

Sorption of Textile Dye from Aqueous Solution by Macroporous Amino-Functionalized Copolymer

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ABSTRACT: Macroporous poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) (PGME) was synthesized by suspension copolymerization and functionalized with diethylene triamine (PGME-deta). The effect of pH, contact time, and sorbent mass on sorption efficiency of initial and functionalized copolymer sample for removal of Acid Orange 10 dye from aqueous solutions was studied. No dye was sorbed by nonfunctionalized copolymer, indicating that sorption of Acid Orange 10 by PGME-deta is specific, through amino groups. The isotherm data are best fitted by Langmuir model, indicating homogeneous distribution of active sites in PGME-deta as well as monolayer sorp-

tion. Sorption kinetics study showed that the sorption of Acid Orange 10 by PGME-deta obeys the pseudo-second-order kinetic model. It was shown that PGME-deta selectively sorbs Acid Orange 10 from binary solution with Bezaktiv Rot reactive dye. The comparison of sorption characteristics of PGME-deta with activated carbon showed that this functionalized copolymer might be used as an alternative sorbent for textile dyes. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 234–242, 2011

Key words: macroporous copolymer; glycidyl methacrylate; dye; adsorption; kinetics

INTRODUCTION

The release of colored effluents from textile plants into the environment is undesirable, not only because of their color but also because many dyes from wastewater and their breakdown products are toxic and/or mutagenic.¹ Without adequate treatment, these dyes are stable and can remain in the environment for an extended period of time. Therefore, dye removal from industrial effluents is a field of research receiving increasing attention. According to the US National Toxicology Program,² Acid Orange 10, the dye chosen for the investigation in this article, showed genotoxicity for Swiss Albino mice³ and might be dangerous for human population as well. Moreover, in USA, this dye was used as a drug and cosmetic colorant until October 1966, when its use for these applications was abandoned. However, this dye is still widely used in textile industry.

Currently, there is no appropriate method for treatment of all textile wastewaters that could be regarded, effective and inexpensive.^{4,5} Usually, the wastewater treatment includes several processes to achieve desired water quality. All techniques have advantages and drawbacks, and their selection depends on the wastewater characteristics. The most thoroughly investigated methods for dye removal are as follows: biological treatment,^{5–7} oxidation,⁸ advanced oxidation,^{9–11} electrooxidation,¹² coagulation,¹³ and adsorption.^{14–17} Recently, adsorption has become one of the most effective and comparable low-cost methods for dye removal from textile industry wastewaters.^{18–20}

Polymeric sorbents have been increasingly investigated as potential alternatives to activated carbon, because of their easily controlled pore structure, stable physical and chemical properties, as well as their ability for regeneration and reuse.²¹ Macroporous hydrophilic copolymers based on glycidyl methacrylate (GMA) produced by radical suspension copolymerization, obtained in the shape of regular beads of required size and porosity, are very attractive. Namely, the epoxy group can be easily transformed under mild reaction conditions into various functionalities such as amino, iminodiacetate, thiol, azole and pyrazole, and pyridine groups. The porous

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structure of these copolymers can be controlled by adjusting the reaction mixture composition.^{22–25}

These copolymers were proven to be very useful as sorbents and column packings in different types of chromatography,^{26,27} as enzyme supports,²⁸ in biotechnological and biomedical applications,²⁹ for heavy and precious metal sorption,^{30–32} the sorption of organic compounds,^{33,34} etc. However, there is a lack of literature data on the textile dyes sorption by copolymers based on GMA.

In this article, macroporous copolymer of GMA and ethylene glycol dimethacrylate (EGDMA), poly(GMA-co-EGDMA) (PGME), was synthesized by suspension copolymerization, and this copolymer additionally functionalized via ring-opening reaction of the pendant epoxy groups with diethylene triamine was used. The effect of pH, contact time, and sorbent mass on sorption efficiency of PGME-deta in Acid Orange 10 removal from aqueous solutions was studied to evaluate this material as wastewater sorbent. The sorption characteristics of the functionalized copolymer were compared with HDTMA-bentonite (bentonite modified with quaternary ammonium cationic surfactant hexadecyltrimethylammonium bromide) and commercial activated carbon. Also, comparative sorption experiments were performed from binary dye mixtures of Acid Orange 10 with Bemacid Gelb acid dye and Bezaktiv Rot reactive dye.

MATERIALS AND METHODS

Materials

All the chemicals used for copolymer synthesis were analytical grade products and used as received: glycidyl methacrylate (Merck), ethylene glycol dimethacrylate (Fluka), diethylene triamine (Merck), 2,2'-azobisisobutyronitrile, AIBN (Merck), poly(*N*-vinyl pyrrolidone) (Kollidone 90, BASF), cyclohexanol (Merck), and dodecanol (Merck). Synthetic textile dye, Acid Orange 10 (7-hydroxy-8-(phenylazo)-1,3-naphthalenedisulfonic acid disodium salt) [CAS: 1936-15-8] (Alfa-Aesar), with chemical purity of 80%, was used without further purification as test model dye; Bemacid Gelb acid dye and Bezaktiv Rot reactive dye both were the products of BEZEMA, Germany. Activated carbon was purchased from Kemika, Croatia.

Methods

The epoxy group content in synthesized PGME was determined by HCl-dioxane method³⁵ The initial and the amino-functionalized samples were analyzed for their carbon, hydrogen, and nitrogen content using the Vario EL III device (GmbH Hanau

Instruments, German). The pore size distributions were determined by mercury porosimetry (Carlo Erba 2000, software Milestone 200). The samples were dried at 50°C for 8 h and degassed at room temperature and at the pressure of 0.5 Pa for 2 h. The values of V_s and $D_{V/2}$ were read from pore size distribution curves determined by mercury porosimetry, whereas specific surface area, $S_{s,Hg}$, was calculated as the sum of incremental specific surface areas from the pore size distribution curves as described in the literature.³⁶

Preparation of poly(GMA-co-EGDMA) and functionalization with diethylene triamine

Macroporous PGME sample was prepared by radical suspension copolymerization of GMA and EGDMA in the presence of inert component (90 mass % of cyclohexanol and 10 mass % dodecanol) as described previously.²⁴ Particles with diameters in the range of 0.15–0.50 mm were used in subsequent reaction.

For functionalization with diethylene triamine, a mixture of 3.6 g of PGME, 15.7 g of diethylene triamine, and 100 cm³ of toluene was left at room temperature for 24 h and then heated at 80°C for 6 h. The modified sample was filtered, washed with ethanol, dried, and labeled as PGME-deta.³⁷

Dye sorption experiments

The Acid Orange 10 sorption by PGME-deta was investigated in aqueous solution in batch system with respect to contact time, pH, and sorbent mass. All the experiments were performed at room temperature (25°C) using the same volume of dye solution ($v = 50.0$ cm³). All experiments were carried out with the same mass of PGME-deta of 25.0 mg. Different copolymer masses were used only when the effect of sorbent mass (m_{sorb}) on sorption was investigated.

The amount of dye sorbed, q_t (mg g⁻¹), by the sorbent at time t was calculated by the following mass-balance relationship:

$$q_t = \frac{(C_0 - C_t)v}{m_{sorb}}, \quad (1)$$

where C_0 and C_t (mg dm⁻³) are initial and dye solution concentrations after sorption time t , respectively.

The pH of the solution was monitored with a Jenway 3320 pH meter. The sorption experiments were carried out in thermostated shaker (Memmert WNE 14 and SV 1422). The solution aliquots were withdrawn from the shaker at regular time intervals, and the dye solution was centrifuged. The absorbance of

TABLE I
Relevant Characteristics of Initial and Amino-Functionalized Copolymer Sample

Property	PGME	PGME-deta
$S_{s,Hg}$ ($m^2 g^{-1}$)	48	53
V_S ($cm^3 g^{-1}$)	0.610	0.635
$D_{V/2}$ (nm)	51	50
Degree of conversion of epoxy groups (%)	–	40
Ligand concentration ($mmol g^{-1}$)	–	1.67
Amino group concentration ($mmol g^{-1}$)	–	5.01

supernatant solution was measured. The spectra were obtained using Thermo Electron Nicolet Evolution 500 UV–vis spectrophotometer, and absorption peaks of Acid Orange 10, Bemacid Gelb acid dye, and Bezaktiv Rot reactive dye at 478, 399, and 542 nm were chosen for monitoring of sorption process.¹⁷

RESULTS AND DISCUSSION

Characterization of sorbents

Macroporous crosslinked PGME was obtained by suspension copolymerization in the presence of inert component (mixture of cyclohexanol and dodecanol) and then subsequently amino-functionalized by ring-opening reaction of the pendant epoxy group with diethylene triamine. The swelling of crosslinked macroporous copolymer particles in aqueous solutions was negligible (<4 vol %). The content of epoxy groups on the surface of crosslinked copolymer sample PGME determined by HCl-dioxane method was 2.08 mmol g^{-1} , and it differed from the theoretical value of 4.22 mmol g^{-1} , calculated on the basis of the feed composition. This discrepancy is understandable, because a certain part of epoxy groups usually remains inside the crosslinked copolymer, not being accessible for subsequent reactions and analytical determinations.³⁸ From the elemental analysis data, the degree of conversion of epoxy groups, ligand concentration, and amino group concentration in PGME-deta were calculated and given in Table I. The degree of conversion of 40% was expected, because similar values were already obtained for reaction with ethylene diamine (50%) and triethylene tetramine (31%).³⁷

The influence of porosity on the dye sorption behavior of the two investigated samples (initial and amino-functionalized) was insignificant, because the porosity parameters of these two samples were similar (see Table I).

First, the Acid Orange 10 sorption by nonfunctionalized PGME was tested. It was confirmed that there

was no Acid Orange 10 sorption by nonfunctionalized PGME. Because the initial copolymer has no functional groups that can bind sulfonate groups in the dye molecule, it was assumed that the Acid Orange 10 sorption by PGME-deta is specific, through amino groups.

In accordance with the previous conclusion, further experiments were performed only on PGME-deta.

The effect of pH

The effect of pH on the Acid Orange 10 sorption by PGME-deta is shown in Figure 1. The pH range between 2 and 11 was tested.

The sorption of Acid Orange 10 by PGME-deta very much depends on the pH value. The dye sorption was almost complete, i.e., 96% at pH 2, and then the sorption capacity decreased with increasing pH and reached plateau of 50% dye removal in the pH interval 4–8. With further increase of pH, dye removal efficiency decreased to only 5% at pH 11. Dye sorption was favored in acidic solutions because of the electrostatic attraction between the positively charged protonated amino groups on the PGME-deta surface ($-\text{NH}_3^+$) and the negatively charged sulfonate groups ($-\text{SO}_3^-$) in Acid Orange 10 dye molecules.^{39,40} It was previously reported that the pH dependence of sorption suggests that dye was sorbed according to complexation and sorption to the surface.⁴¹

The main goal of this research was the synthesis of a sorbent for the purification of textile industry wastewaters. Because they already have fluctuating pH, adjusting pH means an additional operation, which increases the procedure cost. Moreover, extreme pH values present additional ecological

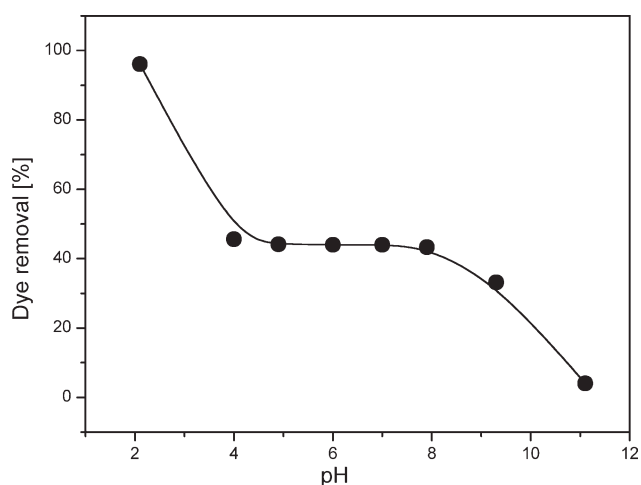


Figure 1 The effect of pH on the sorption of Acid Orange 10 ($C_0 = 50 \text{ mg dm}^{-3}$ for 60 min at 25°C) by PGME-deta.

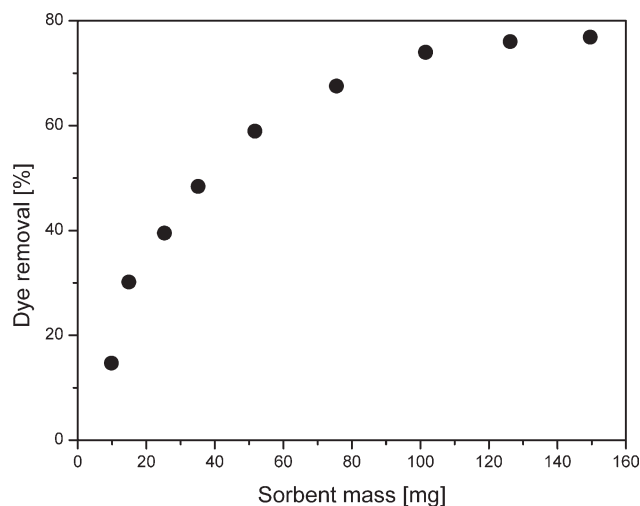


Figure 2 The effect of PGME-deta mass on the sorption of Acid Orange 10 by PGME-deta.

problem that should be avoided. Therefore, the sorption investigations in this article in all further experiments were carried out at the unadjusted pH value of 7.45. The sorption was less efficient, but satisfactory (44% removal of Acid Orange 10 from water) under given experimental conditions.

The effect of sorbent mass

To determine optimal quantity of PGME-deta required for Acid Orange 10 sorption, the influence of sorbent mass on dye removal was investigated and presented in Figure 2. The masses of sorbent were in the interval 10.0–150.0 mg, while the initial dye concentration was 50 mg dm^{-3} and the sorption time was 60 min.

The dye removal percent sharply increased up to 50 mg of sorbent mass, and for masses $\geq 110 \text{ mg}$ it gradually leveled off at 80% dye removal. The increase of sorption with the sorbent mass can be ascribed to the increased sorbent surface area and the availability of more sorption sites.⁴² For further experiments, the mass of 25 mg of PGME-deta was chosen.

Concentration–time profile

Because dye sorption is time-dependent process, the effect of contact time on the amount of Acid Orange 10 sorbed by PGME-deta (Fig. 3) was investigated in the range of the initial dye concentration of 20–70 mg dm^{-3} .

The rate of Acid Orange 10 removal by PGME-deta was high initially, and the process then gradually slowed down. The time profile of dye sorption by PGME-deta was a single smooth and continuous curve leading to saturation, suggesting the possible monolayer coverage of Acid Orange 10 on the sur-

face of the sorbent.⁴³ On the other hand, there were two different trends of dependence of the sorption capacity on the initial dye concentration. The best way to quantify these differences is by comparison of sorption half times (time required to reach 50% of the total sorption capacity, $t_{1/2}$). For three lower initial concentrations 20, 30, and 40 mg dm^{-3} , $t_{1/2}$ was $\sim 45 \text{ min}$, whereas for higher concentrations $t_{1/2}$ was 55 min. According to the results presented in Figure 3, the equilibrium contact time exhibited similar behavior. The equilibrium contact time was estimated to be 180 min for concentrations of 20, 30, and 40 mg dm^{-3} , because there was almost no further increase in sorption with time. For higher concentrations of 50, 60, and 70 mg dm^{-3} , the equilibrium contact time was much higher, i.e., 480 min.

To the best of our knowledge, no sorption studies performed with Acid Orange 10 under the same experimental conditions using macroporous cross-linked PGME-deta have been published. For comparison purposes, it is possible only to use available sorption data published for other polymeric sorbents, synthesized or commercial. For instance, for grafted poly(glycidyl methacrylate) by poly(styrene-co-divinyl benzene) and functionalized with diethyl amine, Senkal et al. reported that within 50 min of contact, the concentration of reactive dye Everzol Red RBN falls to zero.⁴⁴ Yu et al. reported that the time required to reach equilibrium sorption on functionalized polymer with dicyandiamide groups for Reactive Brilliant Blue 19 was 24 h and for Reactive Orange 25, Reactive Red 24, Acid Black 7, and Acid Blue 25 was 48 h.⁴⁵

Valderrama et al. studied sorption of reactive dye Acid Red 14 by Macronet polymeric sorbents based on crosslinked poly(styrene) MN200 (nonfunctionalized) and MN300 (containing tertiary groups).³⁹

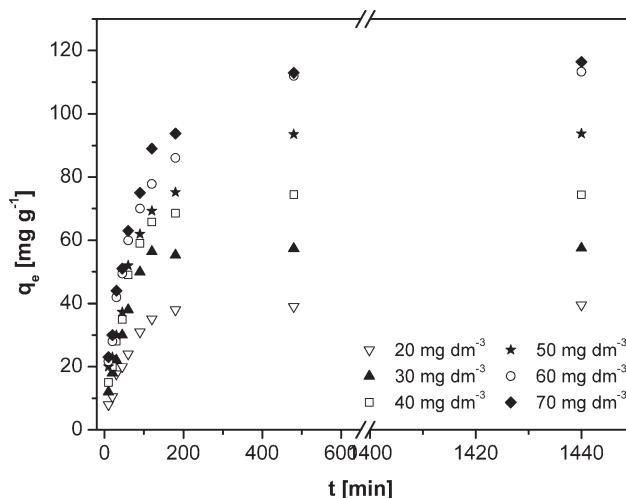


Figure 3 The effect of contact time on sorption of Acid Orange 10 by PGME-deta.

They found that the time required to reach half of the initial dye concentration was 140 and 280 min for MN200 at pH 2 and 7 and 60 and 70 min for MN300 at pH 2 and 7.

Isotherm models

The equilibrium sorption data presented in Figure 3 were fitted into Freundlich and Langmuir equations to determine the model that is the most appropriate to describe the obtained results. The linear form of the Freundlich equation⁴⁶ is as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e, \quad (2)$$

where q_e is the amount of dye adsorbed by sorbent (mg g^{-1}) at equilibrium, C_e is the equilibrium dye concentration in solution (mg dm^{-3}), while K_F ($\text{dm}^3 \text{g}^{-1}$) and n are the Freundlich adsorption constants characteristic for the system.

The value of K_F is related to the degree of adsorption. Higher K_F values indicate higher affinity to the investigated sorbent. The Freundlich equation is used to describe heterogeneous systems and reversible adsorption and is not restricted to the formation of monolayers. The Freundlich constant ($1/n$) is also a measure of the deviation of adsorption from linearity. If n is equal to unity, adsorption is linear. This means that the adsorption sites are homogeneous (as in the Langmuir model) in energy, and no interaction takes place between the adsorbed species. If the value of $1/n$ is smaller than 1, reflecting favorable adsorption, then the sorption capacity increases and new adsorption sites occur. When the value of $1/n$ is larger than 1, $1/n \gg 1$, the adsorption bond becomes weak; unfavorable adsorption takes place, as a result of the adsorption capacity decreases.^{47,48}

The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogenous sites within the adsorbent and is the most appropriate for monolayer adsorption.⁴⁹ Well-known expression of the Langmuir model is as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}}, \quad (3)$$

where q_{\max} is the monolayer capacity of the sorbent (mg g^{-1}) and K_L is the Langmuir adsorption constant ($\text{dm}^3 \text{mg}^{-1}$), whereas all other symbols are the same as in eq. (2).

The characteristics of Langmuir isotherm can be expressed by dimensionless constant called Langmuir equilibrium parameter R_L given in eq. (4):

$$R_L = \frac{1}{1 + K_L C_0}. \quad (4)$$

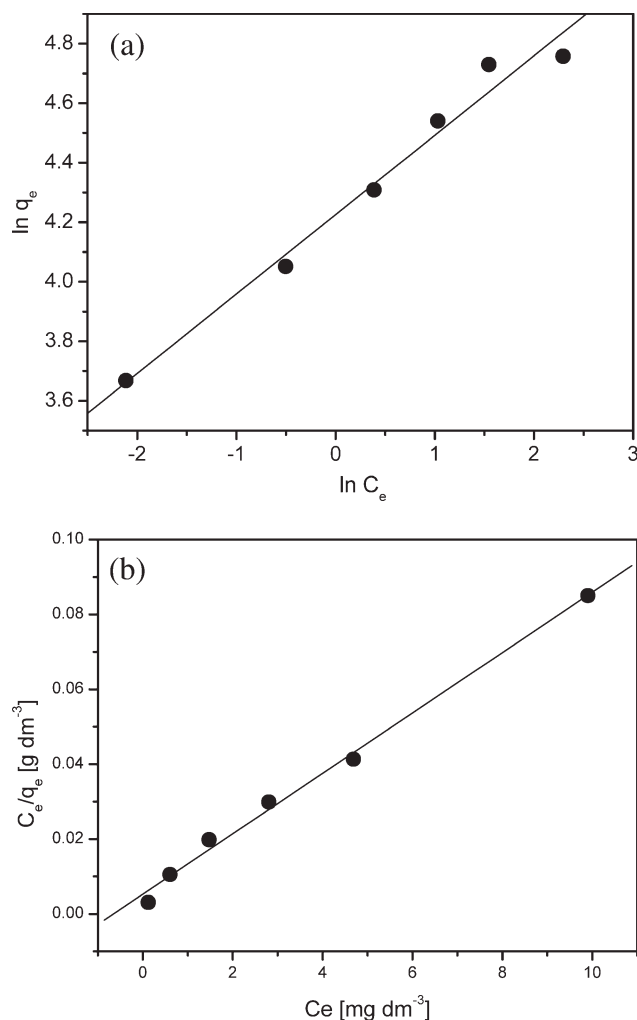


Figure 4 Freundlich (a) and Langmuir (b) isotherm linear plots for sorption of Acid Orange 10 by PGME.

The value of R_L indicates unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) sorption. The experimental data were fitted by Freundlich [Fig. 4(a)] and Langmuir [Fig. 4(b)] models, and the corresponding constants were calculated from the intercepts and the slopes and are given in Table II.

According to the results presented in Table II, both models can be applied to experimental data, but the correlation coefficient in Langmuir model is closer to unity and therefore somewhat more appropriate. At the same time, the values of the coefficients obtained from both isotherms, i.e., $1/n = 0.267$ and $R_L = 0.01$, lie within the favorable limits. The fact that the Langmuir isotherm better fits the experimental data indicates that the distribution of active sites in PGME-deta is homogeneous.

Sorption dynamics

The kinetics data were treated with both the pseudo-first-order and the pseudo-second-order kinetic

TABLE II
Calculated Model Constants and Correlation Coefficients

Freundlich isotherm			Langmuir isotherm			
N	K_F (dm ³ g ⁻¹)	r_F	q_{\max} (mg g ⁻¹)	K_L (dm ³ mg ⁻¹)	R_L	r_L
3.75	68.41	0.9897	123.9	1.528	0.01	0.9972

models.⁵⁰ The integrated rate law for the pseudo-first-order and the pseudo-second-order reactions in linear forms is presented in eqs. (5) and (6), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{\ln 10} \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t, \quad (6)$$

where q_t is the amount of sorbed dye (mg g⁻¹) at any time t , q_e is the amount of sorbed dye at equilibrium (mg g⁻¹), k_1 is the pseudo-first-order rate constant (min⁻¹), and k_2 is the pseudo-second-order rate constant (g mg⁻¹ min⁻¹).

Both models were tested, and the values for q_e , k_1 and k_2 , as well as the corresponding correlation coefficients for each initial dye concentration are presented in Table III. The values for the pseudo-first-order constant were calculated from the plots of $\log(q_e - q_t)$ versus t for each initial dye concentration, whereas for the pseudo-second-order constant, these parameters were calculated from the t/q_t versus t plot (Fig. 5).

Because the correlation coefficients for the pseudo-second-order kinetic model were higher than the corresponding correlation coefficients for the pseudo-first-order kinetic model, the pseudo-second-order kinetic model was proven to be more adequate. Besides, q_e^{exp} and q_e values obtained for the pseudo-second-order reaction showed excellent agreement, particularly for lower initial dye concentrations. Moreover, the correlation coefficients for the pseudo-second-order kinetics model were higher than 0.99 for all experimental data, undoubtedly

confirming that the sorption of Acid Orange 10 by PGME-deta obeys the pseudo-second-order kinetic model.

The rate of intraparticle diffusion can be calculated according to equation⁵¹:

$$q = k_p \cdot t^{1/2}, \quad (7)$$

where k_p is the intraparticle diffusion coefficient.

In the case of linear plot of q versus $t^{1/2}$, and if the line passes through the origin, intraparticle diffusion is the only rate-controlling step. If not, some other mechanisms are also involved. There are opinions in the literature that multilinear $q-t^{1/2}$ plots might present different stages of intraparticle diffusion. The plots of Acid Orange 10 sorption by PGME-deta for all investigated dye concentrations showed the similar trends. Therefore, for the sake of clarity, only the plots for the initial concentrations of 20, 40, and 60 mg dm⁻³ are presented in Figure 6.

The plot of the square root of time ($t^{1/2}$) versus the uptake (q_t) for the adsorption results in a linear relationship passing through origin. This implied that the first rate-limiting step of adsorption may be intraparticle diffusion. According to presented data, there was at least one more controlling step, beside intraparticle diffusion for Acid Orange 10 sorption in PGME-deta.

Comparative study

Some additional tests were performed to establish the quality of synthesized sorbent. The PGME-deta sample was tested on somewhat more complex effluents. The sorption experiments were carried out

TABLE III
Kinetic Parameters for Acid Orange 10 Sorption by PGME-deta

C_0 (mg dm ⁻³)	q_e^{exp} (mg g ⁻¹)	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
		q_e (mg g ⁻¹)	$k_1 \times 10^2$ (min ⁻¹)	r_1	q_e (mg g ⁻¹)	$k_2 \times 10^4$ (g mg ⁻¹ min ⁻¹)	r_2
20	39.5	32.7	1.16	0.9351	40.4367	5.55	0.9992
30	57.5	44.7	1.30	0.9204	58.9623	4.89	0.9995
40	74.4	76.3	1.43	0.9796	77.2798	2.45	0.9989
50	93.7	79.9	0.62	0.9014	99.5025	1.12	0.9985
60	113.3	93.5	8.68	0.9829	117.6471	1.57	0.9997
70	116.5	122.1	7.97	0.9845	128.041	0.58	0.9973

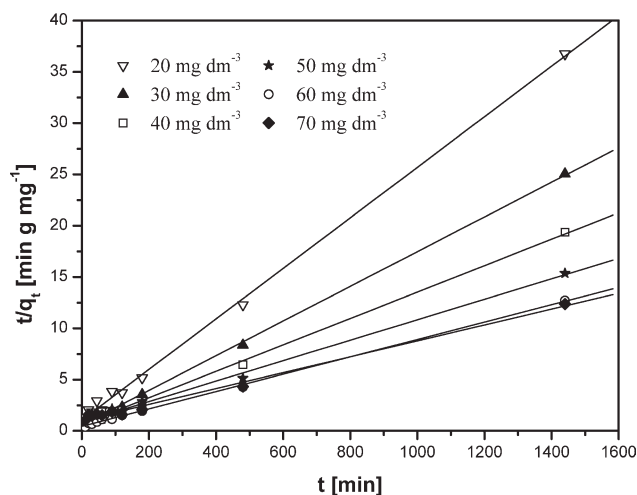


Figure 5 Pseudo-second-order kinetics of Acid Orange 10 uptake by PGME-deta.

on two binary mixtures. These were the mixtures of Acid Orange 10 (originally chosen representative dye) and either Bemacid Gelb acid dye (Fig. 7) or Bezaktiv Rot reactive dye (Fig. 8).

It is obvious that in the case of acid dyes, Acid Orange 10 and Bemacid Gelb, the similar sorption profiles were obtained, with the maximum sorption capacities about 35 mg g^{-1} and $t_{1/2}$ of 45 min for both dyes. On the other hand, maximum sorption capacity of PGME-deta for reactive dye, Bezaktiv Rot was 17 mg g^{-1} , twice lower than for Acid Orange 10, although the $t_{1/2}$ values were around 50 min for both dyes.

The sorption ability of PGME-deta was compared to activated carbon. The most commonly used sorbent is activated carbon, because it has highly porous structure, extremely large surface area to volume ratio, and high degree of surface reactivity and,

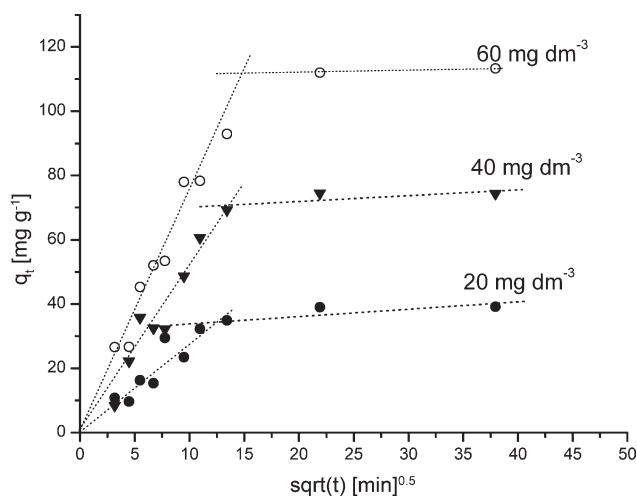


Figure 6 The plots of q_t versus $t^{1/2}$ plots for Acid Orange 10 sorption by PGME-deta at indicated concentrations.

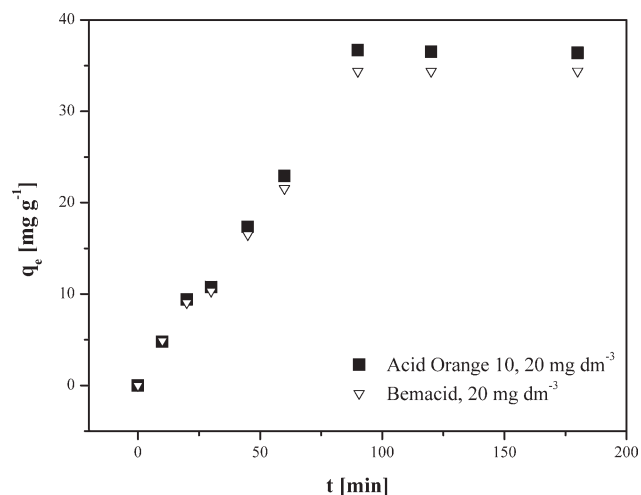


Figure 7 Competitive sorption of Acid Orange 10 and Bemacid Gelb by PGME-deta.

thus, high dye-binding capacity.⁵² However, activated carbon has some drawbacks. Its high cost, expensive disposal by thermal degradation after the sorption, the production of additional effluents, and the loss of adsorbent during the sorption process inspired researchers to find cheaper and more efficient alternative materials. For these reasons, polymeric sorbents have attracted attention as they can easily be regenerated and reused, in addition to the possibility of functionalization, to achieve selective removal of targeted contaminant.

The sorption experiments were performed under the same experimental conditions (temperature 25°C , $C_0 = 70 \text{ mg dm}^{-3}$, and $m_{\text{sorb}} = 25 \text{ mg}$) with PGME-deta and commercial activated carbon for the purpose of more accurately comparing the efficiency of these two sorbents. The effect of contact time on the

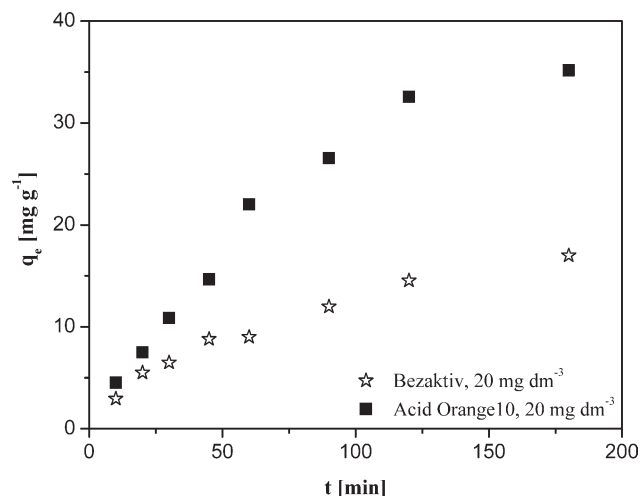


Figure 8 Competitive sorption of Acid Orange 10 and Bezaktiv Rot by PGME-deta.

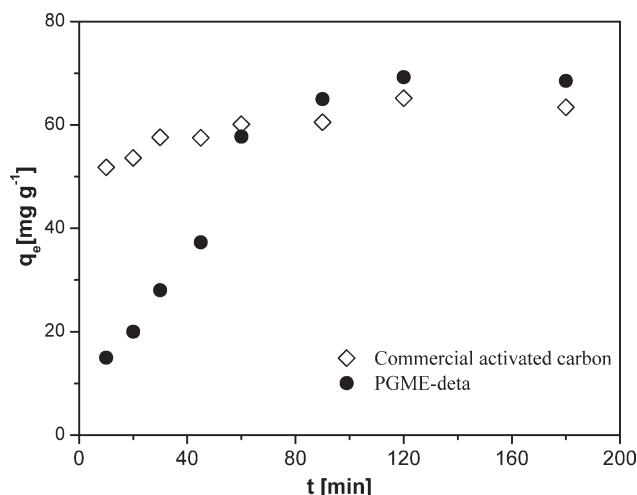


Figure 9 The effect of different sorbents on Acid Orange 10 sorption.

amount of Acid Orange 10 sorbed by PGME-deta and commercial activated carbon is presented in Figure 9.

For comparison purposes, we could use the results previously published by Tsai et al., which show that the monolayer adsorption capacity of activated carbons prepared from agricultural waste bagasse is in the interval from 2.3 to 5.8 mg g⁻¹.⁵³ According to Mall et al., q_{\max} for Acid Orange 10 on bagasse fly ash is 18.8 mg g⁻¹.⁵⁴ Donia et al.⁴⁰ reported q_{\max} for Acid Orange 10 on monoamine-modified silica particles of 27 mg g⁻¹ at the initial concentration of 30 mg dm⁻³ and 298 K.³⁷ These values are significantly lower than the result obtained for PGME-deta sample (68 mg g⁻¹) and particularly for hexadecyltrimethyl-ammonium-bentonite ($q_{\max} = 142$ mg g⁻¹).¹⁷

Undoubtedly, hexadecyltrimethylammonium-bentonite, with the equilibrium sorption capacity of 142 mg g⁻¹ and very fast sorption (after 30 min, the sorption capacity reaches 90% of the total capacity), is the most efficient amongst investigated sorbents, because the amount of sorbed dye by HDTMA-bentonite is more than two times greater than on commercial activated carbon.¹⁷ However, the fineness of organobentonite and activated carbon particles hinders the separation process, which increases the cost of the application of these sorbents. Therefore, more robust PGME-deta is more appropriate for further separation techniques.

On the other hand, the sorption rate of Acid Orange 10 dye on PGME-deta is much lower during the first 60 min when compared with the other two sorbents. However, after 90 min, PGME-deta has higher sorption capacity than activated carbon. The equilibrium capacity for activated carbon was 63 mg g⁻¹, and for PGME-deta, the value was somewhat higher, i.e., 68 mg g⁻¹.

The preliminary experiments with the concentrated HCl and particularly with the concentrated NaOH showed the ability of loaded PGME-deta for regeneration and the possibility of its reuse in several sorption/desorption cycles. This indicates that PGME-deta might be used as an alternative sorbent for textile dyes, because it can be functionalized to achieve selective removal of particular sorbate, and it could be regenerated and reused using the appropriate stripping agent.

CONCLUSION

Macroporous crosslinked PGME was synthesized by suspension copolymerization and functionalized via ring-opening reaction of the pendant epoxy groups with diethylene triamine. The ability of Acid Orange 10 sorption by PGME-deta from single and binary dye solutions was tested. The functionalization enabled dye sorption because of the presence of amino groups that attract anionic sulfonate groups in the Acid Orange 10 dye molecule. The sorption is pH sensitive, reaching maximum at pH = 2 and decreasing with the increase of pH. The sorption kinetics study showed that the sorption of Acid Orange 10 by PGME-deta obeys the pseudo-second-order kinetic model. The isotherm data were best fitted by Langmuir model, indicating homogeneous distribution of active sites on PGME-deta and monolayer adsorption.

It is evident from the experimental data that PGME-deta selectively sorbs Acid Orange 10 from the binary solution with Bezaktiv Rot reactive dye. The comparison of PGME-deta sorption characteristics with activated carbon confirmed that PGME-deta was able to reach the sorption efficiency of activated carbon. PGME-deta might be used as an alternative sorbent for textile dyes, because it can be regenerated and reused using the appropriate stripping agent.

NOMENCLATURE

C_0	initial dye solution concentration (mg dm ⁻³)
C_e	equilibrium dye solution concentration (mg dm ⁻³)
k_1	pseudo-first-order rate constant (min ⁻¹)
k_2	pseudo-second-order rate constant (g mg ⁻¹ min ⁻¹)
K_F	Freundlich adsorption constant (dm ³ mg ⁻¹)
K_L	Langmuir adsorption constant (dm ³ mg ⁻¹)
m_{sorb}	mass of sorbent (mg)
n	Freundlich adsorption constant (–)
q_e	estimated amount of sorbed dye at equilibrium (mg g ⁻¹)
q_e^{exp}	experimentally obtained amount of sorbed dye at equilibrium (mg g ⁻¹)

q_t	the amount of sorbed dye at time t (mg g^{-1})
q_{max}	monolayer capacity of the sorbent (mg g^{-1})
r_1	correlation coefficient for pseudo-first-order kinetic (–)
r_2	correlation coefficient for pseudo-second-order kinetic (–)
r_F	correlation coefficient for Freundlich isotherm (–)
r_L	correlation coefficient for Langmuir isotherm (–)
R_L	Langmuir equilibrium parameter (–)
t	time (min)
v	volume of solution (cm^3)

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