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Adsorptive removal of methylene blue from aqueous solution by polyaniline-nickel ferrite nanocomposite: a kinetic approach

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ABSTRACT

This work deals with the development of a new efficient method for the removal of methylene blue dye from aqueous solutions by using polyaniline (PANI)–nickel ferrite ($NiFe_2O_4$) nanocomposite. It is successfully synthesised *in situ* through self-polymerisation of monomer aniline. Adsorptive removal studies are carried out for water-soluble methylene blue dye using PANI–nickel ferrite nanocomposite in aqueous solutions. Different parameters such as dose of adsorbent, contact time, different initial concentrations and pH have been observed to optimise reaction condition. It is observed that the adsorptive removal by PANI–nickel ferrite nanocomposite is good comparable with other method for removing methylene blue dye from aqueous solutions. The optimum conditions for the removal of the dye are initial concentration 40 mg/L, adsorbent dose 8 g/L and pH 9. The adsorption capacity is found to be 6.65 mg/g. The adsorption followed pseudo-second-order kinetics. The experimental isotherm is analysed with Freundlich and Langmuir equations. Desorption experiment was performed for recycle and reused study of nanocomposite. The characterisation of prepared adsorbent has been done by techniques such as SEM, XRD and EDS.

Keywords: Adsorptive removal; Methylene blue dye; PANI–$NiFe_2O_4$ nanocomposite; SEM; XRD

1. Introduction

Textile dyeing and printing industries produce large amounts of coloured wastewater. It is found that nearly 1–15% of the dye is lost and released into wastewater from textile industries [1]. The presence of dyes in water is not favourable since even a very small concentration of these dyes are highly visible and may be toxic to aquatic environments [2]. Wastewater-containing dyes are very difficult to treat since the dyes are disobedient molecules and are resistant to aerobic digestion. It is very difficult to treat wastewater containing even low concentrations of dye molecules [3].

Adsorption is an affordable and effective technique for the removal of dyes and coloured pollutants from wastewater [4]. Many low-cost adsorbent materials have been proposed and studied for their ability to remove dyes [5–12]. Nanosized magnetic iron oxide particles have a wide range of applications in ferrofluids, high-density information storage and magnetic resonance imaging. Biological cell labelling and storing, separation of bio-chemicals targeting and drug delivery [13]. Fast removal and recovery of Congo red

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by modified iron oxide magnetic nanoparticles [14]. Also, the adsorption of methylene blue from aqueous solutions using Fe_3O_4/bentonite nanocomposite [15]. Mostly photocatalytic degradation method has been used for degradation of carcinogenic textile dyes [16,17].

The present investigation reports on a new, simple and faster method for the removal and recovery of methylene blue using PANI–$NiFe_2O_4$ nanocomposite as an adsorbent. It can be compared with other methods of removal such as methylene blue adsorption from aqueous solutions to carbon nanotubes [18]. In this report, PANI/$NiFe_2O_4$ is easily recovered as it is magnetic and reused, but carbon nanotube does not easily recovered and reused. The main objective of the present work is to solve the problem of dyes from industry which causes wastewater pollution.

2. Experimental

2.1. Materials and methods

Methylene blue (as shown in Fig. 1), $NiCl_2.6H_2O$, $FeCl_3.6H_2O$, monomer aniline, distilled water, ammonium persulphate $(NH_4)_2S_2O_8$. The water-soluble methylene blue dye which has M.F. $\mathbf{C_{16}H_{18}N_3SCl}$, M.W. **319.85 g**/mole, M.P. **105˚C** and PANI–$NiFe_2O_4$ is used as an adsorbent. All chemicals and reagents were of analytical grade purity. The structure of dye presented in Fig. 1. The stock solution 100 mg/L of dye was prepared in double-distilled water. In 100 ml of dye solution of the desired concentration of different adsorbent doses is added and stirred with magnetic stirrer. At specific time interval, suitable aliquot of the sample is withdrawn and analysed after centrifugation. The changes of dye concentration are determined by UV–Visible double beam spectrophotometer (systronics model-2203) at λ max 665 nm in our laboratory.

2.2. Preparation of PANI–$NiFe_2O_4$ nanocomposite

2.2.1. Synthesis of $NiFe_2O_4$ nanoparticles

$NiFe_2O_4$ nanoparticles were synthesised according to the following procedures: 1.0 g of nickel chloride ($NiCl_2.6H_2O$) (5 mmol) in 5 ml of deionised water and 1.63 g of ferric chloride ($FeCl_3.6H_2O$) (6 mmol) in 5 ml of deionised water were mixed at room temperature. The above mixture was dropped into 200 ml aqueous ammonia solution (0.6 M) in 20 min with vigorous stirring. The pH values of the reaction mixture were kept in the range of 11–12 with the addition of a concentrated ammonium hydroxide solution. The resulting nanoparticles were separated by centrifugation at 2,800 rpm for 10 min. The product was washed with distilled water three times and then further washed with ethanol (C_2H_5OH) three times and dried in oven.

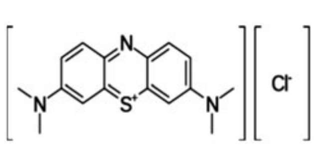

Fig. 1. Structure of methylene blue dye.

2.2.2. Synthesis of PANI–$NiFe_2O_4$ nanocomposite

PANI–$NiFe_2O_4$ nanocomposite was synthesised via self-assembly method using ammonium persulphate (APS) as an oxidant without the addition of organic surfactant. The synthesis process is as followed: 0.64 mol/L aniline monomer into polymerisation vessel containing 1 g $NiFe_2O_4$ in 100 ml of 1.14 mol/L H_2SO_4 acid solution at room temperature and magnetic stirring for 8 h. Then, 50 ml (1 M) of ammonium persulphate $(NH_4)_2S_2O_8$ was added to the above mixture reaction. Resulting precipitate was collected by filtration and then washed with deionised water and methanol three times, respectively. The product was dried in oven at 70˚**C** for 24 H to obtain green–black powder of PANI–$NiFe_2O_4$ nanocomposite [19,20].

3. Results and discussion

3.1. SEM analysis

Scanning electron microscopy is widely used to study the morphological features and surface characteristics of adsorbent materials. The PANI–$NiFe_2O_4$ nanocomposite is analysed by SEM before adsorption of methylene blue dye as shown in Fig. 2(a) and after adsorption as shown in Fig. 2(b). It shows SEM micrographs of PANI–$NiFe_2O_4$. Fig. 2(a) shows surface texture and porosity on PANI–$NiFe_2O_4$. It has heterogeneous surface, micropores and mesopores as seen from its surface micrographs. Fig. 2(b) shows adsorption of methylene blue dye on PANI–$NiFe_2O_4$ surface. It shows dark greyish colour PANI surface which is covered on whitish surface of $NiFe_2O_4$. Some whitish spot of $NiFe_2O_4$ is shown in Fig. 2(a).

3.2. XRD analysis

The XRD diagram of PANI–$NiFe_2O_4$ is shown in Fig. 3(a). It shows match scan with JCPDS-PDF-NO: 00-044-1485, as shown in Table 1.

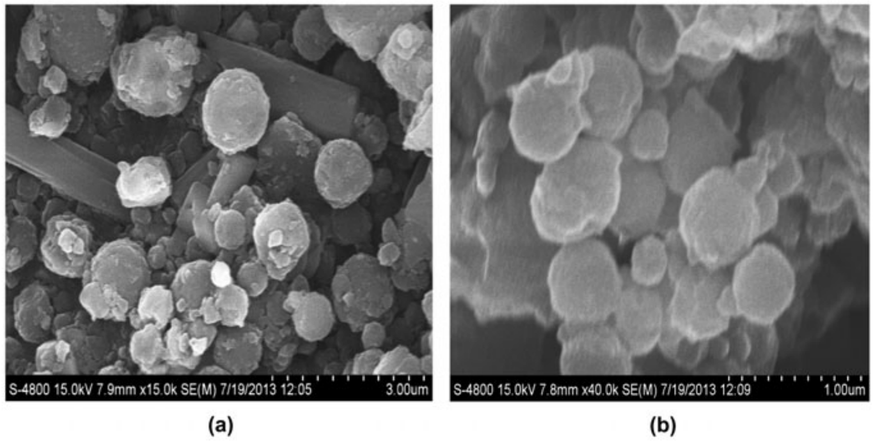

Fig. 2. (a) SEM images of prepared PANI–$NiFe_2O_4$ nanocomposite before adsorption; (b) SEM image of PANI–$NiFe_2O_4$ nanocomposite after adsorption of dye.

The high intensity of peaks indicates the crystalline nature of PANI–$NiFe_2O_4$. The average particle size of PANI–$NiFe_2O_4$ is estimated by Scherrer formula is 15 nm. Some noise in graph is found due to amorphous nature of polyaniline (PANI) [20].

3.3. EDS analysis

EDS (energy dispersive X-ray spectroscopy) has been used to find the chemical composition of materials down to a spot size of a few nanometres and to create element composition maps over a much broader raster area. Together, these capabilities provide fundamental compositional information for a wide variety of materials. From the analysis, it is known that PANI–$NiFe_2O_4$ nanocomposite consists of an exact elemental composition of specific elements such as Ni-1.25%, Fe-2.55%, O-22.02%, C-57.19, N-15.63%, etc. as shown in the Fig. 3(b). As PANI–$NiFe_2O_4$ is a conducting material, therefore, it needs to coat with gold (Au-1.46%) metal. From these results, it is concluded that there is an exact formation of $NiFe_2O_4$ in a ratio 1:2 with PANI consisting C, O, N, etc. elements.

4. Parametric studies

The adsorptive removal of methylene blue is studied at λ max 565 nm. The optimum conditions for removal of dyes are 40 mg/L, pH 9, PANI–$NiFe_2O_4$ and 8 g/L. The results obtained during this study are shown in Figs. 4–8.

4.1. Effect of initial dye concentration with different adsorbent doses

The effect of initial dye concentration with different adsorbent doses on the removal of methylene blue dye is investigated. The percentage removal of methylene blue dye by PANI–$NiFe_2O_4$ nanocomposite at different adsorbent doses 2–8 g/L for 20–60 mg/lt of dye conc. were studied as shown in Fig. 4. Adsorptive removal of methylene blue increases rapidly from 58 to 82.5% with an increasing amount from 2 to 8 g/L of PANI–$NiFe_2O_4$ nanocomposite. As the number of active sites for the adsorption increases, removal of methylene blue also increases is shown in Fig. 4. It is also observed that the conc. of dye increases from 20 to 60 mg/L. Removal percentage of dye decreases from 82.5 to 75.5% for adsorbent dose 8 g/L.

4.2. Effect of pH

The adsorptive removal of dye was studied at different pH values as it is an important parameter for reaction taking place on the particular surface. The role of pH on the adsorptive removal of methylene blue was studied in the pH range 0–10 at dye concentration 40 mg/L and PANI–$NiFe_2O_4$ concentration 8 g/L. It was observed that the rate of adsorption increases with an increase in pH up to 9 as shown in Fig. 5. As the pH increases, the number of anions on dye surface also increases. These anions form a bond with PANI–$NiFe_2O_4$ nanocomposite. This adsorption is based on electrostatic interaction [21]. When the pH increases onwards 9, the repulsion of the dye anions by negatively charged PANI–$NiFe_2O_4$, therefore surface would result in reduction in efficiency of adsorption of methylene blue dye. At lower pH, hydrogen ions can bind on to the surface of adsorbent and then removal efficiency of methylene blue(+ve ions) may decrease.

The effect of Pka on the rate of percentage removal of dyes can be excused along the basis of relations

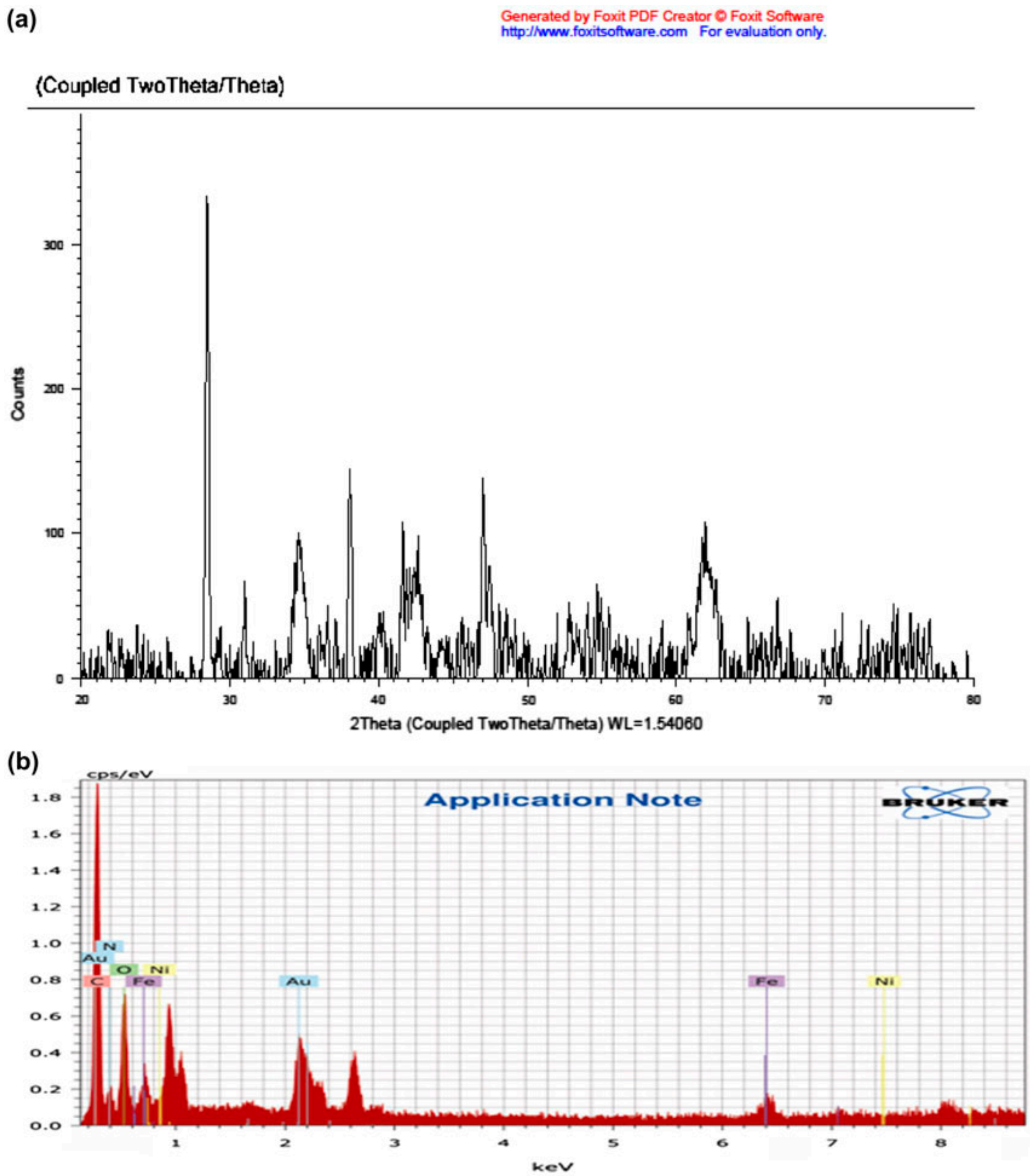

Fig. 3. (a) XRD image of prepared PANI–$NiFe_2O_4$ nanocomposite; (b) EDS image of prepared gold-(Au)coated PANI–$NiFe_2O_4$ nanocomposite.

between pH and Pka. As MB is a cationic dye, therefore, it is a stable conjugate base, which can be easily adsorbed with increasing Pka value on the surface of PANI/$NiFe_2O_4$.

4.3. Effect of contact time

The effect of contact time and initial dye concentration on percentage removal of methylene blue dye is shown in Figs. 6 and 7. It is observed that the rate of dye removal is faster in first 45 min after that it decreases gradually; then, it attains equilibrium at 165th min and after that it remains constant. The percentage removal at equilibrium decreases from 91.5 to 85.5% as dye concentration is increased from 20 to 60 mg/L for 8 g/L adsorbent dose. The amount of dye adsorbed q_t (mg/g) increases from 5.17 to 6.65 mg/g as shown in Fig. 7.

Table 1
Comparison of the pseudo-first-order and pseudo-second-order adsorption rate constants, and calculated and experiments q_e values for different initial concentrations

Adsorbent dose (g/L)	Initial conc. (mg/L)	q_e (exp)(mg/g)	q_e (cal)(mg/g)	K_1 (min^{-1})	R^2
Pseudo-first-order					
8	20	1.807	0.7603	0.01957	0.9759
	40	4.48	0.6295	0.0221	0.9791
	60	6.65	0.3784	0.04214	0.9722
4	20	1.3	0.65	0.027	0.967
	40	2.34	0.45	0.025	0.963
	60	3.5	0.55	0.0293	0.975
Pseudo-second-order					
8	20	2.062	1.807	0.0172	0.9959
	40	6.15	4.48	0.0023	0.9908
	60	6.7	6.65	0.2207	0.9997
10	20	1.5	1.3	0.022	0.998
	40	2.8	4.16	0.033	0.997
	60	4.8	5.73	0.021	0.999

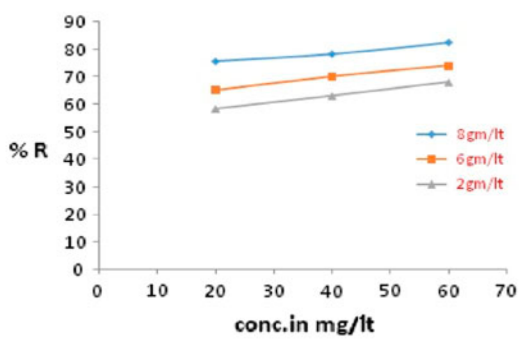

Fig. 4. Effect of initial dye conc. on percentage removal of methylene blue dye for different adsorbent doses with contact time 165 min and pH 9.

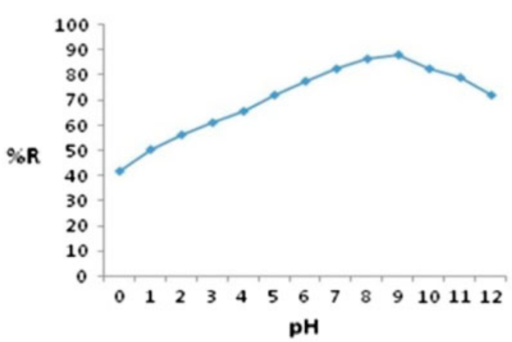

Fig. 5. Effect of pH on percentage removal of methylene blue dye by PANI–$NiFe_2O_4$ catalyst dose 8 g/lt at 40 mg/L.

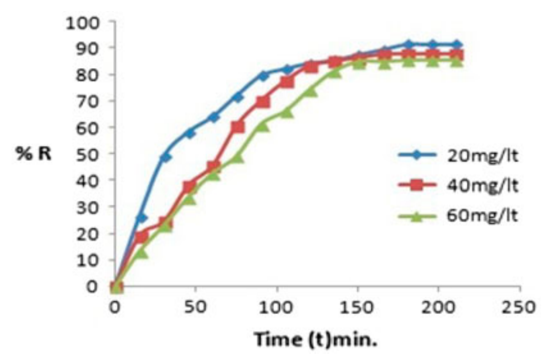

Fig. 6. Effect of contact time and initial concentration of methylene blue dye on % removal at adsorbent dose 8 g/L at pH 9.

5. Adsorption kinetics study

The adsorption kinetics gives the idea about mechanism of adsorption, from which efficiency of process estimated.

5.1. Pseudo-first-order

The integrated form of equation is

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (1)$$

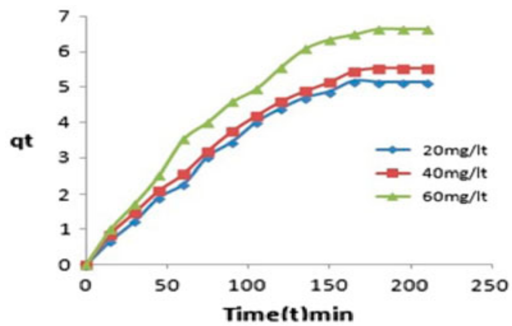

Fig. 7. Amount of dye adsorbed q_t (mg/g) with time for different initial dye concentrations: pH 9 and adsorbent dose 8 g/L.

where q_e and q_t are the amounts of dye adsorbed (mg/g) on PANI–$NiFe_2O_4$ at equilibrium and at time t (min), respectively; while K_1 is the rate constant obtained from the slope of the plot log (q_e − q_t) vs. time as shown in Fig. 8. The linear relationship of the plot for 20, 40 and 60 mg/L dye concentration indicates validity of equation. These calculated K_1 and correlation coefficient r^2 values are shown in Table 1. The correlation coefficient r^2 for the plots is >0.979, the calculated q_e values from first-order kinetic plots are too small as compared to experimental q_e values (as shown in Table 1). This shows that the pseudo-first-order kinetic model is not applicable to predict the adsorption kinetics of methylene blue on PANI–$NiFe_2O_4$ nanocomposite.

5.2. Pseudo-second–order

Adsorption kinetics was explained by second-order model is represented by the following equation.

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

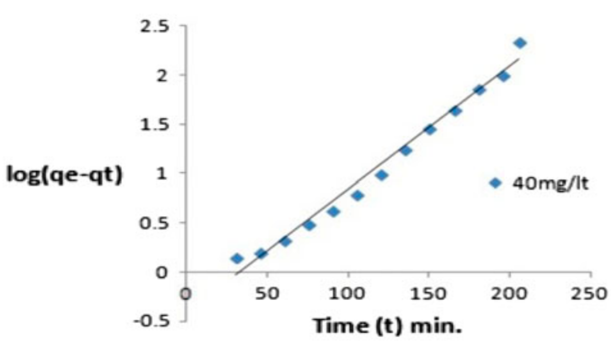

Fig. 8. Pseudo-first-order kinetics plots for the removal of methylene blue at 40 mg/L dye concentration: adsorbent dose 8 g/L and pH 9.

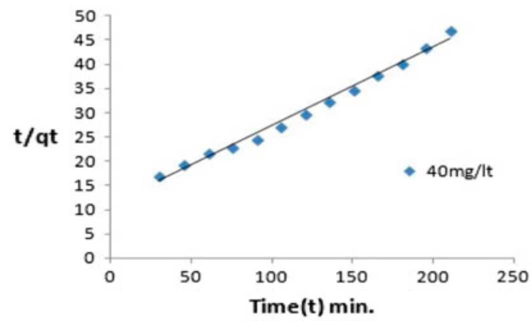

Fig. 9. Pseudo-second-order kinetics plots for the removal of methylene blue at 40 mg/L dye concentration: adsorbent dose 8 g/L and pH 9.

where K_2 is rate constant for second-order adsorption (g/mg/min), while k_2 and q_e are determined from slope and intercept of plot t/q_t vs. t (Fig. 9). The linear plot with correlation coefficient (r^2) from 0.97 to 0.999 (as shown in Table 1) shows a good agreement with the experimental q_e. It shows that adsorption belongs to the second-order kinetic model.

6. Equilibrium adsorption studies

6.1. Freundlich isotherm

The Freundlich isotherm is an empirical equation used to describe heterogeneous systems can be expressed in its logarithmic form as Eq. (3). The Freundlich adsorption isotherm equation is applied for methylene blue dye.

$$\log q_e = \log kf + \left(\frac{1}{n}\right) \log C_e \tag{3}$$

where q_e is the amount of dye adsorbed (mg/g) and C_e is the equilibrium concentration of dye in solution

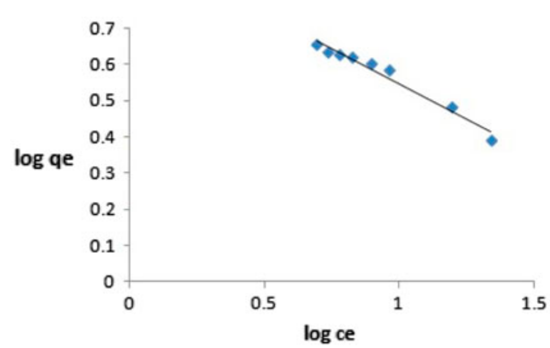

Fig. 10. Freundlich plot for adsorption of methylene blue by PANI–$NiFe_2O_4$.

Table 2
Freundlich and Langmuir coefficients for adsorption of methylene blue on PANI–$NiFe_2O_4$ for different dye concentrations at pH 9

	Freundlich coefficients						Langmuir coefficients		
Adsorbent dose (mg/L)	Dye conc. (mg/L)	*Kf* (l/g)	*n*	1/*n*	R^2	Q_o (mg/g)	*b*	RL	R^2
10	20	2.229	3.68	0.2712	0.951	1.12	1.08	0.043	0.9925
	40	8.433	2.56	0.39	0.966	3.12	0.68	0.035	0.996
	60	20.85	1.83	0.54	0.8937	3.31	0.24	0.064	0.9771
8	20	29.35	1.1	0.909	0.9012	0.87	1.89	0.025	0.987
	40	15.67	1.55	0.6451	0.9365	0.879	2.37	0.03	0.995
	60	11.12	1.31	0.7633	0.9422	0.987	0.5	0.032	0.914

(mg/L). The *Kf* and *n* are the constants incorporating and factors affecting adsorption process. The linear plot of log q_e vs. log c_e shows Freundlich adsorption. In adsorption, if *Kf* value increases, the quantity of dye adsorbed onto the surface of PANI–$NiFe_2O_4$ will also increase (Fig. 10 and Table 2). The slope 1/*n* ranging between 0 and 1 is the measure of adsorption extent or surface becomes heterogeneous as its value gets closer to zero [17]. The values of 1/*n* is between 0.2712 and 0.7633 for 20–60 mg/L dye conc. and adsorbent dose 8 g/L. It indicates chemisorption. The calculated *Kf* and 1/*n* values are presented in Table 2.

6.2. Langmuir isotherm

Langmuir isotherm is a test on the assumption that adsorption occurs at specific homogenous sites within the adsorbent. Once an adsorbate molecule occupies a site, no further adsorption can take place. Thus, adsorption reaches to an equilibrium value. The saturated monolayer curve can be expressed in the equation given below. It has been successful for the explanation of monolayer adsorption. The linear form of Langmuir equation is given as:

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

where C_e is the equilibrium concentration (mg/L), q_e is the amount of dye adsorbed at equilibrium (mg/g), Q_o (mg/g) is the monolayer coverage capacity and *b* is the Langmuir isotherm constants (l/mg). The values of Q_o and *b* are determined from the slope and intercepts of the linear plots of c_e/q_e vs. c_e. It is shown in Fig. 11 and Table 2. Calculated Q_o and *b* values are presented in Table 2. The Langmuir adsorption suggests the monolayer coverage of dye on PANI–$NiFe_2O_4$ nanocomposite. The essential characteristics of the Langmuir isotherm can be expressed by dimensionless constant called equilibrium parameter.

where *b* is the Langmuir constant and C_i is the initial dye concentration (mg/L). According to the rule of *RL*. $RL \geq 1$ unfavourable, $RL = 1$ linear, $1 \geq RL \geq 0$ favourable, $RL = 0$ irreversible. When the rule $1 \geq RL \geq 0$ is obeyed, Langmuir isotherm becomes favourable. The correlation coefficient of r^2 values for Langmuir and Freundlich isotherms are shown in Table 2. Both the isotherms are found to fit well with experimental data.

$$RL = \frac{1}{1 + bC_i} \tag{5}$$

7. Dye desorption experiment

The experiment was performed to do regeneration, recycle and reuse study. In this study, MB adsorbed PANI/$NiFe_2O_4$ adsorbent is dissolved in methanol, MB dye was easily desorbed by methanol solvent molecules. For reusability, PANI/$NiFe_2O_4$ nanocomposite was further separated from the methanol solution using external magnet. The nanocomposite was collected magnetically from the methanol, as the PANI/$NiFe_2O_4$ is sufficiently magnetic [22]. The percentage recovery

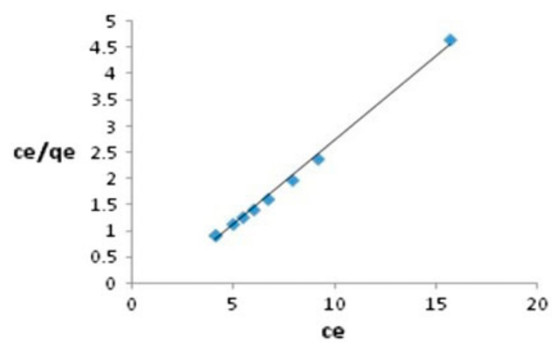

Fig. 11. Langmuir plot for adsorption of methylene blue by PANI–$NiFe_2O_4$.

was about 90% of PANI/$NiFe_2O_4$ nanocomposite. The PANI/$NiFe_2O_4$ nanocomposite was washed with deionised water and reused and recycled for again 2nd, 3rd, 4th and 5th time, respectively. After every recycle and reuse, adsorption efficiency of dye decreases nearly about 15–20%. This is due to loss in the surface texture.

8. Conclusions

PANI–$NiFe_2O_4$ nanocomposite is successfully synthesised *in situ* through self-polymerisation of monomer aniline. Adsorptive removal of methylene blue dye using adsorbent dose (PANI–$NiFe_2O_4$) is successfully applied. The adsorption rate increased significantly by increasing the amount of adsorption dose, while with an increasing dye concentration, adsorption rate decreases. Basic pH condition is found, which significantly affects the dye adsorption efficiency of methylene blue dye is 87.8% and after elution the concentration of dye is 40 mg/L. The present study shows that PANI–$NiFe_2O_4$ can be used as an adsorbent for the removal of methylene blue dye from aqueous solutions. The amount of adsorbed dye is found from 5.14 to 6.65 (mg/g) increased with an increase in contact time and increase in initial dye concentration with an increasing adsorbent dose. The rate of adsorption is found to confirm the pseudo-second-order kinetics with good correlation with R^2 values. Adsorption isotherms are described by Langmuir isotherm and Freundlich isotherm models. Langmuir isotherm model is found to be more suitable with experimental data due to higher r^2 values. The Langmuir adsorption is a physical adsorption which suggests the monolayer coverage of dye on PANI–$NiFe_2O_4$ nanocomposite. As MB is a cationic dye, there is an electrostatic interaction exists [17, 21, 22]. From the desorption experiment, it is concluded that the PANI/$NiFe_2O_4$ nanocomposite could be recycled and reused.

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