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Melamine-anchored magnetic multiwall carbon nanotubes: tailoring functional groups reactivity for efficient adsorption of anionic dye

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ABSTRACT

Herein, onestep prepared magnetic multi-walled carbon nanotubes were anchored with melamine and applied as a magnetic recyclable dye sorbent. Direct blue 71 was used as a sample anionic dye and the results showed that the sorbent has good efficiency for uptake of it. Equilibrium time was 30 min and maximum adsorption capacity of 250 mg/g was obtained. Prepared material was regenerated using ethanol–NaOH solution. The study of kinetic and isotherm models showed that adsorption process followed second-order and Langmuir models, respectively.

Keywords: Adsorption; Carbon nanotubes; Dye; Melamine

1. Introduction

Dyes are organic compounds consisting of auxochromes and chromophores which are responsible for their intensity and color. Dyes are primarily classified based on chemical structures and types of application. Azo (around 70%) and anthraquinone (around 15%) composed the largest classes of dyes [1,2]. Discharge of dyes into the environment from the residues of textile as well as other coloring industries significantly affects the aquatic life and plants by reducing sunlight transmission through water. Owing to being mutagenic and carcinogenic, dyes impart toxicity to human; additionally, they may cause afflictions, such as vomiting, headache, as well as severe damages to liver, brain and central nervous system. In consequence, the effective removal of dyestuff from effluents is of a great importance in both pollution control and environmental protection [3,4].

Treatment of dye contaminant has been undertaken by several physical and chemical methods, such as biodegradation, adsorption, coagulation–flocculation, and oxidation processes. Among mentioned techniques, adsorption appears as a successful effective alternative due to its high efficiency, cost-effectiveness, and ease of operation [5–8]. A lot of adsorbents have been tested for the possibility to lower dye concentrations in aqueous solutions, namely biosorbent [9], metal oxide [10,11], chitosan [12], clay [13], and activated carbon [14]. Over the past decade, considerable attention has been drawn to the carbon nanotubes (CNTs) as efficient adsorbents to adsorb trace pollutants from wastewater owing to their unique physical

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and chemical properties such as large specific surface areas, small size, as well as hollow structures [15–19].

One thing that could be problematic in the adsorption technique is that it is difficult and time-consuming to separate and recover the adsorbents from solution, with this in mind, there is a growing interest in the use of the magnetic and magnetizable adsorbents as a quick and easy method for collecting adsorbents from aqueous solution [20,21]. Based on these considerations, we used magnetic MWCNTs as a magnetic separable adsorbent for anionic dye. In order to enhance the adsorption of anionic dyes, an organic agent consisting of aromatic rings and amine functional groups could be a good choice for the modification ofmagnetic MWCNTs. In this study, melamine has been selected as an amine source in the modification process. Anchoring of melamine to the magnetic MWCNTs was done through amide formation. The synthesized composite has been used as a novel adsorbent for removal of Direct Blue-71, which is a hazardous azo dye. The effects of various parameters on the removal of dye such as pH, contact time and initial dye concentration were also properly investigated.

2. Experimental

2.1. Materials and instrumentation

Direct Blue-71 (DB-71) which was used as a model dye was supplied from chemistry and chemical engineering research center of Iran. The stock dye solution was prepared by dissolving an appropriate amount of dye powder in distilled water. The pH was adjusted using 0.1 mol/L of HCl or NH_3. Dimethyl formamide (DMF), thionyl chloride, $Fe(NO_3)\cdot 9H_2O$ and Melamine (Merck, Darmstadt, Germany) were used to synthesize adsorbent. A pH-Meter model 781 from Metrohm (Herisau, Switzerland) equipped with glass combination electrode was used for the pH measurements. Adsorption studies of the test solutions were carried out using a Lambda 25 UV–vis spectrophotometer (Perkin Elmer). The FT-IR study of the samples was done by Equinox 55 Bruker with ATR method over the wavelength of 400–4,000 cm^{-1}. Magnetization investigation was done using a vibration sample magnetometer (VSM), (Lake Shore Model 7400, Japan).

2.2. Preparation of modified magnetic MWCNTs

Magnetic MWCNTs was prepared by the one-step approach as to our previous work, using iron source as the catalyst [22]. A mixture of MWCNTs (0.2 g) and concentrated nitric acid (20 mL) has been stirred at 60˚C for 12 h to activate MWCNTs. The suspension was filtrated, then was rinsed with distilled water until the pH of the suspension was reached about the neutral value. The solid product was dried at 80˚C for 5 h. In order to acylation of CNTs, the oxidized CNTs (0.2 g) was added to a mixture of thionyl chloride (5 mL) and DMF (50 mL) and was stirred for 6 h. The resulting mixture was filtered and was washed with DMF and dried at 60˚C for 5 h. For amine functionalization of CNTs, 1.0 g melamine was separately dissolved in DMF (50 mL) followed by the addition of chloro-CNTs (0.2 g). After stirring for 5 h at room temperature, modified magnetic CNTs was separated by filtration and dried in oven at 60˚C for 5 h.

2.3. Characterization of prepared composite

In the FT-IR spectrum of oxidized MWCNT (Fig. 1(a)), several significant bands are attributed to carboxylic acid groups introduced by acid oxidizing, including the appearance of C=O stretching band at 1723 cm^{-1}, C=C at 1278 cm^{-1}, $-CH_2$ at 2924 cm^{-1} and O–H stretching band at 3440 cm^{-1}. The FT-IR spectra of melamine functionalized CNTs composites appear at 3430 cm^{-1} (N–H stretching), 1570 cm^{-1} (N–H bending), 1505 cm^{-1}(N–H bending) and 1000–1600 cm^{-1} (aromatic carbon–carbon vibration). These results reveal that amine compounds were successfully anchored on the surface of MWCNTs.

The magnetic property of the prepared composite was carried out using a vibrating sample magnetometer (VSM) at room temperature. Fig. 1(b) reveals that the value of saturation magnetization is 5.43 emu/g. Moreover, remnant magnetization and coercivity are 10.86 Oe and 0.19 emu/g, respectively which are negligible and indicate that the prepared magnetic composite has the superparamagnetic characteristic.

2.4. Adsorption procedure

Dye adsorption experiments were adequately performed using batch equilibrium technique. To do so, modified composite (10 mg) was added to the dye solution of known concentration (50 ml). After adjustment of pH to 2.0, it was shaken for 30 min to reach the equilibrium. At the end of the adsorption period, the adsorbent was separated from dye solution by applying magnetic field. Subsequently, the concentration of residual analyte was determined by measuring the absorbance at 583 nm using a UV–vis spectrophotometer. The dye removal percent (%R) at optimum conditions was calculated by following equation:

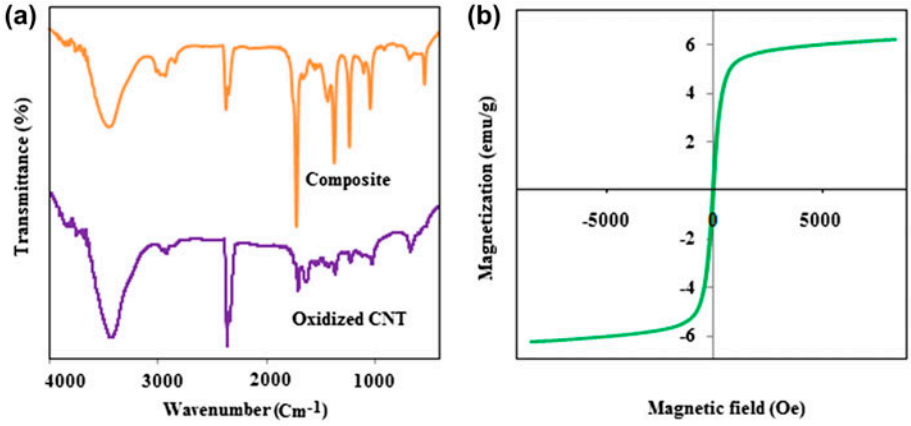

Fig. 1. FT-IR spectra of oxidized CNTs and amine functionalized CNTs (a), and VSM pattern of magnetic modified MWCNTs (b).

$$\%R = (C_0 - C_e) \times 100/C_0 \quad (1)$$

where C_0 and C_e (mg/L) are initial and equilibrium liquid phase concentrations of dye, respectively.

3. Results and discussion

3.1. Effect of pH

In this study, the influence of pH in the range of 1–9, on adsorption capacity of DB-71 onto the modified magnetic composite was investigated. For this purpose, a fixed dye concentration of 20 mg/L and also fixed adsorbent optimum dosage of 10 mg were employed. The adsorption efficiency decreased with an increase in pH from 2 to 8 (Fig. 2(a)). Maximum efficiency was obtained at pH 2, and as a result, this value was used for subsequent works. One of the effective parameters on analyte adsorption is the ionization state, or electrical properties of the sorbent functional groups. This parameter can be estimated using zeta potential measurements. According to zeta potential curves in Fig. 2(b), the amine functionalized CNTs have a pH_{PZC} of 4.5, which is due to the basic properties of amino groups. Based on the results, surface of the modified MWCNs is positively charged at pH values below pH_{PZC} and has negative charge ata-bove that. In consequence, a significant potential mechanism for dye adsorption includes electrostatic interactions. In the other words, at pH 2.0 ion exchange between dye and H^+ is the main mechanism.

As to increasing pH, it is expected that adsorption could be decreased due to the rejection between the anionic dye and negative charge of the sorbent. It can be seen that in alkali solution adsorption removal

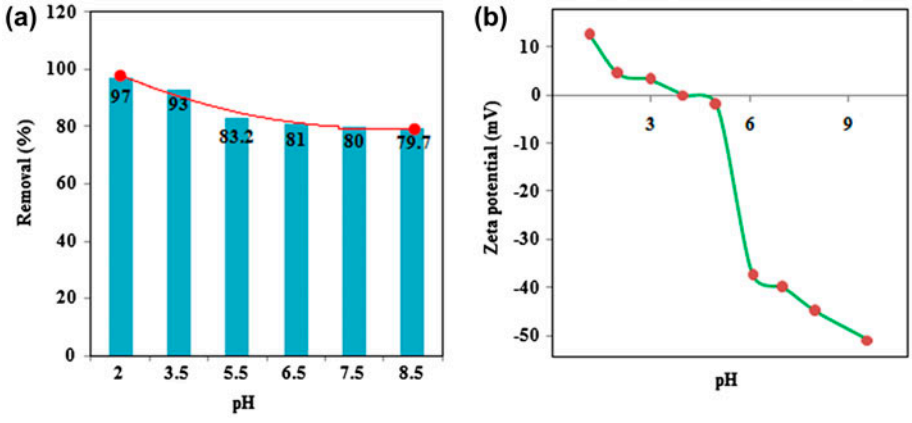

Fig. 2. Effect of pH (a) on dye removal and the zeta potential curve (b) of melamine functionalized CNTs.

efficiency is also high (80%). This situation can be owing to the various mechanisms which act simultaneously in dye adsorption. Hydrophobic interaction between organic compounds and the outer surface of individual CNTs is the main reason for efficient uptake of organic compounds by the nanomaterial. Other mechanisms include π–π interactions between bulk π systems on CNT surfaces and organic molecules. Each carbon atom in a CNT has a π electron orbit perpendicular to CNT surface [23]. Therefore, organic molecules containing π electrons can form π–π bonds with CNTs such as organic molecules with C=C double bonds or benzene rings. In fact, CNTs could be considered as either electron-donors or acceptors. The π–π bond strength is also determined by the tendency of CNTs and analyte to accept or donate electrons. The introduction of carboxylic groups to CNTs made them electron acceptors, which increased adsorption of benzenoid rings on CNTs. Hydrogen bonds also participate in dye adsorption, due to the functional groups on CNT surfaces. On the other hand, the adsorption tends to increase with increased CNT oxygen contents in polar organic chemicals, because of the enhanced H-bond. Morphology of CNTs has the main role in the adsorption process. CNTs tend to aggregate together as bundles as a result of Van der Waals interactions [24]. Formation of groove areas between the CNTs is the direct effect of the aggregation. These sites are generally available for adsorption. Modification of the CNTs with the melamine increases the functional groups of the CNTs, resulted in the improved strength of π–π and hydrogen bonds. Furthermore, groove areas in CNTs structure group as a result of its modification with melamine. Accordingly, dye adsorption efficiency of the adsorbent can be improved by melamine anchoring.

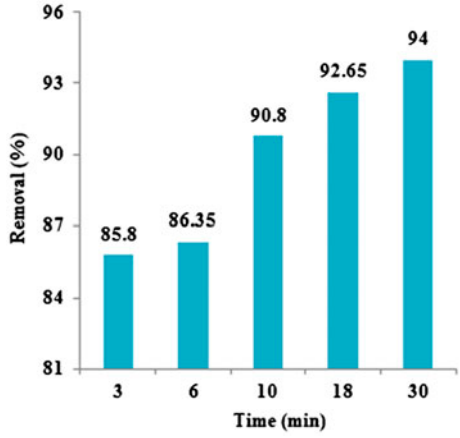

Fig. 3. Effect of time on adsorption of DB-71 by magnetic nanocomposite.

Table 1
The data of kinetic models for adsorption of DB-71 using magnetic nanocomposite

First order	R^2	0.96
	K_1	0.13
	Q (mg/g)	13.06
Second order	R^2	0.99
	K_2	0.02
	Q (mg/g)	100
	Q_{exp} (mg/g)	94
Diffusion model	R^2	0.94
	K_P	2.72
	C	83.0
Liquid film	R^2	0.96
	K_{fd}	0.13
	C	1.95

3.2. Kinetic study

Four of the main kinetic models were applied to the experimental data to determine the kinetic parameters and investigate the mechanism of adsorption of dye by the prepared sorbent. Kinetic measurements were made under the optimum conditions by the batch extraction at different times. Results in Fig. 3 showed that removal efficiency increases in first 10 min since more than 80% of dye was removed at this period and slowly was increased to 30 min after that the removal not changed. The adsorptive interactions rate can be evaluated by using the linear form of integrating the pseudo-first and a second order equation which is the most widely used procedures for the adsorption of solute from aqueous solution.

$$\ln\ (Q_e - Q_t) = \ln\ Q_t - K_1 t \tag{2}$$

$$t/Q_t = 1/K_2 Q_e^2 + t/Q_e \tag{3}$$

where K_1 and K_2 are the pseudo-first and second order adsorption rate constant and Q_e, Q_t are the values of the amount adsorbed per unit mass at equilibrium and at any time, t, (mg/g). The values of constants can be determined experimentally by plotting ln $(Q_e - Q_t)$ and t/Q_t vs. t, as it is shown, obtained plots (Fig. 4(a) and (b)) are linear $R^2 > 0.96$ but according to first-order model there is high difference between the experimental Q_e value and that from the Lagergren

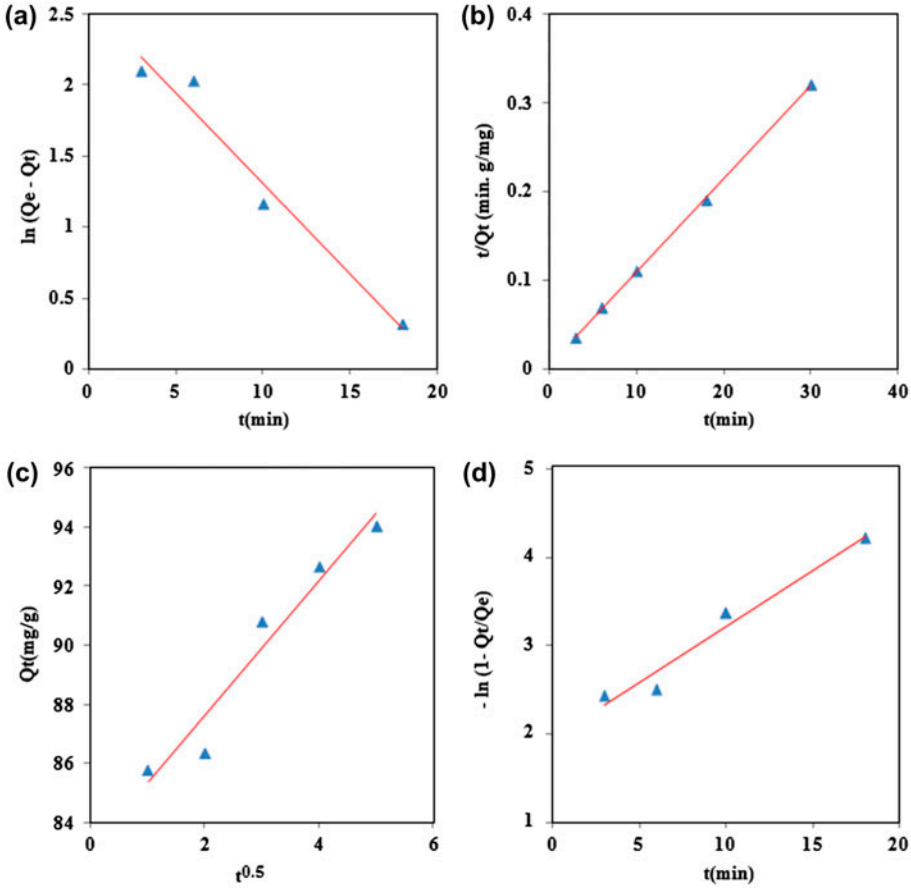

Fig. 4. Pseudo-first-order (a), pseudo-second-order (b), intraparticle diffusion (c) and liquid film (d) plots for DB-71 adsorption by magnetic nanocomposite.

plot (Table 1). Hence, this model cannot be accepted as a kinetic mechanism and adsorption follow second order [25].

If the diffusion of ions on internal surfaces of pores and capillaries of the adsorbent is the rate limiting step, the adsorption can be presented intraparticle diffusion model [26]:

$$Q_t = K_P t^{0.5} + C \quad (4)$$

where K_P represents intraparticle diffusion rate constant (mg/g $min^{0.5}$) and C is a constant which gives information about the thickness of boundary layer. The plot of Q_t against $t^{0.5}$ yields a straight line passing through the origin in case of intraparticle diffusion (Fig. 4(c)) the line has good linearity ($R^2 = 0.94$) but ithas high value of intercept. Thus, it was not the rate limiting parameter.

The liquid film diffusion model can be expressed as follows:

$$\ln(1 - Q_t/Q_e) = -K_{fd}t \quad (5)$$

in which K_{fd} is the adsorption rate constant. The plot of-ln($1 - Q_t/Q_e$) vs. t is illustrated in Fig. 3(d). As can be seen, the plots showed correlation coefficient value of 0.96 and low level of intercept (1.95) which proved the role of film diffusion in the adsorption of DB-71.

3.3. Adsorption isotherms

In order to understand the adsorption properties of the adsorbent and illustrate how adsorbate interacts with adsorbent, the Langmuir and Freundlich isotherm models were investigated. The Langmuir model is based on the assumption that adsorption occurs at specific homogeneous monolayer surface containing sites with uniform energy then the adsorption of adsorbate stops, and no more interactions take place between the adsorbent and adsorbate molecules.

Freundlich isotherm describes that adsorption occurs on a heterogeneous surface. Thus, it does not assume monolayer capacity. Additionally, the adsorption occurs at sites with different energies [27,28].

The linear Langmuir and Freundlich isotherm equation can be written as followed:

$$C_e/Q_e = C_e/Q_m + 1/Q_m K_a \quad (6)$$

$$\ln Q_e = \ln K_F + 1/n \ln C_e \quad (7)$$

where C_e and Q_e are the equilibrium concentration (mg/L) and the amount adsorbed dye at equilibrium (mg/g), Q_m is the maximum adsorption capacity of a monolayer (mg/g) and K_a, K_F and n are the energy of adsorption and Freundlich constants. Langmuir model favorability can be evaluated with dimensionless parameter R_L according to Eq. (8):

$$R_L = 1/(1 + C_0 K_a) \quad (8)$$

According to results, the R_L value was found in the range of $0 < R_L < 1$ which indicated a favorable adsorption process.

The plots and values of Langmuir and Freundlich constants for dye adsorption with the composite are depicted in Fig. 5(a) and (b) and in Table 2. As it can be seen, experimental data fit with both models as values of the correlation coefficient (R^2) are 0.99. The applicability of these two isotherms for the dyes adsorption shows that both monolayer homogeneous adsorption and heterogeneous energetic distribution of active sites on the surface of the adsorbent are possible, and the adsorption on CNTs could not be described using a single adsorption coefficient. The presence of high-energy adsorption sites such as CNT defects [29] and functional groups [30], is the main

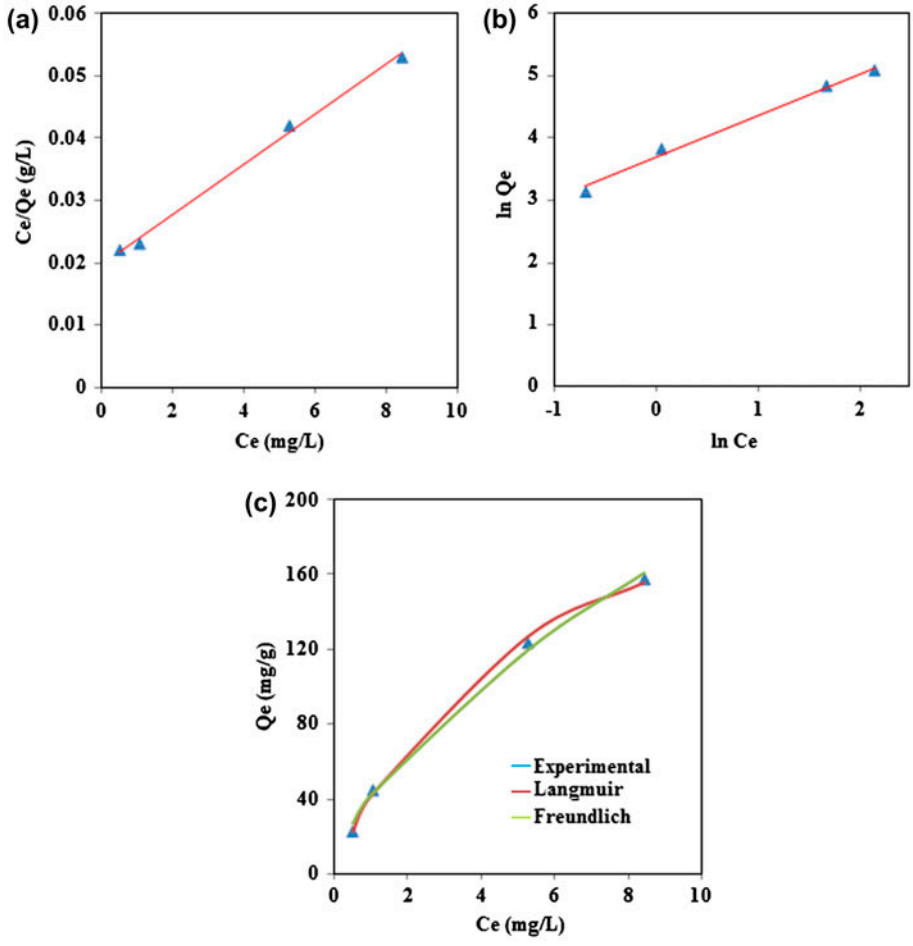

Fig. 5. The Langmuir (a), Freundlich (b) and chi-square test graphs (c) for DB-71 adsorption by magnetic nanocomposite.

Table 2
The data of isotherm for DB-71adsorption using magnetic nanocomposite

Langmuir	
Q_m (mg/g)	250.0
R^2	0.99
K	0.21
R_L	0.10–0.48
χ^2	0.21
Freundlich	
n	1.42
K_F	38.86
R^2	0.99
χ^2	1.01

reason that has been provided to explain the heterogeneous adsorption along with the monolayer process. Surface and capillary condensation of liquid adsorbates could be another reason for this case. In fact the first couple of layers interacts with the surface while molecules beyond the first two layers interacts with each other which cause multilayer adsorption, especially in the case of adsorption of organic chemicals on CNT surfaces [31]. Capillary condensation is responsible for load-dependent adsorption energy [32]. This condensation could be occurred in the hollow column at the inner pore of an open-end CNT or interstitialarea in a CNT bundle. In brief, these explanations indicate that the mechanism of dye adsorption is complex, and both the homogenous and heterogeneous adsorption exists at the same time in this adsorption process.

In order to determining the best-fitting model, chi-square (χ^2) test have been employed [33]. The χ^2 can be defined mathematically as follows:

$$\chi^2 = \sum \left[\left(Q_{e,exp} - Q_{e,cal} \right)^2 / Q_{e,cal} \right] \quad (9)$$

in which $Q_{e,exp}$ and $Q_{e,cal}$ are the experimental data and the calculated from nonlinear models. According to the results (Table 2 and Fig. 5(c)), the Langmuir isotherm model shows better fitness. Moreover, this model show a lower value of chi-squared test compared to Freundlich isotherm and suggests that the Langmuir model is a better model for describing sorption behavior.

3.4. Desorption and reusability

In order to find the best eluent, desorption experiments were performed under the optimized condition. According to the effect of pH on dye removal, the adsorption was not feasible in alkaline solution. Hence, ethanol–NaOH solution (0.1 mol/L) was investigated, and results showed that more than 90% of adsorbed dye desorbed from the sorbent. Therefore, ethanol–NaOH solution was selected as an effective eluent.

3.5. Comparison with other methods

Table 3 compares the adsorption capacity and equilibrium time of the modified magnetic CNTs with different types of adsorbents previously used for the removal of anionic dyes. It can be seen that adsorption capacity of anionic dye on this modified sorbent is higher than that of many other previously reported adsorbents. Moreover, the adsorption process on this adsorbent is faster than the other adsorbents. This indicates that the melamine anchored magnetic MWCNTs can be considered as a promising adsorbent for the easy removal of anionic dyes from aqueous solutions.

Table 3
Comparison of obtained results with other methods for adsorption of anionic dye by melamine functionalized magnetic CNTs

Sorbent	Analyte	Adsorption capacity (mg/g)	Time (min)	Refs.
MgO	Reactive blue	166.7	5	[1]
Activated carbon from coir pith	Congo red	6.72	10	[2]
Sawdust—cetyltrimethyl ammonium bromide	Congo red	42	10	[9]
Crosslinked chitosan	Direct red 81	2,383	5 d	[12]
CNTs	Direct red 224	61.3	100	[16]
CNTs	Procion Red	42.5	180	[17]
Activated carbon	Reactive Red	260.37	60	[19]
MWCNT-starch-iron oxide	Methyl orange	135	60	[20]
γ-Fe_2O_3—chitosan	Methyl orange	29.37	120	[21]
Melamine–magnetic MWCNTs	Direct blue 71	250	30	This work

4. Conclusions

In summary, melamine anchored magnetic MWCNTs nanocomposite was prepared as a magnetic recyclable adsorbent for adsorption of anionic dye. The results of this study show that the prepared composite is a promising adsorbent which was effectively used for the removal of dye. The equilibrium time and adsorption capacity are in good levels compared to other adsorption techniques. Removal of DB–71 was pH dependent, and the maximum removal was attained at pH 2.0. Desorption of the dye carried out by using alkali ethanol. Hence, the modified magnetic composite found to be an effective regenerable adsorbent.

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