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ORIGINAL PAPER

Removal of cationic dyes from aqueous solutions with poly (*N*-isopropylacrylamide-*co*-itaconic acid) hydrogels

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Abstract In this study, *N*-isopropylacrylamide-based temperature and pH-sensitive hydrogels were synthesized by free radical polymerization for removal of cationic dyes from aqueous solutions. For this purpose, *N*-isopropylacrylamide was copolymerized with various amounts of sodium salt of itaconic acid in the presence of crosslinking agent (*N*,*N*-methylene bisacrylamide). The chemical structures of hydrogels were characterized by FT-IR analysis. In order to investigate swelling properties of the hydrogels, water absorption (swelling) and shrinking (deswelling) kinetics, the equilibrium swelling ratios in water and different pH buffer solutions, and the temperature dependent swelling ratios were determined. Then, their adsorption properties such as adsorption capacities, kinetics, isotherms were investigated in case of their usage in removal of Safranine T (ST), Brilliant Green (BG), and Brilliant Cresyl Blue (BCB) aqueous solutions. According to adsorbed dye amount, the adsorption capacities are followed the order BG $>$ ST $\cong$ BCB. In addition, the results indicated that the pseudo-second-order kinetic model fitted better than the data obtained from pseudo-first-order model for the adsorption of all dyes onto hydrogels. Furthermore, according to effect of the initial dye concentration findings, it is concluded that, Freundlich isotherm explains the adsorption better than Langmuir isotherm.

Keywords *N*-isopropylacrylamide · Itaconic acid · Hydrogel · Swelling · Adsorption · Cationic dye · Temperature and pH-sensitive polymers

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Introduction

Hydrogels are three dimensionally crosslinked polymer network structures composed of hydrophilic homo or hetero copolymers, which have the ability to absorb significant amounts of water [1]. The characteristics features of polymeric hydrogels are hydrophilicity, insolubility in water, softness, elasticity, and swelling with water [2]. The hydrophilicity of these materials is due to the presence of water compatible groups such as –OH, –COOH, $-CONH_2$, and $-SO_3H$, and those are related to the existence of capillary areas and differences in osmotic pressure [3]. In addition, the ability to swelling with water depends firstly on the type of polymers and on the degree of crosslinking [4].

Some hydrogels are stimuli sensitive; they exhibit significant changes in their swelling and mechanical properties in response to changes in pH, ionic strength, or temperature of the external environment [5, 6]. All the pH-sensitive hydrogels contain ionizable groups on polymer chains [5, 7, 8]. Poly (*N*-isopropylacrylamide) (pNIPAm) hydrogel is the best known temperature sensitive polymeric network, which exhibits a lower critical solution temperature (LCST) at about 32–34 °C [9, 10]. Below the LCST, the PNIPAm gel is swollen in water. As the temperature is increased above LCST, it undergoes abrupt changes in volume and shrinks quickly [9, 11–13]. Hydrogels have been used in the fields of medicine, pharmacy, biotechnology, agriculture, food industry, and controlled drug delivery systems [14, 15]. Stimuli sensitive hydrogels have attracted great interests for an expansive variety of applications such as sensors, controlled drug or gene delivery, biotechnology, protective coatings, and recyclable absorbents [16–19]. However, today there are few studies on the research of stimuli responsive materials for waste treatment and separation processes [20]. In general, applications of poly (*N*-isopropylacrylamide)-*co*-itaconic acid hydrogels were focused on controlled release and drug delivery systems [21–23] thus their usability in waste water treatment is not explained detail yet.

Synthetic dyes are widely used in many fields of technology, for example, the textile, leather, paper, rubber, plastics, cosmetics, pharmaceutical, and food industries [24]. Synthetic dyes usually have a complex aromatic molecular structure and exhibit considerable structural diversity [24, 25]. The extensive use of dyes usually causes serious pollution problems because of their toxic nature. The conventional methods for removal of dyes from wastewaters include coagulation and flocculation, oxidation or ozonation, membrane separation, and adsorption [26–30]. Among them, adsorption method is very useful and important to treat or even purify the wastewaters [31–33].

The aim of this work is investigating the usage of p(*N*-isopropylacrylamide-*co*-itaconic acid) p(NIPAm-*co*-IA) temperature sensitive hydrogels for removal of cationic dyes from aqueous solutions. For this purpose, *N*-isopropylacrylamide was copolymerized with various amounts of sodium salt of itaconic acid in the presence of crosslinking agent *N*,*N*-methylene bisacrylamide to obtain temperature sensitive hydrogels. The chemical structure, swelling, and deswelling properties of these hydrogels were investigated. In addition, their adsorption properties (i.e., adsorption capacities, kinetics, isotherms) were investigated in case of their usage in removal of Safranine T (ST), Brilliant Green (BG), and Brilliant Cresyl Blue (BCB) aqueous solutions.

Experimental

Materials

N-isopropylacrylamide (NIPAm) was purchased from Sigma-Aldrich (USA) and recrystallized from toluene before use. Itaconic acid (IA); the cross linking agent (*N*,*N*-methylenebisacrylamide (NMBA); the initiator and accelerator pair, potassium persulfate (PPS), and potassium bisulfide (PBS) were all purchased from Merck AG (Darmstadt, Germany). Cationic dyes (ST, BG, and BCB) were also obtained from Merck AG (Darmstadt, Germany). The rest of the materials were synthesis or analytical grade. All solutions and standards were prepared using distilled water. The chemical structures of the dyes are shown in Fig. 1.

Instruments

Spectrophotometric measurements were carried out with an Optima SP-300 Visible spectrophotometer (Tokyo, Japan). Differential Scanning Calorimeter (DSC) analyses of the hydrogels were carried out with Setaram 131 model apparatus

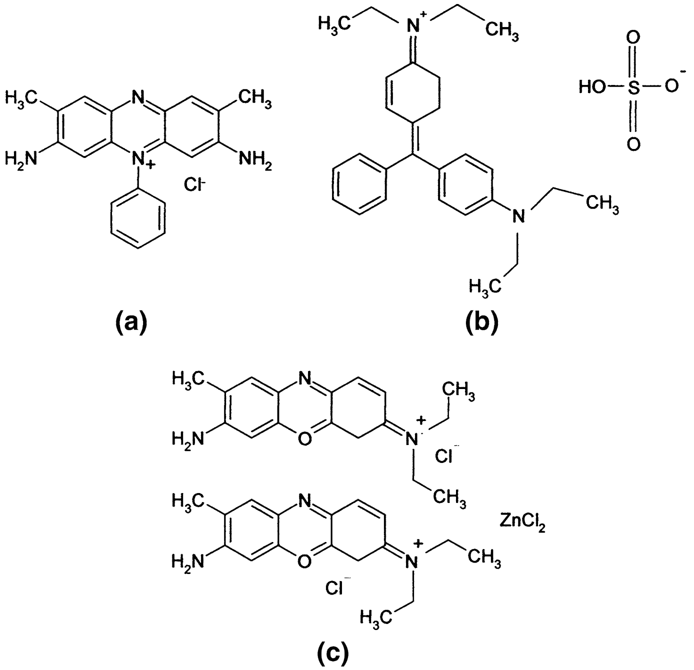


Fig. 1 Chemical structure of the basic dyes used in this study: **a** ST, **b** BG, **c** BCB

(France). The infrared spectra of hydrogels were obtained with Digilab Excalibur-FTS 3000MX model FTIR Spectrophotometer (Randolph, MA, USA) using KBr pellets.

Synthesis of hydrogels

The NIPAm-*co*-IA hydrogels were prepared by free radical polymerization in the presence of NMBA as crosslinker in aqueous solution. Before the synthesis of hydrogels, IA was treated with NaOH in order to obtain sodium salt of itaconic acid (IA-Na). Different amounts of monomers and the crosslinking agent (1% molar ratio of the total mixture) were dissolved in deionized water in glass tubes (12 cm × 1.5 cm; length × diameter). After sealing the tubes with rubber caps, the solution was purged with nitrogen gas for 30 min to eliminate dissolved oxygen in the system, and the tubes were placed in a water-bath at 10 °C. Then, the required amounts of $K_2S_2O_8$ (PPS) and $KHSO_3$ (PBS) were added as their aqueous solutions. The polymerization reactions were carried out for 24 h at 10 °C. In all experiments, the initiator concentration (PPS) was 1% (mol) with respect to total amount of monomers, and the amount of accelerator (PBS) was equal to the PPS in weight. At the end of the polymerization, the hydrogels were taken out by breaking the glass tubes. The hydrogels were put into distillate water and held at room temperature for 4 days. In order to remove any unreacted monomers and initiators, water was changed with fresh water periodically (twice in a day). After 4 days, the hydrogels were dried under vacuum at 50 °C during 24 h for using in swelling and dye adsorption experiments. The feed compositions of the hydrogels are given in Table 1.

Swelling measurements

In order to investigate swelling properties of the hydrogels, water absorption (swelling), and shrinking (deswelling) kinetics, the equilibrium swelling ratios in water and different pH buffer solutions, and the temperature dependent swelling ratios were determined.

Swelling kinetic experiments were carried out at room temperature by "demand absorbency test" method as described in literature [34–37]. The measurements were performed until the swelling equilibrium was reached. The water uptake was calculated by the following equation:

$$Q_t = \left(W_{\text{wet}} - W_{\text{dry}}\right)/W_{\text{dry}} \qquad (1)$$

Table 1 The feed compositions of the hydrogels

Hydrogel	NIPAm (mol%)	IA-Na (mol%)	NMBA (mol%)
N-5	95.0	5.0	1
N-7.5	92.5	7.5	1
N-10	90.0	10	1

where Q_t is the swelling ratio for a given time, W_{wet} and W_{dry} are the weights of the swollen gel and the dry sample, respectively.

The equilibrium swelling ratio of hydrogels was measured gravimetrically. In order to determine the equilibrium swelling ratio, dry copolymer disks were immersed in distilled water at for 24 h at required temperature. After 24 h, the hydrogel sample was weighted. The equilibrium swelling ratio (Q_{e}) was calculated from the following equation:

$$Q_{\mathrm{e}} = \left(W_{\mathrm{wet}} - W_{\mathrm{dry}}\right)/W_{\mathrm{dry}} \times 100 \tag{2}$$

where Q_{e} is the equilibrium swelling ratio for a given time, W_{wet} and W_{dry} are the weights of the swollen gel and the dry sample, respectively.

Temperature dependent swelling ratios of hydrogels were also investigated by gravimetrically. Dry hydrogel samples were immersed in distilled water and kept for 24 h in the temperature range from 5 to 50 °C (5, 10, 15, 20, 30, 40, 50 °C). After 24 h, the hydrogel samples were weighted and the temperature dependent equilibrium swelling ratio (Q_{e}) was calculated using Eq. 1 for a given temperature.

In order to determine the pH sensitivity of hydrogels, dry hydrogel samples were immersed in buffer solutions at different pH values (1.95, 4.83, 7.00, 9.06, 9.94) and kept for 24 h to obtain equilibrium swelling at room temperature. After 24 h, the hydrogel samples were weighted and the pH dependent equilibrium swelling ratio (Q_{e}) was calculated using Eq. 1.

Shrinking kinetic experiments were carried out at 55 °C using a thermostated water-bath by gravimetric method. A given amount of swollen hydrogel at room temperature was immersed in water at 55 °C. The weight changes versus time (5, 10, 20, 40, 60, 80, 100, 120 min) of the hydrogels were recorded during the deswelling. The water retention value was calculated using Eq. 1. The all swelling/deswelling experiments were repeated three times for each hydrogel sample and the averages of the results were reported.

DSC measurements

Lower LCSTs of the hydrogels were determined by using DSC technique. Swollen gels were heated from 10 to 70 °C, with a heating rate of 0.5 °C/min under static atmosphere, using distilled water as reference.

Adsorption kinetics and isotherm experiments

Adsorption kinetics experiments were carried out in 50 mL of synthetic dye solution at room temperature. About 0.05 g hydrogel was added to the ST, BG, and BCB solutions with concentrations of 500 mg/L for the determination of adsorption capacity. ST, BG, and BCB solutions were prepared by the dissolution of dye in distilled water to the required concentrations. After desire treatment period (1, 3, 5, 7, 24, 48, and 96 h) the residual dye concentration was determined colorimetrically with a spectrometer at the specific absorption wavelength, 530, 618, and 622 nm for

ST, BG, and BCB, respectively. All of the experiments were done at their natural pH value of dye solutions and were carried out in triplicate.

Adsorption isotherms were obtained by holding the hydrogel samples in dye solutions with various initial concentrations. In the equilibrium adsorption isotherm experiments, a fixed amount of sorbent (0.05 g) was contacted with 50 mL of aqueous solutions of ST, BG, and BCB with different concentrations (50, 100, 200, 300, 400, 500 mg/L). The amount of residual dye in aqueous solution was determined with a visible spectrophotometer after 24 h. The adsorption capacities (mg dye/g hydrogel) of hydrogels were calculated using the following equation:

$$q_e = (C_o - C_e)V/m \tag{3}$$

where q_e (mg/g) is the adsorbed amount of dye per gram hydrogel, C_o and C_e are the initial dye concentration (mg/L) and equilibrium concentration (mg/L), respectively; V is the volume of the solution; and m is the amount of the hydrogel used (g). Then, the Langmuir and Freundlich models were used to describe the relationship between the amount of dye adsorbed and its equilibrium concentration in solution.

Results and discussion

FTIR analysis

FTIR spectrum of N-10 hydrogel was given in Fig. 2. The characteristic peaks for NIPAm segments in the network were seen as; 1660 cm^{-1} (amide I), 1577 cm^{-1} (amide II), 1177 cm^{-1} (amide III), 1350 and 1444 cm^{-1} (symmetric and asymmetric stretching of C–H bonds of isopropyl group), 3355 and 3416 cm^{-1} (symmetric and asymmetric stretching of N–H bond). The peaks at about 1368 and

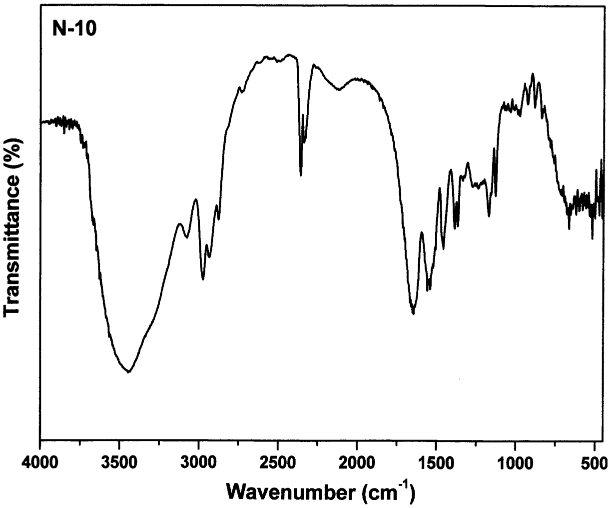


Fig. 2 FTIR spectrum of N-10 hydrogel

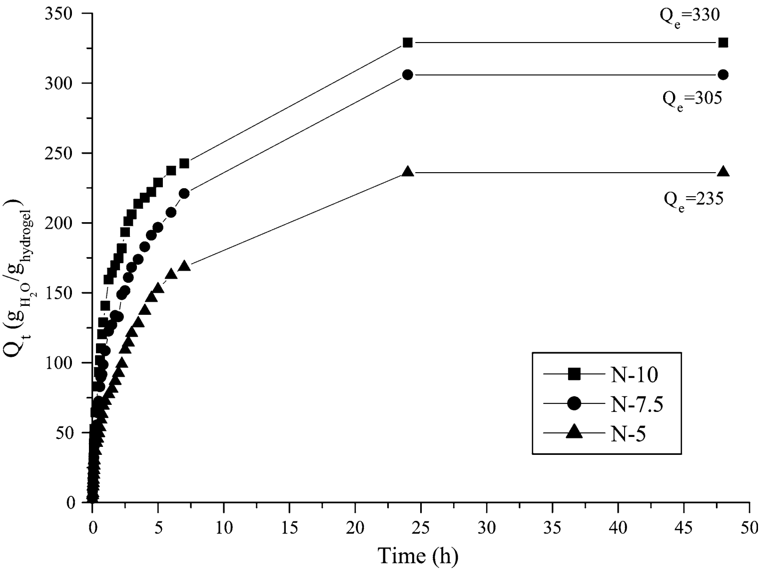


Fig. 3 Swelling properties of the hydrogels in distilled water

1540 cm^{-1} were attributed to asymmetric stretching of $–COO^-$ groups (in Na form) of the IA segments of the network. These so-called IR bands confirm the presence of IA-Na and NIPAm segments in the hydrogel structure [34, 38, 39].

Swelling properties

The swelling mechanism of a hydrogel is affected from several factors such as hydrophilic and hydrophobic character of the network, ionization degree of the hydrophilic groups, dynamic volume, etc. [40, 41]. In case of thermosensitive hydrogels, the medium temperature takes an important role on swelling properties of the hydrogels. Also, in case of pH-sensitive hydrogels, the most important parameter for the swelling becomes the pH of the medium.

The synthesized hydrogels in this study are both thermo and pH sensitive because of the nature of the monomers used. Thus, temperature and pH take important roles on swelling properties. The all swelling properties of the hydrogels were illustrated in Figs. 3, 4, 5, 6, 7 and Table 2 in following sections.

Equilibrium swelling ratios

Figure 3 shows the equilibrium swelling ratios (Q_e) and swelling kinetics of the hydrogel in distilled water at room temperature. As it seen from the figure, all hydrogels exhibit similar swelling behaviors and rates. Increasing the mole ratio of hydrophilic comonomer (IA-Na) content in feed composition from 5 to 7.5 and 10, increases the Q_e values from 235 to 305 and 330 g H_2O/g hydrogel, respectively. These 1.3 and 1.5 times greater capacities are expected results, because it is well

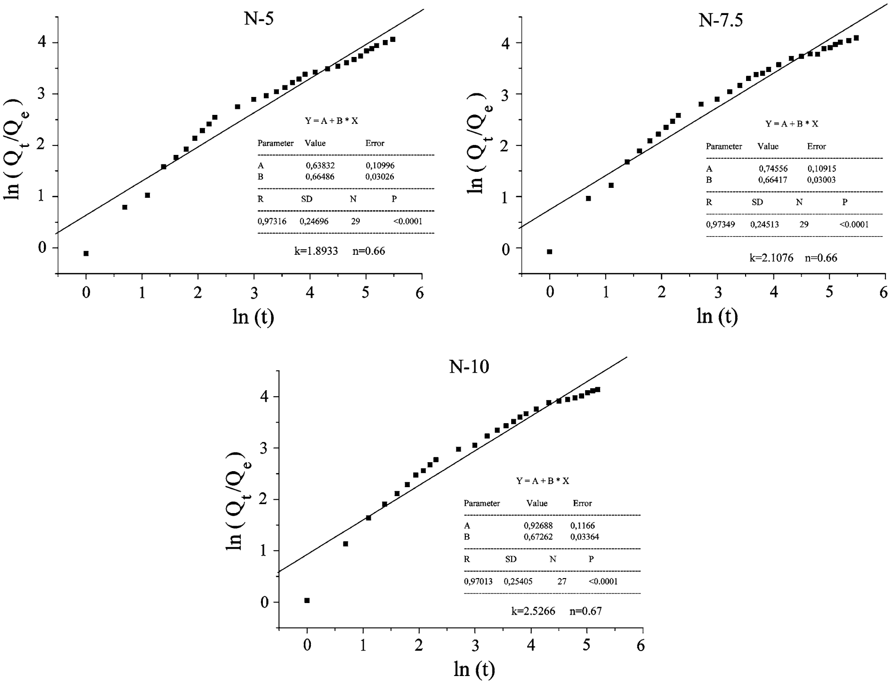


Fig. 4 Swelling kinetic parameters of the hydrogels

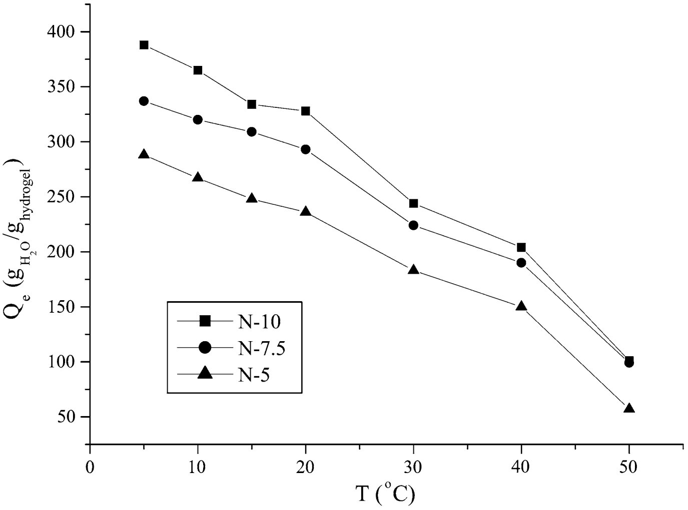
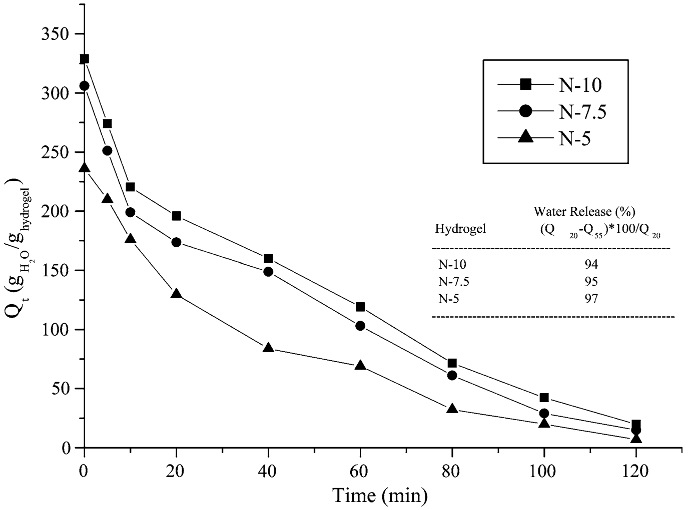


Fig. 5 Temperature dependent swelling values of the hydrogels

known that increasing the hydrophilic character of the network increases the ionization degree of the hydrogel and this yields higher water absorption capacity [42].



Hydrogel	Water Release (%) (Q_{20}-Q_{55})*100/Q_{20}
N-10	94
N-7.5	95
N-5	97

Fig. 6 Deswelling properties of the hydrogel in distilled water at 55 °C

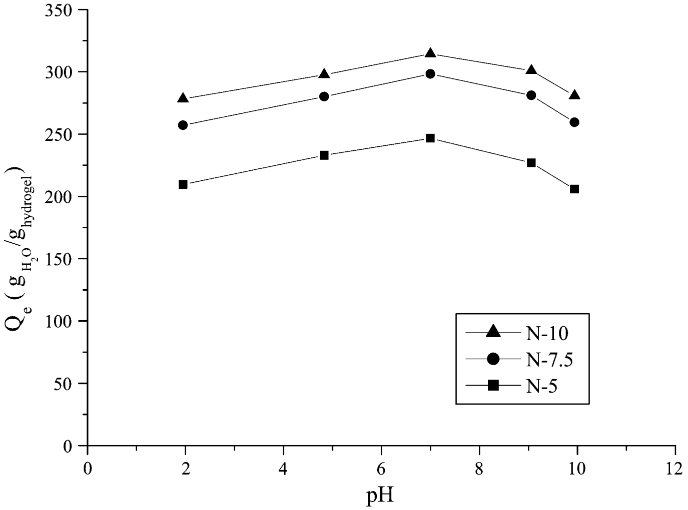


Fig. 7 The effect of medium pH on swelling values of the hydrogels

Swelling kinetic

Kinetic parameters of the swelling of hydrogels in distilled water at room temperature are given in Fig. 4. As it seen from the figure, all *n* values are in the range of 0.5–1 which indicates non-fickian type swelling. Also, it is clearly seen that the composition of the hydrogel does not affect the type of swelling characteristic because all *n* values of the hydrogels are very closed each other and in a range of 0.66–0.67.

Table 2 On-set and off-set points of peaks in the DSC curves of hydrogels

Hydrogel	Number of peaks	DSC peaks (°C)	
		On-set	Off-set
N-10	4	36.5	41.1
		42.1	44.4
		47.2	49.8
		50.3	57.2
N-7.5	3	34.7	36.8
		38.2	41.1
		47.6	53.7
N-5	1	33.7	45.2

LCST of the hydrogels

In order to determine the effect of temperature on swelling (in other words to determine LCST of the hydrogels), DSC technique was employed. In general, in DSC analysis of the thermosensitive hydrogels, homogenous networks (monodispers polymers) show a sharp endothermic peak at LCST indicating discontinuous phase transition while inhomogeneous ones (polydispers polymers) show several sharp and/or a large endothermic peak indicating continuous phase transition [42–45]. As it given in Table 2, the synthesized hydrogels show a large endothermic peak (N-5) or several sharp endothermic peaks (N-7.5 and N-10) in their DSC thermographs, which indicate continuous phase transition. For all hydrogel types, first peaks were all appeared in the region of 33.7–36.5 °C which indicate first thermal response of the polymer network and close to LCST of pNIPAm. The several peaks which were observed in N-7.5 and N-10 hydrogels indicate that the phase transition occurs in several discontinuous stages, but it can be said that the whole phase transition take place as continuous. In case of N-5 hydrogel, there has been only one, but large endothermic peak was observed, which indicates a continuous phase transition. According to these findings, it can be concluded that increasing the hydrophilic comonomer content in the feed composition, changes the phase transition from continuous to discontinuous. Also it affects the onset points of the first peak which means higher LCST values. As expected, the higher the hydrophilic comonomer, the higher the LCST is [42].

The effect of temperature

In Fig. 5, the temperature dependent swelling results were given. As it seen from the figure, a significant decrease was observed in Q_e values of the hydrogels in the range of 30–50 °C. This case confirms the DSC results, and it can be easily said that all hydrogels have LCST value in a range of 30–50 °C. Figure 6 shows deswelling rates of hydrogels and water releases (%) at 55 °C. Holding the hydrogels at 55 °C causes a dramatic decrease in Q_e values and all hydrogels desorbs ~95% of water that absorbed at lower temperatures. Since the hydrogels desorbs ~95% of water, the rate of deswelling is important parameter. As it seen from figure, all hydrogels desorbs 90% of their water content in 100 min and 95–97% in 120 min. According to these results, it can be concluded that the synthesized hydrogels have LCST values in the range of 40–50, and they have fast responsive characteristics.

The effect of pH

The last swelling property; pH sensitivity of the hydrogels were given in Fig. 7. Because of –COOH groups, the hydrogels have pH sensitivity and they have lower Q_e values at lower pH's, and increasing pH to higher values increases the Q_e values, until pH 9, then a decrease is began. It is an expected results; in low pH, the COO^-Na^+ groups turn COOH form and cannot be ionized with increasing the pH (4–9), the COOH groups turn to more ionizable COO^-Na^+ group which causes higher Q_e values. Finally, in high alkaline medium pH > 9.5–10 the sodium ions cannot be dissociated from the carbonyl groups due to higher sodium ion concentration in the medium, and this case causes a dramatically decrease in Q_e value.

Dye adsorption studies

The adsorption properties data of ST, BG, and BCB on the hydrogels were given in Figs. 8, 9, 10 and Tables 3, 4, 5 in following sections.

Effect of the contact time

In Fig. 8, the effect of treatment time on adsorption efficiency was given. As it seen from figure, all hydrogels reach their adsorption equilibrium with in 40 h. Increasing treatment time up to 96 h does not have a significant effect on adsorbed dye amount for three types of dyes. For the adsorption of the cationic dyes onto hydrogels, there are two main reactions take place; the electrostatic interaction between the dyes and adsorbent, and the possible chemical reaction of N^+ groups of the dyes and COO^- groups of the hydrogels [46, 47]. According to obtained adsorption data, two main conclusions can be drawn:

First one: hydrogel composition effects adsorption capacity for all three type dyes. Increasing IA-Na content in feed composition increases the dye adsorption capacity. Since the higher the $-COO^-$ group content, the higher the dye and hydrogel interaction is, this case is an acceptable situation. Strong hydrophilic COO^- groups improve the cationic dye adsorption rates and capacities of the hydrogels. Second one: when the adsorption data were analyzed according to dye type, it is clearly seen that the adsorption capacities of ST and BCB are almost same but a bit lower than that of BG. In an adsorption process, the active cites' locations of adsorbate and adsorbant have an effective role on adsorption capacity. The higher the isolation of active cites, the lower the adsorption capacity is. Since the adsorption of basic dye onto hydrogels occurs by electrostatic interactions, and exchange of electrons between dye and adsorbent [47] and the positively charged ions of BCB and ST are more isolated than that of BG (Fig. 1), it can be concluded

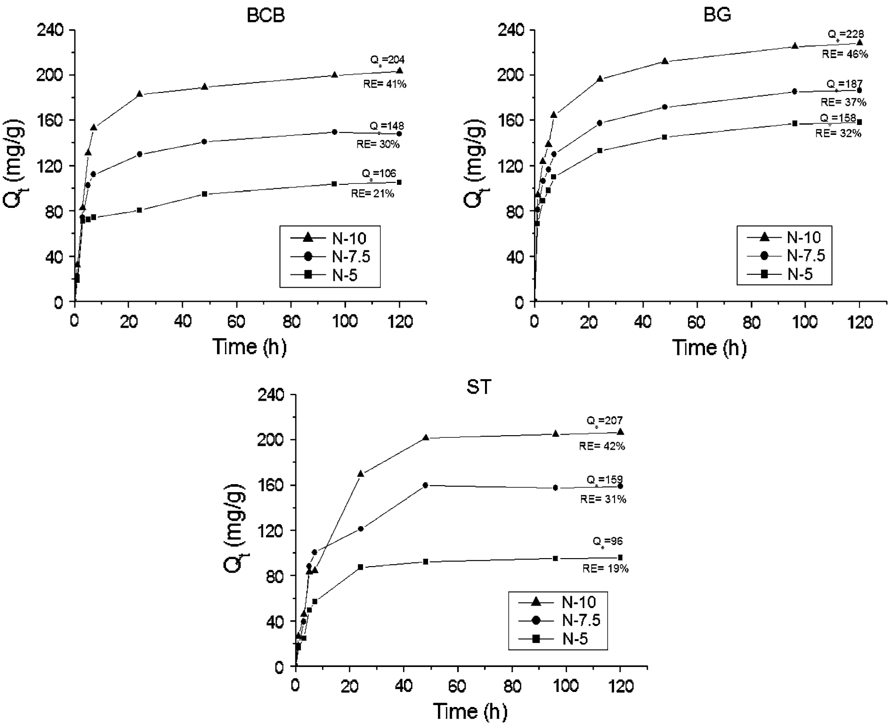


Fig. 8 The effect of treatment time on adsorption efficiencies of the hydrogels and the dye removal efficiency percentage of the hydrogels

that ST and BCB have lower interactions than that of BG. The higher the interactions the higher the adsorption capacity, thus BG has the highest adsorption capacity. Figure 8 also illustrates the dye removal efficiency (RE) percentage of the hydrogels. Because of the same concluded reasons given above, maximum RE value was monitored in case of BG and the RE percentage values are followed the order BG > ST $\cong$ BCB.

Adsorption kinetic

The experimental adsorption data were also analyzed by pseudo-first-order and pseudo-second-order kinetic models for examine the controlling mechanism of adsorption process. The first order rate expression of Lagergren [48, 49] is given as:

$$\log(q_\mathrm{e} - q_t) = \log q_\mathrm{e}(k_1 t/2.303) \tag{4}$$

where q_e and q_t are the amounts of dye adsorbed on adsorbent at equilibrium and at time t, respectively (mmol/g), and k_1 is the rate constant of first-order adsorption (h^{-1}). In many cases, the first-order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the

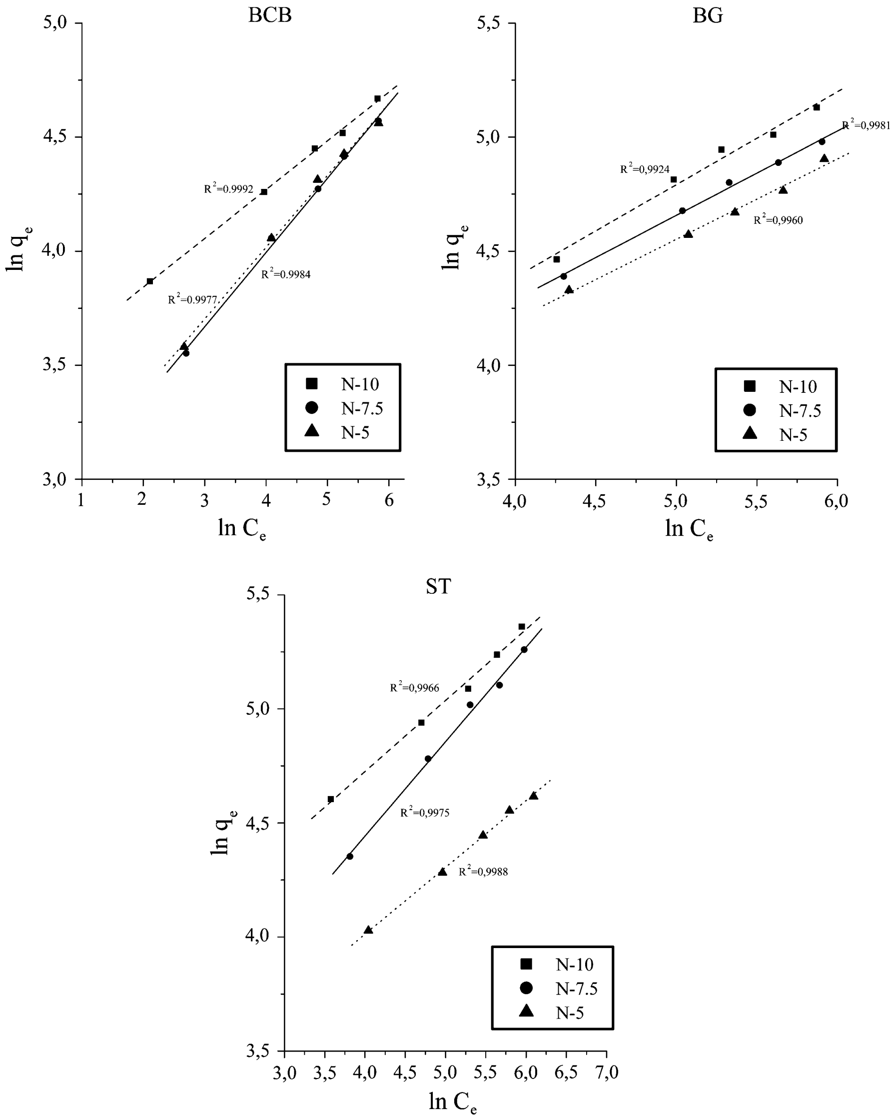


Fig. 9 Freundlich isotherms for the adsorption of the basic dyes onto hydrogels

adsorption processes [48–50]. The second-order kinetic model [50, 51] is expressed as:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \tag{5}$$

where k_2 (g/mmol h) is the rate constant of second-order adsorption. If second-order kinetic is applicable, the plot of t/q_t versus t should give correlation coefficient above 0.990. This kinetic model is more likely to predict the behavior over the whole range of adsorption and is in agreement with chemical sorption being the

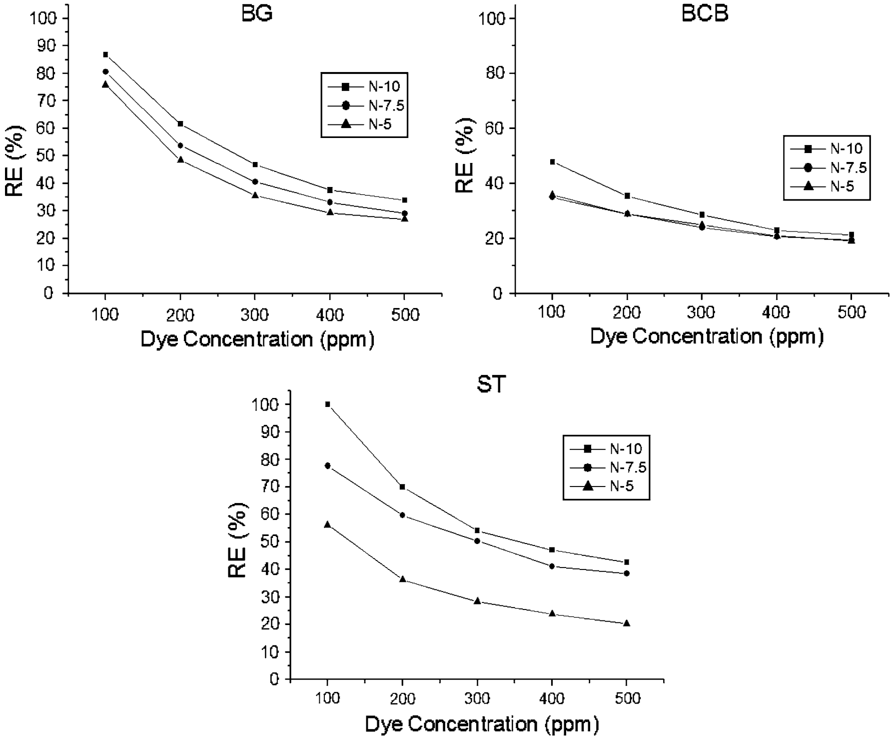


Fig. 10 The effect of dye concentration on removal efficiency after 24 h treatment period

Table 3 Dynamic swelling values and water release at 55 °C of hydrogels

Hydrogel	Equilibrium swelling degree, Q_e, g H_2O/g hydrogel							Water release (%)
	Temperature (^{o}C)							
	5	10	15	20	30	40	50	
N-5	388	365	334	328	244	204	101	94
N-7.5	337	320	309	293	224	190	99	95
N-10	288	267	248	236	183	150	57	97

rate-controlling step [50, 51], which may involve valence forces through sharing or exchange of electrons between metal ions and adsorbent. Table 4 lists the calculated results with the correlation coefficients (R^2) for first-order and second-order kinetic models. The correlation coefficients for the first-order kinetic model are low. Also, the calculated q_e values obtained from the first-order kinetic model do not give reasonable values, which are low compared with experimental q_e values. This suggests that the adsorption of dye molecules onto the hydrogels is not a first-order reaction. The correlation coefficients for the second-order kinetic model are very close to 1,000 for almost all the cases. Also, the calculated q_e values almost agree with the experimental data. These findings indicate that the adsorption system

Table 4 Kinetic parameters for the adsorption of ST, BG and BCB onto hydrogels

Hydrogel	$q_{e,exp}$	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			h_o
		k_1	$q_{e,cal}$	R^2	k_2	$q_{e,cal}$	R^2	
ST								
N-5	96.2	0.0470	61.5	0.9579	1.72×10^{-3}	101.2	0.9994	17.62
N-7.5	159.9	0.0571	114.2	0.9587	0.84×10^{-3}	170.4	0.9987	24.38
N-10	207.0	0.0504	159.5	0.9667	0.49×10^{-3}	224.7	0.9989	24.74
BG								
N-5	158.2	0.0468	91.1	0.9838	2.03×10^{-3}	160.0	0.9992	51.97
N-7.5	186.5	0.0477	107.1	0.9841	1.75×10^{-3}	188.7	0.9992	62.30
N-10	228.3	0.0400	121.1	0.9723	1.50×10^{-3}	229.9	0.9996	79.27
BCB								
N-5	105.3	0.0381	58.5	0.9593	2.23×10^{-3}	107.9	0.9988	25.95
N-7.5	148.0	0.0429	81.5	0.9618	1.70×10^{-3}	154.1	0.9997	40.36
N-10	203.6	0.0386	109.3	0.9367	21.19×10^{-3}	209.2	0.9997	52.08

Table 5 Freundlich constants of adsorption isotherm for cationic dyes

Hydrogel	Langmuir isotherm	Freundlich isotherm		
	R^2	R^2	K_f	n
ST				
N-5	0.9580	0.9988	17.10	3.41
N-7.5	0.9670	0.9975	16.22	2.42
N-10	0.9200	0.9966	32.38	3.21
BG				
N-5	0.9570	0.9960	16.27	2.84
N-7.5	0.9710	0.9981	16.56	2.71
N-10	0.9760	0.9924	15.79	2.46
BCB				
N-5	0.9170	0.9984	15.77	3.18
N-7.5	0.9650	0.9977	14.76	3.08
N-10	0.9270	0.9992	30.41	4.68

belongs to the second-order kinetic model. By using pseudo-second-order kinetic model data, the initial sorption rate, h, can be calculated as given below;

$$[t \to 0] \quad h = k_2 \times q_e^2 \tag{6}$$

As it seen from Table 4, the initial sorption rates for the adsorption of BG to hydrogels are approximately 1.5–2 times greater than those of ST and BCB. This case is probably, occurred due to the easiness of the electrostatic interactions. As it said before the positively charged cites of ST and BCB are more isolated than this of BG, and this case causes a hinderance for electrostatic interactions, which causes decreased adsorption rate and capacity. In case of the effect of hydrogel composition on initial sorption rate, it can be said that increasing COO^- group content in the hydrogel composition increases the initial sorption rate. Since the higher the negatively charge group content in the hydrogel network the higher the electrostatic interaction between the positively charge cites of the dyes; this case is an acceptable finding.

Effect of the initial dye concentration

Several models have been published in the literature to describe adsorption isotherms. The adsorption isotherm defines the relationship between the amount of adsorbate and the concentration of dissolved adsorbate in the liquid at equilibrium. The Langmuir and Freundlich models are the most frequently used models [52–54]. Langmuir and Freundlich models were used to describe the relationship between the amount of dye adsorbed on the absorbent and its equilibrium concentration in solution. The Langmuir isotherm is a valid monolayer sorption on a surface containing a finite number of binding sites, and it assumes uniform energies of sorption on the surface and no transmigration of adsorbate in the plane of the surface [55]. Its linear form is given as:

$$1/q_{\mathrm{e}} = 1/q_{\mathrm{o}} + 1/q_{\mathrm{o}} b C_{\mathrm{e}} \tag{7}$$

where q_{e} is the amount of dye adsorbed (mg/g) onto hydrogel, q_{o} is the maximum adsorption capacity according to Langmuir monolayer adsorption (mg/g), C_{e} is the adsorbate equilibrium concentration in solution (mg/L).

Freundlich isotherm points a heterogeneous surface energy system and describes the adsoption process as “the ratio of the amount of solute adsorbed onto a given amount of adsorbent to the concentration of the solute in the solution is not constant at different concentrations” [56]. Its linear form is given as:

$$\log q_{\mathrm{e}} = \log K_{\mathrm{f}} + 1/n \log C_{\mathrm{e}} \tag{8}$$

where K_{f} and n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The n values between 1 and 10 indicate beneficial adsorption [52, 57–61] and relatively high K_{f} values reflect high adsorption capacity.

In this study, all the regression coefficient values for Langmuir isotherm were found to be in the range of 0.92–0.97 (Table 5) while these of Freundlich isotherm were all above 0.99 (Table 5 and Fig. 9). According to these findings, it was concluded that the Freundlich isotherm describes the adsorption of the cationic dyes onto the hydrogels better than Langmuir isotherm. It is well known that the n values between 1 and 10 indicate beneficial adsorption; since all calculated n values for the hydrogels are in a range of 2.4–4.6, it can be easily concluded that the adsorption is beneficial. Moreover, high K_{f} values also reflect the favorable and high-adsorption capacities for the basic dyes.

The effect of initial dye concentration on RE percentage was also studied. Figure 10 illustrate the effect of dye concentration on RE after 24 h treatment period. According to figure, two main conclusions can be drawn: Increasing dye concentration dramatically decreases the RE percentage of the hydrogels; but increasing IA-Na content in the feed composition of the hydrogels increases the

RE% values. The best RE % values were monitored in case of 100 ppm dye concentration for BG and ST. In case of BCB, the RE% values are almost 60% and quite low than those of BG and ST. This case occurred probably due to the hindrance of the active cites and the difficulty of the possible reaction of N^+ groups of the dye molecule and COO^- groups of the hydrogel, as discussed before.

Conclusions

In this study, temperature and pH-sensitive hydrogels were synthesized from NIPAm and IA-Na by free radical polymerization for using in adsorption of basic dyes (ST, BG, and BCB) from their aqueous solutions. The following conclusions can be drawn:

- Increasing IA-Na monomer in the feed composition yields high-swelling ratios but causes a slight increase in LCST. All hydrogels have fast temperature responsive characteristics and desorbs 95–97% of their water content in 120 min.
- All hydrogels adsorb relatively high amounts of cationic dyes in 40 h, and increasing IA-Na content in the feed composition increases the adsorption capacity.
- According to adsorbed dye amount, the adsorption capacities are followed the order BG $>$ ST $\cong$ BCB.
- Dye RE percentages of the hydrogels are in the range of 90–100% for 100 ppm dye concentration for BG and ST which means almost purified wastewater.
- The adsorption of the cationic dyes onto hydrogels occurs by electrostatic interactions and exchange of electrons between dye and adsorbent. Thus, the isolation of the charged group has an effective role on adsorption rate and capacity. The higher the isolation (i.e., ST and BCB) the lower the adsorption rate and capacity.
- According to the adsorption studies findings, it is concluded that pseudo-second-order kinetic model and Freundlich isotherm explain the adsorption properties of the hydrogels.

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