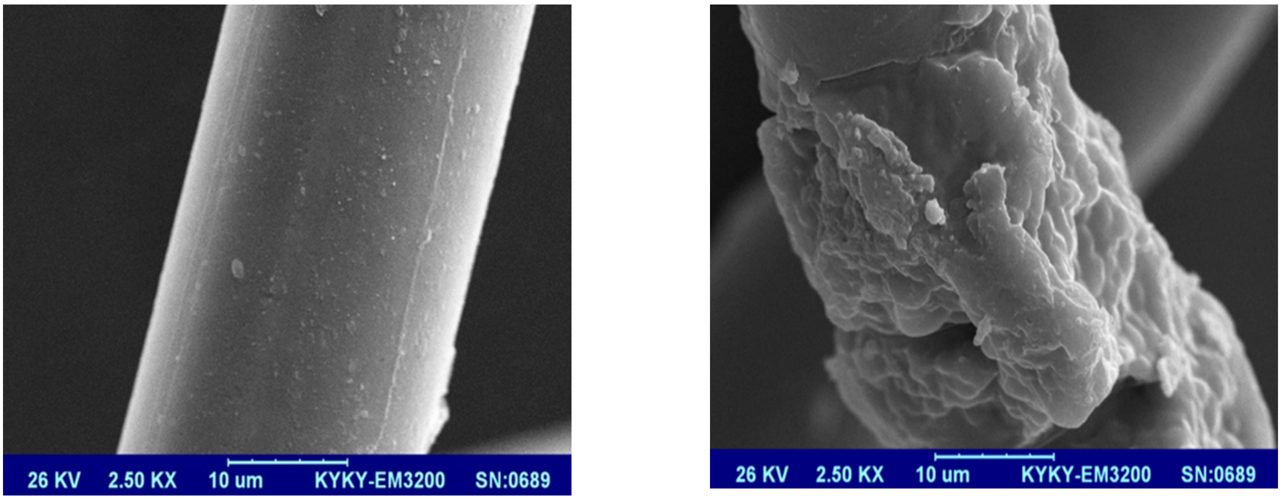


(a)

(b)

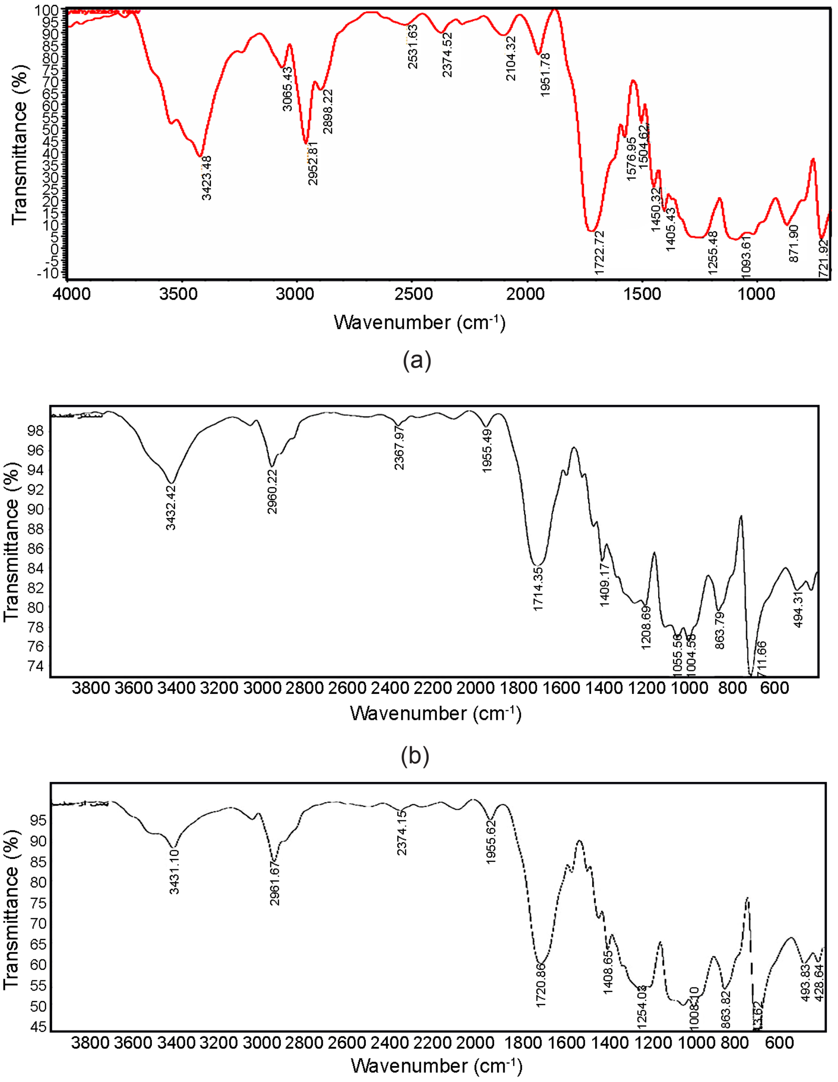
(c)

Fig. 4(a,b,c). Thermograms of (a) ungrafted PET fibers (b) grafted PET fibers(c) after adsorption(c).



(a) (b)

Fig. 5(a,b). SEM micrograph of (a) ungrafted PET fibers, (b) after adorption by grafted fibers.



(a)

(b)

(c)

Fig. 6. FTIR spectrums of (a) ungrafted PET (b) grafted PET (c) after adoption.

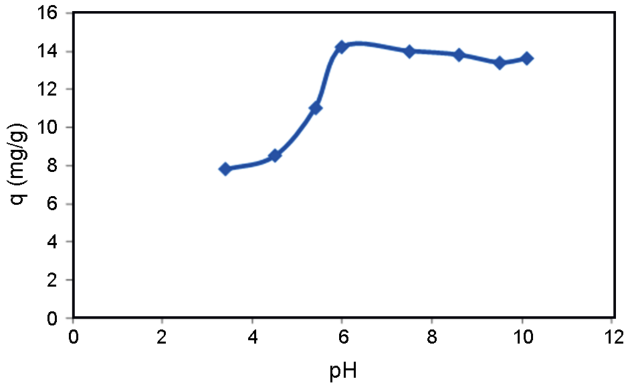


Fig. 7. Effect of pH on the adsorption.

cm^{-1} relate to stretching O-H and 1710 cm^{-1} relates to stretching C=O which are evident in all three spectrums (Fig. 6 a,b,c).

The Impact of Different Parameters on Surface Adsorption

The impact of pH in the adsorption of CPB, in 3-10 pH range in constant conditions (0.1 g adsorbent, CPB=100 mg/L, t=120 min, shaker speed=150 rpm, T = 298Kand V=20 ml) has been investigated. The best pH for maximum adsorption of cetylpyridinium bromide was 6.0. In acidic environment, the H$^+$ cetylpyridinium bromide ions compete together in adsorption o fibers' active sites and they will be adsorbed faster because of higher motion of H$^+$ ions. In alkaline environments, cetylpyridinium bromide sediment in aqueous solution (Fig. 7) to determine the best time impact, the adsorption experiments have been done in a time duration of 10-110 min and under a condition which all other variables are kept constant (adsorbent=0.1 g, CPB=100 mg/L, T= 298 K, shaker speed=150 rpm, pH=6.0, and V=20 ml). The adsorption process has been quantified every ten minutes and the adsorption rate was the same in any tie interval and will be completed after 90 minutes. The maximum adsorption of cetyl pyridinium bromide is 14.2 mg/g (Fig. 8) shows the impact of time in the process of adsorbing CPB. By changing the adsorbent quantity within 0.05-0.2 g range and under constant conditions, the experiments or determining the optimized adsorbent value have been conducted. After increasing the adsorbent due to higher functional groups of –OH and –COOH grafted to PET structure and the increase in active sites in modified fibers, the adsorption rate increased. The results are illustrated in (Fig. 9) with a C_0 value equal to 100 mg/L. In order to determine the maximum adsorbent capacity, the concentration of cetyl pyridinium bromide has changed in the range of 40-200 mg/L as an adsorbate. The maximum adsorbent capacity of 17.8 mg/g in a solution containing 180 mg/L has been observed and recorded. The results are illustrated in (Fig. 10). These values illustrate the adsorption efficiency in the process of adsorbing CPB to the solution.

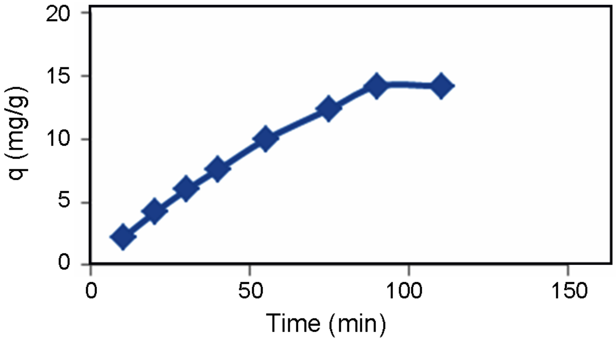


Fig. 8. Effect of contact time.

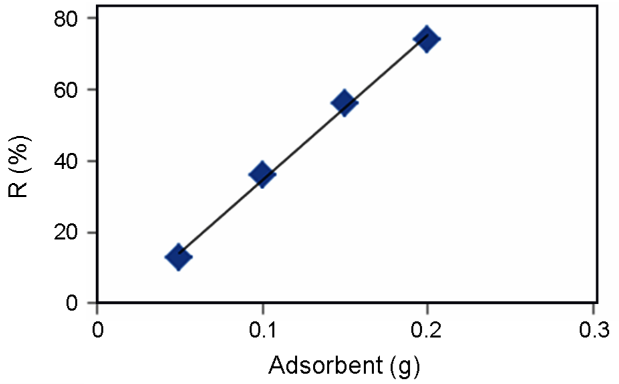


Fig. 9. Effect of adsorbent quantity.

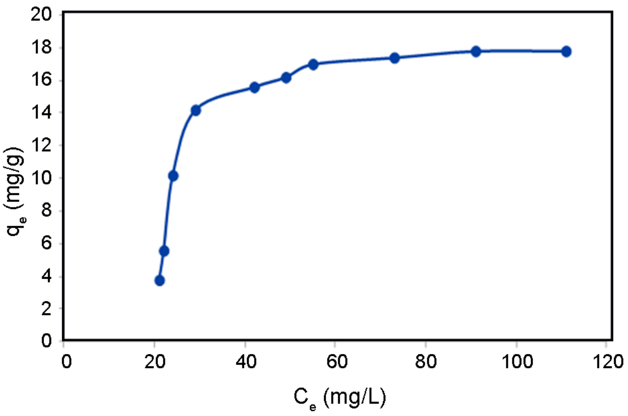


Fig. 10. Effect of adsorbate concentration.

CONCLUSIONS

In this study, modified polyethylene terephthalate fibers grafted by the mixture of 2-hydroxy propyl methacrylate-acrylic acid have been used to remove the cationic surfactant of cetyl pyridinium bromide from aqueous solution. The measurements in surfactant maximum wavelength were by using UV spectrometry. Considering the results of this study, it's recommended to use polyethylene terephthalate fibers due to their high stability in acid or alkaline environments as an industrial adsorbent for removal or adsorption of surfactants from industrial sewages after being modified with various monomers containing functional groups. Besides, due to the low specific area of the fibers, the main adsorbent will be attributed to acid and alkaline functional groups.

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AUTHOR (S) BIOSKETCHES

Fariborz Azizinezhad, Assistant Professor, Department of Chemistry and Chemical Engineering, College of Science, Varamin-Pishva Branch, Islamic Azad University, Varamin, Iran, *Email: fazizinejad@ yahoo.com, fazizinejad@iauvaramin.ac.ir*

Neda YAahyazadeh, PhD. Student, Department of Chemistry and Chemical Engineering, College of Science, Varamin-Pishva Branch, Islamic Azad University, Varamin, Iran

Elham Moniri, Associate Professor, Department of Chemistry and Chemical Engineering, College of Science, Varamin-Pishva Branch, Islamic Azad University, Varamin, Iran