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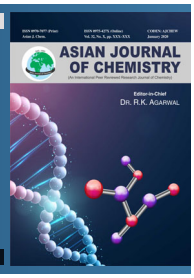

Adsorptive Removal of Anionic Azo Dye Acid Black 194 from Aqueous Solution using NNMBA-Crosslinked Poly *N*-Vinyl Pyrrolidone Hydrogel

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N,N-Methylene *bis*-acrylamide crosslinked poly-*N*-vinyl pyrrolidone hydrogels were synthesized and binding of the hydrogel with the dye solution was followed spectrophotometrically. The chemical structure and morphology of the hydrogel before and after adsorption of acid black 194 was confirmed by FT-IR and SEM. Effect of various physico-chemical parameters such as concentration, temperature, pH, time and the amount of hydrogel used were investigated by batch adsorption studies. Hydrogel used as adsorbent in this study was characterized by UV-Vis spectrophotometer before and after adsorption of acid black 194. Kinetic studies suggested pseudo second order reaction. Langmuir and Freundlich isotherms were applied on equilibrium adsorption data and found that Freundlich isotherm fit better for the present investigation. *N,N*-methylene *bis*acrylamide crosslinked poly-*N*-vinyl pyrrolidone hydrogel displayed excellent properties for the removal of the azo dye, acid black 194 from aqueous solution.

Keywords: Hydrogel, Crosslinking agent, Azo dye, Adsorption.

INTRODUCTION

Water pollution due to effluents from textile dyeing industries is a serious threat to the environment. Azo dyes account for about 50 % of all types of dyes used throughout the world [1]. In recent years, extensive efforts have been devoted for the removal of textile azo dyes from wastewater stream. Depending on the dye class, between 2 % and as much as 50 % of the dye used ends up in wastewater [2]. This discharge is undesirable, not only because of their colour but also because of the toxic and/or mutagenic [3] breakdown products of many azo dyes. Azo dyes can be converted into carcinogenic aryl amines under anaerobic condition [4]. So it is essential to remediate these azo dyes from industrial effluents before it is being discharged in to the wastewater stream.

Acid black 194 (AB194) is 1:1 chromium complex of a mono azo dye produced by coupling 1,2-diazoxynaphthalene-4-sulphonic acid and 2-naphthol [5]. It is used to dye leather, wool, silk and silk blended with wool fabric [4].

Conventional biochemical oxidative treatment of wastewater containing azo dye often results in coloured water unfit for reuse, while other methods such as coagulation, absorption, chemical oxidation, ozonation, reverse osmosis, ultrafiltration, photo decomposition *etc*. alone or in combination, are found to be not effective due to their cost, regeneration or reusability. These results in generation of large amount of sludge, which is difficult to dispose and are not environmental friendly [6]. Among these the adsorption process is one of the most effective and accepted techniques that have been successfully employed for the removal of dyes from wastewater [7] because it is economical, effective and simple in design [8].

Crosslinked polymers which can imbibe large amounts of water of the order of 1000 times its dry weight are called hydrogels [9]. These hydrophilic polymers are elastomeric in nature and are stable. As a result of crosslinking, the polymer become brittle, less elastic and less viscous in nature. Crosslinking is a stabilization process in which two polymeric chains are joined with ionic or covalent bond, which in turn restrict

the movement of the polymeric chain [10]. The polymer of *N*-vinyl pyrrolidone is hydrophilic but the crosslinking makes the polymer, water insoluble. Thus *N,N*-methylene *bis*acrylamide (NNMBA)-crosslinked poly *N*-vinyl pyrrolidone (PVP) hydrogel is insoluble in solvents but can imbibe large amount of water. It is a very effective hydrogel for the adsorptive removal of the azo dye, acid black 194 from aqueous solution.

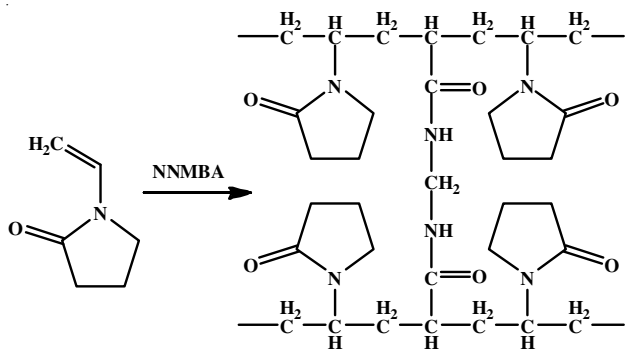
EXPERIMENTAL

The monomer *N*-vinyl 2-pyrrolidone (NVP) and crosslinking agent NNMBA were purchased from Sigma Aldrich, USA. Acid black 194 was obtained from a dye manufacturing company named Jay Chemicals, Ahmadabad, India. Other solvents were purified by distillation unless, otherwise stated. All other reagents used were of analytical grade. IR spectra were recorded on a Shimadzu IR-470 spectrophotometer and UV spectra using Shimadzu UV-Vis 2450 spectrophotometer. SEM photographs were taken on a JEOL JSM-6390 instrument. In the present work, NVP was the monomer used, NNMBA was the crosslinking agent and AIBN was the initiator. Crosslinked polymeric hydrogel formed was equilibrated with the dye solution, acid black 194 and the dye binding studies were followed spectrophotometrically.

Preparation of 2-20 mol % NNMBA-crosslinked PVP hydrogel: A 2-20 mol % NNMBA-crosslinked poly *N*-vinyl pyrrolidone hydrogels were prepared by suspension polymerization. Dissolved 20 g Na_2SO_4 in 80 mL distilled water, 0.25 g Na_2HPO_4 is added to it, heated and stirred. Required amount of the monomer, NVP and NNMBA, the crosslinking agent were mixed to the above solution. When the temperature reached 80-85 °C, fixed amount of AIBN initiator was added, heated and stirred. The polymer was collected by filtration, washed with water, methanol and dried (**Scheme-I**). The yields of 2-20 mol % NNMBA-crosslinked PVP hydrogels are given in Table-1.

RESULTS AND DISCUSSION

Synthesis of 2-20 mol % NNMBA-crosslinked PVP hydrogel: A 2-20 mol % NNMBA-crosslinked poly *N*-vinyl pyrrolidone hydrogels were prepared by suspension polymerization.



Scheme-I: Synthesis of NNMBA-crosslinked poly(*N*-vinyl pyrrolidone)

TABLE-1
SYNTHESIS OF 2-20 mol %
NNMBA-CROSSLINKED PVP HYDROGELS

NNMBA (mol %)	Yield (g)	NNMBA (mol %)	Yield (g)
2	4.4196	12	10.1774
4	5.3122	20	12.0450
8	7.9915	–	–

Characterization

SEM studies: The SEM micrograph of hydrogel and dye bound hydrogel are shown in Fig. 1. From the images, it is observed that the plain hydrogel surface is fairly rough but that for the dye bound hydrogel is quiet smooth. It may be due to the filling of available space on adsorbent particles by the dye molecules. It can be taken as a physical evidence for the adsorption of dye on polymeric hydrogel.

FT-IR analysis: FT-IR spectra of the hydrogel systems were evaluated. It indicate that after binding with the dye the characteristic –OH stretching vibration peak of the hydrogel at 3537.20-3236.33 cm^{-1} is shifted to lower frequency, 3454.27 cm^{-1}. The infrared spectral analysis of NNMBA-crosslinked PVP indicated characteristic absorption peak at 1652.88 cm^{-1} due to amide carbonyl of the pyrrolidone unit and that at 1292.22 cm^{-1} is due to C-N stretching of the vinyl pyrrolidone. A sharp peak at 1018.3 cm^{-1} is attributed to the C-OH stretching mode, which further confirmed dye binding.

Dye binding studies: Required concentration of acid black 194 dye solution was mixed with the polymeric hydrogel

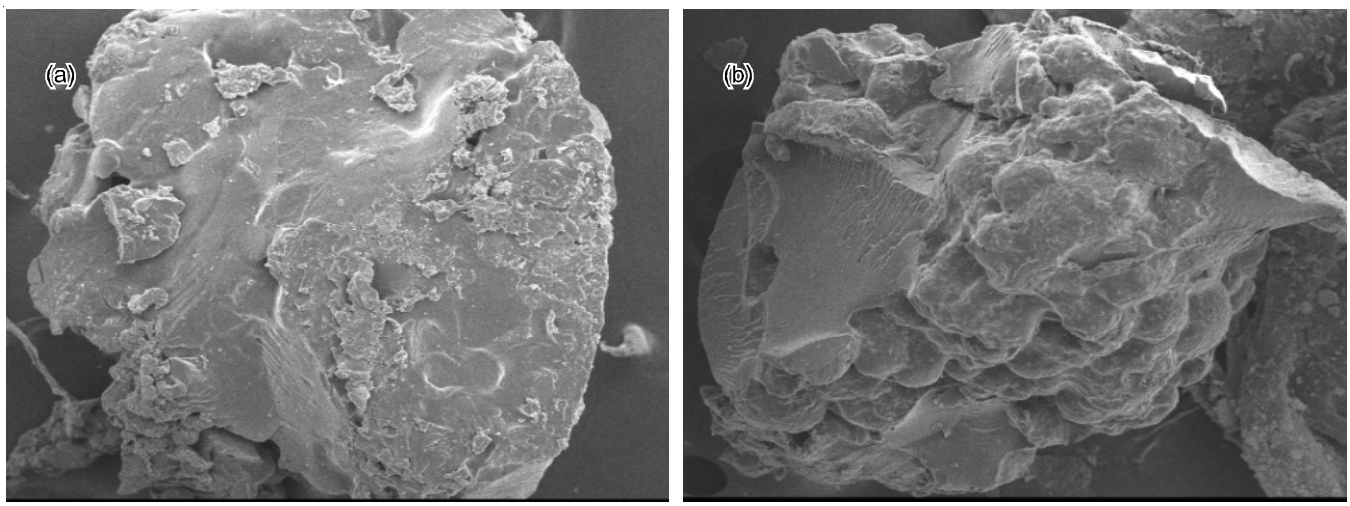


Fig. 1. SEM micrographs of NNMBA-crosslinked PVP on (a) acid black 194 unadsorbed; (b) acid black 194 adsorbed

in an amber coloured bottle and shaken well in a thermostated water bath shaker for 5 h. The dye bound polymer was collected by filtration and repeatedly washed with distilled water to remove the uncomplexed dye. The amount of dye bound was determined by calculating the differences between the absorbance of dye solution before binding with the hydrogel and the combined filtrate, which was measured spectrophotometrically.

Effect of concentration on dye binding capacity: Acid black 194 dye solution of five different concentrations were mixed with definite amount of NNMBA-crosslinked PVP hydrogel and incubated in a water bath shaker for 5 h at constant temperature and the amount of dye bound were calculated as discussed earlier. The amount of dye bound is increased as the concentration of dye solution is increased (Fig. 2). When the dye was lightly loaded on the crosslinked polymer, the dye molecules were 'site isolated' as suggested by Jerzy and Neckers [11]. When the polymer was heavily loaded with the dye moieties, the distance between the dye molecules were decreased and the repulsion between them are effectively controlled by the extent of crosslinked polymer loaded with the dye [12]. This is due to the utilization of all the available activated sites at high concentration [13]. The number of dye molecules compete for the vacant sites of the adsorbent is increased at increased dye concentration, which is resulted in an increased dye adsorption [14].

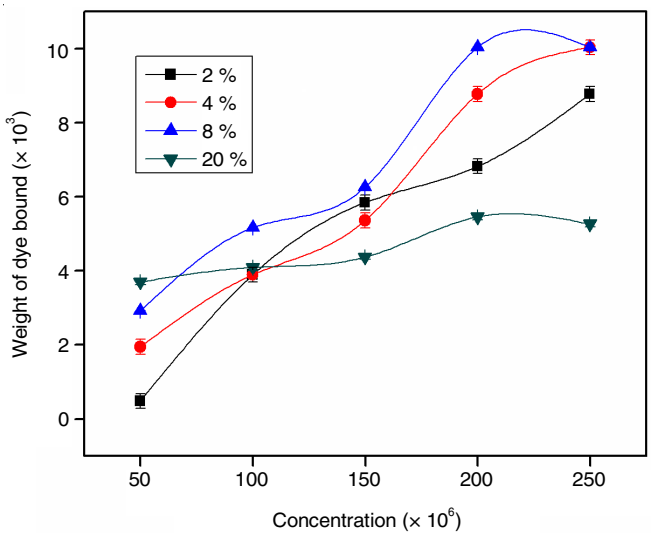


Fig. 2. Effect of concentration on binding of acid black 194 by 2-20 mol % NNMBA-crosslinked PVP

Effect of pH on dye binding capacity: The optimum pH of the medium for maximum uptake of dye solution by the hydrogel can be studied by equilibrating fixed weight of the polymer with the dye solution. The dye solution of three different pH were prepared by using distilled water (pH 6.8) and buffers of pH 4.0 and pH 9.0 at room temperature and was shaken with the hydrogel. Adsorption was minimum at neutral pH and increased with low or high pH. For an acid dye, the binding with the polymer is decreased with increasing pH up to 7 and then it is increased at a faster rate (Fig. 3) [15].

Effect of temperature on dye binding capacity: The effect of temperature on dye binding was investigated by carrying

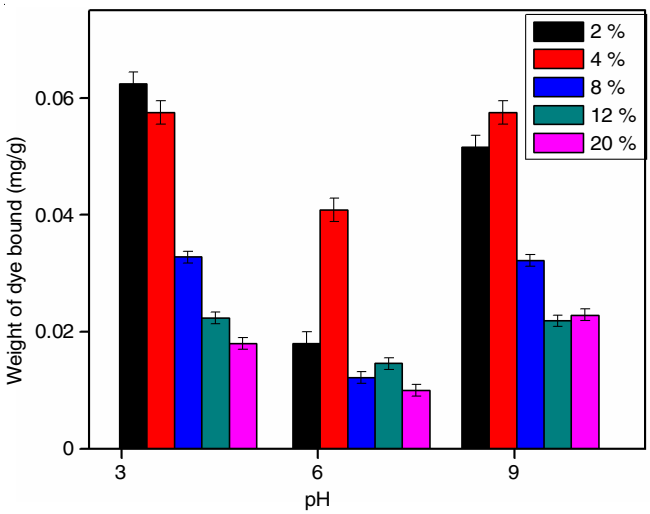


Fig. 3. Effect of pH on the binding of acid black 194 by 2-20 mol % NNMBA-crosslinked PVP

out equilibrium adsorption studies with the crosslinked polymer at four different temperatures 30, 40, 50 and 60 °C. From Fig. 4, it is clear that the optimum temperature for binding of acid black 194 on NNMBA-crosslinked poly *N*-vinyl pyrrolidone is 40 °C. With rise in temperature from 30 to 40 °C, the interaction between dye and the hydrogel is increased, exposing more number of adsorption sites for the dye molecules. From 40 °C onwards, dye binding were decreased sharply indicating exothermic nature of the process [16]. The initial increase was due to the heat supplied, which act as activation energy, but later it was decreased due to exothermic nature of adsorption of dye to the polymer. High temperature caused breaking the bond between dye and the polymer. This may be due to the fact that the kinetic energy of the adsorbate molecules were increased with temperature, thus weakening the adsorbate-adsorbent interaction [17]. Adsorption processes were exothermic for acid dyes [15].

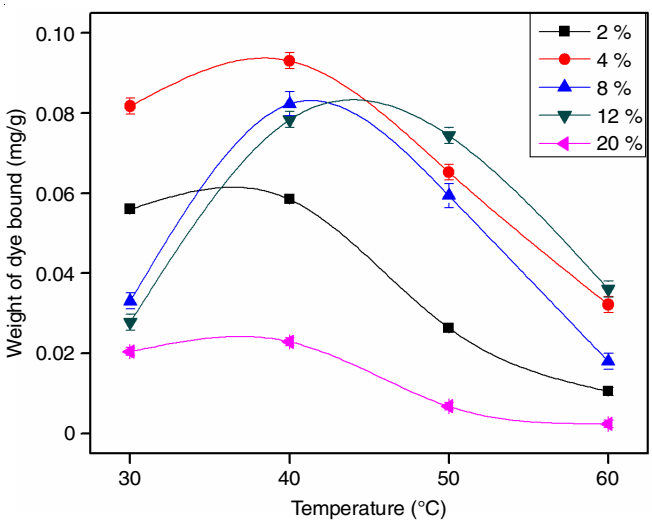


Fig. 4. Effect of temperature on the binding of acid black 194 by 2-20 mol % NNMBA-crosslinked PVP

Effect of amount of polymer added on dye binding capacity: Lower weight of hydrogel showed much better performance of adsorption. As the amount of hydrogel added was

increased from 10 to 40 mg, the dye binding is decreased (Fig. 5). The reason is that the sites remaining unsaturated during the adsorption process [13]. The total available surface area of the adsorbent is decreased due to the overlapping or aggregation of adsorption sites and an increase in adsorption path-length [18].

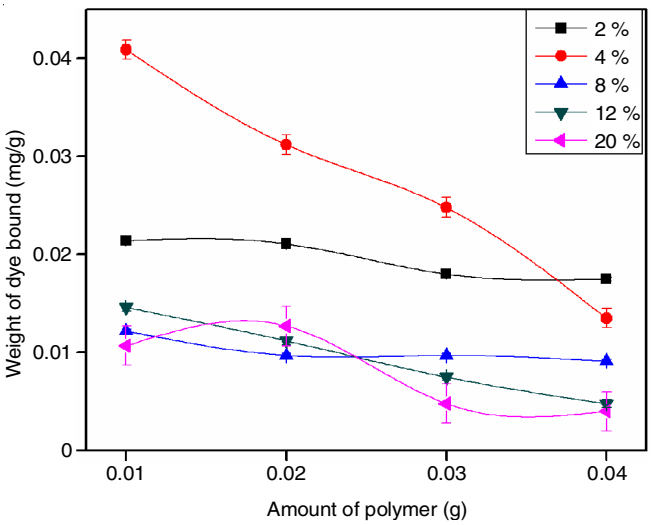


Fig. 5. Effect of weight of polymer added on binding of acid black 194 on 2-20 mol % NNMBA- crosslinked PVP

Effect of contact time: Batch equilibration studies were carried out at gradually increasing time. Dye bound to the polymer was calculated at different intervals of time. It was found that initially dye binding was increased at a rapid rate, reached at equilibrium and then it was decreased. This was due to the availability of active binding sites in the beginning of adsorption, but it gradually slowed down with gradual occupancy of binding sites. Fig. 6 showed that the maximum adsorption capacity occurred at 20 min. The adsorption happened quickly between the interval 0-20 min due to large availability of empty sites to be occupied by the hydrogel [19]. So dye binding experiments were conducted for 20 min [17].

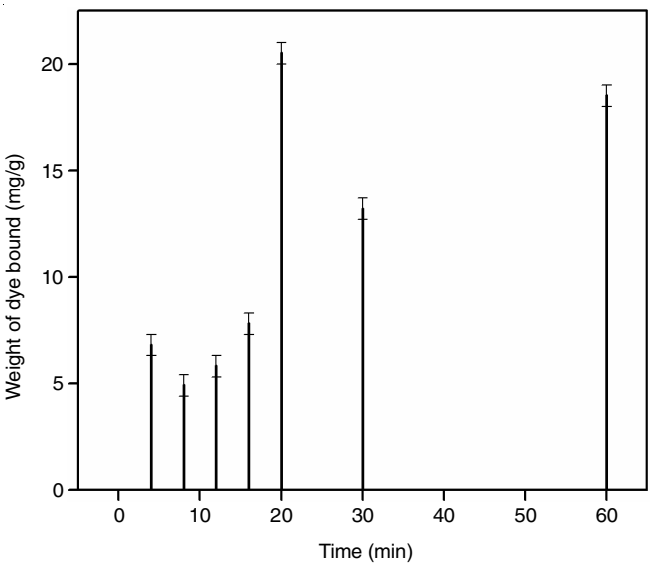


Fig. 6. Effect of time on binding of acid black 194 on NNMBA-crosslinked PVP

Effect of crosslink density: Hydrogels of different crosslink density were equilibrated with dye solution of a fixed concentration and dye binding were studied spectrophotometrically. Crosslinking increases the rigidity of the polymeric chain. When the crosslinking is too low, the hydrogel is flexible which prevents the effective binding of the dye moiety. At very high crosslinking, the hydrogel is too rigid where there is limited accessibility of the dye on to the binding cavities of hydrogel. Thus, from the experimental result (Fig. 7) it was found that 4 % NNMBA-crosslinked poly-*N*-vinyl pyrrolidone is the best adsorbent for the dye, acid black 194.

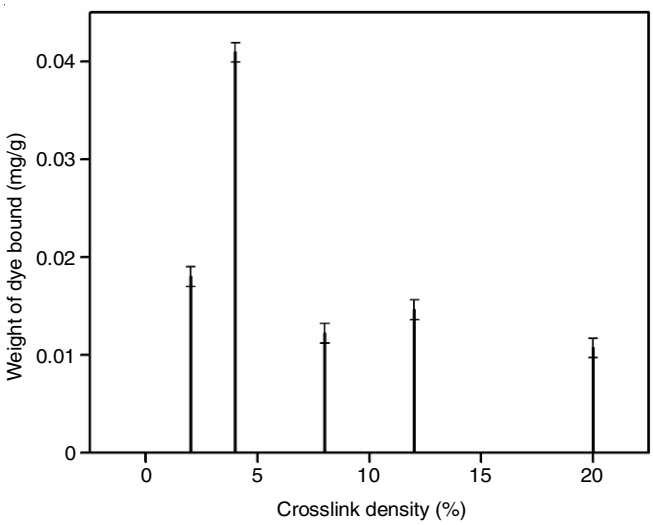


Fig. 7. Effect of varying crosslink density on binding of acid black 194 on NNMBA-crosslinked PVP

Adsorption isotherm: The equilibrium adsorption isotherm is fundamental in describing interactive behaviour between adsorbate and adsorbent. Equilibrium adsorption studies were carried out at different initial concentrations of the dye solution and were analyzed by two models *viz.*, Langmuir adsorption isotherm and Freundlich adsorption isotherm. The basic assumption of Langmuir adsorption model is that the maximum adsorption capacity consists of monolayer adsorption with no interaction between the adsorbent molecules [21]. The Langmuir isotherm is represented by the following equation [22]:

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \quad (1)$$

where q_e (mg/g) is the amount of dye adsorbed at equilibrium, C_e is the equilibrium concentration (mg/L), K_L (L/mg) is the Langmuir constant and Q_o (mg/g) is the adsorption capacity corresponding to complete monolayer coverage. In Langmuir isotherm, a linear plot is obtained by plotting C_e/q_e against C_e.

Freundlich adsorption isotherm model is an empirical equation that describes the surface heterogeneity of the sorbent accompanied by interactions between adsorbed molecules and can be expressed as:

$$q_e = K_F C_e^{1/n} \quad (2)$$

It can be represented in the logarithmic form as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration mg/L, K_F and n are Freundlich constants. The value of K_f and 1/n can be calculated from the intercept and slop of the plot of ln q_e *vs*. ln C_e. In the current study, the adsorption of acid black 194 by NNMBA-crosslinked PVP were analyzed at room temperature using Langmuir and Freundlich isotherms. Fig. 8(a) shows Freundlich isotherm where a linear plot is obtained between ln q_e and ln c_e with a linear regression value of 0.9835. The value of Freundlich constants K_f and n were found to be 10.203 and 1.12, respectively. The regression value obtained is fair, it can be inferred that adsorption of acid black 194 is best interpreted in terms of Frendlich adsorption isotherm model. But the Langmuir adsorption obtained by plotting C_e/q_e against C_e as shown in Fig. 8(b) gave an unfair regression value of 0.7167. Thus it is confirmed that adsorption of acid black 194 by NNMBA-crosslinked PVP followed Freundlich model with maximum adsorption capacity at room temperature.

Adsorption kinetics: The contact time is one of the important parameters in adsorption process. To investigate the adsorption kinetics a fixed mass of the adsorbent is equilibrated with the dye solution at different intervals of time and dye binding is studied spectrophotometrically. The kinetic data of adsorption can be analyzed by pseudo-first-order and the pseudo-second order equations [23]. The differential equation of the pseudo-first-order kinetic model is [21]:

$$\frac{dQ_e}{dt} = k_1(Q_e - Q_t) \quad (4)$$

where Q_e and Q_t refer to the amount of dye adsorbed in mg/g at equilibrium and at a given time, t in minute, respectively and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}) [24].

Integrating eqn. 1 for the boundary conditions (from t = 0, Q_t = 0 to t) gives the equation:

$$\log\left(\frac{Q_e}{Q_e - Q_t}\right) = \frac{\log(Q_e - k_1)}{2.303}t \quad (5)$$

Rate constant (k_1) and the theoretical maximum amount of dye adsorbed (Q_e) can be determined from the slope and intercept of the straight line plot of log (Q_e – Q_t) against t.

The differential equation of pseudo second order reaction is expressed as the following form [21]:

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \quad (6)$$

where k_2 is the rate constant of pseudo-second-order reaction.

Integrating eqn. 3 for the boundary conditions gives the equation:

$$\frac{1}{Q_e - Q_t} = \frac{1}{Q_e} + k_2 t \quad (7)$$

Eqn. 4 can be linearized to the following form:

$$\frac{1}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e}t \quad (8)$$

The value of k and Q_e can be obtained from the slope and intercept of the plot of t/Q_t against t.

The linearized plots of these two models can be analyzed to check the validity of these two models. The fitted results are given in Fig. 9 from which it is clear that pseudo-second-order reaction fitted better than the data obtained from pseudo first order reaction for the adsorption of acid black 194 on NNMBA-crosslinked PVP. The correlation coefficient (r^2) are higher for second order kinetic model than those of first order as explained by Table-2.

TABLE-2
PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER RATE CONSTANT FOR THE ADSORPTION OF ACID BLACK 194 ON NNMBA-CROSSLINKED PVP

Pseudo-first-order			Pseudo-second-order		
Q_e (mg/g)	K (min^{-1})	r^2	Q_e (mg/g)	K (min^{-1})	r^2
-2.9437	0.0254	0.8238	50.86	44.57	0.9755

Thus the adsorption of acid black 194 on NNMBA-crosslinked PVP can be well explained by pseudo-second-order reaction.

Desorption studies: The regeneration of hydrogel after use is very important so that the adsorbent can be recovered and reused which makes the process more economical. 1:1 Ammonia solution was selected as a desorbing agent. In basic solutions the electrostatic interactions between NNMBA-crosslinked

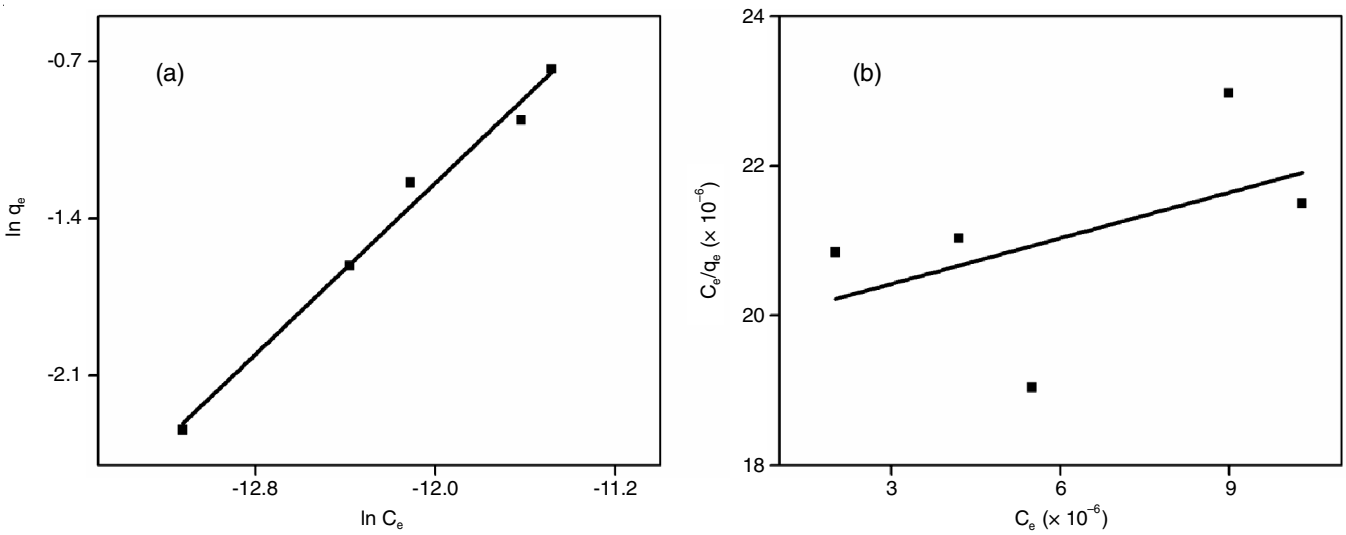


Fig. 8. Adsorption isotherm of acid black 194 on NNMBA-crosslinked PVP (a) Freundlich isotherm (b) Langmuir isotherm

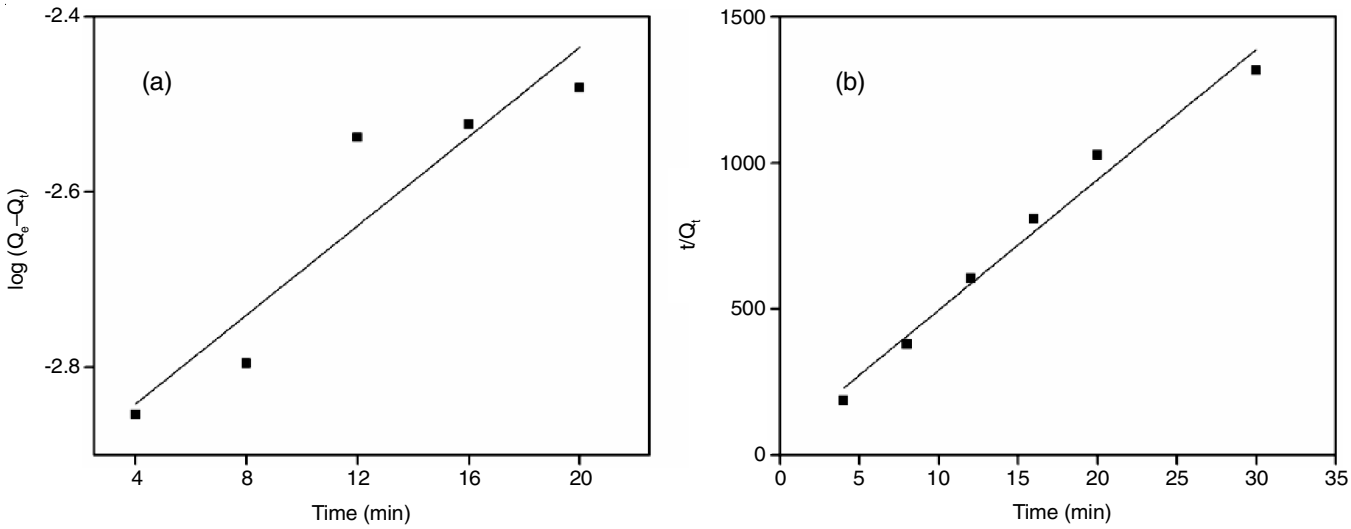


Fig. 9. Adsorption kinetics of acid black 194 on NNMBA-crosslinked PVP by (a) pseudo-first-order and (b) pseudo-second-order reaction

PVP and the acid dye become much weaker and the adsorbed dye leaves the adsorption sites of polymeric hydrogel. The dye bound polymer was equilibrated with 1:1 ammonia solution of different concentration and it is found that it is a best desorbant for the anionic dye, acid black 194.

Conclusion

From the investigation, it is concluded that NNMBA-crosslinked poly *N*-vinyl pyrrolidone is a very effective hydrogel for the adsorptive removal of the anionic dye, acid black 194. The dye removal from aqueous solution is maximum at lower and higher pH rather than neutral pH. The optimum temperature for dye removal is 40 °C. When the crosslink density of the hydrogel is 4 mol %, the dye removal is found to be maximum. The optimum time for adsorption of dye is found to be 20 min. Thus it is clear that the dye concentration, solution pH, mass of the hydrogel, temperature and time of dye binding has a significant role in the removal of acid dye from aqueous solution. In the current study, the adsorption isotherm data was derived at room temperature using Langmuir and Freundlich models. It showed that the adsorption corresponded well with Freundlich model rather than monolayer adsorption. The kinetic data of adsorption can be analyzed by pseudo-first-order and the pseudo-second-order equations and found that adsorption of acid black 194 on NNMBA-crosslinked PVP can be well explained by pseudo-second-order reaction.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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