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ADSORPTION OF CONGO RED ON MULTIWALL CARBON NANOTUBES: EQUILIBRIUM ISOTHERM AND KINETIC STUDIES

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ABSTRACT

In this work, the adsorption capacity of an aqueous solution of Congo Red (CR) dye was used as a model of wastewater treatment to study the treatment activity of multiwall carbon nanotubes (MWCNTs). The adsorption capacity of an aqueous solution of CR onto MWCNTs surface was investigated, particularly focusing on the influence of the experimental parameters on the kinetics adsorption at constant conditions, such as MWCNTs dosage, initial concentration, pH, ionic strength and temperature. Langmuir and Freundlich isotherms were used as the model adsorption equilibrium data. The constants of Langmuir and Freundlich models are obtained from fitting the adsorption equilibrium data. The correlation coefficients of Langmuir and Freundlich models are 0.9906 and 0.9662, respectively. The pseudo-first order, pseudo-second order and intraparticle diffusion models were used to describe the adsorption kinetics. The experimental adsorption data fitted with the pseudo-second order kinetic.

Key words: Adsorption, MWCNTs, Congo Red (CR), Kinetics, isotherms.

INTRODUCTION

Nanotechnology represents one of new sciences that promise to provide a broad range of novel uses and enhanced technologies for several applications. A unique aspect of nanotechnology is the "vastly increased ratio of surface area to volume," present in many nanoscale materials, which opens new possibilities in surface-based sciences. Nanoscale materials have the potential to improve the environment, both through direct applications of these materials to detect, prevent, and remove pollutants, as well as indirectly by using

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nanotechnology to design cleaner industrial processes and create environmentally responsible products[1,2].

One of the main environmental pollutants is wastewater. Wastewater is the leftover water after industrial processes. This polluted water comes from industry due to increasing population and industrial expansion, especially from the developed countries. One of the most important of these pollutants dye, which is becoming a great concern to the environment and public health[3].

Dyes have long been used in different types of industries such as, dyeing, textiles, paper, plastics, leather and cosmetics. Color stuff discharged from these industries pose hazards and has an environmental impact[4]. The presences of dyes in water are causing problems, such as, reducing oxygen levels in water; interfering with penetration of sunlight into waters; retarding photosynthesis and interfering with gas solubility in water bodies.

Azo dyes are divided according to the presence of azo bonds (–N=N–) in the molecule; these include mono azo, diazo, triazo etc[5]. Azo dyes resist the effect of oxidation agents and light, thus they cannot be completely treated by conventional methods of anaerobic digestion.

Huge types of dye uses led to pollute the surface water and groundwater. There are different methods used for water treatment in our previous work[6-53].

The adsorption technique proved to be an effective and attractive process for removing dyes from aqueous solutions in term of initial cost, ease of operation, insensitivity to toxic substance, high efficiency, easy recovery and simplicity of design[24,25]. Carbon nanotubes (CNTs) are relatively new adsorbents that can absorb organic pollutants from wastewater[24]. CNTs were discovered in 1991 as a minor byproduct of fullerene synthesis. CNTs are made up of concentric rolled graphene sheets. CNTs include single wall (SWCNTs) and multiwall (MWCNTs) depending on the number of sheets comprising them.

The interaction of CNTs with gases or any species adsorbed on their internal or external surface open up the possibility of using them for gas storage. It has been shown that the curvature of graphene sheets can result in a lower heat of adsorption compared with a planar graphitic surface. In fact, the rolling of the graphene sheet around itself to produce a tube causes a re-hybridization of the carbon orbital, thus leading to a modification of the π density of the graphene sheet[54].

CNTs tend to aggregate together as bundles because of Van der Waals interactions. The aggregation of CNTs leads to a reduction in their surface area, while generating interstitial channels between nanotubes and grooves on the periphery of the nanotube bundles. The available sorption sites of CNTs bundles include the external surface, the interstitial and groove areas formed between the CNTs, and the inner pores of the tubes, as depicted in Fig. 1.

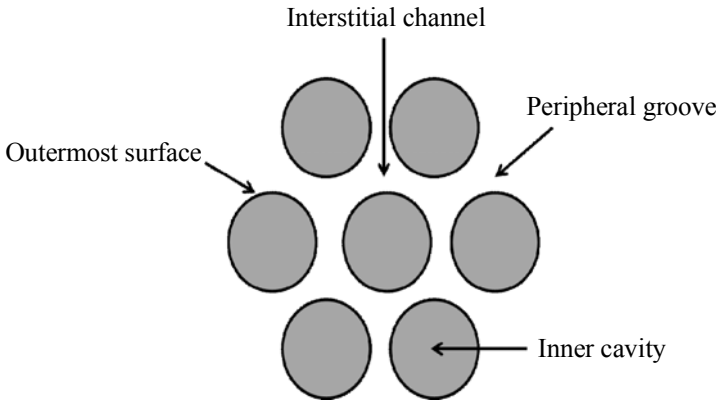

Fig. 1: Schematic structure of CNTs bundles

In this work, commercial MWCNTs were used as an adsorbent to remove CR from aqueous solution. The effects of MWCNTs dosage, initial dye concentration, pH, ionic strength and temperature on adsorption capacity were studied. Kinetic and equilibrium models were used to fit experimental data.

EXPERIMENTAL

Materials and methods

Adsorbent

Multiwall carbon nanotubes (MWCNTs) with diameter of 20-30 nm and length of 10-30 μm was purchased from NANOSHEL. MWCNTs were used without further treatment.

Adsorbate

CR, having molecular formula $C_{32}H_{22}N_6Na_2O_6S_2$ was chosen as the adsorbate. CR is the sodium salt of 3, 3'-([1, 1'-biphenyl]-4, 4'-diyl) bis (4-aminonaphthalene-1-sulfonic acid). The structure of CR is shown in Fig. 2.

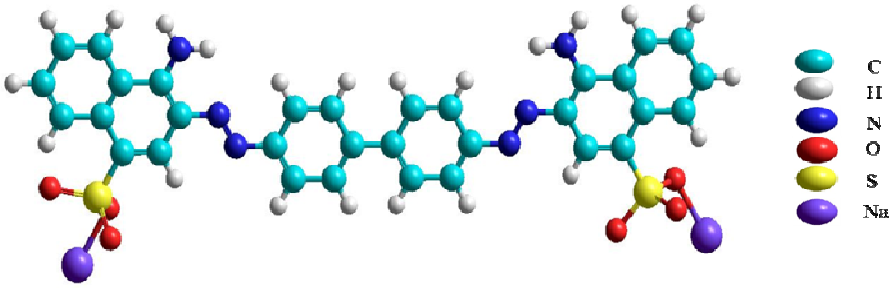

Fig. 2: Chemical structure of CR dye

Adsorption equilibrium experiments

For equilibrium studies, solutions of 40 ppm CR, at the initial concentration, were treated with 0.025 g of MWCNTs. The mixtures were agitated on shakers (Gemmy orbit, van 480 Gemmy Industrial Corp-Taiwan) continuously for 60 min, as the equilibrium time, at different temperature and pH. After 60 min, the suspensions were filtered using a centrifuge and the filtrates were analyzed for residual CR concentration by UV visible spectrophotometer (PG instruments Ltd-Japan) at 499 nm in pH above 5 and at 566 nm at pH below 3. The amount of CR uptake by MWCNTs in each flask was calculated using the mass balance equation:

$$q_e = \frac{(C_o - C_e) \times V}{W} \quad \ldots(1)$$

Where q_e is the amount of congo red adsorbed by CNTs at equilibrium, C_o and C_e are the initial and final dye concentrations (M), respectively, V is the volume of solution (L), and W is the adsorbent weight (g).

The dye percent removal (%) was calculated using the following equation:

$$\text{Removal } \% = \frac{C_o - C_t}{C_o} \times 100 \quad \ldots(2)$$

Adsorption kinetic experiments

For kinetic studies, solutions of 40, 50, 60 and 80 ppm CR, as the initial concentration, were treated with 0.025 g of MWCNTs at a constant temperature of 298 K. The mixtures were then subjected to agitation using a shaker. In all cases, the working pH of solution was not controlled. Mixtures were taken from the shaker at appropriate time

intervals (10, 20, 30, 40, 50, 60 min) and the remaining concentration of the CR solution was determined.

RESULTS AND DISCUSSION

Adsorption isotherms

The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful application in many sorption processes of monolayer adsorption[55]. Fig. 3 shows the Langmuir isotherm for adsorption CR on MWCNTs. The following equation is the Langmuir isotherm:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \ldots(3)$$

Where q_m is the maximum amount of CR adsorbed per unit mass of MWCNTs and K_L is the Langmuir constant related to rate of adsorption.

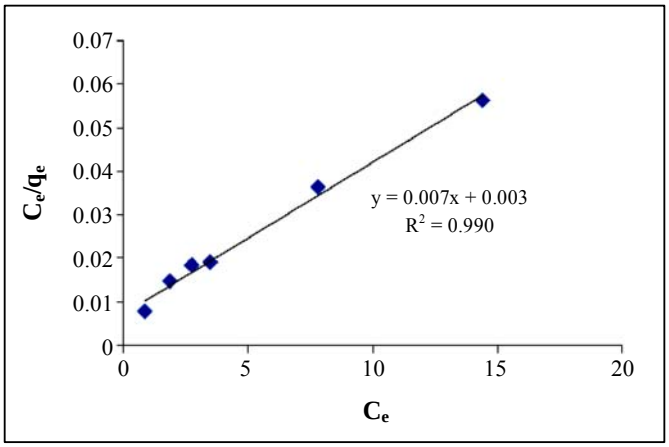

Fig. 3: Langmuir isotherm for CR adsorption onto different mass from MWCNTs

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich model is based on the distribution of adsorbate between the adsorbent and aqueous phases at equilibrium[56]. Fig. 4 shows the Freundlich isotherm for adsorption CR on MWCNTs. The basic Freundlich equation is:

$$\log (q_e) = \log K_F + \frac{1}{n} \log C_e \quad \ldots(4)$$

where K_F and n are Freundlich constants, which give a measure of adsorption capacity and adsorption intensity, respectively. The values of the isotherm parameters are given in Table 1.

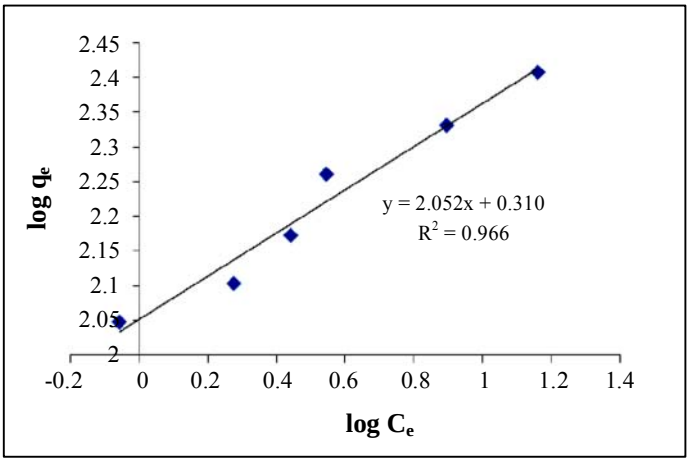

Fig. 4: Freundlich isotherm for CR adsorption onto different mass from MWCNTs

Table 1: Isotherm parameters for CR adsorption on different mass from MWCNTs

Isotherms	Parameters	Values
Langmuir	Q_m	285.7
	K_L	0.4729
	R^2	0.9906
Freundlich	K_F	112.9
	n	3.2
	R^2	0.9662

Adsorption kinetics

Three kinetic models: Pseudo-first order, pseudo-second order and intra particle diffusion kinetic models were used to fit experimental data to examine the adsorption kinetics. Equations 5, 6 and 7 represent the linear forms of the pseudo-first order, pseudo-second order models and Intra particle diffusion kinetic model, respectively.

$$\ln (q_t - q_e) = \ln (q_e) - k_1 t \quad \ldots(5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \ldots(6)$$

$$q_t = k_3 t^{1/2} + C \quad \ldots(7)$$

The straight-line plots of ln (q_e-q_t) versus t for the pseudo-first order reaction (Fig. 5), t/q_t versus t for the pseudo-second order reaction (Fig. 6) and q_t versus $t^{1/2}$ for the intra particle diffusion reaction (Fig. 7) for adsorption of CR onto different mass from MWCNTs. From R^2 values pseudo-second order model best represents this experimental data.

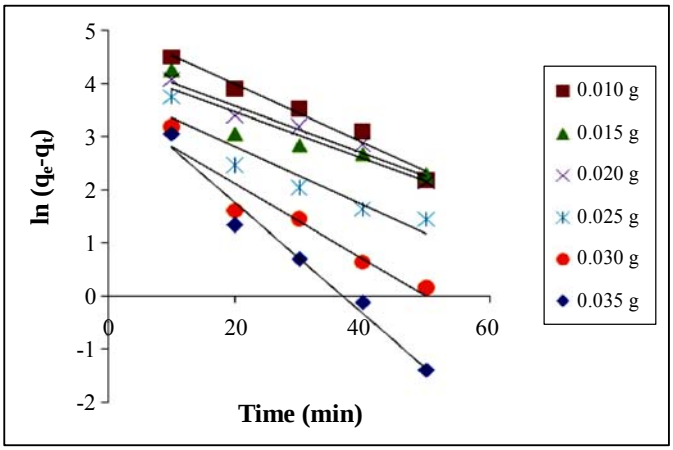

Fig. 5: Pseudo-first order kinetic model for the adsorption of CR on MWCNTs

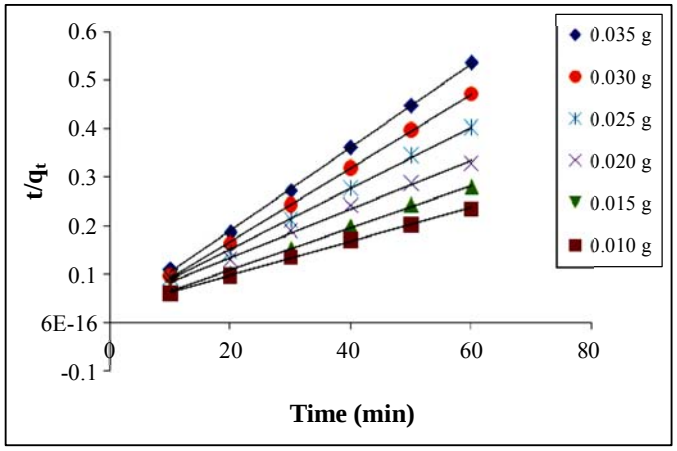

Fig. 6: Pseudo-second order kinetic model for the adsorption of CR on MWCNTs

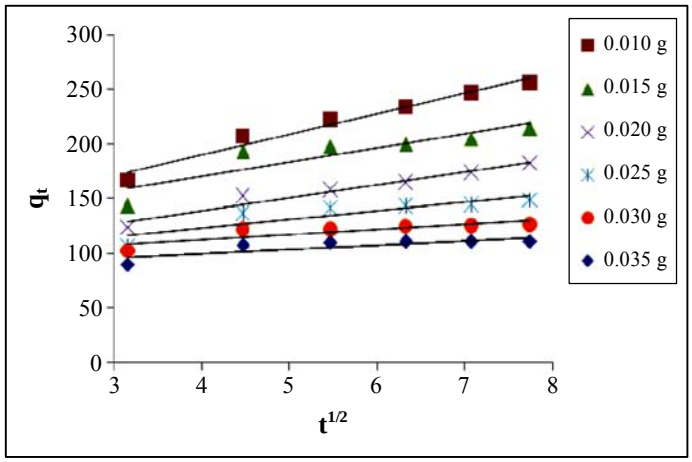

Fig. 7: Intra particle diffusion model for the adsorption of CR on MWCNTs

CONCLUSION

This study shows that MWCNTs can be used effectively for the removal of CR from aqueous solution. The adsorption kinetics was fitted by a pseudo-second order kinetic model. The adsorption of CR on MWCNTs has been described by the Langmuir and Freundlich adsorption isotherm models. The equilibrium data were fitted with the Langmuir isotherm by depending on the correlation coefficient R^2.

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