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Adsorption of Acid Blue 225 dye by Multi Walled Carbon Nanotubes: Determination of equilibrium and kinetics parameters

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ABSTRACT

Batch studies were conducted for kinetics and equilibrium studies on the biosorption of Acid Blue 225 (AB 225) from aqueous solution by Multi Walled Carbon Nanotubes (MWCNTs). The different parameters studied were initial dye concentration, biomass concentration, contact time and solution pH. Results show that the pH value of 3 is favorable for the biosorption of AB 225 dye. The biosorption data have been analysed using Langmuir, Freundlich and Temkin isotherms. The isothermal data for biosorption followed Langmuir Model. The biosorption processes conformed to the pseudo-second-order rate kinetics. Overall, the study demonstrated that MWCNTs can effectively remove AB 225 dye from aqueous solution under a wide range of experimental conditions.

Keywords: Multi Walled Carbon Nanotubes, Adsorption, Acid Blue 225, Kinetics, Isotherms

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INTRODUCTION

Traditionally, the impact of chemical pollution has focused almost exclusively on the conventional priority pollutants[1, 2]. The synthetic dyes are one of important class of chemical which they are synthesized in large amount in the world[1]. It is expressed that the annual production of dyes is more than 700000 tones[3]. The dyes are discharged from various industries such as dyestuffs, textile, paper, printing, leather, cosmetics, plastics, paints, pharmaceuticals, food and petrochemicals; however the textile dye is known as major dye consumer[4, 5]. The dyes and colorful effluents which are released from the industries create many problems for environment and human[6,7]. The unpleasant aesthetic and prevention of light penetration is considered as problem due to discharge the dyes into water body and consequently, it can reduce the photosynthetic phenomenon and oxygen level in water[8-10]. Therefore, the alleviation of the hazardous effects of dyes for environment and public health is significant subject.

It have been confirmed that the adsorption process is the common and promising method to remove the dyes due to its properties including effectiveness, efficiency, economy and no secondary pollution[11-13]. Although the activated carbon has been known as a commercially adsorbent, however there is several disadvantage along with the activated carbon such as limited availability, low adsorption capacity and difficult recovery[14]. Recently, the carbon nanotubes (CNTs) which it discovered by Iijima in 1991 is used to remove the organic and anthropogenic pollutant such phenols, dyes and heavy metal and etc [15-17]. The CNTs are going to become more popular adsorbents due to special characteristics such as chemically inert surfaces for physical adsorption, and their high specific surface areas[18, 19]. In the present study, MWCNTs were chosen as sorbent for removal of AB-225 dye. The aim of this study is to investigate the adsorption of AB-225 dye on MWCNTs under various conditions. So, the influence of different parameters such as initial dye concentration, contact time, adsorbent dose, and initial pH of solution was investigated. Isotherms were used to identify the possible mechanism of the adsorption process.

MATERIALS AND METHODS

The Acid Blue 225 (AB-225) was purchased from Merck Company (Germany). The chemical structure and some properties of the AB-225 dye are presented in Table 1 and fig 1. Also, all other chemicals and reagents used were analytical grade (Merck Company, Germany). Stock solution of AB-225 dye (1000 mg/L) was prepared by dissolving the 1 g dye in 1 L double distilled water. For treatment experiments, the dye solutions with concentrations in the range of 10–200 mg/L were prepared by successive dilution of the stock solution with double distilled water.

MWCNTs (provided from Research Institute of Petroleum Industry (RIPI), Tehran, Iran) were selected as adsorbents to study the adsorption characteristics of AB-225 dye from aqueous solutions. On the basis of the information provided by the manufacturer, the MWCNTs were synthesized by catalytic chemical vapor deposition (CVD) method. The size and morphology of MWCNTs were examined by scanning electron microscope (JEOL JSM 6500F) and transmission electron microscopy (TEM) (using a Philips XL30).

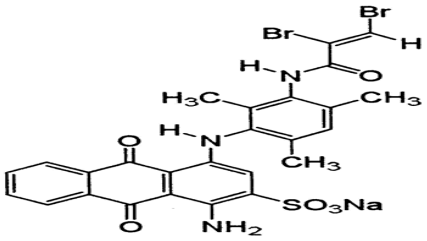


Fig. 1. Chemical structure of AB 225 dye

Table 1: Properties of AB 225 dye[20]

C.I. name	type	Molecular weight	λ_{max} (nm)	Molecular formula
Acid Blue 225	Anionic	533.99	628	$C_{26}H_{20}Br_2N_3O_6S$

Adsorption eperiments

All experiments were carried out with biosorbent samples (0.1 g/L) at 30◦C in 100 mL beakers in an magnetic stirrer operating at 200 rpm to elucidate the optimum conditions (contact time, adsorbent dose and initial dye concentration and pH). Before analysis of the dye concentration, samples were centrifuged at 3600 rpm for solid–liquid separation. Concentration of the dye in solution was analysed using UV-DR 5000. Earlier the wavelength at which maximum absorbance λ_{max} (nm) occurred for AB 225 dye in aqueous solution was determined by performing full range of (200–700 nm) wavelength scans. Concentrations of dyes in solution were estimated quantitatively using the linear regression equations obtained by plotting a calibration curve for dye over a range of concentrations. The dye adsorption capacities of biosorbent were determined at a certain time intervals (10-120 min) and at various adsorbent dose (0.02–0.2 g/L). The effect of pH on biosorption was studied by adjusting dye solutions (100 mg/L) to different pH values (3–11) and agitated with 0.1 g/L of biosorbent for 75 min. The dye solutions were adjusted to the required initial pH values with the addition of HCl or NaOH (0.1M). Dye adsorption Experiments were also accomplished to obtain isotherms at range of 10–200 mg/L dye concentrations. The amount of dye adsorbed by biosorbent, q_e (mg/g) was calculated by the following mass balance relationship[21, 22]:

$$q_e = (C_O - C_e)\, V/M$$

Where C_0 and C_e are the initial and equilibrium dye concentrations in solution, respectively (mg/L), V the volume of the solution (L) and M is the mass (g) of the adsorbent used.

RESULTS AND DISCUSSION

Fig. 1 displays the surface morphology of MWCNTs. The SEM and TEM figures show that the MWCNTs were cylindrical and the range of main external and internal diameters was 2-3.5 and 1.2-1.7 nm, respectively. The specific surface area of the adsorbent used in this study was 782.8 m^2/g.

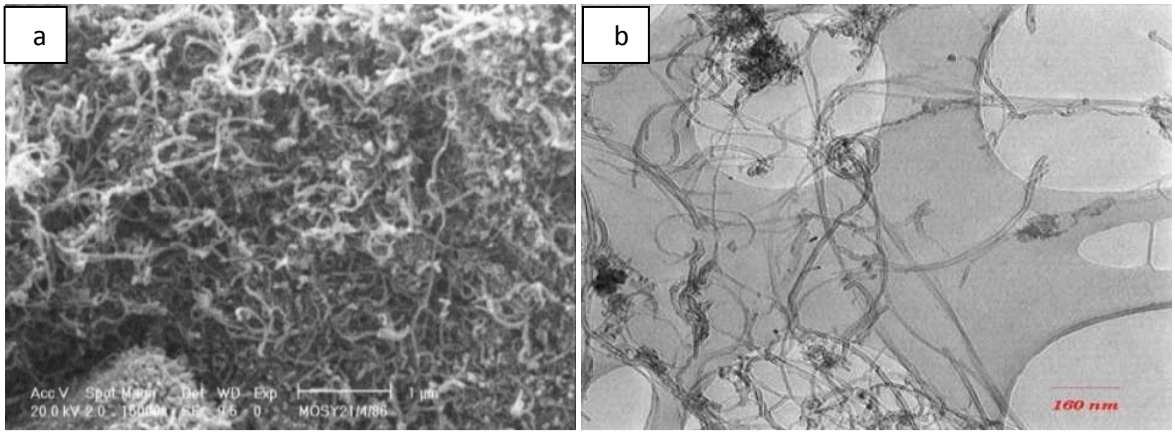


Fig. 2. Micrographs of MWCNTs (a) SEM and (b) TEM

Effect of adsorbent dose

The adsorbent dose is an important parameter in the determination of adsorption capacity. The effect of the adsorbent dose was investigated by addition of various amounts of MWCNTs in 200 mg/L AB 225 dye solution for 75 min. The result is shown in Fig. 3. It was observed that the removal efficiency increased from 42.3% to 92.1% with an increase in adsorbent dose from 0.02 to 0.1 g/L. This can be attributed to the increase in the adsorbent specific surface area and availability of more adsorption sites[23, 24]. However, the further increase in the amount of the adsorbent did not affect the removal efficiency significantly. It is also observed that the adsorption capacity decreases from 2115 to 460.5 mg/g as the adsorbent dose increases from 0.02 to 0.2 g/L. Consequently, the adsorbent dose was maintained at 0.1 g/L in all the subsequent experiments, which was considered to be sufficient for the removal of AB 225 dye.

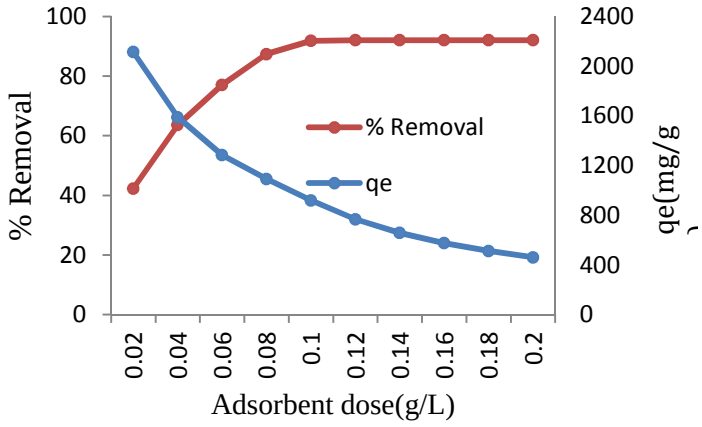


Fig 4: Effect of adsorbent dosage on AB-225 adsorption onto MWCNTs. (C_0 = 100 mg/L, Contact time = 75 min, pH = 3, temperature = 30 ± 2∘C)

Effect of Initial pH: The solution pH would affect both aqueous chemistry and surface binding sites of the adsorbent. So the solution pH is an important parameter during the dye adsorption process. As can be seen from Fig. 4, the maximum adsorption capacity of the adsorbent was 373.9 mg/g at pH 3 and initial concentration of 100 mg/L, when 92.1% of the dye was removed. The adsorption of this dye takes place when the adsorbents present a positive surface charge. On the other hand at lower pHs, more protons would be available, thereby a significantly high electrostatic attraction existed between the positively charged adsorption sites and negatively charged dye anions, which caused the enhanced dye adsorption[25, 26]. But as the pH of solution increased, besides the decrease of negative charge of acidic dyes, the positive charge of adsorbent surface also decreased due to the abundance of OH^-, which can weaken the reaction of dye and adsorbent, and thereby causing a decrease in adsorption[27, 28]. In order to continue the adsorption studies, the initial pH was fixed at 3.0.

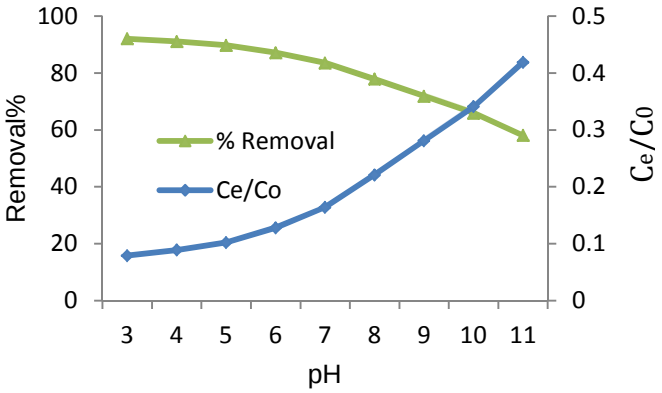


Fig 5: Effect of initial pH on the adsorption of AB-225 onto MWCNTs. (C_0 = 20 mg/L, contact time = 75 min, dosage = 0.12 g/L, temperature = 30 ± 2∘C)

Biosorption isotherms

Isotherms are the equilibrium relations between the concentration of the adsorbate on the solid phase and its concentration in the liquid phase[29]. The equilibrium biosorption data have been analysed using Langmuir, Freundlich and Temkin isotherms. Analysis of such isotherms is important in order to develop an equation that accurately represents the results and could be used for design purposes[30].

The Langmuir isotherm model assumes the uniform energies of adsorption onto the adsorbent surfaces. Furthermore, the Langmuir equation is based on the assumption of the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent where all sorption sites are identical. The Langmuir equation is given as follows[31, 32]:

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

Where q_e is the equilibrium dye concentration on the adsorbent (mg g^{-1}); C_e, the equilibrium dye concentration in solution (mg L^{-1}); q_{max}, the monolayer capacity of the adsorbent (mg g^{-1}); K_L is the Langmuir constant. The plots of C_e/q_e vs. C_e for the biosorption of AB 225 onto MWCNTs give a straight line of slope ($1/q_{max}$) and intercept ($1/q_{max}$ K_L). The essential features of Langmuir can be expressed in terms of dimensionless constant separation factor R_L which is calculated using the following equation[33, 34]:

$$R_L = \frac{1}{1+K_L C_O}$$

Values of R_L indicate the shapes of isotherms to be either unfavorable (R_L>1), linear (R_L= 1), favorable (0 <R_L<1). The Freundlich isotherm model equation is expressed as[35, 36]:

$$\text{Log } q_e = \frac{1}{n} \log Ce + \log K_F$$

Where q_e is the equilibrium dye concentration on the adsorbent (mg g^{-1}); C_e, the equilibrium dye concentration in solution (mg L^{-1}); and K_F is the Freundlich constant. In this function, it is assumed that the sorbent has a surface with a non-uniform distribution of sorption heat. This equation was primarily proposed on a purely empirical basis for adsorption phenomena occurring on gas–solid interfaces, although it can be theoretically derived for an adsorption model in which the heat of adsorption varies exponentially with surface coverage. The slope of plot 1/n ranging 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero.

Temkin considered the effect of some indirect sorbate/adsorbate interactions on the adsorption isotherm. This isotherm assumes that; the heat of adsorption of all the molecules in a layer decreases linearly with surface coverage of adsorbent due to sorbate-adsorbate interactions. This adsorption is characterized by a uniform distribution of binding energies. The linear form of the Temkin isotherm equation is represented by the following equation[37, 38]:

$$q_e = B \ln A + B \ln C_e$$

Where B = RT/b, T is the absolute temperature in K, R the universal gas constant (8.314 J K^{-1} mol^{-1}), A the equilibrium binding constant and the constant B is related to the heat of adsorption. Values of B and A were calculated from the plot of q_e against ln C_e. The results of the isotherm parameters for the biosorption are given in Table 2 and Fig. 6 a-c. As shown in Table 5 that the correlation coefficients for the Langmuir isotherm model for AB 225 were close to 1.0. The correlation coefficients for the Freundlich and Tempkin isotherm models were lower than that of the Langmuir isotherm model. Fig 6 a-c also confirm that the Langmuir isotherm has better fitting than the other isotherm models tested.

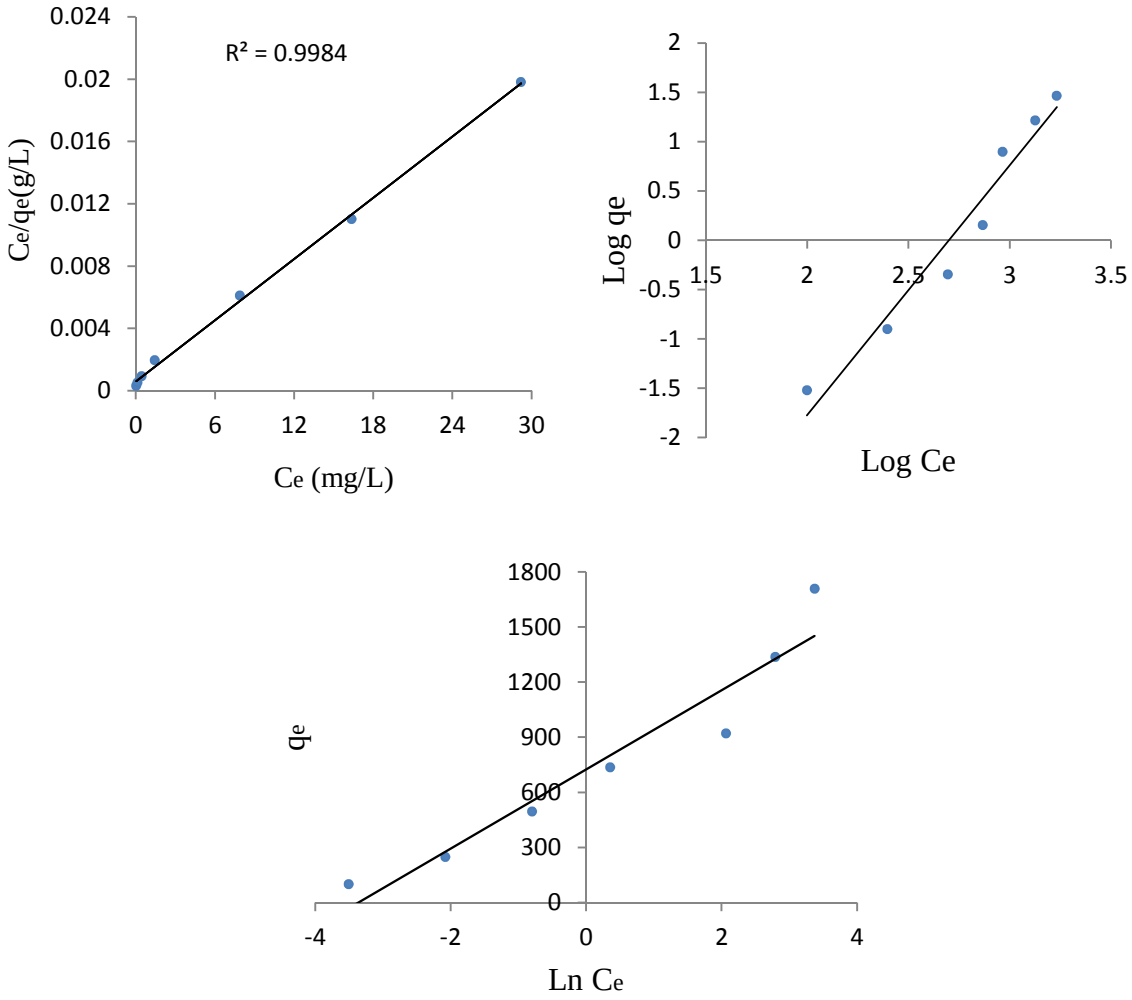


Fig. 6. Adsorption isotherms (a); Langmuir (b); Freundlich (c), Temkin

Table 2: Isotherms constants for the removal AB 225 onto MWCNTs

Langmuir model				Freundlich model			Temkin model		
q_m	R_L	K_L	R^2	n	K_F	R^2	B	A	R^2
923.14	0.826	0.0021	0.998	3.11	17.25	0.953	22.83	0.446	0921

Biosorption kinetics

In order to analyze the biosorption kinetics of acidic dyes, the pseudo-first-order, the pseudo-second-order and intraparticle diffusion models were applied to data obtained from the experiments.

The pseudo-first-order rate expression given as[39, 40]:

$$\text{Log } (q_e - q_t) = \log q_e - \frac{K_1}{2.303}t$$

Where q_e and q_t are the amounts of dye (mg/g) adsorbed at equilibrium and time t, respectively, and k_1 is the rate constant of adsorption (min^{-1}) biosorption. The values of k_1 calculated from the slope of the plots of $1/q_t$ vs. 1/t as shown in Figs. 7 a.

The pseudo-second-order kinetic model is expressed as[41, 42]:

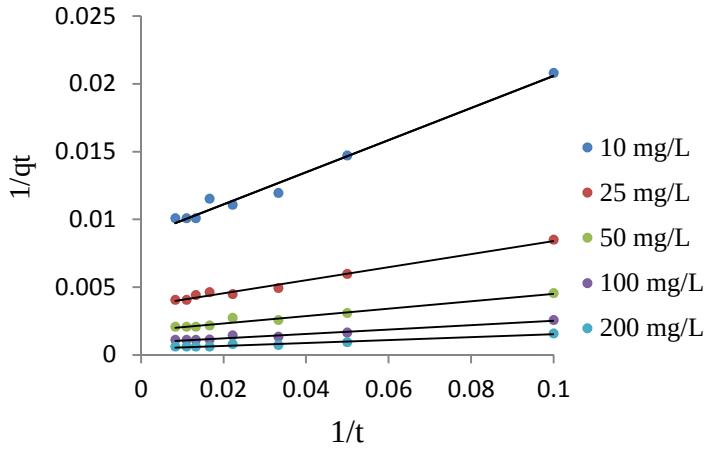
$$\frac{t}{q_t} = \frac{1}{k_2 q e^2} + \frac{1}{qe\, t}$$

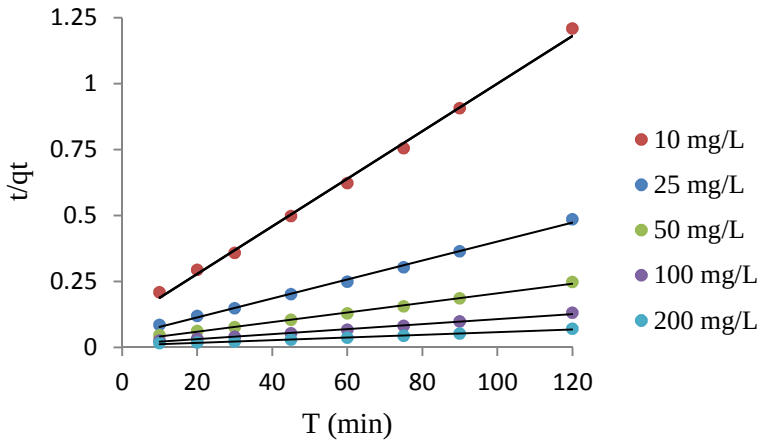
where q_e is the biosorbed dye amount at equilibrium (mg/g) for the pseudo-second-order biosorption, q_t is the amount of dye biosorbed at time t (mg/g) and k_2 is the pseudo-second-order kinetic rate constant (g/mg min). A plot of t/qt vs. t should give a linear relationship for the applicability of the pseudo-second-order kinetic, as shown in Figs. 7 b. The rate constant (k_2) and adsorption at equilibrium (q_e) can be obtained from the intercept and slope, respectively.

The intraparticle diffusion equation can be written as follows[43-45]:

$$q_t = k\, t^{1/2} + C$$

where C is the intercept, and k is the intraparticle diffusion rate constant (mg g^{-1} $min^{-1/2}$) (Figs 7 c). The results of the kinetic parameters for biosorption are given in Table 3. The correlation coefficients for the pseudo-second-order kinetic model were close to 1.0 for all cases. The correlation coefficients for the first-order kinetics and intraparticle diffusion equation models were lower than that the pseudo-second-order.





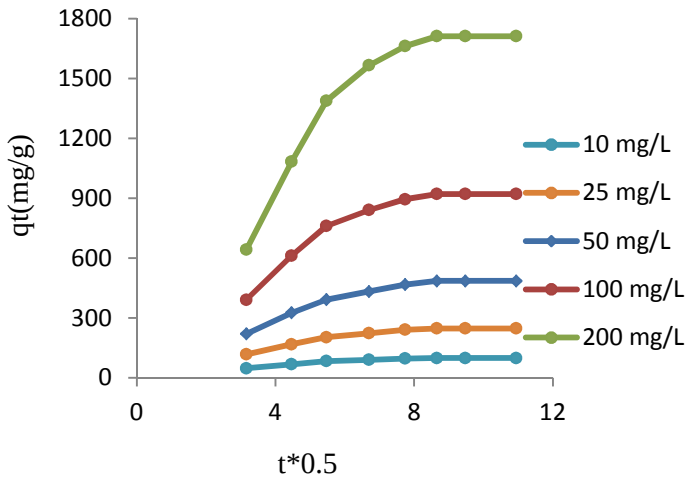


Fig 7: Biosorption kinetics (a): pseudo first-order (b): pseudo-second-order (C): intraparticle diffusion

Table 3: kinetic parameters for AB-225 adsorption onto MWCNTs

Pseudo second-order model				Pseudo first-order model			Intraparticle diffusion		
C_o	k_2	R^2	q_e	K_1	R^2	q_e	K_{dif}	C	R^2
10	0.0011	0.998	98.51	0.048	0.975	71.25	5.59	1.71	0.751
25	0.0027	0.999	242.25	0.059	0.981	163.89	4.77	1.45	0.772
50	0.0041	0.998	481.54	0.068	0.969	395.73	4.05	2.22	0.793
100	0.0076	0.999	914.2	0.081	0.972	645.56	3.55	2.76	0.786
200	0.0095	0.999	1695.5	0.121	0.958	1045.5	2.86	3.11	0.802

CONCLUSION

This paper reports kinetic and equilibrium studies on biosorption of AB 225 dye by MWCNTs. The maximum biosorption capacities of biomass was 923.14 mg/g, at optimum conditions of pH=3 and temperature (30 ◦C) according to Langmuir isotherm model and pseudo-second-order kinetic model. The biosorption equilibrium was reached in 75 min.

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