

## Article

# Composite Activated Carbon Modified with AlCl<sub>3</sub> for the Effective Removal of Reactive Black 5 Dye from Wastewaters

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**Abstract:** Many industries use huge amounts of synthetic dyes which may release into the wastewater in dyeing processes causing serious damage to aquatic life as they are recalcitrant, nonbiodegradable, stable to oxidizing agents, and toxic. Adsorption on activated carbon has been found to be a very efficient treatment method. In this work, a new adsorbent material composed of activated carbon and aluminum chloride (AC-Al) was prepared for the removal of a commercial anionic and anthraquinonic reactive dye, i.e., Reactive Black 5 (RB5) under various experimental conditions. Several parameters, such as the adsorbent's dosage, initial RB5 concentration, pH, and contact time, were studied in order to determine the feasibility of AC-Al. According to the results, it was found that there was an increase in RB5 removal as the adsorbent's dosage increased, especially, in pH  $2 \pm 0.1$ , where the removal rate increased, and reaching 100% by 1.0 g/L of AC-Al. Freundlich isotherm and pseudo-second-order kinetic models adequately fit the experimental data, indicating that favorable and heterogeneous adsorption occurred, closer to chemisorption. According to thermodynamics, it was found that the adsorption procedure was endothermic in nature ( $\Delta H^0 = 62.621$  kJ/mol) and spontaneous ( $\Delta G^0 < 0$ ), and according to the positive value of  $\Delta S^0$  0.0293 (kJ/mol·K), there is an increase in random interaction between solid and liquid interfaces. Finally, the AC-Al adsorbent was successfully regenerated and reused for four cycles.



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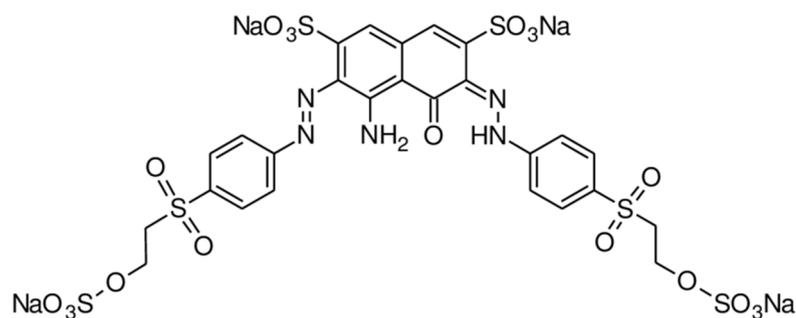
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**Keywords:** Reactive Black 5; activated carbon; adsorption; wastewater treatment; anthraquinone; aluminum

## 1. Introduction

Effluent pollution is a major environmental issue, with one of the critical concerns being the presence of highly toxic substances, specifically synthetic dyes that can lead to carcinogenic problems. These types of effluents can be classified as industrial wastewater with high levels of pollutants [1]. There are three types of dyes, i.e., nonionic, cationic, and anionic. All three are soluble in water and can be harmful even in small amounts. Colorants can be categorized as either natural or synthetic, with synthetic dyes being the more commonly used type and available in a variety of colors [2]. Synthetic dyes are classified according to their specific applications, i.e., reactive, direct, disperse, basic, and vat. They are also classified based on their chemical structure and different functional groups, such as azo, anthraquinone, sulfur, phthalocyanine, and triarylmethane [3,4].

RB5 is a commonly used anionic azo dye (C<sub>26</sub>H<sub>21</sub>N<sub>5</sub>Na<sub>4</sub>O<sub>19</sub>S<sub>6</sub>; molecular weight: 991.82 g/mol) (Figure 1) [5]. Reactive dyes have the ability to chemically bond with the fibers they are applied to, creating a covalent linkage. They are extensively utilized in the textile sector to dye cellulose-based fibers, such as cotton and rayon [6]. The presence of synthetic azo dyes in industrial processes such as dyeing and textile production is a significant threat to water resources as they persist for extended periods in aquatic environments and may have mutagenic and carcinogenic effects. These dyes are a hazard and pose a severe threat to the environment [7].



**Figure 1.** Structure formula of Reactive Black 5 (RB5) ( $C_{26}H_{21}N_5Na_4O_{19}S_6$ ) [8].

Various approaches, such as physical, biological, chemical, or a combination of these, have been used for the elimination of dyes from wastewater [9]. However, some physical and chemical methods have been found to be insufficient in completely deactivating dyes, which can lead to secondary pollution upon discharge into the environment. In contrast, biological treatment is cost-effective and produces less sludge compared to physical and chemical treatments, but it may not be as effective for decolorization, depending on the microorganism employed in the treatment process. Techniques, such as ozonation [10], coagulation [11], electrocoagulation [12], adsorption [13], and membrane separation [14], have been employed for the treatment of wastewater. Nonetheless, adsorption is an inexpensive, straightforward, and commonly used technique for removing organic dyes from wastewater [13,15].

Numerous adsorbent materials, such as zeolites [16], chitosan [5,13,15], magnetic nanocomposites [17,18], graphene oxide [5,7], and activated carbon [19], have been extensively employed to eliminate dyes from wastewater. Activated carbon (AC), a porous material, is a highly effective and widely used adsorbent in wastewater treatment due to its simplicity, reusability, and operational efficiency [19]. However, despite its widespread application, commercial activated carbon can be economically unviable. This has led researchers to explore alternative sources of activated carbon that offer cost-effective and safe dye removal from wastewater while maintaining the advantages of the process [3,13]. As a result, several studies have produced activated carbon from various low-cost materials, such as agricultural waste and by-products (e.g., seed shells [19] like coconut shells [20,21] and rubber seed shell [22], husks [23], nuts [24], roots [25], fruit peels [26], coffee waste [27], fishes [28], and plants [29]) and bacteria [8]. Hence, there is a need to develop advanced and composite activated carbon materials that exhibit superior dye removal performance and efficiency.

Recently, a commercially modified AC with aluminum chloride (Al) was used for the cleaning of cationic dye in wastewater [30]. This study focuses on using activated carbon made from coconut shells, i.e., an economical origin material, and treated with aluminum (AC-Al) as an adsorbent to eliminate reactive azo dye RB5. The objective is to produce an effective adsorbent material that uses a small amount of additional substances to completely remove the dye. As far as we know, there are no studies that have investigated the use of aluminum-modified activated carbon derived from coconut shells for RB5 dye. Several parameters, such as the adsorbent's dosage, initial RB5 concentration, pH, and contact time, were studied. Various isotherm and kinetic models are used to interpret the adsorption process, and several factors, such as thermodynamics, ionic strength, and regeneration studies, are examined.

## 2. Materials and Methods

### 2.1. Materials

RB5 dye was used as an adsorbate and supplied by Kahafix. A stock dye solution (1000 mg/L; 1.0 g diluted in 1000 mL) was created and utilized to generate the necessary concentrations.  $AlCl_3 \cdot 6H_2O$  (Merck) was used for activated carbon's modification. Then,

0.01–0.1 M solution prepared from the concentrated 37% HCl (Panreac) or from  $\geq 97.0\%$  pellets of ACS reagent NaOH (Sigma-Aldrich-Merck KGaA, Darmstadt, Germany) was utilized to adjust the pH. Furthermore, 1.0 M NaOH was utilized for the regeneration study, and 0.1–1.0 M NaCl (Sigma-Aldrich) and NaNO<sub>3</sub> (Sigma-Aldrich) to examine the changes in ionic strength in the removal of dye.

## 2.2. Synthesis of AC-Al

Coconut shells were used as the origin material for the synthesis of activated carbons according to previous studies [20,21] and then modified with aluminum chloride. In short, 0.8 g of AlCl<sub>3</sub> was added to 5.0 g of AC samples in 25 mL, in order to achieve its modification. Content is first mixed (1 h at 298 K), then sonicated (2 h), filtrated, and washed with distilled water. The mixture was then dried overnight at 333 K and calcined for 5 h (773 K) to gain the AC-Al composite-modified activated carbon. After cooling at room temperature, the produced adsorbent was ready to be used in the following experiments.

## 2.3. Analytical Determinations

The remaining concentration of RB5 dye was determined by using a UV-Vis spectrophotometer (WTW Spectroflex 6100, Weilheim, Germany) at its maximum absorption wavelength of 603 nm [5]. This was performed by correlating the absorbance to the RB5 standard curve.

## 2.4. Adsorption Experiments

Experiments were performed to study the effectiveness of AC-Al on RB5 adsorption. The adsorbent was introduced into falcon tubes containing 10 mL RB5 dye solution at different initial concentrations keeping the temperature. The mixture was stirred at 80 rpm by using a Trayster overhead shaker and Loopster rotator. During the experiments, various experimental factors were manipulated independently while keeping other parameters constant. These factors include pH levels ranging from 2 to 10, initial concentrations of RB5 dye ranging from 2 to 300 mg/L, adsorbent doses ranging from 0.2 to 1.0 g/L (by adding 0.002–0.01 g to the working volume 10 mL), and contact time ranging from 5 to 240 min. After adsorption, samples were collected from the tubes and passed through a nylon filter (0.45  $\mu$ m) and the filtrate was saved for the following determinations. The experiments were performed three times, and the results presented are the average of these three measurements.

The percentage removal (%R) of Reactive Black 5 dye (RB5) was calculated from the equation below (Equation (1)):

$$R (\%) = \left( \frac{C_0 - C_f}{C_0} \right) \times 100\% \quad (1)$$

where  $C_0$  symbolizes the initial RB5 concentration (mg/L), and  $C_f$  symbolizes the final RB5 concentration after the experiment (mg/L).

To determine the adsorption capacity of AC-Al,  $Q_e$  (mg/g) was considered using Equation (2) as follows:

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where  $C_e$  symbolizes the RB5 concentration (mg/L) at equilibrium,  $V$  is the volume of solution in L, and  $m$  is the mass of the adsorbent added in g.

### 2.4.1. Equilibrium Experiments

In the isothermal experiments, a consistent quantity of adsorbent AC-Al (g) was introduced into 15 mL falcon tubes containing 10 mL of RB5 dye solution with concentrations ranging from 30 to 200 mg/L, and the data obtained from these experiments were evaluated by Langmuir and Freundlich isotherm models.

The Langmuir model was represented by Equation (3).

$$Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where  $Q_e$  symbolizes the concentration of the adsorbate in the solid phase to the concentration in the liquid phase at equilibrium (mg/g),  $Q_m$  symbolizes the maximum adsorption capacity, in other words, the theoretical monolayer capacity, (mg/g), and  $K_L$  symbolizes the energy associated with the adsorption of RB5 dye (L/mg).

The Langmuir theory states that during adsorption, the adsorbate forms a single layer on the surface of the adsorbent without interaction between the adsorbed molecules. Additionally, the theory assumes that the adsorbent possesses a finite adsorption capacity ( $Q_m$ ), which describes the maximum amount of adsorbate that can be adsorbed by the adsorbent surface under equilibrium conditions.

The Freundlich model describes the correlation between the equilibrium concentration of RB5 in mg/L and the adsorption capacity of the adsorbent,  $Q_e$  in mg/g. This relationship is expressed mathematically as Equation (4).

$$Q_e = K_F C_e^{1/n} \quad (4)$$

where  $K_F$  is a constant that pertains to the adsorption capacity, and  $1/n$  is a constant that pertains to the adsorption intensity or to the heterogeneity of the surface.

#### 2.4.2. Kinetics Experiments

The study examined both the pseudo-first-order (PFO) (Equation (5)) and pseudo-second-order (PSO) (Equation (6)) kinetics of RB5 dye adsorption and used the obtained values for the estimation of adsorption and determine the appropriate rate expressions for potential reaction mechanisms. These analyses were performed to understand better the process of RB5 dye adsorption.

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad (5)$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (6)$$

where the variables  $Q_t$  and  $Q_e$  indicate the amount of RB5 dye adsorbed (mg/g) at time  $t$  (min) and at equilibrium, respectively. The rate constants  $k_1$  and  $k_2$  represent the rate of adsorption for the PFO and PSO models, respectively, with  $k_1$  being measured in L/min and  $k_2$  being measured in g/mg min. The variable  $t$  indicates the duration of contact time (min).

#### 2.5. Thermodynamics

For a better understanding of the adsorption reaction and its feasibility, it is necessary to calculate thermodynamic factors, such as Gibbs free energy change ( $\Delta G^0$ , kJ/mol), entropy change ( $\Delta S^0$ , kJ/mol·K), and enthalpy change ( $\Delta H^0$ , kJ/mol), at various temperatures (298 K, 308 K, 318 K, and 338 K) using Equations (7)–(9) [31].

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (7)$$

$$\Delta G^0 = -RT\ln(K_c) \quad (8)$$

$$K_c = \frac{C_s}{C_e} \quad (9)$$

The value of  $\Delta G^0$  was obtained using Equation (8), while the values of  $\Delta H^0$  and  $\Delta S^0$  were determined by analyzing the slope and intercept of the graph obtained by plotting  $\ln(K_c)$  against the  $1/T$ , as shown below in Equation (10).

$$\ln(K_c) = \left( -\frac{\Delta H^0}{R} \right) + \frac{\Delta S^0}{R} \tag{10}$$

where R is the universal gas constant (8.314 J mol/K).

### 2.6. Characterization Techniques

The surface of AC-Al activated carbon was characterized according to commonly applied techniques, such as Scanning Electron Microscopy (SEM) (Jeol JSM-6390 LV, Japan scanning electron microscope)/EDS, Fourier Transform Infrared Spectroscopy (FT-IR, Perkin Elmer, New York, NY, USA), and Brunauer, Emmett, and Teller (BET) analysis software.

## 3. Results and Discussion

### 3.1. Characterization of AC-Al

Several techniques were used for the characterization of the surface of AC-Al-modified activated carbon, and the obtained relative values and images are presented in Table 1 and Figure 2.

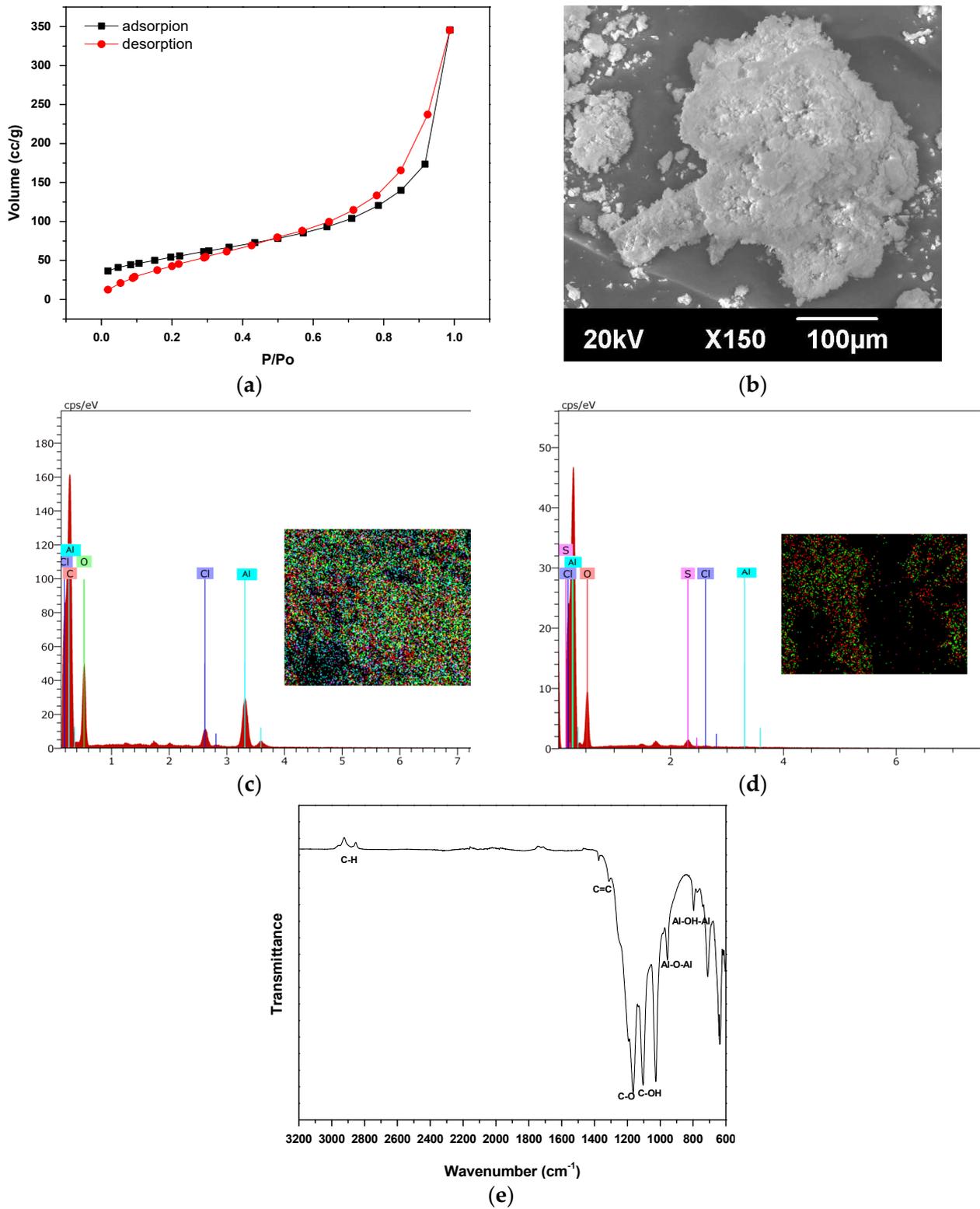
**Table 1.** Characterization parameters of AC-Al.

Physical Properties		
BET surface area, $S_{BET}$ (m <sup>2</sup> /g)		342.32
Micropore volume, $V_{micro}$ (cm <sup>3</sup> /g)		0.007
Total pore volume, $V_T$ (cm <sup>3</sup> /g)		0.740
SEM/EDS analysis		
Element % (w/w)	AC-Al	AC-Al_RB5
Carbon (C)	45.45	54.92
Aluminum (Al)	3.46	0.10
Chlorine (Cl)	0.96	0.14
Oxygen (O)	49.13	44.36
Sulfur (S)	-	0.48
FTIR spectra		
Wavenumber cm <sup>-1</sup>	Speciation	Assigned vibrations
2840–2930	C-H	Stretching
1395.3	C=C	Ring stretching
1200	C-O	Symmetric stretching
1188.3	C-OH	Stretching
938–1000	Al-O-Al	Asymmetric stretching
831–833	Al-OH-Al	Stretching and bending

As depicted in Figure 2a, AC-Al displays Type IV isotherms with hysteresis loops, according to N<sub>2</sub> adsorption–desorption isotherms versus relative pressure ( $P/P_0$ ), confirming the mesoporous structure of this adsorbent [32]. The relative values of BET-specific surface area, median Barrett–Joyner–Halenda (BJH) pore size, and pore volume for AC-Al are presented in Table 1, indicating a surface area of 342 m<sup>2</sup>/g.

In addition, as shown in Figure 2b, the surface of AC-Al exhibits a spread rough texture according to the SEM image. Furthermore, from the SEM-EDS analysis of AC-Al (Figure 2c and Table 1), the presence of Al was noticed on the surface of activated carbon, verifying carbon modification. Furthermore, in Figure 2d, the EDS analysis after the adsorption of RB5 on AC-Al is shown. A greater percentage of carbon and the appearance of sulfur on the surface of AC-Al is observed, which is possibly due to the additional carbon and sulfur that resulted from the structure of the adsorbed dye [33]. In addition, after adsorption, a

decrease in the percentage of aluminum is observed, probably related to the removal and binding of the dye.



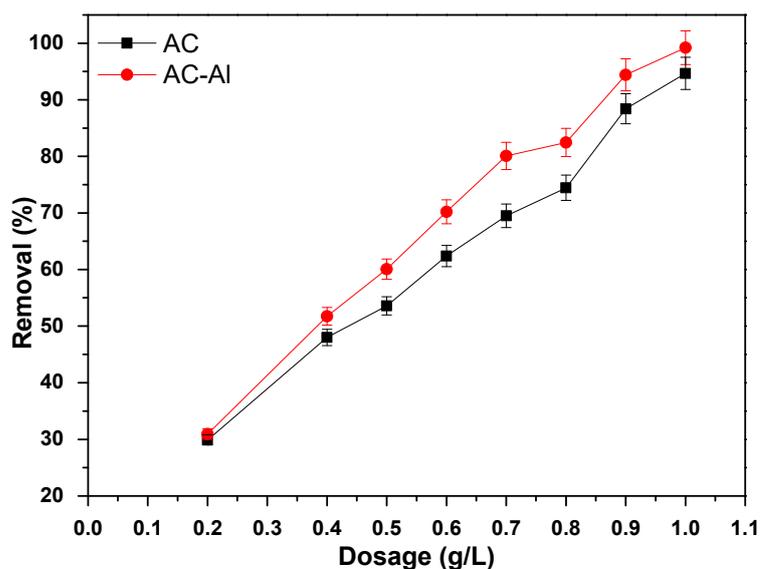
**Figure 2.** Characterization of AC-Al: (a) N<sub>2</sub> adsorption–desorption isotherms versus relative pressure ( $P/P_0$ ) ranging from 0 to 1; (b) SEM image; (c) SEM/EDS analysis before adsorption; (d) SEM/EDS analysis after adsorption; and (e) FTIR spectra.

The spectra of the FTIR analyses for the Al-modified activated carbon are presented in Figure 2e and the main peaks are summarized in Table 1. Noticeably, characteristic peaks for carbonaceous materials appear at  $1190\text{ cm}^{-1}$  to  $2930\text{ cm}^{-1}$  for stretching vibrations (C-OH, C-O, C=C, and C-H) [34] as well as for Al-O-Al and Al-OH-Al bonds at  $938$  and  $833\text{ cm}^{-1}$  [30,35], confirming the modification of activated carbon.

### 3.2. Effect of Adsorbent Dose

Batch experiments were conducted to investigate the potential of a particular material for removing RB5 dye. In the experiments carried out, the dosage of the material, AC-Al, was varied and its efficiency was tested in the adsorption of RB5 from aqueous solutions with an initial concentration of  $100\text{ mg/L}$ , at pH 2, temperature  $298\text{ K}$ , and contact time  $24\text{ h}$ . The AC-Al dosages used were between  $0.2$  and  $1.0\text{ g/L}$  in deionized water. Moreover, similar experiments were conducted using unmodified activated carbon (AC) to compare the efficiency of the two materials. The results are presented in Figure 2.

The plot in Figure 3 shows that the removal rate of RB5 increased as increasing the dosage. For instance, the percentage removal increased from  $31\%$  (using  $0.10\text{ g/L}$ ) to  $99\%$  (using  $1.0\text{ g/L}$ ) as the adsorbent dosage was increased. Additionally, the data show that a dose of  $0.8\text{ g/L}$  resulted in an RB5 removal rate of  $82.5\%$ . Compared with unmodified activated carbon, the adsorption capacity is enhanced during its modification, as evidenced by the higher RB5 removal rates achieved.

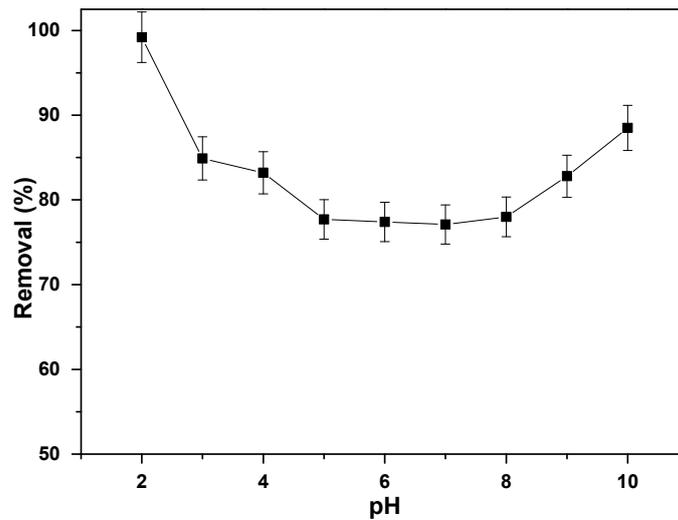


**Figure 3.** Effect of AC-Al dose on RB5 adsorption, in comparison with AC; RB5  $100\text{ mg/L}$ , pH  $2.0 \pm 0.1$ ,  $T = 298\text{ K}$ , and  $t = 24\text{ h}$ .

The wettability of adsorbent can be an additional factor influencing the adsorption ability, as shown in the study of Xu et al. 2016 [36], which investigates the surface wettability, but in this research work, the effect was not taken into account.

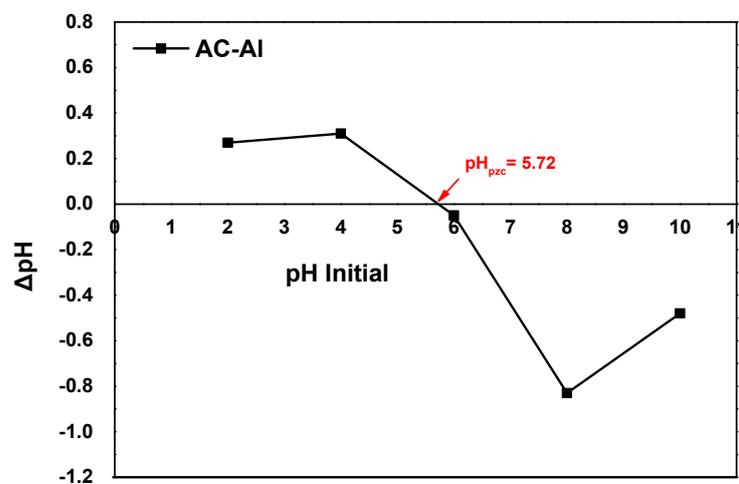
### 3.3. Effect of Initial Solution pH

To gain further insight into how Al-modified activated carbon adsorbs RB5, the impact of pH was studied within a range of 2 to 10. The study maintained a constant adsorbent dosage of  $1.0\text{ g/L}$ , RB5  $100\text{ mg/L}$ , and  $24\text{ h}$  at an ambient temperature of  $298\text{ K}$ . The pH was adjusted before introducing the adsorbent by adding either  $0.01\text{--}0.1\text{ M NaOH}$  or  $0.01\text{--}0.1\text{ M HCl}$ , as required. As represented in Figure 4, AC-Al demonstrated a preference for removing RB5 under low pH conditions, specifically in mildly acidic environments. To clarify, at a pH of 2, a  $100\%$  removal of RB5 was achieved using  $1.0\text{ g/L}$  of AC-Al and as the pH value increased, the removal of RB5 decreased.



**Figure 4.** Effect of initial solution pH on the adsorption of RB5 on AC-Al; RB5 100 mg/L, dose 1.0 g/L, pH 2.0–10.0 ± 0.1, T = 298 K, and t = 24 h.

The point of zero charge ( $pH_{pzc}$ ) of AC-Al was determined by measuring it within a pH range of 2–10 ± 0.1. The  $pH_{pzc}$  is the point at which the surface charge of the material becomes neutral. This was carried out by plotting a relative curve against  $\Delta pH$  versus  $pH_{initial}$  using the pH drift method [37] (Figure 5), which enabled the calculation of the  $pH_{pzc}$ . However, as the pH increased, the efficiency of RB5 adsorption decreased due to the repulsion between the negative charge on the adsorbent surface and RB5. The adsorbent surface becomes positively charged when the adsorption pH is less than the point of zero charge ( $pH_{pzc}$ ) of the adsorbent (which was found to be 5.72) due to protonation of acidic groups on the surface. On the other hand, RB5 is negatively charged due to deprotonation of sulphonate groups ( $-SO_3^-$ ), resulting in electrostatic interactions between the adsorbent and the adsorbed medium. Most likely the major mechanism governing dye removal by specific adsorbent is surface complexation, as sulfuric groups appear on the surface after adsorption takes place (as shown in Figure 2d). However, at pH levels above the  $pH_{pzc}$ , the adsorption efficiency decreased due to the repulsion between the negative-charge surfaces [18].

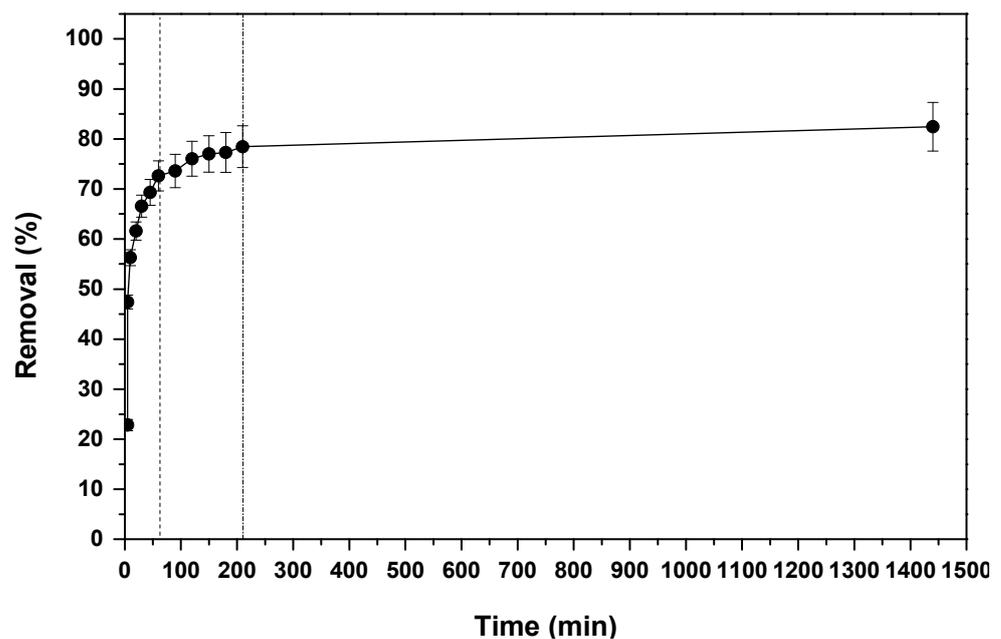


**Figure 5.** Determination of  $pH_{pzc}$  of AC-Al using the pH drift method.

### 3.4. Effect of Contact Time

Figure 6 illustrates how the adsorption process is affected by the contact time. The study examined a range of contact time, from 5 to 1440 min (equivalent to 24 h), and

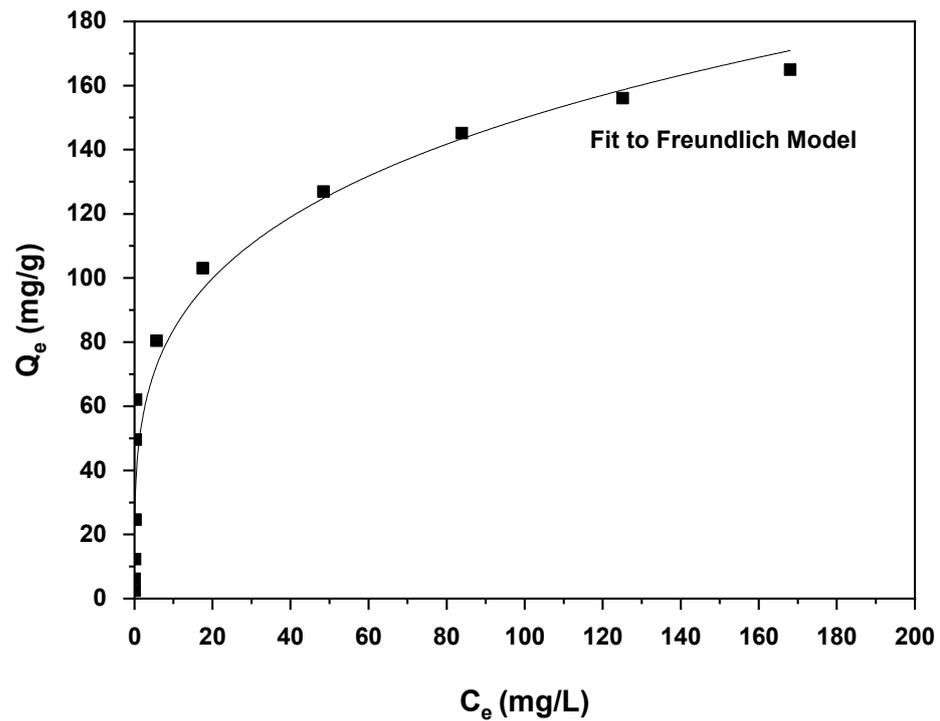
found that after 210 min (3.5 h) of reaction, there was no increase in dye removal performance. Therefore, 210 min was determined as the optimal contact time for further batch experiments. The results showed that there was instantaneous dye adsorption of up to 70% removal within the first 60 min, indicating that the surface was readily available for adsorption. Between 60 and 210 min, the removal rate increased slowly until it reached just under 80%. After 1440 min, an equilibrium state was achieved. This suggests that the adsorption of RB5 occurs quickly in the early stage of the contact time when many surface sites are available for adsorption. However, the process is slowed progressively until equilibrium is reached because of the repulsion between the solute molecules of the solid and the bulk phase, making the remaining surface sites difficult to occupy.



**Figure 6.** Effect of contact time on the adsorption of RB5 on AC-Al; RB5 100 mg/L, dose 0.8 g/L, pH  $2.0 \pm 0.1$ , and  $T = 298$  K.

### 3.5. Adsorption Isotherms

The adsorption isotherms of RBBR dye on AC-Al were evaluated using two different models—Freundlich and Langmuir. Based on the correlation coefficient ( $R^2$ ), the Freundlich isotherm model ( $R^2 = 0.96392$ ) was found to better describe the adsorption of RB5 dye. According to the Freundlich isotherm model, when the value of  $n$  is less than 1, adsorption is a chemical process, when it is equal to 1, adsorption is linear, and when it is greater than 1, adsorption is physical. In this study, as depicted in Figure 7 and Table 2 which display several isotherm parameters, the value of  $n$  was found to be 3.9605, indicating that the adsorption of RB5 dye onto AC-Al is a favorable physical process. The high value of  $n$  suggests a strong interface between the adsorbent surface and RB5, based on the strong affinity of cationic exchange sites of AC-Al with dye. Furthermore, the effectiveness of the adsorption performance increases with higher values of  $K_F$ . It should be noted that the Freundlich adsorption isotherm model applies to heterogeneous surfaces [25]. The Langmuir isotherm model was utilized to determine the maximum adsorption capacity ( $Q_{\max}$ ) of AC-Al for RB5, which was found to be 135.23 mg/g. This value represents the total amount of RB5 that can be adsorbed by AC-Al.



**Figure 7.** Freundlich isotherms for the adsorption of RB5 on AC-Al; RB5 2–300 mg/L, dose 0.8 g/L, pH  $2.0 \pm 0.1$ , T = 298 K, and t = 24 h.

**Table 2.** Freundlich isotherm model parameters for the adsorption of RB5 onto AC-Al (0.8 g/L), pH  $2.0 \pm 0.1$ , T = 298 K.

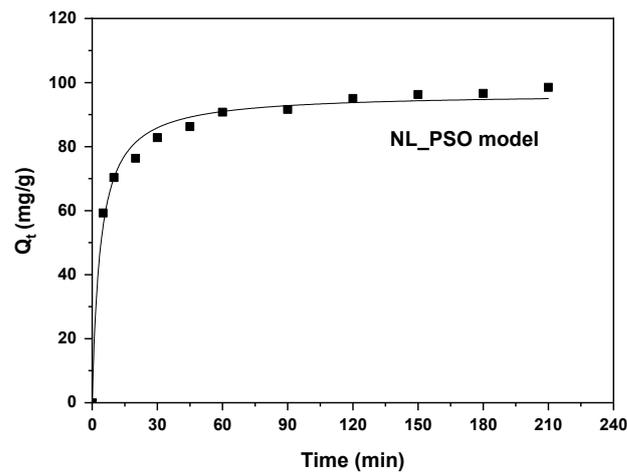
Freundlich Isotherm Model			
1/n	n	$K_F$ (mg/g) (L/mg) <sup>1/n</sup>	R <sup>2</sup>
0.25249	3.96058	46.869	0.96392

### 3.6. Adsorption Kinetics

Table 3 displays the parameters obtained for the adsorption of RB5 by AC-Al using the nonlinear regression analysis method for the PSO kinetic model. The correlation coefficient (R<sup>2</sup>) indicates that the PSO model provides the best fit, suggesting chemisorption [27], in contrast to PFO which suggests physisorption. In this study, the reaction was found to be more inclined towards the PSO model, as shown in Figure 8. Additionally, the Q<sub>e,cal</sub> (96.773 mg/g) obtained from the pseudo-second-order kinetics model was found to be closer to the experimental Q<sub>e,exp</sub> (103.069 mg/g).

**Table 3.** Constants of pseudo-second-order kinetic parameters model for the adsorption of RB5 onto AC-Al (0.8 g/L), pH  $2.0 \pm 0.1$ , T = 298 K.

Pseudo-Second Order Model (PSO)			
Q <sub>e,exp</sub> (mg/g)	K <sub>2</sub> (L/mg·min)	Q <sub>e,cal</sub> (mg/g)	R <sup>2</sup>
103.069	0.0276	96.773	0.99087

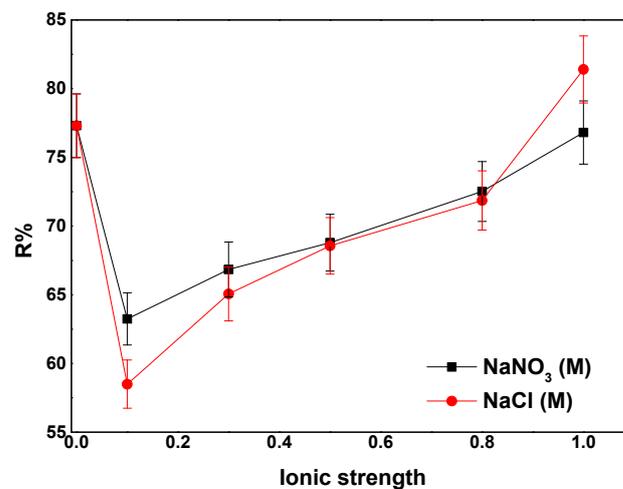


**Figure 8.** Kinetic pseudo-second-order model for the adsorption of RB5 onto AC-Al; RB5 100 mg/L, dose 0.8 g/L, pH  $2.0 \pm 0.1$ , and  $T = 298$  K.

### 3.7. Effect of Ionic Strength

The adsorption behavior of dyes can be influenced by ionic strength as a result of the electrostatic interaction between the adsorbent and the adsorbate [38]. The efficiency of the adsorption process on AC-Al was investigated by studying the effects of ionic strength in an aqueous solution. To conduct the experiment, solutions containing sodium chloride (NaCl) and sodium nitrate ( $\text{NaNO}_3$ ) were prepared, with varying concentrations of 0.1, 0.3, 0.5, 0.8, and 1 M, and a fixed RB5 concentration of 100 mg/L. The experiment was conducted at pH 2, using 0.8 g/L of adsorbent, and the duration of the experiment was 3 h at 298 K. The aim was to understand how the concentration of these electrolytes affected the adsorption process on AC-Al.

According to Figure 9, the investigated electrolytes appeared to have a positive impact on the adsorption of RB5 dye. As the concentration of the electrolytes increased, the ability of AC-Al to decolorize the RB5 solution also increased, which could be attributed to the enhancement of electrostatic interaction between the dye molecules and the adsorbent due to the increase in negative charge on the surface of the adsorbent. However, it is worth noting that the increase in the percentage of adsorption caused by the presence of these electrolytes was about the same compared to the case without using NaCl or  $\text{NaNO}_3$ .



**Figure 9.** Effect of ionic strength on the adsorption of RB5 on AC-Al; RB5 100 mg/L, dose 0.8 g/L, pH  $2.0 \pm 0.1$ , contact time 3 h, and  $T = 298$  K.

### 3.8. Thermodynamics

The values of  $\Delta H^0$  and  $\Delta S^0$  were obtained by analyzing the plot of  $\ln(K_c)$  versus  $1/T$  (with an  $R^2$  value of 0.997, but the data are not presented) [31]. A negative  $\Delta G^0$  value indicates that the process is spontaneous, while a positive  $\Delta G^0$  value indicates that external energy is required for the process to occur. The negative  $\Delta G^0$  values obtained in this study (which are listed in Table 4) recommend that the process of removing RB5 through adsorption occurred spontaneously. The  $\Delta H^0$  value for RB5 was determined to be 62.621 kJ/mol, indicating that the adsorption process was endothermic. The positive  $\Delta S^0$  (0.0293 kJ/mol·K) for RB5 is due to the increased randomness of the adsorbates at the solid–solute interface during the adsorption process [39].

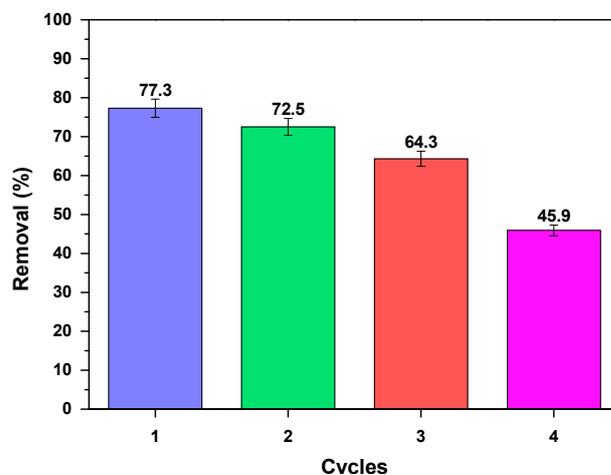
**Table 4.** Thermodynamic parameters for the adsorption of RB5 onto AC-Al; RB5 100 mg/L, dose 0.8 g/L, pH 2.00 ± 0.1, contact time 1.5 h.

T (K)	$\Delta G^0$ (kJ/mol)	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (kJ/mol·K)	$R^2$
298	−2.474			
308	−2.767			
318	−3.060	62.621	0.0293	0.9970
338	−3.646			

### 3.9. Regeneration Study

The reuse of AC-Al for the removal of RB5 from wastewater was investigated through recycling studies. The experiments were conducted, using initially 100 mg/L RB5 and 0.8 g/L of adsorbent at pH 2. Following the first cycle, the AC-Al particles that were utilized were subjected to a treatment process using a 0.01 M NaOH solution for around 2 h. After this, the particles were rinsed with distilled water to eliminate any residual base. A repetitive time that was deemed acceptable was selected to enable the reuse of the adsorbent for the subsequent cycles.

The study results are presented in Figure 10. The desorbed AC-Al was able to be reused for up to four cycles for RB5 removal after successful regeneration with 1 M NaOH treatment. The percentage removal of RB5 was about 77.3% in the first cycle and decreased to about 45.9% after the fourth cycle. Overall, this study demonstrated the potential for reusing AC-Al adsorbent for four cycles in the removal of RB5 from wastewater.



**Figure 10.** RB5 on AC-Al; RB5 100 mg/L, dose 0.8 g/L, pH 2.0 ± 0.1, T = 298 K, contact time 3 h, for four adsorption–desorption cycles after regeneration at alkalic pH values, by using 1 M NaOH treatment.

### 3.10. Comparison with Literature

Table 5 presents a comparison between the new adsorbent material developed in this research (AC-Al) and several other materials found in recent literature, along with their optimal parameters for removing RB5. The results show that acidic conditions with a pH of around 3 are the best for RB5 removal. The adsorbent can be regenerated and reused for four to five cycles while still maintaining its effectiveness. It is noticeable that the maximum adsorption capacity of AC-Al for RB5 removal was found to be 135.23 mg/g. This value suggests that the AC-Al material is an effective adsorbent compared to other materials mentioned in the literature. Additionally, the amount of AC-Al needed for effective removal is significantly less than other materials listed in Table 5, 1.0 g/L is needed to achieve a full removal of RB5 (100%).

**Table 5.** Comparison of adsorption capacity of adsorbents in literature with AC-Al for RB5 removal.

Adsorbent	[RB5] <sub>0</sub> (mg/L)	Dosage (g/L)	pH <sub>init</sub>	Contact Time (min)	Adsorption Capacity (mg/g)	R%	Recycling Cycles	Ref.
GO-Ch <sup>1</sup>	250	1.0	2	900	277.00	86.0	NR <sup>2</sup>	[5]
GO-MnO <sub>2</sub> <sup>3</sup>	60	0.5	3	60	NR <sup>2</sup>	85.0	NR <sup>2</sup>	[7]
Fe <sub>3</sub> O <sub>4</sub> @L-arginine <sup>4</sup>	50	0.8	3	NR <sup>2</sup>	89.20	97.6	5	[17]
MMC-850 <sup>5</sup>	100	0.5	5	4320	106.07	97.0	4	[18]
CMBPP <sup>6</sup>	300	1.67	3	180	211.80	NR <sup>2</sup>	5	[40]
BR-PAC <sup>7</sup>	100	0.5	6.8	120	285.71	60.0–70.0	NR <sup>2</sup>	[41]
MWCNTs <sup>8</sup>	25	1.0	3	60	231.84	94.5	NR <sup>2</sup>	[42]
SWCNTs <sup>9</sup>	25	1.0	3	60	829.20	95.3	NR <sup>2</sup>	[42]
AC-Al <sup>10</sup>	100	1.0	2	210	135.23	100.0	4	this study

<sup>1</sup> Graphite oxide–chitosan, <sup>2</sup> Not referred, <sup>3</sup> Graphene oxide supported manganese oxide, <sup>4</sup> Amine-functionalized Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles with L-arginine, <sup>5</sup> Magnetic mesoporous carbon from *Macadamia* nutshell with chemical activation at 850 °C, <sup>6</sup> Chemically modified banana peel powder, <sup>7</sup> Modified activated carbon from *Bauhenia Racemose* fruit pods, <sup>8</sup> Multi-walled carbon nanotubes, <sup>9</sup> Single-walled carbon nanotubes, <sup>10</sup> Aluminum-chloride-modified activated carbon from coconut shells.

### 4. Conclusions

The performance of the AC-Al adsorbent was evaluated, and the results indicated that at pH 2.0 ± 0.1, a removal rate of 82.5% was achieved with the addition of 0.8 g/L, while complete removal was achieved with 1.0 g/L. Additionally, at pH 2.0, which is lower than the pH<sub>pzc</sub> (5.72) of the adsorbent utilized, the positively charged surface of the AC-Al material would be attracted to the RB5 via electrostatic forces. At acidic pH levels, the RB5 behaves as a cation due to deprotonation of sulphonate groups, resulting in an electrostatic attraction between the adsorbent and the adsorbate.

The Freundlich isotherm and PSO kinetic models were found to best fit the adsorption process, with R<sup>2</sup> values of 0.96 and 0.99, respectively, indicating that the adsorption of RB5 on AC-Al was multilayer and closer to chemisorption. From the Langmuir isotherm model calculated, the maximum adsorption capacity was determined to be 135.23 mg/g and from the kinetic study, the contact time to reach the equilibrium was 210 min. Thermodynamic analysis revealed that the adsorption procedure was endothermic in nature (ΔH<sup>0</sup> = 62.621 kJ/mol) and spontaneous (ΔG<sup>0</sup> < 0), and according to the positive value of ΔS<sup>0</sup> (0.0293 kJ/mol·K), there is an increase in random interaction between solid and liquid interfaces. Finally, the AC-Al adsorbent was successfully regenerated and reused for four cycles.

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