

Original Article

Removal of Anionic Dyes (Direct Blue 106 and Acid Green 25) from Aqueous Solutions Using Oxidized Multi-Walled Carbon NanotubesSoheil Sobhanardakani¹ *Raziyeh Zandipak²

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Abstract

Background and purpose: The presence of dyes in wastewaters may cause serious problems for the environment because of their high toxicity to aquatic organisms and unfavorable aesthetical impact. In the present study, multi-walled carbon nanotubes (MWCNTs) were used for removal of anionic dyes Direct Blue 106 (DB106) and Acid Green 25 (AG25), from water samples.

Materials and Methods: MWCNTs were oxidized and characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). In batch tests, the effects of various parameters such as pH solution (2.0-7.0), oxidized MWCNT dose (0.01-0.04 g), contact time (7-60 minutes), initial dye concentration (30-350 mg/l), and temperature (25-55° C) were investigated.

Results: The optimum pH for removing of investigated anionic dyes from water solutions was found to be 2.0. The adsorption of the dyes reached equilibrium at 15 minutes. Langmuir, Freundlich and Temkin models were used to study the adsorption isotherms and the equilibrium adsorption was best described by Langmuir isotherm model. Kinetic adsorption data were analyzed using pseudo-first-order kinetic model and pseudo-second-order model. The regression results showed that the adsorption kinetics was more accurately represented by pseudo-second-order model.

Conclusion: The results suggest that oxidized MWCNT could be employed as an effective material for the removal of anionic dyes from aqueous solutions and the maximum adsorption capacity was found to be 500 and 333 mg/g for DB106 and AG25, respectively.

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Key words: Adsorption, Direct Blue 106, Acid Green 25, Oxidized Multi-Walled Carbon Nanotube, Removal Efficiency

1. Introduction

Dyes are widely used in various industries including textile, cosmetic, paper, plastics, rubber, and coating and their discharge into water causes serious environmental and health problems (1-3). Most of these dyes contain aromatic rings, which make them carcinogenic and mutagenic. These dyes also cause serious ecological problems; for example, they significantly affect the photosynthetic activity of aquatic plants by reducing light penetration, and they may be toxic to some aquatic organisms (4,5).

Therefore, various methods have been developed for the removal of dyes, such as adsorption, coagulation, photo-degradation, electrochemical, membrane separation, and biological method (6,7). The adsorption is an excellent alternative selection especially using high adsorption capacity adsorbent without requiring any additional pre-treatment step before application (8,9). In general, the activated carbon is an effective adsorbent for dyes removal, but the high cost of activated carbon has restricted its widespread use (10).

Recently, more researchers have been focused on using carbon nanotubes (CNTs) as an adsorbent due to large specific surface areas (SSA), small pore sizes and unique structures (11,12). CNTs include single-walled CNTs and multi-walled CNTs (MWCNTs) depending on the amount of layers. CNTs have been used for the removal of dyes, zinc(II), fluoride, lead(II), chromium(VI), and mercury(II) (13,14).

The adsorption capacity of CNTs can be improved by oxidation with KMnO_4 , H_2O_2 , NaOCl , or HNO_3 . Oxidation can remove impurities of CNTs, increases the surface area, and introduces oxygen-containing functional groups, thus altering adsorption characteristics (15).

Yao et al. (16) investigated the adsorption behavior of methylene blue on CNTs. Machado et al. (17) investigated the adsorption of Reactive Red M-2BE dye from

water solutions by MWCNTs and activated carbon. Yang et al. (18) reported adsorption of Ni(II) on oxidized MWCNTs. Ghaedi and Nasiri Kokhdan (19) reported the oxidized MWCNTs for the removal of methyl red: kinetics and equilibrium study. Comparative study of maximum adsorption capacity of different adsorbents indicates that adsorption capacity for the oxidized MWCNTs were higher than non-oxidized MWCNTs.

In the present study, oxidized MWCNTs were used for removal of anionic dyes from aqueous solution. The influence of variables including the initial pH value, initial dye concentration, amount of adsorbent, contact time, and temperature on dyes adsorption was investigated. Isotherm and kinetics of adsorption were evaluated.

2. Materials and Methods

2.1. Instruments and reagent

All chemicals used were of analytical reagent grade and purchased from Merck (Darmstadt, Germany). Double-distilled water (DDW) was used in all experiments.

MWCNTs with lengths of 5-15 μm , outer diameter of 50-80 nm, inner diameters of 5-10 nm and purity of ≥ 95 were purchased from Sigma-Aldrich (Madrid, Spain).

Stock solutions of dyes were prepared by dissolving an appropriate amount of their powder in 100 ml DDW. Dye solutions of initial concentrations of 30-350 mg/l were prepared by diluting the stock solution in appropriate proportions.

All concentrations of solutions were measured using a UV-Vis spectrophotometer (Lambda 45, Perkin-Elmer, USA). A pH meter (780, Metrohm, Switzerland), equipped with a combined Ag/AgCl glass electrode was used for pH measurements. Morphology and structure of the oxidized MWCNTs were characterized by scanning electron microscope (SEM-EDX, XL30 and Philips, Eindhoven, Netherland). SSA was defined by N_2 adsorption-desorption

porosimetry (77 K) using a porosimeter (Bel Japan, Inc., Osaka, Japan).

2.2. Oxidation of MWCNTs

For oxidation, 2 g MWCNTs were placed in a 1 L round bottom flask with reflux condenser and 300 ml concentrated nitric acid (65%) were added. The mixture was refluxed for 48 hours at 120° C, cooled to room temperature, diluted with 500 ml DDW, and vacuum-filtered through filter paper (3 μm porosity, Whatman, Maidstone, UK). Washing was repeated until the pH became neutral, followed by drying in a vacuum oven at 100° C (20).

2.3. Batch adsorption experiments

Dye removal experiments with the oxidized MWCNTs were performed in 50 ml beakers containing 2.5 ml of anionic dyes Direct Blue 106 (DB106) and Acid Green 25 (AG25) solutions (30 mg/l) and 0.025 g of oxidized MWCNTs. The pH of the solution was adjusted at 2.0, using 0.1 mol/l HCl and/or 0.1 mol/l NaOH solutions. The mixture was shaken at room temperature in a temperature controlled shaking water bath for 15 minutes and the dye loaded oxidized MWCNTs was separated, and the concentrations of the dyes which remained in the solution were determined by UV-visible spectrophotometry (Lambda 45, Perkin- Elmer, Waltham, USA) at 594 and 640 nm for DB106 and AG25, respectively.

The dyes removal efficiency was calculated using Equation 1.

$$\text{Dye removal efficiency(\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

Where: C_0 and C_e (mg/l) were the initial and final dye concentrations (21).

The equilibrium adsorption capacity was calculated using Equation 2.

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (2)$$

Where: q_e (mg/g) is the equilibrium adsorption capacity, C_e is the dye concentration at equilibrium, V (L) is the volume of solution and W (g) is the weight of adsorbent (22).

3. Results

Figure 1a shows the morphological structure of oxidized MWCNTs. Figure 1b shows the FTIR spectrum of oxidized MWCNTs.

Primary study shows that the adsorption efficiency depends strongly on the solution pH, CS dose, initial dye concentration, contact time, and temperature.

The effect of initial pH of solution in the range 2.0-7.0 with a contact time of 15 minutes on the removal of two dyes was investigated with the initial dye concentration fixed at 30 mg/l. The results are shown in figure 2. It was observed that, for all the investigated dyes, adsorption quantity decreased when the pH of the solution increased from 2.0 to 7.0.

The dependence of the adsorption of dyes to the amount of oxidized MWCNTs was studied at temperature 25° C and at pH 2.0 by varying the adsorbent amount from 0.01 to 0.04 g in contact with 30 mg/l of each dye. The results are shown in figure 3.

The effect of contact time on the adsorption DB106 and AG25 using oxidized MWCNTs was investigated individually. The initial dye concentrations for all test solutions were 30 mg/l and pH 2.0 and oxidized MWCNTs dose were fixed at 0.025 g. The results are shown in figure 4. It is clear from the figure 4 that anionic dyes uptake is rapid in the first 15 minutes.

Figure 5 shows the effect of initial dyes concentration on the adsorption of the dyes at pH 2.0, oxidized MWCNTs dose 0.025 g, and at temperature 25° C. Equilibrium uptake has been decreased with increase in the initial dyes concentration in the range of concentrations 30-350 mg/l.

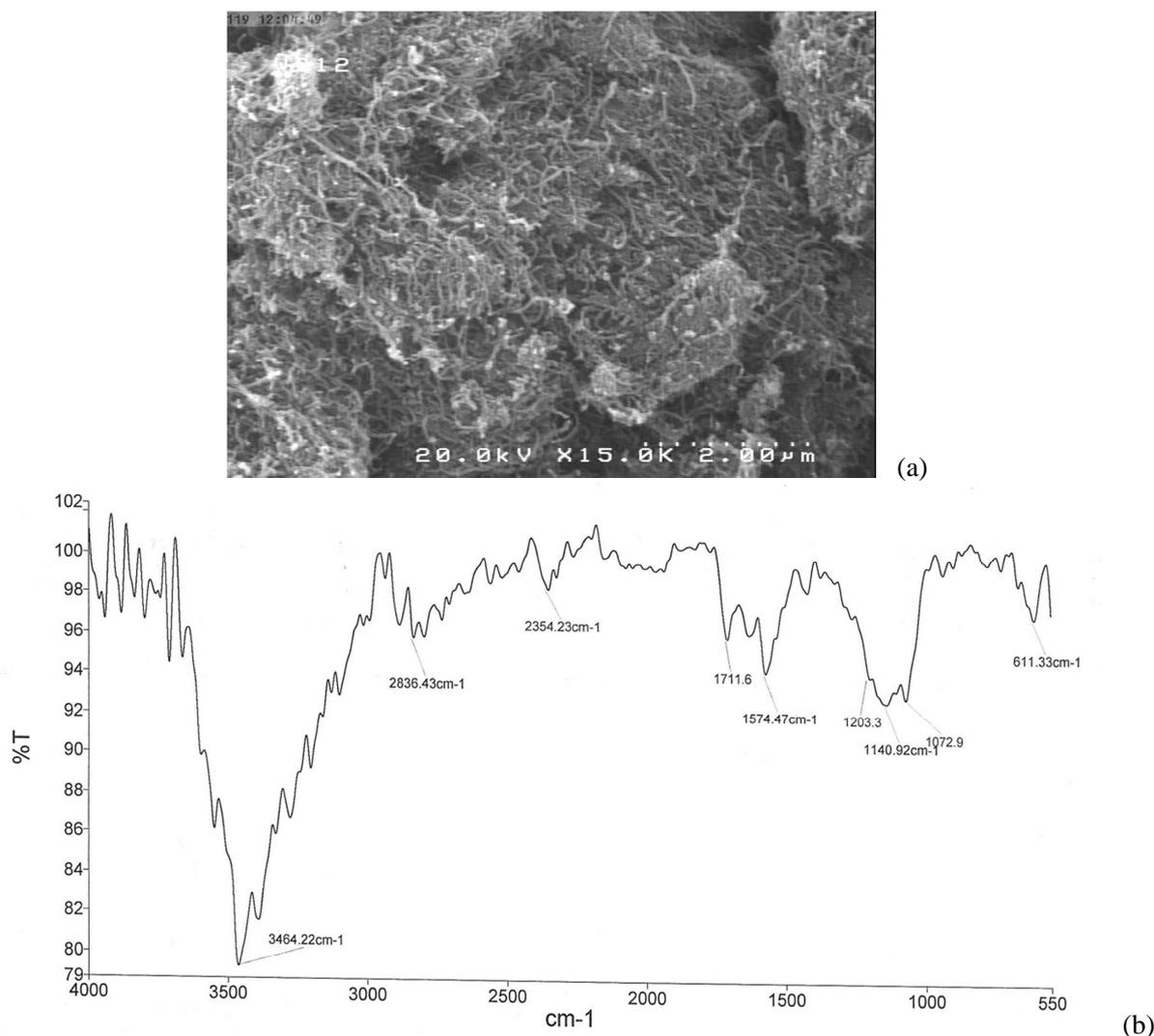


Figure 1. (a) Scanning electron microscope image of oxidized multi-walled carbon nanotubes (MWCNTs). (b) Fourier transform infrared spectrum of oxidized MWCNTs.

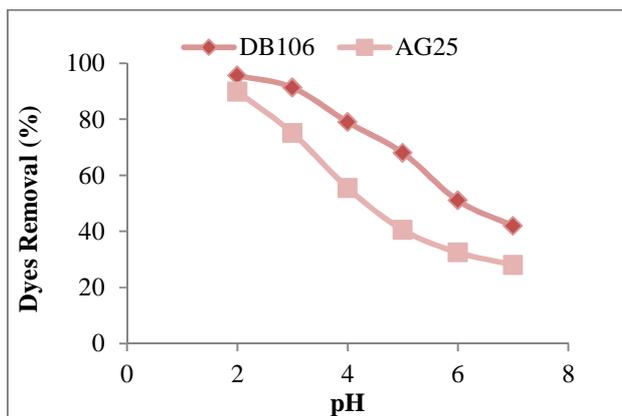


Figure 2. Effect of pH on the removal of dyes from aqueous solution by oxidized multi-walled carbon nanotubes (MWCNTs), ($C_0= 30$ mg/l, contact time = 15 minutes, dose of oxidized MWCNTs = 0.025 g/l, temperature = 25° C)

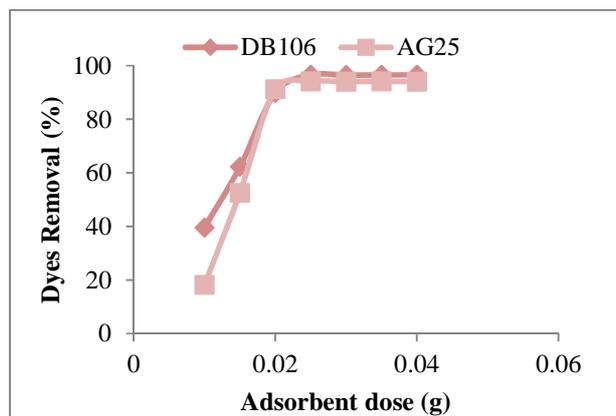


Figure 3. Effect of dose of oxidized multi-walled carbon nanotubes (MWCNTs) on the removal of dyes ($C_0= 30$ mg/l, initial pH = 2.0, contact time = 15 minutes, temperature = 25° C)

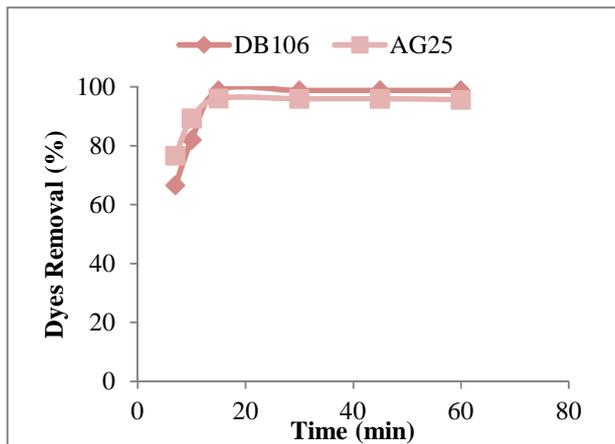


Figure 4. Effect of contact time on the removal of dyes by oxidized multi-walled carbon nanotubes (MWCNTs) ($C_0 = 30$ mg/l, initial pH = 2.0, dose of oxidized MWCNTs = 0.025 g/l, temperature = 25° C)

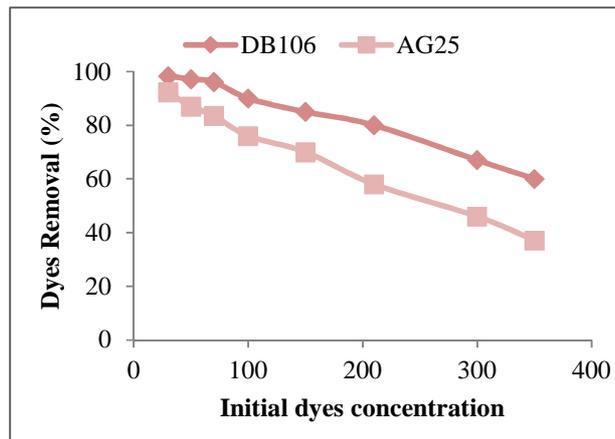


Figure 5. Effect of initial dyes concentration on the removal of dyes by oxidized multi-walled carbon nanotubes (MWCNTs) (Initial pH = 2.0, contact time = 15 minutes, dose of oxidized MWCNTs = 0.025 g/l).

In order to observe the effect of temperature on the adsorption capacity, experiments were carried out at four different temperatures (25, 35, 45, 55° C) for each dye using 0.025 g of oxidized MWCNTs and dye concentration of 30 mg/l (Figure 6).

In order to explore the adsorption mechanism of DB106 and AG25 onto oxidized MWCNTs, two kinetic models including the pseudo-first-order and the pseudo-second-order models were used (Figures 7 and 8). The kinetic parameters and the correlation coefficients (R^2) were determined by linear regression, and the results are given in table 1.

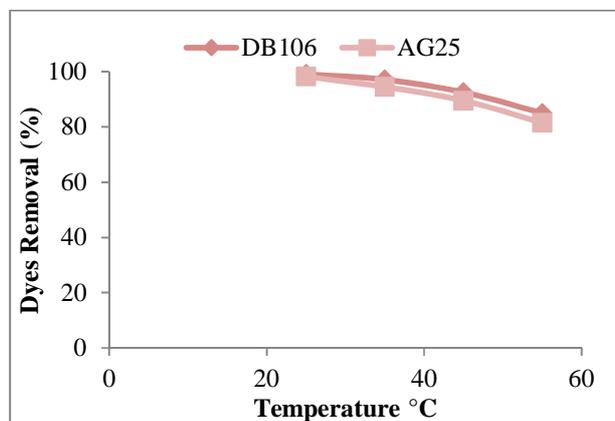


Figure 6. Effect of temperature on the removal of dyes by oxidized multi-walled carbon nanotubes (MWCNTs) ($C_0 = 30$ mg/l, initial pH = 2.0, contact time = 15 minutes, dose of oxidized MWCNTs = 0.025 g/l).

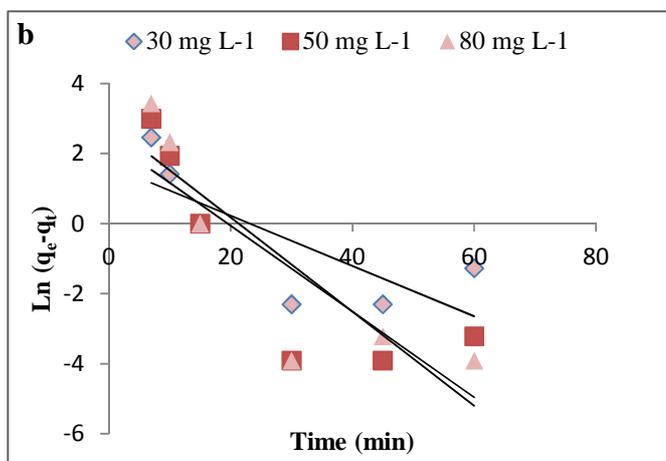
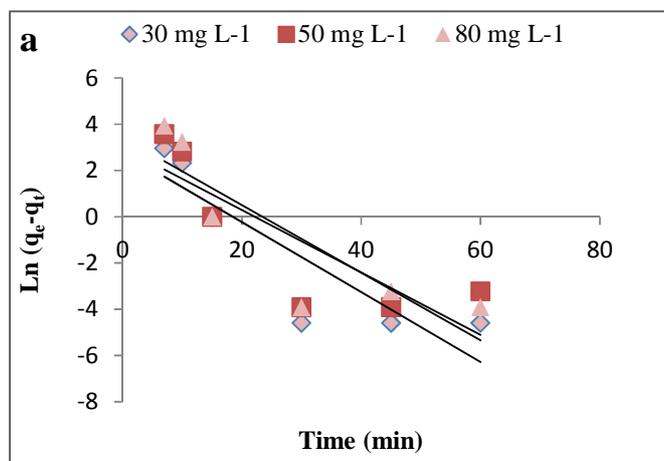


Figure 7. Pseudo-first-order kinetic plot for the adsorption of (a) Direct Blue 106, and (b) Acid Green 25 onto oxidized multi-walled carbon nanotubes at 25° C

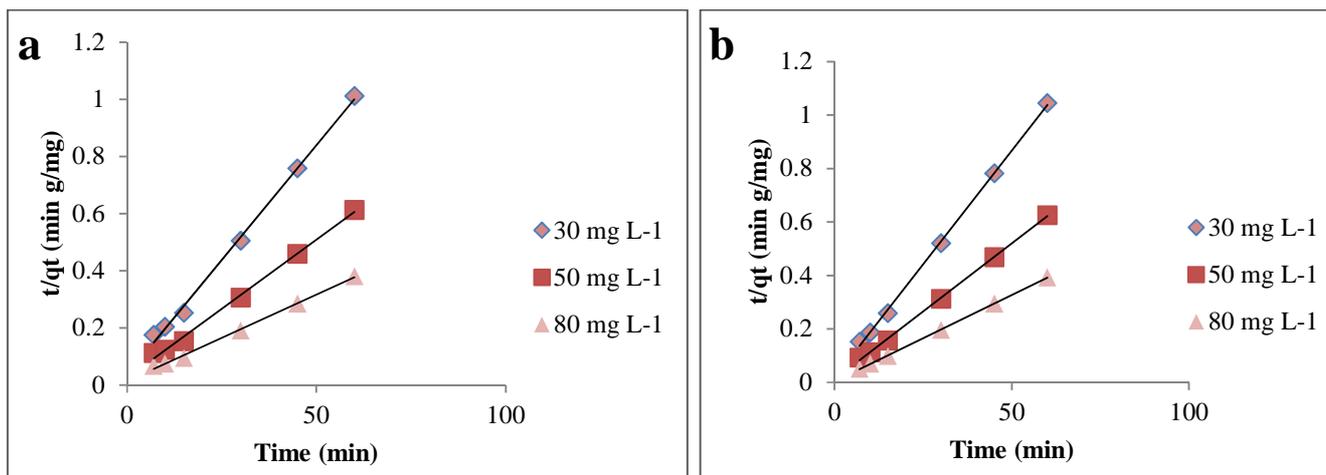


Figure 8. Pseudo-second-order kinetic plot for the adsorption of (a) Direct Blue 106, and (b) Acid Green 25 onto oxidized multi-walled carbon nanotubes at 25°C

Table 1. Pseudo-first order and pseudo-second order kinetic model parameters for the adsorption of dyes onto oxidized multi-walled carbon nanotubes (MWCNTs)

Dye	C ₀ (mg/l)	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model		
		q _e exp (mg/g)	q _{e1} (mg/g)	k ₁ (min ⁻¹)	R ²	q _{e2} (mg/g)	k ₂ (g/mg/min)	R ²
DB106	30	59.3	16.23	0.151	0.783	62.5	0.0060	0.997
DB106	50	98.0	19.80	0.135	0.706	111.1	0.0032	0.996
DB106	80	157.5	30.81	0.146	0.747	166.6	0.0027	0.997
AG25	30	57.7	5.29	0.071	0.593	58.0	0.0180	0.999
AG25	50	96.0	10.95	0.122	0.713	100.0	0.0090	0.999
AG25	80	153.0	17.49	0.134	0.760	165.0	0.0120	0.999

DB106: Direct Blue 106, AG25: Acid Green 25, MWCNTs: Multi-walled carbon nanotubes

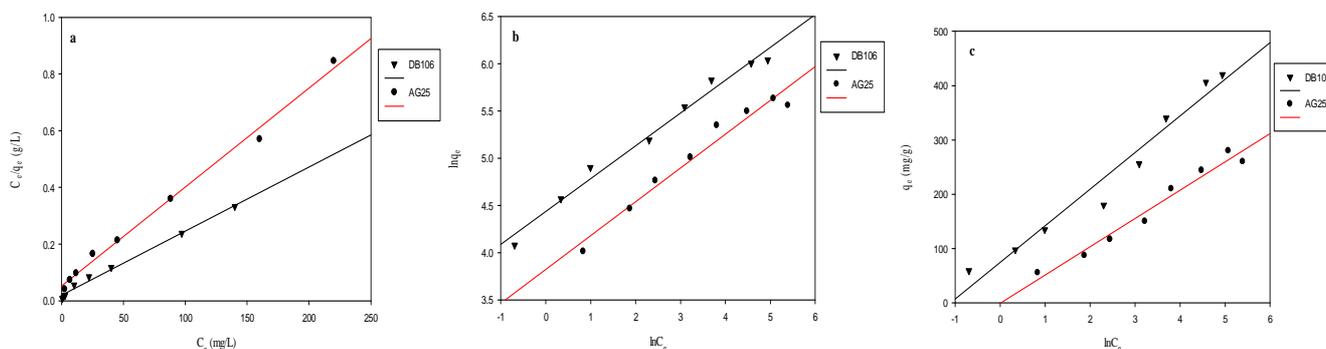


Figure 9. (a) Langmuir, (b) freundlich, and (c) temkin isotherms for dyes adsorption onto oxidized multi-walled carbon nanotubes at 25°C

Table 2. Isotherm parameters of adsorption of dyes onto oxidized Multi-walled carbon nanotubes (MWCNT)

Dye	Adsorbent	Langmuir			Freundlich			Temkin		
		b (l/mg)	q _m	R ²	K _f (mg ^{1-1/n})	n	R ²	K _T (l/mg)	b	R ²
DB106	Oxidized	0.10	500	0.992	27.1	2.88	0.984	1.100	67.510	0.962
DB106	MWCNT	0.03	250	0.996	20.9	2.71	0.947	9.206	0.368	0.947
AG25	Oxidized	0.05	333	0.994	66.5	2.80	0.963	0.017	52.030	0.968
AG25	MWCNT	0.09	125	0.998	30.3	3.89	0.770	13.540	0.257	0.770

DB106: Direct Blue 106, AG25: Acid Green 25, MWCNTs: Multi-walled carbon nanotubes

The adsorption isotherms of DB106 and AG25 on oxidized MWCNTs were studied under the optimized conditions: adsorbent dose of 0.025 g, contact time of 15 minutes and solution pH 2.0. Figure 9 and table 2 show the adsorption isotherms of two dyes onto oxidized MWCNTs at temperature 25° C.

4. Discussion

Figure 1a shows the morphological structure of oxidized MWCNTs. SEM clearly suggests the crystalline tubular structure of nanotubes. Figure 1b shows the FTIR spectrum of oxidized MWCNTs, indicating that the acid treatment process introduces new functional groups. The peak at 3464.22/cm, 1574.47/cm, and 1711.6/cm is attributed to the hydroxyl groups, carboxyl groups and carbonyl groups. These functional groups provide a large number of chemical adsorption sites and thereby can increase the adsorption capacity of oxidized MWCNTs.

SSAs are commonly reported as BET surface areas obtained by applying the theory of Brunauer, Emmett, and Teller (BET) to nitrogen adsorption or desorption isotherms measured at 77 K. This is a standard procedure for the determination of the SSA of sample. The SSA of the sample is determined by physical adsorption of gas on the surface of the solid and by measuring the amount of adsorbed gas corresponding to monomolecular layer on the surface. The data are treated according to the BET theory (23,24).

The results of the BET method showed that the SSA of MWCNTs and oxidized MWCNTs were 115 m²/g and 158 m²/g, respectively.

Pore size distributions of MWCNTs and oxidized MWCNTs were measured using the Barrett, Johner, and Halenda method. The average pore diameter and pore volume were 29 nm, and 0.17 cm³/g for MWCNTs and 36

nm, and 0.24 cm³/g for oxidized MWCNTs, respectively (25).

The results indicated that the pore volume and average pore diameter of MWCNTs are less than oxidized MWCNTs. This can be comprehended considering the structure change of oxidized MWCNTs with nitric acid which can easily break up the MWCNTs into smaller pieces with large amount of defects on their surface and open the tips, probe the holes through the MWCNTs (26).

The pH of the system is very effective on the adsorption amount of dye molecules presumably due to its influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecules. Figure 2 presents the results of the effect of the solution pH on the removal efficiency of each dye. It was observed that removal percent decreased from 95% to 42% for DB106 and from 89 to 28% for AG 25, when the pH of solution increased from 2.0 to 7.0 and the maximum adsorption capacity for both dyes, observed at pH 2.0. The zero point charge (pH_{ZPC}) for the oxidized MWCNTs was determined around 5.0 (18). At lower pH values (pH < pH_{PZC}) the oxidized MWCNTs surface will be positively charged and the electrostatic interaction between the negatively charged dyes molecules and the oxidized MWCNTs surface sites increased which favored the uptake of dye anions. At higher pH values (pH > pH_{PZC}) the oxidized MWCNTs surface becomes more negatively charged and the electrostatic repulsion between the dyes molecule and the oxidized MWCNTs surface sites increased which lead to decrease in uptake of dyes. At high pH, also there is competition between OH⁻ and dye anions for positively charged adsorption sites. Similar phenomenon has also been shown in the adsorption of sunset yellow dye from water with cadmium hydroxide nanowires loaded on activated carbon (27).

As shown in figure 3, by increasing the oxidized MWCNTs dose from 0.01 to 0.025 g,

the removal efficiency (%) of dyes increased from 39% to 96% for DB106 and from 18% to 94% for AG25 and remained nearly constant at higher doses. This can be attributed to the increase in the adsorbent surface area and availability of more active adsorption sites on the oxidized MWCNTs surface with increasing the dose of the adsorbent.

Contact time also played major role during adsorption process. The decrease in the concentration of dyes with increase time is due to its adsorption on oxidized MWCNTs (Figure 4). It was found that the adsorption rate is rapid at the initial stages and the system reach equilibrium about 15 minutes. The rapid adsorption at the initial contact time can be attributed to the availability of the reactive site of adsorbent, while at higher time due to the saturation of adsorbent the removal rate do not change significantly. Similar results were observed by Afkhami who investigated the effect of contact time on the removal of Congo red from aqueous solution by maghemite nanoparticles and indicated that adsorption increases with increasing contact time (28).

The adsorption capacity is dependent on the initial dyes concentration. Figure 5 shows the effect of initial dyes concentration on the adsorption of the dyes. At a constant oxidized MWCNTs dose, the decrease in the adsorption efficiency is probably due to the saturation of the active binding sites on the oxidized MWCNTs surface at higher dyes concentrations. On the other hand, by increasing the initial DB106 and AG25 concentrations the actual amount of dyes adsorbed per unit mass of the oxidized MWCNTs increased. The higher initial DB106 and AG25 concentrations provides an important driving force to overcome the mass transfer resistance for DB106 and AG25 transfer between the solution and the surface of the oxidized MWCNTs. Similar results were observed by Karami who investigated the effect of initial concentration of metals

ions on removal of heavy metal from aqueous solution by magnetite nanorods and indicated that adsorption decreases with increasing initial concentration of metals (29).

Furthermore, the results showed that the adsorption capacity of dyes onto oxidized MWCNTs decreased with increase in temperature for both the dyes that indicating the process is exothermic in nature and by the weakening of bonds between dye molecules and oxidized MWCNTs of adsorbents at high temperatures (Figure 6).

Adsorption kinetics expresses the nature of adsorption interaction dependence (physical and/or chemical) of the adsorbents with adsorbate species. In this study, two kinetic models (pseudo-first-order equation and pseudo-second-order equation) were applied (Figures 7 and 8). It can be seen that values of correlation coefficients for pseudo-second-order model are greater than those of pseudo-first-order model (Table 1). Moreover, the calculated values of q_e for pseudo-second-order model are in good agreement with the experimental values of q_e which indicates that the adsorption process follows the pseudo-second-order kinetics.

Analysis of equilibrium data is important for evaluating adsorption properties of oxidized MWCNTs adsorbent. The adsorption isotherm experiments of different dyes onto oxidized MWCNTs were fitted to Langmuir, Freundlich, and Temkin isotherm models (Figure 9).

The values of the parameters are given in table 2. By comparing the correlation coefficient values obtained from the Langmuir, Freundlich, and Temkin isotherm models, it can be evaluated that the Langmuir isotherm model is more suitable for describing DB106 and AG25 adsorption onto oxidized MWCNTs. The Langmuir isotherm model assumes that a monolayer adsorption exists on the adsorbent surface with a finite number of identical sites that all sites are energetically equivalent, and that there is no interaction

between the adsorbed molecules and homogeneous distribution of active sites on the surface of oxidized MWCNT and indicates that the maximum adsorption capacity of oxidized MWCNT for DB106 and AG25 is 500 and 333 mg/g.

Oxidized MWCNT used as an effective adsorbent for the removal of anionic dyes from aqueous solutions. The batch adsorption process was dependent on some experimental parameters such as pH, initial dye concentration, contact time, adsorbent dose, and temperature. It was observed that the adsorbed amount of dyes increased with increase in contact time and reached the equilibrium after 15 minutes. The optimum pH for the maximum removal of dyes was found at in strong acidic solutions. Furthermore, adsorption capacity of dyes on oxidized MWCNTs decreases with temperature. The isotherm parameters for the Langmuir, Freundlich, and Temkin models were determined and the equilibrium data were best described by the Langmuir isotherm model. The adsorption kinetics was well described by pseudo-second-order model.

Conflict of Interests

The Authors have no conflict of interest.

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