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Synthesis, Characterization, and Application of a Triazene-Based Polysulfone as a Dye Adsorbent

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ABSTRACT: Novel triazene-based polysulfone, poly 4-(4-aminophenylsulfonyl)diazobenzene, was synthesized from 4-[(4-aminobenzene)sulfonyl]aniline (Dapsone) in the presence of sodium nitrite/silica sulfuric acid system, under solvent-free conditions, and also in aqueous media to compare their polymerization process and the products. The structures of the obtained polymers under the two conditions were characterized for the first time in this investigation by several analytical and spectroscopic methods such as FT-IR, ^{1}H-NMR, UV–vis, thermogravimetric and differential thermal analyses, gel permeation chromatography, mass spectrometry, and CHN micro-elemental analysis. The results showed that both polymerization processes had made the same product; nevertheless, the solvent-free conditions afforded silica-coated poly 4-(4-aminophenylsulfonyl)diazobenzene. In another study, the ability of the silica-coated polymer, to remove some usual applied water-soluble dyes by spectrophotometric detection, was measured in which cationic structure dyes such as Rhodamine B and Cationic blue 41 were preferably adsorbed. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

KEYWORDS: adsorption; applications; dyes/pigments; properties and characterization; synthesis and processing

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INTRODUCTION

Recently, triazenes have been received much attention due to their novel physical and chemical properties, and prospects of their application in the synthesis of photosensitive polymers,[1–5] ^{13}N-labeled azo compounds,[6] conductive polymer,[7] and hybrid nanocomposites are used for detecting metal ions.[8] Moreover, they have been applied as coordination agents in inorganic chemistry,[9,10] triazene linkers,[11–15] photolabile linker in solid-phase chemistry,[16] solid-phase extraction,[17] thiophenol synthesis,[18] and improvement in semiconductor laser printing.[19] Hence, triazene-group-containing polymers can be potentially interesting due to the possibilities of its applications such as each of the above uses.

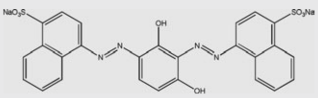
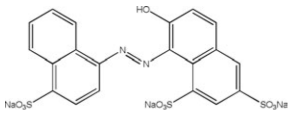
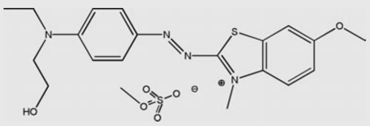
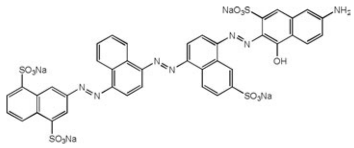
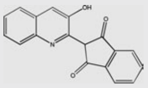
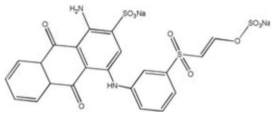
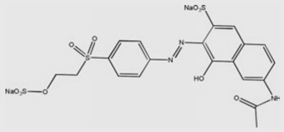
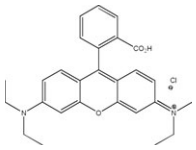
Many industries generate wastewater concomitant dyes daily. Elimination of dye materials from wastewater in refinement process is very important, since a negligible amount of dye is highly visible, is unpleasant, or is poisonous and even causes cancer. Adsorption techniques have been widely used to remove industrial water-soluble dyes, especially dyes that are not easily reactive and biodegradable; thus, they remain within the environment for a long time; consequently, dyes are one of a biggest problematic water pollutant groups. Utilization of polymers in different ways is one of the common methods for removal of dyes from wastewater.[20–26]

Synthesis of poly(triazene-1,3-diyl-di-1,4-phenylene) by diazotization and azo-coupling of 4,4-diaminodiphenyl in aqueous media and the same synthesis of polymers containing 1-triazene-1,3-diyl and 1,4-phenylene groups, from p-phenylenediamine, was reported by Durgaryan et al.[7]

We hypothesized that triazene group can substantially increase the interactions of polymer with water-soluble dyes, and, accordingly, adsorbing process becomes improved. In the present work, not only do we offer a novel route for one-pot synthesis of poly 4-(4-aminophenylsulfonyl)diazobenzene as a new triazene-group-containing polymer under solvent-free conditions, but also in aqueous media. It is noteworthy that the solvent-free procedure can be a beneficial synthetic route toward silica-coated poly 4-(4-aminophenylsulfonyl)diazobenzene, which can be used as a hybrid composite for adsorb dyes.

Due to the insolubility of this synthesized polymer in water, it can be potentially used for water refining purposes without

Table I. Basic Properties of Investigated Dyes

Dye (commercial name)	Chemical formula	Molecular structure	Molecular weight (g mol^{-1})
Acid brown 14	$C_{26}H_{16}N_4Na_2O_8S_2$		622.02
Acid red 18	$C_{20}H_{11}N_2Na_3O_{10}S_3$		603.93
Cationic blue 41	$C_{20}H_{26}N_4O_6S_2$		482.52
Direct blue 71	$C_{40}H_{23}N_7Na_4O_{13}S_4$		1028.98
Disperse yellow 54	$C_{18}H_{11}NO_3$		289.07
Reactive blue 19	$C_{22}H_{16}N_2Na_2O_{11}S_3$		625.97
Reactive orange 16	$C_{20}H_{17}N_3Na_2O_{11}S_3$		616.98
Rhodamine B	$C_{28}H_{31}ClN_2O_4$		479.01

having any bad side effect on water quality or the environment. In addition, the selected constitutive monomers of this polymer is Dapsone, a well-known medicine,[27–30] which has not any fatal toxicity, flammability, or poisonous vapor. Furthermore, our recommended synthesis procedure does not need any organic solvent or hazardous chemicals. After performing the adsorption process, due to the differences between solubility of the polymer and adsorbed dye, the dye-loaded adsorbent could be washed (in a green organic solvent like ethanol as eluent), separated and recovered. Finally eluate, which contain redissolved dye, could be afforded. Upon the above mentioned benefits, it was very interesting to conduct more investigation on this kind of triazene-based synthesized polysulfone.

EXPERIMENTAL

Materials

Water was used after deionization (DI) with pH range 5.8–6.2 and conductivity 6.0 $\mu S\ m^{-1}$. Investigated dyes, whose basic properties are mentioned in Table I, were of commercial grade prepared from Alvan-Sabet, Hamedan, Iran. Silica sulfuric acid was prepared by the reported procedure.[31] Deuterated dimethylsulfoxide (DMSO) was purchased from Sigma-Aldrich, Munich,

Table II. Spectral and Adsorption Data of Investigated Dyes

Dyes (commercial names)	C_0 (ppm)	λ_{max} (nm)	Adsorbed percentage on Silica gel	 Adsorbent	q_e (mg g^{-1})
Acid brown 14	110	424	01.11	18.56	11.47
Acid red 18	110	509	00.00	03.00	00.00
Cationic blue 41	110	608	55.98	96.78[a]	59.81
Direct blue 71	110	584	01.54	17.06	10.54
Disperse yellow 54	160[b]	415	33.60	38.35	34.48
Reactive blue 19	110	593	00.00	20.05	12.39
Reactive orange16	110	493	00.00	00.00	00.00
Rhodamine B	110	554	43.46	98.72[a]	61.01

[a] Due to the cationic structures, these dyes have shown maximum adsorption efficiency.
[b] In this case, due to lower peak intensity, more concentrated solution was produced.

Germany. Dapsone, sodium nitrite, α-naphthol, and other chemicals were of analytical grade purchased from Merck Chemical Company, Tehran, Iran and used as received without any further purification.

Methods

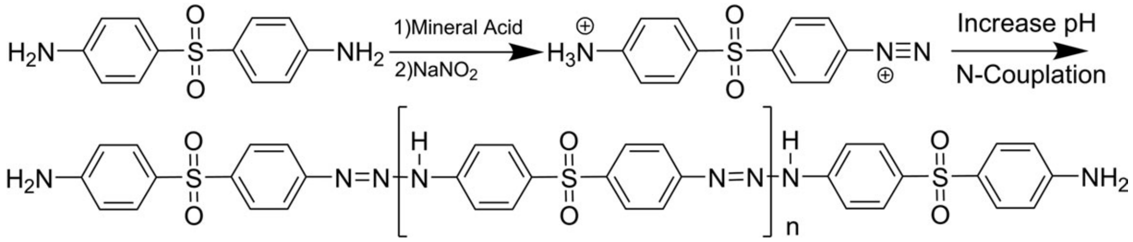
^{1}H-NMR spectra were obtained from deuterated DMSO (d_6) with tetramethylsilane (TMS) as an internal standard using Bruker 300 MHz NMR spectrometer. The UV–vis spectra of the polymer samples in *N*,*N*-dimethylformamide (DMF) were recorded by 1 cm quartz cell and Agilent UV/Vis spectrometer. FT-IR Perkin Elmer spectrometer was served to obtain FT-IR spectra in the range of 4000–400 cm^{-1} by KBr powder-pressed pellets. Gel permeation chromatography (GPC) chromatogram was obtained from 1,2,4-trichlorobenzene (TCB) as solvent at 145°C by 0.8 mL L^{-1} flow rate, the column was filled by Styragel HT, and polystyrene was used as standard. A Perkin Elmer Pyris-Diamond thermogravimetric and differential thermal analyzer (TG–DTA) was used by nitrogen gas flow and ceramic pan. Agilent mass spectrometer 5973 was used with network mass-selective detector and a 70 eV electron impact as the ion source and quadrupole analyzer.

Preparation of Silica-Coated Poly 4-(4-Aminophenylsulfonyl)-diazobenzene under Solvent-Free Conditions. First, a mixture of 4-[(4-aminobenzene)sulfonyl]aniline (Dapsone; 1.24 g, 5 mmol), sodium nitrite (0.42 g), and silica sulfuric acid (1.5 g; optimum ratio achieved after eight times) was ground in a glass mortar with a pestle for 5 min to afford a homogeneous mixture. Then, a few drops of water were added gradually, and the resulting mixture was ground fast to lose its moisture accompanied by gradual change of color into orange. This step was repeated several times for 30 min (mixture must not become wet or dough in this step), and diazonium silica sulfate was formed, which can be tested by mixing a small amount of reaction mixture with α-naphthol in acetone to become extremely colored in the presence of NaOH. Afterward, DI water (20 mL) was added to reaction mixture, mixed well, and maintained for 20 min. The mixture was neutralized by sodium carbonate and remained for 12 h. The precipitated polymeric powder coating on silica was collected by Büchner filtration, was washed with DI water thoroughly, and was then dried in the air and desiccator vacuum/concentrated sulfuric acid, respectively, and 94.4% yield was obtained.

Preparation of the Poly 4-(4-Aminophenylsulfonyl)diazobenzene in Aqueous Media. To a mixture of Dapsone (1.0 g, 4 mmol) and DI water (200 mL) in a 500 mL Erlenmeyer flask, was slowly added hydrochloric acid 37% (25 mL), while being mixed by a magnetic stirrer, at room temperature until Dapsone was dissolved completely. The flask put in ice/acetone bath to cool down the reaction mixture to about 0–3°C. Afterward, sodium nitrite solution (0.3 g in 100 mL cold DI water) was added dropwise with continuous stirring for about 30 min accompanied by gradual change of color to pale yellow as the diazotization was continued on. To prove formation of diazonium salt, some drops of the reaction mixture was added to a test tube filled by basic (NaOH) α-naphthol solution, which became extremely colored. When the reaction was completed, the flask was removed from ice bath, diluted, and buffered at pHs 4–5 through addition of reaction solution in 2000 mL beaker containing sodium acetate (40 g) in 1700 mL DI water. Change of color to red and formation of the orange polymeric precipitate occurred, and the resulting mixture maintained at room temperature for 2 days to complete reaction. The solution was neutralized with sodium carbonate (20.0 g) having been kept overnight; during this time, the polymeric product was precipitated, which was collected by Büchner filtration, washed with DI water thoroughly, and dried. Then, the polymer was dried in desiccator vacuum/concentrated sulfuric acid, and 86% yield was obtained by weighing.

Dye Removal Experiments

The precipitated polymeric powder coating on silica, produced in solvent-free conditions, was used as a hybrid composite for adsorption of Table I mentioned dyes from water samples. The experiments were conducted individually for each of the dyes, but the same procedure was used for them, as detailed below, and repeated three times. In this procedure, first, the adsorbent (0.02 g) was added in a centrifuge tube containing desired dye solutions (5 mL) with the known initial concentration of C_0 as



Scheme 1. Diazotization reaction of the primary aromatic diamine and polymerization with subsequent N-coupling.

recorded in Table II. The pH of the solution was adjusted at 6 by the addition of 0.01 mol L^{-1} NaOH and/or 0.01 mol L^{-1} HCl solutions, and the solution was stirred vigorously by a magnetic stirrer for 8 h as a predefined maximum time. All the experiments were performed at room temperature, and amount of adsorbed dye on the flask surfaces was zero. Then, the dye-loaded adsorbent was separated by centrifuge, and mixture was decanted to remove the above solution of the adsorbent completely. Removal percent and adsorbed amount of each dye were determined spectrophotometrically by measuring the UV–vis absorbance of the sample solutions before and after removing process at appropriate wavelengths corresponding to the maximum absorbance of each dye according to Table II. In addition, the adsorption of investigated dyes on the silica gel, in the same way as a blank for comparison, was also studied. The adsorption percent for each dye, i.e., the dye removal efficiency, was determined using the mentioned expressions in "Results and discussion" section.

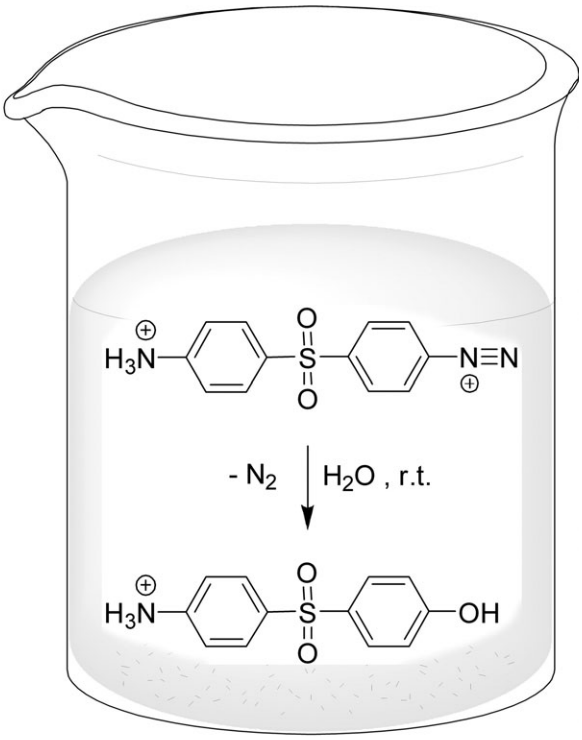


Figure 1. Unwanted phenol formation through the healthy monomer decomposition in aqueous media.

RESULTS AND DISCUSSION

Polymerization Process Description

Polymerization process is based on the diazotization reaction of a primary aromatic diamine that performs self-N-coupling to form linear triazene (Scheme 1). Diazotization in aqueous media was accompanied by unwanted phenol formation (Figure 1) due to diazonium salt decomposition[32]; and, it resulted in decreasing the yield. The formation of unwanted phenol was proved by observation of the FT-IR spectra of extracted monomers from reaction solution including decomposed monomers (unwanted phenol). IR (KBr): ν = 3530–3380 (b; ν_s (OH)), 1305 (m; ν_s (CO)), 2559 (m; ν_s (NH_3^+)), 3058, 3075 (m; ν_s (CH)), 1164, 1384 (s; ν_s (SO_2)), and 2289 cm^{-1} (w; ν_s (N_2^+) for healthy monomers).

Recently, chemists have reported diazonium silica sulfate as a solid stable form of diazonium salt at room temperature,[33–36] which is prepared easily. In the present article, both approaches (solvent-free and aqueous media) were used for diazotization reaction. The new triazene-based polymer was synthesized through solvent-free conditions and had the same mechanism as in aqueous media. The polymer was prepared under similar acidic conditions, provided with mineral acids for the diazonium salt synthesis, except for solvent-free procedure in which instead of aqueous HCl solution, silica sulfuric acid was used.

Characterization

^{1}H-NMR spectra of the obtained polymer in both routes have unique peaks that show similar structure; hence, we ignore showing the second results. Interpretations of peaks are given pictorially (Figure 2). It must be noticed that, because of the solubility of the smaller polymeric chains in deuterated solvent,

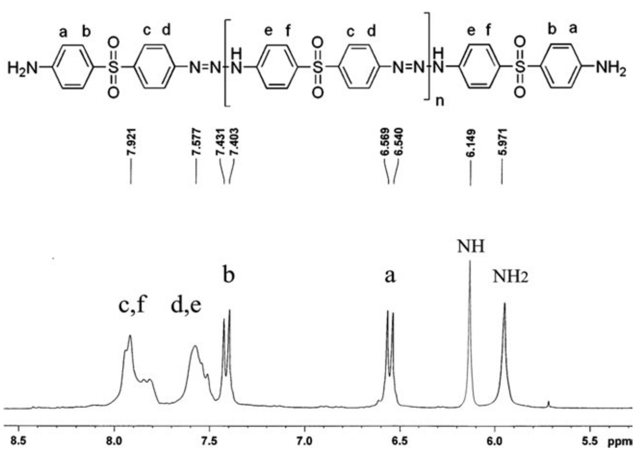


Figure 2. ^{1}H-NMR of polymer sample (300 MHz, DMSO-d_6, δ).

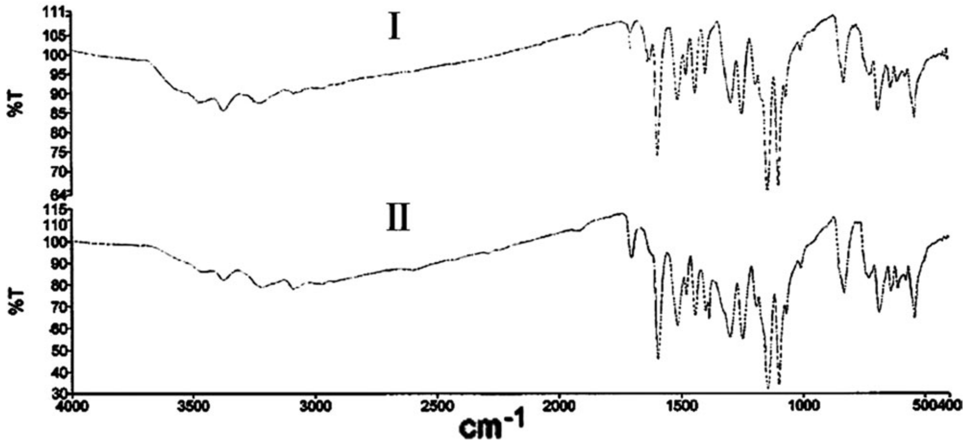


Figure 3. FT-IR spectra of synthesized polymer in aqueous media (I) and solvent-free conditions (II).

the peaks integrals are ignored. The a and b protons belong to the terminal rings of polymer chains appearing in chemical shift such as its monomer. Nevertheless, proton of the fused rings by triazene group appears in downfield, due to one of the protons of primary amine group replaced by azo-withdrawing group.

Comparing the FT-IR spectroscopic characterization results of the polymer produced in both solvent-free and aqueous solution conditions (Figure 3) showed that they are the same and provide a comparison showing both routes make unique functional groups.[37] IR (KBr): $v = 3373, 3470$ (w; v_s (amine NH_2)), 1595 (m; v_b (amine NH_2)), 3224 (m; v_s (triazene NH)), 1514 (m; v_b (triazene NH)), 3055, 3089 (m; v_s (CH)), 1145, 1295 (w; v_s (SO_2)), and 1101 cm^{-1} (s; v_s (CN)).

The UV–vis spectra of the both obtained polymer sample solutes in DMF, which were another evidence to confirm the polymerization processes, have the same absorptions $\lambda_{max}(\varepsilon) = 383$ nm. The UV–vis data show (Figure 4) how this polymer has photoactive potential; also, both polymerization processes have made unique structure, while the maxima of absorption for monomer appear at $\lambda_{max}(\varepsilon) = 298$ nm.

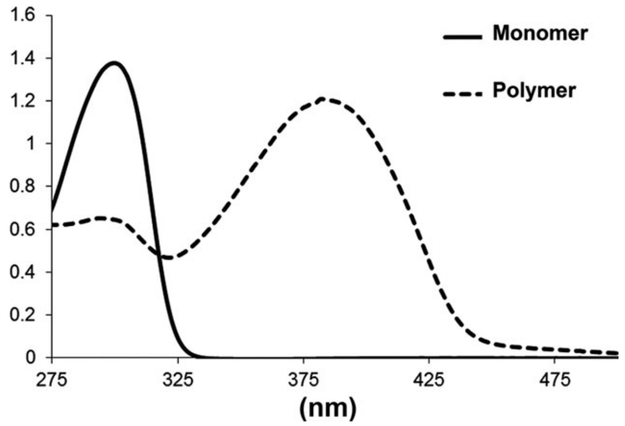


Figure 4. UV–vis (DMF): polymer sample and related monomer.

Table III. Average Molecular Weight and Polydispersity of Polymers Obtained from the GPC Chromatograms

Polymerization procedure	M_w ($\times 10^3$)	M_n ($\times 10^3$)	PDI
Aqueous media	576	268	2.14
Solvent free condition	488	240	2.03

GPC chromatograms were obtained from TCB as solvent at 145°C by 0.8 mL L^{-1} flow rate, the column was filled by Styragel HT, and polystyrene was used as our standard. The GPC results, which show similar molecular weight and polydispersity for both polymerization routes, have been shown in Table III.

The mass spectra show proportionate mass amounts of fractions according to the main structure (Figure 5). Also, CHN microelemental analysis results proved the structure (%): anal. calcd

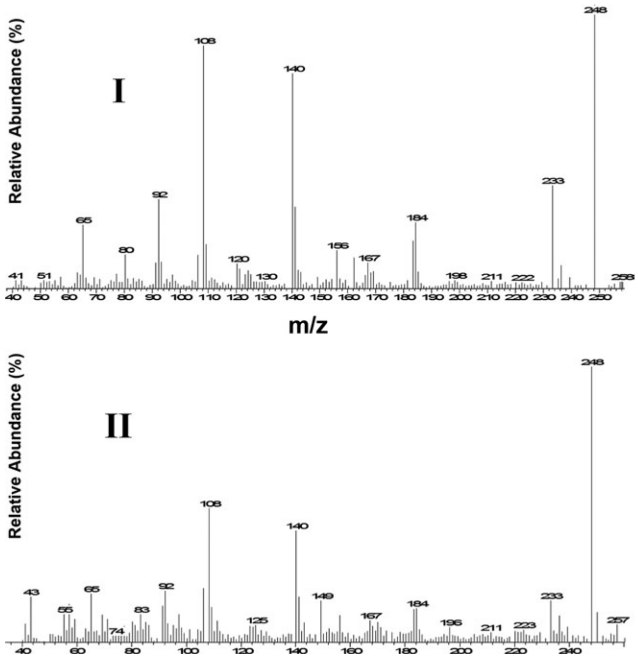


Figure 5. The mass spectra of polymer sample which synthesize by polymerization procedure in aqueous media (I) and in solvent-free condition (II).

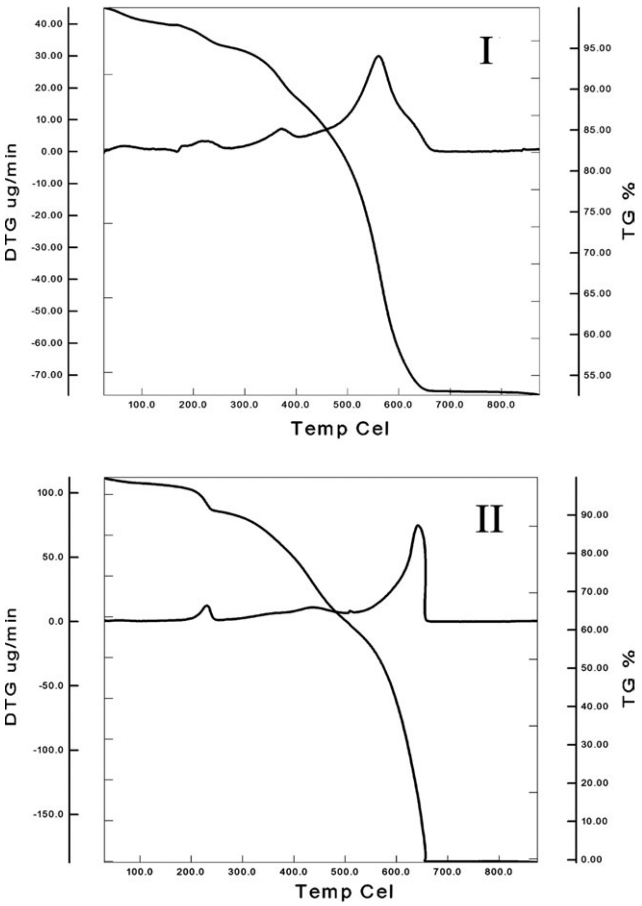


Figure 6. TG/DTA thermograms of investigated polymer synthesis in solvent-free conditions coated on silica (I) and polymer synthesis in aqueous media (II).

for $C_{12}H_9N_3O_2S$: C 55.59, H 03.50, N 16.21, S 12.37, O 12.37; found: C 55.52, H 03.46, N 16.18.

Coating and Thermogravimetric Analysis

Because of strong hydrogen bonding between silica sulfate and triazene groups, the polymer was coated strongly on the silica surface in polymerization via the solvent-free procedure, which could be a beneficial one-pot coating method for silica particles, to make a novel organic–inorganic hybrid composite. In the thermal gravimetric (TG) and differential TG of the polymer (Figure 6), the first weight-loss step (70–130°C) can be assigned to the loss of physically and chemically bound water. The first stage (230–250°C) of decomposition corresponds to the depolymerization, because of triazene bonding breakage with nitrogen gas releasing by about 5% losing of total weight. The second stage (450–640°C) of decomposition, which corresponds to an important loss of weight, could be mainly due to the final decomposition of aromatic residue of cracked polymer structure. The bond breakage occurred in lower temperature for polymer coated on silica. Perhaps, silica plays a catalytic role in decomposition of triazene bondings.[38] The decomposition takes place up to the almost complete degradation of the polymer. It is to be noticed that these results were compatible with the main steps of decomposition, but silica maintained without any change.

Spectral and Adsorption Results

Because of possible electrostatic interactions between electron-rich triazene groups and cationic structures of dyes, such as Rhodamine B and Cationic blue 41 (Table I), cationic dyes are preferred to be adsorbed. This phenomenon could clarify the reason of selective adsorption of dyes (Table II).

Effect of Solution pH

Solution pH is an important parameter, which would affect aqueous chemistry, surface binding sites of the adsorbent, and electrical charges of dye molecules. The effect of the solution pH on the adsorption of dyes onto adsorbent was assessed at different values, ranging from 4 to 10, at the room temperature for 4 h. In these experiments, the initial concentration of dye and adsorbent dosage were set at 100 mg L^{-1} and 0.10 g, respectively, for all batch tests. Figure 7 presents the results of the effect of the solution pH on the removal efficiency of each selected cationic dye. For both of investigated cationic dyes, Cationic blue 41 and Rhodamine B, at the wide range of acidic pHs, it was found that the adsorption efficiency was not significantly affected by solution pH in the range 4–7. Therefore, routine works were performed at pH 6. As Figure 7 shows, removal of these mentioned dyes is decreased, from 98.4% to 80.1% and 99.2% to 69.3 %, for Cationic blue 41 and Rhodamine B, respectively, when the pH increased from 6 to 10. Since the removal of dyes increased to its maximum value in the pH range 5–7, the electrostatic attraction between the dye molecules (positively charged) and adsorbent surface (electron rich structure) might be the predominant adsorption mechanism. Due to the adsorption amount of dyes remained maximum at pH 6, the following studies were conducted at a fixed pH of 6. The chemical structures of Rhodamine B and Cationic blue 41 are shown in Table I, which contain exchangeable proton on some functional groups such as hydroxyl and carboxyl groups, so at high pHs these investigated dyes owing to the losing of an exchangeable proton become zwitterionic, and electrostatic force of

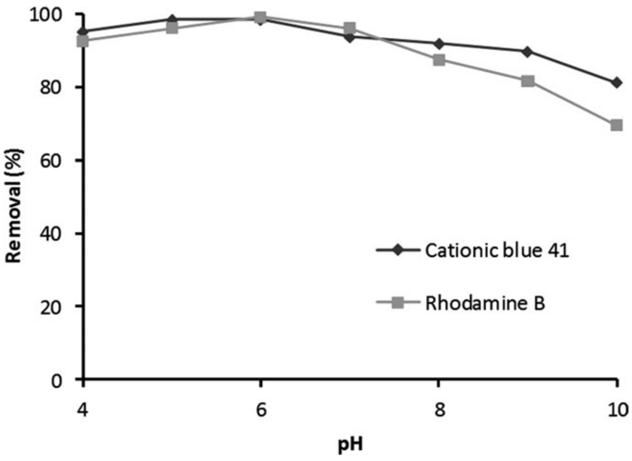


Figure 7. Percentage of dye removal at different pHs. *Conditions*: 0.1 g of adsorbent, 25 mL of 100 mg L^{-1} of dye, agitation time of 4 h, temperature: 25°C.

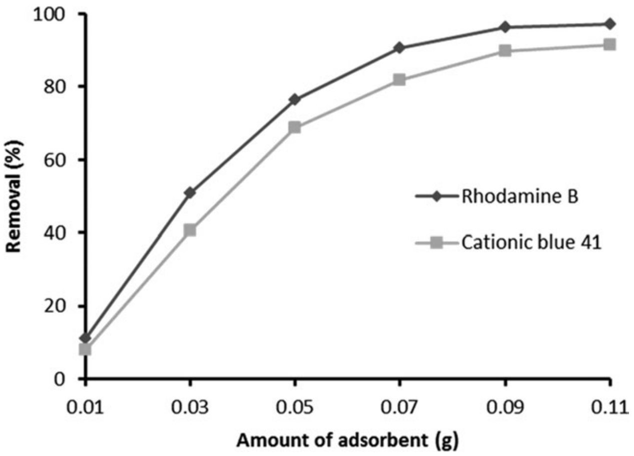


Figure 8. Percentage removal of dye at different amounts of adsorbent. *Conditions*: 25 mL of 100 mg L^{-1} of dye, pH 6, agitation time of 4 h., temperature: 25°C.

adsorbency decreased. Therefore, adsorption efficiency decreases at pH values higher than 6.

Effect of the Adsorbent Amount

The effect of adsorbent quantity for dye removal was investigated by adding various amounts of adsorbent in the range 0.01–0.11 g into the beaker containing 25 mL of dye solution (100 mg L^{-1}) at pH 6 and 4 h for all batch experiments. The results are shown in Figure 8, which indicated the addition of 0.09 g of adsorbent per 25 mL solution of dye (100 mg L^{-1}) leads to maximum separation of dye. The supernatant was analyzed for the remained dye. It was observed that, by increasing the adsorbent dosage from 0.01 to 0.09 g, the removal efficiency (%) of dyes increased from 11.1% to 96.2% for Rhodamine B and from 8.135% to 89.90% for Cationic blue 41. The greater number of adsorption sites made available at greater adsorbent dosages can explain this observation. Above 0.09 g of adsorbent dosage, the removal ratio of dyes held almost no variety.

Recovery of Adsorbent and Dyes

The dye-loaded adsorbent was separated by centrifuge from mixture, dried, washed with small amount of absolute ethanol for three times, and filtrated off. Then, solvent was evaporated under reduced pressure to afford recycled dye, and recovered adsorbent can be reused again.

The calculations of the solid-phase adsorbate concentration of a specific adsorbent represent its adsorptive characteristics, which are very important to introduce adsorption ability. Calculations of the solid-phase adsorbate concentration (q_e, mg g^{-1}) are defined as follows:

$$q_e = \frac{(C_0 - C_e) \times V}{W_p} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of dye in mg L^{-1}, V is the volume of experimental solution in L, and W_p is the weight of polymeric part of adsorbent composite in g. Where q_e is the equilibrium relationship between the quantity of adsorbate per unit of adsorbent (Table II).

The TGA thermogram proved that only 44.5% weight of composite belongs to polymer. We calculated the weight of polymer in composite with eqs. (2) and (3).

$$W_p = W_a - W_s \tag{2}$$

where W_p is the weight of polymeric part of composite, W_a is the weight of anhydrous composite (at 180°C), and W_s is the weight of residue silica remained (at 875°C).

$$\%P = \frac{W_p}{W_t} \times 100 \tag{3}$$

where $\%P$ is the percentage of polymer in composite, W_p is the weight of polymeric part of composite, and W_t is the total weight of composite.

CONCLUSIONS

Polymerization process based on the new applied method of diazotization (diazonium silica sulfate) became optimized, in which there was no need to use solvent, and monomers were not decomposed, in turn, resulting in the increase of the yield, while having least time and material consumed. In addition, polymerization procedure in solvent-free condition was simple in comparison with aqueous media and generated purer product at room temperature (without unwanted phenol formation). We have also compared the results of some recently reported methods for the removal of Rhodamine B, with our method (Table IV). As the results indicates, our method is superior with respect to the reported methods in terms of efficiency, energy consumption with low costing, and environmentally friendly; hence, it can be widely used in water refinery purposes. Moreover, our novel polymer could adsorb cationic dyes selectively and release easily; thus, it could recycle successfully.

Table IV. Comparison of the Proposed Methods for the Removal of Rhodamine B with Some Current Methods

Type of adsorbent	Dye concentration (mg L^{-1})	Wt. of adsorbent (g L^{-1})	Adsorption capacity (mg g^{-1})	% adsorbed	Ref.
Kaolinite	90	3.00	46.08	83.00	39
Sodium montmorillonite	200	0.30	42.19	93.67	40
AlMCM-41	4.79	0.025	41.86	78.15	41
$BiFeO_3$	7.0	0.50	11.90	N/A	42
Triazene-based polysulfone	110	3.60	61.01	98.72	This work

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