

Synthesis of amine-functionalized methacrylic acid-g-poly(ethylene terephthalate) fiber and its Congo red removal ability

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Abstract The two kinds of amine-type adsorbents were synthesized by reacting hexamethylenediamine (HMDA) and tetraethylenepentamine (TEPA) with methacrylic acid-g-poly(ethylene terephthalate) (MAA-g-PET) fiber for the removal of Congo red (CR) dye from an aqueous solution. The effect of solvents (toluene, ethanol, 2-propanol, and water) on modification of carboxylic acid group of MAA-g-PET fiber to amine groups (HMDA and TEPA) was investigated. Ethanol and 2-propanol provided a higher amination amount of PET fibers for HMDA and TEPA, respectively. The amination amount of PET fibers increased with increasing concentration of amine (vol%) and graft yield. Effect of various parameters such as pH, graft yield, treatment time, and initial dye concentration on the removal amount of CR on chelating fiber was studied. The removal of CR was higher on the TEPA-MAA-g-PET fiber than on HMDA-MAA-g-PET fiber. The effective pH was 3 for adsorption on HMDA-MAA-g-PET fiber and 6 for adsorption on TEPA-MAA-g-PET fiber. The maximum removal capacities of HMDA-MAA-g-PET fiber and TEPA-MAA-g-PET fiber were 11 and 21 mg/g fiber adsorbent for CR. Consequently, the amine-functionalized MAA-g-PET fiber has demonstrated potential as an effective adsorbent for the removal of acidic dyes from aqueous media.

Keywords Poly(ethylene terephthalate) fibers · Graft copolymerization · Removal · Congo red · Amine modification

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Introduction

There is an undesirable amount of synthetic dyes in the wastewater from various industries such as textile, paper, rubber, plastics, paints, printing, inks, leather, food, drug, and cosmetic, which is released directly into the environment without pre-processing. The industrial wastewater containing synthetic dyes is among the most dangerous organic water pollutions, which is a threat to human and environment health. Even a very small amount of synthetic dye in water is highly visible and can be toxic to life in water [1]. The effective removal of synthetic dyes from wastewater has been one of the major issues owing to their toxicities. Therefore, chemical and physical methods of synthetic dyes removal have been studied [2, 3]. Adsorption process is the most widely used physicochemical treatment to remove synthetic dyes from wastewater due to its simplicity, low cost, efficiency, and high selectivity. Several adsorbents have been tried for synthetic dye removal [4, 5]. New adsorbents have been widely investigated because it is highly desirable to develop novel adsorbents with large surface area, active functional groups, high adsorption capacity, and fast separation [6].

Synthetic dyes can be removed by the adsorption on polymers through physical and chemical modification [7]. In recent years, research interest has been focused on synthesizing fibrous polymers having different functional groups such as amine, amide, carboxylic acid, epoxy, pyridine, and hydroxyl for use in removal of various pollutants [8, 9]. This is mainly attributed to the relatively large external specific surface area, high adsorption kinetics, effective functional groups, and low cost of these polymer fibers [10]. The fibrous polymers having functional groups can be obtained by graft copolymerization of vinyl monomers with different functional groups.

Poly(ethylene terephthalate) (PET) fibers are one of the most important synthetic fibers and are widely used in many different industries. PET fibers have good properties but do not contain chemically reactive groups. Certain desirable functional groups can be imparted to PET fibers by grafting. Chelating PET fibers are a preferred alternative adsorbent due to their low cost, simple processing, variety of structural and surface properties, chemical stability, high removal capacity, and kinetics. Our previous investigations have shown that PET fibers are good fibrous polymeric material for the removal of different types of heavy metal ions and synthetic dye [8, 11].

In the study, methacrylic acid (MAA) was grafted onto PET fibers by chemical method. The carboxylic acid groups of MAA-*g*-PET fibers were converted to amide and amine adsorbent using hexamethylenediamine (HMDA) and tetraethylenepentamine (TEPA) by chemical modification. Removal of Congo red (CR) dye from aqueous solution by HMDA-MAA-*g*-PET fibers and TEPA-MAA-*g*-PET fibers was investigated. Amine-MAA-*g*-PET fibers may be a preferred alternative adsorbent due to their low cost, simple processing, variety of structural and surface properties, chemical stability, high removal capacity, and kinetics.

Experimental

Materials

The polyester (PET) fibers (122 dTex) were from SASA Co. (Turkey). The models were cleared for 10 h by dimethyl ketone and dried in an oven at surrounding temperature. Benzoyl peroxide was doubly recrystallized from chloroform in methanol and dried. Other reagents were used as received. Total chemicals were Merck products.

Swelling procedure

The fibers were immersed in dichloroethane at 90 °C for 2 h. The swollen fibers were wiped with cleansing tissue to remove dichloroethane and placed in the polymerization medium [10].

Graft copolymerization process

Graft copolymerization was allotted in a three-necked polymerization glass tube. The polymerization tube containing PET fiber of about 0.3 g, acceptable quantity of MAA monomer, and benzoyl peroxide at needed concentration in 2 mL of dissolving agent (acetone) was made up to 20 mL with demineralized water. The polymerization tube was instantly placed into the water bathtub adjusted to the polymerization temperature (at 85 °C). At the tip of the preset chemical change time (2 h), the grafted fibers were taken out and residual solvent, monomer and homopoly (MAA) were removed with methanol for 8 h. The modified fibers were then dried at 25 °C for 24 h and weighed. The graft yield (GY) was calculated from the weight increase in grafted fibers as follows:

$$\text{GY}(\%) = [(m_g - m_i)/m_i] \times 100 \quad (1)$$

where m_i and m_g represent the weights of the original and grafted fibers, respectively.

Preparation of amine-MAA-g-PET fibers

MAA-g-PET fibers were immersed in 30 mL of 50% (v/v) amine (HMDA, TEPA) in solution (water, toluene, ethanol, and 2-propanol). The contents were shaken at 110 rpm for 60 min at 30 °C using orbital shaker (Selectra). Then, the aminated fibers were separated from the amine solution and washed with methanol. Subsequently, the aminated fibers were washed repeatedly with deionized water. Aminated fibers were vacuum dried at 50 °C for 24 h and weighed. The amount of amine (%) was calculated from the weight increase in aminated fibers as follows:

$$\text{Amine}(\%) = [(w_s - w_g)/w_s] \times 100 \quad (2)$$

where w_g and w_s denote the weights of grafted PET fibers and aminated MAA-g-PET fibers, respectively.

FTIR spectra

FTIR spectra of ungrafted, MAA-grafted and aminated PET fibers were obtained. The fibers were cut into roughly 1 mm size, mixed with KBr, and then pressed. The spectra were recorded on a Bruker Vertex 70 V FTIR photometer.

Scanning electron microscopy analysis

Scanning electron microscopy (SEM) analysis was carried out to research the surface morphology of original and MAA-g-PET fibers employing a JEOL Model JSM 5600 scientific instrument. The fibers were covered with a thin evaporated layer of gold and SEM was performed.

Removal process

A volume of 25 mL of CR solution was added onto a certain amount of aminated MAA-g-PET fiber adsorbent in a glass container. The ingredients were agitated on a shaker (Selectra) set at 110 rpm for a fixed period at 25 °C. The charged adsorbent was separated and cleaned. The pH of the solution was adjusted to 6.8, the remaining CR was analyzed employing UV/visible photometer ($\lambda = 497$ nm, Perkin Elmer Lambda 25). The amount of CR dye adsorbed by the adsorbent was analyzed using the following equation:

$$q \text{ (mg g}^{-1}\text{)} = (C_o - C_e)V \text{ (L)}/w \text{ (g)} \quad (3)$$

where C_o is the initial dye concentration (ppm), C_e is the last concentration of dye solution, V is the volume of the dye solution used, and w is the quantity of the adsorbent used.

Desorption of aminated MAA-g-PET fibers

Desorption of CR dyes was studied with 25 mL of 1 M KOH, NaOH, and Ca(OH)_2 . The dye was desorbed in 45 min., then diluted with water, and analyzed as above. The desorption percent was calculated employing the following equation:

$$\% \text{Desorption} = \frac{\text{Amount of CR dye (mg) desorbed}}{\text{Adsorbed amount of CR dye (mg) by adsorbent}} \times 100 \quad (4)$$

Results and discussion

The aim of the current study is the novel practice of an effective fiber containing amine groups to removal a hazardous CR dye. First, poly(ethylene terephthalate) (PET) fibers were grafted with methacrylic acid (MAA-g-PET) after MAA-g-PET fibers were aminated with HMDA and TEPA. Amine functional groups were placed

into graft copolymer chains. Modified PET fibers were characterized by scanning electron microscopy (SEM) and FTIR spectra.

SEM analysis

Scanning electron micrograph is a primary instrument to characterize the surface morphology of the PET fiber surface. We examined the surface morphologies of ungrafted and grafted PET fibers by SEM and observed a significant change in the surface morphology of the MAA-*g*-PET fiber (Fig. 1). The surface of ungrafted PET fibers appeared clean, smooth, and relatively homogenous, and grafted fibers appeared rough and heterogeneous; this change can be ascribed to the grafting reaction.

Amination of MAA-*g*-PET fibers

HMDA and TEPA were attached to MAA-*g*-PET fibers to make chelating PET fibers having various amino groups by varying conditions such as solvent, concentration, and graft yield. Figure 2 shows the effect of different solvents on amination of carboxylic acid groups to amine groups (HMDA, TEPA) on MAA-*g*-PET fibers. The maximum values of conversion of carboxylic acid groups to HMDA and TEPA were obtained with ethanol and 2-propanol as solvents, respectively. The lowest values of conversion of carboxylic acid groups to HMDA and TEPA are obtained with water as solvent. The conversion of carboxylic acid groups to HMDA and TEPA depends on nature of the solvent. The effect of the amine concentration in solvent on the attached amount of amine (%) was investigated at 25 °C. The results are shown in Fig. 3. The amine (%) increases significantly by increasing the amine concentration in solvent up to 50% (v/v) and then MAA-*g*-PET fibers were deformed. The effect of graft yield on the attached amount of amine (%) was

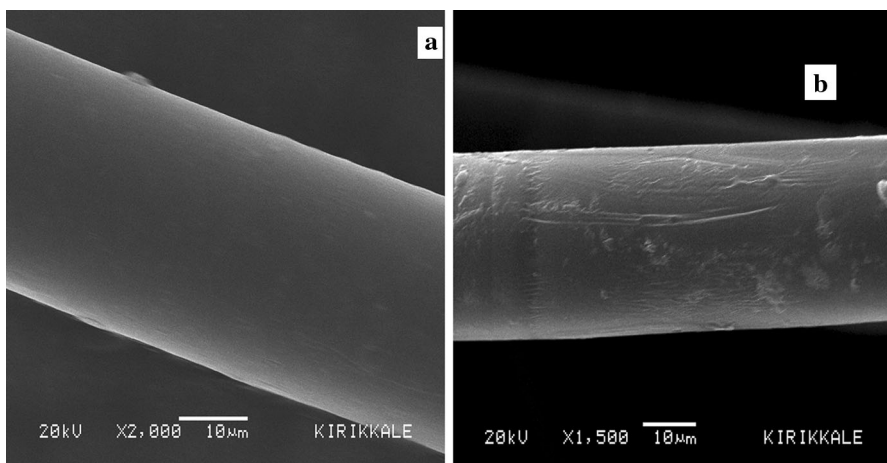


Fig. 1 SEM photographs of **a** original and **b** MAA-*g*-PET fibers (150%)

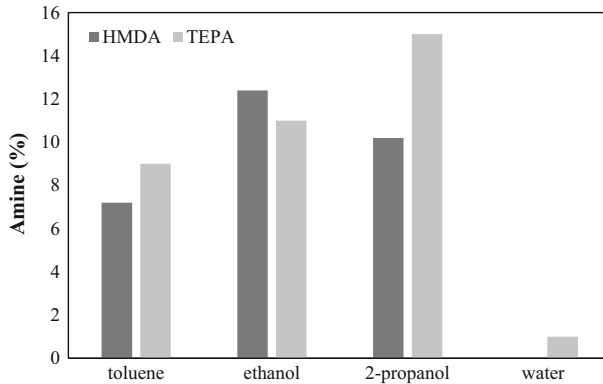


Fig. 2 Effect of solvent on modification of carboxylic acid group to amine groups on MAA-g-PET fiber: amine = 50% (v/v); graft yield = 70%; $T = 30\text{ }^{\circ}\text{C}$; $t = 60\text{ min}$

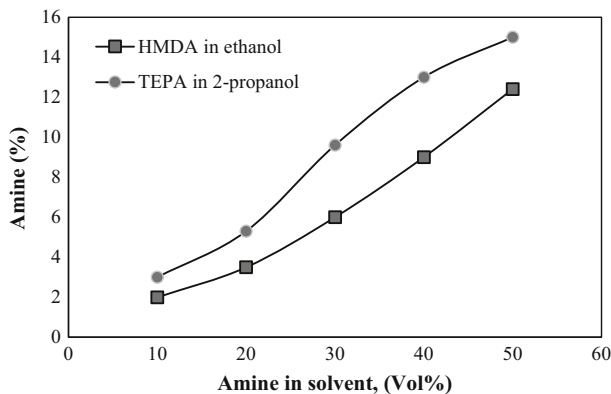


Fig. 3 Effect of the amine concentration in solvent on the attached amount of amine (%): graft yield = 70%; $T = 30\text{ }^{\circ}\text{C}$; $t = 60\text{ min}$

investigated. The results are shown in Fig. 4. The amine (%) increases significantly by increasing the graft yield up to 100 and 150% for HMDA and TEPA, respectively, then falls down upon further increase in graft yield. The number of carboxyl groups increased with increase in the graft yield. However, decreasing trend may be due to the graft layer thickening with the increase in the graft yield [3].

FTIR spectrum

The FTIR spectra of original, MAA-grafted, and amino-functionalized fibers are given in Fig. 5. After the amination, the new characteristic peaks were observed at 1539 cm^{-1} (Fig. 5), related to N–H bonding vibration. In spectra of aminated PET fibers (Fig. 5), the absorption peaks originating from C=O groups of amide at 1627 cm^{-1} and COOH group of MAA and COOR of PET fiber units at 1720 cm^{-1}

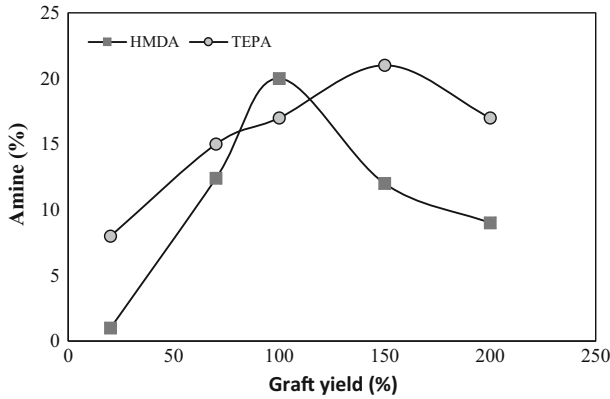


Fig. 4 Effect of the graft yield on the attached amount of amine (%) on MAA-g-PET fiber: amine = 50% (v/v); $T = 30\text{ }^{\circ}\text{C}$; $t = 60\text{ min}$

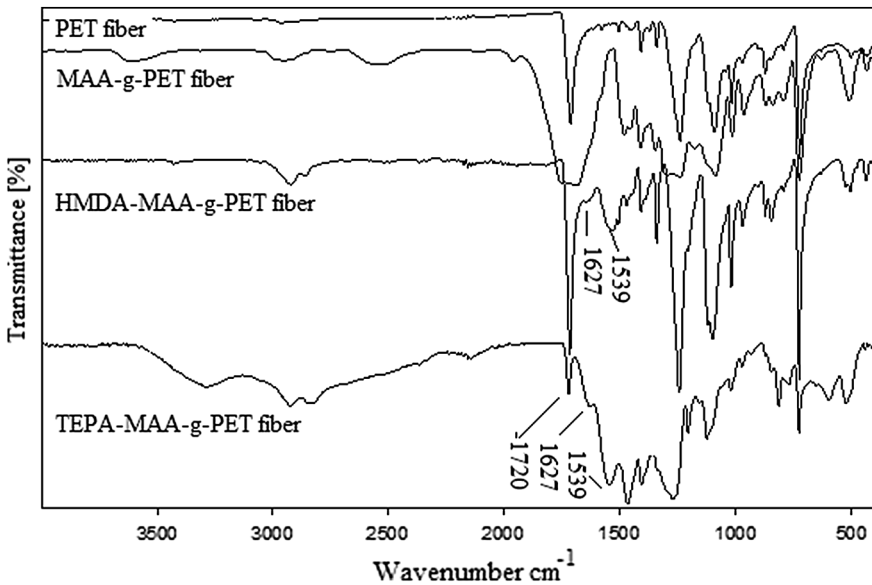


Fig. 5 FT-IR spectra of PET fibers

are present. Hence, FTIR results confirm that the amine groups attached to the MAA-g-PET fibers and certain chemical bonds were formed [12, 13].

Effect of pH

The pH value of the synthetic dye solution is a very important parameter in investigating removal process. Solution pH not only influences the surface property of the aminated PET fibers but also affects the CR dye. The uptake of CR as a

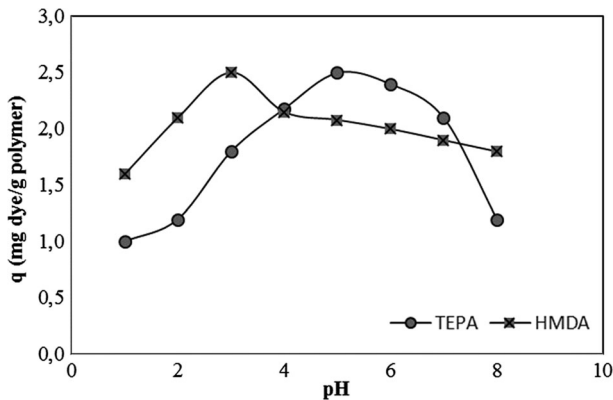


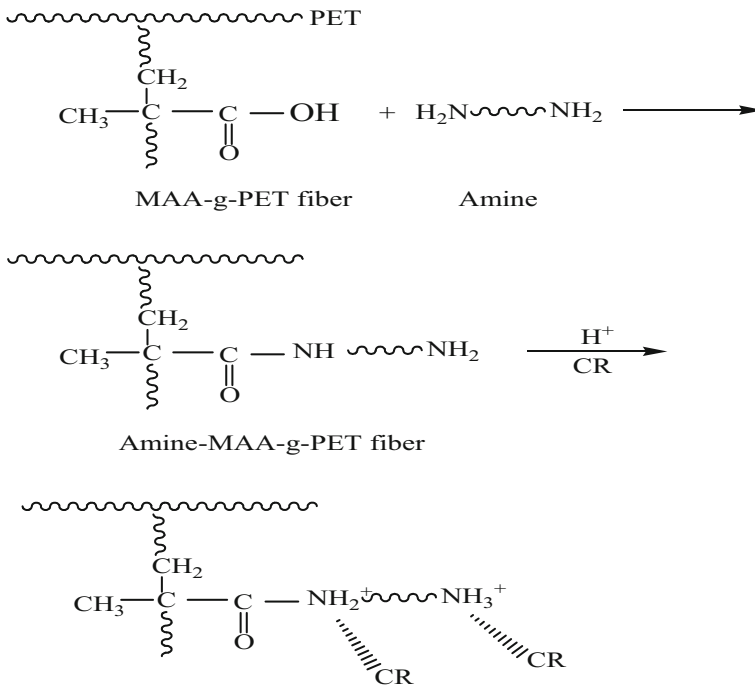
Fig. 6 Effect of the pH on removal

function of pH values was investigated (Fig. 6). HMDA-MAA-g-PET and TEPA-MAA-g-PET fibers were incubated for 60 min with aqueous CR solution (10 ppm) adjusted to required pH values in the range of 1–8 using buffer solution (Britton–Robinson buffer). It can be seen from the figure that increasing the pH value of the CR aqueous solution increases the removal amount significantly and reaches a maximum value at pH 3 and 6 for HMDA-MAA-g-PET and TEPA-MAA-g-PET fibers, respectively, beyond that point it decreases [14–16]. Amine-MAA-g-PET fibers removed 100% of CR dye (10 ppm) at optimum pH.

To explain the observed behaviour of CR removal with various pHs, two possible mechanisms of removal of CR on amine-MAA-g-PET fibers may be considered such as electrostatic interactions and chemical reactions that are responsible for removal on aminated PET fibers surfaces. The dye solution is acidified by strong acid (HX), and the surface of the amine-MAA-g-PET fibers of the positively charged interface will be associated with X^- ions. There is competition between X^- (at a low pH) and anionic ions of CR for positively charged removal sites. At optimum pH, a significantly high electrostatic interaction exists between the positively charged surface of the fibers adsorbent and CR dye. As the pH of the dye solution increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface sites on the fiber adsorbent does not favour the removal of CR. At an alkaline pH, the removal of the CR dye on the fibers adsorbent occurs. This suggests that chemisorption might be effective [17]. This is illustrated in Scheme 1 and Fig. 7.

Effect of contact time

The contact time to reach removal equilibrium is a very significant factor to know when removal process is used in aqueous medium treatment. The rapid removal of the dye by the fiber adsorbent is significant for practical use. The effect of contact time between CR dye and aminated PET fibers was studied. Figure 8 shows the amount of CR dye adsorbed by amine-MAA-g-PET fiber adsorbent from aqueous



Scheme 1 Removal of CR dye on the adsorbent

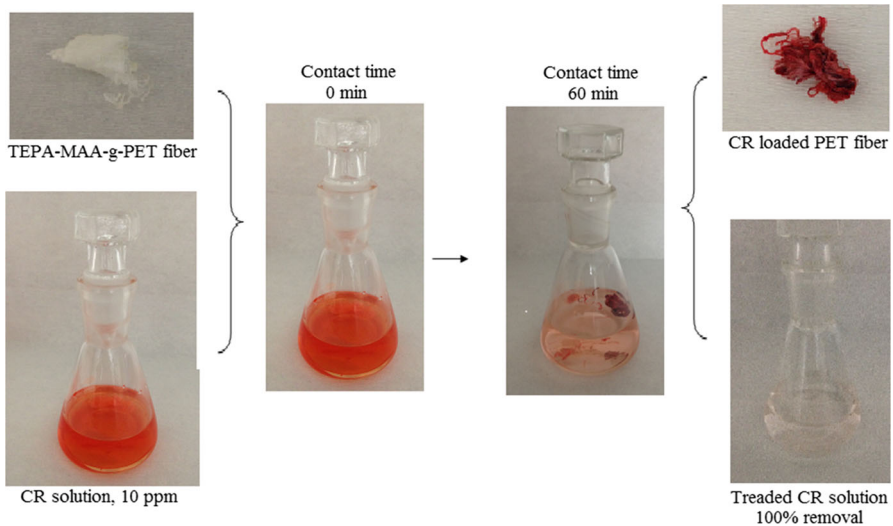


Fig. 7 Photograph showing the CR dye removal process

solution. It is observed that the removal takes place rapidly at first, then slows down and levels off. The removal equilibrium was attained within 45 min. Generally, removal kinetics includes two stages: the first initial removal stage is rapid and

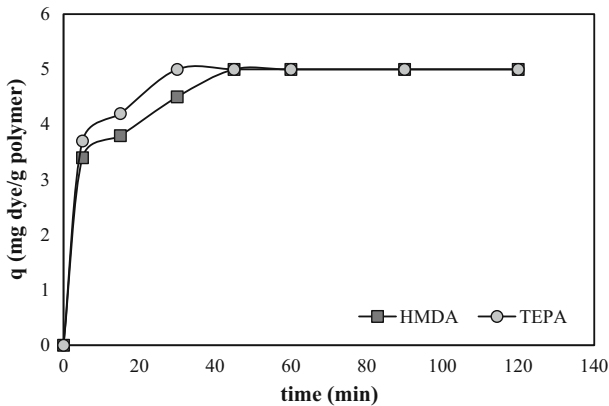


Fig. 8 Adsorption time of CR dye on aminated MAA-g-PET fibers

contributed to equilibrium uptake. It is thought to be outer surface removal due to the availability of many active removal sites. The second stage is slower and interpreted to be a gradual removal stage [18].

Effect of dye concentration

Removal capacity of a fiber adsorbent is dependent on the initial concentration of the adsorbed synthetic dye. The effect of initial concentration on the removal of CR dye by HMDA-MAA-g-PET and TEPA-MAA-g-PET fibers was studied at 25 °C by varying CR concentration from 10 to 200 mg L⁻¹. As shown in Fig. 9, the removal rapidly increased with increasing initial CR concentration then slows down. The removal capacities of the HMDA-MAA-g-PET and TEPA-MAA-g-PET fibers are 11 and 21 mg g⁻¹, respectively. TEPA-MAA-g-PET fibers were highly adsorptive for CR in aqueous solution.

This may be explained by the availability of many removal binding sites during initial stage. However, at higher initial concentrations significant effect was not

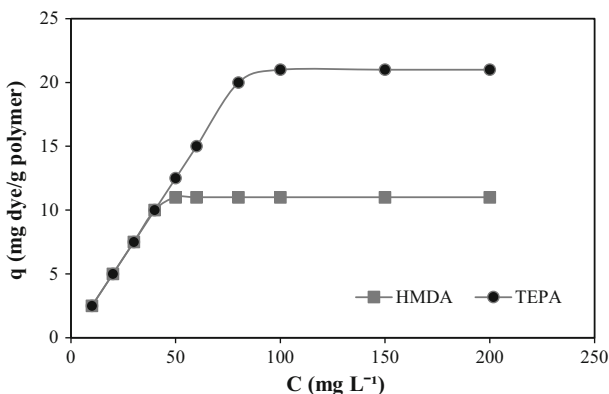


Fig. 9 Sorption of CR dye with amine-MAA-g-PET fibers at different dye concentrations

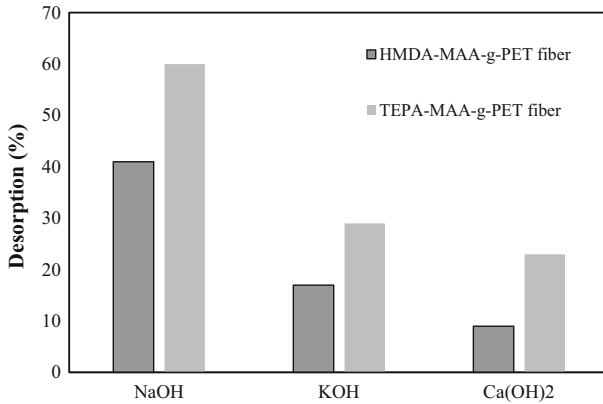


Fig. 10 Effect of solution types on the desorption of CR-loaded fiber adsorbents

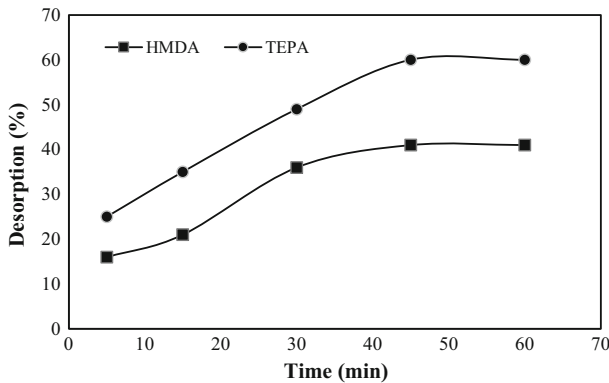


Fig. 11 Effect of time on desorption

observed, likely due to the saturation of the active sites on the aminated PET fiber adsorbent surfaces. Aminated PET fibers have $-NH_2$ groups which are polar and very hydrophilic, while CR is water soluble and has polar amino groups and sulfonic groups in the structure. Therefore, aminated PET fibers displayed very high adsorption capacity. The increase of the removal capacity is mainly due to the presence of such interaction as ion change and hydrogen bonding between the amino groups of the fibers adsorbent and functional groups presented in the CR dye. Aminated PET fiber adsorbent possesses higher surface area and a high number of active sites [19, 20]. Therefore, it would be an interesting alternative and an economical industrial fibrous adsorbent.

Desorption studies

Aminated fiber adsorbents did not adsorb CR dye significantly at $pH > 8$, suggesting that the adsorbed CR dye on the fiber adsorbents may be possibly desorbed in a

basic solution with a high pH value. Therefore, the adsorbed CR dye was desorbed by treatment of the HMDA–MAA-g-PET and TEPA–MAA-g-PET fibers with the different basic solutions (1 M) shown in Fig. 10. The highest desorption amounts were obtained with NaOH. At 25 °C within 45 min (Fig. 11), the highest desorption percentages were found as 41 and 60% for HMDA–MAA-g-PET and TEPA–MAA-g-PET fibers, respectively. The investigation in the desorption studies confirms the mechanism of removal stated in the pH effect.

Conclusions

Fibrous adsorbents containing amine (HMDA, TEPA) groups were prepared by a reaction between amine and carboxylic acid group on MAA-g-PET fibers prepared by grafting MAA monomer onto PET fibers. Removal of CR dye from aqueous solution by HMDA–MAA-g-PET and TEPA–MAA-g-PET fibers was investigated. The maximum value of modification of carboxylic acid groups to HMDA and TEPA on MAA-g-PET fibers was obtained at graft yield 100 and 150%, respectively. Among the different solvents, ethanol for HMDA and 2-propanol for TEPA were found to be good solvents for modification of carboxylic acid groups on MAA-g-PET fibers. It was observed that pH is the most important parameter. The removal rates of CR dye were much higher on the TEPA–MAA-g-PET fibers than on HMDA–MAA-g-PET fibers. TEPA–MAA-g-PET fibers removed 100% of CR dye (up to 80 ppm) at optimum pH. A treatment time of 45 min was sufficient to reach the adsorption equilibrium value. It was recognized that TEPA–MAA-g-PET fibers are alternative adsorbent for CR dye removal from aqueous solution. Thus, the fibrous adsorbent should be addressed for other acidic dyes. In the future, the amine-functionalized MAA-g-PET fiber can be used as an effective adsorbent for the removal of acidic dyes from wastewater.

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