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Adsorptive removal of organic dyes from aqueous solutions using acrylic acid–acrylonitrile–N-isopropylacrylamide polymeric gels as adsorbents: linear and non linear isotherms

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ABSTRACT

The polymeric gels, acrylic acid–acrylonitrile–*N*-isopropylacrylamide with varying contents of *N*-isopropylacrylamide (NS1, NS2, NS3, and NS4), were prepared via free radical polymerization. Adsorption studies of methylene blue and bromophenol blue were carried out on the synthesized gels at 298 and 308 K. Among all the adsorbents, the gel NS4 showed better adsorption percent for the removal of methylene blue from aqueous solutions. This gel was characterized by scanning electron microscopy and Fourier transform infrared spectroscopy before and after adsorption of methylene blue. The equilibrium data were fitted to both linear and nonlinear models in an urge to find the accurate results. It was found that the adsorption of methylene blue on the adsorbent NS4 was well described by the Langmuir adsorption isotherm in both linear and nonlinear analyses. The adsorption capacity calculated from the Langmuir model was 2.79 mg/g for the adsorption of methylene blue dye on the adsorbent NS4. The kinetic data followed pseudo-second-order model revealing that both the internal and external mass transfers were taking place. Keeping in view the higher value of adsorption capacity, it is suggested that the synthesized adsorbent NS4 can be effectively used for the removal of methylene blue dye from aqueous solutions.

Keywords: Adsorption; Polymeric gels; Langmuir model; Adsorption kinetics; Double exponential model

1. Introduction

In the recent years, the water bodies polluted with organic dyes is a global environmental problem. Triphenyl methane dyes such as methylene blue and bromophenol blue are most frequently used dyes in various industries such as paper, food, textile, leather, pulp mills, and plastics [1–3]. In addition to their industrial applications, they also have a number of dangerous effects. These dyes are carcinogenic in nature [4]. The eyes of terrestrial and aquatic animals are affected by their contact to methylene blue. Irritation to skin and gastrointestinal tract [5] is also caused by the exposure to this dye. Methylene blue has also been noticed to cause serious toxicity in central nervous system [6]. Bromophenol blue can originate mutagenic [7] and heterogenic effects in human beings [8]. Many industries discharge their sewage into the nearby streams, rivers, and lakes without paying their attention to its effect on living bodies [9]. There are

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more than 100,000 commercially available dyes and ca. 800,000 tons per year enter into the environment as waste material. These dyes give color to the water bodies due to which the sunlight becomes unable to go through the lower layers; thus, the process of photosynthesis is affected. Sometimes, these dyes are changed into poisonous intermediates which can damage the aquatic life even when these are present in very low concentration [8]. Hence, management of effluent containing these dyes is of much importance to circumvent their hazardous effects. Several physical and chemical methods have been used for the exclusion of such colored effluent from water. These are coagulation [10], reverse osmosis [11], photodegradation [12], electrochemical oxidation [13], ozonation [14], and adsorption [15], etc. Adsorption is, however, more convenient among all these methods because of its low cost, simple design, and easy operation [16]. The most commonly used adsorbent for the removal of dyes is the activated carbon but it is costly [17,18]. Many researchers have attempted to replace carbon adsorbents with some other adsorbents such as sepiolite [19], bagasse fly ash [20], diatomite [21], sludge ash [22], rice husk [23], silica [24], sawdust [17] hen feathers [25], and polymeric gels [5]. The polymeric gels have gained much attention in the field of biomedicine [26] and super adsorbents [27].

In the present investigations, three novel polymeric gel adsorbents (NS2, NS3, and NS4) have been tried for the elimination of methylene blue and bromophenol blue from the aqueous solutions. Fit of linear isotherm and kinetic models to the experimental data commonly reported in the literature has been criticized (because of transformation of the original equations) for its less accuracy. In the present work, the adsorption data have been subjected to both linear and nonlinear analyses to obtain reliable results.

2. Experimental

2.1. Materials

In this study, acrylic acid (99%, Fluka), N-isopropylacrylamide (97%. Aldrich), acrylonitrile (99%, DAE Jung), ethyl alcohol (99.8%, BDH), benzoyl peroxide (100%, merck), diethyleneglycoldimethacrylate (100%, Aldrich), bromophenol blue (98%, Sigma Aldrich), and methylene blue (99%, Merck) were used.

2.2. Synthesis of acrylic acid–acrylonitrile–N-isopropylacrylamide (AA-AN-NIPAAm) gels

The AA-AN-NIPAAm gels were synthesized by free radical polymerization process. Two monomers acrylic acid and acrylonitrile were mixed in equal volume ratio with various NIPAAm contents (0.25, 0.50, 0.75, and 1.0 g for NS1, NS2, NS3, and NS4 polymeric gels, respectively). Ethyl alcohol (100% v/v of monomers volume), diethyleneglycoldimethacrylate (1.5 mL), and benzoyl peroxide (1.0% w/v) were added as solvent, cross-linking agent, and initiator, respectively. The contents of the tube were mixed thoroughly and nitrogen gas was bubbled through the reaction mixture to avoid the possible interference of oxygen. The screw-capped tubes were placed in the water bath. The polymerization reaction was carried out by following slow heating scheme to prepare the uniform polymeric column. The temperature of the reaction mixture was raised gradually, and for each 5 K rise, the temperature was maintained constant for at least one hour up to 343 K. The polymeric column started to build up at this temperature and the reaction mixture was kept at the same temperature for 24 h to ensure the completion of polymerization reaction. The smooth columns of the gels were removed from the tube, washed with ethanol then with deionized water to remove un-reacted materials. The gels were then dried at the room temperature for 24 h. The columns of the gels were then cut into the disks and saved for further investigations.

2.3. Adsorption studies

In the present work, the synthesized polymeric gels (NS2, NS3, and NS4) were used as adsorbents and methylene blue and bromophenol blue dyes as adsorbates. Dyes solutions of various concentrations (2.0–12.0 mg/L) were prepared by diluting their 100 ppm stock solutions with deionized water. The experiment was conducted at optimized pH (7.0) and at two temperatures, i.e. 298 and 308 K. In a typical experiment, 0.05 g of the adsorbent was added in 25-ml conical flask already containing 10 ml of the dye solution of known concentration. The solution was shaken in a thermostat shaker for optimized time (50 min) at the rate of 120 strokes/min. Afterward, the residues were separated and the solutions were analyzed for dye concentration using UV/visible spectrophotometer (Biochrome-52,000). The absorbance data were recorded for each dye solution at their respective λ_{max}. The amount of dye adsorbed (q_e) was calculated using the absorbance data.

2.4. Optimization of pH

Fig. 1 displays the effect of pH on the adsorption of methylene blue on the gel NS4 at 298 K. It can be

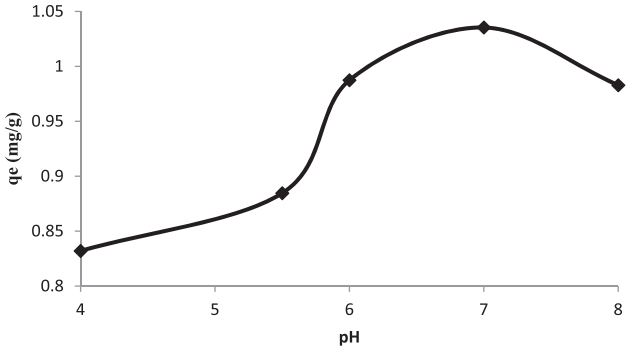

Fig. 1. Effect of pH on the adsorption of methylene blue on the NS4 gel at 298 K.

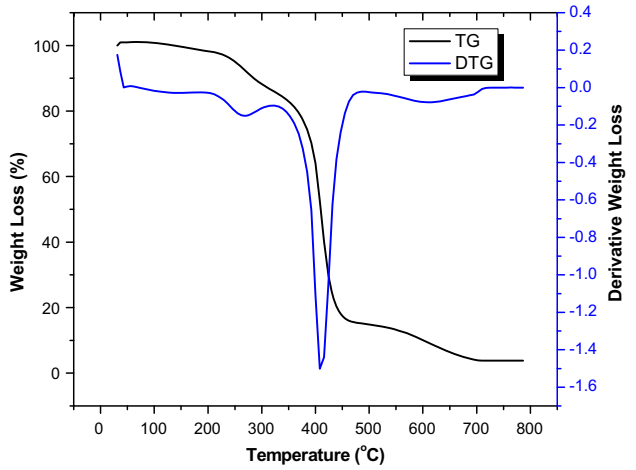

Fig. 2. TG/DTG pattern of the synthesized polymer NS4 at heating rate of 10°C/min.

seen from the figure that the adsorption of methylene blue on NS4 adsorbent rises as the pH of the solution increases from 4.0 to 7.0, while at higher pH (8.0), it slightly decreases. Therefore, the neutral pH (7.0) was chosen for further experiments of the adsorption process.

2.5. Thermogravimetric (TG) analysis

Thermogravimetric analysis of the synthesized hydrogel (NS4) at heating rate of 10°C/min was carried out using Universal 4.2E TA Instruments.

2.6. Scanning electron microscopy

A scanning electron microscope JEOL-JSM-6700F was used to envisage the surface of the synthesized adsorbent before and after adsorption of the dye.

2.7. Fourier transform infrared spectroscopy

To study the interaction between adsorbate and adsorbent, the FTIR spectra of the gel NS4 before and after adsorption of methylene blue dye were recorded using FTIR spectrometer NICOLET 6700 thermoscientific USA.

3. Results and discussion

3.1. Thermal analysis

The TG curve of the synthesized hydrogel NS4 at the heating rate of 10°C/min is displayed in Fig. 2. It shows the degradation of the synthesized polymer in three distinct steps. The first step of degradation occurs in the temperature range of 203.961–358.91°C with the weight loss of 14.30%. The peak temperature (T_P) of this step is 260°C which is close to that for degradation of DEGDMA (T_P = 240.24°C); hence, it may be assumed that the weight loss of this step is due to the evaporation of DEGDMA. The 2nd step (358.91–454.63°C) with maximum weight loss of 69.19% may be related to the burning of carbonaceous material of the polymer. The third drop in weight (14.76%) occurring in temperature range of 454.63–710.198°C may correspond to the breakdown of the polymer side chains.

3.2. SEM analysis

Scanning electron micrographs of adsorbent NS4 before and after adsorption of methylene blue are displayed in Fig. S1 (provided in supplementary material). It can be seen from the figure that the adsorbent surface is rough and porous before adsorption (Fig. S1a). These pores are filled by the adsorbate molecules and surface becomes smooth after adsorption (Fig. S1b) which confirms the adsorption of the dye on the adsorbent NS4.

3.3. FTIR analysis

Fig. S2a (given in supplementary materials) presents the FTIR spectrum of the synthesized gel NS4 before adsorption of methylene blue. In this figure, a broad band at 3,410 cm^{-1} may be related to the stretching vibrations of hydrogen bonded –OH of acrylic acid. The peak at 2,964 cm^{-1} may be attributed to the methylene (CH_2=) C–H asymmetric stretching vibrations of vinyl group present in all the monomers used for the synthesis. The band at 2,243 cm^{-1} may be ascribed to the nitrile group (–C=N) of acrylonitrile.

The carbonyl group (=C=O) present in the monomers is located in the polymer at 1,732 cm^{-1}. The amide group (–NH–) of *N*-isopropylacrylamide and C–H bending vibrations of methylene (CH_2=) in vinyl group are observed at 1,616 and 1,448 cm^{-1}, respectively. The peaks at 1,392 and 1,174 cm^{-1} may correspond to iso-dimethyl (isopropyl) group in *N*-isopropylacrylamide and C–C skeletal vibrations, respectively. The bending vibrations (out of plane) of –OH of ethanol are registered at 613 cm^{-1} in the synthesized gel [28].

After the adsorption of methylene blue on the polymeric gel NS4 (Fig. S2b, given in supplementary material), the shifts of frequencies from 3,410 to 3,417 cm^{-1}, 2,964 to 2,968 cm^{-1}, 2,243 to 2,237 cm^{-1}, 1,732 to 1,728 cm^{-1}, 1,392 to 1,386 cm^{-1}, and 1,174 to 1,165 cm^{-1} are observed which is indicative of interaction (though weak) of adsorbate molecules with the adsorbent.

3.4. Percent (%) removal of the dyes

Removal efficiency of the adsorbent was calculated in terms of % removal (Eq. (1)) of the dyes from aqueous solutions under the given experimental conditions:

$$\text{Removal}\,\% = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

Here, C_i is the initial concentration (mg/L) of the dye and C_e is the equilibrium concentration (mg/L). The obtained % age removal of methylene blue and bromophenol blue dyes on all the adsorbents at both the temperatures studied are tabulated in Tables 1 and 2, respectively.

It is clear from the tables that the synthesized polymeric gels provide better removal efficiency for methylene blue than that of bromophenol blue at 298 K. By increasing the temperature (308 K), the removal percent decreases in both the cases. Among all the adsorbents, the polymeric gel having higher contents of NIPAAm (NS4) shows better adsorption in case of methylene blue and hence is discussed here in detail. Greater porosity of the gel NS4 may be responsible for the higher adsorption of methylene blue on this gel as compared to the other adsorbents.

3.5. Kinetic studies

To evaluate the kinetic order of the adsorption process, the data were subjected to pseudo-first- and pseudo-second-order model in linear analysis and modified second-order and double exponential model in nonlinear analysis. Better value of R^2 and comparable values of experimental and calculated q_e (Table 3) suggest pseudo-second-order kinetic model to be more suitable to elucidate the adsorption data. Therefore, it is thought that both the internal and external mass transfer are likely to occur during the adsorption process [5,29]. The pseudo-second-order plot for the adsorption of methylene blue on the adsorbent NS4 at 298 K is represented in Fig. 3.

The nonlinear analysis yields minimum χ^2 value for double exponential model to explain the kinetic data of the adsorption process. Fit of the experimental data to modified second-order and double exponential kinetic models is depicted in Fig. 4, and the parameters calculated from these models are listed in Table 3.

The parameters *D*1 and *D*2 obtained from double exponential model are utilized to calculate the rapid (RF) and slow (SF) adsorbed fractions using Eqs. (2) and (3), respectively:

$$\text{RF}\,\% = 100\left[\frac{D1}{D1 + D2}\right] \quad (2)$$

$$\text{SF}\,\% = 100\left[\frac{D2}{D1 + D2}\right] \quad (3)$$

Table 1
Percent (%) removal of methylene blue on the NS2, NS3, and NS4 adsorbents at 298 and 308 K

	298 K			308 K		
Conc. range (mg/L)	NS2	NS3	NS4	NS2	NS3	NS4
2.0	81.30 ± 0.13	88.30 ± 0.83	93.90 ± 0.09	92.60 ± 0.82	90.50 ± 0.54	91.60 ± 0.45
4.0	89.30 ± 0.75	88.00 ± 0.59	93.40 ± 0.36	91.90 ± 0.87	90.70 ± 0.23	87.60 ± 0.65
6.0	88.70 ± 0.37	85.40 ± 0.48	91.60 ± 0.1	90.60 ± 0.08	87.70 ± 0.24	87.00 ± 0.34
8.0	88.20 ± 225	86.90 ± 0.82	90.80 ± 0.09	91.40 ± 0.30	88.40 ± 0.45	84.70 ± 0.10
10.0	80.40 ± 0.85	78.70 ± 0.74	88.40 ± 0.16	82.60 ± 0.05	78.00 ± 0.54	97.40 ± 0.25
12.0	77.20 ± 0.82	78.70 ± 0.51	85.60 ± 0.59	85.20 ± 0.25	82.00 ± 0.08	76.80 ± 0.35

Table 2
Percent (%) removal of bromophenol blue on the NS2, NS3, and NS4 adsorbents at 298 and 308 K

	298 K			308 K		
Conc. range (mg/L)	NS2	NS3	NS4	NS2	NS3	NS4
2.0	92.90 ± 0.51	88.70 ± 0.44	83.80 ± 0.57	71.65 ± 0.24	58.20 ± 0.76	60.60 ± 0.72
4.0	91.80 ± 0.19	84.90 ± 0.08	76.80 ± 0.66	70.20 ± 0.02	52.10 ± 0.92	58.80 ± 0.35
6.0	93.00 ± 0.54	90.30 ± 0.10	72.70 ± 0.99	61.00 ± 0.79	53.20 ± 0.84	50.50 ± 0.67
8.0	75.30 ± 0.53	73.20 ± 0.87	66.30 ± 0.47	57.50 ± 0.45	48.30 ± 0.66	46.40 ± 0.65
10.0	74.00 ± 0.31	72.90 ± 0.40	57.50 ± 0.35	50.70 ± 0.01	41.40 ± 0.737	44.60 ± 0.23
12.0	65.00 ± 0.30	62.60 ± 0.36	50.25 ± 0.44	49.10 ± 0.38	37.44 ± 0.77	40.30 ± 0.68

Table 3
Linear and Nonlinear kinetic models and their parameters calculated for the adsorption of methylene blue on the adsorbent NS4 at 298 K

Analysis	Models and mathematical forms	Parameters
Linear	Pseudo-first-order: $\ln(q_e - q_t) = \ln q_e - k_1 t$	R^2 value = 0.95 Exp. q_e (mg/g) = 0.73 Calc. q_e(mg/g) = 1.431 k_1 = 0.099 min^{-1}
	Pseudo-second-order: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	R^2 value = 0.99 Exp. q_e (mg/g) = 0.73 Calc. q_e (mg/g) = 1.123 k_2 = 0.035 g/mg/min
Non Linear	Double exponential model: $q_t = q_e - \left(\frac{D_1}{m_{ads}}\right)^{(-K_{D1}t)} - \left(\frac{D_2}{m_{ads}}\right)^{(-K_{D2}t)}$	$D1$ = 1.723 $D2$ = 0.1466 $KD1$ =0.0070 $KD2$ = 0.0075 m = 0.0.006 χ^2 = 0.00058 RF (%) = 92.15 SF (%) = 7.84
	Modified second-order: $q_t = q_e\left[1 - \frac{1}{\beta_2 + k_2 t}\right]$	k_2 = 0.1303 β = 0.5619 χ^2 = 0.027

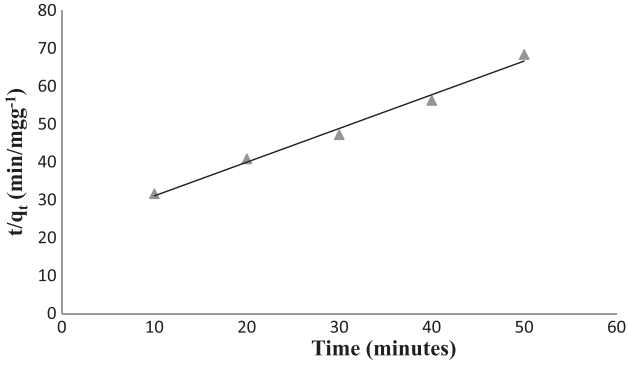

Fig. 3. Plot of pseudo-second-order model for adsorption of methylene blue on NS4 at 298 K.

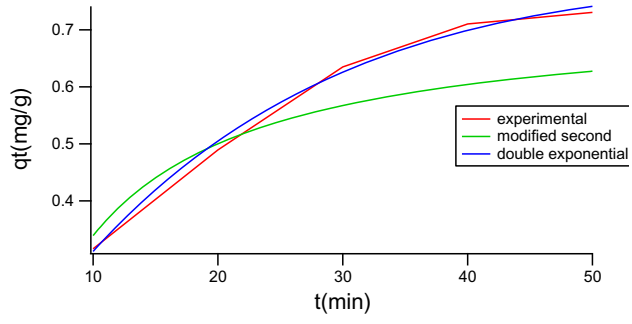

Fig. 4. Nonlinear kinetic models for the adsorption of methylene blue on NS4 at 298 K.

It is evident from Table 3 that the rapid adsorbed fraction of methylene blue on the adsorbent NS4 at 298 K is greater than the slower adsorbed fraction.

The value of β in modified second-order model gives information about the impurities adsorbed on the adsorbent. It is assumed that the value of β should be greater than one if impurities are adsorbed during the adsorption process. In the present work, the value of β is less than 1, thereby indicating no pre experimental adsorption.

3.6. Equilibrium adsorption isotherms

In this study, the results of adsorption experiments were analyzed by one parameter isotherm; Henry, two parameters isotherm; Henry, Langmuir, Freundlich, Dubinin–Radushkevich, three parameters isotherms; Redlich–Peterson, Toth, Sips, Hill, Khan, four parameters isotherm; Fritz–Schulnder model and five parameters isotherm; Frotz–Sch model.

Scrutiny of the experimental data by linear regression method (usually used because of its simplicity) may produce inaccurate results owing to the use of transformed equations [30]. Hence, it is strategic to examine the data by both the linear and nonlinear regression analysis. The choice of better fit adsorption model was made on the basis of maximum value of R^2 in linear and minimum value of χ^2 in nonlinear [31] analysis. The mathematical forms (linear and nonlinear) of all the adsorption isotherms used in this study have already been reported in the literature [32].

For convenience, linear Langmuir isotherm and the plots of all the nonlinear adsorption models for the adsorption of methylene blue on the adsorbent NS4 at 298 K are presented in Figs. 5 and 6, respectively.

Adsorption parameters calculated from the models are tabulated in Table 4.

It is evident from Table 4 that among two parameters isotherm, Langmuir isotherm models better describe the adsorption data of methylene blue on the adsorbent at 298 K. The adsorption capacity (q_m) gives the amount of adsorbate adsorbed per gram of adsorbent and is calculated from Langmuir model. The value of q_m obtained for methylene blue on the adsorbent NS4 is 2.79 mg/g. This value of q_m is higher than many of adsorption capacities of methylene blue on various adsorbents already reported [5].

Another important characteristic of this model is dimensionless separation factor R_L which can be defined by the following equation (Eq. (4)):

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

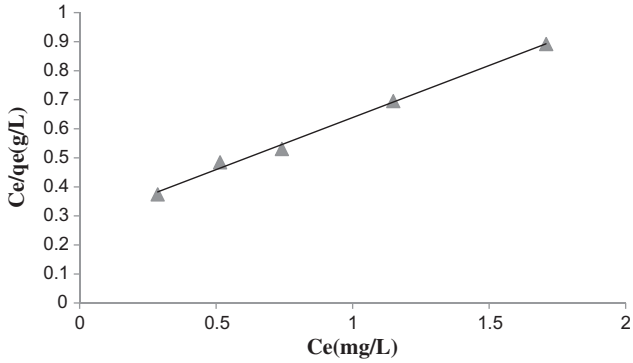

Fig. 5. Langmuir isotherm for adsorption of methylene blue on the adsorbent NS4 at 298 K.

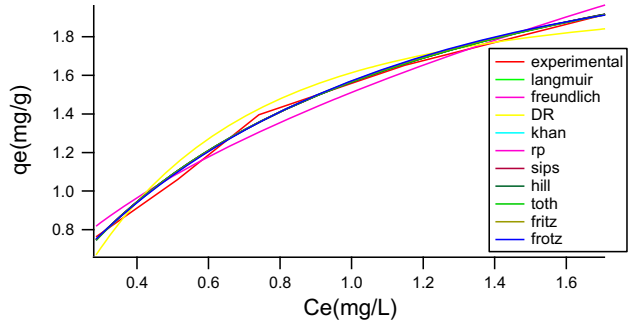

Fig. 6. Nonlinear isotherms for the adsorption of methylene blue on NS4 at 298 K.

The value of this factor calculated from the above equation determines favorability of the adsorption process. It has been suggested [5] that if the value of $R_L = 1$, the process is linear, and for $0 > R_L < 1$, the adsorption process is favorable. The value of R_L greater than 1 shows that the process is unfavorable. When $R_L = 0$, the process is irreversible. The magnitude of R_L obtained in this study is less 1 and greater than zero which indicates that the adsorption of methylene blue on the adsorbent NS4 is favorable. The value of $n > 1$ obtained from Freundlich model also endorses the favorability of the adsorption process [29].

It is apparent from Table 4 that among the three parameters isotherms, Redlich–Peterson model is more favored for the adsorption process. It has been reported [32] that the value of g in this model should be between zero and 1. The value of g near to unity supports the applicability of Langmuir isotherm, and its value close to zero favors the suitability of Freundlich isotherm model to the adsorption data. In the present work, the value of g obtained from RP model is more close to unity than zero, thus advocating the argument in favor of Langmuir isotherm model.

Table 4
Results obtained from the linear and nonlinear analysis of adsorption of methylene blue on NS4 adsorbent at 298 K

	Isotherm models	Parameters	Linear method	Nonlinear method
2	Freundlich	K_f (mg/g)	1.5	1.5113 ± 0.0347
		n	1.912046	2.0435 ± 0.178
		R^2	0.9835	–
		χ^2	–	0.015
2	Langmuir	K_L	3.5688	1.2727 ± 0.119
		q_m (mg/g)	2.790179	2.7968 ± 0.118
		R^2	0.9956	–
		χ^2	–	0.0039
2	Dubinin–Rudeshkevich	K_{DR}	7.00e-08	3.866e-007 ± 4.62e-008
		q_s	2	2.0446 ± 0.0914
		E (kJ/mol)	2.672	
		R^2	0.9661	–
		χ^2	–	0.024
3	Redlich–Peterson	K_R	3.9	3.5537 ± 0.83
		a_R	1.5	1.2688 ± 0.555
		g	0.922	1.0015 ± 0.214
		R^2	0.9922	–
		χ^2	–	0.0039
3	Sips	K_S	1.943	3.4879 ± 0.966
		a_s	1.3	1.2291 ± 0.589
		β_S	0.523	0.9845 ± 0.204
		R^2	0.9835	–
		χ^2	–	0.0039
3	Hill	K_D	1.08	0.81365 ± 0.39
		q_{sH}	2.83	2.8378 ± 0.576
		nH	0.7604	0.98446 ± 0.204
		R^2	0.9345	–
		χ^2	–	0.0039

The mean sorption energy is calculated by DR model which is less than 8.0 kJ/mol indicating the physical nature of the adsorption of methylene blue dye on the adsorbent NS4.

4. Conclusions

Among the adsorbents tested, the NS4 gel proved better adsorbent for the exclusion of methylene blue dye from aqueous solution. SEM pictures confirm the occurrence of the process of adsorption of methylene blue dye on the adsorbent NS4. Langmuir model gave better fit for the adsorption of methylene blue on the NS4 gel indicating homogenous surface of the adsorbent. Outcomes of the linear regression analysis agreed well with nonlinear analysis showing reliability of the adsorption data. Adsorption of methylene blue on the gel NS4 followed pseudo-second-order kinetic model. Fit of double exponential model indicated that the rapid adsorbed fraction of methylene blue on the adsorbent NS4 was much higher than the slow adsorbed fraction.

Supplementary material

The supplementary material for this paper is available online at http://dx.doi.10.1080/19443994.2015.1132393.

References

[1] M. Zhao, P. Liu, Adsorption behavior of methylene blue on halloysite nanotubes, Microporous Mesoporous Mater. 112 (2008) 419–424.

[2] M. Zhao, P. Liu, Removal of basic dye (methylene blue) from wastewaters utilizing beer brewery waste, J. Hazard. Mater. 154 (2008) 73–78.
[3] M. Zhao, P. Liu, Batch removal of malachite green from aqueous solutions by adsorption on oil palm trunk fibre: Equillibrium isotherms and kinetic studies, J. Hazard. Mater. 154 (2008) 237–244.
[4] G. McKay, M.S. Otterburn, J.A. Aga, Fuller's earth and fired clay as adsorbents for dyestuffs, Water Air and Soil Pollut. 24 (1985) 307–322.
[5] M.A. Malana, S. Ijaz, M.N. Ashiq, Removal of various dyes from aqueous media onto polymeric gels by adsorption process: Their kinetics and thermodynamics, Desalination 263 (2010) 249–257.
[6] P.K. Gillman, CNS toxicity involving methylene blue: The exemplar for understanding and predicting drug interactions that precipitate serotonin toxicity, J. Psychopharmacol. 25 (2011) 429–436.
[7] G.H. Lin, D.J. Brusick, Mutagenicity studies on two triphenylmethane dyes, bromophenol blue and tetrabromophenol blue, J. Appl. Toxicol. 12 (1992) 267–274.
[8] N. Daneshvar, M. Ayazloo, A.R. Khataee, M. Pourhassan, Biological decolorization of dye solution containing Malachite Green by microalgae *Cosmarium* sp. Bioresour. Technol. 98 (2007) 1176–1182.
[9] C.M. Kao, M.S. Chou, W.L. Fang, B.W. Liu, B.R. Huang, Regulating colored textile wastewater by 3/31 wavelength admi methods in Taiwan, Chemosphere 44 (2001) 1055–1063.
[10] O. Tunay, I. Kabdasli, G. Eremektar, D. Orhon, Color removal from textile wastewaters, Water Sci. Technol. 34 (1996) 9–16.
[11] E. Forgacs, T. Cserháti, G. Oros, Removal of synthetic dyes from wastewaters: A review, Environ. Int. 30 (2004) 953–971.
[12] K. Wu, Y. Xie, J. Zhao, H. Hidaka, Photo-Fenton degradation of a dye under visible light irradiation, J. Mol. Catal. A: Chem. 144 (1999) 77–84.
[13] E. Kusvuran, O. Gulnaz, S. Irmak, O.M. Atanur, H.I. Yavuz, O. Erbatur, Comparison of several advanced oxidation processes for the decolorization of Reactive Red 120 azo dye in aqueous solution, J. Hazard. Mater. 109 (2004) 85–93.
[14] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative, Bioresour. Technol. 77 (2001) 247–255.
[15] J. Mittal, D. Jhare, H. Vardhan, A. Mittal, Utilization of bottom ash as a low-cost sorbent for the removal and recovery of a toxic halogen containing dye eosin yellow, Desalin. Water Treat. 52 (2014) 4508–4519.
[16] G. Annadurai, M. Chellapandian, M.R.V. Krishnan, Adsorption of reactive dye on chitin, Environ. Monit. Assess. 59 (1999) 111–119.
[17] F.A. Batzias, D.K. Sidiras, Dye adsorption by prehydrolysed beech sawdust in batch and fixed-bed systems, Bioresour. Technol. 98 (2007) 1208–1217.
[18] M. Dogan, Y. Ozdemir, M. Alkan, Adsorption kinetics and mechanism of cationic methyl violet methylene blue dyes onto sepiolite, Dyes Pigm. 75 (2007) 701–713.
[19] M. Alkan, Ö. Demirbaş, S. Çelikçapa, M. Doğan, Sorption of acid red 57 from aqueous solution onto sepiolite, J. Hazard. Mater. 116 (2004) 135–145.
[20] I. Deo, V. Mall, C. Sivastava, N.K. Agawal, I.M. Misha, Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses, J. Colloids Surf. A: Physicochem. Eng. Aspect 264 (2005) 17–28.
[21] M. Al-Ghouti, M.A.M. Khraisheh, M.N.M. Ahmad, S. Allen, Thermodynamic behaviour and the effect of temperature on the removal of dyes from aqueous solution using modified diatomite: A kinetic study, J. Colloid Interface Sci. 287 (2005) 6–13.
[22] C.H. Weng, Y.F. Pan, Adsorption characteristics of methylene blue from aqueous solution by sludge ash, Colloids Surf., A: Physicochem. Eng. Aspects 274 (2006) 154–162.
[23] V.K. Gupta, A. Mittal, R. Jain, M. Mathur, S. Sikarwar, Adsorption of Safranin-T from wastewater using waste materials- activated carbon and activated rice husks, J. Colloid Interface Sci. 303 (2006) 80–86.
[24] W.T. Tsai, K.J. Hsien, J.M. Yang, Silica adsorbent prepared from spent diatomaceous earth and its application to removal of dye from aqueous solution, J. Colloid Interface Sci. 275 (2004) 428–433.
[25] J. Mittal, A. Mittal, Green Chemistry for Dyes Removal from Wastewater, Scrivener Publishing LLC, USA, 2015, pp. 409–457.
[26] J. Filipovik, M.K. Krusic, Copolymer gels based on *N*-isopropylacrylamide and itaconic acid, Polymer 47 (2006) 148–155.
[27] S. Jin, M. Liu, F. Zhang, S. Chen, A. Niu, Synthesis and characterization of pH-sensitivity semi-IPN hydrogel based on hydrogen bond between poly(N-vinylpyrrolidone) and poly(acrylic acid), Polymer 47 (2006) 1526–1532.
[28] J. Coates, Interpretation of Infrared Spectra, A Practical Approach, John Wiley & Sons Ltd, Chichester, 2000.
[29] M.A. Malana, R.B. Qureshi, M.N. Ashiq, Adsorption studies of arsenic on nano aluminium doped manganese copper ferrite polymer (MA, VA, AA) composite: Kinetics and mechanism, Chem. Eng. J. 172 (2011) 721–727.
[30] Y. Ho, W. Chiu, C. Wang, Regression analysis for the sorption isotherms of basic dyes on sugarcane dust, Bioresour. Technol. 96 (2005) 1285–1291.
[31] D. Schimmel, K.C. Fagnani1, J.B. Oliveira, D. Santos, M.A.S.D. Barros, E.A.D. Silva, Adsorption of turquoise blue QG reactive bye commercial activated carbon in batch reactor: Kinetic and equilibrium studies, Braz. J. Chem. Eng. 27 (2010) 289–298.
[32] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, Chem. Eng. J. 156 (2010) 2–10.