



Adsorption of scarlet red dye from industrial wastewater using multiwall carbon nanotubes

Ola A. Shabaan^a, Hossam S. Jahin^a, Maher M.I. Eldessouky^b, Gehad G. Mohamed^b

^a Central Laboratory for Environmental Quality Monitoring (CLEQM), National Water Research Center, Egypt

^b Chemistry Department, Faculty of Science, Cairo University, Giza 12613, Egypt

Abstract

The problem of water pollution with organic compounds such as dyes is a big challenge. Many of water purification techniques were developed. The most technique that used is adsorption. In this paper, multiwall carbon nanotubes (MWNTs) were used as adsorbent for removal of scarlet red dye from industrial wastewater. So, in this paper the efficiency of MWNTs in removal of scarlet red dye under effect of pH = 7, concentration of MWNTs, concentration of dye, agitation time were studied. At equilibrium, the removal reaches 98% of dye. The kinetic studies were described by Langmuir model. To sum up, the results obtained showed that MWNTs had high efficiency in removal of dye from wastewater.

Keywords: Adsorption; scarlet red dye; industrial wastewater; carbon nanotubes.

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1. Introduction

Since dye was entering many of industry, the pollution caused by it increase. So the demands of dye removal increase [1]. The threat of dye is for all living organisms not for the human only but for all aquatic life also [2, 3]. Many techniques and methods were developed in order to get rid of it either chemical or physical or biological [4, 5]. An important example for synthetic dye that used is acid red dye where it was used as coloring agents in the leather, textile, paper, food industries, pharmaceutical and gasoline. After the dye was used, the remaining gushes were poured into the aquatic territory, which caused the toxicity to aquatic life. The degradation of dye affects the aquatic life by adsorbing oxygen from water. Because of complexity of dye structure and its color it causes undesirable color to water, prevent photochemical, and prevent sunlight penetration. From the degradation products of dye is aromatic amine which proved that aromatic amine has carcinogenic effect, rise both COD and BOD level in water resource [6].

Because of the previous reasons that mentioned before as their complexity, carcinogenicity, synthetic origin they make it stable for biodegradation, photo degradation and oxidizing agent. So many technologies were applied in order remove dyes from wastewater as membrane filtration, aerobic or anaerobic treatment, coagulation, and adsorption.

In this paper, the carbon-based nanoparticles as MWNTs was used as adsorbent. The adsorption is the most popular technique used for removal of organic pollutants from wastewater using different adsorbent with different efficiency [7]. There is much advantage

in using adsorbent technique due to its high efficiency, simplicity and low cost. The addition of using MWNTs as adsorbent give our technique the best advantage and priority to be used in purification of wastewater which has high sorption ability [8]. The success of adsorption is determined by measuring the adsorption capacity at equilibrium [9]. MWNTs has high surface area, large number of pore size, high conductivity, thermal stability and in this paper its efficiency was measured in removal of acid scarlet red dye under different conditions which affect the adsorption process as pH, dose of adsorbent (MWNTs), agitation speed and initial concentration of dye itself [10].

2. Experimental methodology:

2.1. Chemicals and materials:

The experiments were performed at room temperature using MWNTs as adsorbent, scarlet red dye as adsorbate, the pH was adjust using 1M of HCl and NaOH. The experiment is performed under different conditions of pH, concentration of both adsorbent and adsorbate.

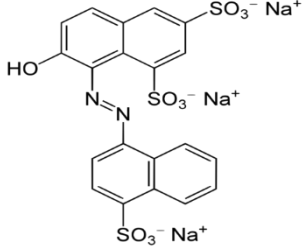
The device that used in measuring the change in the concentration is DR3900 laboratory VIS Spectrophotometer for water analysis.

2.2. Methods

Firstly: preparation of contaminated sample by using double distilled water, weight specific amount of Acid Scarlet Red dye, using ethanol in order to get best solubility of Acid Scarlet Red dye. Determine maximum wavelength of dye, prepare different concentration of Acid Scarlet Red dye from 10 mg into 50 mg to perform calibration curve.

Information of dye:

Table (1). The chemical formula, Molecular weight (g/mol), Maximum wavelength, Uses, Molecular structure of dye.

| Dye | Chemical formula | Molecular weight (g/mol) | Maximum wavelength | Uses | Molecular structure |
|-----------------|--------------------------------|--------------------------|--------------------|-----------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| Acid Scarlet 3R | $C_{20}H_{11}N_2Na_3O_{10}S_3$ | 604.47 | 506 nm | coloring agents in the textile, paper, leather, gasoline, pharmaceutical, and food industries |  |

Characterization of MWNTs:

MWNTs was characterized using both SEM (Figure 1) and TEM (Figure 2).

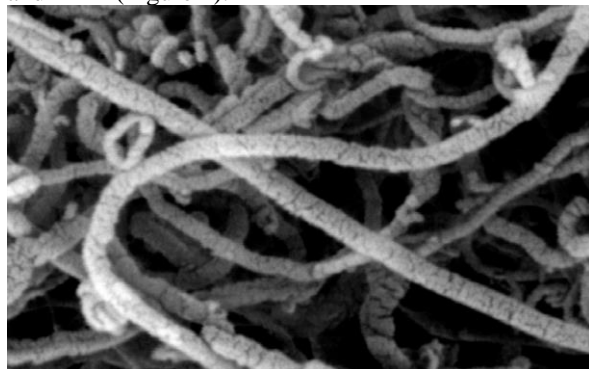


Fig (1): SEM image of MWNTs before adsorption of dye.

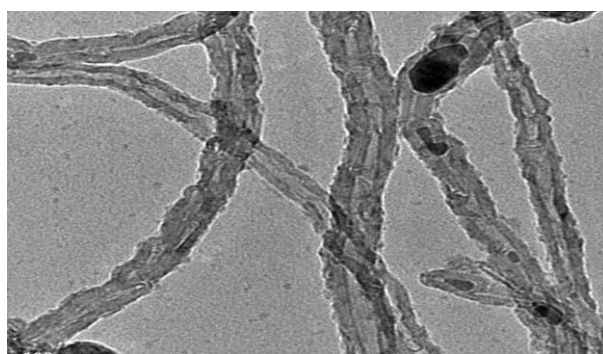


Fig (2): TEM image of MWNTs before adsorption of dye.

3. Results and discussion**3.1. Effect of dosage of adsorbent**

The amount of adsorbent in the water is a critical factor, which affects the adsorption capacity. The adsorption experiment was carried out by using unequal amounts of MWNTs from 10 mg to 30 mg but the agitation speed, contact time and pH were fixed at 40 minutes, 240 rpm and 7, respectively. It was observed that the adsorption capacity is directly proportional with the dose of adsorbent whereas the

adsorbent dosage increases the adsorption capacity increase until adsorbent dosage reach equilibrium at 40 min, then remains almost constant for the remaining dosage range. For the range after 40 min, the higher percentage removal and the higher dosage rate were expected due to the increase in the dose of adsorbents in the solution and hence, the greater the availability of exchangeable sites for ions. Although, after specific dosage rate [11].

3.2. Effect of pH on removal

In this experiment, the change of pH range was taken in pH =4, 7 and 10 as three point in order to scope most of pH range, and their effect on adsorption capacity by using MWNTs. The other conditions as contact time, dosage of adsorbent, and agitation speed were kept constant, 40 min, 30 mg and 240 rpm, respectively. It was observed that the neutral pH is the best point that gives best removal of dye with high adsorption capacity, while the acidic and basic point gives low percent of removal and low adsorption capacity. This is may be due to difference in H and OH concentrations which cause competition on active site to be adsorbed on surface of MWNTs[12, 13].

3.3. Effect of initial concentration of dye

At this experiment, the effect of dye with different concentrations against contact time was studied by varying contact time from 10 min to 80 min with respect to the concentration of adsorbent was fixed at 30 mg, pH = 7 and agitation speed of 240 rpm. It was observed that as the concentration of dye increase the precents of removal decrease due to decreases of active sites on the surface of adsorbent. This means that the rate of adsorption is inversely proportion with concentration of dye [13, 14].

3.4. Adsorption isotherms

The adsorption is a process usually studied through the graphs known as adsorption isotherm. The graph is relation between the amount of adsorbate that adsorbed on the surface of adsorbent at constant temperature and its concentration in the equilibrium solution which indicates either the reaction is homogenous or heterogeneous. The layer formed on the surface adsorbent monolayer or multilayer[15].

Langmuir and Freundlich models of isotherms were graphed as shown in Figures (3 and 4). The Langmuir model is applied on homogenous adsorption, expressed by the following equation (Langmuir 1)

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{C_e K_L q_m} \dots\dots\dots 1$$

Moreover, the Freundlich model is applied to describe the heterogeneous adsorption, also expressed by the following equation [16, 17]:

$$q_e = K_f C_e^{\frac{1}{n}}$$

Where q_m is the maximum adsorption capacity (mg/g), c_e is the equilibrium concentration of adsorbate (mg/l), q_e is the adsorption capacity (mg/g), b is adsorption reaction constant (l/mg), and K_f and n are empirical constants.

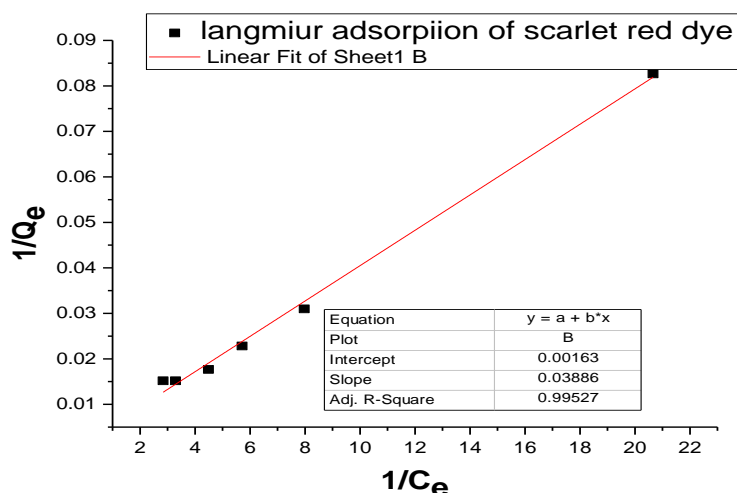


Fig (3): Langmuir isotherm of scarlet red dye.

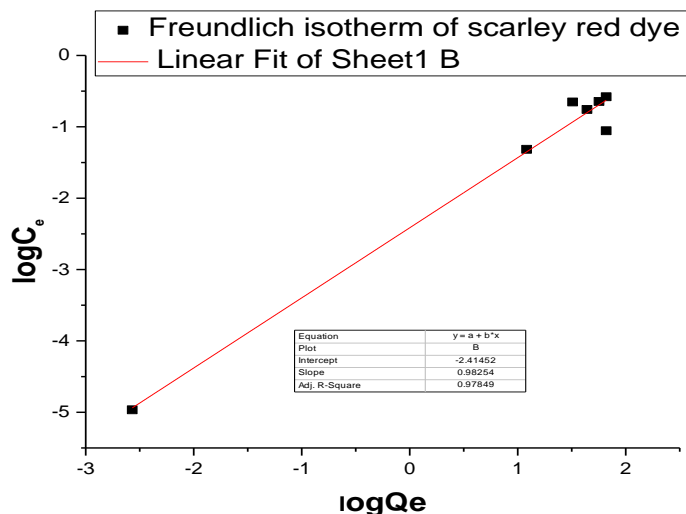


Fig (4): Freundlich isotherm of scarlet red dye.

Table (2): Model parameters of Langmuir and Freunlich isotherms.

| | | | | |
|------------------|---------|--------|--------|-------|
| Langmuir model | Q_m | k_L | R_L | R^2 |
| | 300mg/g | 0.0163 | 0.5312 | 0.99 |
| Freundlich model | K_f | N | R_L | R^2 |
| | 982 | 6.4 | 0.467 | 0.98 |

The constants of both models of acid scarlet 3R are represented in Table 2. According to the correlation coefficient (R^2), Langmuir model is much better in

description of adsorption isotherm data with a higher R^2 than Freundlich model.

Conclusion

Most of adsorption parameter as concentration of dye, agitation speed, contact time, and adsorbent dose have the effect on removal of different dye by using MWNTs were the perfect condition to achieved high adsorption capacity at room temperature was contact time 40min, agitation speed 240 rpm, dose of MWNTs

30 mg. The maximum loading capacity that was determined according Langmuir model 300 mg/g, so it was concluded from that results that MWNTs was a highly effective adsorbent for removal of different dye from wastewater.

References

1. Rashed, M.N., *Adsorption technique for the removal of organic pollutants from water and wastewater*. Organic pollutants-monitoring, risk and treatment, 2013: p. 167-194.
2. Hassaan, M.A. and A. El Nembr, *Health and environmental impacts of dyes: mini review*. American Journal of Environmental Science and Engineering, 2017. **1**(3): p. 64-67.
3. Yusuff, R. and J. Sonibare, *Characterization of textile industries' effluents in Kaduna, Nigeria and pollution implications*. Global Nest: the int. J, 2004. **6**(3): p. 212-221.
4. Ariga, K., J.P. Hill, and Q. Ji, *Layer-by-layer assembly as a versatile bottom-up nanofabrication technique for exploratory research and realistic application*. Physical Chemistry Chemical Physics, 2007. **9**(19): p. 2319-2340.
5. Villeneuve, P., et al., *Customizing lipases for biocatalysis: a survey of chemical, physical and molecular biological approaches*. Journal of molecular catalysis B: enzymatic, 2000. **9**(4-6): p. 113-148.
6. Pieleesz, A., et al., *Detection and determination of aromatic amines as products of reductive splitting from selected azo dyes*. Ecotoxicology and environmental safety, 2002. **53**(1): p. 42-47.
7. Zou, Y., et al., *Processing and properties of MWNT/HDPE composites*. Carbon, 2004. **42**(2): p. 271-277.
8. Mazov, I., et al., *Structural and physical properties of MWNT/polyolefine composites*. Fullerenes, Nanotubes and Carbon Nanostructures, 2012. **20**(4-7): p. 510-518.
9. Kim, M.-S., et al., *Mechanical properties of MWNT-loaded plain-weave glass/epoxy composites*. Advanced Composite Materials, 2009. **18**(3): p. 209-219.
10. Kiso, Y., *Factors affecting adsorption of organic solutes on cellulose acetate in an aqueous solution system*. Chromatographia, 1986. **22**(1-6): p. 55-58.
11. Yang, P., et al., *Preparation of modified pomelo peel's pulp adsorbent and its adsorption to uranyl ions*. Royal Society open science, 2019. **6**(3): p. 181986.
12. de la Cruz, E.F., et al., *Zeta potential of modified multi-walled carbon nanotubes in presence of poly (vinyl alcohol) hydrogel*. 2012.
13. Calvete, T., et al., *Application of carbon adsorbents prepared from Brazilian-pine fruit shell for the removal of reactive orange 16 from aqueous solution: Kinetic, equilibrium, and thermodynamic studies*. Journal of Environmental Management, 2010. **91**(8): p. 1695-1706.
14. Huangfu, X., et al., *A review on the interactions between engineered nanoparticles with extracellular and intracellular polymeric substances from wastewater treatment aggregates*. Chemosphere, 2019. **219**: p. 766-783.
15. Darwish, A., M. Rashad, and H.A. AL-Aoh, *Methyl orange adsorption comparison on nanoparticles: Isotherm, kinetics, and thermodynamic studies*. Dyes and Pigments, 2019. **160**: p. 563-571.
16. Reed, B.E. and M.R. Matsumoto, *Modeling cadmium adsorption by activated carbon using the Langmuir and Freundlich isotherm expressions*. Separation science and technology, 1993. **28**(13-14): p. 2179-2195.
17. Chung, H.-K., et al., *Application of Langmuir and Freundlich isotherms to predict adsorbate removal efficiency or required amount of adsorbent*. Journal of Industrial and Engineering Chemistry, 2015. **28**: p. 241-246.