Preparation and Characterization of Strong Cation Exchange Terpolymer Resin as Effective Adsorbent for Removal of Disperse Dyes

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In this study, (hydroxypropylmethacrylate-*co*-ethyleneglycol dimethacrylate-*co*-glycidylmetharylate) terpolymer resin functionalized with sulfonic acid groups was prepared and used as cation exchange resin for removal of two different disperse dyes (i.e., Direct Red R [DR-R] and Disperse Violet 28 [DV-28]) from aqueous solution. The properties of the adsorbent were determined using Fourier transform infrared, dynamic light scattering, scanning electron microscopy, and Brunauer, Emmett, and Teller methods. The maximum adsorption capacity of the resin for the DR-R and DV-28 was found to be 86.1 and 179.6 mg/g, respectively. Desorption study was realized to evaluate the reusability of the resin and the percent desorption from the resin for DR-R and DV-28 dyes was found to be approximately 89.4% and 91.7%, respectively. The experimental data were evaluated using different kinetics and isotherm models. These results show that the experimental data could be designated with the second-order kinetic model and both Langmuir and Temkin isotherm models. Finally, the presented resin was able to remove large amounts of organic pollutants in a short process time with a low amount of adsorbent. Thus, it was shown that the prepared resin has high potential for use as an effective and sustainable adsorbent for the treatment of industrial wastewater.
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INTRODUCTION

Mostly industrial wastewaters have been discharged into the aqueous ecosystems and various treatment technologies have been developed according to the chemical properties of the pollutants. Removal of the dyes from textile wastewaters were not achieved to desired level with the existing conventional treatment technologies. On the other hand, natural treatment systems are insufficient to remove or neutralize these substances [1–4]. In particular, most textile products containing aromatic amines and benzidine are known to be toxic to living things [5, 6]. The largest elements of textile dyes consist of azo group dyes. Among these, disperse dyes contain one or more azo bonds as color-forming chromophore groups and they also contain functional groups such as $-NH_2$ and $-SO_3H$ [7–10]. The dyes to be used in the textile industries should be selected by considering the possibility that they will produce metabolites in the mammalian systems [9–13]. Some aromatic amines used in the synthesis of azo dyes cause bladder, lung, and soft tissue cancer and these have been confirmed by laboratory toxicity tests [14, 15]. Carcinogenic or mutagenic synthetic organic molecules could be originated after metabolic transformation of the pollutants molecules. These nucleophilic molecules interact with electron-rich regions in DNA and cause mutation and cancer. Additionally, the presence aromatic ring substitutions in a molecule increase its hydrophobic character as well as its carcinogenic potential [16, 17].

Several methods have been presented for the treatment of contaminated waste water, including adsorption, chemical precipitation, electrochemical reduction, and reverse osmosis [18–22]. Among them, adsorption has several advantages such as economy, design and working flexibility, effectiveness, efficiency, and high removal efficiency of pollutant in a short time. A wide variety of adsorbents (such as natural or synthetic) have been used for removal of organic or inorganic pollutants and these adsorbents have been used repeatedly in the adsorption studies. For dye removal, conventional adsorbents include chitosan, zeolite, kaolinite, montmorillonite, graphene oxide, modified porous silica, synthetic terpolymer resin [18–23], and biological biomasses [4, 7] have been used. Using of synthetic polymer for preparation of adsorbents provide some outstanding properties. For example, they can be easily prepared in suitable forms such as films, membranes, and microbeads and they can be repeatedly used in the adsorption tests [12, 13]. The later crosslinked synthetic porous microbeads are mainly preferred for the preparation of adsorbents due to their high surface areas, porosity, ease of preparation with required size, high stability, greater mobility and easy recovery from medium [12, 13]. In addition, glycidylmethacylate (GMA) has a reactive pendant epoxide ring and is appropriate for the preparation of functionalized porous microbeads with desired size, and also its polymer surface can be easily modified into various functional groups via ring opening reaction. Thus, the GMA permits attachment of various ligands or macromolecules under mild experimental conditions which have amine or thiol groups.

For the removal of organic dyes by adsorption method, a high adsorption capacity is expected to be reached in a short processing time. The efficiency of the dye removal capacity of an adsorbent is highly dependent on the presence and properties of the functional groups on the surface of the adsorbent [24–29]. According to the characteristics of these groups, the interaction between a pollutant and an adsorbent can be physical or chemical, depending on the nature of the adsorption [24–29]. The adsorption of various dyes onto sulfonated and other adsorbents has been studied extensively. For examples, Zarezadeh-Mehrizi et al., [1] prepared sulfonate-functionalized nanoporous silica spheres by conversion of epoxide to sulfonate with sulfonic acid salts. The equilibrium adsorption data were described by the Langmuir isotherm.

Additional Supporting Information may be found in the online version of this article.

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A maximum monolayer sorption capacity for methylene blue dye was found to be 208 mg/g. Ghamsari and Madrakian [7] synthesized sulfonated activated carbon by using nitric acid and concentrated sulfuric acid. The adsorbent was used for removing of methylene blue, crystal violet, and thionin acetate dyes from aqueous solutions. The experimental data were well described by the Freundlich adsorption isotherm. Zhou et al. [10] prepared a water-soluble sulfonated poly(arylene ether nitrile) polymer. The functional carboxyl, sulfonic acid, and rigid benzene rings were crosslinked using aluminum (III) ions. The prepared adsorbent was used for removal of three cationic dyes (i.e., Rhodamine B, neutral red, methylene blue) and three anionic dyes (i.e., Orange G, methyl orange, acid fuchsin). The adsorbent was highly efficient in selective adsorption for cationic dyes. Zhao et al. [29] prepared a composite membrane from poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)/cellulose acetate and coated with chitosan and the composite membranes morphology, mechanical properties, and ultrafiltration performance were evaluated. The composite membrane was used to remove disperse dye and metal ion for water purification, and, the membrane exhibited high durability, low operating pressure, and had environmentally friendly fabrication process.

Direct Red R (DR-R) and Disperse Violet 28 (DV-28) dyes are benzidine-derived and anionic diazo dyes [7, 26, 29]. These textile dyes are resistant to biological and chemical degradation methods due to their complex aromatic structures. Since these dyes have high persistence in the wastewater, they will preserve their toxicity for a long period of time, therefore, many studies have been conducted on the removal of the disperse dyes.

In this work, a new strong cation-exchange resin was prepared (i.e., (hydroxypropylmethacrylate-*co*-ethyleneglycol dimethacrylate-*co*-GMA) [HPMA-co-EGDMA-*co*-GMA]) via suspension polymerization. The surface of the (HPMA-*co*-EGDMA-*co*-GMA) resin was functionalized with sulfonic acid groups to prepare cationic (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin. It was characterized using various imaging, spectrometric, gravimetric, and analytical techniques. Adsorption of DR-R and DV-28 dyes from aqueous solutions with cation-exchange resin was studied to determine the optimization of different experimental parameters. The experimental data were analyzed using different adsorption isotherms and kinetics models. The thermodynamic parameters were also determined.

EXPERIMENTAL

Chemicals

GMA (2,3-epoxypropyl methacrylate), HPMA, EGDMA, poly(vinyl alcohol) (PVA), α,α-azobis(isobutyronitrile) (AIBN), DR-R, and DV-28 were obtained from Sigma (St. Louis, MO). The characteristic properties of DR-R and DV-28 dyes were presented in Table S1. Sodium sulfate and isopropyl alcohol were supplied from Merck A.G. (Darmstadt, Germany).

Preparation of (HPMA-co-EGDMA-co-GMA) Microbeads

The crosslinked (HPMA-*co*-EGDMA-co-GMA) terpolymer with reactive epoxy groups were synthesized from GMA, HPMA, and EGDMA monomers via suspension polymerization. The continuous phase was prepared using purified water (100 mL), PVA (20 mL, 5.0%) and NaCl solution (150 mL, 1.0 mol L^{-1}) and transferred to a three-necked reactor (500 mL). Then, the reactor was equipped with a mechanical stirrer, a reflux condenser, and an on line N_2 gas system. The reactor was placed in a water bath and polymerization mixture (i.e., HPMA [5.0 mL], EGDMA [5.0 mL], GMA [10 mL], isopropyl alcohol [10 mL], and AIBN [100 mg]) was added into reactor using a dropping funnel. Then, the polymerization reaction was carried out at 70°C for 2.0 h under nitrogen atmosphere while continuous stirring at 250 rpm. After this period, the system temperature was raised to 85°C and reactor was further operated for 1.0 h. After this process, the reactor was cooled down to room temperature and the formed microbeads were collected by filtration and washed with ethanol (70%, 250 mL) under continuous stirring for 3.0 h to remove polymerization impurities. Then, the product was dried under reduced pressure at 25°C for 24 h. The resulting reactive epoxy groups bearing microbeads were referred as (HPMA-*co*-EGDMA-*co*-GMA).

Preparation of Strong Cationic Groups Containing (HPMA-co-EGDMA-co-GMA)-SO_3H Terpolymer Resin

The (HPMA-*co*-EGDMA-*co*-GMA) terpolymer from above step (10.0 g, 75–150 μm size) were transferred into anhydrous methanol, ethanol, and isopropyl alcohol mixture (1:1:1, v/v ratio, 150 mL) and stirred at 25°C for 2.0 h. Then, $NaHSO_3$ (2.0 mol/L) and Na_2SO_3 (2.0 mol/L) solutions (60:40 ratio, 10 mL) were added to the above mixture. The reaction of epoxy groups with $NaHSO_3$/Na_2SO_3 salt has been reported in the earlier studies [30–34]. The temperature was raised to 50°C and kept 2.0 h at this temperature. At the end of the modification process, the modified resin with sulfonic acid groups was collected and washed with ethanol (70%, 250 mL) and purified water. The functionalized (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H was referred as terpolymer resin. Available epoxy groups of the terpolymer microbeads were converted into hydroxyl groups, and used as a control system in the dyes adsorption experiments. To hydrolyze epoxy groups into hydroxyl groups, the (HPMA-*co*-EGDMA-*co*-GMA) terpolymer was transferred into H_2SO_4 solution (0.5 mol/L, 50 mL) and stirred at 50°C for 2.0 h. Then, it was dried at room temperature for 24 h.

Characterization Studies

The amount of accessible oxiran groups of the (HPMA-*co*-EGDMA-*co*-GMA) terpolymer microbeads was determined using the pyridine–HCl method given in the literature [14]. For this purpose, the microbeads (0.5 g) were reacted with pyridine–HCl solution (50 mL) under reflux for 20 min. Then, the sample was titrated with NaOH solution (0.1 mol/L) in the presence of phenolphthalein indicator. The amount of sulfonic acid groups of the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin was determined with a titrimetric method. For this purpose, approximately 0.1 g resin was transferred into NaOH solution (0.1 mol/L, 20 mL) and stirred at 25°C for 6 h. Then, the sample was titrated with HCl solution (0.05 mol/L).

The dried (HPMA-*co*-EGDMA-*co*-GMA) terpolymer microbeads were sieved by sieve shaker using molecular sieves (52, 75, 150, 212, 300, 425 μm) and the size distribution was determined by weighing the resin of each size. Mean particle diameter of the (HPMA-*co*-EGDMA-*co*-GMA) terpolymer in the range 75–150 was determined by a dynamic light scattering instrument (DLS-Nano ZS, Zetasizer; Malvern Instrument Ltd., Malvern, UK). The specific surface area of (HPMA-*co*-EGDMA-*co*-GMA) and

(HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin was measured with a surface area apparatus (AUTOSORPII 6B; Quantachrome Instruments) and calculated using the Brunauer, Emmett, and Teller (BET) method.

The surface morphology of the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin was determined by scanning electron microscopy (SEM). The dry samples were coated with thin gold layer under reduced pressure. The SEM micrographs were obtained using scanning electron microscope (JMS 5600; JEOL, Tokyo, Japan). The attenuated total reflection-Fourier transform infrared (ATR-FTIR) measurements of (HPMA-*co*-EGDMA-*co*-GMA) and (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin were performed using an ATR-FTIR spectrometer (Spectrum 100; PerkinElmer Inc., Norwalk, CT) equipped with a universal ATR accessory. Samples were screened between 4,000 and 525 cm^{-1}. Prior to FTIR measurements, samples were incubated at 40°C in a vacuum oven overnight.

Hydrolysis or release of the sulfonate groups from the terpolymer resin were investigated in 0.1 mol/L HCl or NaOH solution. The terpolymer resin was stirred for 18 h at room temperature in these medium. After this period, the terpolymer resin was removed and washed with deionized water, and the concentration of the sulfonate groups on the terpolymer resin was determined with a titrimetric method as described above.

The swelling ratio of (HPMA-*co*-EGDMA-*co*-GMA) and (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin was determined in distilled water. Approximately, 1.0 g of the resin was added in a graduated cylinder and placed in a water bath at 25°C. After 24 h, the height observed in a volumetric cylinder was recorded. The swelling ratio of the terpolymer and terpolymer resin was calculated using the following equation:

$$\text{Swelling ratio} = \text{Measured final height}/\text{first measured height} \quad (1)$$

Adsorption Studies

The adsorption of DR-R and DV-28 dyes on (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin was studied in a batch system. The (HPMA-*co*-EGDMA-*co*-GMA)-OH resin was used for control purposes in the adsorption studies. For the adsorption of DR-R and DV-28 dyes on the resin, the dye solutions in the concentration range of 10–500 mg/L were prepared by diluting the stock dye solutions (1,000 mg/L). In a typical adsorption experiment, 10 mg adsorbent was added in the adsorption medium (10 mL) and stirred at a rate of 150 rpm at 25°C for 2.0 h. After adsorption process, the resin was separated from the adsorption medium by centrifugation at 1,000 rpm for 5.0 min. The remaining concentrations of the DR-R and DV-28 dyes were determined in the resulting supernatant at 498 and 560 nm, respectively. Calibration graphs were prepared for DR-R and DV-28 at different concentrations using a double-beam ultraviolet–visible spectrophotometer (PG Instrument Ltd., Model T80 +; PRC).

The effect pH on the adsorption rate of the DR-R and DV-28 dyes on the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H resin was investigated in the pH range from 3.0 to 8.0. The effect of the ionic strength of the adsorption medium on the removal of DR-R and DV-28 dyes by (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin was studied by adding NaCl in the range of 0.0 and 1.0 mol/L. The effect of sorbent dose on adsorption of DR-R and DV-28 dyes on the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin was realized by varying the amount of adsorbent dosage between 0.1 and 2.0 g/L. The effect of temperature on dye removal efficiency of the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin was investigated at four different temperatures (15°C, 25°C, 35°C, and 45°C). The effect of the initial dye concentration (i.e., DR-R and DV-28) on the adsorption capacity of the (HPMA-*co*-EGDMA-*co*-GMA)-OH and (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin was investigated by changing the initial dye concentration between 10 and 500 mg/L. All experiments were carried out as described above and repeated three times and averaged.

The amount of dye (i.e., DR-R and DV-28) in the medium before and after adsorption was calculated using the calibration curves and the following equation:

$$q = (C_0 - C)\,V/m \quad (2)$$

In this equation, q (mg/g) is the amount of adsorbed dye per gram of resin; C_0 and C are the residual amount of dye in the solution before and after adsorption (mg/L), respectively. V is the volume of solution (L) and m is the dry weight of the resin (g). The percentage removal (removal [%]) of dye from the aqueous medium was calculated using the following equation:

$$\text{Removal}\,(\%) = [(C_0 - C)/C_0] \times 100 \quad (3)$$

Desorption Studies

Sodium hydroxide solution (0.1 mol/L, 20 mL) was used for desorption of DR-R and DV-28 dyes from dye laden resin as a desorption agent. In desorption studies, the temperature and desorption time were 25°C and 2.0 h, respectively. The residual dye concentration in the desorption medium was determined as described above. The amount of dye desorbed from the resin was calculated using *Eq. 4*.

$$\text{The desorption}\,(\%) = [C_{\text{des}}/C_{\text{ads}}] \times 100 \quad (4)$$

where C_{des} and C_{ads} are the desorbed and adsorbed concentration of dye (mg/L), respectively.

In order to determine the reusability of the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin, the adsorption–desorption cycles with the same resin were repeated five times.

RESULTS AND DISCUSSION

Properties of the (HPMA-co-EGDMA-co-GMA) Microbeads

The size distribution of the prepared (HPMA-*co*-EGDMA-*co*-GMA) resin was 52–425 μm using molecular sieves (Fig. S1). The resin in the size fraction of 75–150 μm was used for the modification to sulfonic acid groups. After modification, the particle size distribution of the resin was measured by DLS. The average particle size and of the resin was found to be 113.7 μm. The particle size distribution of the resin was found to be in the range from 79.6 to 156.8 μm, (Fig. 1). As observed in this figure, after modification epoxy groups into sulfonic acid groups, the particle size of the resin was not changed significantly. The surface areas of (HPMA-*co*-EGDMA-*co*-GMA) and (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H functionalized resin were measured by nitrogen gas

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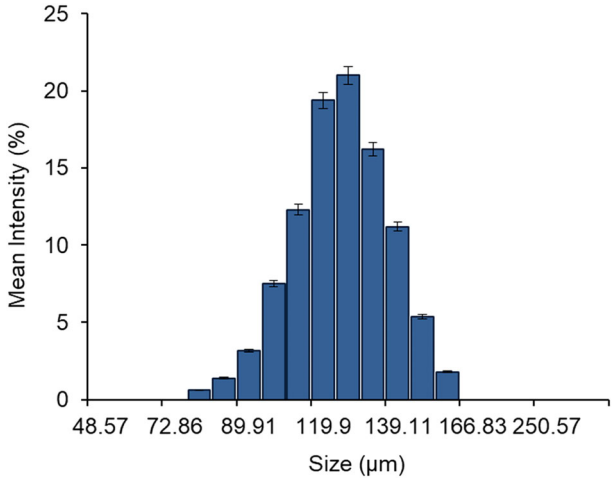


FIG. 1. DLS distribution of (HPMA-*co*-EGDMA-*co*-GMA) terpolymer in the range of 79.6–156.8 μm. [Color figure can be viewed at wileyonlinelibrary.com]

adsorption desorption studies and calculated by the BET method, and the total surface area was found to be 14.3 and 12.1 m^2/g, respectively, and the surface area was decreased approximately 1.18-fold upon introducing sulfonic acid groups. Surface morphology of the (HPMA-*co*-EGDMA-*co*-GMA) resin was investigated by SEM. It has a spherical geometry and smooth surfaces (Fig. 2).

The FTIR spectra of (HPMA-*co*-EGDMA-*co*-GMA) and (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin are given in Fig. 3. For the (HPMA-*co*-EGDMA-*co*-GMA) resin, a characteristic vibration band is observed at around 3,453 cm^{-1} and refers to the stretching vibration of hydrogen bonds between alcohols. The characteristic vibration bands of GMA and EGDMA include methylene and ester configuration vibrations are observed at 2953 and 1,724 cm^{-1}, respectively. The epoxy group gives an epoxy ring vibration band at approximately 909 cm^{-1}. After modification of epoxy groups in to sulfonic acid groups, some new absorption bands are observed. The symmetric and asymmetric stretching vibration bands of the sulfonic acid groups are observed at 1,130 and 1,055 cm^{-1}, respectively, indicate that the sulfonic acid groups were successfully introduced onto the resin structure.

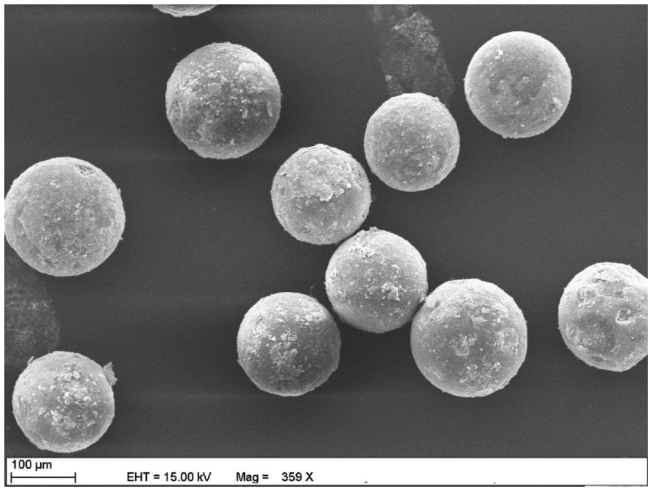


FIG. 2. SEM micrograph of (HPMA-*co*-EGDMA-*co*-GMA) terpolymer.

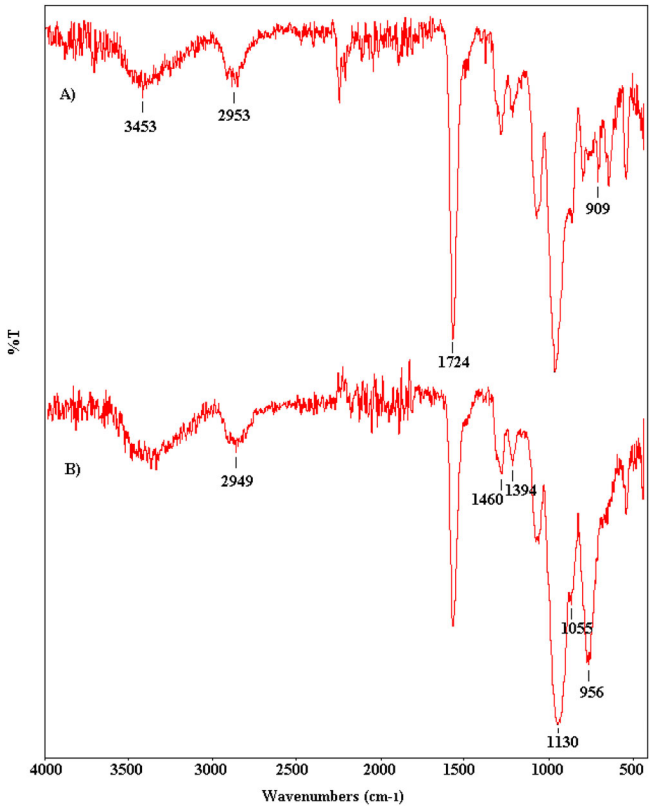


FIG. 3. FTIR spectra: (HPMA-*co*-EGDMA-*co*-GMA) terpolymer (a); (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin (b). [Color figure can be viewed at wileyonlinelibrary.com]

The stretching vibration band at about 956 cm^{-1} is attributed to the S═O bond. The band at around 1,394 cm^{-1} is characteristic stretching vibration of the pendant sulfonic acid groups (S═O).

The equilibrium swelling ratio of (HPMA-*co*-EGDMA-*co*-GMA) and (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin in distilled water was found to be 32.6% and 41.7%, respectively. The GMA units in the structure of the polymeric resin have a low polarity, therefore, it does not well swell in aqueous medium; on the other hand, the HPMA units in the polymer structure has many hydroxyl groups, therefore, more water molecules can be interact with the hydroxyl groups of the (HPMA-*co*-EGDMA-*co*-GMA) microbeads. After modification of epoxy group into sulfonic acid groups, an increase in the swelling ratio of about 1.28-fold was observed due to the presence of net negative charge on the resin structure. The chemistry of (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin is schematically given in Fig. 4. The amount of epoxy groups of (HPMA-*co*-EGDMA-*co*-GMA) terpolymer were calculated to be 3.55 mmol/g, whereas the amount of accessible epoxy group of (HPMA-*co*-EGDMA-*co*-GMA) terpolymer were found to be 2.31 mmol/g by pyridine–HCl method. The sulfonic acid groups of the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin was found to be 2.08 mmol/g. More than 90% epoxy groups were converted into sulfonic acid groups under given reaction conditions.

The hydrolysis or/and leakage of the sulfonate groups from the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin were studied and any decrease in amounts of sulfonate groups were not observed from the terpolymer resin when incubated in 0.1 mol/L HCl or NaOH solutions at room temperature.

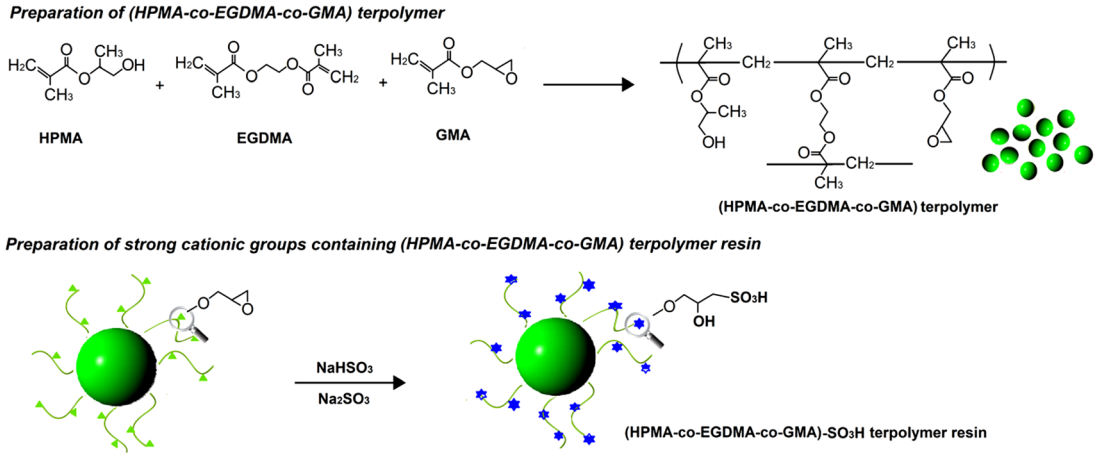


FIG. 4. Chemistry of (HPMA-*co*-EGDMA-*co*-GMA) terpolymer. [Color figure can be viewed at wileyonlinelibrary.com]

Adsorption Studies

The adsorption mechanism of (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin is presented in Fig. 5. The epoxy groups of the (HPMA-*co*-EGDMA-*co*-GMA) terpolymer were converted into hydroxyl group via acid hydrolysis and used as a control system in the presented adsorption system. The surface of the (HPMA-*co*-EGDMA-*co*-GMA) terpolymer microbeads contains only hydroxyl group and which permits only hydrogen bonding interaction with hydrogen donor site of the tested both dye molecules. After modification into sulfonic acid groups, the decoration of pendant sulfonic acid groups on the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin resulted creation of net negative charged on surfaces of the resin. Thus, the acidic sulfonic acid groups of the terpolymer resin interact with the amine groups of the tested both dye molecules mainly via ion-exchange interactions (Fig. 5 and Table S1).

Effect of pH on DR-R and DV-28 Dyes Removal Efficiency

The effect of pH on the adsorption capacity of (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin for DR-R and DV-28 dyes was studied in the pH range of 3.0–8.0 (Fig. 6). As observed from this figure, maximum amounts of DR-R and DV-28 dyes were absorbed at between pH 5.0 and 6.0 on the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H cationic terpolymer resin. The maximum amounts of adsorbed dyes were found to be 58.4 and 98.7 mg/g for DR-R and DV-28 dyes at pH 6.0, respectively, on the cationic resin. As seen from Fig. 6, the amounts of adsorbed dyes were increased with increasing the medium pH from 3.0 to 6.0. Then, the adsorption amount was decreased by further increasing pH. The ionization state of the DR-R and DV-28 dyes and the functional groups on the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H cationic resin surface are mainly influenced by the pH of the solution, and thus, the ionic interactions between the dye and

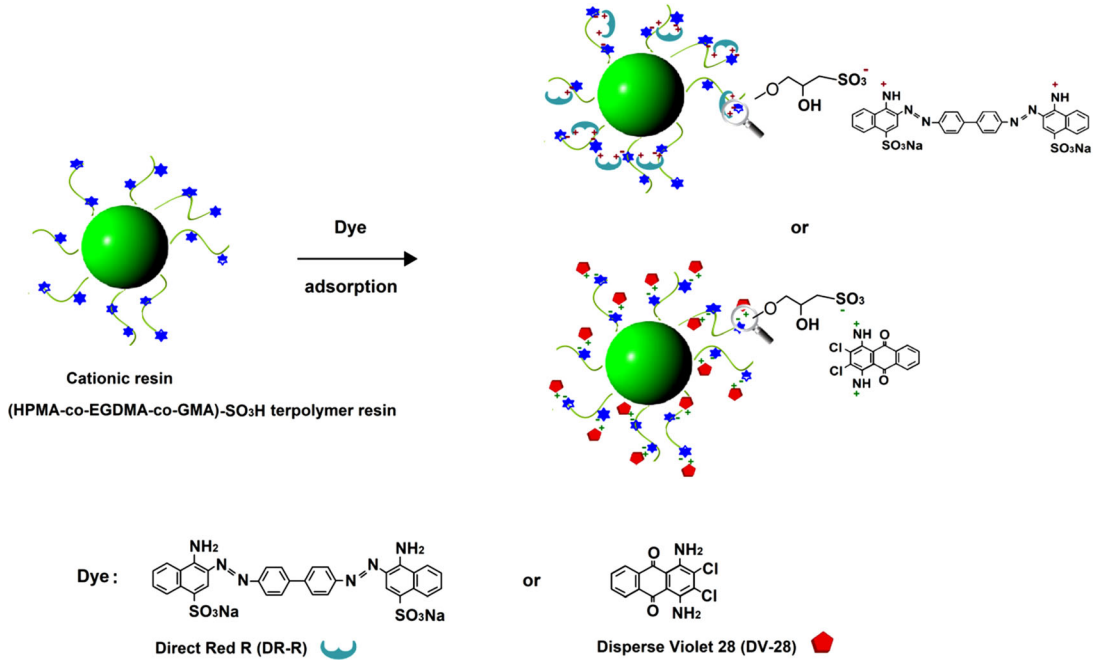


FIG. 5. Adsorption mechanism of the tested dyes on the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin. [Color figure can be viewed at wileyonlinelibrary.com]

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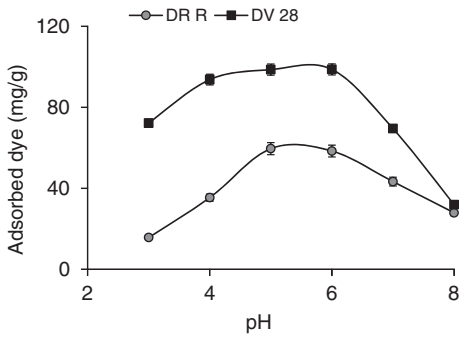


FIG. 6. Effect of pH on disperse dyes adsorption on the cationic terpolymer resin.

adsorbent were varied depending on the medium pH [6, 20]. It should be noted that the DR-R dye has two acidic sulfonic acid groups and two primary amino groups, and the DV-28 dye has two primary amino groups (Table S1). On the other hand, the resin has net negative charge and its pK_a value is approximately 0.8. Both dyes (i.e., DR-R and DV-28) are positively charged approximately pH 8.5. Both tested dyes were interacted with sulfonic group of the resin at moderate acidic pH range from pH 5.0 to 6.0. Thus, the adsorption of both dyes on the resin can be resulted from the electrostatic interactions between positively charged amine groups of dye molecules and negatively charged sulfonic acid groups of the resin. Therefore, the adsorption experiments for both dyes were studied at pH 6.0 for the remaining experiments.

Effect of Ionic Strength

As can be seen from Fig. 7, the amount of dye adsorbed to the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin showed a decrease as the ionic strength increased. By increasing NaCl concentration in the medium from 0.0 to 1.0 mol/L, the amount of the adsorbed dye on the resin was decreased from 58.4 to 6.1 mg/g for the DR-R dye and from 98.7 to 3.8 mg/g for the DV-28 dye. The dependence of dye adsorption on ionic strength of the medium showed that noncovalent interaction played an important role for adsorption of dye on the cationic resin. As the salt concentration of the adsorption medium increases, the sulfonic acid groups of the adsorbent and the amine groups present on both DR-R dye and DV-28 dyes will also be neutralized by sodium and chlorine ions of the salt (i.e., NaCl). Thus, this neutralization process causes a lower amount of adsorbed dye on the resin [6, 13]. It should be noted that both dyes and resin have electrostatic and hydrogen bonding groups, thus, these forces will be contributed together to the adsorption process. As the salt concentration in the medium increases, the electrical dual layer around the molecules provided by the Debye–Huckel length is reduced. These effects cause a reduction in electrostatic power between the adsorbent surface and the dye molecules.

Effect of Adsorbent Dosage on Dye Removal Efficiency

The effect of resin dosage on DR-R and DV-28 dyes adsorption was investigated between 0.1 and 2.0 g/L (Figs. S2 and S3, respectively). As seen from these figures, when the amount of resin was increased from 0.1 to 1.0 g/L, the adsorption percentage of the DR-R and DV-28 increased from 17.8% to 58.4% and 41.7% to 91.2%, respectively. On the other hand, the adsorbed amount of the tested dyes decreased from 178.0 to 30.4 mg/g for DR-R and 471 mg/g to 99.4 mg/g for DV-28 dye by increasing the resin dose from 0.1 to 2.0 g/L. This can be due to the increase in the quantity of adsorptive sites in the medium that interact with the dye molecules in bulk solution. For this reason, 1.0 g/L resin dosage was found to be optimal dosage, and used as the ideal amount in the remaining experiments.

Effect of Initial Dye Concentration on Removal Efficiency

The effect of the initial dye concentration on the adsorption capacity of the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin is presented in Fig. 8. From this figure, the amount of DR-R and DV-28 dyes adsorbed on the resin was increased from 6.8 to 86.1 and from 10.0 to 179.7 mg/g by increasing the initial concentrations of the dye from 10 to 500 mg/L, respectively. On the other hand, DR-R and DV-28 dyes were showed different initial saturation value, and they were found to be 200 and 400 mg/L, respectively. At initial stage, the amount of adsorbed dye on the resin can be explained by the increases of the dye concentration in the medium. This can be due to the high binding affinity of both disperse dyes molecules to the acidic groups of the adsorbent at the low dye concentration. Thus, the adsorption capacity of the resin for both dyes was increased with increasing the initial concentration of each tested dye. After equilibrium, increase in the

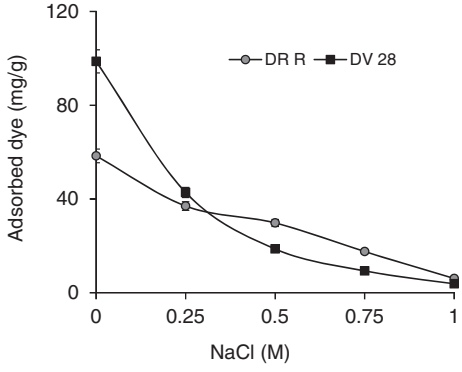


FIG. 7. Effect of ionic strength on the disperse dye adsorption to cationic terpolymer resin.

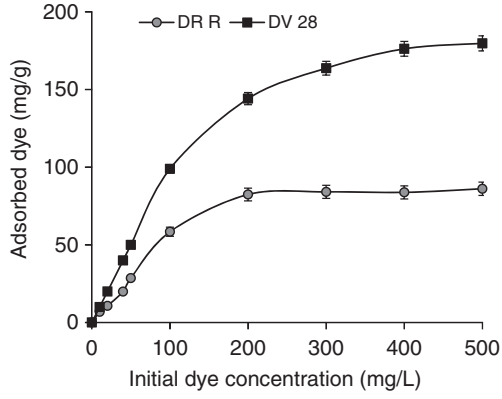


FIG. 8. Effect of initial concentration of disperse dyes on adsorption capacity of the terpolymer and terpolymer resin.

initial concentration of each dye in the medium was not affected the adsorbed amount of dyes. As can be seen in Fig. 8, the amount of adsorbed DV-28 dye was about 2.1 times more than the DR-R dye. In addition, the acid hydrolyzed (HPMA-*co*-EGDMA-*co*-GMA)-OH microbeads were used as a control system for adsorption of DR-R and DV-28 dyes, and the amounts of adsorbed DR-R and DV-28 dyes were found to be 6.5 and 9.2 mg/g, respectively. Thus, the creation of sulfonic acid groups was caused an increase in the adsorption capacity for DR-R and DV-28 dyes about 13.3 and 19.5 times, respectively. These can be attributed to the ion-exchange and hydrogen bonds interactions between the azo and amine groups of the dyes and sulfonic acid groups of the resin.

Adsorption Isotherms

Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Temkin isotherm models were used to analyze experimental data. The Langmuir adsorption isotherm is established on the statement of a dynamic equilibrium. The Langmuir isotherm equation is:

$$C_e/q_e = 1/q_m\, b + (1/q_m)\, C_e \tag{5}$$

where q_e is the amount of adsorbed onto the surface of the unit adsorbent (mg/g), q_m is the theoretical maximum adsorption capacity of adsorbent (mg/g), b indicates the Langmuir adsorption constant (L/mg), and C_e refers to the equilibrium concentration (mg/L) of the adsorbed substance.

The Temkin isotherm is not based on homogenous surface, it assumes uniform distribution of bounding energy up to some maximum binding energy. The Temkin model equation is:

$$q_e = B \ln A + B \ln C_e \tag{6}$$

where A and B (= RT/b_T) are the Temkin isotherm constants (L/g), b_T is the Temkin constant (J/mol). T and R are the temperature (K) and universal gas constant (8.314 J/mol/K).

The Freundlich isotherm model that expresses adsorption to heterogeneous surfaces and valid in the limited concentration range and the linear Freundlich isotherm model equation are as follows.

$$q_e = K_F\, C_e^{\,1/n} \tag{7}$$

where K_F and n are isotherm model constants including the features of the adsorption capacity and adsorption intensity, respectively.

D–R isotherm is used to refer to the heterogeneous surface adsorption mechanism with the assumption of micropore volume filling [12]. D–R model is expressed mathematically as:

$$\ln q_e = \ln q_m - K\,\varepsilon^2 \tag{8}$$

where ε is the Polanyi constant [RT ln(1 + 1/C_e)], K is the adsorption energy constant (mol^2/kJ), and E is the adsorption energy (kJ/mol) and defined by expression $E = (2\ \mathrm{K})^{-1/2}$.

The experimental results for the adsorption of DR-R and DV-28 dyes at different temperatures on the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin were applied to the Langmuir isotherm model equation and the calculated model constants were tabulated in Table 1. The obtained theoretical maximum adsorption capacities using the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin at 298 K were 98.9 and 178.2 mg/g for DR-R and DV-28 dyes, respectively, (Table 1). Experimental and theoretical adsorption capacity of the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin for DR-R and DV-28 dyes were observed to be very close to each other at different temperatures. In addition, high R^2 values were obtained for adsorption of DR-R and DV-28 with the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin in the range of 0.992–0.999 and 0.997–0.999, respectively. These results showed that Langmuir equation represents the best fit of experimental data than the other isotherm equation.

The Langmuir isotherm equilibrium parameter "R_L" (R_L = 1/(1 + b C_o)) can be defined as a dimensionless constant (or separation factor). If the R_L value is greater than 1.0; equal to 1.0; between 0.0 and 1.0; or equal to 0.0, it means that the adsorption process is unfavorable, linear, favorable, or irreversible, respectively. The R_L value was found to be 0.035–0.099 for DR-R and 0.002–0.009 for DV-28 at 500 mg/L dye concentration.

The Freundlich isotherm model explains nonideal and reversible adsorption that can be useful to multi-layer adsorption on the basis of a hypothesis about the heterogeneous surfaces. 1/n is a measure of surface heterogeneity ranging from 0.0 to 1.0 and becomes more heterogeneous as its value approaches zero. The n value less than 1.0 indicates poor adsorption with low affinity, a range between 1.0 and 2.0, a moderate adsorption phenomenon, or a high adsorption trend of 2.0–10.0. The constants of the model

TABLE 1. Langmuir and Temkin isotherm model constants and correlation coefficients determined in the adsorption process of DR-R and DV-28 dyes to (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin.

			Langmuir constant			Temkin constant				
Dye	T (K)	$q_{e,\,exp}$ (mg/g)	q_m (mg/g)	$K_a \times 10^{-5}$ (M^{-1})	R^2	[a]R_L	B (L/g)	$b \times 10^1$ (J/mol)	A (mg/L)	R^2
DR-R	288	84.5	97.8	0.107	0.992	0.099	19.3	1.78	0.178	0.962
	298	86.1	98.9	0.125	0.996	0.093	19.6	1.82	0.271	0.956
	308	90.3	102.0	0.136	0.994	0.078	20.3	1.83	0.317	0.923
	318	92.8	97.8	0.390	0.999	0.035	20.6	1.90	0.362	0.959
DV-28	288	148.6	147.4	0.178	0.997	0.009	14.6	5.11	68.6	0.979
	298	179.7	178.2	1.032	0.999	0.006	16.3	4.72	187.5	0.991
	308	184.2	183.8	2.487	0.998	0.003	16.7	4.80	395.1	0.996
	318	205.9	204.1	4.089	0.999	0.002	16.9	4.94	1890.4	0.989

[a]C_0 = 500 mg/L.

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were calculated and presented in Table S2. At 288–318 K temperature range, the n values were found to be 1.45–2.39 for DR-R and 3.98–6.14 for DV-28 dyes. The high n values obtained from the Freundlich model indicate that the adsorption of both dyes on the resin is appropriate. In addition, the increase in n values, which indicates an increased tendency of adsorption with increasing temperatures, is consistent with increasing adsorption capacity values. These results showed that the prepared strong cationic resin provides high affinity for both tested dyes. In general, as adsorption capacity of adsorbent increases, Freundlich constant K_F increases. In the process of adsorption of DR-R and DV-28 dyes onto the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H resin, K_F values in the temperature range (288–318 K) were found to be between 4.14 and 9.97, and 46.3 and 93.7 for DR-R, and DV-28, respectively (Table S2).

The D–R isotherm model parameters were determined from the linearized form of the D–R equation and listed in Table S2. The correlation coefficients "R^2" were calculated from the D–R model equation, and found to be between 0.713 and 0.875 for DR-R and 0.883 and 0.960 for DV-28 dyes. Analysis of Table 1 and Table shows that the Langmuir and Temkin models have higher value of the correlation coefficients in almost all of the cases and that the Freundlich and D–R models.

Adsorption Time and Kinetics

The adsorption time during the adsorption process to reach equilibrium between adsorbents and dye molecules is vital in order to the design of economic adsorption wastewater management system. To develop a highly effective adsorbent for utilization in wastewater treatment system, the adsorbent should have a high adsorption capacity for target pollutant and a short equilibrium time. The adsorption of DR-R and DV-28 dyes on the resin was studied at between 0 and 120 min to determine the equilibrium adsorption time. As seen from Fig. 9, the dye adsorption rate and capacity of each dye changed with contact time but reached equilibrium at the end of a certain processing time. The amount of adsorbed DR-R and DV-28 dyes on the resin was higher at the beginning (at initial 30 min) and reached equilibrium approximately within 60 min. Then, there was no significant change in the amount of adsorbed dye by the resin (Fig. 9).

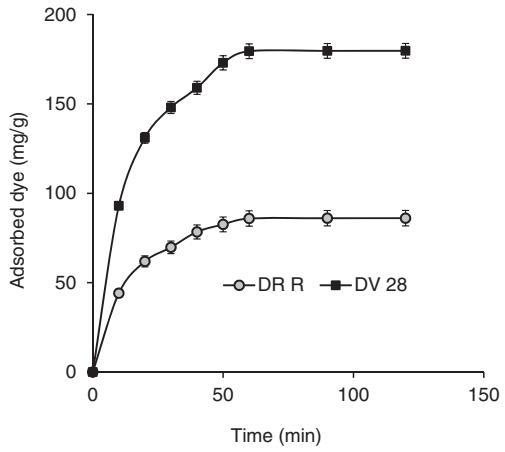


FIG. 9. Effect of contact time on adsorption of DR-R and DV-28 dyes on cationic terpolymer resin.

The adsorption kinetics of the DR-R and DV-28 adsorption on the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H resin were investigated by using pseudo-first and pseudo-second-order kinetic models. The linear pseudo-first-order kinetic equation defined by Lagergren is given as the following equation:

$$\log\left(q_{e,\mathrm{cal}} - q_t\right) = \log q_{e,\mathrm{cal}} - (k_1/2.300)\, t \tag{9}$$

where k_1 is the first-order kinetic rate constant (min^{-1}), $q_{e,\mathrm{cal}}$ and q_t are the amount of dye adsorbed at equilibrium and time t (mg/g), respectively.

Theoretical adsorption capacity ($q_{e,\mathrm{cal}}$) was also calculated using second-order kinetic equation, and the pseudo-second-order kinetic equation based on adsorption capacity is:

$$1/q_t = 1/\left(k_2\, q_{e,\mathrm{cal}}{}^2\right) + \left(1/q_{e,\mathrm{cal}}\right) t \tag{10}$$

In this equation, k_2 (mg g^{-1} min^{-1}) is the pseudo-second-order adsorption rate constant. The adsorption initial rate constant is indicated by h and defined as $h = k_2\, q_e{}^2$. The results in Table S3 showed that the pseudo-second-order kinetic model was more appropriate with a high correlation coefficient (R^2) close to unity, compared to the first-order model. Moreover, a large difference in the equilibrium adsorption capacity between the experimentally and theoretically was observed for first-order model. Thus, the pseudo-first-order model did not fit well the experimental data.

Adsorption Thermodynamics

The effect of temperature for the adsorption of DR-R and DV-28 dyes from the aqueous medium by the resin is an important factor for the evaluation of temperature-dependent dye adsorption mechanisms. The adsorption capacity of terpolymer resin was increased with increasing temperature. When the temperature was increased from 288 to 318 K, the amount of adsorbed DR-R and DV-28 dyes was increased from 84.5 to 92.8 and 148.6 to 205.9 mg/g, respectively (Fig. S4).

Thermodynamic parameters such as standard free energy change (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0) were determined to evaluate the feasibility, spontaneity, and the nature of adsorbate–adsorbent interactions of the cationic resin for the adsorption process and calculated using the following equations;

$$\Delta G^0 = -\mathrm{RT} \ln K_a \tag{11}$$

$$\Delta \mathrm{G}^0 = \Delta H^0 + T\Delta S^0 \tag{12}$$

The equilibrium constants K_a for the DR-R and DV-28 dyes adsorption on the resin are equal to the "b" values determined from the Langmuir model equation at four different temperatures (*Eq. 5*) and presented in Table 1. The thermodynamic parameters ΔH^0 and ΔS^0 were determined from the slope and intercept of the 1/T versus ln K_a plot according to the van't Hoff equation, respectively. Thermodynamic evaluations state that the standard free energy change is the primary criterion for determination of adsorption process characteristics. As seen in Table 2, while the temperature was increased from 288 to 318 K, the ΔG^0 values were decreased. The negative values of $\mathbf{\Delta}\mathrm{G}^0$ imply that the adsorption of DR-R and DV-28 dyes on the resin is spontaneous.

TABLE 2. Thermodynamic parameters for the adsorption of DR-R and DV-28 dyes to (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin.

Dye	T (K)	q_{exp} (mg/g)	First order			Second order			h (mg/g min)
			q_{eq} (mg/g)	$k_1 \times 10^2$ (min^{-1})	R^2	q_{eq} (mg/g)	$k_2 \times 10^4$ (g/mg/min)	R^2	
DR-R	288	84.5	186.2	9.88	0.954	96.86	7.55	0.998	7.09
	298	86.1	163.3	9.60	0.978	97.10	8.83	0.999	8.32
	308	90.3	128.7	8.78	0.993	100.8	9.56	0.997	9.72
	318	92.8	190.6	10.7	0.985	102.7	10.2	0.998	10.8
DV-28	288	148.6	245.5	8.20	0.929	167.2	3.28	0.996	9.20
	298	179.7	331.1	9.44	0.948	196.1	5.31	0.998	20.4
	308	184.2	303.4	9.69	0.971	198.4	6.77	0.999	26.7
	318	205.9	323.6	10.6	0.979	217.3	8.14	0.999	38.5

The ΔG^0 value was decreased with the temperature, indicating that the spontaneous nature of adsorption was directly proportional to the temperature. The ΔH^0 values for the adsorption of DR-R and DV-28 dyes on the resin were found to be 26.99 and 46.32 kJ/mol, respectively (Table 2). The positive ΔH^0 values indicate that the adsorption process is endothermic. Therefore, an increase in the temperature leads to a higher adsorption of dye at equilibrium. The ΔS^0 values were determined as 0.171 and 0.253 kJ/mol/K for adsorption of DR-R and DV-28 dyes on the resin, respectively. The positive entropy values indicate that randomness increases during the adsorption process.

Activation energies (E_a) for the adsorption of both dyes were calculated from the slope of the $1/T$ versus ln k_2 (k_2 calculated from second-order kinetic equation) curves. The activation energies for adsorption of DR-R and DV-28 dyes on the (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin were calculated as 11.9 and 22.7 kJ/mol, respectively (Table 2). The positive values of E_a show that the adsorption of DR-R and DV-28 dyes on the cationic resin is endothermic.

Desorption of Dyes and Reusability of Cationic Resin

For desorption of dyes from DR-R and DV-28 laden resin, sodium hydroxide solution (0.1 mol L^{-1}) was used as desorption agent (Fig. S4). As shown in this figure, desorption efficiencies obtained for the resin were found to be 89.4% and 91.7% for DR-R and DV-28 dyes, respectively. Therefore, the reusability of an adsorbent is very significant for large-scale applications. The reusability of the resin was studied using the same resin five adsorption/desorption cycles. After five times adsorption/desorption cycle, a negligible decrease in the adsorption capacity was observed for both tested dyes (Fig. S6).

CONCLUSIONS

In this work, a new cationic (HPMA-*co*-EGDMA-*co*-GMA)-SO_3H terpolymer resin was synthesized and used for removal of two different positively charged organic pollutants. The negatively charged resin give good adsorption properties towards two disperse dyes (i.e., DR-R and DV-28). The resin was rapidly interacted with these dyes and approximately 70% its capacity saturated within 20 min. The adsorption capacity of the resin for DR-R and DV-28 dyes was reached up to 86.1 and 179.6 mg g^{-1}, respectively, which is better to that for most reported adsorbents. The high adsorption capacity of the resin can be attributed to ion-exchange and the strong electrostatic interaction between the abundant sulfonic acids groups on the mainly external surface of the resin and the amine groups of both the dyes. Thermodynamic studies showed that the adsorption of dyes on the resin was reasonable and spontaneous and mainly controlled physically. Accordingly, the prepared resin had a great potential as an environmental and operative adsorbent in the adsorption process of many different dyes from solutions. Additionally, the resin can be regenerated and reused in the removal of disperse dyes from aqueous solution. Due to its easy synthesis, stable structure, and efficient performance, the resin could be used as an operative candidate for removal of positively charged pollutants from wastewaters.

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