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Utilization of dried activated sludge for the removal of basic dye from aqueous solution

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ABSTRACT

Textile dye wastewater can easily lead to environmental pollution issues because of its toxicity and difficult treatment. If the waste sludge produced from sewage treatment plant is used as an adsorbent to treat textile dye wastewater, waste recycling can be achieved. This study investigated the use of dried activated sludge (DAS) for the removal of Basic Red 29 dye from aqueous solution and used granular-activated carbon to compare differences in adsorption capacity. Influence on adsorption capacity of various factors, such as adsorbent properties, initial dye concentration and dye solution temperature, were investigated on the original dye solution. Kinetic data followed well both pseudo-first-order model and pseudo-second-order model. Equilibrium data fitted well with the Langmuir isotherm model. The monolayer adsorption capacity was found as 224.72 $\mathrm{mg\,g^{-1}}$ at 30°C. Thermodynamic studies indicated that adsorption process was exothermic in nature and the adsorption heat was $-17.70\,\mathrm{kJ\,mol^{-1}}$. The Fourier transform infrared spectroscopy analysis showed that because DAS had an extremely strong amide group, it could be an effective adsorbent for the removal of basic dye from aqueous solution.

Keywords: Dried activated sludge; Basic dye; Adsorption capacity; Adsorption kinetics

1. Introduction

Dyestuff, which possesses a complex molecular structure [1,2] and colored properties, pollutes the environment when released into water supplies. Therefore, the treatment of wastewater from dyestuff manufacturing industries has become a problematic issue. Traditional wastewater treatments such as applying chemicals are expensive and cause secondary pollution [3]. Furthermore, biological processes are inefficient because most dyestuffs have low biodegradability [1]. Therefore, the textile dye wastewater treatment efficiency is not fulfilling.

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Recently, some of the scholars have proposed using various adsorbents, such as sugarcane bagasse [4], papaya leaf [5], durian peal [6] and coffee residue [7], to treat basic dye wastewater. However, current adsorbent manufacturing processes are either excessively cumbersome or produce adsorbents with a low basic dye adsorption capacity. Thus, other simple and economical adsorbent manufacturing processes must be established to improve basic dye wastewater treatment.

Regarding biological treatments, wastewaters released from commercial and residential facilities worldwide are processed in aeration tanks, forming activated sludge, which is transferred into sedimentation tanks. Only 50 to 90% of these wastewaters are recycled [8]. The remaining sludge is concentrated, dehydrated and disposed of at a sanitary landfill site. Therefore, the use of waste-activated sludge to treat the pollutants in wastewater is not only economical, but can also reduce the extent of environmental pollution.

The surface of activated sludge consists of negative charges [9–11]. Therefore, several research scholars have recommended treating wastewater using activated sludge to absorb the heavy metal content in wastewater [12–14]. Basic dyes (also known as cationic dyes) are positively charged; therefore, in this study, we investigated the feasibility of treating basic dye wastewater using waste-activated sludge as an adsorbent. This treatment is not only economical, but also provides a solution for treating wastewater from dyestuff industries.

In this study, the dried activated sludge (DAS) was utilized to conduct batch adsorption of Basic Red 29 (BR-29) dyes. We investigated several aspects of this adsorption process, such as the influential factors, adsorption kinetics, adsorption isotherms, and thermodynamics. Furthermore, using the results obtained from Fourier transform infrared spectroscopy (FTIR) analysis, we identified the reason why activated sludge adsorbs basic dyestuffs.

2. Materials and methods

2.1. Preparation of basic dye solution

BR-29 dyes used in the adsorption studies were 99% pure and supplied by BASF Taiwan Ltd. To provide BR-29 dye solution of different concentrations (300 ppm or other) for use in these studies, the dyes were dried in an oven at 105℃ for 2 h. Various weights of dyes were dissolved in 1 L of double-distilled water and mixed for 3 h. The COD concentration was analyzed using a dichromate method [15] and stored at 4℃ until used. In these studies, different dye wastewaters were prepared only at an original condition without pH adjustment, and the pH value of BR-29 dye wastewater was about 5.06.

2.2. Preparation of adsorbents

DAS was obtained by collecting recycled activated sludge from the Taipei, Min-Shen wastewater treatment plant. The sludge settled and the supernatant water was decanted and replaced by fresh tap water several times. Washing was repeated with doubled-distilled water until the COD concentration of the supernatant water was less than 15 mg L^{-1}, and the sludge was recovered by settling. The sludge was dried in an oven at 115℃ for 24 h [16], ground with a mortar and pestle, sieved into a discrete particle size range (150–300 μm) and then stored in a desiccator at room temperature until used.

The granular-activated carbons (GAC) were reagent grade and purchased from Merck Taiwan Ltd. They were dried in an oven at 105℃ for 24 h and sieved with different mesh screens. A mesh range from 50 to 100, which is the same particle size of DAS, was utilized for adsorption studies, then stored and used in the same procedure as DAS.

2.3. Adsorption experiments

Adsorption experiments were conducted in a water bath shaker at a constant temperature (30℃ or other) and a shaking rate (120 rpm), using 250 mL screw top flasks containing the same volume (100 mL) of BR-29 dye solutions and the same quantity (0.08 g) of adsorbent. Controls that contained the same dye solutions but no adsorbent were run in each experiment. Furthermore, the COD concentrations produced by adsorbents were also deleted by using the same volume (100 mL) of double-distilled water in each adsorption experiment.

Batch contact time studies were carried out at selected time intervals (1 h) until 10 h of contact time for two adsorbents at 30℃, and adsorption equilibrium experiments were conducted at 12 h of contact time for BR-29 dye adsorbed only by DAS at different dye solution temperatures. After each adsorption experiment was finished, the remaining dye solution was separated from the adsorbents, and the COD concentrations analyzed using a dichromate method.

2.4. Analytical methods

In each adsorption experiment, samples from prepared dye solutions or subsequent filtrates were stored in a low-temperature incubator at 20℃ for 3 h, and their COD concentrations were then measured by a COD reactor and a DR 2010 spectrophotometer (HACH, USA). The determination of COD concentration followed the procedures described in standard methods [15].

The DAS was characterized by FTIR using a Japan Spectroscopic FT/IR-3 spectrophotometer. The test sample was spread as a thin layer on a KBr tablet for examination. Spectra were recorded in the region 4,000–650 $\mathrm{cm^{-1}}$ at 4 $\mathrm{cm^{-1}}$ resolution over 32 scans.

3. Results and discussion

3.1. Effect of adsorbent properties

The isothermal adsorption experiments were conducted to compare the maximum adsorption capacities and equilibration times of the adsorbents DAS and GAC for BR-29 dye solution in equilibrium adsorption conditions at 10 h of contact time; the results are shown in Fig. 1. An examination of the data shows that the maximum adsorption capacities and equilibration times for DAS and GAC are 213.89 $\mathrm{mg\,g^{-1}}$ and 4 h and 364.13 $\mathrm{mg\,g^{-1}}$ and 6 h, respectively. The differences in BR-29 dye adsorption between the two adsorbents result from the properties of DAS (surfaces with negative charges and specific sites [17]). These properties facilitate the maximum adsorption capacity and lower equilibration time of BR-29 dye adsorptions. Furthermore, the results of this study showed that the replacement of GAC with DAS for treating basic dye wastewater provided a 58.75% adsorption capacity and 2 h reduction in equilibration time.

3.2. Effect of initial dye concentration and dye solution temperature

A series of adsorption experiments were carried out for BR-29 dye solutions with 50–500 ppm initial dye concentration at the same contact time (10 h) and dye solution temperature (30℃). The results are given in Fig. 2, which reveals that for BR-29 dye, the adsorption capacity increases from 50 to 250 ppm and then becomes constant from 300 to 500 ppm at the initial dye concentration. The experimental results indicated that for the same biomass dose (0.8 g $\mathrm{L^{-1}}$), 300 ppm of initial dye concentration was not only sufficient but also economical for the maximum uptake of BR-29 dyes on the biomass; that is, the optimum initial dye concentration was 300 ppm for BR-29 dyes, and this was also suitable for further adsorption experiments.

Batch adsorption experiments were also conducted with BR-29 dye using another dye solution temperatures (40 and 50℃), the same biomass dose (0.8 g $\mathrm{L^{-1}}$), and contact time (10 h). The results are also plotted in Fig. 2, and we observed that for BR-29 dyes, the maximum adsorption capacity occurred at 30℃ dye solution temperature, and the serial order of the three temperatures was 30℃ > 40℃ > 50℃. Therefore, we

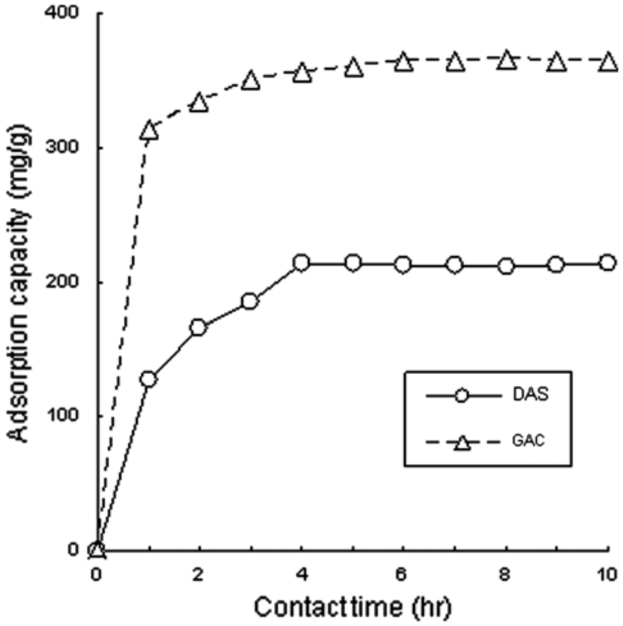

Fig. 1. Adsorption capacity vs. contact time for the removal of BR-29 dye from aqueous solution by DAS and GAC at 30ºC.

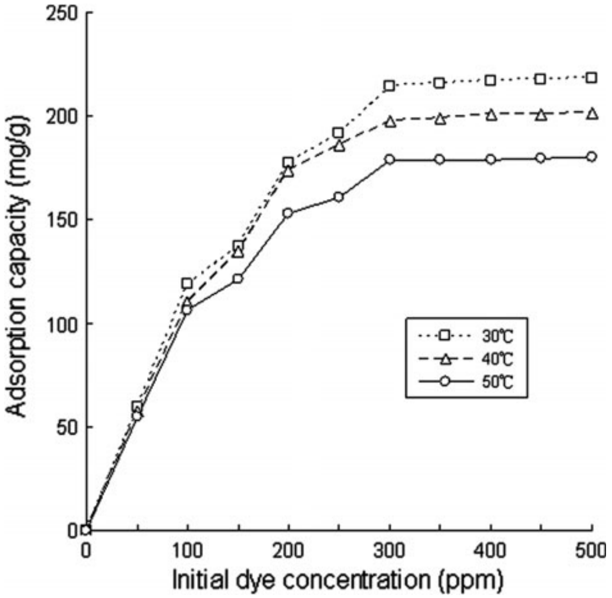

Fig. 2. Adsorption capacity vs. initial dye concentration for the removal of BR-29 dye from aqueous solution by DAS at different temperatures.

selected the optimum dye solution temperature of 30° C for further absorption experiments. Also, the uptake of BR-29 dye decreased with an increase in temperature, so we confirmed that the adsorption process is exothermic in nature.

3.3. Adsorption kinetics

In order to better understand the kinetics of BR-29 dye adsorption on the DAS, the pseudo-first-order and pseudo-second-order models were used to describe the experimental data.

3.3.1. Pseudo-first-order model

Pseudo-first-order equation [18] is the first equation for the adsorption of liquid/solid system based on solid capacity. The equation is represented as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$

where q_e and q_t are the amount adsorbed (mg g^{-1}) at equilibration time and any contact time, respectively, and k_1 is the equilibrium rate constant of pseudo-first-order equation (min^{-1}).

On the basis of a least-squares regression method [19], the plot of $\log(q_e - q_t)$ vs. contact time for the adsorption of BR-29 dye was linearized and its correlation coefficient ($R^2 = 0.9801$) and probability ($P = 0.0100$, $R = 0$) were calculated. The results of linearized value indicated that the adsorption of BR-29 dyes on a biomass at 300 ppm initial dye concentration fit well with the pseudo-first-order equation. Thus, k_1 and q_e are determined from the slope and intercept of the plot, and their values are given in Table 1.

3.3.2. Pseudo-second-order model

The experimental data were also analyzed using the pseudo-second-order [20] and the equation is represented as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e}t \tag{1}$$

where q_e and q_t are the amount adsorbed (mg g^{-1}) at equilibration time and any contact time, respectively and k_2 is the equilibrium rate constant of pseudo-second-order equation (g mg^{-1} min^{-1}).

Table 1
Kinetic parameters for the adsorption of Basic Red 29 dye onto DAS at 30°C

Parameter	DAS
Pseudo-first order	
q_e (mg g^{-1}) (exp)	213.89
q_e (mg g^{-1}) (cal)	190.85
k_1 (min^{-1})	0.6547
R^2	0.9801
Pseudo-second order	
q_e (mg g^{-1}) (exp)	213.89
q_e (mg g^{-1}) (cal)	272.11
k_2 (g mg^{-1} min^{-1})	0.00298
R^2	0.9863

The plot of t/q_t vs. contact time for the adsorption of BR-29 dye was also linearized and its correlation coefficient ($R^2 = 0.9863$) and probability ($P = 0.0069$, $R = 0$) were calculated. The linearized results showed that the adsorption of the BR-29 dye on a biomass at the same adsorption condition also fit well the pseudo-second-order equation. Thus, k_2 and q_e are determined from the slope and intercept of the plot and their values are also given in Table 1.

3.4. Adsorption isotherms

We also analyzed the results obtained from the effect of initial dye concentration and dye solution temperature using the well-known adsorption models given by Langmuir and Freundlich.

3.4.1. Langmuir adsorption isotherm

The Langmuir adsorption isotherm [21,22] has been used by many workers to study the adsorption of a variety of compounds. This adsorption model [17] assumes that adsorbed molecules are localized as a monolayer on the surface of the adsorbent, that all definite sites are energetically equivalent, and that the rate of adsorption is proportional to the initial concentration of the adsorbate. The linear form of the Langmuir equation is given as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0}$$

where q_e is the amount adsorbed (mg g^{-1}) at adsorption equilibrium, C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), and Q_0 and K_L are the

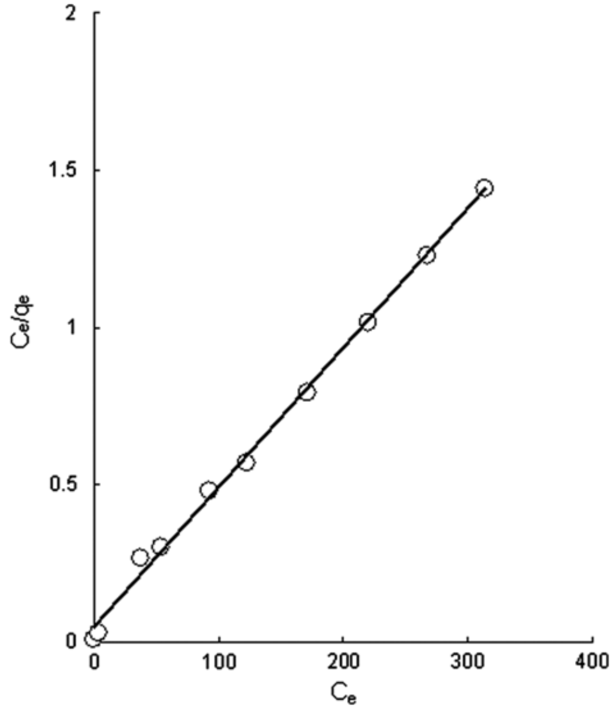

Fig. 3. Langmuir isotherm of BR-29 dye onto DAS. Conditions: adsorbent dosage 0.8 g L^{-1}; contact time 12 h; temperature 30˚C.

Langmuir constants related to the monolayer capacity [17] and adsorption energy, respectively.

On the basis of a least-squares regression method, the plots (Fig. 3) of C_e/q_e vs. C_e for the adsorption of BR-29 dye were linearized and their correlation coefficients ($R = 0.998$–0.999) and probabilities ($P < 0.01\%$, $R = 0$) were calculated. An inspection of these values ($R > 0.80$, $P < 1\%$) [19] indicated that the adsorption of BR-29 dye on a biomass at 50–300 ppm initial dye concentration fit well with the Langmuir isotherm. Thus, the Langmuir constants Q_0 and K_L were calculated and their values at different dye solution temperatures (30, 40 and 50˚C) are given in Table 2.

3.4.2. Freundlich adsorption isotherm

The Freundlich equation [21,22] is the most widely used mathematical description of absorption in an aqueous system and the logarithmic form of this equation is expressed as follows:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$

where q_e is the amount adsorbed (mg g^{-1}) at adsorption equilibrium, C_e is the equilibrium concentration (mg L^{-1}) of the adsorbate, and K_F and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The plots (Fig. 4) of log q_e vs. log C_e for the adsorption of BR-29 dye were also linearized and their correlation coefficients ($R = 0.953$–0.966) and probabilities ($P < 0.0255\%$, $R = 0$) were calculated. The linearized results ($R > 0.80$, $P < 1\%$) [19] showed that the adsorption of BR-29 dye on a biomass at 50–300 ppm initial dye concentration also followed the Freundlich adsorption isotherm. Thus, Freundlich constants K_F and n were calculated, and their values at different dye solution temperatures (30, 40 and 50˚C) are also given in Table 2.

3.4.3. Thermodynamic calculations

On the basis of analyzing the experimental data of adsorption isotherms for BR-29 dye, we calculated the thermodynamic parameters, such as Gibbs free energy (ΔG^0), adsorption heat (ΔH^0), and entropy (ΔS^0), using the thermodynamic equilibrium, Clausius–Clapeyron, and Gibbs–Helmholtz equations, respectively. These equations [23] are as follows and the calculated values are given in Table 3.

$$\Delta G^0 = -RT\ln K_L$$

$$\ln K_L = -\frac{\Delta H^0}{RT} + C$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$

where K_L are the Langmuir constants at different dye solution temperatures, R is the ideal gas law constant (8.314 J mol^{-1} K^{-1}), and C is a constant of integration.

Table 2
Comparison of the adsorption isotherm constants for the absorption equilibrium of Basic Red 29 dye onto DAS

	Langmuir constants						Freundlich constants					
	Q_0 (mg g^{-1})			K_L (L mol^{-1}) × 10^{-4}			n			K_F		
Basic dye	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
Basic Red 29	224.72	208.77	189.04	3.61	3.32	2.33	5.10	4.01	3.86	76.92	55.14	45.14

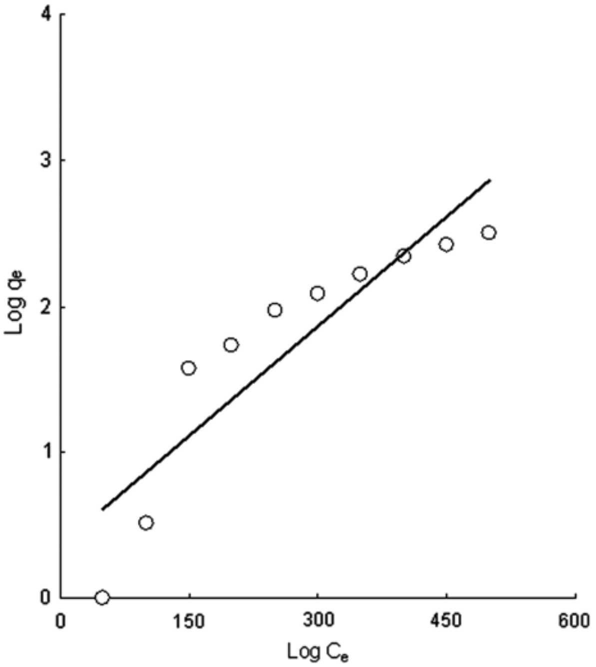

Fig. 4. Freundlich isotherm of BR-29 dye onto DAS. Conditions: adsorbent dosage 0.8 g L^{-1}; contact time 12 h; temperature 30˚C.

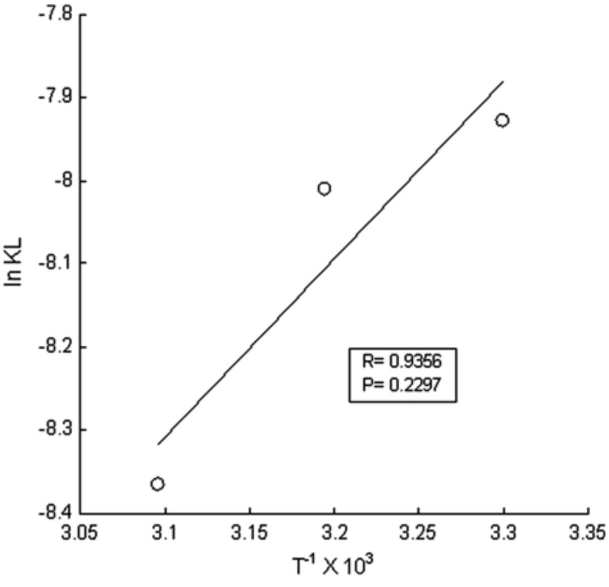

Fig. 5. Determination of adsorption heat for the adsorption of BR-29 dye onto DAS.

An inspection of ΔG^0 of the BR-29 dye (Table 3) shows that the negative values are as expected, because the basic dye (cationic dye) is expected to be more concentrated on the surface of negatively charged biomass than in the bulk solution. On the basis of a least-squares regression method [19], the plot (Fig. 5) of ln K_L vs. T^{-1} allowed us to calculate the correlation coefficients ($R = 0.936$) and probabilities ($P = 0.2297$, $R = 0$). This calculated result is close to 0.95 for a linear relationship reported by Bell [16], and it could be concluded that the temperature independence of ΔH^0 for BR-29 dye adsorbed by biomass is reasonable for the 30–50˚C experimental temperature range. In addition, the negative value of ΔH^0 (Table 3) also indicated that the absorption process is exothermic in nature.

3.5. FTIR analysis

The FTIR spectra analysis of DAS was shown in Fig. 6. The spectra showed that peak in 3,413 cm^{-1} and 1,037 cm^{-1} indicated the presence of N–H stretching vibration and C–N bending vibration, peak in the range 2,924 and 2,853 cm^{-1} indicated the presence of C–H stretching vibration, and peak in the range 1,546 cm^{-1} and 1,454 cm^{-1} indicated the presence of –CH_2-bending vibration. The presence of sharp and strong band at 1,651 cm^{-1} denotes the presence of C=O stretching vibration. The results of FTIR analysis

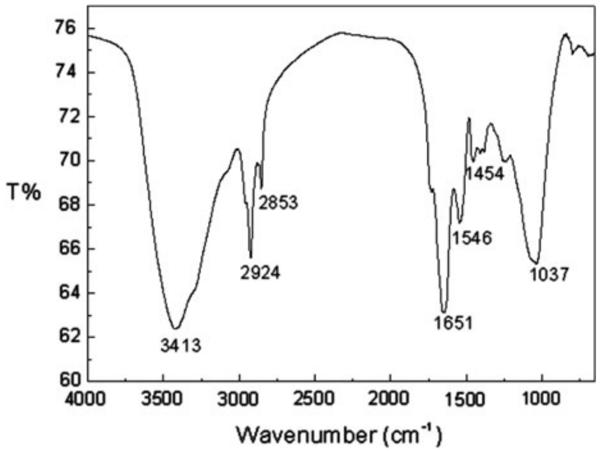

Fig. 6. FTIR spectra of DAS.

Table 3
Thermodynamic parameters for the absorption equilibrium of Basic Red 29 dye onto DAS

Basic dye	ΔG^0 (kJ mol^{-1})			ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
	30ºC	40ºC	50ºC		
Basic Red 29	−26.44	−27.09	−27.01	−17.70	29.23

indicate that DAS has an extremely strong amide group, forming a negatively charged biomass body in the dye solution with excellent attraction for positively charged metal ions or cationic dyes. Therefore, this type of adsorption can reasonably explain that DAS can effectively remove the basic dye from aqueous solution.

4. Conclusion

In this study, the utilization of DAS as a low-cost adsorbent was investigated for the removal of BR-29 dye from aqueous solution in the bath mode. The results of adsorbent properties experiments indicated that the kind of adsorbent influenced the maximum adsorption capacity and equilibration time of BR-29 dye in reaching adsorption equilibrium. The results of kinetics studies followed well both pseudo-first-order model and pseudo-second-order model. Isotherm studies indicated that the Langmuir isotherm produced a preferable experimental data with a monolayer adsorption capacity of $224.72\,\text{mg}\,\text{g}^{-1}$ at 30˚C compared with Freundlich isotherm. Calculations of thermodynamic parameters revealed that the adsorption process was exothermic in nature and the adsorption heat was $-17.70\,\text{kJ}\,\text{mol}^{-1}$. The results of FTIR analysis indicated that because DAS had an extremely strong amide group, it could be an effective adsorbent for the removal of basic dyes from aqueous solution.

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