

Research Article

Environmentally Friendly Mesoporous Nanocomposite Prepared from Al-Dross Waste with Remarkable Adsorption Ability for Toxic Anionic Dye

Inas A. Ahmed (),¹ Najlaa S. Al-Radadi (),² H. S. Hussein (),³ and Ahmed H. Ragab¹

¹Department of Chemistry, Faculty of Science, King Khalid University, Abha, Saudi Arabia
 ²Department of Chemistry, Faculty of Science, Taibah University, Madinah Monawara, Saudi Arabia
 ³Chemical Engineering & Pilot Plant Department, Engineering Division, National Research Centre, Cairo, Egypt

Correspondence should be addressed to Inas A. Ahmed; inas.2011@yahoo.com

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In this work, a mesoporous nanocomposite composed of nanogibbsite (α -Al(OH)₃) and nanosilica was prepared. Gibbsite nanoparticles (GNPs) with a crystal size of \approx 38 nm were prepared from Al-dross industrial waste products in an acidic environment at 100°C. Nanosilica (NS) with a crystal size of \approx 13 nm was prepared from sodium silicate using dilute hydrochloric acid. The deposition of nanosilica onto gibbsite particles was investigated. The mesoporous silica-gibbsite (NSG) nanocomposite was examined by evaluating its ability to adsorb the toxic anionic dye Eriochrome black T (EBT) from aqueous solution. The compositional and morphological properties of NSG nanocomposites were studied by means of the FTIR spectroscopy, X-ray fluorescence (XRF), XRD, SEM, and TEM techniques. The effect of dye concentration, pH, adsorbent dose, contact time, and temperature was investigated. The sorption models, the isotherms, and the thermodynamic parameters ΔH° , ΔG° , and ΔS° were evaluated. The N₂ adsorption-desorption isotherms revealed that mixing the two prepared materials (NS and GNPs) to form the NSG nanocomposite resulted in good properties (a surface area of 62.34 m²·g⁻¹, a pore radius of 22.717 nm, and a pore volume of 0.7081 cm³·g⁻¹). The results show that the prepared NSG nanocomposite has a remarkable ability to adsorb toxic anionic dyes.

1. Introduction

Pollution of the environment is one of the society's main problems. There is an urgent need to reduce the quantities of industrial solid waste materials that are currently being landfilled. At present, water pollution that arises from the discharge of industrial wastes is considered to be a serious environmental problem, especially in developing countries [1]. The presence of only small amounts of dyes in water (<1 ppm for some dyes) can negatively affect the quality of the water and aquatic life in it. The use of synthetic dyes in the textile, rubber, paper, plastic, pharmaceutical, and food industries is increasing, as they are low in cost, stable, easy to synthesize, have several colors in comparison to natural dyes, and raw materials for them are readily available. Now, more than 10,000 dyes are commercially available, and most of these are not biodegradable due to their complicated aromatic molecular structure [2]. Eriochrome black T (EBT), which is a type of azo dye, accounts for over 50% of the dye industry in the world. Moreover, it is a toxic and carcinogenic compound. Hence, the removal of this dye from industrial effluents must be considered [3, 4].

Various methods for water treatment have been developed. However, the physical adsorption method is the most attractive as it is simple, easy to perform, convenient, effective, environmentally friendly, and economic [5–8]. The use of nanotechnology in wastewater treatment has attracted a great deal of interest [9]. Nano adsorbents offer considerable decontamination potential due to their unique properties as nanoscale materials [10]. They are known for their high surface area to volume ratio, small size, high capacity for regeneration, and ability to make available a large number of reactive sites [11]. Nanoadsorbents based on inorganic iron and aluminum nanomaterials [12-16] were the first studied nanoadsorbents due to their low cost and high pollutant removal efficiency. Nanoalumina is one of the most remarkable adsorbents for water and wastewater treatment [17-22]. Abiyu Kerebo et al. found that nanoaluminum oxy hydroxide has a superior adsorption capacity. Aluminum trihydroxide (Al(OH)₃) and aluminum monohydroxide (AlOOH) exist in many structural forms [23]. As the surface of an adsorbent is positively charged and electrostatically attracted to the anionic dye species, it has a higher rate of adsorption. Moreover, nanosilica has been successfully applied in wastewater treatment. Amorphous silica's effectiveness as an adsorbent depends on the hydroxyl groups in many cases. Hydroxyl groups act as molecular adsorption centers through which the adsorbent interacts with the pollutant material [24]. The surface characteristics of an adsorbent, such as its surface area and functional groups, can alter its efficiency. A higher specific surface area is essential to improving the adsorption capacity of adsorbents. Leonard et al. [25] found that the use of substances with various surface potentials causes an increment in the attraction of ions within the adsorption process. The adsorption of anionic dyes has been insufficiently studied. Since water contaminants include both cationic and anionic pollutants, it is of particular importance to study the adsorption of anionic pollutants.

In this study, we developed an environmentally friendly mesoporous nanocomposite from industrial solid waste materials for the efficient removal of EBT from contaminated water based on a low-cost, simple, and reliable method. The synthesized mesoporous nanocomposite was found to have a great adsorption capacity. The synthesized mesoporous nanocomposite is composed of nanogibbsite prepared from Al-dross industrial waste products and nanosilica prepared from sodium silicate. The effect of dye concentration, solution pH, adsorbent dose, temperature, and contact time was investigated. Sorption models using Mories-Weber and Lagrange equations were used to identify the adsorption mechanism and the reaction order. An isotherm model of the adsorption was developed by using the Langmuir equation and the Freundlich equation to determine the adsorption capacity and the type of adsorption, respectively. The thermodynamic parameters ΔH^{o} , ΔG^{o} , and ΔS^{o} were determined to identify the reaction temperature, the change in entropy, and the reaction spontaneity, respectively.

2. Experimental Methods

2.1. Starting Materials. The starting materials were Al-dross, sodium silicate, hydrochloric acid (HCl), ammonium hydroxide (NH₄OH), and Eriochrome Black T. All chemicals were obtained from commercial sources and used without further purification. Deionized water was used in all synthesis steps.

2.2. Synthesis of Nanosilica. Nanosilica was synthesized via acid hydrolysis of sodium silicate using dilute hydrochloric acid. The acid was slowly added to sodium silicate at 60°C

with stirring for 30 min to carry out the acid hydrolysis of sodium silicate. The pH value ranged between 1 and 2. The sol-gel mixture was well-washed at 50°C for 3 h to remove the sodium chloride that was formed [26, 27].

2.3. Synthesis of Nanogibbsite. Nanogibbsite was prepared as a reference sample. Fine (0.1 mm) Al-dross waste was provided by MCA. The Al-dross waste was used to precipitate fine and pure nanogibbsite after leaching in dilute HCl solution. The leaching conditions in terms of the acid solution's concentration and solid/liquid ratio as well as the leaching temperature and time were optimized. The leaching of the Al-dross powder in a 1:4 HCl/tap water solution for 8 h at 100°C resulted in the filtrate with the maximum Al³⁺ ion content (~60%). The optimal leaching conditions were adopted to precipitate pure gibbsite as a gel in the HCl-leached filtrate using ammonia solution (1:1) at a pH of ~8. After that, the sample was heated at 200°C for 12 h to form nanogibbsite [27, 28]. The nature and thermal behavior of this powder were revealed by XRD and TEM.

2.4. Synthesis of Silica-Gibbsite Nanocomposites. Figure 1 shows a flowchart of the synthesis process for the silica-gibbsite (NSG) nanocomposite. The NSG nanocomposite was prepared by mixing certain amounts of nano silica (NS) and gibbsite nanoparticles (GNPs). Then, the composite was grinded and stirred in deionized water for 30 min until complete homogeneity was achieved. The obtained composite powder was dried and stored in an airtight container until further analysis.

2.5. Structural and Surface Characterization of the NSG Nanocomposite

2.5.1. Analytical Instruments. The final product was characterized by X-ray diffraction using a BRUKER D8 AD-VANCE apparatus with a Cu target wavelength of 1.54 A, 40 kV, and 40 mA (Germany). X-ray fluorescence (XRF) was used to identify the elements in the sample and to estimate their concentrations as oxides (mass %) using an AXIOS, WD-XRF Sequential Spectrometer (P analytical, 2005). The structure of the composite was analyzed using a scanning electron microscope (SEM). The surface morphology of our adsorbent was analyzed using a JXA-840A electron probe microanalyzer (Japan) attached to an EDAX unit, with an accelerating voltage of 30 kV and a magnification of 10-400.000x. Transmission electron microscopy (JEM 2100, HRTEM, JEOL) was also used. The functional groups in the NSG nanocomposite and the interfacial modification were analyzed by Fourier-transform infrared spectroscopy (FTIR). The FTIR spectrometer was used at frequencies in the 4000–400 cm⁻¹ range. The surface area was determined using BEL SORB-max (made in Japan). To determine the parameters that had an influence on the adsorption process, measurements of the amounts of EBT adsorbed on the used composite were analyzed at a wavelength of 530 nm using an **OPTIMA SP-300** Visible Spectrophotometer.



FIGURE 1: A flow chart of the synthesis process of the silica-gibbsite (NSG) nanocomposite.

2.5.2. EBT Dye Adsorption Studies. The EBT dye adsorption studies were carried out as follows: 50 mL of EBT dye solution was stirred with different doses of composite under different reaction conditions. The effect of adsorption parameters (pH, contact time, initial concentration, adsorbent dosage, and temperature) on the EBT adsorption behavior of the NSG nanocomposite was investigated using batch experiments. The initial pH value of the dye solutions was adjusted with acetic acid or ammonium hydroxide solution using a pH meter. All experiments were performed at a temperature of $27 \pm 1^{\circ}$ C. The adsorption study's variables were as follows: dye concentration (10, 20, 30, 40, 50, and 80 mg/L), initial pH of solution (2, 3, 5, 7, and 9), adsorbent dosage (0.02, 0.04, 0.08, and 0.1 g/50 mL), and contact time (1, 3, 5, 10, 20, and 30 min). Table 1 shows characteristics of Eriochrome black T dye [29].

The equilibrium adsorption capacity $q_e (mg/g)$ and the percentage removal were determined using the following equations [30]:

adsorption capacity
$$q_{\rm e} = \frac{(C_0 - C_{\rm e})V}{W}$$
,
adsorption% = $\frac{(C_0 - C_{\rm e})}{C_0} \times 100$, (1)

where q_e (mg/g) denotes the equilibrium adsorption capacity, C_0 and C_e are the initial and equilibrium concentration (mg/L) of the EBT dye, respectively, and V (L) and W (g) are the volume of the solution and weight of the adsorbent, respectively.

2.5.3. Error Analysis. The validity of each model was analyzed by the coefficient of determination (R^2), a Pearson's Chi-square test (v^2) (equation (2)), and the normalized standard deviation Δq (equation (3)):

$$\chi^2 = \frac{(q_e, \exp - q_e, \operatorname{cal})^2}{q_e, \operatorname{cal}},$$
(2)

$$\Delta q = \frac{\sqrt{\sum (q_e, \exp - q_e, \operatorname{cal})^2 / (q_e, \operatorname{cal})}}{(N-1)},$$
(3)

where q_e , exp is the experimental value of sorption capacity $(\text{mg} \cdot \text{g}^{-1})$, q_e , cal is the calculated sorption capacity $(\text{mg} \cdot \text{g}^{-1})$, and N is the number of measurements. The most suitable model can be determined when the R^2 value is equal or close to 1 and the Chi-square test (v^2) result and the normalized standard deviation (Δq) are as small as possible [31].

3. Results

3.1. Structural and Surface Characterization of the Adsorbent

3.1.1. XRF of the Starting Materials. Table 1 shows the composition of the prepared NS and GNPs. It is evident that the prepared NS and GNPs both have limited amounts of SiO₂, R₂O₃, RO, and R₂O. The prepared NS was mainly composed of SiO₂ (87.59%) and loss on ignition (LOI, 9.60%). Similarly, the main constituents of the GNPs were Al₂O₃ (55.73%) and LOI (36.40%) [32].

3.1.2. FTIR Study. The ability of an NSG nanocomposite to adsorb the EBT dye is related to its physicochemical characteristics, such as pore structure and surface functional groups. The functional groups on the NSG nanocomposite's surface were identified from the FTIR spectrum that was obtained after the completion of the adsorption process. Figure 2 shows the peak assignments in the residue FTIR spectra. The FTIR spectrum of the blank NSG nanocomposite shows characteristic bands at around 3457, 1635, 1350, 1095, 792, and 466 cm⁻¹.



TABLE 1: Chemical analysis of the prepared nanosilica (NS) and gibbsite nanoparticles (GNPs) (wt%).

FIGURE 2: FTIR spectra of the NSG nanocomposite: (a) after adsorption and (b) before adsorption.

The broad absorption peak at 3457 cm⁻¹ was due to the O-H stretching vibration that resulted from the hydroxylation of OH nanoparticle surfaces by adsorbed water molecules [33]. The 1635 cm^{-1} peak corresponds to the H–O–H bending vibration. The absorption peak at 1350 cm⁻¹ concerns Al-OH and Si-OH [34]. Moreover, the strong peak at 1095 cm^{-1} , along with the shoulders, indicates the existence of Si-O-Si and Al-O-Al bonds [35, 36]. The characteristic bands at 792 and 466 cm⁻¹ were assigned to the bending vibration of O-Al-O and O-Si-O. Taken together, these results confirm that the NSG nanocomposite was successfully prepared and has a considerable number of hydroxyl groups on the nanomaterial surface. The EBT-loaded NSG nanocomposite intensities show that there were weak bands at 1560 and 1528 cm⁻¹, which were attributed to -NO2 and the N=N stretching vibration, respectively. Since this band is very weak, it cannot be detected at a low concentration [37]. The shifting of the peak from 3457, 1635, and 1384 cm⁻¹ to 3432, 1636, and 1383 cm⁻¹, respectively, indicates the presence of H-bonded OH stretching in the NSG nanocomposite's adsorption of EBT.

3.1.3. XRD Study. Figure 3 shows the XRD patterns of the NS, GNPs, and NSG nanocomposite. The data show a broad peak at $2\theta = 22^{\circ}$, which indicates that the prepared NS is an amorphous material [31]. Additionally, the XRD pattern proves that no ordered crystalline structure was present. The XRD diagram of GNPs shows that the major phase is ultrafine gibbsite (α -Al(OH)₃) and the minor phase is bayerite (β -Al(OH)₃) with a weak degree of crystallinity [38]. The XRD patterns of the NSG nanocomposite show the same peaks as the individual materials.

3.1.4. SEM Study. The SEM images revealed the characteristics of the adsorbent's surface morphology. Figure 4 shows SEM images of the blank and EBT-loaded NSG



FIGURE 3: The XRD patterns of NS, GNPs, and the NSG nanocomposite.

nanocomposites. The NSG nanocomposites exhibit remarkable variations in their surface morphology (before and after dye adsorption). The SEM images show that, before adsorption, the NSG nanocomposite's surface was rough and had a porous structure with holes and small openings. The homogeneously distributed pore structure was also supported by the high porosity and the high number of open pores. Moreover, Figure 4(b) shows some agglomeration of NS. After the adsorption of EBT onto the NSG nanocomposite, the surface seemed fine and intact, and there was a lower number of pores because most of the pores on the surface were filled with dye [39].

3.1.5. TEM Study. Figure 5 shows TEM images of the NS, GNPs, and NSG nanocomposite. The TEM micrograph





FIGURE 4: SEM images of the NSG nanocomposite before absorption (a) at $200 \,\mu$ m and (b) at $30 \,\mu$ m and (c) after absorption.

shows that the synthesized GNPs have a dense and porous structure with a crystal size of ≈ 38 nm. The dense structure is related to the gibbsite concentration; a concentration that is too high brings about a risk of aggregation. The compositions of the NS particles are spherical and highly dispersed with a crystallite size of ≈ 13 nm. The TEM image of the NSG nanocomposite in Figure 6(c) shows that the surfaces were densely sheltered. This irregular surface indicates that the NS was nucleating on the GNPs. In other words, the surface-covering layer of NS particles was nucleating on the gibbsite, and this is clearly visible in the TEM pictures.

(a)

3.1.6. Adsorption-Desorption Measurements. The properties of the NS, GNPs, and NSG nanocomposites were also analyzed by BET adsorption-desorption measurements. Figure 6 illustrates the N_2 adsorption-desorption isotherms and pore size distribution curves of the composite's constituents that were obtained at 77 K. As shown in Figures 6(a) and 6(e), the adsorption and desorption isotherms that were obtained for the GNPs and the NSG nanocomposite are of type V, which is

a specific characteristic of mesoporous materials [40, 41], and the shape of the pores indicates that the hysteresis loop is of the H1 type [42]. As shown in Figure 6(c), the adsorption and desorption isotherms that were obtained for the NS are of type IV, and the shape of the hysteresis loop is between types H2 and H3 [43]. The data reveal that the amount of adsorbed EBT increased when using the NSG nanocomposite adsorbent, which explains the high removal percentage. Moreover, the adsorbent's uptake continuously increased (but not into the limiting zone), which means that it was still able to adsorb the dye molecules at its active sites. The peak of the NS, the GNPs, and the NSG nanocomposite pore size distribution was 4, 21, and 21 nm, respectively. The pore size distribution evidences the mesoporous nature of the synthesized materials. Table 2 summarizes the BET data (surface area, pore volume, and average pore radius) of the synthesized NS, GNP, and NSG nanocomposite samples. The results show that the surface area of the NS $(94 \, \text{m}^2 \cdot \text{g}^{-1})$ is high compared to that of the GNPs (10.1 $\text{m}^2 \cdot \text{g}^{-1}$). In contrast, the pore radius of the GNPs (43.657 nm) is about 10 times larger than that of the NS (4.6645 nm). Mixing the two prepared materials (NS and



FIGURE 5: TEM images of (a) NS; (b) GNPs; (c) the NSG nanocomposite (100 nm); and (d) the NSG nanocomposite (200 nm).

GNPs) to form the NSG nanocomposite resulted in good-tomoderate properties (a surface area of $62.34 \text{ m}^2 \cdot \text{g}^{-1}$, a pore radius of 22.717 nm, and a pore volume of $0.7081 \text{ cm}^3 \cdot \text{g}^{-1}$). Consequently, the prepared NSG nanocomposite shows potential for utilization as an adsorbent due to its good porous structure.

3.2. Effect of pH on EBT Dye Concentration. The pH of a dye solution plays a significant role in the adsorption process and particularly in an adsorbent's ability to adsorb the EBT dye. The experimental conditions were a pH in the range of 2-9, $10 \text{ mg} \cdot \text{L}^{-1}$ of EBT dye, 0.1 g/50 mL of NSG nanocomposite, and a contact time of 20 min. Figure 7 shows the adsorption capacity of the NSG nanocomposite with the dye solution's pH. The maximum adsorption of the EBT dye took place at a pH of 2.0, and it decreased as the pH increased up to 9. The efficiency of the EBT dye's removal at the optimum pH of 2 was elevated to 100% [32, 44]. The decrease in the adsorption capacity with the increase in pH up to 9 is related to the increase in the number of hydroxide ions that may compete with anionic ions in the dye. Consequently, the adsorption capability is reduced as the number of positively charged sites decreases. The negatively charged sites on the adsorbent surface will not favor the adsorption of dye ions due to the electrostatic repulsion of OH- groups [43, 45, 46]. Additionally, the sulfonic group on the EBT dye may be blinded through the ion exchange process [47].

3.3. Effect of Contact Time on EBT Dye Concentration. Figure 8 illustrates the change in the number of adsorbed dye molecules (removal%) as a function of contact time from 1 to 30 min. The experiments were carried out in the pH range of 3–10 with 20 mg·L⁻¹ of EBT dye and 0.1 g/50 mL of NSG nanocomposite. The results show that the adsorption of EBT dye started rapidly at the initial time point and became slower as time passed. This is related to the nanoparticles being characterized by a large specific surface area, a low diffusion resistance, and a large adsorption of EBT onto the NSG nanocomposite at this time may be due to the large numbers of unoccupied sites on the NSG nanocomposite's surface, which were loaded with dye molecules as time proceeded. Equilibrium was attained within 20 min.

3.4. Effect of Initial EBT Dye Concentration. Figure 9 shows the effect of the EBT's initial concentration on the removal percentage. The dye concentration was varied from 10 to $80 \text{ mg} \cdot \text{L}^{-1}$, the experimental conditions were held at a pH of 3 and an adsorbent dosage of 0.1 g/50 mL, and the contact time was fixed at 20 min. It is clear that the adsorption of the dye decreases as the dye's concentration increases. The reason for this may be that a higher concentration led to the presence of large numbers of dye molecules with a limited number of adsorption sites on the NSG nanocomposite's surface. Hence, no extra dye molecules could be adsorbed onto the adsorbent's surface.



FIGURE 6: N_2 adsorption-desorption isotherms of (a) NS, (c) GNPs, and (e) the NSG nanocomposite and the pore size distribution curves of (b) NS, (d) GNPs, and (f) the NSG nanocomposite.

Sample	Surface area $(m^2 \cdot g^{-1})$	Pore volume $(cm^3 \cdot g^{-1})$	Pore size (nm)	Pore radius (nm)
NS	94	0.1598	4	4.6645
GNP	10.1	0.2224	21	43.657
NSG	62.34	0.7081	21	22.717

TABLE 2: The data on surface area, pore volume, and average pore radius.



FIGURE 7: Influence of pH on the adsorption of 10 mg-L^{-1} (EBT) dye by 0.1 g/50 mL NSG nanocomposite for a contact time of 20 min.



FIGURE 8: Influence of contact time on the adsorption of $10 \text{ mg} \cdot \text{L}^{-1}$ EBT dye by 0.1 g/50 mL NSG nanocomposite at a pH of 3 and a contact time of 20 min.

3.5. Effect of Adsorbent Dose on EBT Dye Removal. The effect of adsorbent dose on the EBT dye's removal was determined using doses of 0.02, 0.04, 0.08, and 0.1 g/50 mL of NSG nanocomposite and 10 mg·L⁻¹ of EBT dye at a pH of 3. The experiments were carried out at different contact times up to 20 min. Figure 10 shows the results of the removal efficiency experiments. The results show that the dye removal percentage increased as the adsorbent dose increased. The increase in dye adsorption with the adsorbent dosage can be attributed to the availability of a larger surface area with more active functional groups [48, 49]. The optimum adsorbent dose for EBT dye removal in aqueous solution was found to be 0.1 g/50 mL, at which the removal efficiency was 99.5%.

3.6. Effect of NS, GNPs, and NSG Nanocomposite on EBT Dye Removal. The effect of NS, GNPs, and NSG nanocomposite



FIGURE 9: Influence of initial dye concentration on the adsorption of EBT dye by 0.1 g/50 mL NSG nanocomposite at a pH of 3 and a contact time of 20 min.



FIGURE 10: The effect of dosage of the NSG nanocomposite on the adsorption of $10 \text{ mg} \cdot \text{L}^{-1}$ EBT dye at a pH of 3 and a contact time of 20 min.

on the EBT dye's removal was determined using dosages of 0.1 g/50 mL of adsorbent, 10 mg·L⁻¹ of EBT dye at a pH of 3, and a contact time of 20 min. Figure 11 shows the results of the removal efficiency experiments. The results show that the NSG nanocomposite had a higher adsorption capacity for the EBT dye, was more efficient, and had a higher adsorption potential for the treatment of water contaminated by anionic dye than either the NS or the GNPs. The higher removal efficiency of the NSG nanocomposite can be ascribed to the properties of the NSG nanocomposite. Moreover, pore volume is one of the parameters with the greatest effect on an NSG nanocomposite's EBT removal rate [43]. It is clear that the removal efficiency of GNPs is higher than that of NS and that this is related to the high pore radius of GNPs or may be due to the presence of an agglomeration of NS as was shown



FIGURE 11: The effect of NS, GNPs, and NSG nanocomposite on the adsorption of 10 mg·L⁻¹ EBT dye at a pH of 3 and a contact time of 20 min.

in the XRD analysis. This indicates that the GNPs' maximum EBT removal rate is higher than that of NS at an acidic pH. Figure 12 shows an outline of the mechanism underlying the adsorption of EBT dyes onto the NSG nanocomposite.

3.7. Sorption Model. The mechanism of adsorption can be identified by determining the rate of adsorption. Therefore, two kinetic models can be applied. The first kinetic model is the pseudo first-order (PFO) kinetic model [46], which is represented by equation (4) and is shown in Figure 13(a):

$$\log(q_{\rm e} - q_{\rm t}) - \log q_{\rm e} = \frac{-K_{\rm ads}t}{2.303},\tag{4}$$

where q_e and q_t (mg·g⁻¹) are the amounts of dye adsorbed at equilibrium and at time *t*, respectively, and k_{ads} is the PFO rate constant (min⁻¹). The rate constant k_{ads} and the amount of dye adsorbed at equilibrium q_e can be determined from the slope and intercept of the plot of $\ln(q_e - q_t)$ versus *t*. The second kinetic model is the pseudo second-order (PSO) kinetic model [50], which is represented by equation (5) and is shown in Figure 13(b):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e},$$
(5)

where k_2 is the PSO rate constant (g·mg⁻¹·min⁻¹). Similar to the PFO kinetic model, the k_2 and q_e , cal parameters are deduced from the linear and angular coefficients of the equations formed by regressing t/q_t versus t, respectively. Table 3 shows the parameters of the PFO and PSO kinetic models that were developed for EBT adsorption on the NSG nanocomposite using 0.1 g/50 mL of adsorbent, 10 mg·L⁻¹ of EBT dye at a pH of 3, and a contact time of 20 min. From the results, it can be concluded that the kinetics of the adsorption process followed the PSO model and had a coefficient of determination (R^2) of 0.999.

In this work, the intraparticle mass transfer diffusion model [51] was investigated using the Mories–Weber equation (equation (6)) and is represented in Figure 14.

$$q = K_{\rm d}(t)^{1/2},$$
 (6)

where q is the amount of dye adsorbed (g/g), K_d is the intraparticle diffusion rate constant, and $t^{1/2}$ is the square root of time. If the data on the adsorption process agree with the intraparticle diffusion, then the intraparticle diffusion is the lone limiting step. On the other hand, the larger the intercept means, the higher the contribution of the film diffusion to the control of the rate. Regarding Figure 14, the EBT adsorption processes have two linear parts within the curve, indicating that several steps occur in the adsorption process. The results show that intraparticle diffusion in EBT dye sorption is not the only rate-determining step; film diffusion may also be included in the sorption process. Film diffusion drives the transfer of dyes from the bulk solution to the outer surface of the composite's particles. In the second step of the sorption process, equilibrium is reached and the intraparticle diffusion decreases the sorption of dye molecules [52]. The magnitude of the rate constant for the intraparticle diffusion K_d was determined to be 0.250 $(g/g \cdot min^{-1})$ for the EBT dye, which indicates the movement of dye molecules to the composite.

3.8. Sorption Isotherms. Sorption isotherms describe the distribution and interaction of EBT dye molecules within the adsorbent at equilibrium. Sorption isotherms illustrate the relationships between the adsorption capacity and the remaining concentration of the adsorbate at constant temperature. Three well-known models were studied in this work: the Langmuir, Freundlich, and Dubinin-Radusekevisch-Kanager isotherms. The Freundlich and Langmuir isotherms are expressed by equations (7) [53] and (8) [54], respectively:

$$\ln q_{\rm e} = \ln K_f + \frac{1}{n} \ln C_{\rm e},\tag{7}$$

where $K_{\rm f} \,({\rm mol}^{1-n} \cdot \ln \cdot {\rm g}^{-1})$ refers to the sorption capacity when the dye's concentration at equilibrium equals 1, and *n* is an empirical parameter that represents the favorability of the adsorption process. The Freundlich constants $K_{\rm F}$ and *n* were determined from a linear plot of $\ln q_{\rm e}$ versus $\ln C_{\rm e}$ that is represented in Figure 15(a).

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{b \cdot q_{\rm max}} + \left(\frac{1}{q_{\rm max}}\right) \cdot C_{\rm e},\tag{8}$$

where *b* denotes the monolayer adsorption capacity of the heat of sorption ($L \cdot mg^{-1}$), and q_{max} is the maximum adsorption capacity ($mg \cdot g^{-1}$). The Langmuir adsorption isotherm shown in Figure 15(b) was established based on the assumption of monolayer adsorption of the adsorbate on the adsorbent's surface with fixed adsorption. Hence, the Langmuir adsorption isotherm usually defines the equilibrium uptake of homogeneous surfaces.

The Freundlich isotherm suggested that a multilayer adsorption occurred on the heterogeneous surface via interaction between adsorbed molecules. The value of n should be higher than 1 for good adsorption conditions. Table 4 shows the isotherm parameters for the EBT dye's removal



Pores

FIGURE 12: Outline of the mechanism underlying the adsorption of EBT dye onto the NSG nanocomposite.



FIGURE 13: The adsorption kinetics. (a) The pseudo first-order equation and (b) the pseudo second-order equation for the adsorption of $10 \text{ mg} \cdot \text{L}^{-1}$ EBT dye by 0.1 g/50 mL NSG nanocomposite at a pH of 3.

TABLE 3: Parameters of the pseudo first-order (PFO) and pseudo second-order (PSO) kinetic models developed for the adsorption of $10 \text{ mg} \cdot \text{L}^{-1}$ EBT dye by 0.1 g/50 mL NSG nanocomposite at a pH of 3.

Adsorbent	(PFO)					(PSO)					
	q _e , exp	q _e ,cal	Kads	R^2	χ^2	Δq (%)	$q_{\rm e}$, cal	K_2	R^2	χ^2	Δq (%)
NSG	4.9	3.08	0.391	0.967	1.7	0.517	5.20	0.234	0.999	0.017	0.0619

onto the NSG nanocomposite. It can be seen that the Langmuir isotherm model fits the adsorption data well, with a correlation coefficient (R^2) of 0.9567, which is higher than that of the Freundlich isotherm (0.937). The Langmuir isotherm model gave an adsorption capacity of 38.46 mg/g

and a $K_{\rm L}$ value of 0.35 L·mg⁻¹. This indicates that the removal of EBT dye occurred in the form of monolayer coverage onto the NSG nanocomposite's surface. Thus, there was no interaction between dye molecules [55]. The obtained results from the Freundlich isotherm model showed a small



FIGURE 14: The Mories–Weber equation for the adsorption of $10 \text{ mg} \cdot \text{L}^{-1}$ EBT dye by 0.1 g/50 mL NSG nanocomposite at a pH of 3.



FIGURE 15: Sorption isotherms: (a) Freundlich adsorption and (b) Langmuir adsorption of $10 \text{ mg} \text{-}1^{-1}$ EBT dye by 0.1 g/50 mL NSG nanocomposite at a pH of 3.

TABLE 4: Isothermal parameters for the adsorption of $10 \text{ mg} \cdot \text{L}^{-1}$ EBT dye by 0.1 g/50 mL NSG nanocomposite at a pH of 3.

Isotherm		Langmuir				Freundlich				D-R			
parameter	q _e , exp	$q_{\rm e}$, cal	$K_{\rm L}$	R^2	X^2	$K_{\rm f}$	п	R^2	X^2	Ε	$q_{(\mathrm{D-R})}$	R^2	X^2
EBT/NSG	4.9 (mg/g)	38.46 (mg/g)	0.3586 (L/mg)	0.9567	0.029	8.5 (L/mg)	3.07	0.937	0.032	7.14 (kJ·mol ⁻¹)	198.3 (mg/g)	0.952	0.18

adsorption capacity $(11.66 \text{ mg} \cdot \text{g}^{-1})$ compared to that of the Langmuir model. Therefore, the results illustrate a good fit to the Langmuir model.

3.8.1. Dubinin-Radusekevisch-Kanager Isotherm. The Dubinin-Radusekevisch (D-R) isotherm is more general than the Langmuir isotherm model as it does not assume a homogeneous surface or constant sorption potential. Generally, the model is convenient for Gaussian energy distribution and adsorption processes on a heterogeneous surface. The D-R equation is expressed by the following equation [56]:

$$\ln q = \ln q_{(\mathrm{D}-\mathrm{R})} - \beta \varepsilon^{2},$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_{\mathrm{e}}}\right),$$
(9)

where $q_{(D-R)}$ is the theoretical adsorption capacity (mg·g⁻¹); β is the activity coefficient ascribed to the mean sorption energy (mol²·kJ⁻²); ε is the Polanyi potential; R is the ideal gas constant (0.008314 kJ·mol⁻¹·K⁻¹); and T is the absolute temperature in Kelvin (K). E (kJ·mol⁻¹) is defined as the change in free energy that is required to transfer 1 mole of dye from a solution to a solid surface, which equals

$$E = \frac{1}{(2\beta)^{1/2}}.$$
 (10)

The value of *E* can be used to identify the type of sorption reaction. If $E < 8 \text{ kJ} \cdot \text{mol}^{-1}$, physical forces may affect the sorption. If *E* is in the range of 8–16 kJ·mol⁻¹, the sorption is governed by chemical ion exchange. Sorption may be controlled by particle diffusion if $E > 16 \text{ kJ} \cdot \text{mol}^{-1}$ [57]. The results of the D-R model simulation shown in Table 4 show

EBT dye	<i>T</i> (K)	$\ln K_{\rm L}$	$\Delta H^{\mathrm{o}} (\mathrm{J} \cdot \mathrm{mol}^{-1})$	$\Delta S^{\rm o} (J \cdot {\rm mol}^{-1} \cdot {\rm K}^{-1})$	$\Delta G^{\rm o} \; ({\rm kJ}{\cdot}{ m mol}^{-1})$	R^2
	300	4.6			-11.4	
$10 \text{ mg} \cdot \text{L}^{-1}$	313	1.47	-101.34	-297.64	-8.2	0.943
-	323	1.11			-7.9	
	300	1.85			-4.6	
$20 \text{ mg} \cdot \text{L}^{-1}$	313	0.14	-69.622	-213.70	-0.36	0.999
	323	-0.64			1.718	

TABLE 5: Thermal parameters for the adsorption of 10 and $20 \text{ mg} \cdot \text{L}^{-1}$ of EBT dye by 0.1 g/50 mL NSG nanocomposite at a pH of 3.

that the *E* value is $7.14 \text{ kJ} \cdot \text{mol}^{-1}$ for the EBT dye, which is $< 8 \text{ kJ} \cdot \text{mol}^{-1}$, indicating that the sorption is governed by physical adsorption [58].

3.9. Sorption Thermodynamics. The experimental data were verified at three temperatures (27, 40, and 50°C). The thermodynamic parameters standard enthalpy (ΔH°), standard free energy (ΔG°), and standard entropy (ΔS°) were calculated to identify the thermodynamic behavior of the uptake of EBT on the NSG nanocomposite. The thermo-dynamic parameters were evaluated using the following equations [59, 60]:

$$\Delta G^{\rm o} = -RT \ln K_L, \tag{11}$$

$$\Delta G^{\rm o} = \Delta H^{\rm o} - T \Delta S^{\rm o}, \qquad (12)$$

$$\ln K_L = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R},\tag{13}$$

where *R* is the gas constant (8.314 $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) and *T* is the absolute temperature (K). $K_{\rm L}$ is the thermodynamic equilibrium constant, which was calculated from the Langmuir constant [59]. The Gibbs free energy (ΔG°) thermodynamic parameter was calculated using equation (11). ΔG° can be calculated using ΔH° and equation (12). The thermodynamic parameters ΔS° and ΔH° were calculated from the intercept and slope of equation (13). The results indicate that the amount of EBT dye that is adsorbed onto the nanocomposite decreases as the temperature increases. An increase in temperature will enhance the solubility of contaminants in a bulk solution to a greater degree than the adsorbent particles [44]. Table 5 shows the thermal parameters for the sorption of EBT dye on the NSG nanocomposite. The negative ΔH° value indicates that the dye's sorption on the NSG nanocomposite is an exothermic process. The ideal value for physisorption is less than 80 kJ·mol⁻¹, which fits the values that were obtained for adsorption of EBT on the NSG nanocomposite. Moreover, the negative ΔG° value indicates that the adsorption of EBT on the NSG nanocomposite is spontaneous and feasible. As the temperature increased from 27 to 50°C, the negative ΔG° value decreased, indicating that the adsorption process is more spontaneous and favorable. The negative (ΔH°) value means that the adsorption phenomenon is an exothermic process. The negative ΔS° value indicates that the EBT dye molecules in the adsorbed phase of the NSG nanocomposite were more highly dispersed than the pollutant molecules in the bulk solution.

4. Conclusion

The preparation of mesoporous silica-gibbsite nanocomposites for the adsorption of dyes in solution is an effective way to remove environmental pollutants from water. The mesoporous NSG nanocomposite could be used as an adsorbent with a remarkable ability to adsorb the EBT dye from aqueous solution. In this study, we examined the adsorption of the EBT dye onto an NSG nanocomposite, and the results showed that the NSG nanocomposite has a high capacity to adsorb the EBT dye. Characterization studies with SEM, TEM, and FTIR indicated that silica, gibbsite, and the NSG composite at the nanoscale with a sufficient number of pores can be applied in the adsorption process. Furthermore, this work revealed that batch adsorption is affected by the operating parameters initial dye concentration, solution pH, temperature, and contact time. The maximum removal percentage was found to reach 99.5% at equilibrium when using an initial dye concentration of $10 \text{ mg} \cdot \text{L}^{-1}$ and 0.1 g/50 mL of sorbent at a pH of 3. The Langmuir adsorption isotherm fits the experimental data well, suggesting that monolayer adsorption took place on the homogeneous surface. The adsorption kinetics belonged to the pseudo second-order model with a determination coefficient (R^2) of 0.999. The removal percentage of the EBT dye on the SHA nanocomposite decreased from 99.5% to 35.4% as the temperature increased from 27 to 50°C, indicating an exothermic process. The D-R model simulation estimated the *E* value to be $7.14 \text{ kJ} \cdot \text{mol}^{-1}$ for the EBT dye, which is < 8 kJ·mol⁻¹, indicating that the sorption was governed by physical adsorption. The negative ΔG° value decreased as the temperature increased, indicating that the adsorption of EBT onto the NSG nanocomposite was favorable and spontaneous. Finally, the values of ΔH° , which were found to be negative, indicate that the adsorption process was exothermic.

Data Availability

Samples of the compounds and composite all are available from the author.

Conflicts of Interest

The authors declare no conflicts of interest.

Authors' Contributions

I. A. contributed to the methodology, analyzed the data, and wrote the paper. N. A. contributed to the methodology and reviewed the paper. H. H. contributed to the methodology and

wrote the paper. A. R. was involved in preparation of reagents and materials and was responsible for handing analysis tools.

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