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Synthesis of Carbon Nanosheets from Onion Peels for Removing Methylene Blue from Aqueous Environments

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ABSTRACT

Background: Nowadays, colored water and, remarkably, wastewaters from dyeing industries are one of the most significant sources of toxic compounds in the environment. On the other hand, waste management and reduction are the most main obstacles governments encounter. Therefore, this study aimed to use waste materials to remove contaminants.
Method: First, we pyrolyzed onion peels, added distilled water, and then sonicated the solution. AFM (Atomic force microscopy) analysis determined the characteristics of produced carbon nanosheets. Batch experiments on the synthesized carbon nanosheets implemented adsorption studies. The effects of adsorbent dose, pH, dye concentration, and temperature were also evaluated.
Results: The isotherm assessments indicated that the data significantly matches the Langmuir model; moreover, the kinetic modeling results showed that the experimental data perfectly matched the pseudo-second-order kinetic model.
Conclusion: Synthesized carbon nanosheets from onion peel as a low-cost adsorbent with good properties; not only are eco-friendly materials that can significantly reduce solid waste generation, but they are efficient adsorbents for methylene blue removal from aquatic solution.

1. Introduction

Fresh water is one of the most fundamental elements for the survival of living creatures [1,2]. Water contamination has been a global concern [3]. Due to a growing tendency of industrialization and population growth, pollution of water resources has occurred worldwide. Furthermore, water requirement for different parts of agricultural, industrial, and domestic needs has dramatically risen with 70%, 22%, and 8% of freshwater consumption, respectively, which has led to wastewater [2]. Dyes and heavy metal ions are among the most important water pollutants. If water is exposed to these materials, it will not be drinkable, and in some cases, it needs a complete treatment, which might be complicated [2]. In this regard, nanoparticles are a proper candidate for water treatment programs. The materials with one or more dimensions in the nanometer size range (1-100 nm) are nanomaterials that have specific features such as large surface area, potential self-assembly, high specificity, high reactivity, high adsorption capacity, low-temperature modification ability, and catalytic potential which make them an outstanding selection for fabricating in water treatment [4]. The first synthetic commercial dye was discovered in 1986. Since then, one hundred thousand types

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of dye have been manufactured, and billions of tons are used annually [5]. Dyes are a major pollutant used in many industries, including textile, painting, paper, plastic, tannery, foodstuffs, cosmetics, etc. [3,6]. Most commercial dyes are chemically constant and hardly degradable. Therefore, they can have carcinogenic and mutagenic effects and cause severe problems in the environment [6,7]. Dyes are one of the most notable industrial pollutants that impede sunlight exposure to water, affecting the aquatic ecosystem [8]. In addition, dyes reduce oxygen levels in the water and have toxic, carcinogenic, mutagenic, and teratogenic effects on aquatic life and humans [6]. There are numerous technologies for water and wastewater treatment[2,4,9]. Among these techniques, adsorption is considered the most reliable, simple, and highly effective[7,10]. It is observed that adsorption will be a suitable water treatment technology in the future [2]. Various adsorbents are used in the adsorption, such as granular/powder-activated carbon, coke, bentonite soil, cellulose phosphohydrate, etc. However, researchers are about to fabricate low-cost absorbents synthesized from waste and by-products. Considering the health issues, the environment, and the cost-effectiveness of using waste as a waste management approach, the purpose oh this study is to developed the process by applying carbon nanosheets synthesized from onion peel to eliminate methylene blue dye as one of the conventional industrial pollutants.

2. Materials and Methods

Onion peel is agricultural waste, easily accessible, and could be collected from an onion farm in Saray, East Azarbaijan, Iran. Other solvents and Methylene blue powder could be purchased from Emertat Chimi Company (Tehran, Iran) in high purity. All the experiments were done in a volumetric flask (25mL), Erlenmeyer, and shaken on the heater-stirrer. Finally, the solution was centrifuged for 5 min and 10000 rpm in order to separate the adsorbent from the solution, and to adsorb residual color was read by UV-vis spectrophotometer (HACH-Germany DR-5000). The residual dye concentration was measured by referring to the calibration curve which was obtained by using standard solutions (1, 2, 3, 4, 5 ppm).

2.1 Preparation of carbon nanosheets

Onion peels were used as waste material for dye removal. Peels were washed using distilled water to remove any interferences and then dried in the oven (150 °C) for two h. To obtain activated carbon, we pyrolyzed dry peels for two h at 700 °C under N_2 flow and then milled them to become powder. Some distilled water was added to the powder, and the solution was sonicated for one h. The ultrasound-assisted treatments were carried out using a Sonics & Materials Inc. 500Watt ultrasonic processor equipped with a ½″ diameter probe. The ultrasonic processor was operated at a frequency of 20 kHz and an amplitude of 40%. Finally, the produced suspension contained carbon nanosheets [11,12,13].

2.2 Characterization

Atomic force microscopy (AFM, XE-100E PSIA) in the pharmaceutical faculty of Zanjan University of Medical Sciences was implemented to identify the morphology of the nanoparticles.

2.3 Preparation of dye

A stock solution of Methylene blue with a concentration of 1000 mgl^{-1} was prepared and further diluted to the desired concentration (20, 50, 100, 150, 200 mgl^{-1}).

2.4 Adsorption studies

The batch adsorption experiments of MB on carbon nanosheets synthesized from onion peels were studied to measure the effect of initial dye concentration, adsorbent [13] dose, contact time, pH, and temperature using a UV-visible spectrophotometer. The parameters were optimized using 20 mgl^{-1} dye and 500 mgl^{-1} of adsorbent. The amount of dye absorbed per unit mass of nanosheets is determined by applying equation (1):

$$q_e = v\left(\frac{c_0 - c_e}{w}\right) \quad (1)$$

Where V is the volume of solution (L), W is the mass of absorbent (g), C_0 is the initial concentration (mgl^{-1}), and C_e is the equivalent concentration (mgl^{-1}).

3. Results and Discussion

3.1 Characterization

3.1.1 AFM study

AFM measured the size of carbon nanosheets sonicated for one hour. AFM accurately provides the lateral and vertical dimensions of a single flake and shows the size distributions. Fig. 1 presents the measured size 50 nm.

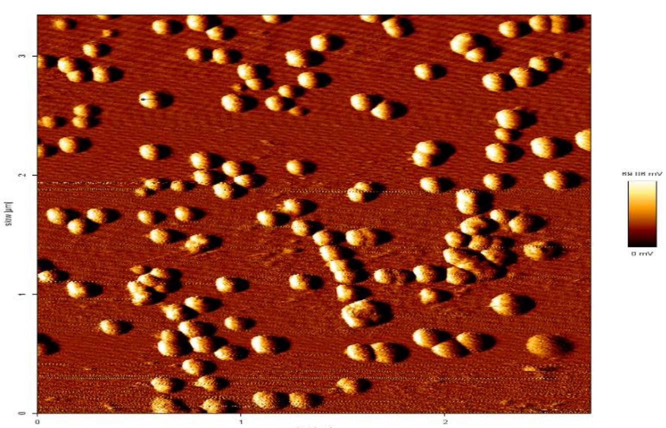

Figure 1: AFM images of graphene oxide[13] carbon flakes

3.2 Adsorption studies

3.2.1 Effect of contact time

Fig. 2 gives information about the effect of contact time on methylene blue removal. The graph indicates the trend of dye removal rising by increasing contact time (5-120 min). After 60 min, the removal proportion is approximately 53.8%, which is a bit lower than 120 min (57.9%), which means by doubling the contact time, the elimination did not increase significantly, so the 60 min was selected as an optimum contact time.

3.2.2 Effect of temperature

Fig. 2 illustrates the effect of temperature on removal percentage. Four temperatures were determined (20, 30, 40, 50 °C). As seen in Fig. 2 the removal gradually increased with a rise in temperature, which is 56.7% for 20 °C and 76.7% for 50 °C. Due to the considerable impact of 50 °C compared with lower temperatures in the adsorption process, the mentioned temperature an optimum temperature.

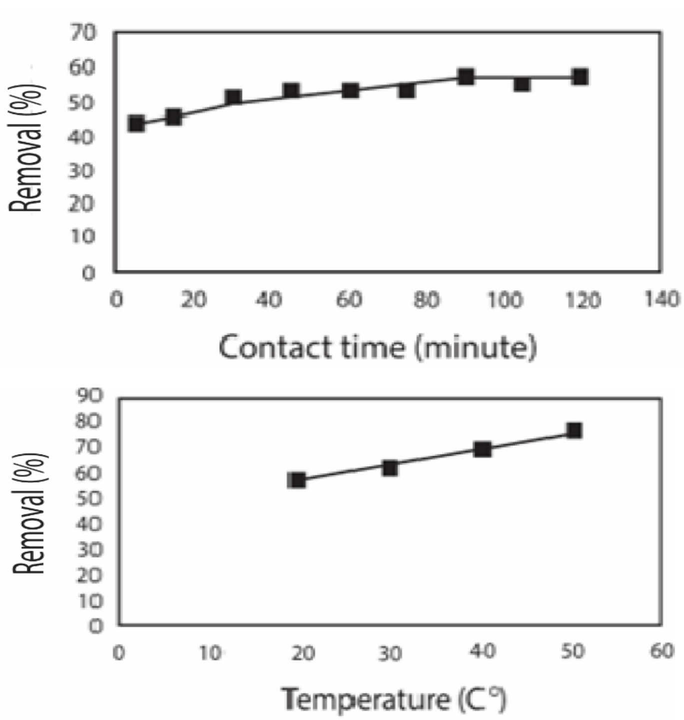

Figure 2: Effect of contact time and temperature on removal efficiency (Initial dye concentration (20 ppm) and the dosage of the absorbent (500 ppm))

3.2.3 Effect of pH

The initial pH of the solution was nearly 6.7, determined using (AZ pH/mV/Temp.meter). The process was studied in different pH (3, 5, 7, 9, 11), and the desired pH was obtained by adding 0.3N NaOH and 0.1N HCL. Fig. 3 gives data on pH performance, showing that the pH=3 adsorption process has high efficiency in dye removal, approximately 94%, with R^2= 0.99.

3.2.4 Effect of adsorbent dose

The effect of the adsorbent dose (10, 50, 100, 250, and 500 ppm) was determined at 50 °C, pH=3 and after one hour of contact time. The results show that the highest removal point occurred when the adsorbent dose was 500 ppm with R^2= 0.99, which is more than 90% removal.

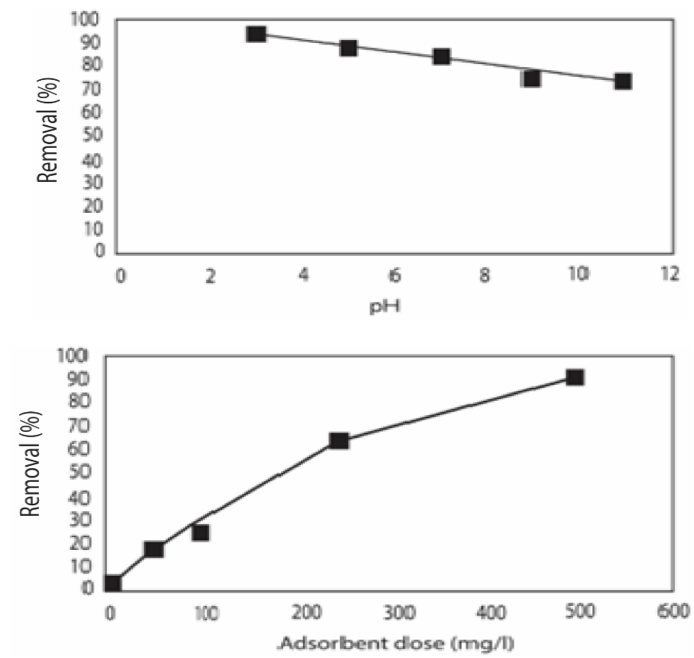

Figure 3: Effect of pH and adsorbent dose on removal efficiency

3.2.5 Effect of initial dye concentration

The amount of initial dye concentration includes 20, 50, 100, 150, and 200 ppm in this study which was evaluated in optimum conditions. According to Fig. 4, the maximum removal percentage is 94% for the initial concentration of 20 ppm, while this amount is less than 50% for further concentrations.

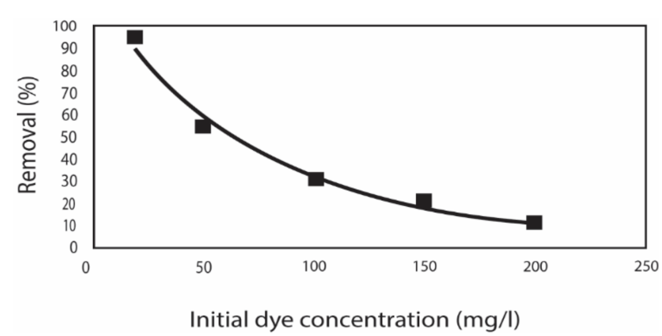

Figure 4: Effect of initial dye concentration on removal efficiency

3.3 Adsorption Isotherm

Adsorption isotherm is a mathematical equation that provides information about the equilibrium condition of adsorbate in the solid and liquid phases which investigates the function and capacity of adsorption that could be explained by some of the most studied and accepted equilibrium isotherms, the Langmuir and Freundlich equations [9,11,12]. Langmuir equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_e} + \frac{1}{k_L q_m}$$

Where q_e is the equilibrium adsorption capacity of dye on the adsorbent (mg g^{-1}); C_e, is the equilibrium dye concentration in solution (mg L^{-1}); q_m, is the maximum capacity of the adsorbent (mg g^{-1}); and k_L, the Langmuir adsorption constant (L mg^{-1}). Freundlich equation:

$$log\, q_e = log\, K_f + \frac{1}{n} log\, C_e$$

Where q_e and C_e are defined above, K_F is the Freundlich constant (L mg^{-1}), and n is the heterogeneity factor. Langmuir isotherm represents the process of homogenous monolayer adsorption in which a molecule adsorbs on the binding site, which gets abortive for further binding to happen in order to be a monolayer formation [11]. As is observed in Fig. 5, the process matches Langmuir isotherm with R_2= 0.97. the constant parameters are shown in the Table 1.

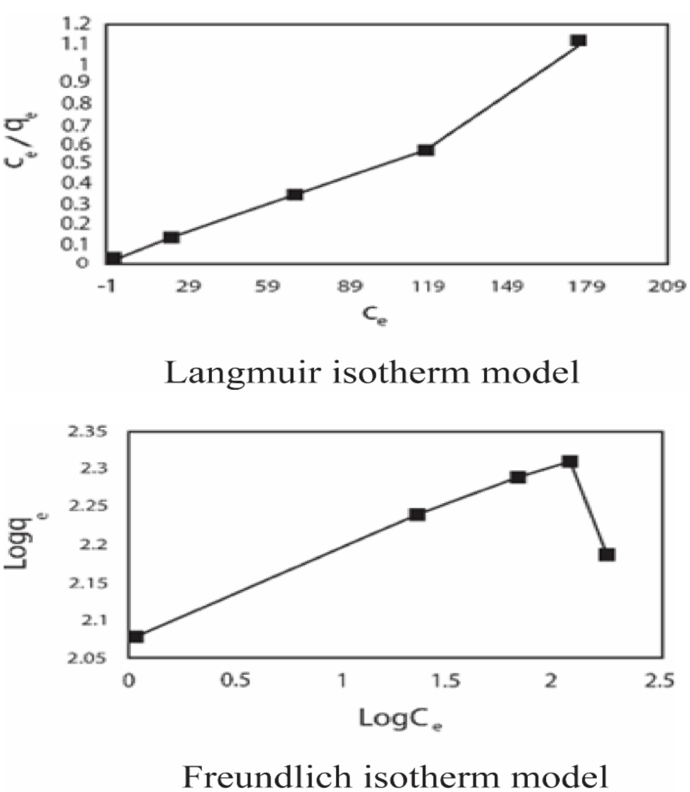

Figure 5: **Kinetic models of the adsorption process of** Methylene blue

3.4 Adsorption kinetics

The effect of various contact times, including 5, 15, 30,..., 120 min and initial dye concentration on the adsorption capacity (q_t) of synthesized nanosheets was checked using 20 mg l^{-1} of MB in an optimum condition as indicated in Fig. 6. The results showed a two-step adsorption process. The trend has a moderate increase in the initial 60 min of contact time, followed by 120 min. No further striking advancement was observed with increasing contact time which in 120 min the adsorption capacity was just beyond the amount in 60 min. We investigated the adsorption kinetics of MB onto nanosheets using two kinetic models, which are shown by Fig.7:the Lagergren pseudo-first order and pseudo-second order models whose equations are mentioned below[14]: Pseudo-first- order:

$$Ln\,(q_e - q_t) = Lnq_e - k_1 t$$

Pseudo-second-order[15]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

where q_t (mg g^{-1}) is the adsorption at time t (min); q_e (mg g^{-1}) is the adsorption capacity at adsorption equilibrium; and k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the kinetic rate constants for the pseudo-first-order and pseudo-second-order models, respectively. The evaluated parameters are shown in table 2. The correlation coefficient (R^2) for the pseudo-first-order and pseudo-second- order were 0.89 and 0.99, respectively. Therefore, the adsorption data may be well illustrated by the pseudo-second-order model.

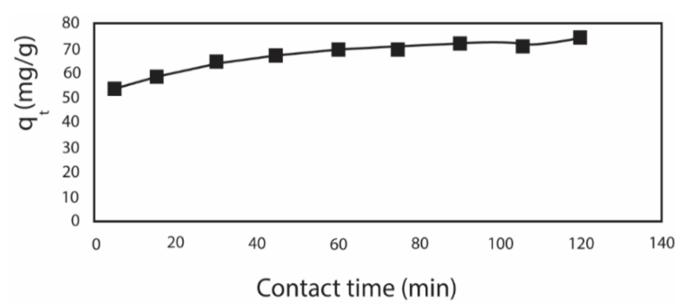

Figure 6: Effect of contact time on adsorption capacity

3.5 Thermodynamic study

To analyze the effect of temperature on MB adsorption on synthesized carbon nanosheets, we studied the adsorption process at four temperatures, including 293, 303, 313 and 323 °K which is shown in fig 8. The thermodynamic constants, such as the standard Gibbs free energy change (△G°), standard enthalpy change (△H°), and standard entropy change (△S°), which are obtained by equations below, are listed in Table 3.

$$KC= \frac{C_S}{C_e} \qquad \triangle G° = RT\, LnKC \qquad LnKC = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

Table 1: Adsorption isotherm models evaluated parameters

Type of isotherm	Langmuir			Freundlich		
Constant	R_2	K_L (L mg^{-1})	q_m (mg g^{-1}/m mol g^{-1})	R_2	n	K_F ($mg^{1-(1/n)} L^{1/n} g^{-1}$)
	0.9701	1.2	163.93	0.6089	12.48	126.29

Table 2: Kinetic models evaluated parameters

Type of kinetic	Pseudo-first order			Pseudo-second order		
Constant	R^2	K_1	q_e (mg g^{-1})	R^2	K_2	q_e (mg g^{-1})
	0.8912	0.000276	63.95	0.9985	0.000314	75.18

Table 3: Thermodynamic parameters

Temperature	∆G(kJ/mol)	∆H(kJ/mol)	∆S(J/molK)
293	-4947.52	341.5	1.404
303	-5733.56		
313	-6677.45		
323	-7921.99		

Where KC is the equilibrium constant; C_S and C_e are the concentration of MB adsorbed on carbon nanosheets and solution, respectively; T is the absolute temperature in Kelvin (K), and R is the universal gas constant (8.314 Jmol/K). The values of ∆H° and ∆S° are evaluated from the inclination and interception of the linear graph of LnKC and 1/T. Table 3 illustrates that ∆G° values are negative, which indicates feasibility and spontaneity of the adsorption process. Furthur, positive values of ∆H° and ∆S° give information about the end otermic and increase of disarray during the MB adsorption on the adsorbent.

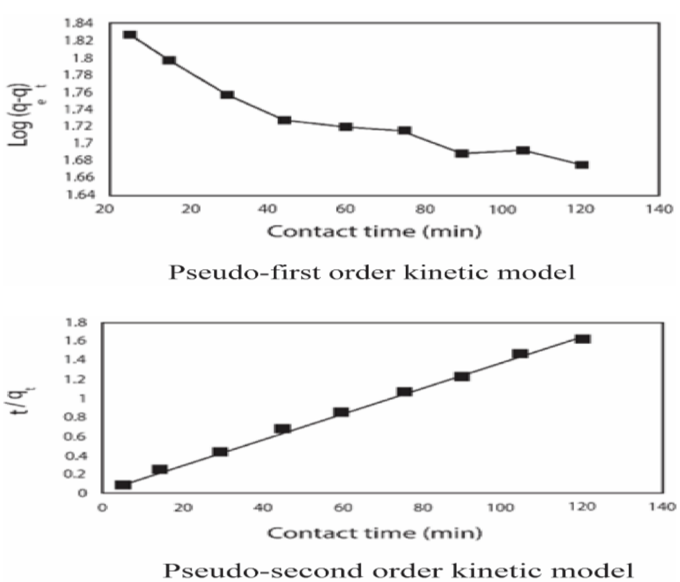

Figure 7: Kinetic models of the adsorption process of Methylene blue

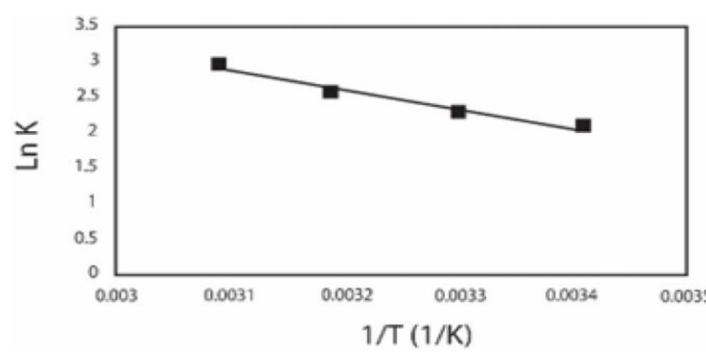

Figure 8: Thermodynamic of the adsorption process of Methylene blue

4. Conclusion

The carbon nanosheets synthesized from onion peel as a low-cost adsorbent with good properties [13], not only are eco-friendly materials that can significantly reduce solid waste generation, but they are also efficient adsorbents for methylene blue removal from aquatic solution. According to the results, the adsorption process fits Langmuir isotherm with a correlation coefficient of 0.97. In addition, it matches the pseudo-second-order kinetic model with R^2= 0.99. Moreover, due to the values of thermodynamic studies, the process is spontaneous.

Authors' Contributions

Negar Hariri: performing the experiment; data analysis; writing-original draft. Hosein Danafar: conceptualization; methodology and reviewing the manuscript. Ali

Mohammadi: advisor. Mehran Mohammadian Fazli: conceptualization; methodology and reviewing the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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