



Proceeding Paper Removal of Brilliant-Green Dye Using Carbon-Loaded Zinc Oxide Nanoparticles: A Comparative Isotherm Study [†]

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Abstract: Adsorption is a phase transfer process extensively utilized for removing substances from fluid phases (either gases or liquids) to the solid phase, also known as the adsorbent particle. This natural method is observable in various environmental compartments. In water or effluent treatments, a solid interacts with a pollutant, such as a dye. The pollutant is termed the adsorbate, and the solid is the adsorbent. This technique has been proven efficient in removing a broad range of contaminants. This study investigates the use of the adsorption technique to eliminate brilliantgreen dye from aqueous solutions, employing different adsorbent materials like AC, CNT, ZnO, and ZnO/AC prepared through the hydrothermal method. The compositions of these composites were elucidated using analytical techniques such as FTIR, EDX, and FE-SEM. The study also compares the efficiency of different carbon sources in removing brilliant-green dye, namely, activated carbon (AC), carbon nanotubes (CNTs), zinc oxide (ZnO), and AC/ZnO nanocomposites as adsorbents. The removal efficiency (E%) for BG dye followed the order: CNT > ZnO/AC > AC > ZnO. Additionally, a comparison was made between sonication and a shaker water bath for different carbon sources in removing brilliant-green dye. The shaker water bath demonstrated an efficiency range of 90.122% to 42.812%, while sonication showed 90.011% to 32.012%. The adsorption data aligned with the Freundlich isotherm model.

Keywords: adsorption; isotherms; removal; brilliant-green dye; activated carbon; carbon nanotube

1. Introduction

Pollution from point sources such as wastewater treatment plants (WWTPs) has a significant impact on freshwater ecosystems. Effluents from WWTPs introduce a variety of chemical stressors to rivers, including excess organic matter, inorganic nutrients, and a plethora of organic micro-pollutants such as pesticides, dyes, drugs, pharmaceuticals, and industrial products [1–4]. In addition to these chemicals, rivers may also be subjected to other concurrent stressors. Notably, disruptions in water flow and elevated water temperatures pose threats to river biota, often leading to local extinctions and an overall decline in biodiversity [5–9]. Such stressors act as environmental filters, exerting additional selective pressures that influence the composition and relative abundance of species within riverine biological communities. Numerous studies have linked exposure to these pollutants with various health issues, including cancers, skin irritations, respiratory



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). complications, and allergies. A significant portion of these dyes are derived from aromatic organic compounds [10,11]. Brilliant green, for instance, is widely utilized as a biological stain, particularly in Gram staining procedures to differentiate bacterial species.

Additionally, it serves as a histological stain and is added to domestic animals to inhibit the proliferation of putrefactive parasites and fungi. Several methods, such as ion exchange, photodegradation, filtration, and adsorption, have been employed to eliminate organic dyes from water [12–15]. Among these, the adsorption technique, being cost-effective and highly efficient, has garnered significant attention from researchers in recent times.

2. Method

2.1. Determination of Maximum Absorption (λ_{max}) of BG Dye

The chemical structure of brilliant-green dye is shown in Figure 1. This dye, with a molecular formula of $C_{27}H_{34}N_2O_4S$ and a molecular weight of 482.6 g/mol, is an odorless yellow-green to green powder. The maximum absorption wavelength of the dye was determined using a UV spectrophotometer. A concentrated dye solution (30 mg/L) was prepared, and the λ_{max} was found to be 630 nm, recorded over a range of 500–700 nm. This is further illustrated in Figure 1.



Figure 1. The chemical structure of brilliant-green dye and its UV-visible absorption spectrum.

2.2. Adsorption Studies

To achieve maximum removal efficiency, tests were conducted in multiple sets. Each set consisted of 0.05 gm of the composite placed in distinct stoppered conical flasks. To each flask, 100 mL of freshly prepared BG dye solution with an initial concentration of 50 mg/L was added. The samples were agitated in a shaking incubator at 160 rpm for 60 min and subsequently separated via centrifugation at 6000 rpm for 10 min. The resulting solutions were analyzed using a UV-visible spectrophotometer PC 1800 at $\lambda_{max} = 630$ nm. The adsorption capacity at equilibrium was determined using the equation:

$$q_e = \frac{V_{\rm sol}(C_o - C_e)}{m} \tag{1}$$

The adsorption efficiency and removal capacity of the dye on the adsorbents were calculated according to:

$$\%E = \frac{(C_o - C_e)}{C_o} \times 100$$
 (2)

3. Results and Discussion

3.1. Characterization of ZnO/AC Nanocomposite

3.1.1. FT-IR Spectroscopy

FT-IR spectroscopy is utilized to identify changes in functional groups, shedding light on the affinity between atoms. After the surface was dried and ground with potassium bromide (KBr), spectra were taken both before and after adsorption to observe the absorption peaks. As shown in Figure 2, the infrared spectra of the AC/ZnO nanocomposite are presented [16]. A broad band observed at 3350 cm^{-1} can be attributed to the stretching vibrations of the OH group. Another vibration identified in the range $3020-2850 \text{ cm}^{-1}$ corresponds to asymmetric stretching vibrations of aliphatic and aromatic C-H groups. The C=O group, present in the nanocomposite, manifested absorption peaks within the range $1620-1740 \text{ cm}^{-1}$. Additionally, the range $480-800 \text{ cm}^{-1}$ revealed absorption peaks associated with C-C, C-N, and C-O bonds. However, the FT-IR analysis of the nanocomposite showed band shifts, indicating interactions between the carboxylic groups on the AC/ZnO nanocomposite [17,18].



Figure 2. FT-IR spectrum of nanocomposite before and after dye adsorption.

3.1.2. Scanning Electron Microscopy and Energy-Dispersive X-ray

Figure 3 presents scanning electron microscopy images captured at a magnification of 200 nm. Through this analysis, insight was gained into the morphology of the particles, the nature of clusters on the adsorbent surfaces, and their porosity, both prior and subsequent to adsorption. According to the figure, the activated carbon surface exhibits a rough texture. However, after the introduction of zinc oxide onto the activated carbon, small clusters, irregular in nature, become evident. This showcases the surface prior to dye adsorption. Post-dye deposition on the ZnO/AC nanocomposite surface, an enlargement of these clusters is observed, indicating the incorporation of the dye within the surface. This depicts the surface following adsorption. EDX serves as a versatile tool for both qualitative and semi-quantitative analyses. The EDX patterns for the nanocomposite presented in Figure 3 confirm the presence of Zn and O within the ZnO-AC EDX pattern delineates the presence of Zn, O, and C within the AC/ZnO nanocomposite [19,20].



Figure 3. FE-SEM of (**a**) activated carbon, (**b**,**c**) nanocomposite before and after BG dye adsorption, and (**d**) EDX analysis of ZnO/AC nanocomposite.

3.1.3. Comparative Adsorption of BG Dye Using Different Carbon Sources

A comparative study was conducted to assess the dye removal efficacy of various adsorbents, namely, activated carbon (AC), carbon nanotubes (CNTs), zinc oxide (ZnO), and AC/ZnO nanocomposites. As observed in Figure 4, the dye removal efficiency (E%) followed the order: CNT > ZnO/AC > AC > ZnO. This can be attributed to the exceptionally high efficiency and large surface area of the carbon nanotube, which resulted in a removal efficiency of 99.12%. In contrast, zinc oxide demonstrated a comparatively lower removal efficiency of 40.22% [21,22].



Figure 4. Comparison of different carbon sources for dye removal at 20 °C, over 1 h, using 0.05 g in 100 mL water, with a concentration of 50 mg/L.

3.1.4. Comparative Adsorption Using Shaker Water Bath and Sonication for BG Dye Removal

A comparative study was conducted between sonication and shaker water bath methods for dye removal using various sources of carbon, namely, activated carbon (AC), carbon nanotube (CNTs), AC/ZnO nanocomposites, and zinc oxide (ZnO), as depicted in Figure 5. The removal efficiency (E%) for the shaker water bath method was found to be 90.122%, 84.21%, 82.812%, and 40.11% for the respective carbon sources, whereas sonication yielded removal efficiencies of 90.011%, 77.2%, 72.2%, and 32.01% for the same carbon sources. This difference can be attributed to the ultrasound waves' capability to break down dye molecules and dissolve the surface in the solution, thus slightly reducing the removal percentage compared to the shaker water bath method [23,24].



Figure 5. Comparison between sonication and shaker methods using different carbon sources.

Further comparison was made using varying amounts of activated carbon (AC) decorated with zinc oxide (ZnO). This was studied using 0.05 g of C/ZnO, 0.1 g of C/ZnO, 0.2 g of C/ZnO, 0.5 g of C/ZnO, and 1 g of C/ZnO nanocomposites, as shown in Figure 6. The highest removal efficiency (E%) was observed for ZnO/AC (1 gm) at 90.451%, followed by efficiencies of 86.56% for ZnO/AC (0.5 gm), 80.59% for ZnO/AC (0.2 gm), 72.26% for ZnO/AC (0.1 gm), and 67.55% for ZnO/AC (0.05 gm) in removing brilliant-green dye.



Figure 6. Effect of comparison between amounts of C decorated with ZnO nanocomposite (experimental conditions: mass of absorbent, 0.5 g; temperature, 20 °C; concentration, 50 mg/L; contact time, 60 min).

4. Adsorption Isotherms

Adsorption isotherms were evaluated using three distinct models: the Langmuir and Freundlich models. The results are depicted in Figure 7. The Freundlich model, which is associated with adsorption on a heterogeneous surface, is expressed using the following equation:

$$Q_e = k_f C e^{\frac{1}{n}} \tag{3}$$

where *Ce* (mg/L) represents the concentration at equilibrium, Q_e is the amount of dye adsorbed (mg/g), n is the adsorption strength, and k_f signifies the adsorption capacity. However, the Langmuir adsorption isotherm describes monolayer adsorption formed on a surface with a consistent number of fixed positions. Table 1 suggests that the adsorption process aligns better with the Freundlich isotherm, suggesting multilayered adsorption [25].



Figure 7. Several adsorption non-linear model fits for dye adsorption onto nano-composite.

Table 1. Constants and correlation coefficients of the Langmuir and Freundlich adsorption isotherms for brilliant-green dye adsorbed onto nano-composite at 20 °C.

Langmuir Equation			Freundlich Equation		
K _L	qm	R ²	K _F	n	R ²
0.145	218.633	0.9435	927.63	0.436	0.9663

5. Conclusions

This study demonstrated the high-quality removal of brilliant-green dye from aqueous solutions using AC/ZnO nanocomposites. The results indicated that the shaker method exhibited better efficiency (E%) compared to sonication for the removal of brilliant-green dye. Furthermore, the most effective adsorption was observed when using 1 gm of C/ZnO nanocomposite. Various analytical tests, including FTIR, FE-SEM, and EDX, were employed to analyze the morphological properties of the adsorbents before and after adsorption. The EDX pattern for the ZnO-AC confirmed the presence of Zn, O, and C elements within the AC/ZnO nanocomposite.

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