STUDY THE ADSORPTION ABILITY OF ALIZARIN RED DYE FROM THEIR AQUEOUS SOLUTION ON SYNTHESIZED CARBON NANOTUBES

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In this research, Carbon nanotubes were fabricated by the electrolysis method using (5 x 50 mm) graphite rod as cathode and anode with 4.7 x10^{-3} mA\cm2 of current density for 6 h. Characterization and identification of the synthesized carbon nanotubes were done using an X-ray diffractometer (XRD), transmission electron microscope (TEM), and scanning electron microscope (SEM). The synthesized carbon nanotubes behave as an attractive adsorbent for alizarin red dye from wastewater. The effects on the dye removal were tested for contact time, temperatures, and initial concentration. The dye adsorption isotherm has been studied and was a good match for Freundlich isotherm models. The maximum adsorption capacity (*q*m*)* of samples 24,070 mg/g. Thermodynamic and kinetic studies were done to calculate the parameters (ΔS, ΔH, ΔG) and the adsorption order respectively.

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1. Introduction

Nanochemistry is one of the important sciences in the modern era, as all materials in the nanoscale are used in various applications in all fields [1-9]. There are broad applications of carbon nanotubes (CNTs) due to their unique properties, a potential uses in electronic equipment, drug delivery systems, storage of hydrogen, processes for adsorption and separation [10–12] But the low solubility of carbon nanotubes in water solutions is one of the significant benefits of their applications in the biomedical field [13]. The difficult regulation of various solvents further limits their use in other fields of biotechnology. Tubular carbon structure may provide greater surface area to volume ratio than other nanostructures because of their hollow internal shape, the large area leading to the increase of adsorption activity, so CNT`s are very useful for wastewater treatment applications [14]. Hollow tube nanostructures from different materials have shown great interest along with adsorption applications since they have been used as building blocks on the nanoscale with unique physical properties [15-21]. Carbon nanoparticle surface usability with functional groups has prompted the arrangement of large nanohybrids that have not only been used for catalysis, gas sensors and fuel cells [22–26], but also for biomedical imaging, supercapacitors, biomanipulation or environmental treatment (adsorption) [27–30]. The aim of this study included the Synthesized Carbon Nanotubes by electrochemical method and Study the Adsorption Ability of Alizarin Red Dye From Their Aqueous Solution.

2. Experimental

2.1. Synthesis of carbon nanotubes

All chemicals were at reagent grade or the highest available commercial grade and were used as received. The electrolysis process used to synthesize CNTs employing 100 ml of KOH 0.08 M at 25 °C as the electrolyte. At atmospheric pressure, a graphite rod (5 x 50 mm) was performed with a current density of 4.7 x10-3 mA\cm2 for 6h in the two electrodes (Cathode and Anode). The

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cleaner solvents (ethanol, acetone, chlorinated and de-ionized water) were sequentially cleaned sonically before installing the substrate in the cells, and every cleaning step took 5 minutes. The voltage was 10 V with D.c applied between the electrodes using a D.c. Power supply (HEWLETT.PACKARD) as shown in Fig. 1.

Fig. 1. Electrochemical cell.

2.2. Adsorption experiments

Adsorption batch processes were performed using distilled water with 125 mg \L alizarin red dye. Further dilution of the solution was needed to concentrate alizarin red dye (5-25 mg / l). All experiments were run with 100 ml of dye solution at the target concentration and 0.1 g of carbon nanotubes in 10 ml glass tubes. At various temperatures (15, 25, 35, 45, and 55) ◦C, the glass tubes were placed on a shaker (HZQ-C) and shaken for 120 min. Using a UV-visible spectrophotometer to evaluate the dye concentration in the liquid phase. The amount of adsorbed dye in the solution was assessed by the following equation [31]:

$$Q_e = \frac{(C_o - C_e)V_{sol}}{M} \tag{1}$$

Where Q_e is Adsorption capacity at equilibrium (mg/g), C_o is the Primary concentration of alizarin red dye (mg L^{-1}), C_e is the equilibrium concentrations of alizarin red dye (mg L^{-1}), V is the volume of the red dye solution (L) and M is the mass of the carbon nanotubes as adsorbent (g).

3. Results and discussion

The synthesized carbon nanotubes by the electrochemical method were investigated via X-Ray Diffraction (XRD), and Electronic microscopes Transmission (TEM), and Scanning (SEM).

XRD patterns of the carbon nanotubes recorded in the 2θ range from 10 to 80º are shown in Figure 2. The diffraction peaks in carbon nanotubes observed around 2θ = 26º and 42º corresponding to the (002) and (100) were due to the carbon structure. The broad peak at 2θ = 26º proves that the carbon tubes were in nano size. A Debye-Scherrer equation [32-36] was used to calculate the crystal size of synthesized CNT. The calculated crystallite size by Scherrer's formula of the maximum reflection peak at 2θ 26° (002) indicated that the crystals of carbon nanotubes had about 19 nm.

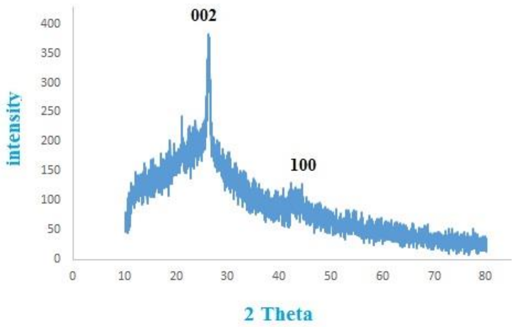


Fig. 2. XRD pattern of carbon nanotubes.

The SEM image of synthesized carbon nanotubes was given in Fig. 3, it shows the surface morphology, particle size, and particle shape, it can be observed that carbon nanostructures have a tubular shape, which affords ultra-thin and homogeneous carbon nanotubes with a diameter ranged from 25 to 50 nm and wall thickness 6.7 nm. which identical to the crystal size calculated from XRD pattern.

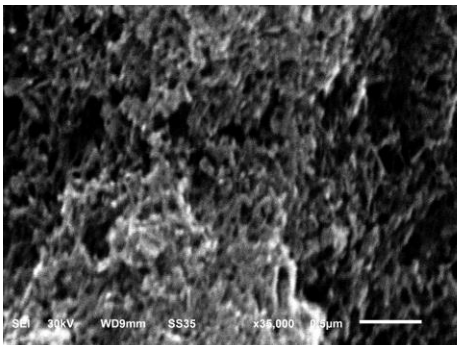


Fig. 3. SEM images of carbon nanotubes.

TEM image of the synthesized carbon nanotubes with a clear appearance of single-wall CNT is shown in Fig. 4; the diameter ranged from 25 to 50 nm. The XRD identity, SEM results, and TEM results prove that the synthesized carbon nanotubes are single-wall type.

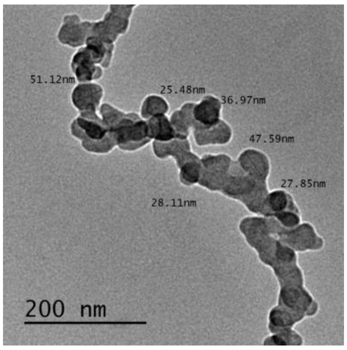


Fig. 4. TEM images of carbon nanotubes.

3.1. Adsorption isotherm

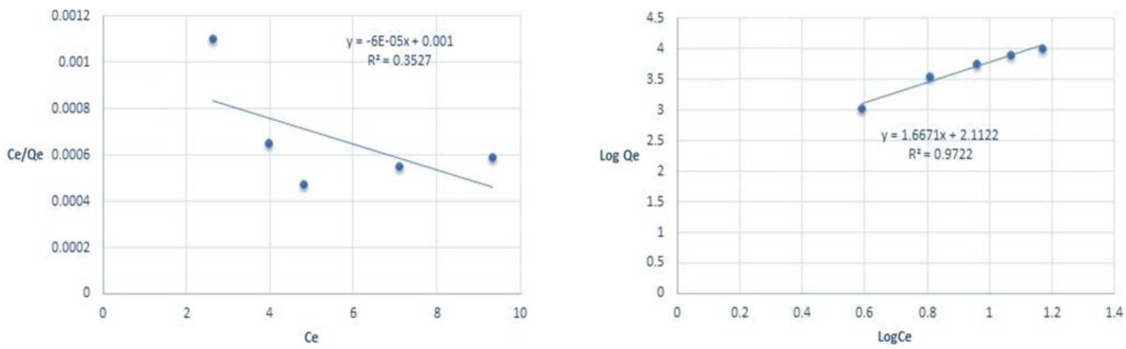
The isotherm of the adsorbing components is typically defined in the adsorption process. As a rule, Adsorption isotherm is a crucial technique to monitor the release by solid-phase at constant temperature and pH of the unwanted materials from the aqueous media. The designing of adsorption isotherms relies on experimental information. The adsorption process on solid surfaces is represented in two main models: Langmuir and Freundlich [37]. The Langmuir isotherm is given by the equation

$$\frac{Ce}{Qe} = \frac{1}{a} + \frac{b}{a} Ce \tag{2}$$

where Q_e is the adsorption amount correlates with monolayer coverage, (a) and (b) refers to the Langmuir constants which are correlated with the energy of adsorption, and C_e is the liquid phase equilibrium concentration. The Freundlich equation which is given by the equation:

$$\text{Log } [Q_e[= \log [k_f] + (1/n) \log [C_e] \tag{3}$$

where K_F and n refer to the Freundlich constants which are the predictor of the adsorption capability (potential) and intensity (strength)., respectively. Freundlich model relies on heterogeneous surface processes of sorption and offers no information about the capability of monolayer adsorption . The adsorption curve of alizarin red dye from its solution was not fitted with the Langmuir equation as shown in the relation between (C_e) versus (C_e / Q_e) in fig. (5 A) and the result shows that it does not undergo the adsorption equation of Langmuir, this can be explained that the equation for Langmuir limited to two main factors, Monolayer surface sorption with a total of similar sites and uniform energy absorption [37]**.** The adsorption curve of alizarin red Dye from its solution was fitted with the Freundlich equation as shown in the relation between (ln Qe) versus (ln Ce) in fig. (5 B) and the result shows that it does undergo the adsorption on this equation.



a) *b)*

Fig. 5. Adsorption curves of Langmuir isotherm (a) and Freundlich isotherm (b), at 298 K.

3.2. Thermodynamic parameters

The results of the effect of temperature on the alizarin red dye adsorption on the surface of carbon nanotubes with various temperatures (15, 25, 35, 45, 55) $^{\circ}$C indicate that the amount of adsorption of alizarin red dye in its aqueous solution increases with increasing temperature, which implies that the process is endothermic, with a positive mean value of ΔH, this confirms the occurs of an absorption process in addition to the adsorption process. Increasing temperature causes an increase in the amount of the diffused molecules which then adsorbed on the inside surfaces of the pores and increases the speed of diffusion. On the other hand, The strength of the relations between the adsorbed and the adsorbent increases adsorbed molecular amounts.

The thermodynamic parameters enthalpy (ΔH°), Free energy (ΔG°) of adsorption and entropy changes (ΔS°) were determined in this study to foretell the adsorption process by equations [37]:

$$\log\ Xm = \frac{-\Delta H}{2.303\,RT} + \frac{\Delta S}{R}. \tag{4}$$

$$\Delta G = \Delta H - T\Delta S \tag{5}$$

where X_m the largest amount of adsorbate (mg/g), R =8.314 J/mol K (gas constant), and T is the temperature by Kelvin. ΔH has determined from the slope of the van Hoff plot (log(X_m) versus 1/T), and (ΔS) was determined from the intercept, as shown in Fig. 6.

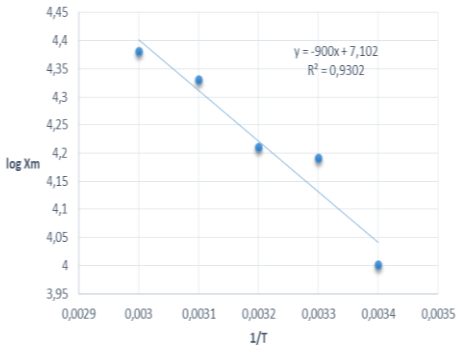


Fig. 6. The relation between log X_m and 1/T for the adsorption of alizarin red dye.

The estimated total value of ΔH was 17.23 kJ/mol, and ΔS was 59.04 J/(mol·K); this suggests that the adsorbed molecules still are in continuous movement on the surface and are due to the absorption and adsorption. The ΔG for the adsorption was calculated as -0.363 kJ/mol at 298 k; this means that the adsorption is spontaneous.

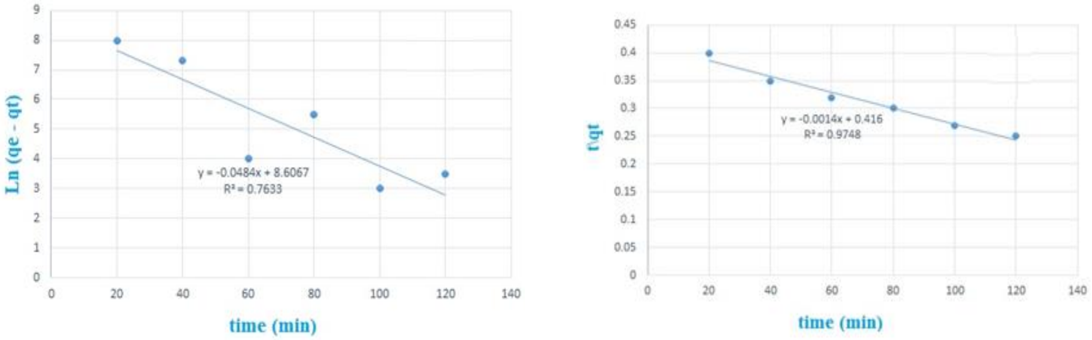
3.3. Adsorption kinetic

Kinetic models have been applied for the identification and analysis of alizarin red dye dynamics on carbon nanotubes obtained from experimental data. Dynamics considered as the reaction rate are characterized as movement or a variation in the reactant or product concentration over time. In this study, it was noticed that the time equilibrium of dye adsorption was approximately 120 min with 0. 1 g of carbon nanotube adsorbents; there have been two kinetic models: a kinetical pseudo-first-order model and a kinetical pseudo-second - order model[37]:

$$\ln\,(qe - q_t) = \ln qe - k_1\, t \qquad \text{(pseudo-first-order model)}$$

$$1/q_t = 1/\,k_2\, q_e + t\,/\,q_e \qquad \text{(pseudo-second-order model)}$$

where, qe is The quantity of red alizarin adsorbed in equilibrium (mg / g), qt is the quantity of red alizarin adsorbed in various time t (mg / g), respectively, k_1 and k_2 are the Kinetic rate constants values. The cinematic data can be correctly characterized with a high correlation coefficient (R2 > 0.9748) in the pseudo-secondary order pattern (Fig. 7).



a) *b)*

Fig. 7. Kinetic curves of the dye adsorption, pseudo first order (a), pseudo second order (b).

4. Conclusion

Single wall carbon nanotubes were synthesized by anodization technique using two graphite electrodes. The synthesized SWCNTs were characterized using XRD, TEM, and SEM techniques; the same results were given by all characterization techniques to show that the synthesized CNT type SWCNT and the diameter was 25 to 50 nm.

The adsorption potential of alizarin red on synthesized SWCNTs has been studied and is consistent with Freundlich's isotherm. Thermodynamical parameters estimation suggested values for ΔH, ΔS, and ΔG equivalent to 17.23 kJ/mol, 59.04 J/(mol·K) and -0.363 kJ/mol, respectively. The adsorption is a random endothermal process with a pseudo-second-order (R2=0.9748).

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