



# An evaluation on S-type adsorption isotherm in the model of crosslinked polyhydroxamates/oxazine dyes/water interactions

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## Abstract

The effects of crosslinker and dye type on swelling and S-type adsorption properties of crosslinked polyhydroxamates (CHP) were investigated. CHPs containing N,N'-methylenebisacrylamide (N), or ethylene glycol dimethacrylate (E) were used in the swelling, diffusion, and adsorption experiments in solutions of oxazine dyes such as Brilliant Cresyl Blue, Nile Blue, and Cresyl Violet. Swelling and diffusion parameters of CHPs in dye solutions (such as equilibrium swelling, half time of swelling, swelling value at half time, network parameter, diffusion exponent, and diffusion constant) were calculated. It is understood from the time of swelling to reach equilibrium that CHPs swell very fast. CHP-E in all dyes solutions swelled considerably more than CHP-N. Dye solution diffusion into CHPs was determined to be of non-Fickian character. It has been observed that the swelling properties of hydrogels are highly influenced by the crosslinker type. The adsorption of oxazine dyes onto CHPs is similar to the S-type adsorption in the Giles classification system. When it was seen that the experimental data fit the Sigmoidal 4 parameter equation with a high correlation ( $r^2 > 0.995$ ), the use of this equation determined the adsorption parameters such as the highest bonding rate or monolayer coverage, the transition point of the isotherm, the magnitude of the absorbent's absorbability and the slope parameter. Site-size, maximum fractional occupancy, the binding ratio at the transition point, binding constant, the initial binding constant, partition coefficient, and adsorption free energy values were also calculated by using the found adsorption values. Dye adsorption from all dyes solutions to CHP-E is considerably higher than CHP-N. An increasing linear relationship was found between swelling and adsorption. In conclusion, the sigmoidal equation approach can be a useful tool for chemists, chemical, agricultural and environmental engineers, polymer scientists to find the adsorption parameters of polymer adsorbents, and at the same time, it can be said that CHP can be used as a good sorbent in the removal of some chemical agents (such as dye molecules, organic molecules, biologically active molecules).

**Keywords** Crosslinked hydroxamate polymer · Swelling · Adsorption · S-type isotherm · Oxazine dye

## 1 Introduction

Environmental pollution caused by dyes is an important universal problem due to their toxicity [1]. Dyes, which are used in high amounts as colorants in paper, printing and textile products, plastics, and paints, are one of the heavy pollutants of water [1, 2]. One of these dyes groups is cationic oxazine

dyes, which have a planar molecular structure and can accept and donate hydrogen bonds in the polar solvents [3–5]. The dyes in this group are mostly used in biological, histological, and medical applications, as well as in industrial applications such as optical data storage, optical recording materials, dye lasers, light-emitting diode, electrochromic display device, semiconductors, thin-film materials, laundry detergent, paper, and textile [6].

Various physical and chemical methods such as coagulation, flocculation, photocatalysis, adsorption, etc. have been used for a long time to remove dyes from water contaminated by dyes [7, 8]. Of all these methods, the adsorption method is preferred over other methods due to its cheaper, more effective, relatively simple design, operation, cost, and

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energy efficiency compared to other chemical or physical techniques [9–11].

Among the absorbents used in dye adsorption, polymers have an important place. The functional structures of polymers, their chemical modification, the addition of a functional co-monomer, or a suitable crosslinker can easily arrange their molecular architecture and their adsorption abilities can be greatly increased [9–13]. Polymers containing hydroxamic group structures are also used as adsorbents [14]. Hydroxamic acid and hydroxamate groups form the strong chelate with different heavy metal cations and interact with dyes. A series of chelating polymers containing these groups have been prepared. These polymers can be used in the adsorption of organic or inorganic pollutants of cationic nature [14–17].

An adsorption isotherm helps to identify the mechanism pathways of binding an adsorbed species to an adsorbent. Adsorption mechanism models of varying complexity and variation have been proposed [18, 19].

While BET isotherm classification (Type-I, Type-II, Type-III, Type-IV, Type-V, and Type-VI) is used for the adsorption of gases to solids [20], Giles isotherm classification (C, H, L, and S) is used for the adsorption of solutes to solids [21]. The Giles classification was made by considering the initial region of the isotherm curve, while the BET classification was made by using the full isotherm (i.e., until the saturated vapor pressure is reached or the relative pressure = 1) [20–22].

Many relations such as one-parameter isotherm (i.e., Henry's), two-parameter isotherm (i.e., Freundlich, Langmuir,

Fowler–Guggenheim, Hill–Deboer, Dubinin–Radushkevich, Temkin, Flory–Huggins, Hill-de Boer, Halsey, Harkin–Jura, Elovich, Kiselev), three-parameter isotherm (i.e., Redlich–Peterson, Sips, Toth, Koble–Carrigan, Kahn, Radke–Prausniiz, Langmuir–Freundlich, Jossens), four-parameter isotherm (i.e., Fritz–Schlunder, Bauder, Weber–Van Vliet Marczewski–Jaroniec), and five-parameter isotherm (i.e., Fritz and Schlunder) have been derived to explain the mechanisms of gas isotherms [23–26].

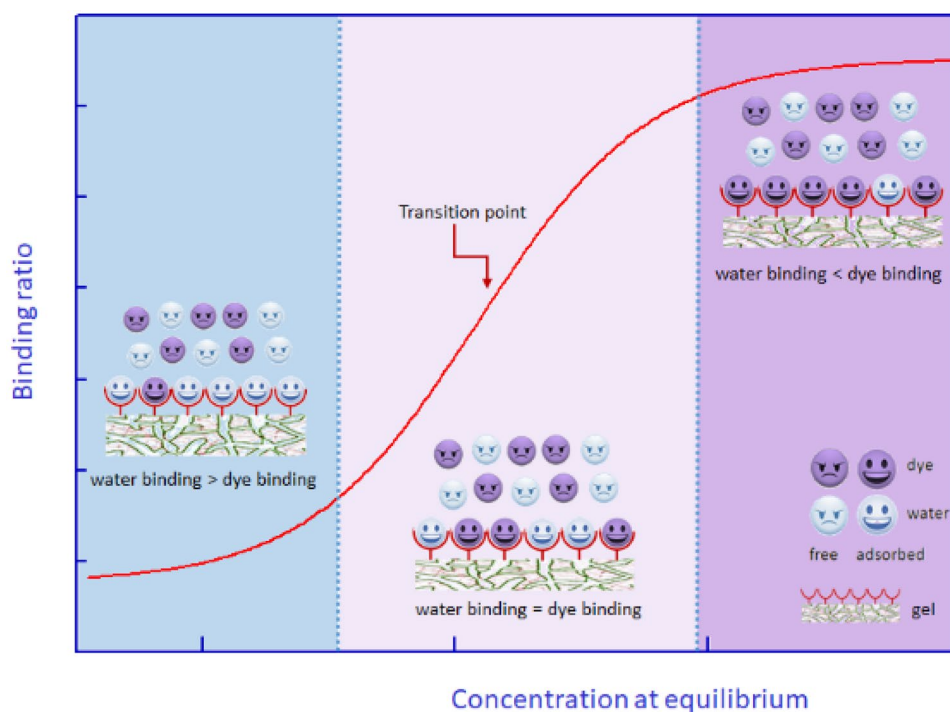
Quite a several researchers have tried to conclude by evaluating the gas isotherm formulas (especially the Freundlich and Langmuir isotherm formulas) as the adsorption of solute from the solution and did not consider the solvent-adsorbent interaction [23–26].

In the Giles classification for solid-solute binding in solution, the S-type adsorption isotherm in which both the solvent and the solute are prominent has a sigmoidal shape and thus has a transition point. The formation of the transition point is the result of at least two opposing mechanisms, in which solvent and solute compete for binding to the adsorbent. S-type isotherms are less common than L- and H- type isotherms [21–23]. In both H and L-type isotherms, a transition point is not clearly observed, since solute adsorption is quite dominant over solvent absorption [9, 22].

The S-type isotherm formed as a result of the binding of a dye onto a hydrophilic solid adsorbent is illustrated in Fig. 1 as a representative.

While the number of publications on adsorption since 1970 is more than 594,000, 25,000 of these publications are on S-type adsorption in SCI. In 26 of these publications,

**Fig. 1** A visual representation of the S-type isotherm



polymer-hydrogel absorbents are mentioned [27]. However, there are no studies on the determination of the transition points, monolayer capacities, and binding constants, which are very important in determining the adsorption mechanism in S-type adsorption systems. As it can be understood from this literature research, detailed investigations of solute-solid systems giving S-Type isotherms were either abandoned or only the adsorption type was indicated.

In line with our research interest in acrylamide-based materials [28–31], we report in this paper the swelling and adsorption of hydroxamate derivatives prepared by chemical modification of crosslinked polyacrylamide in aqueous dye solutions. In this study, it is aimed to find adsorption parameters such as minimum and maximum binding ratio, monolayer capacity, the width of adsorption, and binding constant, etc. by using the sigmoidal 4 parameter relation in the adsorption of cationic oxazine group dyes such as Brilliant Cresyl Blue (CB), Nile Blue (NB), and Cresyl Violet (CV) [32, 33] onto crosslinked hydroxamate polymers (CHP), which are thought to give S-type isotherm. In addition to determining the S-type isotherm parameters, swelling behaviors of CHPs in dye solutions were investigated, swelling parameters were calculated, and the relationship between the binding and swelling of CHPs containing different crosslinkers such as N,N'-methylenebisacrylamide (N), or ethylene glycol dimethacrylate (E) in dye solutions was also investigated.

## 2 Experimental methods

In our previous studies [34], the preparation and characterization of CHPs were studied and its use as an adsorbent in the removal of cationic heavy metal ions [35] or dyes [36–38] was investigated. In this study, CHPs were used for the adsorption of oxazine dyes. As described elsewhere, for obtaining of CHPs, crosslinked polyacrylamides were converted by chemical modification to poly(hydroxamic acid) with hydroxylamine hydrochloride and then to polyhydroxamates with NaOH solution [34]. The CHP samples were labeled as, CHP-N and CHP-E, for crosslinkers; N,N'-methylenebisacrylamide or ethylene glycol dimethacrylate, respectively.

The oxazine dyes containing a six-membered heterocyclic structure with one oxygen and one nitrogen atom; Brilliant Cresyl Blue (BCB), Nile Blue (NB), and Cresyl Violet (CV) were purchased from Merck (Darmstadt, Germany). The names, chemical structures, molar masses, and wavelength maxima of these dyes are shown in Table 1.

By using stock solutions of oxazine dyes prepared in distilled water, aqueous solutions at certain concentrations were prepared with appropriate dilutions.

To determine swelling and diffusion parameters, CHPs were accurately weighed and transferred to 20 mg L<sup>-1</sup> aqueous oxazine dye solutions contained in the glass beaker. The swelling of the CHPs was monitoring at some periodic time intervals by removing the polymer from the dye solution, rapid blot drying, and reweighing. The swelling process was carried out in a thermostated water bath at 25 ± 0.1 °C. The swelling (S) was determined from the following equation.

$$S = \frac{a_{ds}}{m_o} \quad (1)$$

where  $a_{ds}$  (=  $m_t - m_o$ ) is the mass of the dye solution adsorbed in the CHPs.  $m_t$  indicates the mass of swollen CHPs at time  $t$ , while  $m_o$  indicates the mass of dry CHPs at time 0.

Adsorption studies were carried out in a temperature-controlled incubator. All experiments were conducted at the original pH of the dye solutions [39–41]. Oxazine dye solutions were prepared in concentration ranges of 8–80 mg L<sup>-1</sup>.

Hundred mg of dry CHP-N or CHP-E were added in 50 mL oxazine dye solutions and allowed to equilibrate at 25 °C for 24 h. After this time, the aqueous oxazine dye solutions were separated from the polymers by filtration. Dye absorbances were monitored by UV–Vis spectrophotometer (Shimadzu, Tokyo, Japan, Model 160) at the wavelengths given in Table 1. Pre-calibrated absorbance versus concentration calibration curves were used to calculate the concentration values.

When the difference between an initial ( $C_i$ ) and an equilibrium dye concentration ( $C_e$ ) gives the concentration of the bound dye ( $C_b$ ) onto adsorbent, the binding ratio can be given as [42].

$$\Phi = \frac{C_b}{P} \quad (2)$$

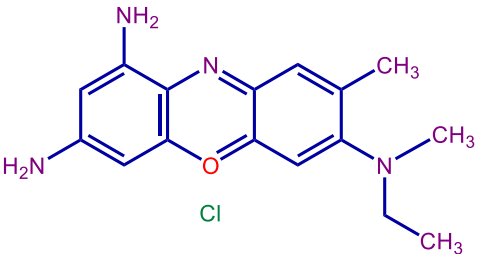
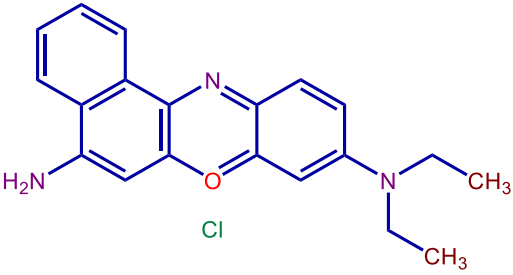
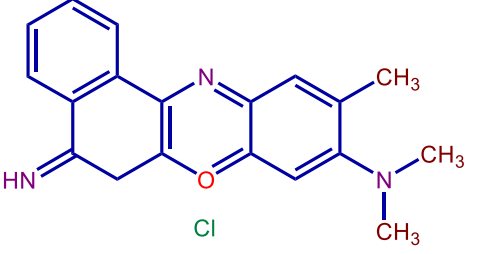
where  $C_b$  in mol L<sup>-1</sup> and  $P$  in base mol (moles of constitutional repeating units of the polymer) per liter solution,  $\Phi$  then indicates the average number of moles of solute bound to each moles of the constitutional repeating unit at that free solute concentration.

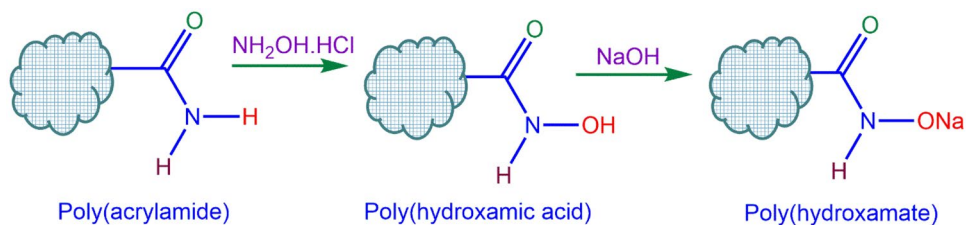
## 3 Results and discussion

In our previous studies, CHPs obtained from crosslinked poly(acrylamide) by chemical modification with hydroxylamine hydrochloride and then to polyhydroxamates with NaOH solution were prepared (Fig. 2) and the adsorptions of cationic heavy metal ions and cationic dyes onto these CHPs were examined [34–38].

In this work, the effect of ionogenicity and hydrophobicity of CHPs on swelling and adsorption behavior of

**Table 1** Oxazine dyes used in the study

Name	Symbol	Chemical structure	Molar mass g mol <sup>-1</sup>	$\lambda_{\max}$ nm
Cresyl Blue <i>Brilliant Cresyl Blue</i>	CB		332.84	622
Nile Blue <i>Basic Blue 12</i> <i>Nile Blue A</i> <i>Nile Blue AX</i>	NB		353.85	638
Cresyl violet <i>Cresyl Fast Violet</i> <i>Cresole Violet</i>	CV		339.82	590

**Fig. 2** Chemical modification of crosslinked poly(acrylamide) to crosslinked poly(hydroxamic acid) and then crosslinked poly(hydroxamate)

oxazine dyes (oxazine dyes are from the class of quinone imines, which are in the scaffold of p-benzoquinone imine or -diimine) such as Brilliant Cresyl Blue (BCB), Nile Blue (NB), and Cresyl Violet (CV) in aqueous solutions was investigated [43].

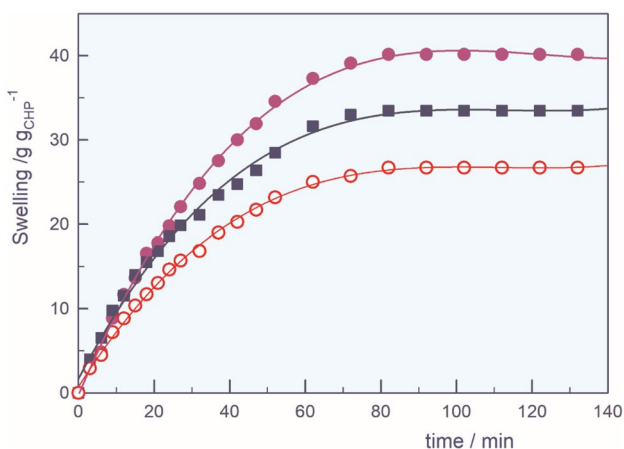
### 3.1 Swelling

Swelling graphs of CHPs in the solutions of cationic oxazine dyes were plotted. As exemplary graphical representations, swelling of CHP-E in different dyes are given in Fig. 3, and swelling of CHP-N and CHP-E in CB are given in Fig. 4.

All CHPs absorbed dye solutions and initially showed a higher rate of swelling, after a certain time the solution

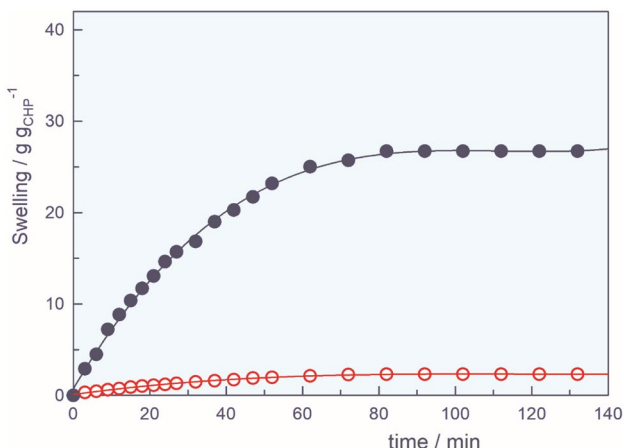
intake stopped and the CHPs reached their equilibrium swelling ( $S_e$ ). The time ( $t_{1/2}$ , min) when the swelling is half of the equilibrium swelling ( $S_{1/2} = S_{eq}/2$ ) was found from the swelling and the swelling parameters of CHP-dye solution systems are given in Table 2.

The  $S_e$  values of CHPs containing semi-flexible N vary between 2.32 and 2.48 g g<sup>-1</sup>, while those of CHPs containing flexible E vary between 26.72 and 40.16 g g<sup>-1</sup> (Table 2). The swelling of CHP-E in dye solutions is 16.12 times higher in CV, 14.19 times in NB, and 11.52 times in CB compared to the swelling of CHP-N. Since the water-loving regions of E are more abundant than those of N crosslinker, the aqueous solution of CHP-E is much greater than that of CHP-N.



**Fig. 3** Swelling graphs of CHP-E in the different oxazine dye solutions; ○: CB, ■: NB, ●: CV

These data also show that CHP-E absorbs the solutions

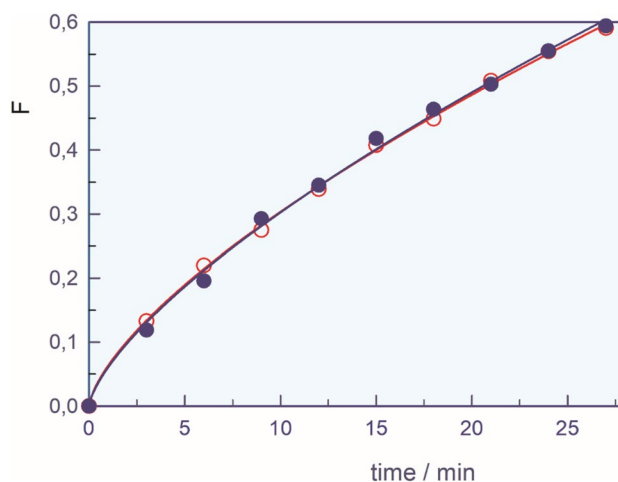


**Fig. 4** Swelling graphs of CHPs in CB solutions; ○: CHP-N, ●: CHP-E

**Table 2** Swelling parameters

Crosslinker dye	$S_e/g\ g^{-1}$	$S_{1/2}/g\ g^{-1}$	$t_{1/2}/min$
N,N' methylene bisacrylamide			
Cresyl Blue	2.32	1.16	22.28
Nile Blue	2.36	1.18	22.21
Cresyl Violet	2.48	1.24	24.30
Ethylene glycol dimethacrylate			
Cresyl Blue	26.72	13.36	21.69
Nile Blue	33.48	16.74	21.40
Cresyl Violet	40.16	21.40	23.77

quite quickly, has a high swelling ratio (~ 13.4–21.4 g g<sup>-1</sup>), and reaches a swelling half time of ~ 21–24 min, while CHP-N absorbs the solutions less (and has a low swelling



**Fig. 5** The NB solution diffusion into the CHPs; ○: CHP-N, ●: CHP-E, ———; model fit

ratio (~ 1.16–1.24 g g<sup>-1</sup>), but to time to reach the swelling half-time is very close to that of CHP-E (~ 22–24 min).

In addition, dye types belonging to the oxazine class and very similar to each other in terms of chemical structure affected the swelling of CHP-E but did not affect the swelling of CHP-N. The swelling of CHP-N in CB solution is 1.07 times higher than CV while swelling in NB is 1.02 times higher than CV. Similarly, the swelling of CHP-E in CB solution is 1.50 times higher than CV, while its swelling in NB is 1.20 times higher than CV. This difference may have been caused by the steric effect of the groups on the dye molecules.

### 3.2 Diffusion

The diffusion of dye solution into a water-loving crosslinked polymer is calculated following equation;

$$F = kt^n \tag{3}$$

where F is the fractional solution uptake at time t; k is a constant incorporating characteristic of the polymer and the solution; and n is the diffusional exponent, indicative of the transport mechanism. This equation is valid for the first 60% of F. It shows Fickian diffusion if n = 0.5, non-Fickian diffusion if 0.5 > n > 1, and Case II transport behavior if n = 1 [37, 38].

The F-t graph of the NB solution is given in Fig. 5 as a representation of the F-t plots for all CHPs. The n and k values determined from the nonlinear regression of the graphs, along with the standard error (SE) and correlation coefficients (r<sup>2</sup>), are summarized in Table 3.

The n values ranged from 0.61 and 0.87, depending on the type of crosslinker and dye. These n values indicate the anomalous or non-Fickian type diffusion. In non-Fickian type diffusion, the relaxation and diffusion time is at the



**Table 3** Diffusion parameters

Crosslinker dye	$n \pm SE$	$(k \pm SE) \times 10^2 / \text{min}^{-n}$	$r^2$	$D \times 10^6 / \text{cm}^2 \text{ s}^{-1}$
<b>N,N' methylene bisacrylamide</b>				
Cresyl Blue	$0.68 \pm 0.02$	$6.05 \pm 0.30$	0.998	1.88
Nile Blue	$0.68 \pm 0.01$	$6.33 \pm 0.11$	0.998	1.79
Cresyl Violet	$0.61 \pm 0.01$	$7.10 \pm 0.31$	0.998	1.51
<b>Ethylene glycol dimethacrylate</b>				
Cresyl Blue	$0.76 \pm 0.02$	$4.88 \pm 0.32$	0.998	4.73
Nile Blue	$0.70 \pm 0.02$	$6.10 \pm 0.40$	0.997	5.75
Cresyl Violet	$0.87 \pm 0.04$	$3.19 \pm 0.37$	0.994	9.05

same level. Therefore, as the fluid diffuses into the network, there is a delay in rearrangement (rupturing) within the polymer chains [38]. Diffusion constants of CHPs are between  $3.2 \times 10^{-22}$  and  $7.1 \times 10^{-2} \text{ min}^{-n}$ . There is no suitable correlation between the  $n$  values of CHPs.

In the dye solution diffusion into cylindrical CHPs, the diffusion coefficients ( $D$ ) were determined by the following equation [38];

$$D = \left(\frac{k}{4}\right)^2 \pi r^2 \quad (4)$$

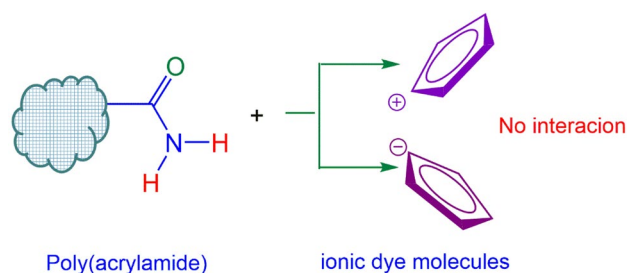
where  $D$  is diffusion coefficient ( $\text{cm}^2 \text{ s}^{-1}$ ),  $t$  is time (second) and  $r$  (cm) is the radius of the cylindrical crosslinked polymer.

The  $D$  values change from  $1.51 \times 10^{-6}$  to  $9.05 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  (Table 3). In cylindrical crosslinked polymers,  $D$  values are calculated at the level of  $10^{-7}$ , but currently, relatively higher diffusion coefficients are an indication of faster penetration of dye solutions into CHPs. The  $D$  values of CHP-E in aqueous dyestuff solutions were 2.5 to 6 times higher than that of CHP-N. The reason for this difference may be as described in the swelling.

### 3.3 Dye binding

The spectral properties of aqueous solutions of some cationic dyes change with concentration due to the metachromatic effect. Deviation from Beer's law with increasing concentration is an indication of the formation of dimers and higher aggregates in the solution [44, 45]. In the calibration plots of the aqueous solution of dyes used in this study, no deviation from linearity, i.e., Beer's law, was observed, so it can be said that the dyes do not dimerize among themselves and do not form aggregates.

To determine the absorbability of the dyes to cross-linked acrylamide polymer or CHP, they were transferred in the solutions of cationic oxazine dyes (i.e., Cresyl Blue, Nile Blue, and Cresyl Violet) or anionic dyes (i.e., Alkali Blue

**Fig. 6** The plausible interactions between oxazine dye molecules and crosslinked PAAM

4B, Alizarin Yellow R, Bromocresol Purple, Carmine, Evans Blue, Metanil Yellow, Cresol Red, and Naphthol Green B), and left for two days. After this process, the cross-linked acrylamide polymer preserved its transparency in all dye solutions, while the CHPs in the oxazine dye solutions showed a darker coloration compared to the original color of the solutions and did not show any coloration in the others. The absence of any coloration on the crosslinked polyacrylamide is due to the non-ionic nature of this polymer. In CHPs formed by chemical modification of polyacrylamide, ionizable groups on the polymer are increased. Thus, many hydroxamate groups have been formed in polymers, which can lead to increased interaction between cationic oxazine dyes and hydroxamate groups. Plausible interactions between oxazine dye molecules and PAAM or CHPs are shown in Figs. 6 and 7 are shown.

### 3.4 Adsorption isotherms

The adsorption isotherm is the curve that gives the distribution of the solute between the fluid phase and the solid phase when the adsorption equilibrium is reached [7–11].

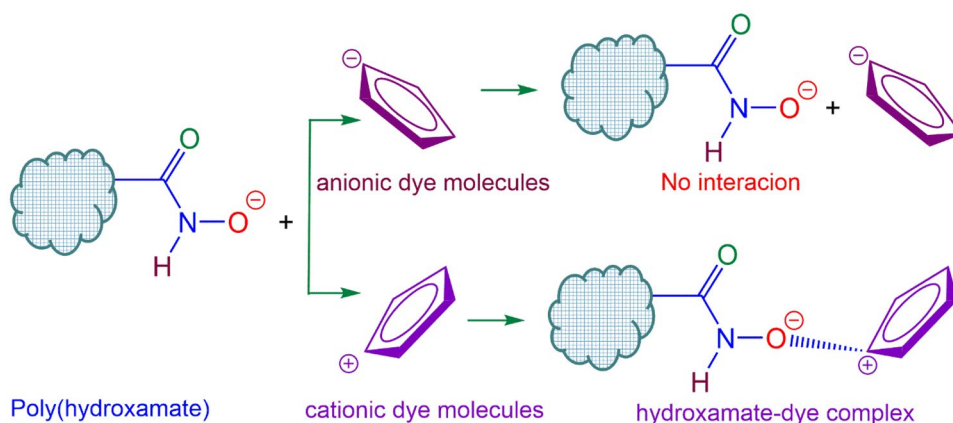
To determine the adsorption of the oxazine dyes onto CHPs, the graphs of the  $\Phi$  versus  $C$  were plotted, and the representative isotherms shown in Fig. 8 (for adsorption of different dyes onto CHP-E), and Fig. 9 (for adsorption of CB onto CHPs).

The shape of the isotherms in our graphs shows the S-type according to the Giles classification [21–23].

In S-Type isotherm curves, before the transition point (TP, where concavity changes direction), the solvent is more strongly adsorbed on the adsorbent than the solute, while after this critical point is exceeded, the solute is more strongly adsorbed on the adsorbent than the solvent. Thus, while the adsorption curve increases in the horizontal axis direction before TP, it increases in the vertical axis direction after TP. In TP, on the other hand, the adsorption of solvent and solute is of equal strength.

The transition points (TP) of S-type adsorption isotherms of the adsorbent–solute–solvent system can be calculated

**Fig. 7** The plausible interactions between oxazine dye molecules and CHPs



from the following equations using sigmoidal 4 parameter relationships [46, 47], adapted by Saraydn’s approach, for binding ratio ( $\Phi$ ) and equilibrium concentration of solute ( $C$ );

$$\Phi = \Phi_0 + \frac{\psi}{1 + e^{-\left(\frac{C-TP}{D_s}\right)}} \quad (5)$$

where  $\Phi_0$  and  $\Phi_m$  are asymptotic lower and upper values of binding ratio (values that the function approaches but never quite reaches).  $\Phi_m$  can also be represented as the  $n_m$  value in this adapted equation, and  $n_m$  is the hypothetical site density i.e., the limiting value of  $\Phi$  for “monolayer” coverage. The value  $\psi$  is the magnitude of the absorbent’s absorbability and is equal to  $\Phi_m - \Phi_0$ . TP is transition points of isotherm. The slope parameter  $D_s$  is the width of the region of points between two asymptotic values and also defines the steepness of the curve.

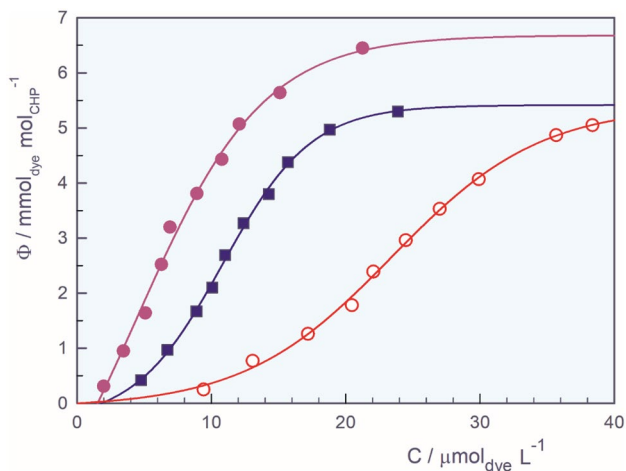
Adsorption parameters of CHPs-oxazine dye systems were calculated from Eq. 5 with the help of SigmaPlot Version 12.5 program using adsorption isotherms. The correlation coefficients ( $r^2$ ) of all graphs drawn according to the

proposed equation are 0.995 and above, indicating that the sigmoidal 4-parameter equation can be used to determine the adsorption parameters of the CHPs-oxazine dyes systems.

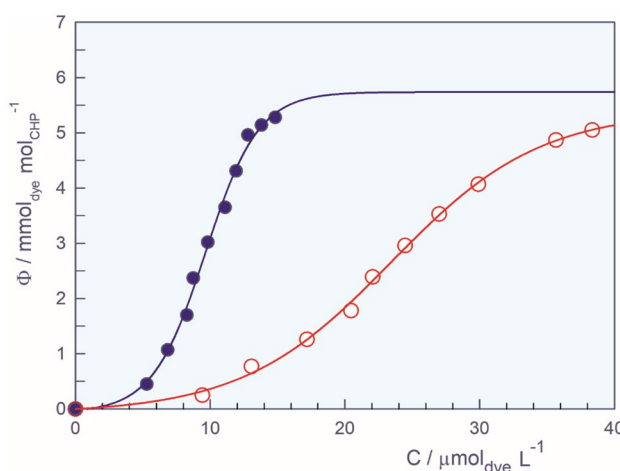
Table 4 presents the values of  $\psi$ ,  $D_s$ , TP, and  $\Phi_0$  with standard error (SE) and coefficients ( $r^2$ ) found from Eq. 6.

Table 4 shows that the monolayer coverage values increase in the order of CB, NB, and CV, respectively, in dye adsorptions in both CHP-N and CHP-E. While TP values decrease in the same order, isotherms also become steeper in this ranking. When crosslinker types in the CHP are compared for the same dye, generally CHP-E has higher  $n_m$  values than CHP-N, adsorption isotherms are steeper and transition points are smaller. In the adsorption of a dye molecule, the higher  $n_m$  and small TP value and steeper isotherm indicate that the dye has a higher affinity for CHP than the others.

The differences in the adsorption parameters resulting from the CHP-oxazine dye-water interactions can be thought to be due to the chemical structure of the crosslinked polymer, the crosslinker, the dye and the water, its ability to form hydrogen bonds, its ionogenicity, hydrophilicity, and hydrophobicity.



**Fig. 8** Adsorption isotherms of CHP-E in the different oxazine dye solutions; ○: CB, ■: NB, ●: CV, —: model fit



**Fig. 9** Adsorption isotherms of CHPs in CB solutions; ○: CHP-N, ●: CHP-E, —: model fit

**Table 4** Sigmoidal curve parameters of CHPs in the oxazine dye solutions

Crosslinker dye	$\psi \pm SE \text{ mmol}_d \text{ mol}_p^{-1}$	$D_S \pm SE \text{ } \mu\text{mol}_d \text{ L}^{-1}$	$TP \pm SE \text{ } \mu\text{mol}_d \text{ mol}_p^{-1}$	$\Phi_o \pm SE \text{ mmol}_d \text{ mol}_p^{-1}$	$r^2$
N,N' methylene bisacrylamide					
Cresyl Blue	$5.48 \pm 0.20$	$5.53 \pm 0.39$	$23.44 \pm 0.35$	$-0.08 \pm 0.09$	0.998
Nile Blue	$5.58 \pm 0.15$	$3.14 \pm 0.16$	$11.02 \pm 0.16$	$-0.19 \pm 0.09$	0.999
Cresyl Violet	$7.86 \pm 0.00$	$3.76 \pm 0.00$	$6.65 \pm 0.00$	$-1.37 \pm 0.00$	1.000
Ethylene glycol dimethacrylate					
Cresyl Blue	$5.80 \pm 0.33$	$1.96 \pm 0.21$	$9.66 \pm 0.22$	$-0.07 \pm 0.15$	0.996
Nile Blue	$6.06 \pm 0.02$	$0.36 \pm 0.03$	$4.38 \pm 0.03$	$0.06 \pm 0.11$	0.995
Cresyl Violet	$7.39 \pm 0.29$	$0.05 \pm 0.00$	$0.12 \pm 0.00$	$-0.73 \pm 0.24$	0.998

The ranking of affinity of CHPs to dyes is  $CV > NB > CB$ , while the affinity of dyes to crosslinked polymers is  $CHP-E > CHP-N$ . This ranking is also valid for the transition point from water-loving to dye-loving.

By using the adsorption parameters found from sigmoidal adsorption isotherms, parameters such as site-size (SS) and maximum fractional occupancy (FO) values can also be calculated. The SS value is equal to  $1/n_m$  and represents both the average number of constitutional repeating units filled by the bound solute and, more generally, the average spacing of solutes when the chains are saturated. Using the  $\Phi_{max}$  value at the maximum experimental free dye concentration, the percentage maximum fractional occupancy (FO%) can be calculated from the given equation [48];

$$FO\% = \frac{\Phi_{max}}{n_m} \times 100 \quad (6)$$

The notations in this equation have already been defined. Table 5 presents the values of  $\Phi_{max}$ , SS, and FO%.

The SS values of CHP-N were calculated as 127.2 to 182.6 mol of polymer (mol dye)<sup>-1</sup>, while those of CHP-E were calculated as 135.3 to 172.9 mol of polymer (mol dye)<sup>-1</sup>. This means that one mole of dyestuff binds to the structural repeating unit of CHPs as much as the numerical values of the site sizes given in Table 5. At binding of 1 mol of dye to CHPs, the active site size of the polymer is lowest for CV and highest for CB. This shows that the binding sites on the polymers are activated in the order  $CV > NB > CB$ .

According to the FO% values, 82 to 95% of the active binding sites of CHP-N were filled by oxazine dyes, while 90 to 100% of CHP-E was occupied by oxazine dyes. These values indicate that the active binding sites in both polymers are occupied by the oxazine dyes by approximately the same amount.

By using the transition points (TP) and slope parameters ( $D_S$ ) found from sigmoidal adsorption isotherms, parameters such as binding ratio at TP ( $\Phi_{TP}$ ), binding constant ( $K_S$ ), the initial binding constant ( $K_i$ ), partition coefficient ( $K_{pc}$ ) and adsorption free energy ( $\Delta G$ ) values can also be calculated.

While  $\Phi_{TP}$  values are found from the adsorption isotherm of the binding ratios corresponding to the TP points,  $K_S$ ,  $K_i$ ,

$K_d$ , and  $\Delta G$  values can be calculated from the Eqs. (7–10) given below, respectively [48, 49];

$$K_S = \frac{\Phi_m - \Phi_o}{4D_S} \quad (7)$$

$$K_i = K_S n_m \quad (8)$$

$$K_{pc} = \frac{C_o - TP}{TP} \quad (9)$$

$$\Delta G = -RT \ln K_{pc} \quad (10)$$

where R is the ideal gas constant and T is the absolute temperature. Other notations were defined earlier.

The values of  $\Phi_{TP}$ ,  $K_S$ ,  $K_i$ ,  $K_d$ , and  $\Delta G$  for the CHP/dye/water systems at the transition points were found and tabulated in Table 6.

As expected,  $\Phi_{TP}$ ,  $K_S$ ,  $K_i$ ,  $K_d$ , and  $\Delta G$  values at the transition points for all CHP/dye/water systems increased in the order  $CV > NB > CB$  for dyes. Considering these values in terms of crosslinker, an increase was observed in the order  $CHP-E > CHP-N$ .

The  $\Delta G$  values of CHP-E are higher than those of CHP-N. Therefore, more energetically favorable adsorption occurred in CHP-E/dye/water systems. When these values are evaluated according to oxazine dyes, the energetic

**Table 5** Adsorption isotherm parameters of CHPs in the oxazine dye solutions

Crosslinker dye	$\Phi_{max} \text{ mmol}_d \text{ mol}_p^{-1}$	$n_m \text{ } \mu\text{mol}_d \text{ mol}_p^{-1}$	SS mol <sub>p</sub> mol <sub>d</sub> <sup>-1</sup>	FO %
N,N' methylene bisacrylamide				
Cresyl Blue	5.05	5.48	182.57	92.20
Nile Blue	5.30	5.58	179.86	95.32
Cresyl Violet	6.45	7.86	127.19	82.04
Ethylene glycol dimethacrylate				
Cresyl Blue	5.28	5.80	172.29	90.97
Nile Blue	6.06	6.06	165.15	100.00
Cresyl Violet	6.71	7.39	135.33	90.81



binding order onto CHPs is CV > NB > CB. In this case, it can be seen from Table 6, that the most energetic coupling is in the CHP-E/CV/water system [50].

### 3.5 Influence of the mass of polymer on adsorption

The mass of the polymer is also an important factor in removing a desired solute in large-scale industrial applications. To investigate the influence of the mass of the CHPs on the adsorption, a series of adsorption experiments are performed with increasing polymer masses at a certain initial oxazine dyes concentration. The percentage removal efficiencies ( $\xi\%$ ) of dyes are calculated from the uptake of dyes by CHPs using the equation below [2].

$$\xi\% = \frac{C_o - C_e}{C_o} \times 100 \tag{11}$$

The notations in this equation have already been defined.

Figure 10 shows that the  $\xi$  values of the dyes increase slightly with the increase in the mass of the CHPs. Increasing the mass of the polymers does not affect the removal efficiency. Also, Fig. 10 shows that CHP-E adsorbs slightly more dye than CHP-N.

### 3.6 Relationship between binding and swelling

To determine the relationship between the swelling of CHPs and the binding of dyes to CHPs, a graph of equilibrium swelling values ( $S_e$ ) versus maximum binding ratio values ( $\Phi_{max}$ ) was drawn and presented in Fig. 11.

Figure 11 shows that the swelling of CHPs in aqueous dye solutions increases linearly with increasing dye binding to CHPs. The high correlation coefficients ( $r^2$ ) of this linear increase indicate a good relationship between swelling and adsorption ( $r^2 = 0.998$  for CHP-N and  $r^2 = 0.994$  for CHP-E). This trend in this linear relationship between swelling and bonding is very high for CHP-E (slope =  $9.734 \pm 0.460$ ), while for CHP-N it is very close to zero (slope =  $0.111 \pm 0.008$ ).

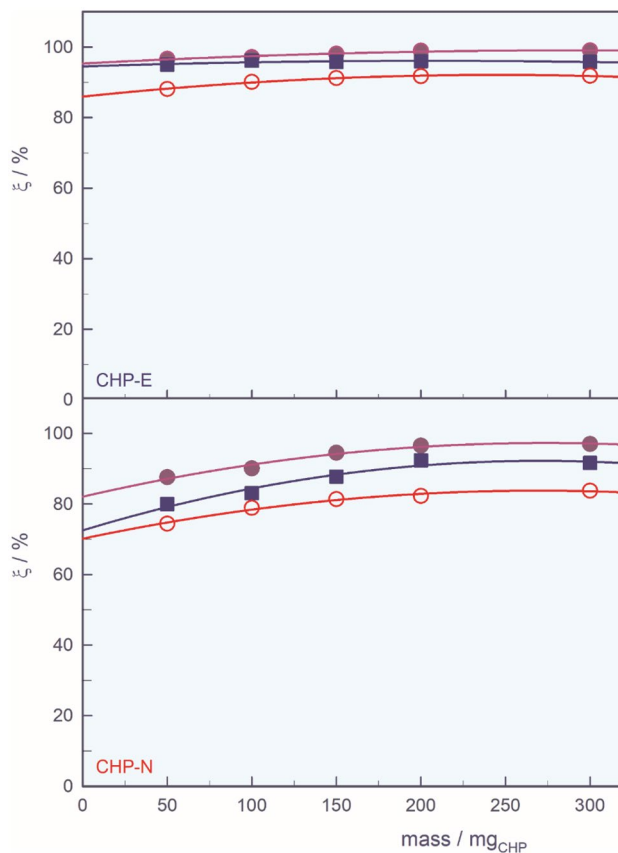


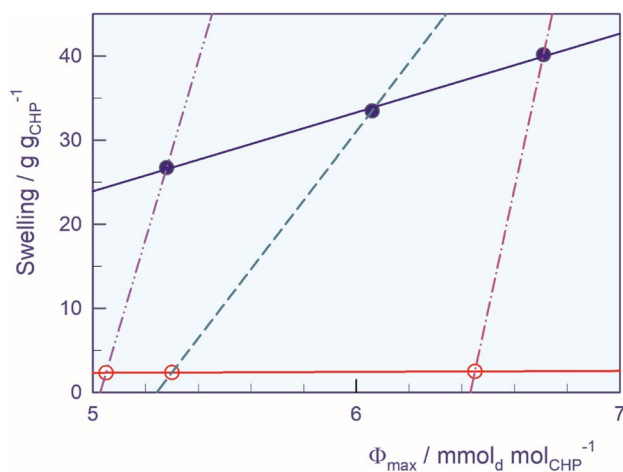
Fig. 10 The influence of the CHP mass on oxazine dye adsorption; ○: CB, ■: NB, ●: CV

There may be some reasons for non-covalent interactions in the adsorption of oxazine group dye molecules by CHPs. Electrostatic interactions would be expected between the positive charge on the cationic oxazine dye molecules and the negative charge of the hydroxamate groups on the anionic CHPs. Another interaction may be hydrogen bonding. Especially, hydrogen bonds are expected to form as follows:

- between the hydrogen atoms of the amine groups on the oxazine dyes and the oxygen atom of the carbonyl groups on the repeating monomeric units of the CHPs,

Table 6 S-type adsorption isotherm parameters of CHPs in the oxazine dye solutions at the transition points

Crosslinker dye	$\Phi_{TP}$ mmol <sub>d</sub> mol <sub>p</sub> <sup>-1</sup>	$K_S$ L mol <sub>p</sub> <sup>-1</sup>	$K_i$ L mol <sub>d</sub> <sup>-1</sup>	$K_d$ dimensionless	$\Delta G$ kJ mol <sup>-1</sup>
N,N' methylene bisacrylamide					
Cresyl Blue	2.74	247.90	1.36	129.46	-12.09
Nile Blue	2.78	443.88	2.47	297.59	-13.96
Cresyl Violet	3.93	522.29	4.11	674.98	-16.14
Ethylene glycol dimethacrylate					
Cresyl Blue	2.90	740.95	4.30	333.09	-14.39
Nile Blue	3.08	4162.29	25.20	765.32	-16.15
Cresyl Violet	3.40	36,798.81	291.91	35,144.85	-25.93

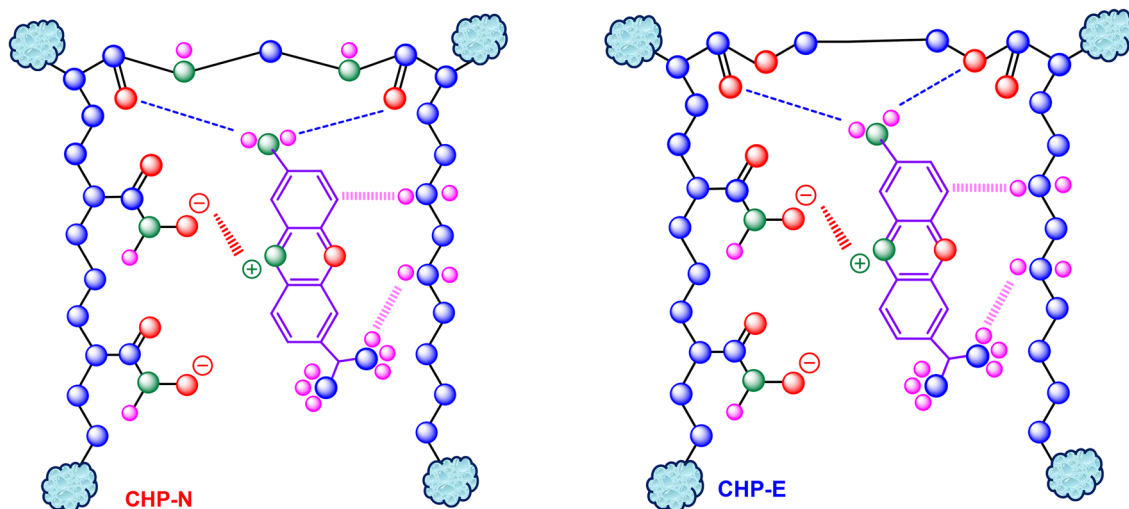


**Fig. 11** The graphs of the relationship between the binding and the swelling, ○; CHP-N, ●; CHP-E

- between the oxygen and nitrogen atoms in the benzoquinone ring of the oxazine dyes and the hydrogens in the amine and amide groups of the CHPs,
- between the hydrogen atoms of the amine groups on the oxazine dyes and the oxygen atoms on the E crosslinker and the oxygen atom of the carbonyl groups, or
- between the hydrogen atoms of the amine groups on the oxazine dyes and the oxygen atom of the carbonyl groups on the N crosslinker.

Finally, another interaction can be hydrophobic interactions between methyl or ethyl groups and aromatic rings on the oxazine dye molecules and methylene groups on the CHP main chains and crosslinkers.

The proposed plausible mechanisms for the binding of the cationic oxazine dyes onto anionic CHPs are illustrated in Fig. 12.



**Fig. 12** Proposed plausible interactions between the dye and CHPs

The results of the bindings were found to parallel the results of the swellings. Although the ionic charge content in the cross-linked structure is important, the swelling of water-loving polymers increases with the increase of hydrophilic units in the adsorbent structure. Therefore, CHPs have many hydroxamate groups that can enhance the interaction between the cationic dye molecules and the anionic groups of the polymer. Thus, it can be seen that the swelling or sorption capacity of CHPs is increased. The most important effect on swelling and binding is the chemical structure of the dyestuff, as well as the anionicity of the CHPs and the hydrophilicity of the crosslinkers. These effects on the swelling and binding follow the order of choosing polymers containing ionizable, hydrophilic, and hydrophobic groups > changing the crosslinker > increasing the cationic, hydrophilic, and hydrophobic groups in the dyes.

## 4 Conclusions

This research gave us quantitative information about the swelling and binding properties of anionic CHP adsorbents and cationic oxazine dyes such as CB, NB, and CV, which were selected as water polluting model dyes. CHPs in dye solutions swelled rapidly and reached equilibrium in a short time. In the same dye solution, CHP-N swelled considerably less than CHP-E. In the diffusion of all dye solutions to the CHPs, diffusion was determined as non-Fickian type.

The binding of cationic oxazine dyes to CHPs was found to be S-type according to the Giles classification. Adsorption parameters, which are difficult to find for S-Type isotherms, could be calculated using the Sigmoidal 4 parameter equation. The binding of dyes onto CHPs in the same dye solution is significantly higher in CHP-E than in CHP-N. It was determined that there was an increasing linear correlation

between swelling and binding values. The removal efficiency of binding oxazine dyes onto CHPs has been calculated between 90 and 100 percent. Swelling and binding properties were more affected by the type of crosslinker in CHP than the structure of the dye.

Finally, it can be said that it may be appropriate to use CHPs as the adsorbent in the removal of cationic chemicals (such as organic molecules, heavy metal ions) and dye molecules. The use of such networks makes crosslinked polymers more popular in agriculture, environment, adsorption, separation, purification, immobilization, and enrichment of some species. In addition, the use of the proposed sigmoidal equation approaches can be a very useful model for chemists, chemical engineers, agriculture engineers, environment engineers, plastic engineers, polymer scientists to determine the adsorption parameters of the adsorbents.

**Author contributions** DS: Conceptualization, methodology, software, formal analysis, investigation, resources, data curation, writing—original draft preparation, writing—review and editing, visualization, supervision, project administration, funding acquisition, YI: Conceptualization, methodology, software, formal analysis, investigation, resources, data curation, writing—original draft preparation, writing—review and editing, visualization, EK: Conceptualization, methodology, formal analysis, investigation, resources. All authors have read and agreed to the published version of the manuscript.

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## Declarations

**Conflict of interest** The authors declare no conflict of interest.

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