THE STUDY OF ADSORPTION EFFICIENCY OF ALIZARIN RED DYE ON THE SOOT-CHITOSAN NANOCOMPOSITE

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ABSTRACT
The goal of this study is to see how well the ACS2 surface removes Alizarin red (AR) dye from its aqueous solution. The ACS2 surface is made from locally available and inexpensive materials (soot and chitosan), and it's frequently utilized in adsorption operations. ACS2 was made by thermally treating ACS1 for 2 hours at 40 ºC. FTIR, SEM, and BET were used to identify the characteristics of ACS2 were identified by FTIR, SEM, BET and XRD technique. The AR dye was adsorbed from aqueous solutions using ACS2, and the results demonstrate that ACS2 produced from ACS1 is an excellent absorbent. On the AR dye adsorption, the effects of pH, temperature, equilibrium time, and adsorbent dosage were investigated. The efficiency of adsorption was shown to decline at PH = 10 and rise at PH=4. The results also revealed that when the temperature rose, the efficacy of the adsorption dye on ACS2 reduced, and the optimum contact time for absorption was 20 min, and the optimum adsorbent weight is 0.01g values of (∆G°) and (∆H°), respectively, revealed that the AR dye adsorption process was spontaneous and exothermic. According to the kinetic finding, the adsorption process is pseudo second order.

Keywords: Soot and Chitosan (ACS1), Activated Soot and Chitosan (ACS2), Adsorption, Alizarin red(AR).

I. INTRODUCTION
Dyes are colorful materials intended to give any colorable substance a color, such as fabrics, and papers [1]. due to the increased use of dyes to paint items such as textiles, paper, plastics, and cosmetics, and the leakage of these highly toxic dyes, dye wastewater contamination has become a serious problem in recent decades. Dye contamination of the water supply is therefore a major environmental problem, as dye-containing wastewater is notoriously difficult to handle [2]. The presence of dyestuff in the water result in major damage to the ecosystem of the receiving surface water contaminates the groundwater resources[3]and can be harmful to human health[4]. The dyes are also carcinogenic and mutagenic. Thus, the removal of these dyes is necessary before they're discharged into water bodies[5]. There area lot of methods of treatment are usable, reliable, simple and inexpensive for the removal of dyes such as oxidation[6], electrochemical degradation, chemical-biological integration, and absorption[7]. The simplest and cheapest of these methods is adsorption[8], the adsorption is a common method among the researchers due to its ease of establishment for the treatment of colored solutions. The typical utilized adsorbent is the active charcoal. Nevertheless, the difficult and the costly process of producing the activated charcoal forced the research for efficient yet inexpensive alternatives[9]. The most frequent difficulty faced in the research for such alternative adsorbents, is the instability of the material prices[10]. Due to this complication, searching for stable, available and reliable material is one of the factors in researching for alternative adsorbents. On the other hand, the diversity of the properties of the different materials and the expansion of manufacturing makes the selection of ideal material is somewhat a tedious task[11].

soot (also known as black carbon and refractory carbon) appears to contain considerable amounts of elemental carbon in the molecular form of graphite, along with organic impurities. All forms of combustion of carbonaceous materials produce some soot, so its presence is ubiquitous in both original and polluted regions. The exact composition is changeful and dependent on the nature of the source, however, characterized by the presence of very small particles (sub micrometer) and correspondingly a large ratio of surface area to mass. The key features of soot are its chemical inertness, its physical and chemical adsorption properties, and its light absorption. The large surface area coupled with the presence of various organic functional groups allow the adsorption of many different materials onto the surfaces of the particles [12]. soot particles contain up to 10
molecules of hydrogen, and even more when they are small. A great deal of this hydrogen can be extracted in organic solvents as it appears mostly in condensed aromatic ring compounds [13].

Chitosan is a natural carbohydrate biopolymer derived by deacetylation (DA) of chitin, a major component of the shells of crustacean such as crab, shrimp[14], has many attractive properties such as hydrophobicity, biocompatibility, biodegradability, non-toxicity and the presence of very reactive amino (–NH2) and hydroxyl (–OH) groups in its backbone, which makes chitosan to be used as an effective adsorbent material for the removal of wastewater pollutants.

Chitosan is a functional polymer, which is facilely soluble in dilute acid solutions. In contrast to other polysaccharides that are either neutral or anionic, chitosan acts as a polycation in solution. It has complex multilateral and ion adsorption properties. Chitosan is a very versatile material in terms of its chemical, physical and biological properties . [15]. In this work, we are studying the absorption of Alizarin red dye on soot and chitosan

The material & instrumentation
The chemical ingredients used in this research were provided by the companies Sigma Aldrich and BDH. FT-IR-800, Shimadzu Fourier transform infrared spectrophotometer captured the FTIR spectrum in the range (400-4000) cm⁻¹. The ultraviolet-visible spectrum was measured in the range of 200-800 using a UV-1800PC Shimadzu UV-Visible spectrophotometer. The XRD analysis was carried out using an Xper Philips Holland Diffractometer. In the 2θ range between (10°-80°), the intensity of Cu Ka radiation generated at 40 Kv was measured. The scanning electron microscope (SEM) of the ACS₂ surface morphology is the FEI Nova Nano SEM 450. The voltage acceleration in SEM is in the range of 15-20 Kv, and images of surface morphology are acquired at various magnifications.

Preparation of alizarin red solution
Prepared the stock solution of Alizarin red dye (100ppm) by dissolving (0.1g) of Alizarin red dye in 1000ml of pure water. After that, using an absorbance spectrum in the range of (200-800nm) and a UV-Visible spectrophotometer, the maximum absorption wavelength (λmax) of Alizarin red dye was calculated. The standard curve was created by measuring dye concentration in aqueous solution using a series of day solutions made at concentrations ranging from 10 ppm to 100 ppm.

Preparation of ACS₂ from ACS₁
The ACS₁ was prepared by mixing candle paraffin and chitosan in 1:2 ratio and was collected in clean and dry beaker. The collected ACS₁ is dried by using oven at 60 °C and for a period of 4 hours. Afterward, this dried ACS₁ is grinded and sieved then was activated to produce ACS₂ by adding nitric acid 10% with stirring for two hours at a temperature of 40°C, then filtering the solution and washing it with distilled water three times and drying it at a temperature of 105°C for an hour to obtain ACS₂ with particle size of 125μm.

The Study factors that affect the adsorption process
The Effect of an Equilibrium time
Alizarin red dye concentration (25 ppm) was selected at different times (10,20, 30, 40, 50, 60, and 90) min, at constant temperature 25°C and the volume of dye solution (25 ml) was constant, and using a constant mass of the ACS₂ (0.01 g) to determine the equilibrium time between the adsorbed amount of the AR dye by the adsorbent.
The test tubes were placed in a water-bath shaker at 25°C at a speed of 125rpm with the dye solution's natural PH. The sample was then filtered. The dye solution's absorbance was then measured using UV – visible spectra set at 516 nm.

**The Effect of an Adsorbent weight**

The weight of the adsorbent on the absorption process is the second studied factor. At 25°C, several weights of adsorbent (0.01, 0.02, 0.5, and 0.1g) were used. The dye was kept at a constant volume (25 ppm, 10 ml), the equilibrium time was 20 minutes, and the pH was not modified. The test tubes were placed in a water bath-shaker at 125 rpm, filtered with micro filter paper, and the dye solutions’ absorbance was measured at 516nm.

**The Effect of the PH on the Adsorption**

The measurement of samples at varying pH on adsorption is the study of PH. At varied PH values (4, 7, and 10), the dye concentration (25ppm) was measured with a constant volume of dye solution (25ml). Dilute solutions of 1M HCl and 1M NaOH were used to change the pH value. The absorbent has a constant weight of 0.01g and the equilibrium time is (20min) at temperature is 25 ºC . The test tubes were then placed in a water bath-shaker at 125 rpm to determine the absorbance of the solutions at 516 nm.

**The Effect of the Temperature**

To determine the effect of temperature on the Alizarin red adsorption process (AR). The dye was prepared at a concentration of 25ppm in a solution. Also (0.01g of ACS2 / 10mL) was added to the flasks. They were shaken for 20 minutes at 125rpm in a water-bath shaker at three different temperatures (25, 35, and 45°C), using the natural pH of the solutions (not changed).

### II. RESULTS AND DISCUSSION

**Characterization of ACS$_2$**

FTIR spectrum of activated surface (ACS$_2$), The hydroxyl groups vibration is attributed to a broad absorption band at 3394.83 cm$^{-1}$, the C-H stretching vibration is attributed to strong bands at 2870.17 cm$^{-1}$, medium bands at 1720.56 and 1653.05 cm$^{-1}$ are attributed to C=O and C=C group respectively, and finally bands at 1427.37 and 1381.42 cm$^{-1}$ are attributed to C-H group bending.

After activation, the surface morphology of ACS$_2$ was investigated. Figure (3) the SEM image demonstrates the presence of regular particle forms on the surface. Several pores of varied sizes and shapes could be seen, indicating the possibility for adsorption, and the surface was smooth. The surface area of ACS$_2$ after activation was large and smooth, with no sharp edges.
ACS₂ Figure (4) XRD pattern revealed two types of diffractions, indicating the presence of two phases. The ACS₂ XRD shows a diffraction peak 2θ = 25.00°, 2θ = 43.00°, and 2θ = 29.00°, indicating the presence of the crystalline phase.

**Effect of equilibrium time on the Adsorption**

The equilibrium time of adsorption onto the ACS₂ surface was determined across a range of time (10, 20, 30, 40, 50, 60, and 90 minutes) at 25 °C, with the volume of dye solution (25 ml) and weight of ACS₂ (0.01g) being constant. The equilibrium time, as seen in Figure(5), is (20 min). The percentage of dyes removed increases with time because initially unoccupied active sites are available more for dye adsorption, and as time passes, the sites become fully saturated[16], indicating that active sites are used up and produces a stable equilibrium, depending on the chemical and physical nature of the dye and saturation of active sites on the surface.
Effect of PH on Adsorption of AR Dye

The PH of the adsorbate solution has a significant impact on its absorption capacity. For the adsorption of various adsorbates, different adsorbents have varied optimal PH levels. The maximum percentage of Alizarin red dye removal was obtained at PH=4, while the least percentage of Alizarin red dye removal was obtained at PH=10. The pH solution can be arranged in the following way: - (4>7>10). The greatest adsorption capability of AR onto ACS2 was observed at PH 4.0, the phenolic functional groups in the dye are protonated, but the sulfonic group is not protonated. This could be related to the fact that these groups are highly acidic, with pKa values in the negative range [17]. The anionic dye was adsorbed in the positively charged ACS2 at pH 4 by electrostatic attraction, based on these findings. An electrostatic interaction between the positively charged ACS2 and the negatively charged AR should constitute the mechanism of adsorption [18].

The amount of adsorbed dye (qe) in Equ. 1 and the percentages of removal dye (E) in Equ.2 calculated as follows:

\[
q_e = \frac{v(c_0 - c_e)}{m} \quad \ldots (1)
\]

\[
R\% = \frac{c_0 - c_e}{c_0} \times 100 \quad \ldots (2)
\]

Where C0, Ce are initial and remaining dye concentrations in the solution (mg/L). qe is the adsorbed amount of the dye (mg/g). And v is dye solution volume (L). m is the weight of adsorbent (g) and R is percentage dye removal (R%).

Effect of temperature

To determine how temperature affects the absorption of a solution of Alizarin red dye with a pH of 4 and a constant volume (10 ml) / 100 ppm of the solution at temperatures of 25, 35 and 45°C. The adsorption results are shown in Figure (7). The study observed that with increasing temperature, the effectiveness of the adsorption dye on ACS2 decreased, indicating that dye adsorption by ACS2 is exothermic in nature[19]. As a result, the study determined that the most suitable working temperature was 25°C.
Effect of adsorbent mass

The appropriate weight of adsorbent is 0.01 g, as shown in Fig (8), and increasing the weight of the adsorbent increases the percentage of AR dye adsorption on the surface of the ACS2. The percentage of adsorption increases with the weight of the adsorbent as a result of an increase in the number of active sites on the ACS2 surface that are designed for dye adsorption, increasing the sorption sites of the adsorbent and thus increasing the effectiveness of the surface and thus increasing the percentage of adsorption. [20].

Adsorption isotherm

The adsorption isotherm provides information about the adsorption process as well as the adsorbed concentration's adsorption capacity. The Frindlish and Langmuir equations for adsorption were used to apply the experimental data. Frindlich's isotherm model describes the adsorption of solutes from a liquid to a solid surface by taking into account several sites and different adsorption energies [21]. By projecting the linear equation of the Freundlich isotherm on the ACS2 surface in various concentrations, Figure(9) shows the Freundlich equation adsorption on the surface in numerous concentrations. The Freundlich constants ($K_f$, $n$) were computed, and they provide information on the amount of adsorption and the quality of surfaces (heterogeneous or homogeneous). In addition, the Langmuir constant ($b$) and ($Q_m$) the maximum adsorption capacity were calculated by the linear equations as following:

The Langmuir equation: 
$$\frac{c_e}{q_e} = \frac{1}{Q_m} * b + \frac{c_e}{Q_m}$$  … (3)

The Freundlich equation: 
$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$  … (4)

| Table1: Values of the Parameters of Freundlich and Langmuir Equations for ACS2 |
|---|---|---|---|---|
| Isotherm constant | Langmuir | Freundlich |
| coefficient of correlation /constants | $q_m$ | $b_e$ | $R^2$ | $n$ | $K_f$ | $R^2$ |
| Values | 87.71 | 0.048 | 0.551 | 1.19 | 8.64 | 0.823 |
As seen in Table (1), the (n) value is less than one (1). As a result, the surface has a heterogeneous appearance. When the coefficient of correlation ($R^2$) readings from the Freundlich isotherm are compared to Langmuir's $R^2$, Freundlich's $R^2$ is larger. As a result, the Freundlich equation is better suited to the adsorption of alizarin red dye in aqueous solution onto the ACS2 surface. As a result, it is a multilayer adsorption system (more than one layer)[22].

**Thermodynamics of adsorption process**

Only the adsorption technique was studied in terms of thermodynamics in order to determine the type of adsorption reaction. As a result, it is important to study the Thermodynamics parameters of adsorption entropy ($\Delta S^o$), Gibbs free energy ($\Delta G^o$), and the change in the standard enthalpy ($\Delta H^o$) at (298 to 318) K. Gibbs free energy change can be estimated from the as:

$$\Delta G^o = - R \ T \ LnK \ ... \ (5)$$

The $\Delta G^o$: is the change in Gibbs free energy (KJ.mol$^{-1}$), and T: is absolute solution temperature (in Kelvin), $R$ is the universal gas constant (8.314 J.mol$^{-1}$.K$^{-1}$), and K: is thermodynamic equilibrium constant to the adsorption. The value of (k) has been calculated by on the equation:

$$K = \frac{q_e* m}{C_e*v} \ ... \ (6)$$

Where the standard enthalpy change ($\Delta H^o$) were calculated by using the values of Lnk against $1/T$ according to Van't Hoff - Arrhenius equation:

$$LnK = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \ ... \ (7)$$

The values of ($\Delta S^o/R$) and ($-\Delta H^o/R$ ) have been determined using the intercept and slope of the linear plots. Table (2) of the thermodynamic study demonstrates that Alizarin red adsorption onto the ACS2 surface was spontaneous and exothermic (physical adsorption), as determined by $\Delta G^o$ and $\Delta H^o$.

**Table 2: Thermodynamic Parameters of the Adsorption Alizarin Red Dye onto ACS2**

![Fig. 9: Langmuir isotherm for adsorption of dye on ACS2.](image)

![Fig. 10: Freundlich isotherm for adsorption of dye on ACS2.](image)
### III. CONCLUSION

1. The adsorption procedure is an effective way to remove dyes from water.

2. The adsorbent is commercially available and inexpensive.

3. At pH=4, the adsorption mechanism is favorable for dye removal.

4. As the adsorbent dose is increased, the adsorption capacity increases.

5. The Freundlich isotherm is more suitable for the adsorption processes.

6. The thermodynamic analysis demonstrates that Alizarin Red adsorption onto the ACS 2 surface is spontaneous and exothermic, as determined by $\Delta G^\circ$ and $\Delta H^\circ$.

### REFERENCES


