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Synthesis of copper oxide nanoparticles on activated carbon for pollutant removal in tartrazine structure

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ABSTRACT

In this study, activated carbon particles were modified by copper oxide to remove the anionic Tartrazine dye from aqueous solutions. Adsorption studies were performed as batch studies and the influences of pH, initial dye concentrations, and contact times were evaluated. Maximum removal percentage was obtained for the initial concentration of 30 mg/L and the equilibrium of the adsorption was achieved within 60 minutes of contact time. The Langmuir and Freundlich kinetic models were used for analyzing the equilibrium data. It was shown that better fitting was observed by the Langmuir model. Pseudo-first-order and Pseudo-second-order kinetic models were also applied to understand the kinetics of the adsorption processes. It was found that the Tartrazine adsorption followed the pseudo-second-order kinetic model.

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1. Introduction

The major environmental pollution source is the discharge of dye-containing wastewater from cosmetics, textiles, food, plastic, and paper industries [1–5]. These residual dyes present in the wastewater endanger the life of fish as well as other organisms. Moreover, these substances absorb sunshine resulting in photosynthesis prevention and an adverse impact on the natural aquatic ecosystem. As a result of their complex structure and high molecular weight, the degradation of organic dyes is usually difficult [1-3]. Different approaches, such as membrane separation, oxidation, flocculation, coagulation, and adsorption, have been proposed for the removal of these dyes [4-6].

Recently, nanoparticles have been widely investigated because of their potential applications such as information storage devices, optoelectronics [7], nanoelectronics [8], nanosensors [9-11], catalysts, microelectronics, and magnetic recording media [12]. Factors such as size distribution and morphology of the nanoparticles can affect their properties and applications [13-15]. The physical and chemical properties of copper oxide nanoparticles make them promising for applications such as solar energy conversion, gas sensors, batteries, catalysis, high-temperature superconductors, and antibacterial agents with low toxicity and low cost [16, 17].

In wastewater treatment, various adsorbents have been investigated for pollutant removal. Among them, activated carbon (AC) is the most extensively utilized adsorbent because of having various structural forms, chemical stability, low density, and large specific surface area [4]. This carbonaceous material with high porosity is widely utilized in water treatment processes to remove organic/inorganic pollutants [18-20] because of its tunable chemical and physical characteristics [21, 22] including modifiable surface, high surface reactivity, large surface area, and highly porosity with controllability [23]. Currently, activated carbons are mostly considered as a catalyst and mild reducing agent with a low cost. Thus, the development of low-cost effective carbons and other efficient material for contaminants removal from wastewater is necessary [24].

The effect of different parameters such as the CuO/AC ratio, pH, temperature, shaking rate, and contact time on the adsorption performance of this system has been studied in various scenarios. Tartrazine or trisodium (IUPAC name) is known as a typical synthetic, anionic dye with water solubility [25, 26]. Tartrazine causes intolerance and allergic reactions, especially for those with aspirin intolerance and asthmatics. Therefore, it is required to treat the wastewater containing various concentrations of tartrazine prior to discharge [4, 27].

Tartrazine is an anionic, synthetic, water-soluble azo dye with yellow color, which consists of one carboxylic functional group, one azo (N=N), and two sulphonic groups. Tartrazine is widely utilized in pharmaceuticals (gels, pills, and capsules), cosmetics, and different food products (jellies, chewing gum, chips, alcoholic beverages, sodas, and cakes). Several side effects have been appeared to be caused by Tartrazine including allergic reactions, attention deficit disorder, hyperactivity in children, damage to DNA, and lethal asthma [28, 29].

Most studies have concentrated on removing one or two of these contaminants, while several contamination forms usually exist in drinking water. Therefore, the development of materials with the potential to remove several pollutants is extremely valuable, as it could suggest...
2. Materials and Methods

2.1. Materials

Tartrazine (Trisodium (4E)-5-oxo-1-(4-sulfonatophenyl)-4-[4- sulfonatophenyl]hydrazono]-3-pyrazolecarboxylate; C.I., 19,140; with a molar mass of 543.40 g mol L⁻¹ and chemical formula of C₆H₇N₄Na₃O₁₂S₂) was selected as an adsorbate. Fig. 1 shows the molecular structure of Tartrazine. Highly pure materials with the analytical grade were used that were obtained from Merck, Iran. The dye concentration was measured at 427 nm. UV–Vis spectrophotometer was used to study the adsorption performance. A pH meter was utilized to measure the pH value of the solution.

2.2. Sample preparation

1 g of active carbon and 0.024 g of Cu (NO₃)₂.3H₂O was added to distilled water (100 mL) followed by stirring for 30 min. 1.85 g of NaBH₄ was dissolved in distilled water (50 mL), and then 10 mL of this solution was added dropwise to the copper nitrate solution and stirred for 2 h at room temperature. The sediments were filtered, washed with distilled water, and dried at 80 °C for 10 h followed by grinding. To study the adsorption performance of CuO-modified AC, 10 mL Tartrazine solution and 2 mL of phosphoric acid buffer solution (pH=7) were dissolved in 100 mL of distilled water. 0.05 g of the adsorbent particles was added to the prepared solution and stirring was applied for 30 min. 10 mL of the solution was centrifuged in determined intervals to measure the adsorption by a UV–vis spectrophotometer at 423 nm indicating the dye concentrations.

2.3. Determination of PZC point

For determination of zero charge point (pH_m), solutions of the absorbent with the ratio of 1 to 1000 (w/v) with different initial pH values (pH_i) were prepared using 0.01 M HCl or NaOH. The dispersed solutions were stirred at ambient temperature for 24 h and the pH values of the final solutions (pH_f) were then measured. The ΔpH values that are the differences between the initial and final values of pH were plotted vs. pH_i and the point at which the pH change was zero was reported as pH_m.

2.4. Kinetic models

During the physicochemical process of adsorption, the mass transfer of a solute occurs from the aqueous phase to the surface of an adsorbent. In this research, pseudo-first-order and pseudo-second-order kinetic models were used to study the Tartrazine adsorption mechanism onto copper oxide-modified AC. Equation 1 represents the Lagergren-first-order kinetic model [30]:

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]

where \( q_t \) denotes the Tartrazine amounts adsorbed at equilibrium (mg/g), \( q_e \) represents the Tartrazine amounts adsorbed at time \( t \) (min), and the rate constant (min⁻¹) was represented by \( k_1 \). The \( q_e \) value was obtained using the curve of \( \ln(q_e - q_t) \) vs. time. The following linear pseudo-second-order model [30] was also used for kinetic studies.

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

In this equation, the rate constant of the pseudo-second-order kinetic adsorption model is denoted by \( k_2 \). The slope of the linear plots presenting the change of \( t/q_t \) with time is 1/\( q_e \) and the intercept value gives 1/\( k_2 q_e^2 \).

2.5. Adsorption isotherms

The interaction between the adsorbents and adsorbates can be described in the equilibrium state. To fit the adsorption isotherm data, the Langmuir and Freundlich models were used. Selecting the best-fit model was done based on the linear regression correlation coefficient values (R²). The assumptions of the Langmuir model are the adsorption in a monolayer and the absence of interaction between the molecules of the adsorbate. Equation 3 is the linear equation of Langmuir isotherm.

\[ \frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \]

where \( q_e \) represent the equilibrium adsorption amount (mg/g) and \( C_e \) denotes the equilibrium concentration (mg L⁻¹). The Langmuir constant and the theoretical maximum adsorption capacity are denoted by \( K_L \) and \( q_m \), respectively. There exists another model that describes the solutes adsorption from a liquid to the solid surface, which is known as the Freundlich model. In this model, it is assumed that different adsorption energies in several sites are involved. The Freundlich model follows the presented equation of:

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]

In this equation, \( C_e \) and \( q_e \) are the equilibrium concentration of Tartrazine (mg L⁻¹) and the adsorbed dye at equilibrium, respectively (mg/g). The adsorbate amount that is adsorbed on the surface for a unit equilibrium concentration is defined by the Freundlich constant of \( K_F \), which is a distribution or adsorption coefficient. The Freundlich constant of \( n \) reveals how favorable the adsorption process is. All experiments were performed on the batch.

Mass balance equation determines the adsorption capacity in the adsorbents equilibrium. The equation is based on the assumption that the dye amount adsorbed on the adsorbent surface is equal to the amount of the removed adsorbate from the solution:

\[ q_e = \frac{V(C_0 - C_e)}{m} \]

where \( C_0 \), \( m \), and \( V \) denote initial adsorbate concentration (mg L⁻¹), adsorbent weight (g), and volume of aqueous solution (L), respectively. For evaluation of the removal efficiency, samples were studied after the flocculation/coagulation and sedimentation. In this regard, the apparent color and the concentration parameters of the yellow dye were characterized. All analyses were carried out based on standard methods and repeated three times for each sample. Equation 6 was employed.
calculate the removal efficiency for each analyzed parameter.

\[
\text{Removal efficiency } \% = \left( \frac{C_i - C_f}{C_i} \right) \times 100
\]  

(6)

In this equation, \( C_i \) is the initial value of each parameter and \( C_f \) is its final value.

3. Results and discussion

3.1. Determination of PZC point

One of the important properties for the surface of solids containing hydroxyl groups is the determination of the PZC point. PZC point is the pH of the surrounding liquid medium, at which the sum of the positive surface charges is in balance with the total negative surface charges and the surface charge density is zero. Determining the PZC point for nanoscale structures is more important because of the increase in surface-to-mass ratio in these particles; subsequently, their surface charge increases. The pH change vs. pH is shown in Fig. 2. It is observed that at pH = 7.1, the pH change is zero, indicating that the adsorbent charge at this point is zero.

3.2. pH effect

To investigate whether the pH changes influence the contaminant removal and apparent color, the adsorption percentage was measured in different pH of the solution. The adsorption percentages were measured by a UV-Vis spectrometer based on a plotted calibration curve with dye concentrations between 1 to 3 mg L\(^{-1}\). In Fig. 3, the effect of pH on the percentage removal of Tartrazine is illustrated. The results showed that the pH value does not significantly affect the dye removal, therefore pH=7 was selected as optimal pH value.

3.3. Effect of the adsorbent amount

Modification of activated carbon with copper oxide nanoparticles affects its textural features including the decrease in diameter, pore volume, and surface area. To evaluate the influence of the absorbent amount on the removal efficiency, the adsorption was measured in solutions with different amounts of the absorbent particles ranging from 0.001 to 0.15 g. According to the observations, with an increase in the absorbent amount, the amount of surface adsorption enhanced (Table 1). The dye removal reached the highest value in 0.05 g of absorbent and the further increase in the dye concentration did not show significant changes in the adsorption. This might be due to the interaction of dye molecules with each other or other molecules in the solution preventing the complete removal of the contaminants. Fig.4 shows the removal percentage vs. Tartrazine concentration.

3.4. Effect of contact time and initial adsorbate concentration

The influences of the initial adsorbate concentration of Tartrazine dye as well as contact time on the dye removal from the aqueous solu-
tion were investigated. The results of these factors are presented in Fig. 5 and Fig. 6, respectively. According to Fig. 4, the increment of the initial concentration of the dye led to the reduction of Tartrazine removal. Principally, the initial concentration of Tartrazine can provide the driving force necessary for overcoming the resistance to the dye mass transfer between the solid surface of AC and aqueous phase. On the other hand, the interaction between the molecules of Tartrazine increases leading to the reduction of removal percentages. As seen in Fig. 6, the adsorption of the dye onto the modified AC was a relatively rapid process, revealing a high affinity between the surface of the absorbent particles and Tartrazine molecules. The accessibility of adsorption sites on the adsorbent surface was indicated by the high adsorption efficiency at an initial stage. The contact time does not significantly affect the dye removal. The required time for reaching an equilibrium was found to be 60 min. Therefore, all subsequent experiments were conducted at the contact equilibrium time of 60 min.

3.5. Study of adsorption kinetics

The kinetics of the Tartrazine adsorption onto copper oxide-modified AC surface was studied using the adsorption data for different initial dye concentrations. The adsorption kinetic curves are illustrated in Fig. 7. The pseudo-first-order and pseudo-second-order models were used to fit the adsorption kinetic data. The parameters of these models are listed in Table 2.

Table 2.
Kinetic parameters of adsorption

<table>
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<td>$R^2$</td>
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3.6. Adsorption isotherms

Considering the values of $C_r$, $C_e$, solution volume of 0.1 L, and the adsorbent weight of 0.05 g, the values of $q_e$ for the dye concentrations of 15, 25, 35, and 40 mg L$^{-1}$ were obtained at the equilibrium time of 60 min. The results are shown in Table 3. The $C_e/q_e$ diagram was then plotted against $C_r$ to obtain the parameters of the two equations, which are listed in Table 4. To show the degree of adsorption tendency to the adsorbent, a non-dimensional parameter called $R_L$ is used, which is calculated by Equation 7 obtained from the Langmuir equation.

$$R_L = 1/(1 + K_L C_r)$$  \hspace{1cm} (7)

where $C$ denotes the initial concentration of the dye (mg L$^{-1}$). If the $R_L$...
value is greater than 1, it reveals that surface adsorption has occurred under undesirable conditions. If \( R_e = 1 \), it will indicate that the adsorption is linear. When the \( R_e \) value is less than 1 and greater than zero, surface adsorption will occur under favorable conditions, and if the \( R_e \) equals to 0, the adsorption will be irreversible. The values of \( R_e \) for the different initial concentrations are shown in Table 5. Based on the obtained \( R_e \) values, surface adsorption has occurred under favorable conditions.

The linear form of Langmuir and Freundlich models was utilized to fit the adsorption isotherms (Fig. 8). The correlation coefficient of \( R^2 \) indicates whether the isotherm equations are applicable for the description of the adsorption process. The higher linearity and \( R^2 \) in the \( C_e/q \) vs. \( C_e \) curve (Fig. 8a) indicated that the Langmuir equation could be applied for fitting the experimental data and interpret the dye adsorption onto copper oxide-modified AC particles. It is worth noting that the theoretical value of \( q_m \) was obtained close to the maximum adsorption capacities \( (q_m) \) obtained from the experimental studies. Moreover, it is interesting to understand whether the adsorption of the dye is favorable or not. In the Freundlich model, when the \( n \) values are in the range of 2–10, the adsorption is good, while the values less than 1 show poor adsorption behavior. The values between 1 to 2 indicate moderately difficult adsorption characteristics. Based on the obtained values, the studied material is a good adsorbent for tartrazine. Surface heterogeneity or adsorption intensity is measured by the slope of \( 1/n \) in the range of 0 to 1. A straight line with slope \( 1/n \) is obtained from the curve of \( 
\frac{\ln q}{\ln C_e} \) vs. \( q \) in \( C_e \) (Fig. 8b). If the value gets closer to 0, it indicates a more heterogeneous surface.

4. Conclusions

In this research, activated carbon was modified with copper oxide to absorb the Tartrazine dye from wastewater and the contributed mechanisms in the adsorption process were investigated. AC particles modified with copper oxide were found to be very efficient in the removal of Tartrazine dye. According to the batch experiments, the adsorption process was conducted rapidly, as maximum removal percentage of the dye obtained within 60 minutes of contact time for the initial dye concentration of 30 mg/L. Based on the equilibrium data related to the Freundlich and Langmuir models, the Langmuir isotherm appeared to be more concise for the description of the Tartrazine adsorption. The adsorption kinetics followed closely the pseudo-second-order kinetic model. Finally, the removal efficiency was found to be more than 98%. Therefore, the modified AC particles can be a good candidate for the removal of Tartrazine from aqueous solutions.

REFERENCES


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