Removal of some cationic dyes from aqueous solutions using magnetic-modified multi-walled carbon nanotubes

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ABSTRACT

An adsorbent, magnetic-modified multi-walled carbon nanotubes, was used for removal of cationic dyes crystal violet (CV), thionine (Th), janus green B (JG), and methylene blue (MB) from water samples. Prepared nanoparticles were characterized by SEM, TEM, BET and XRD measurements. The prepared magnetic adsorbent can be well dispersed in the water and easily separated magnetically from the medium after loaded with adsorbate. The influences of parameters including initial pH, dosage of adsorbent and contact time have been investigated in order to find the optimum adsorption conditions. The optimum pH for removing of all the investigated cationic dyes from water solutions was found to be 7.0. The experimental data were analyzed by the Langmuir adsorption model. The maximum predicted adsorption capacities for CV, JG, Th and MB dyes were obtained as 227.7, 250.0, 36.4 and 48.1 mg g^{-1}, respectively. Desorption process of the adsorbed cationic dyes was also investigated using acetonitrile as the solvent. It was notable that both the adsorption and desorption of dyes were quite fast probably due to the absence of internal diffusion resistance.

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1. Introduction

Dyes are widely used in the textile and dyestuff industries. Effluents from these industrial facilities are typically of high organic contents and color strength. Thus, dyestuff wastewaters must be treated before discharge, as to minimize the threat to the environment. The strong color in wastewater can decrease the transparency of water and influence photosynthesis activity, which hinders the microbial activities of submerged organisms. However, removal of color from wastewater is of a great challenge. The common dyes include reactive, disperse, acid, and direct dyes. Usually the dyes are low in toxicity, easy to dissolve in water and can be applied for various industrial uses, including inks, cosmetics, soap, and foods [1–4].

The methods used for the removal of organic dyes and pigments from wastewaters are classified into three main categories: physical [5], chemical [6,7] and biological [8,9]. Adsorption methods is the most applied in the removal of organic dyes and pigments from wastewaters, since it can produce high-quality water and also be a process that is economically feasible [10]. Although activated carbon commonly used as adsorbent for color removal [11,12], but the main disadvantage of activated carbon is its high production

and treatment costs [12]. The biological process is difficult to start up and control [13]. Furthermore, the organics in the wastewater cannot be degraded completely by biological processes, and as a result the total treatment cost can increase because of the need of further treatment. Thus, many researchers throughout the world have focused their efforts on optimizing adsorption and developing novel alternative adsorbents with high adsorptive capacity and low cost. In this regard, much attention has recently been paid to nanotechnology.

Magnetic nanoparticles as an efficient adsorbent with large specific surface area and small diffusion resistance has been recognized [14,15]. The magnetic separation provides suitable route for online separation, where particles with affinity to target species are mixed with the heterogeneous solution. Upon mixing with the solution, the particles tag the target species. External magnetic fields are then applied to separate the tagged particles from the solution.

The synthetic dyes represent a relatively large group of organic chemicals that are met in practically all spheres of our daily life. The cationic dyes such as MB, Th, JG and CV are an important group of organic compounds, which have a variety of scientific and industrial applications [16–22]. So it would be likely that such chemicals have some undesirable effects on humans as well as on environment. In order to minimize the possible damages to humans and the environment arising from the production and applications of cationic dyes, research was carried out around the world.

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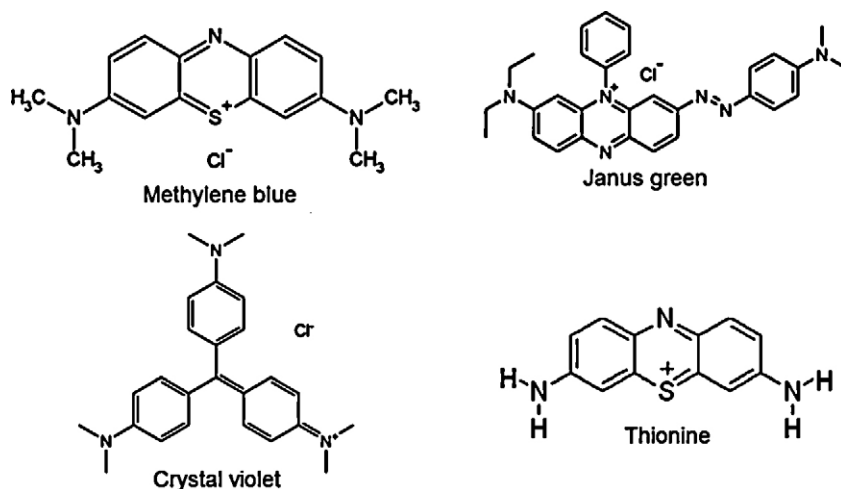
Scheme 1. The structure of the investigated dyes.

Removal of cationic dyes methylene blue, neutral red and brilliant cresyl blue from aqueous solution using magnetic multi-wall carbon nanotubes (MMWCNTs) nanocomposite as adsorbent has been reported by Gong et al. [23]. The morphologies of the adsorbent and the synthesized MMWCNT adsorbent were obtained by SEM. It was observed that iron oxide nanoparticles were successfully coated on the surface of multi-wall carbon nanotubes (MWCNTs) to form multi-walled carbon nanotube iron oxide nanocomposites. In the other work, Qu et al. used multi-walled carbon nanotubes filled with Fe_2O_3 particles for removal of methylene blue and neutral red from aqueous solutions. The TEM images of this synthesized multi-walled carbon nanotubes demonstrated that the tip of MWCNTs was opened and the inside of the nanotubes were filled with in situ produced Fe_2O_3 nanoparticles [24].

Carbon nanofibers can remove cationic and anionic dyes from water samples. The selectivity of adsorption is obtained by adjustment of adsorption pH [25]. But the separation of MWCNTs from solution is very difficult. In this study the multi-walled carbon nanotube that modified with magnetic nanoparticles was synthesized by a simple method and used for removal of cationic dyes from wastewater samples. The technique was found to be very useful and cost-effective for a better removal of dyes. Separation of the dye loaded magnetic-modified multi-walled carbon nanotubes (MMMWCNTs) from the solution was then occurred by an external magnetic field. The adsorption isotherms of the dyes into adsorbent were investigated.

2. Experimental

2.1. Reagents and materials

All chemicals were of analytical reagent grade or the highest purity available from Merck (Darmstadt, Germany) and double distilled water (DDW) was used throughout the study. In addition, all glassware were soaked in dilute nitric acid for 12 h and finally rinsed for three times with DDW prior to use.

Scheme 1 shows the structure of the investigated dyes. Stock solutions of dyes were prepared by dissolving the powder in DDW. Dye solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions.

2.2. Instrumentation

A Metrohm model 713 pH-meter was used for pH measurements. A single beam UV-mini-WPA spectrophotometer was used for determination of dye concentration in the solutions. The size, morphology and structure of the nanoparticles were characterized by transmission electronic microscopy (TEM, Philips, CM10, 100 KV) and scanning electron microscope (SEM-EDX, XL30, Philips Netherland). The crystal structure of synthesized materials was determined by an X-ray diffractometer (XRD, 38066 Riva, d/G. Via M. Misone, 11/D (TN) Italy) at ambient temperature. Specific surface area and porosity were defined by N_2 adsorption–desorption porosimetry (77 K) using a porosimeter (Bel Japan, Inc.).

2.3. Synthesis of magnetic-modified multi-walled carbon nanotubes

The synthesis of MMMWCNTs was achieved according to the literature previously reported with some modification [26]. Typically, MWCNTs were first dispersed in concentrated nitric acid at 130 °C for 30 min under stirring to remove the impurities and then washed by DDW until the filtrate is neutral. MWCNTs filled with Fe_3O_4 or Fe_2O_3 nanoparticles prepared using a simple solution method, in which 0.6 g of ammonium iron (II) sulfate hexahydrate was dissolved in 20 mL of DDW and hydrazine hydrate solution (volume ratio 3:1) to form a grass-green solution, then pretreated MWCNTs of 0.25 g was added. The mixture was sonicated and stirred vigorously. Subsequently, the pH of the mixture was adjusted to 11–13 and kept refluxed at boiling point for 2 h. Finally, the iron oxides nanoparticles-filled MWCNTs were filtered and washed with DDW and anhydrous alcohol for several times, and dried under vacuum for 24 h.

2.4. Removal dyes experiments

Fifteen milligram of MMMWCNTs were added to 20 mL of 20 mg L^{-1} of each of cationic dyes MB, Th, JG and CV solutions with predetermined concentration, and the pH of the solution was adjusted at 7.0 with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH solutions. The mixed solution was then shaken at room temperature for 15 min. Subsequently, the MMMWCNTs with adsorbed dyes were separated from the mixture via a permanent hand-held magnet within 30 s. The residual amounts of dyes in the solution were determined spectrophotometrically at 663, 618, 596, and 601 nm for MB, JG, CV and Th, respectively. The adsorption percentage for each dye, i.e. the dye removal efficiency, was determined using the following expression:

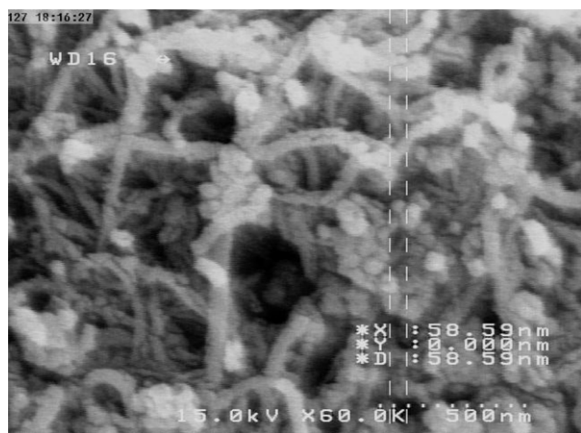$$\%R = \left[\frac{(C_o - C_t)}{C_o}\right] \times 100 \tag{1}$$

Fig. 1. The SEM image of MMWCNTs. Conditions: voltage: 15 KV, resolution.

Fig. 3. X-ray diffraction patterns of (a) MWCNTS, (b) Fe_3O_4, (c) MMWCNTs.

where C_o and C_t represent the initial and final (after adsorption) concentrations of dyes in $mg\,L^{-1}$, respectively. All tests were performed in triplicate to insure the repeatability of the results; the mean of the three measurements was then reported. All the experiments were performed at room temperature.

3. Results and discussion

3.1. Characterization of the adsorbent

The SEM and TEM images of the MMMWCNTs, as shown in Figs. 1 and 2, revealed that the diameter of synthesized MMMWC-NTs was around 58 nm. The XRD profile of MWCNTs, MMMWCNTs and Fe_3O_4 are shown in Fig. 3. Fig. 3a shows the XRD of MWCNTs and the typical peaks of MWCNTs at $2\theta = 25.91°$ can be observed. At Fig. 3b the typical peaks of Fe_3O_4 and Fe_2O_3, at $2\theta = 30.2°$, $35.6°$, $43.3°$ and $57.2°$ are observed that can be assigned to maghemite or magnetite [27]. Other peaks are also observed at $2\theta = 53.7°$ and $62.8°$ may be related to the presence of hematite [28,29] and Fig. 3c shows the XRD of MMMWCNTs that includes all the carbon nanotube and iron oxide nanoparticles peaks. The results have a good agreement with other reported [26,30]. The results confirm that iron oxide nanoparticles are encapsulated into the interiors of MWCNTs or adsorbed on the surface of MWCNTs.

Specific surface areas are commonly reported as BET surface areas obtained by applying the theory of Brunauer, Emmett, and Teller (BET) to nitrogen adsorption/desorption isotherms measured at 77 K. The specific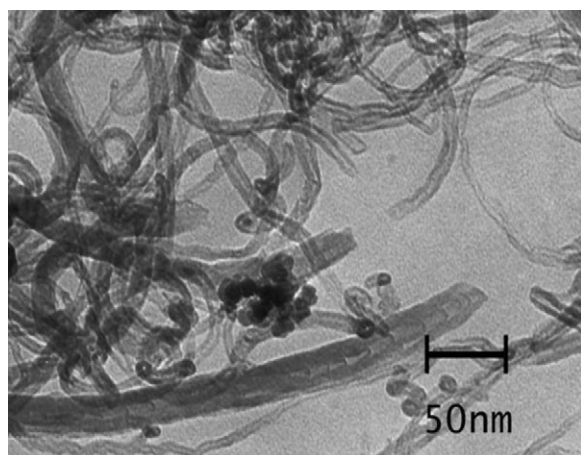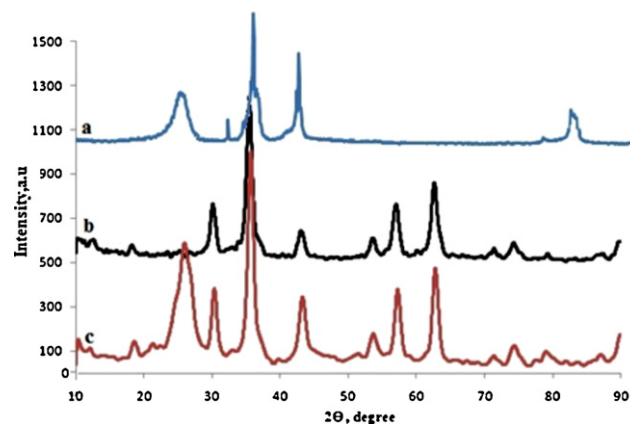 surface area of the sample is determined by physical adsorption of a gas on the surface of the solid and by measuring the amount of adsorbed gas corresponding to a monomolecular layer on the surface. The data are treated according to the BET theory [31–34]. The results of the BET method showed that the average specific surface area of MMMWCNTs was $144.68\,m^2\,g^{-1}$, which was higher than that of MWCNTs ($44.29\,m^2\,g^{-1}$) [29] since the MMWCNT adsorbent was a nanocomposite of MWCNTs and iron oxide nanoparticles.

3.2. Effect of pH

Solution pH is an important parameter that affects adsorption process of dye molecules. The solution pH would affect both aqueous chemistry and surface binding-sites of the adsorbent. The effect of the initial pH of the solution in the range 4.0–12.0 with a stirring time of 15 min on the removal of four dyes was investigated using $0.1\,mol\,L^{-1}$ HCl or NaOH solutions for pH adjustment, with the initial dye concentration fixed at $20\,mg\,L^{-1}$. The results are shown in Fig. 4. It was observed that, for all the investigated dyes, adsorption quantity increased when the pH of the solution increased from 4 to 7 and remained nearly constant at higher pHs. This can be due to the negative charge of the surface of MMMWCNTs in a wide pH range. The negative charge of the surface of the nanoparticles was also confirmed from the data on the zeta potential [28]. Therefore, the fact that cationic dyes adsorption on MMMWCNTs adsorbent increased with pH values suggested that one of the contributions of MMMWCNTs adsorption toward cationic dyes resulted from electrostatic attraction between the negatively charged MMMWCNTs adsorbent surface and the positively charged cationic dyes [28]. Ideally, wastewater is neutralized and this is an advantage for application of adsorbent in removal cationic dyes from wastewaters.
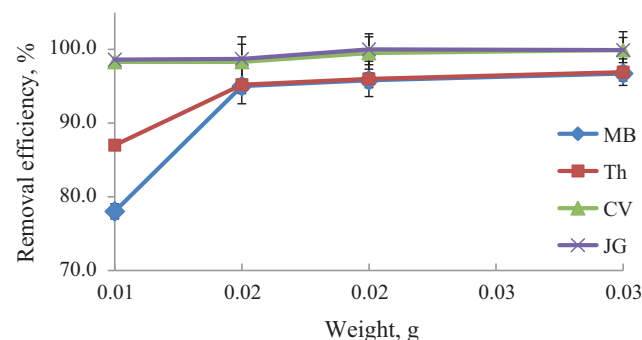

Fig. 2. TEM images of MMWCNTs.

Fig. 4. Percentage of dye removal at different pHs for JG, MB, Th and CV. Conditions: 0.015 g of MMWCNTs, 20 mL of $20\,mg\,L^{-1}$ of dye, agitation time of 15 min.
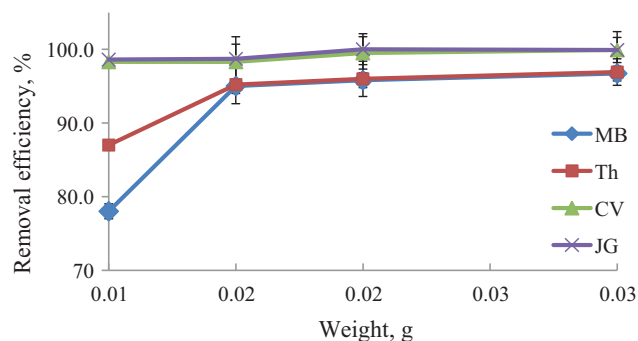
Fig. 5. Percentage of dye removal at different amount of MMWCNTs for cationic dyes. Conditions: pH 7.0, 20 mL of 20 mg L^{-1} of dye, agitation time of 15 min.

3.3. Effect of the amount of adsorbent

The dependence of the adsorption of dye on the amount of modified nanoparticles was studied at room temperature and at pH 7.0 by varying the adsorbent amount from 0.01 to 0.03 g in contact with 20 mL solution of 20 mg L^{-1} of each dye. The results are shown in Fig. 5. Apparently, the percentage removal of dyes increased by increasing amount of MMMWCNTs due to the availability of higher adsorption sites. The adsorption reached a maximum with 0.015 g of adsorbent that maximum percentage removal was about 95% for MB and Th and 100% for JG and CV.

3.4. Effect of contact time

The effect of contact time on the adsorption of dyes was studied to determine the time taken by MMMCNTs to remove 20 mg L^{-1} dye solution at pH 7.0. A 0.015 g of adsorbent was added into a 20 mL of dye solution. Absorbance of the solution at related wavelength of each dye with time was determined to monitor the dye concentration. It can be seen that after about 15 min, almost all the dye became adsorbed. The results are shown in Fig. 6. Agitation time of 15 min was selected for further works.

3.5. Adsorption isotherms

In order to optimize the use of MMMWCNTs adsorbents, it is important to establish the most appropriate adsorption isotherm. Thus, the correlation of equilibrium data by either theoretical or empirical models is essential to practical operation. Langmuir [35] and Freundlich [36] equations were used to analysis the experimental data of the MMMWCNTs adsorbents for four dyes in our work.
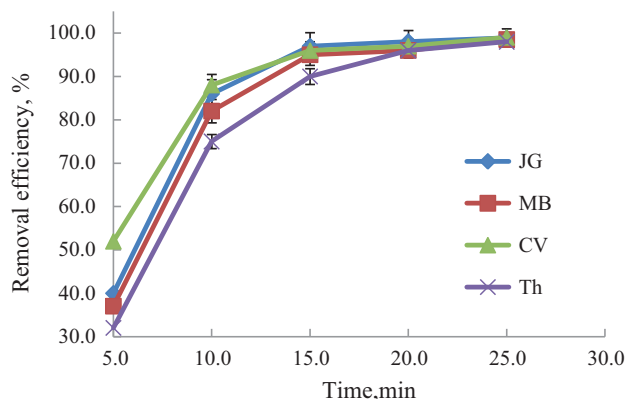

Fig. 6. The effect of contact time on the adsorption of cationic dyes on MMMWCNTs. Conditions: 20 mL of 20 mg L^{-1} of dye, pH 7, adsorbent dosage 0.015 g.
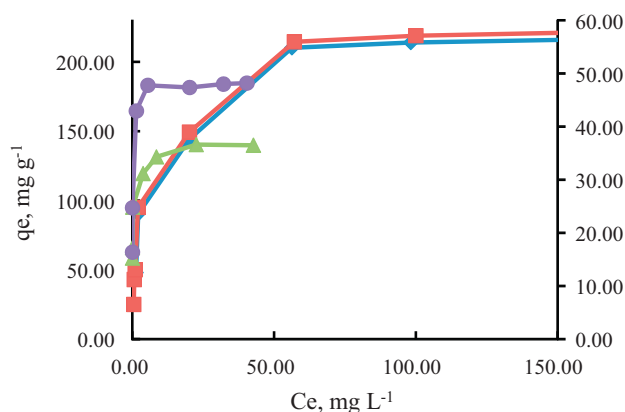

Fig. 7. Langmuir adsorption isotherm of JG, CV, MB and Th for MMWCNTs.

The absorption equilibrium curves of the four dyes to MMMWCNTs were evaluated by adding weighted samples of MMMWCNTs to 50.0 mL solutions of different concentrations of each dye at pH 7.0. The amounts of dyes in the solution were determined after equilibration.

The general form of the Langmuir isotherm is:

$$\frac{q_e}{q_m} = \frac{K_L C_e}{(1 + K_L C_e)} \tag{2}$$

where K_L is a constant and C_e is the equilibrium concentration (mg L^{-1}), q_e is the amount of dye adsorbed per gram of adsorbent (mg g^{-1}) at equilibrium concentration C_e, and q_m is the maximum amount of solute adsorbed per gram of surface (mg g^{-1}), which depends on the number of adsorption sites. The Langmuir isotherm shows that the amount of dyes adsorbed increases as the concentration increases up to a saturation point. As long as there are available sites, adsorption will increase with increasing dye concentrations, but as soon as all of the sites are occupied, a further increase in concentrations of dyes does not increase the amount of dyes on adsorbents (Fig. 7). After linearization of the Langmuir isotherm, Eq. (2), we obtain:

$$\frac{C_e}{q_e} = \left(\frac{C_e}{q_m} \right) + \left(\frac{1}{K_L q_m} \right) \tag{3}$$

The parameters of this equation for dye were calculated and are given in Table 1.

The Freundlich empirical model is represented by:

$$q_e = K_f C_e^{1/n} \tag{4}$$

where K_f (mmol$^{1-1/n}$ L$^{1/n}$ g^{-1}) and $1/n$ are Freundlich constants depending on the temperature and the given adsorbent–adsorbate couple, n is related to the adsorption energy distribution, and K_f indicates the adsorption capacity.

The linearized form of the Freundlich adsorption isotherm equation is

$$\ln q_e = \ln K_f + \left(\frac{1}{n} \right) \ln C_e \tag{5}$$

the parameters of Eqs. (3) and (5) for investigated dyes were calculated and are given in Table 1. The results indicate that the experimental data for four dyes do not fit the Freundlich model.

Table 2 shows the evaluated parameters of Eqs. (3) and (5) for investigated dyes on to CNTs. The results show capacity factor for the adsorption of JG and CV on the MMMWCNTs is higher than that for MB and Th. Therefore CNTs is the more efficient adsorbent than MMMWCNTs for the adsorption of Th and MB.

As the results show, the capacity factor for JG and CV is higher than that for MB and Th. The difference in capacity may be due to the difference in the structure of dyes. JG and CV have quaternary

Table 1
Adsorption isotherms parameters of dyes onto MMMWCNTs.

Dyes	Langmuir model				Freundlich model		
	q_{max} (mg g^{-1})	K_L (L mg^{-1})	$K_L q_{max}{}^{-1}$	r	K_f (mg$^{1-1/n}$L$^{1/n}$g^{-1})	$1/n$	r
JG	250.00	51.02	0.204	0.9989	48.23	0.343	0.914
CV	227.27	38.46	0.169	0.9980	44.74	0.351	0.879
MB	48.08	400.00	8.319	0.9982	32.69	0.134	0.842
Th	36.63	166.67	4.550	0.9997	26.26	0.108	0.925

Table 2
Adsorption isotherms parameters of dyes onto CNTs.

Dyes	Langmuir model				Freundlich model		
	q_{max} (mg g^{-1})	K_L (L mg^{-1})	b ($K_L q_{max}{}^{-1}$)	r	K_f (mg$^{1-1/n}$L$^{1/n}$g^{-1})	$1/n$	r
JG	166.67	60.24	0.36	0.9999	59.41	0.23	0.8966
CV	163.93	55.86	0.34	0.9996	85.42	0.14	0.8844
MB	76.92	144.92	1.88	0.9949	44.31	0.13	0.9156
Th	56.49	142.85	2.53	0.9998	33.20	0.12	0.9838

Table 3
Effect of type of eluting agent on recovery (%) for dyes adsorbed on MMMWCNTs ($N = 5$).

Eluent	Recovery (%)			
	Th	CV	MB	JG
Methanol	85 ± 2	93 ± 2	82 ± 3	94 ± 2
N,N-Dimethylformamide	92 ± 4	88 ± 5	91 ± 3	95 ± 4
Acetonitrile	98 ± 1	99 ± 4	99 ± 1	98 ± 2

Table 4
Comparison the calculated capacity factor for some synthetic adsorbents with proposed method.

Sorbent	Capacity factor (mg g^{-1})				Ref.
	MB	Th	JG	CV	
Maghemite modified by SDS	–	200	172	–	[29]
MMWCNTs	15.87	–	–	–	[23]
MMWCNTs(Fe$_2$O$_3$)	42.3	–	–	–	[24]
MMMWCNTs	48.1	36.4	250	227	Proposed method

ammonium group and MB and Th are cationic sulfide dyes. In the JG and CV the positive charge is dispersed on the molecule and in two other dyes the positive charge is located on the heteroatom ring. Therefore the adsorption of CV and JG on the adsorbent is better than that for MB and Th dyes.

3.6. Desorption and reuse study

In order to evaluate the possibility of regeneration and reuse of the MMMWCNTs adsorbent, desorption experiments have been performed.

Dye desorption from the MMMWCNTs was conducted by washing the dyes loaded on MMMWCNTs using 5.0 mL of methanol, N,N-dimethyl formamide and acetonitrile. For this purpose 5.0 mL of eluent was added to the 0.015 g of dye loaded MMMWCNTs in a beaker. The MMMWCNTs were collected magnetically from the solution. The concentration of dyes in the desorbed solution was measured spectrohotometrically. The results are given in Table 3. As the results show, desorption efficiencies for acetonitrile were higher than other solutions. It was notable that the equilibrium of desorption was achieved within about 2 min, that was fast, similar to the adsorption equilibrium. This was due to the absence of internal diffusion resistance. After elution of the adsorbed dyes, the adsorbent was washed with DDW and vacuum dried at 25 °C overnight and reused for dye removal. The reusability of the sorbent was greater than 5 cycles without any loss in its sorption behavior. Therefore, the MMMWCNTs can be a good reusable and economical sorbent.

4. Conclusion

A simple and effective method was presented for removal of cationic dyes from water samples using MMMWCNTs. When iron oxide nanoparticles were adsorbed on the surfaces of MWCNTs, dispersed among the MWCNTs, or encapsulated into the interiors of MWCNTs. The prepared magnetic adsorbent can be well dispersed in the water and can be easily separated magnetically from

the medium after adsorption. The rapid adsorption rate is mainly attributed to their unique carbon nanotubes multi-walled structure and carboxylic groups on the carbon nanotube shell providing large surface area and good affinity for the facile and fast adsorption of dye molecules. Table 4 shows the comparison results of our procedure with some methods [23,24,36]. It should be highlighted that the major advantages that the magnetic separation offers is the ability to recover the dye from the nanoparticles and reticulate the particles for further dye separations and easily separated magnetically from the medium after adsorption vs. MWCNTs. Also, the short duration of these experiments have significant practical importance, as it will facilitate smaller reactor volumes ensuring efficiency and economy.

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