Dyes removal by use carbon nanotube and carbon nanotube functional group.

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Abstract. Batch experiments were accomplished to remove methylene blue as a cationic dye onto multi wall carbon nanotubes (MWCNTs) and carbon Nano tube functional group (fMWCNTs). The results of predominant variables governing the efficiency of the manner which include, dye concentration, MWCNTs dosage, contact time, stirring speed and pH have been studied. Experimental effects have shown that, the quantity of dye adsorption elevated with elevating CNTs dosage and stirring velocity. in addition to its far lower with decreasing of the initial concentration of the dye. The dye elimination using 400 mg/L of MWCNTs changed into extra than 98%. The dosage (400 mg/L) is the optimum dosage of functionalized CNTs (fMWCNTs) to remove of methylene blue with removal more than 98%. The adsorption kinetic information was analysed the use of pseudo-2nd-order models. It has become determined that the pseudo-2d-order kinetic version became the most suitable version, describing the adsorption kinetics. Adsorption isotherm onto the (fMWCNTs) has become determined with 40 mg/L as methylene blue concentration. Equilibrium time turned into 80 min. Equilibrium statistics had been suited for the Langmuir and Freundlich isotherm models and isotherm constants have been determined.

Key words: Multi wall Carbon nanotubes, methylene blue, adsorption, equilibrium and kinetic

Introduction: Industrial dyes materials are one of the most important pollutants of water and wastewater. Its infection troubles in different ways: Even at very low concentration of dye in water, is noticeably seen and unwanted; prevent the penetration of sunlight through water; Discouraged aquatic life; reduce photosynthesis and obstruct gas solubility in water bodies. Those materials cannot decay effortlessly (Wang et al., 2008b; Baldez et al., 2008), (Garg et al., 2004;)

Consequently, it's far essentially to remove dye component from wastewater. The manners which followed for treating wastewaters containing dye are electrochemical, chemical oxidation, coagulation and flocculation, liquid–liquid extraction and adsorption (Shahryari et al., 2010). Adsorption is an effective manner for eliminating organic matter
from aqueous solutions in terms of cost, ease of design, facility of operation and insensitivity to poisonous components (Lata et al., 2007; Wang et al., 2005b).

Methylene blue (MB) need totally requisitions (coloring paper, impermanent hair colorant, coloring cottons, wools and covering for paper stock). MB was employed as the organic pollutant to be treated by CNTs in this work. The consequences of pH, contact time, agitation speed, MB concentration and fMW CNTs dosage have been scrutinized.

**Adsorbent.** A MWCNTs from (Sigma-Aldrich company) products of USA with outer diameter =10 nm ±1nm, the interior diameter is 4.5nm ± 0.5 nm and the particles length is 3-6 µm surface area of 220 m2/g with purity more than 98%. Fig1 shows functionalization of Carbon Nanotubes steps.

**Adsorbate** the MB that utilized for this research as a basic dye which is collected from scientific bureaus in the local markets. The maximum wave length 637.5 nm as the UV spectrophotometer scan chart. The choice of MB dye as an adsorbate was due to its known strong adsorption onto solids, adsorption capacity 11-28 g/100g, [Cheung et al., 2009].

**Preparation of MB:** To determine the calibration curve of MB dye, stock solution of 40 mg/l was prepared, a (10, 15, 20, 25, 30 and 35) mg/l was collected from the stock by use dilution equation (C1V1=C2V2). The absorbance of each concentration collected by use A spectrophotometer at predetermined maximum wavelength (λ max =637.5 nm). The calibration curve shown in fig (2) was drawn by MB concentration versus the absorbency, the MB dye concentration in solution (Ce) can be calculated from the straight line equation . Fig (3. A) shows the treatment application, (3.B) shows the preparation of stock solution and diluted concentration.

![Fig1. Functionalization of Carbon Nanotubes MWCNTs, A. Raw MWCNTs, B. Sonication C. Vacuum filter system and D.fMWCNTs](image)

![Fig.2: Calibration Curve of MB Dye at (λ max=637.5nm).](image)
**Tools and Equipment: Tools and equipment are utilized in this work are listed in table 1.**

| NO. | Tools and equipment | Manufacturing |
|-----|---------------------|--------------|
| 1-  | Electronic balance (Sartorius BL 210S), M-Power Gem, Gold |                  |
| 2-  | pH meter type (5011A, Ezodo) | Japan |
| 3-  | Spectrophotometer, (6800 UV- Jenway Type) | Germany |
| 4-  | Conical flasks (100 ml) |                  |
| 5-  | Filter paper (type WINLAB qualitative, D=15cm) | Germany |
| 6-  | Sulfuric acid and nitric acid for functionalization the MWCNTs. | England |
| 7-  | Vacuum motor. | China |
| 8-  | Vacuum filtration system as shown in fig(3.8) | Germany |
| 9-  | 1. Hydrochloric acid (HCl) and Sodium hydroxide (NaOH)to control the pH. | England |
| 10- | Oven for drying the sample, (DZF, 2060) | China |
| 11- | Flow meter to control the flow inter to the column. | China |
| 12- | Shaker type (Daihan Lab tech) | Korea |
| 13- | 1.5 CM in diameter Pyrex glass adsorption column | Germany |
| 14- | 20 L Plastic tank with its fittings | China |
| 15- | Sonication 60 KHz | China |
| 16- | Magnetic stirrer | China |

**Adsorption equilibrium experiments**

Batch approach gets to be utilized due to its effortlessness. Content of 40 mg/l methylene blue, concerning illustration those beginning concentration, needed been treated with 200, 300, 400, 500, 600, Furthermore 700 mg/l for fMWCNTs individually. The combos were agitated on magnetic stirrer for 80 min, as the equilibrium time, at 25°C. After an 80 min, The suspension might have been separated utilizing An 0. 2 µm filter,(Schleicher and Schuell, ref. No. 104 62 200) and the filtrates were analysed for remaining methylene blue concentration using spectrophotometer toward An wave period 637.5 nm. The measure for methylene blue uptake by means of fMWCNTs for each might have been ascertained utilizing the equation below:

\[
q = \frac{(C_0 - C_e)v}{w} \quad (1).
\]

Collection efficiency (%) was estimated by subsequent equation:

\[
\text{collection efficiency (\%)} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100\% \quad (2)
\]

in which; \(q\) will be methylene blue adsorbed by utilizing fMWCNTs (mg g\(^{-}\)), \(C_0\) and \(C_e\) are the initial and effluent dye concentrations (mg L\(^{-}\)), respectively, \(v\) will be those volume of solution (L), Also \(W\) will be the adsorbent dosage (g).

**RESULTS AND DISCUSSION**
Effluence of initial dye concentration:

Figure (4) shows the Effluence of initial dye concentration on adsorption rate of MB. It can be notice that the equilibrium contact time was at 80 min. The initial MB concentration has been expanded from 40 to 120 mg L-1, the quantity of dye that adsorbed by fMWCNTs has been expanded from 98.23 (98 %) to 189.1 (65 %) under the equilibrium conditions at a consistent temperature of 25 °C. Consequently, the percentage of adsorption falls with growth of adsorption amount at increasing dye concentration this is coming from the truth that the preliminary concentration of MB supplies an essential driving force frustrate the resistance to mass transfer. In addition, fMWCNTs with increasing initial MB concentration may increase their loading capacity.

![Graph of Effluence of initial dye concentration on adsorption rate of MB](image)

Fig. 4: Effect of Initial MB Concentration on Removal Efficiency by fMWCNTs, (pH=6, Adsorbent Dose=0.04 g, S =250 rpm).

Effluence of pH: The value of PH ranging between (2-10) was taken for MB dye. Fig (5) shows that firstly, increase in removal efficiency from 99.92 at pH 2 to 100% at pH 6. Then, there are slightly decreases in removal efficiency equal to 99.64 at pH 10 .The optimum pH was obtained as 6 with maximum removal of MB dye was found to be 100% . At acidic phase, a positively charged on fMWCNTs sites and the positively charged MB dye increase, the same finding recorded by, P. S. Kumar et al, 2014.

![Graph of Effluence of pH](image)

Fig. 5: Effect of pH on Adsorption of MB by fMWCNTs, (C0=40 mg/L, Adsorbent Dose = 0.04 g, and S =250 rpm).
Influence of Adsorbent dose: Doses between 0.02 to 0.07 g of MWCNTs were taken in 100-ml volumetric flasks having initial MB dye concentration of 40 mg/L at contact time 80 and 120 min at pH 6. The removal profile of MB versus different dosages of MWCNTs is shown in Figure 6. The efficiency of removing MB growth as the dosage of MWCNTs increase. 99.7% of MB was removed after 80 min using 0.4 g/L of fMWCNTs, the dosage of fMWCNTs reduced to 0.2 g/L, the removal efficiency of MB was still 80%. While at 120 min contact time the removal efficiency was 99.96% and 94.5% by using 0.4 g/L and 0.2 g/L respectively. At larger dosage of fMWCNTs resulted in more adsorptive active sites. 0.4 g/L is the optimal dosage of fMWCNTs at the equilibrium condition at 80 min.

Fig. 6: Removal Efficiency of MB by fMWCNTs (C0=40 mg/L, pH=6, Temp. =25±1°C, S=250 rpm).

Effluence of agitation speed: Agitation speed value between (100 – 300) was taken to examine the removal efficiency of MB in solution and maintaining other parameters (pH6, T=25C, fMWCNTs dosage =400ppm, contact time =80min and Co=40 ppm). Fig. 7 shows that the elimination of MB increase in shaking rate. At 100 rpm the removal efficiency was 93.9 and between (150 – 300) rpm the MB removal was almost the same value. That may be due to the increase in agitation speed encourage the diffusion of dye ion towards the surface media. Maximum removal efficiency was 99.45 at agitation speed 250 rpm to ensure absorption by surface bonding sites, this is the same reason cited by [Wadie, A., and Al-Khawaja, E., 2018].

Fig. 7: Effect of Agitation Speed, (pH 6, Adsorbent Dose =0.04 g, =40 mg/L, Time=120 min.

Adsorption kinetics: The straight-line plots of t/qt versus t for the pseudo-second order reaction Figure (8) for adsorption of MB onto CNTs.
The pseudo-second order condition created by Ho can be composed as:

$$\frac{dq}{dt} = k_2 \left( q_e - q_t \right)^2$$

Where: $K_2 \, (g/mg.min)$ is the rate constant of the pseudo second order. Which has a linear form of

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

Where $k_2$ and $q_e$ can be obtained from the intercept and slope of plotting $\frac{t}{q_t}$ vs. $t$. As documented in table 2.

**Table 2: The Values of Parameters and Correlation Coefficients of Kinetic Models.**

| MB | Pseudo-second order model | $C=40 \, ppm$ | $C=60 \, ppm$ | $C=80 \, ppm$ | $C=100 \, ppm$ | $C=120 \, ppm$ |
|----|---------------------------|----------------|----------------|---------------|----------------|----------------|
| K1 |                           | 0.0303         | 0.0637         | 0.0604        | 0.0694         | 0.0757         |
| Qe  |                           | 0.0099         | 0.0071         | 0.006         | 0.005          | 0.0042         |
| $R^2$ |                        | 0.9999         | 0.9994         | 0.9973        | 0.9941         | 0.9945         |

**Adsorption mechanism:** The active test results of Weber's intra-particle diffusion were suited to pick up understanding into the instruments influencing the energy of adsorption (Weber and Morris 1963). The intra-particle diffusion expressed as:

$$q_t = K_p \sqrt{t}$$

Where; $K_p$ is the intra particle diffusion rate constant (mg g-1 min-1/2).

Figure (10), the primary, sharper component is the outside surface adsorption or instant stage. The second one component is the gradual adsorption stage, in which the intra particle diffusion is rate controlled. The third component is the very last equilibrium stage in which the intra particle diffusion starts to slow down because of extremely low solute concentrations within the solution (Hameed, 2009).
Figure 10: MB uptake Mechanism onto CNTs (intra particle diffusion model).

**Adsorption isotherms:**
Table 3 indicates experimental equilibrium statistics of MB dye on functionalized MWCNTs as adsorbents, Figure 11 and figure. 12 represent freundlich add Langmuir respectively.

Figures. (11) shows the way to find unique coefficients from the plot of ln(qe) versus ln (Ce). n magnitude indicated that nonlinearity degree of among solution concentration and adsorption. If the n values from (1–10) represented excellent adsorption. In the present study, because $n=(6.64)$ for MB dye via functionalized MWCNTs lies among 1 to 10, indicating the physical adsorption onto adsorbents and representing favourable adsorption condition. This is the same finding obtained by using, Ozer and Pirinc, 2006.

Freundlich was excellent model for adsorptive the MB onto functionalized MWCNTs at $R^2$ equal to (0.996). The best fit to the Freundlich model indicates the surface is relatively heterogeneous in phrases of functional groups.

The important feature of Langmuir isotherm parameter, that it could be utilized to be expecting the unattractive between the sorbate and sorbent referred to as dimensionless constant separation factor, or equilibrium parameter ($RL$). The $RL$ value within the present research become observed in the range of (0.0545to 0.0188). This indicated that the adsorption of MB onto functionalized MWCNTs was favorable adsorption technique.

Figure. (13) display the equilibrium adsorption Isotherm of MB onto functionalized MWCNTs.

**Table 3: Experimental Equilibrium Data (pH=6, Dose=0.04 g, S=250 rpm, Time= 80 min.**

| C₀ (mg/L) | Cₑ (mg/L) | qₑ (mg/g) |
|-----------|------------|-----------|
| 40        | 0.78       | 13.073    |
| 60        | 1.254      | 19.583    |
| 80        | 2.888      | 25.704    |
| 100       | 7.68       | 30.77     |
| 120       | 11.424     | 36.192    |

Table 4: Sorption Isotherm Constants for MB sorption on fMWCNTs.

| Adsorbents | Langmuir constants | Freundlich constants |
|------------|---------------------|----------------------|
|            | $q_{max}$ (mg/g) | b (L/mg) | $R^2$ | $K_F$ (mg/g) | I/n | $R^2$ |
| fMWCNTs    | 192.3077          | 0.4333   | 0.9931 | 102.7707     | 0.1506 | 0.9961   |
Conclusion:
This research about appears that fMWCNTs have a high adsorptive capacity for MB. The amounts of adsorption increase with an increase in the initial concentration of methylene blue. The optimum dosage of fMWCNTs to remove methylene blue was considered to be 400 mg L\(^{-1}\). PH and agitation speed plays an important role in this process. A pseudo-second order kinetic equation could fit the adsorption kinetics quite successfully and a three-step intra particle diffusion process dominates the adsorption. The adsorption isotherm models of the Langmuir and Freundlich were used to express the methylene blue adsorption situation. The Freundlich model described the equilibrium data well.

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