Polym. Bull. (2011) 67:125–140
DOI 10.1007/s00289-011-0463-6

ORIGINAL PAPER

Removal of cationic dye from aqueous solution by adsorption onto crosslinked poly(4-vinylpyridine/crotonic acid) and its N-oxide derivative

Ramazan Coşkun

Received: 9 November 2010 / Revised: 15 February 2011 / Accepted: 16 February 2011 /

Abstract In this study, crosslinked poly(4-vinylpyridine/crotonic acid) [poly(4-VPy/CrA)] and its N-oxide derivative were synthesized to compare the adsorption of cationic methylene blue (MB) dye on these materials. The adsorptive removal of MB from aqueous solution onto adsorbents was studied by using column adsorption method. Experimental results showed that MB was removed more effective by poly(4-VPy/CrA)–N-oxide than poly(4-VPy/CrA) resins. The percentage removal of MB increased with pH, and it was observed that basic pH was favorable for the adsorption of MB. The adsorption capacity for poly(4-VPy/CrA)–N-oxide resin was found to 19.96 mg/g. It was found that the adsorption isotherm of the MB-fitted Langmuir-type isotherm. For the adsorption of MB, the pseudo-second-order chemical reaction kinetics provides the best correlation with the experimental data. Ten adsorption–desorption cycles demonstrated that the resins were suitable for repeated use without considerable change in adsorption capacity.

Keywords Resin · Methylene blue dye · Removal · Adsorption–desorption · Isotherms and adsorption kinetics

Introduction

It is well known that textile industries, pulp mills and dyestuff manufacturing discharge highly colored wastewaters which have provoked serious environmental concerns all over the world [1–3]. Methylene blue (MB), a cationic dye, has wide applications, which include paper coloring, cottons or wools dyeing, and coating for paper stock [4]. Although the dye is not regarded as a very toxic dye, it can have various harmful effects on living things [5]. Once inhaled, it can cause heart rate

---

R. Coşkun (✉)
Department of Chemistry, Faculty of Science and Arts, Bozok University, Yozgat, Turkey
e-mail: rcoskun66@hotmail.com

increasing, nausea and vomiting. If the amount of intake is large, severe symptoms such as difficulties in breathing, mental confusion, and methemoglobinemia-like syndromes may take place [6]. Dyes even in low concentrations are visually detected and meanwhile affect the aquatic life and food web. The removal of dye from textile wastewaters is a major environmental problem due to the difficulty of treating such waters by conventional methods. Most studies have focused on the development of a technique and a method for the treatment of dye wastewater. Adsorption has been found to be superior to other techniques for dye remove due to its low operating cost, easy of design and insensitivity to toxic substances [7]. Activated carbon is widely used as adsorbent because of its high adsorption abilities for a large number of organic compounds [1]. However, the cost of activated carbon is relatively high and the generation is difficult, which limits its usage in dye treatment [8].

In recent years, the development of new adsorbents having superior properties such as high adsorption capacity, fast adsorption rate, and mechanical strength has generated great interests for wastewater treatment. Polymeric adsorbents, due to their wide variations in porosity and surface chemistry, especially regenerability on site and reuse for continuous process, have been increasingly used to remove and recover organic pollutants from waste streams [9–11].

In addition, a wide variety of materials such as bioadsorbents [12–24], fibers [25, 26], hydrogels [27, 28], and functional polymers [29, 30] are used for the removal of various dyes.

Cross-linked copolymers based on vinylpyridines (VPy) have a great potential for many applications as ion-exchange resins, gas separation membranes, catalyst supports, in the water purification industry, in monitoring heavy metals, and as other useful materials [31–34]. The VPy ring can be chemically modified by oxidation, producing a VPy–N-oxide. These modified materials could be used as catalyst supports and ion-exchange resins to remove heavy metals because of the presence of VPy–N-oxide groups [35]. However, dye removal study of the poly(4-VPy/CrA)–N-oxide has not reported in the literature.

Main advantage of the resins is that they have both (+) and (−) charge so they are suitable for anionic and cationic dye. In this work, poly(4-VPy/CrA)–N-oxided resin was prepared and the potential use of this resin as alternative adsorbent for cationic dye removal from aqueous solutions was investigated. The adsorption properties in terms of adsorption capacity were described. The influence of several parameters such as initial dye concentration, and pH on the adsorption capacity was evaluated and discussed. The equilibrium data have been analyzed using various adsorption isotherms and adsorption kinetic models. Moreover, desorption and reusability of resin was examined.

Experimental

Instruments

FT-IR spectra of the resins were recorded with Jasco 460 Plus Fourier Transform IR spectrometer using KBr disc in the range of 4000–700 cm^{-1}. Elemental analyses were carried out on a Leco CHNS-932 elemental analyser. A Schimadzu UV-1208 model UV–Vis spectrophotometer was used to determine MB dye at 665 nm. The pH measurements were made with Consort C931 model digital pH-meter.

Reagents

Crotonic acid (CrA) (Aldrich) was used after recrystallization from distilled water, m.p. 72–74 °C, divinylbenzene (DVB) (Merck) and 4-vinylpyridine (4VPy) (Aldrich) were used as received. α,α'-Azobisisobutyronitrile (AIBN) (Merck) was purified by recrystallization from methanol. The other reagents were commercially purchased, namely *n*-butanol, propanone, methanol, hydrogen peroxide (H_2O_2) (30% w/v), glacial acetic acid, toluene used as received. As adsorbate, chloride salt of MB, a cationic dye, was used as a Merck product without further purification. The following buffer solutions were used for the solid phase extraction procedures: CH_3COOH/CH_3COONa buffer for pH 3–6, Na_2HPO_4/NaH_2PO_4 buffer for pH 7, and NH_3/NH_4Cl buffer for pH 9–11. Aqueous solutions were prepared using distilled deionized water.

Synthesis of resins

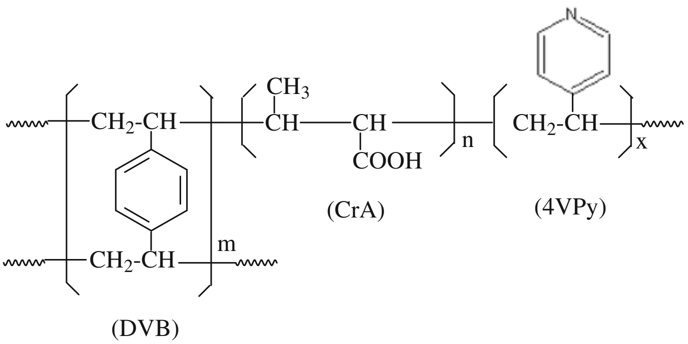
Crosslinked poly(4-vinylpyridine/crotonic acid) and its N-oxide derivative were synthesized in two steps [36]. In the first step (*radicalic polymerization*), the synthesis of the 4VPy/CrA/DVB networks were carried out with a radical initiator (Scheme 1). To a polymerization flask, the two appropriate monomers 4VPy and CrA, the crosslinking reagent DVB, and the initiator AIBN were added. The system was kept under N_2 for 3 h at 60 ± 0.1 °C. Subsequently, the resins was filtered and washed with abundant distilled water and dried in oven at 50 °C until a constant weight was obtained. The amounts of monomeric units in the copolymers were determined by elemental analysis (N content for 4VPy).

In the second step (*oxidation reaction*), the oxidation reaction of 4VPy crosslinked copolymers (Scheme 2) was carried out in n-butanol. The polymers were heated at 75 °C in glacial acetic acid (5.25 mol) with H_2O_2 (1 mol using 30% w/v H_2O_2 solution) under mechanical stirring for 24 h [35, 37]. The modified networks was filtered off, thoroughly washed with water and propanone to remove excess reagents and then dried at 50 °C for 24 h.

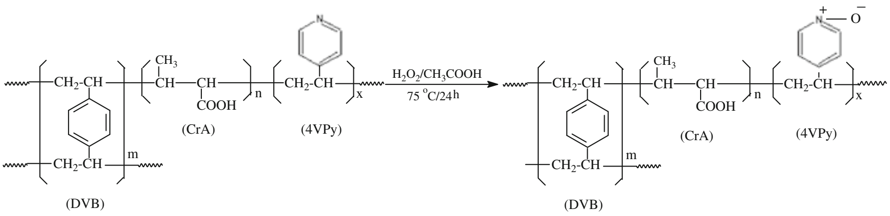
The detailed characterization of unmodified and modified resins has been described previously published in our study [36].

Column dynamic method

The glass column (Vensil, size: 7 mm diameter and 12 cm length) was packed with 0.3 g of the resin and washed three to four times with deionized water. 100 mL of MB dye (25 ppm) solution adjusted to desired pH was taken and passed through the column at a flow rate of 1 mL min^{-1}. Dye concentration was determined at wavelength 665 nm by an UV–Vis spectrophotometer. The removal percentage (R %) and the adsorption amount (Q, mg/g) were calculated as follows:



Scheme 1 Structure of 4VPy/CrA/DVB networks



Scheme 2 Oxidation reaction of 4VPy/CrA/DVB networks

$$\%R = \frac{(C_1 - C_2) \times 100}{C_1} \tag{1}$$

$$Q = \frac{V(C_1 - C_2)}{W}, \tag{2}$$

where C_1 and C_2 are the concentrations (ppm) of dye before and after adsorption, W is the weight of the resin (g), and V is the volume of solution.

Desorption and reuse of the resins

Desorption of dye from dye adsorbed resins was studied with HNO_3 in column experiment. 100 mL of HNO_3 (1 M) solution was taken and passed through the column at a flow rate of 1 mL min^{-1}. Thereafter, the column was washed with buffer (pH = 9) and deionized water, and then again reused adsorption processes. The adsorption/desorption procedure was repeated ten times, each times with fresh solution.

Adsorption kinetic

All adsorption kinetic experiments were studied by batch method. Dried samples (0.1 g each) of resin were added in 100 mL Erlenmeyer including volumes of 30 mL of each the dye solution (25, 50, 75 ppm) adjusted to desired pH.

The mixture was stirred at 25 °C. Every other period of time, 0.1 mL of dye solution was taken out to dilute to 10 mL with deionized water, and its concentration was determined at wavelength 665 nm. The adsorption amount was calculated as follows:

$$Q = \frac{V(C_1 - C_2)}{W}, \tag{3}$$

where Q is adsorption amount (mg/g), W is the weight of the reactive fibers (g), V is the volume of solution (l), and C_1 and C_2 are the concentrations of ion before and after adsorption, respectively (mg/l).

Results and discussion

Effect of N-oxide on the removal of MB

Removal of MB preparation of various mol ratio poly(4-VPy/CrA) resins is shown in Table 1. As seen from the Table 1, with increase of amount CrA in the poly(4-VPy/CrA) resins the removal of MB dye slightly increased. This could be implied that the removal of MB by poly(4-VPy/CrA) resins by cation exchange between the MB cation and –COOH groups of CrA.

Percentage removal of poly(4-VPy/CrA) resins was compared with its N-oxide derivatives in Fig. 1. It is clearly seen from Fig. 1 that MB was removed more effectively by poly(4-VPy/CrA)–N-oxide than by poly(4-VPy/CrA) resins. This could be implied that the removal of MB by N-oxide derivatives is done not only by cation exchange but also via the electrostatic attraction between the MB cation and the negatively charged surface of poly(4-VPy/CrA) resins.

Effect of pH on the removal of MB

The pH value of the solution, which affects the surface charge of the adsorbent and the degree of speciation of adsorbate, was an important controlling parameter in the adsorption process. The effect of pH on the removal of MB was investigated by the column method. 100 mL of MB solutions containing 25 ppm of MB dye was passed at various pH changing from 2 to 10, and the experimental results were shown in Fig. 2.

Table 1 Distribution of 4-VPy and CrA in crosslinked poly(4-VPy/CrA) and removal of MB dye

4-VPy/CrA (mol/mol)	*N* (%)	Distribution of monomers in poly(4-VPy/CrA) (%mol)		Removal of dye (%)
		4-VPy	CrA	
90/10	7.481	51.14	48.86	8.2
70/30	3.851	24.96	75.04	14.1
50/50	3.114	19.97	80.03	15.3
10/90	2.371	15.05	84.95	27.8

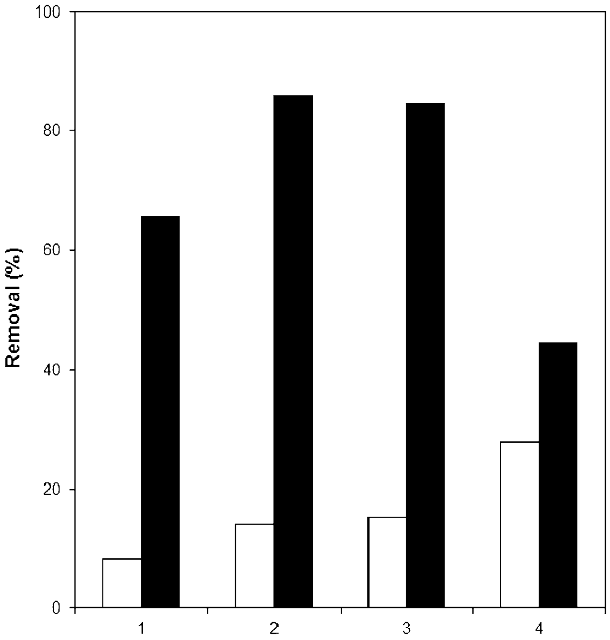


Fig. 1 Adsorption percentages of MB with polymers 1: ☐ 90/10 4-VPr/CrA; ■ 4-VPr/CrA-N okside; *2*: ☐ 70/30 4-VPr/CrA; ■ 4-VPr/CrA-N okside; *3*: ☐ 50/50 4-VPr/CrA; ■ 4-VPr/CrA-N okside; *4*: ☐ 10/90 4-VPr/CrA; ■ 4-VPr/CrA-N okside

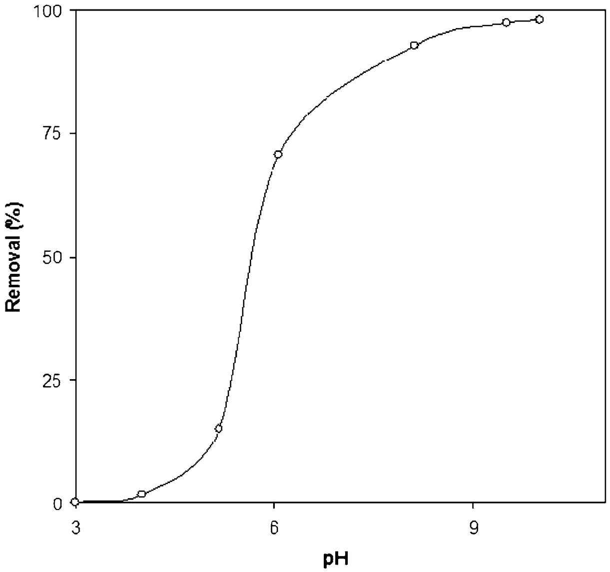


Fig. 2 Effect of pH on the adsorption amount of MB onto resin [$T = 25$ °C; $C_i = 25$ ppm; flow rate = 1 mL min^{-1}]

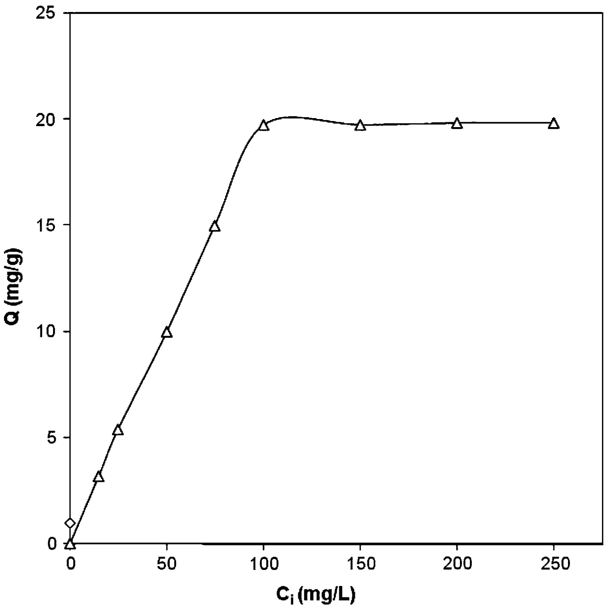


Fig. 3 Effect of initial concentration of MB on the adsorption amount onto resin [pH = 9.0; $T = 25$ °C; flow rate = 1 mL min^{-1}]

As can be seen from Fig. 2, the removal of MB dye onto poly(4-VPy/CrA)–N-oxide increase significantly with increasing pH. The maximum removal of MB dye onto poly(4-VPy/CrA)–N-oxide resin was observed at pH 9. The MB dye is positively charged in solution and it has an affinity to materials with net negative charges. The high removal is due to the strong electrostatic interaction between the COOH group of CrA, –N-oxide group of 4-VPy units and cationic dye molecule. At higher pH, a significantly high electrostatic attraction exists between the negatively charged adsorption sites and positively charged dye molecule, thereby causing the increase in dye adsorption. Also, lower removal of MB dye at lower pH is also due to the abundance of H^+ ions competing with the cationic dye (MB) molecule for the adsorption sites.

Effect of initial dye concentration on the removal

Figure 3 shows the relationship between initial concentration of MB dye and the adsorption amount. It is clear from the Fig. 3, the adsorption amount of MB dye increased with increasing initial dye concentration then reached a plateau value at higher concentration. This is attributed to the adsorption sites of the resin become saturated when the dye concentration is reached at 100 ppm. Equilibrium adsorption isotherms relate the adsorbate concentration in the bulk and the adsorbed amount on the interface. The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes [38]. Experimental data obtained from the effect of initial concentration on

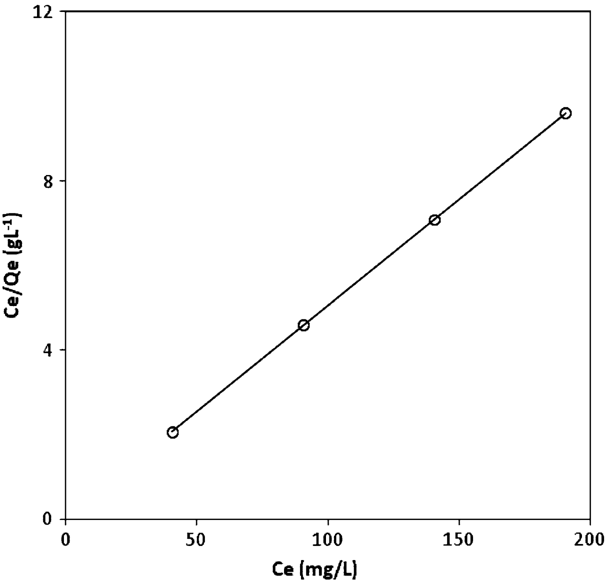


Fig. 4 Langmuir isotherm plot

adsorption capacity were evaluated with the three popular adsorption models which are Langmuir, Freundlich, and DR models. The Langmuir isotherm assumes that the adsorbent surface is homogeneous and the adsorption sites are energetically identical. The linear form of Langmuir equation is given as [39]:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_o} + \frac{1}{Q_o b} \tag{4}$$

where the parameters of the equations are the following: C_e (mg/g) and Q_e (g/mg) the amount of dye remained in the solution and adsorbed onto the resin at equilibrium, respectively. Q_0 (mg/g) is the saturated adsorption capacity and b is the Langmuir isotherm constant (L/mg), related to the affinity of the adsorption sites. The plot of C_e/Q_e versus C_e in Fig. 4 was drawn from the experimental data given in Fig. 3 and the values of Q_o and b can be calculated from the intercept and slope of the plots, respectively.

Freundlich equation is derived to model the multilayer adsorption and for the adsorption on heterogeneous surfaces. The Freundlich model is formulated as [40];

$$Q_e = K_f C_e^{1/n} \tag{5}$$

where Q_e is the equilibrium solute concentration on adsorbent (mg g^{-1}), C_e is the equilibrium concentration of the solute (mg L^{-1}), K_f is Freundlich constant (mg g^{-1}) which indicates the adsorption capacity also represents the strength of the adsorptive bond, and n is the heterogeneity factor which also represents the bond distribution. A linear form of the Freundlich equation can be obtained by taking logarithms of the equation,

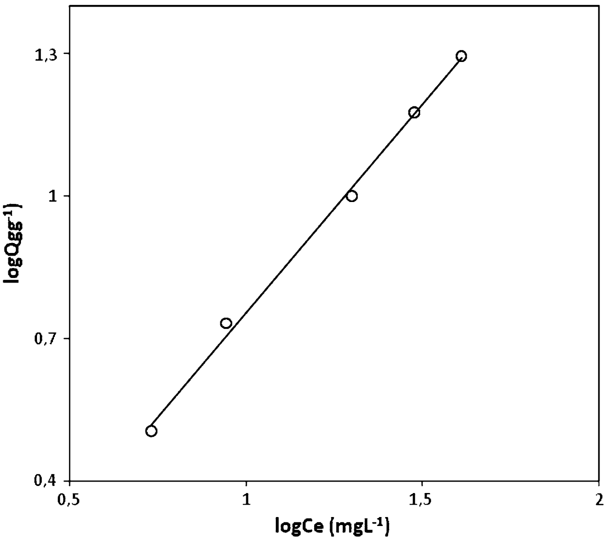


Fig. 5 Freundlich isotherm plot

$$\log Q_\mathrm{e} = \log K_\mathrm{f} + \frac{1}{n}\log\ C_\mathrm{e} \tag{6}$$

Experimental data obtained from the effect of initial concentration to the adsorption of MB on resin was also evaluated by applying this equation and the plots of log Q_e versus log C_e was shown in Fig. 5. The values of K_f and n can be calculated from the intercept and slope of the plots, respectively. Langmuir and Freundlich isotherms do not give any idea about adsorption mechanism. D–R isotherm describes adsorption on a single type of uniform pores. In order to understand the adsorption type, D–R isotherm was obtained (Fig. 6). The D–R isotherm which is given with the following equation [41]:

$$\log Q_\mathrm{e} = \log Q_\mathrm{m} - k\varepsilon^2 \tag{7}$$

where Q_m is the D–R monolayer capacity (mg/g), Q is the amount of solute adsorbed per unit weight of adsorbent (mg g^{-1}), k is a constant correlated to sorption energy ($(\mathrm{mol/J})^2$), and ε is the Polanyi potential related to the equilibrium concentration (J/mol), illustrated as follows:

$$\varepsilon = RT\ln(1 + \frac{1}{C_\mathrm{e}}) \tag{8}$$

where R is the universal gas constant (8.314 J/(mol K)), and T is the absolute temperature (K). The mean free energy of adsorption (E) was calculated from the k values using the equation

$$E = (2k)^{-0.5} \tag{9}$$

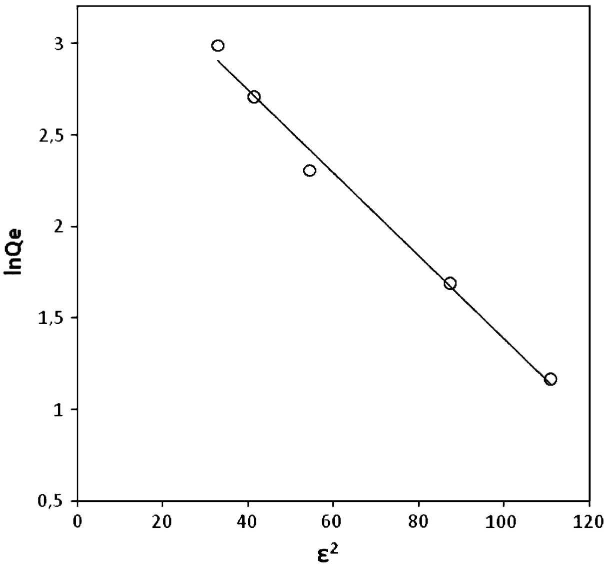


Fig. 6 D–R isotherm plot

Table 2 Langmuir, Freundlich and Dubinin–Radusckevich parameters for MB adsorption

Langmuir model			Freundlich model			Dubinin–Radusckevich model			
Q_o (mg/g)	b (L/mg)	R^2	K_F (mg/g)	$1/n$	R^2	Q_m (mg/g)	k (mol^2/kJ^2)	E (kJ/mol)	R^2
20	2.381	1	0.752	1.138	0.996	38.28	0.022	4.76	0.990

The magnitude of E is useful for estimating the type of adsorption process. If this value is between 8 and 16 kJ mol^{-1} adsorption process can be explained by ion-exchange [42]. The constant parameters and correlation coefficients were calculated from the Langmuir; Freundlich and D–R equations mentioned above, as summarized in Table 2. It can be seen that the values of correlation coefficients of Langmuir equation were higher than the other two isotherm values, which indicated the Langmuir isotherm correctly fitted the equilibrium data, confirming the monolayer coverage of MB onto the poly(4-VPy/CrA)–N-oxide and E values are calculated to be 4.76 kJ/mol which is not within the energy range of ion-exchange reactions. Hence, it is possible to say that adsorption mechanism of MB on resin can be explained with a simple physical adsorption. But chelating effect of the functional groups onto the poly(4-VPy/CrA)–N-oxide are also thought to take part in the adsorption process.

Adsorption kinetic

Using various dye concentration (25, 50, 75 ppm) and resin (0.1 g/30 mL), the concentrations of the dye in solution were determined at regular times. The experimental data obtained was given in Fig. 7. The amount of dye adsorbed

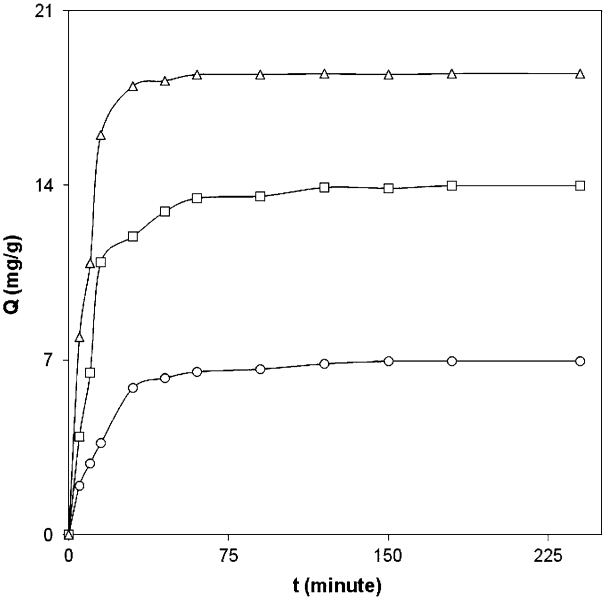


Fig. 7 Adsorption kinetic of MB on resin (*circle*) 25 ppm, (*square*) 50 ppm, (*triangle*) 75 ppm, [pH = 9.0; $T = 25$ °C]

increased with increasing contact time and reached equilibrium after 60 min for the three different initial concentrations of MB. It is known that adsorption process could be dependent on and controlled with different kinds of mechanisms, such as mass transfer and chemical reaction. So as to clarify the adsorption process, the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were tested. A pseudo-first-order kinetic model of Lagergren [43] is given as;

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{10}$$

A pseudo-second-order kinetic model of Ho [44] is given as

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \tag{11}$$

Intraparticle diffusion model is expressed with the equation given by Weber and Morris [45];

$$Q_t = k_{id} \,.\, t^{1/2} \tag{12}$$

where, Q_t and Q_e (mg g^{-1}) are the amount of adsorption on the resin at time t and equilibrium, k_1 ($\min^{-1}$), k_2 (gmg^{-1} $\min^{-1}$), and k_{id} (mg g^{-1} $\min^{-1/2}$) are the rate constant for the pseudo-first-order, the pseudo-second-order and the intraparticle diffusion models, respectively. The values of k_1, k_2, and k_{id} at 25 °C were calculated from the slopes of the linear plot of $\frac{t}{Q_t}$ versus t (Fig. 8), $\ln(Q_e - Q_t)$ versus t (not given) and Q_t versus $t^{1/2}$ (not given), respectively, and the kinetic parameters obtained for

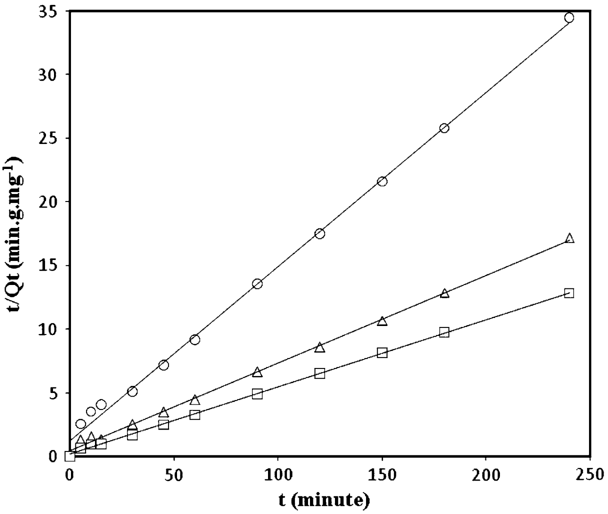


Fig. 8 Pseudo-second-order plots for MB on resin (*circle*) 25 ppm, (*square*) 50 ppm, (*triangle*) 75 ppm, [pH = 9.0; $T = 25$ °C]

adsorption of MB dye onto resin were listed in Table 3. It can be seen from Table 3, over all adsorption process fitted to the pseudo-second-order kinetic model. This behavior can be explained with the existence of chemisorptions. The structural nature of the adsorbent and the functional groups on it thought to be effective in such behavior. Actually this kind of behavior is in accordance with the literature that for such exchangers' adsorption kinetics is expected to follow second-order kinetics model [46]. The theoretical q_e values calculated from graphical interpretation of the first-order kinetic model were not found to fit experimental q_e values. For all initial concentrations second-order kinetic model fitted better with high correlation coefficient and resulted in reasonable theoretical and experimental q_e values.

Reusability

The most an important properties of the adsorbent is its reusability after a particular process. For obtaining the reusability of the resins, the adsorption–desorption cycle was repeated ten times with the same adsorbent and the results are shown in Fig. 9. It was observed that the adsorption capacity of poly(4-VPy/CrA)–N-oxide did not considerably change after ten adsorption–desorption cycles. This results shows that poly(4-VPy/CrA)–N-oxide are good reusable adsorbent for the removal of MB from aqueous solution.

Conclusion

In this paper, poly(4-VPy/CrA)–N-oxided resin was prepared and the adsorption properties of MB from aqueous solution by the resins were investigated. As results, the following conclusions were obtained.

Table 3 Comparison of the pseudo-first-and second-order and intraparticle diffusion adsorption constants at different initial concentrations of MB onto poly(4-VPy/CrA)–N-oxide resin

Kinetic model										
[MB] (ppm)	Pseudo-first-order				Pseudo-second-order				Intraparticle diffusion	
	Q_e(exp) (mg g^{-1})	Q_e(theor.) (mg g^{-1})	k_1 (min^{-1})	R^2	Q_e(exp) (mg g^{-1})	Q_e(theor.) (mg g^{-1})	k_2 (gmg^{-1} min^{-1})	R^2	k_{id} (mg g^{-1} $min^{-1/2}$)	R^2
25	6.95	3.76	0.029	0.972	6.95	7.35	0.0148	0.997	0.454	0.648
50	14.00	5.31	0.030	0.949	14.00	14.70	0. 0104	0.997	0.605	0.615
75	18.51	1.83	0.020	0.641	18.51	19.23	0. 0155	0.999	0.588	0.505

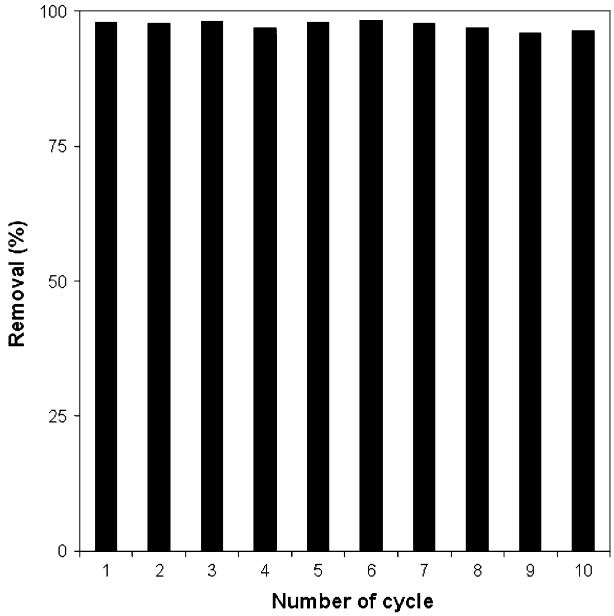


Fig. 9 MB adsorption capacity of resin after adsorption/desorption cycle [pH = 9.0; $T = 25$ °C; $t = 24$ h; $C_i = 25$ ppm]

(1) The adsorption amount of MB efficiently increased with N-oxide.
(2) The adsorption of MB onto poly(4-VPy/CrA)–N-oxide is favored at basic pH.
(3) Adsorption on resin can be expressed better with Langmuir-type adsorption isotherms which show the homogenous characteristics of the adsorption sites on resin.
(4) Adsorption of MB dye onto resin was found to occur with a simple physical adsorption. But chelating effect of the functional groups onto the poly(4-VPy/CrA)–N-oxide are also thought to take part in the adsorption process.
(5) The kinetic studies indicate that the adsorption equilibrium of MB is ~60 min and independent initial dye concentration (25–75 ppm). For all initial concentrations, second-order kinetic model fitted better with high correlation coefficient.
(6) The regeneration of resins without losing its original activity is found at least ten cycles.

References

1. Faria PCC, Orfao JJM, Pereira MFR (2004) Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. Water Res 38:2043–2052
2. Qin Q, Ma J, Liu K (2009) Adsorption of anionic dyes on ammonium-functionalized MCM-41. J Hazard Mater 162:133–139

3. Namasivayam C, Radhika R, Suba S (2001) Uptake of dyes by a promising locally available agricultural solid waste: coir pith. Waste Manage 21:381–387
4. Vadivelan V, Kumar KV (2005) Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. J Colloid Interface Sci 286:90–100
5. Cengiz S, Cavas L (2008) Removal of methylene blue by invasive marine seaweed: *Caulerpa racemosa* var. *cylindracea*. Bioresour Technol 99:2357–2363
6. Bhattacharyya KG, Sharma A (2005) Kinetics and thermodynamics of methylene blue adsorption on neem (*Azadirachta indica*) leaf powder. Dyes Pigment 65:51–59
7. Garg VK, Amita MR (2004) Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste. Dyes Pigment 63:243–250
8. Waranusantigul P, Pokethitiyook P, Kruatrachue M, Upatham ES (2003) Kinetics of basic dye (methylene blue) biosorption by giant duckweed (*Spirodela polyrrhiza*. Env Pollut 125:385–392
9. Xu ZY, Zhang QX, Fang HHP (2003) Applications of porous resin sorbents in industrial wastewater treatment and resource recovery. Crit Rev Env Sci Technol 33(4):363–389
10. Azanova VV, Hradil J (1999) Sorption properties of macroporous and hypercrosslinked copolymers. J React Funct Polym 41:163–175
11. Senkal BF, Yavuz E (2006) Preparation of poly(vinyl pyrrolidone) grafted sulfonamide based polystyrene resin and its use for the removal of dye from water. Polym Adv Technol 17:928–931
12. Gupta VK, Suhas I, Ali V, Saini K (2004) Removal of rhodamine B, fast green, and methylene blue from wastewater using red mud, an aluminum industry waste. Ind Eng Chem Res 43:1740–1747
13. Gupta VK, Jain R, Shrivastava M (2010) Adsorptive removal of cyanosine from wastewater using coconut husks. J Colloid Interface Sci 347:309–314
14. Mall ID, Srivastava VC, Agarwa NK (2006) Removal of orange-G and methyl violet dyes by adsorption onto bagasse fly ash—kinetic study and equilibrium isotherm analyses. Dyes Pigment 69:210–223
15. Mittal A, Mittal J, Malviya A, Gupta VK (2010) Removal and recovery of chrysoidine Y from aqueous solutions by waste materials. J Colloid Interface Sci 344:497–507
16. Barka N, Assabbane A, Nounah A, Laanab L, Ichou YA (2009) Removal of textile dyes from aqueous solutions by natural phosphate as a new adsorbent. Desalination 235:264–275
17. Gupta VK, Jain R, Malath S, Nayak A (2010) Adsorption–desorption studies of indigocarmine from industrial effluents by using deoiled mustard and its comparison with charcoal. J Colloid Interface Sci 348:628–633
18. Sun D, Zhang X, Wu Y, Liu X (2010) Adsorption of anionic dyes from aqueous solution on fly ash. J Hazard Mater 181:335–342
19. Ponnusami V, Kritika V, Madhuram R, Srivastava SN (2007) Biosorption of reactive dye using acid-treated rice husk: factorial design analysis. J Hazard Mater 142:397–403
20. Benguella B, Yacouta-Nour A (2009) Adsorption of bezanyl red and nylomine green from aqueous solutions by natural and acid-activated bentonite. Desalination 235:276–292
21. Gomez V, Larrechi MS, Callao MP (2007) Kinetic and adsorption study of acid dye removal using activated carbon. Chemosphere 69:1151–1158
22. Wang L, Zhang J, Zhao R, Li C, Li Y, Zhang C (2010) Adsorption of basic dyes on activated carbon prepared from *Polygonum orientale* Linn: equilibrium, kinetic and thermodynamic studies. Desalination 254:68–74
23. Cestari AR, Vieira EFS, Tavares AMG, Bruns RE (2008) The removal of the indigo carmine dye from aqueous solutions using cross-linked chitosan—evaluation of adsorption thermodynamics using a full factorial design. J Hazard Mater 153:566–574
24. Bulut Y, Aydın H (2006) A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. Desalination 194:259–267
25. Arslan M, Yiğitoğlu M (2008) Use of methacrylic acid grafted poly(ethylene terephthalate) fibers for the removal of basic dyes from aqueous solutions. J Appl Polym Sci 110:30–38
26. Arslan M, Yiğitoğlu M (2008) Adsorption behavior of Congo red from an aqueous solution on 4-vinyl pyridine grafted poly(ethylene terephthalate) fibers. J Appl Polym Sci 107:2653–2846
27. Şolpan D, Duran S, Torun M (2008) Removal of cationic dyes by poly(acrylamide-co-acrylic acid) hydrogels in aqueous solutions. Radiat Phys chem 77:447–452
28. Üzüm ÖB, Karadağ EJ (2006) Synthetic polymeric absorbent for dye based on chemically crosslinked acrylamide/mesaconic acid hydrogels. J Appl Polym Sci 101:405–413
29. Crini G (2008) Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer. Dyes Pigment 77:415–426

30. Dhodapkar R, Rao NN, Pande SP, Kaul SN (2006) Removal of basic dyes from aqueous medium using a novel polymer: Jalshakti. Bioresour Technol 97:877–885
31. Malik MA, Mukhtar R, Zaidi SAR, Ahmed S, Awan MA (2002) Ion-exchange properties of 4-vinylpyridine-divinylbenzene-based anion exchangers for ferric chloride complex anions. React Funct Polym 51(2–3):117–120
32. Li XG (1999) High-resolution thermogravimetry of poly(4-vinylpyridine-co-divinylbenzene). React Funct Polym 42(1):53–58
33. Wu RSS, Lau TC (1996) Polymer-ligands: a novel chemical device for monitoring heavy metals in the aquatic environment? Pollut Bull 32(5):391–396
34. Beauvais RA, Alexandratos SD (1998) Polymer-supported reagents for the selective complexation of metal ions: an overview. React Funct Polym 36(2):113–123
35. Balakrishnan T, Rajendran V (2000) Polymer supported reagents. III. Kinetic study of synthesizing *n*-octylacetate using insoluble titanium tetrachloride. J Appl Polym Sci 78(12):2075–2080
36. Soykan C, Coşkun R, Delibaş A (2007) Thermodegradation of poly(4-vinylpyridine-*co*-crotonic acid-*co*-divinylbenzene) and N-oxide derivatives. Thermochim Acta 456:152–157
37. Lambert JB, Shurvell HF, Lightner DA, Cooks RG (1998) Organic structural spectroscopy. Prentice-Hall, New Jersey
38. Özkan D, Alkan M, Doğan M (2002) The removal of victoria blue from aqueous solution by adsorption on a low-cost material. Adsorption 8:341–349
39. Liu Y, Wang W, Wang A (2010) Adsorption of lead ions from aqueous solution by using carboxymethyl cellulose-*g*-poly (acrylic acid)/attapulgite hydrogel composites. Desalination 259: 258–264
40. Freundlich HMF (1906) Uber die adsorption in lasungen. Z Phys Chem 57:385
41. Ünlü N, Ersöz M (2006) Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions. J Hazard Mater 136:272–280
42. Kilislioglu A, Bilgin B (2003) Thermodynamic and kinetic investigations of uranium adsorption on amberlite IR-118H resin. Appl Radiat Isot 58:155–160
43. Lagergren S (1898) About the theory of so-called adsorption of soluble substances. K Sven Vetenskapsakad Handl 24:1–39
44. Ho YS, McKay G (1998) Sorption of dye from aqueous solution by peat. Chem Eng J 70:115–124
45. Weber WJ Jr, Morris JC (1962) Removal of biologically-resistant pollutants from waste waters by sorption. Advances in Water Pollution Research, Pergamon Press, New York, pp 231–266
46. Kantipuly G, Katragadda S, Chow A, Gesser HD (1990) Chelating polymers and related supports for separation and preconcentration of trace metals. Talanta 37:491–517