Adsorption Characteristics of Allura Red AC onto Sawdust and Hexadecylpyridinium Bromide-Treated Sawdust in Aqueous Solution

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ABSTRACT: The Allura red AC (ARAC) dye adsorption onto natural sawdust (NSD) and hexadecylpyridinium bromide-treated sawdust (MSD) was investigated in aqueous solution as a function of contact time, solution pH, particle size, adsorbent dosage, dye concentration, temperature, and ionic strength. The adsorbents were characterized by Fourier transform infrared spectroscopy and X-ray diffraction crystallography. The dye adsorption onto both adsorbents was confirmed by field emission scanning electron microscopy and energy-dispersive X-ray spectroscopy. The maximum dye adsorption was found within 120 min at pH 2.0 for NSD and pH 3.0 for MSD, respectively, with a particle size of 0–75 μm and an adsorbent dosage of 0.07 g/50 mL ARAC dye solution (50 μmol/L). The batch adsorption kinetic data were followed by the pseudo-second-order kinetic model rather than the pseudo-first-order and Elovich kinetic models. Equilibrium adsorption isotherms were explained by the Langmuir isotherm model, and the maximum extent of adsorption was found to be 52.14 μmol/g for NSD and 151.88 μmol/g for MSD at 55 °C. The values of activation energy (E_a) and thermodynamic parameters (ΔG°, ΔH°, ΔS°, ΔG°, ΔH° and ΔS°) proved that the ARAC dye adsorption onto both adsorbents NSD and MSD is a spontaneous-endothermic physiosorption process. ARAC (98–99%) was released from dye-loaded adsorbents in aqueous solution (pH ≥ 12) within 120 min. The adsorbents NSD and MSD were reused for a second time without significant loss of their adsorption efficiency.

INTRODUCTION

Dyes are a kind of organic compounds with a complex aromatic molecular structure which makes them more stable and non-biodegradable.1,2 Various industries often use large amount of dyes that are responsible for producing wastewater and discharged into water bodies. The removal of dyes from these industrial effluents is desired not only for aesthetic reasons but also this wastewater could have high levels of BOD, COD, color, toxicity, surfactants, fibers, and turbidity.3,4 Moreover, the breakdown products of dyes are toxic to aquatic life and carcinogenic to humans. A number of methods such as photodegradation,5 coagulation,6 flotation,7 ultrafiltration-exchange,8 chemical oxidation,9 ozonation,10 membrane filtration,11 and electrochemical12 have been recommended to clean wastewater. However, these techniques are highly complicated and overpriced. Therefore, these techniques are not reasonable to clean effluents of textile and food industries in developing countries such as Bangladesh.

The adsorption technique has received great importance for the protection of environment by eliminating textile and food dyes from wastewater.13,14 Literature survey shows that various low-cost adsorbents such as peanut shell,15 sugarcane bagasse,16 banana peel,17 activated carbon prepared from rice hull,18 jackfruit seed,19 and chitosan20–23 have been used to remove organic dyes from water. However, these adsorbents do not have good adsorption capacity. Therefore, new adsorbents are still under development to improve the adsorption performance.

Sawdust is an enormous and accessible byproduct of sawmills in our country, Bangladesh. Thus, the appropriate use of this biomaterial must bring conspicuous economic and social benefits. The raw and modified sawdust (MSD) were used to eliminate organic dyes such as methylene blue,24–26 acid green and acid red 14,27 Congo red,28 torque blue,29 and tartrazine30 from aqueous solution. It is noted that the adsorption of Allura red AC (ARAC; Figure 1a) azo dye onto sawdust and surfactant-MSD in aqueous solution was not reported in literature yet. However, chitosan,31 cross-linked chitosan,32 Spirulina platensis,33 vine-trimming waste,34 and activated carbons35–37 were used to remove ARAC from aqueous solution.

In this study, the natural sawdust (NSD) and cationic surfactant hexadecyl peridinium bromide (CPB; Figure 1b)-MSD were prepared and characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD).
The adsorption characteristics of ARAC onto NSD and MSD were investigated in aqueous solution as a function of contact time, solution pH, particle size of the adsorbents, adsorbent dosages, dye concentration, ionic strength, and solution temperature, respectively. To understand the kinetics and mechanisms of ARAC dye adsorption onto NSD and MSD, the batch adsorption kinetic data were examined by using various kinetic models. The dye adsorption equilibrium was studied at different temperatures. The equilibrium dye adsorption data were examined by various isotherm models. The FTIR spectra of dye-loaded NSD and MSD were investigated. The adsorption capacity of the present adsorbents was compared with other adsorbents reported in the literature. The thermodynamics of the dye adsorption process was also investigated.

## RESULTS AND DISCUSSION

### Characterization of Adsorbents.

The FTIR spectra of NSD and MSD are shown in Figure 2. The spectrum of NSD (Figure 2a) showed the characteristic bands at 3420 (broad) cm$^{-1}$ for the N–H and O–H stretching, 2922 cm$^{-1}$ for alkyl C–H stretching, 1647 cm$^{-1}$ for amide I (C=O group), 1559 cm$^{-1}$ for amide II (N–H bending), 1458 cm$^{-1}$ for –CH$_2$ bending, 1373 cm$^{-1}$ for overlapping of C–H bending and symmetric CH$_3$ deformation, 1317 cm$^{-1}$ for C–N, 1113 cm$^{-1}$ for overlapping of asymmetric bridge oxygen (C=O–C) and C–O stretching, 1057 and 1036 cm$^{-1}$ for overlapping of C–O and C–N stretchings, and 669 cm$^{-1}$ for O–H deformation (out of plane). In the spectrum of MSD (Figure 2b), the intensity of the characteristic vibration band at 2918 cm$^{-1}$ for symmetric C–H stretching was increased while the shoulder peak at 2852 cm$^{-1}$ was attributed to the asymmetric C–H stretching vibration of saturated hydrocarbon. This is because of the increase in the aliphatic carbon content (from CPB) in MSD.$^{38}$ These results indicate the existence of CPB on the surface of MSD.

Crystalline nature of the material is determined through an efficient technique known as XRD. Crystalline materials show well-defined peaks while noncrystalline or amorphous materials show a hallow instead of a well-defined peak.$^{39}$ The XRD pattern of NSD showed no sharp peak (Figure 3a), which indicates that NSD was noncrystalline in nature. On the other hand, the XRD pattern of MSD showed two sharp peaks at 2θ: 26.43 and 39.44°, respectively (Figure 3b), which suggests that MSD is crystalline in nature.

The point of zero charge (pH$_{pzc}$) describes the condition when the electrical charge density on a surface is zero. The pH$_{pzc}$ values of NSD and MSD were determined by using the pH drift method.$^{40}$ The values of pH$_{pzc}$ were estimated to be 5.03 for NSD (figure not shown) and 7.43 for MSD (figure not shown), respectively. These results indicate that the surfaces of NSD will act as the positive-charged surface at pH < 5.03 and as the negative charged surface at pH > 5.03. On the other hand, the surfaces of MSD will act as the positive-charged surface at pH < 7.43 and as the negative-charged surface at pH > 7.43. A similar result was also observed in cationic surfactant CPB-modified peanut husk.$^{38}$

## Effect of Contact Time on Adsorption Capacity.

Contact time is one of the important parameters for the assessment of practical application of the adsorption process. In order to determine the equilibrium time, the adsorption of ARAC dye (50 μmol/L) onto both adsorbents was studied as a function of contact time at pH 2.0 for NSD and at pH 3.0 MSD, respectively. The typical changes in UV-visible spectra of ARAC with time during adsorption onto NSD and MSD in aqueous solution are shown in Figure 4. It is noticed that NSD adsorbed 60% of ARAC (50 μmol/L) within 120 min (Figure 4a), whereas MSD adsorbed 100% of ARAC (50 μmol/L) within 120 min (Figure 4b). The initial rate of dye adsorption onto MSD was faster than that of NSD in aqueous solution (Figure 4).

The plots of $q_i$ versus contact time, $t$, are shown in Figure 5. It is noted that the adsorption of dye onto both adsorbents occurred rapidly in the first 20 min, and thereafter, no noticeable dye adsorption was observed beyond a contact time of about 120 min. This may be because of strong attractive forces between the dye molecules and the adsorbents. The fast adsorption of dye molecules occurred on the external surface of the adsorbents followed by the pore diffusion into the adsorbents matrix to attain equilibrium. Further increase in contact time shows that there was no significant progress in the adsorption of ARAC dye onto both adsorbents (NSD and MSD) in aqueous solution. A similar result was found in textile dye adsorption onto activated carbons made from DVD and CD wastes.$^{41}$ Hence, all the adsorption experiments were conducted for 120 min.

## Effect of pH.

The functional groups of the adsorbent and adsorbate can be protonated or deprotonated in aqueous solution depending on its pH. This causes electrostatic attraction or repulsion between charged adsorbates and adsorbents. The kinetics of dye adsorption onto NSD and

![Figure 1. Structure of Allura red AC dye (ARAC; a) and hexadecylpyridinium bromide (CPB; b).](image1)

![Figure 2. FTIR spectra of natural sawdust (a: NSD) and modified sawdust (b: MSD). The spectra were recorded in KBr.](image2)
MSD at various solution pHs is depicted in Figure 6. The adsorption of ARAC dye onto NSD was examined in aqueous solution at pH ranging from 2 to 6. The time of equilibrium dye adsorption gradually increased with increasing solution pH (Figure 6a). It is noticed that the initial dye adsorption rate and the extent of dye adsorption capacity of NSD was significantly decreased with an increase in solution pH (Figure 6a). The maximum amount of ARAC dye adsorbed onto NSD was obtained to be 22.08 μmol/g at solution pH 2 (Figure 7). The ARAC dye behaves as an anionic dye molecule, and two sulfonate (−SO₃⁻) groups (Figure 1a) may be electrostatically attracted by protonated amino (−NH₂⁺) groups of NSD in acidic solution (pH 2). This electrostatic attraction between dye molecules and adsorption sites may become the reason to observe highest dye adsorption onto NSD at solution pH 2 (Figure 7).

The adsorption of ARAC dye onto MSD was examined in solution at pH ranging from 2 to 10. The results are depicted in Figure 6b. The MSD was unstable in very acidic solution (pH 2). It is observed that the initial rate of dye adsorption, h (μmol/g min), amplified with rising solution pH up to pH 3 (Table 3), and thereafter, it significantly reduced with expanding solution pH from 4 to 10 (Table 3). After 120 min, the amount of equilibrium dye adsorption (qₑ) onto MSD versus solution pH is shown in Figure 7. The dye binding capacity of MSD at equilibrium increased from 32.05 to 35.21 μmol/g with increasing pH 2 to 3, slightly decreased in the region of 5 < pH < 6 and then significantly decreased at pH > 6. The maximum amount of ARAC adsorbed onto MSD was estimated to be 35.21 μmol/g at solution pH 3. A similar result was also observed in the adsorption of light green anionic dye onto CPB-modified wheat straw in aqueous solution. Therefore, all further kinetic studies were implemented in solution at pH 2.0 for NSD and at pH 3.0 for MSD, respectively.

**Effect of Particle Size.** The effects of adsorbent particle size on the adsorption kinetics of ARAC onto NSD and MSD in aqueous solution are depicted in Figure 8. It is noticed that the initial dye adsorption rate and the extent of dye adsorption capacity of NSD was significantly decreased with an increase in solution pH (Figure 6a). The maximum amount of ARAC dye adsorbed onto NSD was obtained to be 22.08 μmol/g at solution pH 2 (Figure 7). The ARAC dye behaves as an anionic dye molecule, and two sulfonate (−SO₃⁻) groups (Figure 1a) may be electrostatically attracted by protonated amino (−NH₂⁺) groups of NSD in acidic solution (pH 2). This electrostatic attraction between dye molecules and adsorption sites may become the reason to observe highest dye adsorption onto NSD at solution pH 2 (Figure 7).
results were also noticed for the removal of Congo red and methylene blue from aqueous solution by using marine alga Porphyra yezoensis Ueda43 and activated carbons prepared from waste biomass,44 respectively.

**Effect of Adsorbent Dosage.** The effects of adsorbent dosages on the dye removal percentage (%) and the extent of equilibrium dye adsorption ($q_e$) onto the both adsorbents are exhibited in Figure 9, where the dye concentration was 50 μmol/L (50 mL) fixed. It is noticed that the dye removal percentage increased with increasing masses of both adsorbents (Figure 9a,b). This is because of the increase in surface areas of adsorbents and expanding the number of adsorption sites available for adsorption. On the other hand, the extent of dye uptake per gram of adsorbent ($q_e$) was remarkably decreased with increasing the masses of both adsorbents (Figure 9a,b). These results can be mathematically explained by combining eqs 21 and 22. As observed in eq 21, the amount of dye uptake ($q_e$) and the mass of adsorbent ($m$) are inversely proportional. For a fixed dye percentage removal, the increase in adsorbent mass leads to a decrease in $q_e$ values because the volume ($V$) and initial dye concentrations ($C_0$) are always constant. Similar results were also observed in the removal of Congo red and brilliant green dye from aqueous solutions by using the marine alga P. yezoensis Ueda43 and home-made activated carbons,45 respectively.

**Effect of Initial Dye Concentration.** It is known that the initial concentration delivers the key driving force to overwhelm all mass transfer resistances of all molecules between the aqueous and solid phases. An increase in the initial adsorbate concentration leads to an increase in the adsorption capacity of the adsorbate onto the adsorbent. The impacts of initial concentration of dye on the kinetic of ARAC dye adsorption on both adsorbents (NSD and MSD) in aqueous solution are depicted in Figure 10. The rate of dye adsorption was significantly rapid for the initial 5 min, and afterward, it progressed at a slow rate and eventually attained

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Figure 6. Effects of solution pHs on the adsorption of ARAC dye onto NSD (a) and MSD (b) in aqueous solution at 25 °C. Experimental conditions [ARAC]₀: 50 μmol/L; volume of dye solution: 50 mL; particle size of adsorbents: 0–75 μm; and adsorbent dosage: 0.07 g. Solution pHs: circle open: pH 2; circle solid: pH 3; triangle up open: pH 4; triangle up solid: pH 5; box: pH6; box solid: pH 7; diamond open: pH 8; diamond solid: pH 9; multiplication: pH 10. All lines are modelled pseudo-second-order adsorption kinetic traces produced by utilizing eq 2, and the $q_{e(cal)}$ and $k_2$ values are recorded in Tables 1 and 2, respectively.

Figure 7. Plot for $q_e$ vs solution pH for the adsorption of ARAC dye onto NSD (circle solid) and MSD (circle open) in aqueous solution at 25 °C. Data were taken from Figure 6.

Figure 8. Effects of adsorbent particle size on the adsorption of ARAC onto NSD (a) and MSD (b) in aqueous solution at 25 °C. Experimental conditions: [ARAC]₀: 50 μmol/L; volume of dye solution: 50 mL; adsorbent dosage: 0.07 g; and pH 2.0 for NSD and pH 3.0 for MSD. Particle size: circle open: 0−75 μm; circle solid: 75−150 μm; triangle up open: 150−300 μm; triangle up solid: 300−600 μm. All lines are modelled pseudo-second-order adsorption kinetic traces produced by utilizing eq 2, and the $q_{e(cal)}$ and $k_2$ values are recorded in Tables 1 and 2, respectively.
equilibrium. The dye adsorption attained equilibrium within 10 min for 50 μmol/L and 60 min for 200 μmol/L ARAC dye solutions, respectively. However, the data were received for 120 min to confirm perfect equilibrium. The rate of initial ARAC dye adsorption, \( h \) (μmol/g min), decreased with rising concentration of dye (Tables 1 and 2), showing that the adsorption of ARAC dye onto NSD and MSD is really dye concentration-dependent. One of the possible reasons for this phenomenon is at lower dye concentration, solute concentrations to the adsorbent site ratio is high, which cause an increase in the color removal rate, and at higher dye concentrations, solute concentrations to the adsorbent site ratio is low because of the saturation of adsorption sites, which results a slower rate of color removal. The values of equilibrium dye uptake (\( q_e \)) were increased from 22.08 to 43.20 μmol/g for NSD (Figure 10a) and 35.07 to 101.33 μmol/g for MSD (Figure 10b) with increasing initial dye concentrations from 50 to 200 μmol/L, respectively. An analogous phenomenon was also found in the adsorption of reactive black 5 (RB5), reactive yellow 145 (RY145), and Remazol Brilliant Violet on chitosan in liquid solution.21−23

Effect of Ionic Strength. The effects of ionic strength on the adsorption of ARAC dye onto both adsorbents (NSD and MSD) were investigated in aqueous solution. The dye solution ionic strength was controlled by using 1 mol/L Na2SO4 solution keeping other parameters constant. It is noticed that the initial rate and the extent of equilibrium dye adsorption onto both adsorbents declined with rising the dye solution ionic strengths (Figure 11a for NSD and Figure 11b for MSD).

It can be stated that the addition of salts allows the neutralization of the negative sites of dye molecules by an extra Na+ ion, and hence, the electrostatic repulsion barrier is hindered, and non-electrostatic interactions between the adsorbent and neutral site can occur. Again, the negative SO₄²⁻ ions compete with dye anions for adsorption. Thus, the adsorption capacity decreases with increasing ionic strength of the aqueous solution. A similar result was also noted in Remazol Brilliant Violet dye adsorption on chitosan in aqueous solution.23

Effect of Temperature. Temperature is a significant issue which can change the rates and equilibrium sorption processes. The temperature has two major effects on the adsorption process.

- Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution.
- And changing the temperature will change the equilibrium capacity (\( q_e \)) of the adsorbent for a particular adsorbate.

Figure 12 shows the effect of temperature on the adsorption kinetics and equilibrium adsorption of ARAC onto both adsorbents NSD and MSD in aqueous solution. It is noticed that both the initial rate (\( h \)) and the extent of equilibrium dye adsorption (\( q_e \)) onto both adsorbents NSD (Figure 12a) and MSD (Figure 12b) increased with increasing solution temperatures. The values of \( q_e \) were estimated to be 22.08 μmol/g at
analyzed by applying the pseudo-second-order kinetic models. The pseudo-second-order rate constant, \( k_2 \) (g/mmol min), can be estimated from the slope of the plot of \( t/q\text{t} \) versus \( t \). The initial adsorption rate, \( h \) (\( \mu \text{mol/g min} \)), can be estimated by eq 4.

The Elovich model is written as

\[
q_t = \frac{k_2q_e^{2}t}{(1 + k_2q_e t)}
\]  

(2)

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}
\]  

(3)

The pseudo-second-order rate constant, \( k_2 \) (g/mmol min), can be computed from the slope of the plot of \( t/q\text{t} \) versus \( t \). The initial adsorption rate, \( h \) (\( \mu \text{mol/g min} \)), can be estimated by eq 4.

\[
h = k_2q_e^2
\]  

(4)

where \( \alpha \) (\( \mu \text{mol/g min} \)) is the rate of initial adsorption and \( \beta \) (g/mmol) is associated to the degree of surface exposure and the activation energy for chemisorption.

The various kinetic plots of the batch adsorption experiments are not shown in this paper. However, the values of correlation coefficients (\( R^2 \)) and kinetic parameters obtained from various utilized kinetic models are presented in Table 1 for NSD and Table 2 for MSD, respectively. It is noted that the values of \( R^2 \) obtained from the pseudo-first-order model (\( \leq 0.913 \)) for NSD and (\( \leq 0.742 \)) for MSD, and from the

Table 1. Comparison of Calculated and Experimental \( q_e \) Values, and Kinetic Parameters for the Adsorption of ARAC onto NSD at Various Solution pHs, Initial Dye Concentration, Ionic Strengths, and Temperatures

| Parameter | \( q_e(\text{exp}) \) (\( \mu \text{mol/g} \)) | \( q_e(\text{cal}) \) (\( \mu \text{mol/g} \)) | \( k_1 \) (min\(^{-1}\)) | \( R^2 \) | \( q_e(\text{cal}) \) (g/\( \mu \text{mol min} \)) | \( h \) (\( \mu \text{mol/g min} \)) | \( R^2 \) | \( \alpha \) (\( \mu \text{mol/g min} \)) | \( \beta \) (g/mmol) | \( R^2 \) |
|-----------|----------------------------------|----------------------------------|----------------|---------|----------------------------------|----------------|---------|----------------|----------------|---------|
| \( \text{pH} \) | [Dye]: 50 \( \mu \text{mol/L} \), Temp.: 25 \( ^\circ \text{C} \), Particle Size: 0–75 \( \mu \text{m} \), Adsorbent: 0.07 \( \mu \text{g} \) | | | | | | | | |
| 2 | 22.08 | 4.79 | 0.049 | 0.931 | 22.27 | 0.036 | 18.02 | 0.999 | 7.70 \( \times \) 10 \( ^1 \) | 0.569 | 0.928 |
| 3 | 16.91 | 3.99 | 0.034 | 0.963 | 17.04 | 0.032 | 9.35 | 0.999 | 7.56 \( \times \) 10 \( ^1 \) | 0.937 | 0.994 |
| 4 | 5.75 | 3.02 | 0.035 | 0.997 | 5.92 | 0.032 | 1.11 | 0.997 | 1.67 \( \times \) 10 \( ^1 \) | 1.392 | 0.970 |
| 5 | 3.84 | 2.49 | 0.032 | 0.996 | 4.01 | 0.030 | 0.49 | 0.995 | 0.35 \( \times \) 10 \( ^1 \) | 1.788 | 0.945 |
| 6 | 2.96 | 1.62 | 0.040 | 0.928 | 3.06 | 0.071 | 0.67 | 0.999 | 0.35 \( \times \) 10 \( ^1 \) | 2.189 | 0.970 |

25 \( ^\circ \text{C} \) and 25.61 \( \mu \text{mol/g} \) at 55 \( ^\circ \text{C} \) for NSD and 35.07 \( \mu \text{mol/g} \) at 25 \( ^\circ \text{C} \) and 35.58 \( \mu \text{mol/g} \) at 55 \( ^\circ \text{C} \) for MSD, respectively.

This may be attributed to increase penetration of dye molecules inside microspores at higher temperatures or the creation of new active sites. The formation of more than one molecular layer on the surface of adsorbent appears to be achieved in the case of ARAC dye. This suggests that the equilibrium time became shorter with increase in the solution temperature (Figure 12). Analogous results were also noticed in the adsorption of RB5 and Remazol Brilliant Violet on chitosan in aqueous solution.21,23

Adsorption Kinetics Modeling. The adsorption kinetic data obtained from different batch adsorption trails were analyzed by applying the pseudo-first-order,46 pseudo-second-order,47 and Elovich48 kinetic models. The pseudo-first-order adsorption kinetics can be written as eq 1.

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.0303}t
\]  

(1)

where \( q_e \) (\( \mu \text{mol/g} \)) and \( q_t \) (\( \mu \text{mol/g} \)) indicate the extent of adsorption at time \( t \) and at equilibrium time, respectively. The pseudo-first-order adsorption rate constant, \( k_1 \) (min\(^{-1}\)), can be estimated from the slope of the plot \( \log(q_e - q_t) \) versus \( t \).

The pseudo-second-order kinetic model can be written by the following equations:

Nonlinear form

\[
q_t = \frac{k_2q_e^{2}t}{(1 + k_2q_e t)}
\]  

(2)

Linear form

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}
\]  

(3)
Table 2. Comparison of Calculated and Experimental \( q_e \) Values, Kinetic Parameters for the Adsorption of ARAC onto MSD at Various Solution pHs, Initial Dye Concentration, Ionic Strengths, and Temperatures

| Parameter | \( \bar{q}_{(exp)} \) (\( \mu \text{mol/g} \)) | \( \bar{q}_{(cal)} \) (\( \mu \text{mol/g} \)) | \( k_1 \) (min\(^{-1}\)) | \( R^2 \) | \( \bar{q}_{(exp)} \) (\( \mu \text{g/(min}\times \text{g} \)) | \( h \) (\( \mu \text{g/g/min} \)) | \( R^2 \) | \( \alpha \) (\( \mu \text{g/min} \)) | \( \beta \) (\( \mu \text{g/}\mu \text{l} \)) | \( R^2 \) |
|-----------|-----------------|-----------------|-----------|-------|-----------------|-------|-------|-----------------|-----------------|-------|
| pH; [Dye]: | 0.5 0  
50 | 3.184 | 10.45 | 0.181 | 2.98 | 32.05 | 0.04 | 41.67 | 1.00 | 2.08 \( \times 10^{5} \) | 0.489 | 0.859 |
| 75 75 | 3.057 | 8.37 | 0.140 | 7.32 | 35.21 | 0.04 | 54.68 | 1.00 | 1.05 \( \times 10^{5} \) | 0.417 | 0.768 |
| 100 100 | 3.459 | 4.97 | 0.055 | 8.83 | 34.84 | 0.04 | 49.05 | 1.00 | 4.34 \( \times 10^{5} \) | 0.396 | 0.823 |
| 125 125 | 3.401 | 5.82 | 0.049 | 9.06 | 34.25 | 0.03 | 37.06 | 0.99 | 7.16 \( \times 10^{5} \) | 0.412 | 0.844 |
| 150 150 | 2.976 | 8.96 | 0.056 | 9.69 | 27.40 | 0.02 | 15.09 | 0.99 | 7.39 \( \times 10^{5} \) | 0.363 | 0.938 |
| 175 175 | 18.64 | 7.38 | 0.032 | 9.09 | 18.94 | 0.01 | 5.31 | 0.99 | 7.61 \( \times 10^{5} \) | 0.431 | 0.982 |
| 200 200 | 16.73 | 8.54 | 0.035 | 9.76 | 17.12 | 0.01 | 3.55 | 0.99 | 3.29 \( \times 10^{5} \) | 0.438 | 0.996 |
| 225 225 | 13.64 | 10.33 | 0.054 | 9.13 | 14.20 | 0.01 | 2.40 | 0.99 | 1.26 \( \times 10^{5} \) | 0.467 | 0.985 |
| 250 250 | 11.84 | 7.31 | 0.037 | 9.68 | 12.42 | 0.01 | 1.77 | 0.99 | 0.59 \( \times 10^{5} \) | 0.468 | 0.988 |

- **Elovich kinetic model** ([≤0.917] for MSD and [≤0.768] for MSD were low. On the other hand, the value of \( R^2 \) obtained from the pseudo-second-order kinetic model was found to be ≥0.998 for both MSD and MSD adsorbents. Moreover, the calculated \( q_e(cal) \) value obtained from pseudo-second-order kinetic model was very similar to the experimental \( q_e(exp) \) values for both adsorbents MSD and MSD (Tables 1 and 2). These results indicate that the adsorption of ARAC onto MSD and MSD followed pseudo-second-order adsorption kinetics.**

**Adsorption Mechanism.** It well known that the adsorption mechanism is regulated by the film diffusion or intraparticle diffusion, that is, one of the methods should be
the rate-limiting step. The film diffusion model suggested by the McKay and intraparticle diffusion model proposed by Weber and Morris equations is expressed as

\[
\ln(1 - F) = -k_{id}t
\] (6)

Intraparticle diffusion model

\[
q_t = k_{id} t^{0.5}
\] (7)

where \(k_{id} \) (μmol/g min^{0.5}) is the intraparticle diffusion rate constant, \(k_{fd} \) (min^{-1}) is the film diffusion rate constant, \(F = q_t / q_{\infty} \) is the fractional attainment of the equilibrium, and \(q_t \) (μmol/g) and \(q_{\infty} \) (μmol/g) are amounts of ARAC adsorbed after \(t \) time and infinite time, respectively. Typical plots of ln(1 − \(F \)) versus \(t \) and \(q_t \) versus \(t^{0.5} \) for ARAC dye adsorption onto NSD and MSD in aqueous solution are shown in Figures 13 and 14. The values of diffusion kinetic parameters \((k_{id} \) and \(k_{fd} \)) and \(R^2 \) found in employed models are shown in Tables 3 and 4, respectively. From Figures 13 and 14, it is noticed that none of the linear plots at any concentration of ARAC solution passed through the origin, which suggests that both film diffusion and intraparticle diffusion are the rate-limiting steps for the ARAC dye adsorption onto NSD and MSD. As expected, the order of
temperatures (Tables 1 and 2). Presuming that the correlation equation expressed by the eq 8

\[ k = \frac{E_a}{RT} + \text{constant} \]

diffusion rate constant \((k_{id1})\) in the first stage was higher than that in the second \((k_{id2})\) and third \((k_{id3})\) stages. At the beginning, the ARAC dye adsorbed on the external surface of the both adsorbents NSD and MSD; hence, the initial dye adsorption rate was very high. The external surface of the adsorbents reached saturation, and the adsorption rate became slower. Then, the dye molecule entered into the internal pores within the particles and finally was adsorbed by the internal structure of the adsorbent material during the adsorption process. The values of \(k_a\) remained the same as earlier, \(k_i\): 1.381 × 10⁻²³ J/K is the Boltzmann constant and \(h_p\): 6.626 × 10⁻³⁴ Js is the Planck constant. The slope and y-intercept of the plot \(ln(k_i/T)\) versus \(1/T\) (\(R^2 = 0.987\) for NSD and MSD) were utilized to determine \(\Delta H^\ddagger\) and \(\Delta S^\ddagger\), respectively (Table 5). The values of \(\Delta H^\ddagger\) were estimated to be 4.07 kJ/mol for NSD and 9.10 kJ/mol for MSD, which is consistent with endothermic nature of the diffusion process. The values of \(\Delta S^\ddagger\) were found to be −167.40 J/mol K for NSD and −148.98 for MSD, which indicates that no significant alteration developed in the internal structure of the adsorbent material during adsorption. The values of \(\Delta G^\ddagger\) were found to be 53.62, 55.62, 57.29, and 58.97 kJ/mol for NSD and 53.50, 54.99, 56.48, and 57.97 kJ/mol for MSD at 25, 35, 45, and 55 °C, respectively (Table 5). The positive \(\Delta G^\ddagger\) values indicate the presence of an energy barrier in the adsorption process.

**Adsorption Isotherm.** An adsorption isotherm is a graphical picture for stating the relation between the extent

### Table 3. Diffusion Rate Constants \((k_{id} \text{ and } k_{ia})\) for the Adsorption of ARAC on NSD at Different Solution pHs, ARAC Dye Concentrations, Ionic Strengths, Particle Size, and Temperatures

| Parameter | Film Diffusion Model | Intraparticle Diffusion Model |
|-----------|---------------------|-----------------------------|
|           | \(k_{id} \text{ (min}^{-1})\) | \(k_{id} \text{ (\mu mol/g min}^{-0.5})\) | \(R^2\) | \(k_{ia} \text{ (\mu mol/g min}^{-0.5})\) | \(R^2\) | \(k_{ia} \text{ (\mu mol/g min}^{-0.5})\) | \(R^2\) |
| pH: 2.0, [Dye]: 50 μmol/L, Tem.: 25 °C, Particle Size: 0.07 g | | | | | | |
| 0–75 | 0.049 | 0.930 | 3.117 | 0.980 | 0.628 | 0.878 | 0.076 | 0.973 |
| 75–150 | 0.046 | 0.953 | 3.183 | 0.999 | 0.865 | 0.894 | 0.154 | 0.791 |
| 150–300 | 0.052 | 0.985 | 2.809 | 1.000 | 0.983 | 0.975 | 0.140 | 0.825 |
| 300–600 | 0.048 | 0.961 | 2.852 | 0.985 | 0.859 | 0.971 | 0.145 | 0.721 |

where \(R\) (8.314 J/mol K) is the ideal gas constant. The slope of the plot of \(ln k_i\) versus \(1/T\) \((R^2 = 0.995\) for NSD and 0.994 for MSD) was employed to assess \(E_a\), which was estimated to be 6.67 kJ/mol for NSD and 11.70 kJ/mol for MSD in the temperature range 25–55 °C (Table 5). The low activation energy range \((4–40 \text{ kJ/mol})\) indicates physisorption, while higher activation energies \((40–400 \text{ kJ/mol})\) suggest chemisorption. The values of \(E_a\) indicate that the ARAC dye adsorption was a physisorption process.

To determine the thermodynamic activation parameters such as changes in enthalpy of activation \((\Delta H^\ddagger)\), entropy of activation \((\Delta S^\ddagger)\), and Gibb’s free energy of activation \((\Delta G^\ddagger)\), the following equations were employed:

\[
\ln \left( \frac{k_i}{T} \right) = -\frac{\Delta H^\ddagger}{RT} + \ln \frac{k_i}{h_p} + \frac{\Delta S^\ddagger}{R}
\]

\[
\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger
\]
of dye adsorbed per unit mass of adsorbent and equilibrium dye concentration in the liquid phase at constant temperature. It shows how dye can be distributed between the liquid and solid phases at various equilibrium concentrations. There are a number of factors that determine the shape of isotherm. The major factors are the number of compounds in the solution, their relative adsorbing abilities, initial concentration of the adsorbate in the solution, and the degree of competition among solutes for adsorption sites. The relationship between the amount of equilibrium dye adsorption onto both adsorbents (NSD and MSD) and the equilibrium dye concentrations in aqueous solution at different temperatures is given in Figure 15. It is noticed that the extent of equilibrium dye adsorption onto NSD was increased with increasing solution temperature (Figure 15a); however, this effect was very insignificant in the case of MSD (Figure 15b).

Table 4. Diffusion Rate Parameters ($k_{fd}$ and $k_{id}$) for the Adsorption of ARAC on MSD at Different Solution pHs, ARAC Concentrations, Ionic Strengths, Particle Size, and Temperatures

| parameter | film diffusion model | | | intraparticle diffusion model | | |
|-----------|----------------------|-----------------|-----------------|-------------------|-----------------|-----------------|
|           | $k_{fd}$ (min$^{-1}$) | $R^2$ | $k_{id1}$ (μmol/g min$^{0.5}$) | $R^2$ | $k_{id2}$ (μmol/g min$^{0.5}$) | $R^2$ | $k_{id3}$ (μmol/g min$^{0.5}$) | $R^2$ |
| pH: [Dye] | 50 μmol/L, Tem.: 25 °C, Particle Size: 0–75 μm, Adsorbent: 0.07 g | | | | | | |
| 2         | 0.051 0.928 5.605 0.999 0.582 0.927 0.095 0.949 | | | | | | |
| 3         | 0.040 0.742 8.449 0.992 0.605 0.959 0.107 0.968 | | | | | | |
| 4         | 0.055 0.883 7.377 0.999 0.750 0.895 0.079 0.829 | | | | | | |
| 5         | 0.049 0.906 6.852 0.999 0.337 0.977 0.174 0.723 | | | | | | |
| 6         | 0.056 0.969 5.223 0.947 1.045 0.977 0.215 0.681 | | | | | | |
| 7         | 0.032 0.909 3.748 0.954 1.193 0.977 0.239 0.926 | | | | | | |
| 8         | 0.035 0.976 3.221 0.974 1.015 0.928 0.494 0.938 | | | | | | |
| 9         | 0.054 0.913 1.835 0.998 1.233 0.971 0.396 0.909 | | | | | | |
| 10        | 0.037 0.968 2.509 0.986 1.367 0.981 0.281 0.984 | | | | | | |
| [Dye] (μmol/L), pH 3.0, Temp.: 25 °C, Particle Size: 0–75 μm, Adsorbent: 0.07 g | | | | | | | |
| 25        | 0.040 0.742 8.449 0.992 0.605 0.959 0.107 0.968 | | | | | | |
| 35        | 0.142 0.871 5.591 0.999 0.833 0.917 0.042 0.653 | | | | | | |
| 45        | 0.055 0.859 5.509 0.999 0.318 0.884 0.036 0.858 | | | | | | |
| 55        | 0.051 0.868 3.903 0.986 0.212 0.989 0.030 0.926 | | | | | | |
| Temperature (°C), pH 3.0, [Dye]: 50 μmol/L, Particle Size: 0–75 μm, Adsorbent: 0.07 g | | | | | | | |
| 0–75      | 0.040 0.742 8.449 0.992 0.605 0.959 0.107 0.968 | | | | | | |
| 75–150    | 0.054 0.983 5.151 0.996 1.849 0.971 0.202 0.852 | | | | | | |
| 150–300   | 0.033 0.911 4.867 0.996 1.592 0.911 0.426 0.975 | | | | | | |
| 300–600   | 0.045 0.918 3.498 0.981 2.513 0.939 0.264 0.932 | | | | | | |
| Ionic Strength (mol/L), pH 3.0, [Dye]: 50 μmol/L, Tem.: 25 °C, Particle Size: 0–75 μm, Adsorbent: 0.07 g | | | | | | | |
| 0.05      | 0.044 0.772 8.964 0.994 0.672 0.912 0.079 0.911 | | | | | | |
| 0.10      | 0.046 0.831 8.268 0.981 0.614 0.791 0.112 0.995 | | | | | | |
| 0.20      | 0.050 0.887 7.880 0.979 0.932 0.834 0.118 0.962 | | | | | | |
| 0.30      | 0.048 0.898 7.888 0.967 0.907 0.864 0.112 0.995 | | | | | | |
| 0.40      | 0.047 0.916 7.833 0.977 1.172 0.920 0.139 0.976 | | | | | | |

Table 5. Values of the Activation Parameters for the Adsorption of ARAC Onto NSD and MSD in Aqueous Solution

| temperature (K) | activation energy | thermodynamic activation parameters |
|-----------------|------------------|-------------------------------------|
|                 | $E_a$ (kJ/mol)    | $R^2$ | $\Delta G^\ddagger$ (kJ/mol) | $\Delta H^\ddagger$ (kJ/mol) | $\Delta S^\ddagger$ (J/mol.K) | $R^2$ |
| Dye Adsorption onto NSD | | | | | | |
| 298             | 6.67 0.995        | 53.95 4.07 | -167.40 | 0.987 |
| 308             | 5.62 0.999        | 57.29 4.07 | -148.98 | 0.987 |
| 318             | 58.97 0.999        | 64.48 4.07 | -133.74 | 0.987 |
| 328             | 66.02 0.999        | 73.79 4.07 | -119.24 | 0.987 |
| Dye Adsorption onto MSD | | | | | | |
| 298             | 11.70 0.994        | 53.50 4.07 | -167.40 | 0.987 |
| 308             | 54.99 0.999        | 66.48 4.07 | -148.98 | 0.987 |
| 318             | 66.97 0.999        | 76.48 4.07 | -133.74 | 0.987 |
| 328             | 60.00 0.999        | 83.48 4.07 | -119.24 | 0.987 |
Freundlich model
Nonlinear form
\[ q_e = K_F C_e^{1/n} \]  
\[ q_e = C_e \left(\frac{1}{a_L + C_e}\right) \]  
Linear form
\[ \ln q_e = \frac{1}{n} \ln C_e + \ln K_F \]  
\[ \ln q_e = \ln b_T + \ln C_e \]  
Temkin model
Nonlinear form
\[ q_e = b_T \ln (K_T C_e) \]  
Linear form
\[ q_e = b_T \ln K_T + b_T \ln C_e \]  
\[ b_T = \frac{R T}{b} \]  

where \( C_e (\mu\text{mol/L}) \) is the equilibrium ARAC concentration in solution, \( q_e (\mu\text{mol/g}) \) is the extent of dye adsorption onto the adsorbent at equilibrium time, \( K_F \) [(\mu\text{mol/g}) (\mu\text{mol/L})^{−1/n}], and \( n \) are Freundlich isotherm constants signifying the ability and strength of the adsorbent, respectively. \( K_T (\mu\text{mol/L}) \) is a Temkin isotherm constant, \( b (J/\text{mol}) \) is a constant associated to the heat of adsorption, \( R (8.314 \text{ J/mol K}) \) and \( T \) (K) remain the same as earlier. \( K_L (\text{L/g}) \) and \( a_L (\text{L/\mu\text{mol}}) \) are the Langmuir isotherm constants, and the ratio of \( K_L/a_L \) denotes

Table 6. Langmuir, Freundlich, and Temkin Isotherm Constants at Different Temperatures for the Adsorption of ARAC Onto NSD (pH 2.0) and onto MSD (pH 3)

| Isotherm        | Parameter          | Temperature (°C) | 25  | 35  | 45  | 55  |
|-----------------|--------------------|-----------------|-----|-----|-----|-----|
| Dye Adsorption onto NSD |                    |                 |     |     |     |     |
| Langmuir model  | \( K_L (\text{L/g}) \) |                 | 2.07| 2.48| 2.71| 3.17|
|                 | \( a_L (\text{L/\mu\text{mol}}) \) |                 | 0.041| 0.048| 0.052| 0.061|
|                 | \( q_m (\mu\text{mol/g}) \) |                 | 50.98| 51.25| 52.04| 52.14|
|                 | \( R^2 \) |                 | 0.999| 0.999| 0.999| 0.999|
| Freundlich model| \( K_F (\text{\mu\text{mol/g}}) (\mu\text{mol/L})^{−1/n} \) |                 | 6.33| 7.72| 8.29| 9.25|
|                 | \( n \) |                 | 2.41| 2.64| 2.59| 2.82|
|                 | \( R^2 \) |                 | 0.998| 0.951| 0.955| 0.929|
| Temkin model    | \( K_T (\mu\text{mol/L}) \) |                 | 0.37| 0.51| 0.57| 0.69|
|                 | \( b (J/\text{mol}) \) |                 | 217.45| 228.16| 227.07| 231.18|
|                 | \( R^2 \) |                 | 0.989| 0.994| 0.994| 0.986|
| Dye Adsorption onto MSD |                    |                 |     |     |     |     |
| Langmuir model  | \( K_L (\text{L/g}) \) |                 | 9.50| 10.27| 10.79| 11.15|
|                 | \( a_L (\text{L/\mu\text{mol}}) \) |                 | 0.063| 0.068| 0.071| 0.074|
|                 | \( q_m (\mu\text{mol/g}) \) |                 | 151.46| 151.65| 151.72| 151.88|
|                 | \( R^2 \) |                 | 0.999| 0.999| 0.999| 0.999|
| Freundlich model| \( K_F (\text{\mu\text{mol/g}}) (\mu\text{mol/L})^{−1/n} \) |                 | 41.59| 43.18| 44.83| 46.83|
|                 | \( N \) |                 | 5.05| 5.17| 5.33| 5.55|
|                 | \( R^2 \) |                 | 0.955| 0.956| 0.959| 0.965|
| Temkin model    | \( K_T (\mu\text{mol/L}) \) |                 | 7.83| 9.85| 13.03| 18.56|
|                 | \( b (J/\text{mol}) \) |                 | 147.62| 150.83| 155.69| 162.18|
|                 | \( R^2 \) |                 | 0.982| 0.979| 0.977| 0.975|

Figure 15. Equilibrium adsorption isotherm of ARAC dye onto NSD (a) and MSD (b) in aqueous solution at different temperatures (particle size 0–75 μm; pH 2.0 for NSD and pH 3.0 for MSD); circle open: 25 °C; circle solid: 35 °C; triangle up open: 45 °C; and triangle up solid: 55 °C. All lines are modeled Langmuir adsorption isotherm using eq 15, and the values of \( K_L \) and \( a_L \) are recorded in Table 6.
the maximum dye adsorption capacity, \( q_{\text{max}} \) (\( \mu \text{mol/g} \)), of NSD and MSD, respectively. The values of isotherm parameters and correlation coefficients are given in Table 6. The Langmuir isotherm showed the highest correlation coefficients (R²), which indicates significantly good fit compared to Freundlich and Temkin adsorption isotherms. The highest extent of dye adsorption was observed to be 52.14 \( \mu \text{mol/g} \) for NSD and 151.88 \( \mu \text{mol/g} \) for MSD at 55 °C, respectively. Thus, the equilibrium constants (\( a_{L} \)) obtained from Langmuir isotherms were used to calculate the thermodynamic parameters for the adsorption process.

An essential dimensionless term R_L is the separation factor (Table 7) which can be used to explain the characteristics of Langmuir isotherm.

\[
R_L = \frac{1}{(1 + a_L C_0)}
\]

Here, \( C_0 \) is highest initial concentration of dye taken in the adsorption isotherm processes.

The calculated values of \( R_L \) were found to be 0.110, 0.094, 0.088, and 0.076 for NSD and 0.011, 0.010, 0.009, and 0.009 for MSD at 25, 35, 45, and 55 °C, respectively, which suggests that the present adsorption was proposing at all temperatures. The maximum amount of ARAC dye adsorption onto various adsorbents are shown in Table 8. The values of \( q_{\text{max}} \) on the adsorbent. Similarly, EDX is also a very useful technique for elemental analysis. The FE-SEM images and EDX data of NSD before and after ARAC dye adsorption are shown in Figure 16. It is noticed that the irregular surface structure of NSD was clearly observed in the FE-SEM image, as shown in Figure 16a, and corresponding EDX data are shown in Figure 16b. The FE-SEM image of the surface of NSD became brighter after ARAC dye adsorption (Figure 16c), and the presence of precipitates also suggest that the layer of ARAC dye was present on the surface of NSD. Moreover, the mass percentage of nitrogen, oxygen, and sulfur were increased in NSD after adsorption of ARAC (Figure 16d). Hence, it is confirmed that the ARAC dye adsorption occurred on the surface of NSD.

The surface morphology and EDX data of MSD before and after ARAC dye adsorption are shown in Figure 17. The figure shows surface texture, porosity, and elemental composition of the materials analyzed. It is noticed that the FE-SEM micrograph of MSD showed rough and microporous surfaces before adsorption of ARAC (Figure 17a). The corresponding elemental compositions of MSD are shown in Figure 17b. The elements of carbon, nitrogen, oxygen, and bromine were present in the surface of MSD before dye adsorption; however, the sulfur peak was not detected in Figure 17b. The brightness of MSD surfaces was increased after dye adsorption (Figure 17c). It is noted that the mass percentage of carbon and nitrogen increased on the surface of MSD after the adsorption of ARAC dye, and the presence of sulfur element was also detected (Figure 17d). These results confirm that the ARAC dye adsorbed onto the surfaces of MSD.

**Table 7. Relation between \( R_L \) Values and the Types of Adsorption**

| values of \( R_L \) | types of adsorption          |
|-------------------|-----------------------------|
| \( R_L > 1.0 \)   | unfavorable                 |
| \( R_L = 1.0 \)   | linear                      |
| \( 0 \gg R_L < 1.0 \) | favorable                   |
| \( R_L = 0 \)     | irreversible                |

The thermodynamic factors associated with the adsorption phenomena, that is, changes in Gibb’s free energy (\( \Delta G \), kJ/mol), enthalpy (\( \Delta H \), kJ/mol), and entropy (\( \Delta S \), J/mol K) were computed by utilizing the Langmuir isotherm constant (\( a_L \), L/mol) and the subsequent equations:

\[
\Delta G = -RT \ln a_L
\]

\[
\ln a_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT}
\]

where \( R \) (8.314 J/mol K) and \( T \) (K) remain the same as before. The \( \Delta H \) and \( \Delta S \) were estimated from the slope and y-intercept of the plot of \( \ln a_L \) versus \( 1/T \) (\( R^2 = 0.982 \) for NSD and \( R^2 = 0.981 \) for MSD). The values of thermodynamic parameters are shown in Table 9. The values of \( \Delta H \) suggest that the dye adsorption pursued endothermic processes. The positive \( \Delta S \) values prove the presence of randomness at the solid–liquid edge throughout ARAC dye adsorption onto NSD and MSD, which develops from the translational entropy produced by the exchanged water molecules as related to that lost as a cause of dye uptake. Negative \( \Delta G \) values suggest that the adsorption of ARAC dye onto NSD and MSD adsorbents was natural adsorption and more promising at high temperature. The growth of adsorption capacities of NSD and MSD at higher temperatures might be ascribed to the enriched movement and permeation of ARAC dye molecules in the porous adsorbents by overwhelming the barrier of activation energy and boosting the intraparticle diffusion rate.

**Table 8. Comparison of ARAC Dye Adsorption Capacities (\( q_{\text{max}} \)) of Different Adsorbents**

| adsorbents                  | pH | temperature (°C) | \( q_{\text{max}} \) (\( \mu \text{mol/g} \)) | references |
|-----------------------------|----|------------------|---------------------------------|------------|
| chitosan                    | 5.7| 25               | 604.33                          | 31         |
| *Spirulina platensis*       | 4.0| 25               | 944.16                          | 33         |
| vine-trimming waste         | 6.0| 25               | 272.23                          | 34         |
| activated carbon            | 3.5| 25               | 8.86                            | 35         |
| activated carbon            | 2.0| 55               | 146.75                          | 36         |
| activated carbon from biological sludge (ACBS) | 2.0 | 55 | 578.34 | 37 |
| natural sawdust (NSD)       | 2.0| 55               | 52.14                           | 38         |
| CPB-treated sawdust (MSD)   | 3.0| 55               | 151.88                          | 39         |

The typical adsorption–desorption-adsorption phenomena of ARAC dye onto NSD and MSD in aqueous are shown in Figure 18. In adsorption steps, the concentration of dye solution was 50
μmol/L fixed with a working solution pH 2 for NSD (Figure 18a) and pH 3 for MSD (Figure 18b) at a temperature of 25 °C, while the discharge of ARAC from dye-included adsorbents was observed in 0.01 mol/L NaOH solution (pH 12) for NSD (Figure 18a) and in 0.1 mol/L NaOH solution (pH 13) for MSD (Figure 18b) at a temperature of 25 °C. In the first adsorption step, the intensity of equilibrium ARAC dye adsorption was estimated to be 22.08 μmol/g for NSD and 35.07 μmol/g for MSD (Figure 18a,b). It is observed that the initial dye desorption rate was very quick, and 90% of ARAC dye was released within 10 min. The 98−99% of ARAC dye was liberated from dye-included adsorbents within 120 min. This is due to the fact that in a strong basic solution, the electrostatic interaction between the adsorbents and the dye molecules was much weaker. Behind the dye-releasing step, the subsequent dye adsorption occurred and found similar adsorption phenomena as observed in the first adsorption step. The extent of dye adsorption was similar as observed in the first adsorption step. These results suggest that the present adsorbents NSD and MSD can be reused for further dye adsorption.

**CONCLUSIONS**

The adsorption characteristic of ARAC onto the both adsorbents (NSD and MSD) was investigated in aqueous solution. Both adsorbents (NSD and MSD) were prepared and characterized by FTIR and XRD methods. The values of pH_{pzc} were estimated to be 5.03 for NSD and 7.43 for MSD, respectively. The dye adsorption onto both adsorbents was confirmed by FE-SEM and EDX analysis. The batch adsorption kinetic experiments were carried as a function of contact time, solution pHs, particle sizes, adsorbent dosages, dye concentrations, ionic strengths, and temperatures, respectively. The equilibrium dye adsorption onto both adsorbents were studied in aqueous solution at various temperatures. The batch adsorption kinetic data were examined by pseudo-first-order, pseudo-second-order, Elovich, intraparticle, and film diffusion models. The equilibrium dye adsorption isotherms were fitted with Temkin, Freundlich, and Langmuir adsorption isotherm models. The acidic solution pH was favorable for the ARAC dye adsorption onto both adsorbents. The maximum dye adsorption was found to be at pH 2.0 for NSD and at pH 3.0 for MSD, respectively. The amount of equilibrium dye adsorption onto both adsorbents was enhanced with rising concentration of dye solutions. The initial rate and amount of equilibrium dye adsorption onto both adsorbents were increased with rising solution temperatures. However, the initial rate and the extent of dye adsorption reduced with rising dye solution ionic strengths. Batch adsorption kinetics of data was followed by the pseudo-second-order kinetic model rather than pseudo-first-order, Elovich, film-diffusion, and intraparticle diffusion models. Moreover, the observed values of $q_{e(\text{exp})}$ in all cases were very similar to the calculated values of $q_{e(\text{cal})}$ obtained from the pseudo-second-order kinetic model. The equilibrium dye adsorption isotherm was fitted well by the Langmuir
adsorption isotherm rather than Temkin and Freundlich isotherm models. The activation and thermodynamic parameters suggest that the present dye adsorption onto both adsorbents (NSD and MSD) is an endothermic spontaneous physisorption process. The ARAC was released from dye-loaded adsorbents in very basic solution. Moreover, dye-loaded NSD and MSD were reused in the adsorption of ARAC in aqueous solution without loss of their adsorption efficiency. Hence, the NSD and MSD could be used to clean dye-containing industrial wastewater.

**EXPERIMENTAL SECTION**

**Chemicals.** The chemicals used in the present research were of pure analytical grade and used without further purification. The sources and purity along with the CAS registration numbers of the chemicals used have been summarized in Table 10. Deionized water was prepared by passing distilled water through a deionizing column (Barnstead, Suyboron Corporation, Boston, USA). Petroleum ether was prepared by distillation of petrol purchased from local gasoline station.

**Preparation and Characterization of NSD and MSD.** Sawdust used in present research was collected from the local sawmill of Savar, Dhaka, Bangladesh. The raw sawdust was frequently rinsed with distilled water to eliminate the dust-like impurities and dried in open air. The dried sample was pulverized into powder. To make it free from organic materials and other impurities, the powder of sawdust was treated with petroleum ether for two days. The organic material free sawdust was washed with warm distilled water (60 °C) and dried in the oven at 120 °C for 24 h. The dried sawdust was sieved using different meshes to separate different particle size sawdust and to preserve in the desiccator for further use. The MSD was prepared according to the method used by Zhao et al. with a little modification. Sawdust (10.0 g) was

---

**Table 9. Thermodynamics of ARAC Dye Adsorption onto NSD and MSD in Aqueous Media**

| Temperature (°C) | ΔG (kJ/mol) | ΔS (J/mol. K) | ΔH (kJ/mol) | R² | ΔG (kJ/mol) | ΔS (J/mol. K) | ΔH (kJ/mol) | R² |
|-----------------|-------------|--------------|-------------|----|-------------|--------------|-------------|----|
| 25              | −26.29      | 123.48       | 10.49       | 0.982 | −27.37      | 106.21       | 4.26        | 0.981 |
| 35              | −27.62      |              |             |     | −28.48      |              |             |     |
| 45              | −28.72      |              |             |     | −29.54      |              |             |     |
| 55              | −30.03      |              |             |     | −30.55      |              |             |     |
Batch Adsorption Experiments. To examine the ARAC dye adsorption features on NSD and MSD, batch adsorption experiments were conducted in 125 mL stoppered bottles having 0.07 g of the adsorbent and 50 mL of dye solution (50 μmol/L). The solution pH was fixed by adding small amounts of 1 mol/L NaOH or HCl solution. The dye solution pH was determined by the pH meter (Adwa 101 pH meter). The sample bottles were agitated in a thermostated shaker at room temperature (25 ± 0.2 °C), with a velocity of 120 rpm, until achieving equilibrium. Each sample bottle was covered to prevent vaporization at elevated temperatures. Sample bottles were removed at preferred time periods for measuring dye concentration in the liquid phase. The samples were centrifuged at a speed of 4000 rpm for 5 min. The dye concentration in the supernatant was analyzed by the spectrophotometric method, using a Shimadzu UV-1800 spectrophotometer (Shimadzu, Japan), at a λ_{max} value of 504 nm (pH 2–10). The molar absorbivity of ARAC was determined to be 21.0 × 10^4 L/mmol cm at 504 nm. The extent of ARAC adsorbed per unit mass of NSD or MSD at time t, q_t (μmol/g) was determined by:

$$ q_t = \frac{V(C_0 - C_t)}{m} $$

where C_0 (μmol/L) and C_t (μmol/L) are the concentration of ARAC dye in the liquid phase at initial and any time t, respectively; V (L) is the volume of ARAC dye solution, and m (g) is the amount of dry NSD or MSD used.

The kinetics of dye adsorption onto both adsorbents was also studied changing particle size of adsorbents (0–600 μm), dosages of adsorbents (0.02–0.20 g), dye concentrations (30–500 μmol/L), ionic strengths (0.05–0.40 mol/L), and temperatures (25, 35, 45, and 55 °C), respectively. Na_2SO_4 solution (1 mol/L) was used to adjust ionic strength of dye solutions. The equilibrium dye adsorption was conducted in aqueous solution at four different temperatures (25, 35, 45, and 55 °C), and at pH 2 for NSD and pH 3 for MSD in the absence of Na_2SO_4.

The extent of ARAC dye adsorption onto NSD or MSD at equilibrium time, q_e (μmol/g), and % removal of ARAC dye were determined by:

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

and

$$ \text{Dye removal} \% = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 $$

where C_e (μmol/L) is ARAC dye concentration in the liquid phase at equilibrium time; C_0, V, and m remain the same as discussed earlier.

In the desorption study, the released amount of ARAC dye was measured in 50 mL of 0.01 mol/L NaOH solution (pH 12) for dye-loaded NSD and in 50 mL of 0.1 mol/L NaOH solution (pH 13) for dye-loaded MSD, respectively. At first, a 20 range (5–70 °C) with a step size of 0.01° 2θ with an X-ray diffractometer (GNR-EXPLORER, GNR Analytical Instruments Group, Italy). The surface morphology and elements of NSD and MSD were examined before and after dye adsorption by using FE-SEM and EDX analysis (JSM-7610F Schottky field emission scanning electron microscope, JEOL Ltd., Japan). The pH_{zpc} values of NSD and MSD were determined by using the pH drift method.

Table 10. CAS Registry Number, Purity and Source of the Chemicals Used

| chemicals          | CAS registry number | source         | purity       |
|--------------------|---------------------|----------------|--------------|
| sodium hydroxide   | 1310-73-2           | Merck (Germany)| ≥98.0%       |
| hydrochloric acid  | 7647-01-0           | Sigma-Aldrich  | ACS reagent  | 37%          |
| potassium chloride | 7447-40-7           | Merck (Germany)| ≥99.0%       |
| allura red AC (ARAC)| 25956-47-6         | Sigma-Aldrich | dye content  | 80%          |
| hexadecylpyridinium| 140-72-7            | Sigma-Aldrich  | ≥97.0%       |

Table taken into a 1000 mL beaker containing 500 mL of 0.5% (w/v) CPB solution. The solution was stirred with a magnetic stirrer hot plate at 120 rpm and at room temperature (30 °C) for 24 h. Then, crude MSD was separated from the solution by filtration and repeatedly washed with distilled water to remove loosely bound CPB with sawdust. Finally, MSD was dried at 80 °C for overnight and stored in an airtight glass bottle for further use.

The FTIR spectra of NSD and MSD were taken in KBr at the frequencies 400–4000 cm^{-1} by utilizing FTIR spectrometer (IR Prestige-21 FTIR Spectrophotometer, Shimadzu, Japan). The X-ray powder diffraction outlines of NSD and MSD were observed by using an X-ray diffractometer maintaining a voltage of 30 kV and a current of 20 mA, using Cu Kα radiation (λ = 1.54 Å) and a frequency range of 10 μHz to 32 MHz. The representative data were collected in a
the adsorbent with dye solution (50 mL of 50 μmol/L) was agitated for 120 min, filtered, and the dye inserted-adsorbent was desiccated at room temperature (25 °C) overnight. The dye inserted-adsorbent was kept in 50 mL desorbing solution, and the mixture was shaken in a thermostated shaker at room temperature (25 ± 0.2 °C), with a speed of 120 rpm, until complete desorption. The extent of dye adsorption was measured in similar way as explained earlier. All data given in this study are the average of double measurements.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Markandeya; Shukl, S. P.; Mohan, D. Toxicity of disperse dyes and its removal from wastewater using various adsorbents: a review. Res. J. Environ. Toxicol. 2017, 11, 72−89.

(2) Wang, S.; Li, H. Kinetic modelling and mechanism of dye adsorption on unburned carbon. Dyes Pigm. 2007, 72, 308−314.

(3) Lellis, B.; Fivaro-Polonio, C. Z.; Pambili, J. A.; Poloni, J. C. Effects of textile dyes on health and the environment and bioremediation potential of living organisms. Biotechnol. Res. Innov. 2019, 3, 275−290.

(4) Berradi, M.; Hsissou, R.; Khudhair, M.; Assouag, M.; Cherkaoui, O.; El Bachiri, A.; El Harfi, A. Textile finishing dyes and their impact on aquatic environs. Heliyon 2019, 5, No. e02711.

(5) Sun, Q.; Li, K.; Wu, S.; Han, B.; Sui, L.; Dong, L. Remarkable improvement of TiO2 for dye photocatalytic degradation by a facile post-treatment. New J. Chem. 2020, 44, 1942−1952.

(6) Moghaddam, S. S.; Moghaddam, M. A.; Arami, M. Coagulation/flocculation process for dye removal using sludge from water treatment plant: optimization through response surface methodology. J. Hazard. Mater. 2010, 175, 651−657.

(7) Shakir, K.; Elkafrawy, A. F.; Ghoneimy, H. F.; Elrab Beheir, S. G.; Refaat, M. Removal of rhodamine B (a basic dye) and thoron (an acidic dye) from dilute aqueous solutions and wastewater simulants by ion flotation. Water Res. 2010, 44, 1449−1461.

(8) Simonic, M. Efficiency of ultracentrifugation for the pre-treatment of dye-bath effluents. Desalination 2009, 245, 701−707.

(9) Saha, T. K.; Fraendorff, H.; John, M.; Dechert, S.; Meyer, F. Efficient oxidative degradation of azo dyes by a water-soluble manganese porphyrin catalyst. ChemCatChem 2013, 5, 796−805.

(10) Gharbani, P.; Tabatabai, S. M.; Mehrizad, A. Removal of Congo red from textile wastewater by ozonation. Int. J. Sci. Environ. Technol. 2008, 5, 495−500.

(11) Kim, T.-H.; Park, C.; Kim, S. Water recycling from desalination and purification process of reactive dye manufacturing industry by combined membrane filtration. J. Clean. Prod. 2005, 13, 779−786.

(12) Gupta, V. K.; Jain, R.; Varshney, S. Electrochemical removal of the hazardous dye Reactofix Red 3 BFN from industrial effluents. J. Colloid Interface Sci. 2007, 312, 292−296.

(13) Wang, Z.; Gao, M.; Li, X.; Ning, J.; Zhou, Z.; Li, G. Efficient adsorption of methylene blue from aqueous solution by graphene oxide modified persimmon tannins. Mater. Sci. Eng., C 2020, 108, 110196.

(14) Yagub, M. T.; Sen, T. K.; Afrozoe, S.; Ang, H. M. Dye and its removal from aqueous solution by adsorption: a review. Adv. Colloid Interface Sci. 2014, 209, 172−184.

(15) Liu, J.; Wang, Z.; Li, H.; Hu, C.; Raymer, P.; Huang, Q. Effect of solid state formation of peanut shell on its dye adsorption performance. Bioresour. Technol. 2018, 249, 307−314.

(16) Amin, N. K. Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sawdust bagasse pulp. Desalination 2008, 223, 152−161.

(17) Amela, K.; Hassen, M. A.; Kerroum, D. Isotherm and kinetics study of biosorption of cationic dye onto banana peel. Energy Procedia 2012, 19, 286−295.

(18) de Luna, M. D. G.; Flores, E. D.; Genuino, D. A. D.; Futalan, C. M.; Wan, M. W. Adsorption of eriochrome black T (EBT) dye using activated carbon prepared from waste rice hulls−Optimization, isotherm and kinetic studies. J. Taiwan Inst. Chem. Eng. 2013, 44, 646−653.

(19) Karmaker, S.; Uddin, M. N.; Ichikawa, H.; Fukushima, Y.; Saha, T. K. Adsorption of reactive orange 13 onto jackfruit seed flakes in aqueous solution. J. Environ. Chem. Eng. 2015, 3, 583−592.

(20) Saha, T. K.; Karmaker, S.; Ichikawa, H.; Fukushima, Y. Mechanisms and kinetics of trisodium-2-hydroxy-1,1,3-trisulfonate adsorption onto chitosan. J. Colloid Interface Sci. 2005, 286, 433−439.

(21) Saha, T. K.; Bhoumik, N. C.; Karmaker, S.; Ahmed, M. G.; Ichikawa, H.; Fukushima, Y. Adsorption characteristics of reactive black 5 from aqueous solution onto chitosan. Cellul. Chem. Technol. 2011, 39, 984−993.

(22) Karmaker, S.; Sen, T.; Saha, T. K. Adsorption of reactive yellow 145 onto chitosan in aqueous solution: Kinetic modeling and thermodynamic analysis. Polym. Bull. 2015, 72, 1879−1897.

(23) Karmaker, S.; Nag, A. J.; Saha, T. K. Adsorption of remazol brilliant violet onto chitosan 10B in aqueous solution: Kinetics, equilibrium and thermodynamics studies. Cellul. Chem. Technol. 2019, 53, 373−386.

(24) Garg, V.; Amita, M.; Kumar, R.; Gupta, R. Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian rosewood sawdust: a timber industry waste. Dyes Pigm. 2004, 63, 243−250.

(25) Hameed, B. H.; Ahmad, A. L.; Latiff, K. N. A. Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. Dyes Pigm. 2007, 75, 143−149.

(26) Ansari, R.; Mosayebzadeh, Z. Removal of basic dye methylene blue from aqueous solutions using sawdust and sawdust coated with polypropylene. J. Iran. Chem. Soc. 2010, 7, 339−340.

(27) Ansari, R.; Seyghali, B. Application of wood sawdust modified with cationic surfactants for efficient removal of acidic dyes from aqueous solutions: Kinetic and thermodynamic studies. Eur. Chem. Bull. 2013, 2, 499−506.
(28) Nimkar, D. A.; Chavan, S. K. Removal of Congo red dye from aqueous solution by using sawdust as an adsorbent. Int. J. Eng. Res. Appl. 2014, 4, 47–51.
(29) Gupta, V.; Agarwal, A.; Singh, M. K.; Singh, N. B. Removal of torque blue dye from aqueous solution by kail sawdust. Asian J. Water, Environ. Pollut. 2016, 13, 59–67.
(30) Banerjee, S.; Chattopadhyaya, M. C. Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product. Arab. J. Chem. 2017, 10, S1629–S1638.
(31) Piccin, J. S.; Dotto, G. L.; Vieira, M. L. G.; Pinto, L. A. A. Kinetics and mechanism of the food dye FD&C red 40 adsorption onto chitosan. J. Chem. Eng. Data 2011, 56, 3759–3765.
(32) Sánchez-Duarte, R. G.; Sánchez-Machado, D. I.; López-Cervantes, J.; Correa-Murrieta, M. A. Adsorption of allura red dye by cross-linked chitosan from shrimp waste. Water Sci. Technol. 2012, 65, 618–623.
(33) Dotto, G. L.; Vieira, M. L. G.; Esquerdo, V. M.; Pinto, L. A. A. Equilibrium and thermodynamics of azo dyes biosorption onto Spirulina platensis. Braz. J. Chem. Eng. 2013, 30, 13–21.
(34) Sütcü, H. Removal of FD&C red no. 40 food dye from an aqueous solution by vine-trimming waste. Int. J. Chem. Eng. Appl. 2014, 5, 420–423.
(35) Özyör, H. D.; van Leeuwen, J. Removal of color from fruit candy waste by activated carbon adsorption. J. Food Eng. 2010, 101, 106–112.
(36) Alkahtani, S. A.; Abu-Alrub, S. S.; Mahmoud, A. M. Adsorption of food coloring allura red dye (E129) from aqueous solutions using activated carbon. Int. J. Food Allied Sci. 2017, 3, 10–19.
(37) Streit, A. F. M.; Côrtes, L. N.; Druzian, S. F.; Godinho, M.; Collazzo, G. C.; Perondi, D.; Dotto, G. L. Development of high quality activated carbon from biological sludge and its application for dyes removal from aqueous solutions. Sci. Total Environ. 2019, 660, 277–287.
(38) Zhao, B.; Xiao, W.; Shang, Y.; Zhu, H.; Han, R. Adsorption of light green anionic dye using cationic surfactant-modified peanut husk in batch mode. Arab. J. Chem. 2017, 10, S3595–S3602.
(39) Guinier, A.; Sainte-Marie Lorrain, D. X-ray Crystallography. (Book Reviews: X-Ray Diffraction in Crystals, Imperfect Crystals, and Amorphous Bodies). Science 1963, 142, 1564.
(40) Kosmulski, M. pH-dependent surface charging and point zero charge. Update and new approach. J. Colloid Interface Sci. 2009, 337, 439–448.
(41) Noorimotlagh, Z.; Mirzaei, S. A.; Martinez, S. S.; Alavi, S.; Ahmadi, M.; Jaafarzadeh, N. Adsorption of textile dye in activated carbons prepared from DVD and CD wastes modified with multi-wall carbon nanotubes: Equilibrium isotherms, kinetics and thermodynamic study. Chem. Eng. Res. Des. 2019, 141, 290–301.
(42) Su, Y.; Zhao, B.; Xiao, W.; Han, R. Adsorption behavior of light green anionic dye using cationic surfactant-modified wheat straw in batch and column mode. Environ. Sci. Pollut. Res. 2013, 20, 5558–5568.
(43) Wang, X. S.; Chen, J. P. Removal of the azo dye Congo red from aqueous solutions by the marine alga Porphyra yezoensis Ueda. Clean: Soil, Air, Water 2009, 37, 793–798.
(44) Nunes, A. A.; Franca, A. S.; Oliveira, L. S. Activated carbons from waste biomass: An alternative use for biodiesel production solid residues. Bioresour. Technol. 2009, 100, 1786–1792.
(45) Calvet, T.; Lima, E. C.; Cardoso, N. F.; Dias, S. L. P.; Ribeiro, E. S. Removal of brilliant green dye from aqueous solutions using home-made activated carbons. Clean: Soil, Air, Water 2010, 38, 521–532.
(46) Lagergren, S. Zur theorie der sogenannten adsorption geloster stoffe. K. Vetens. Vetenskapakad. Handl. 1898, 24, 1–39.
(47) Ho, Y. S.; McKay, G. Pseudo-second order model for sorption processes. Process Biochem. 1999, 34, 451–465.
(48) Elovich, S. Y.; Larionov, O. G. Theory of adsorption from nonelectrolyte solutions on solid adsorbents. Russ. Chem. Bull. 1962, 11, 198–203.
(49) Weber, W. J.; Morris, J. C. Kinetics of adsorption on carbon from solution. J. Sanit. Eng. Div. 1963, 89, 31–60.
(50) Laidler, K. J. The development of the Arrhenius equation. J. Chem. Educ. 1984, 61, 494–498.
(51) Freundlich, H. Adsorption solution. J. Phys. Chem. 1906, 57, 384–470.
(52) Temkin, M. I.; Pyzhev, V. Kinetics of ammonia synthesis on promoted iron catalyst. Acta Phys. Chem. USSR 1940, 12, 327–356.
(53) Langmuir, I. Adsorption of gases on plain surfaces of glass mica platinum. J. Am. Chem. Soc. 1918, 40, 1361–1403.
(54) Karmaker, S.; Sintaha, F.; Saha, T. K. Kinetics, isotherm and thermodynamic studies of the adsorption of reactive red 239 dye from aqueous solution by chitosan 8B. Adv. Biol. Chem. 2019, 9, 1–22.