

# Use of Aluminium Hydroxide Sludge as Adsorbents for the Removal of Reactive Dyes: Equilibrium, Thermodynamic, and Kinetic Studies

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## Abstract

This study investigated the removal of RR-2 and RB-4 dyes from aqueous solutions by adsorption using poppy bagasse, sugar beet bagasse, aluminium hydroxide sludge, phosphogypsum, ferrochromium plant waste, and orange peel. Aluminium hydroxide sludge had the highest adsorption capacity for both dyes. The equilibrium time was 2 days. The effects on adsorption of pH, adsorbent concentration, and stirring rate were investigated. The highest removal percentage was 80.75% and 99.74% for RR-2 and RB-4, respectively. Adsorption of RR-2 was expressed better with a Freundlich adsorption equation, while adsorption of RB-4 was expressed better with a Langmuir adsorption equation. Adsorption of RR-2 agreed with the pseudo-first-order rate equation and adsorption of RB-4 followed the pseudo-second-order rate equation. Moreover, both removal processes are endothermic. Various thermodynamic parameters, such as  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ , were calculated.

**Keywords:** Solid waste; Adsorption; Wastewater; Aluminium hydroxide sludge; Reactive red 2; Reactive Blue 4

**Nomenclature:**  $C_A$ : Adsorbent concentration (mg/L);  $C_e$ : Equilibrium concentration (mg/L);  $C_0$ : Initial dye concentration (mg/L);  $C$ : Dye concentration (mg/L);  $k_i$ : Rate parameter of intraparticle diffusion model (mg dye/g adsorbent min<sup>0.5</sup>);  $k_1$ : Rate constant of pseudo-first-order model (min<sup>-1</sup>);  $k_2$ : Rate constant of pseudo-second-order model (g adsorbent/mg dye min);  $K$ : Langmuir constant (L/mg);  $K_F$ : Freundlich constant ((mg/g)(L/mg)<sup>1/n</sup>);  $n$ : Freundlich constant;  $N$ : Stirring rate (rpm);  $q_e$ : Adsorption capacity in equilibrium (mg dye/g solid);  $q_{e,exp}$ : Experimental adsorption capacity in equilibrium (mg dye/g solid);  $q_{e,cal}$ : Calculated adsorption capacity in equilibrium (mg dye/g solid);  $q_t$ : Amount of dye adsorbed onto 1 g solid at time  $t$  (mg dye/g solid);  $Q^0$ : Maximum adsorption capacity (mg dye/g solid);  $R$ : Universal gas constant (=8.314 J/mol/K); RB-4: Reactive Blue 4; RR-2: Reactive Red 2;  $t$ : Time;  $T$ : Temperature;  $\Delta G^\circ$ : Gibbs free energy of adsorption (kJ/mol);  $\Delta H^\circ$ : Enthalpy change of adsorption (kJ/mol);  $\Delta S^\circ$ : Entropy change of adsorption (J/mol/K)

## Introduction

Dyes are used in large quantities in many industries including textile, leather, cosmetics, paper, printing, plastic, pharmaceuticals, and food to colour their products [1]. Dyeing in the textile industry uses large amounts of water and generates high volumes of coloured wastewaters. A fair estimation of dye losses to the environment is about 1-2% during their production and 1-10% during their use [2].

The remaining dye molecules, even at very low concentrations, in the wastewater of textile industries are common water pollutants. Some dyes are either toxic or mutagenic and carcinogenic due to the presence of metals and other chemicals in their structure. In addition, their presence in water is highly visible and undesirable and may significantly affect photo-synthetic activity in aquatic life due to reduced light penetration [3,4].

Textile dyeing effluents are composed of complex mixtures of dyes, auxiliary chemicals, salts, acids, bases, organochlorinated compounds, and occasionally heavy metals. Colour removal is, however, one of the main problems in the treatment of this kind of effluent, due to dye resistance to biodegradability, light, heat, and oxidizing agents [2]. Considerable research has been done on colour removal from

industrial effluents to decrease their impact on the environment. These technologies include adsorption onto inorganic or organic matrices, decolourization by photocatalysis or photo-oxidation processes, microbiological decomposition, chemical oxidation, ozonation, and coagulation [5]. There are many studies in the literature about the removal of Reactive Red 2 and Reactive Blue 4 textile dyes by different methods. Kalyani et al. studied the biodegradation and detoxification of Reactive Red 2 by newly isolated *Pseudomonas* sp. SUK1. The isolate was able to decolourize sulfonated azo dye (Reactive Red 2) in a wide range (1-5 g/L), at a temperature of 30°C, and pH range 6.2-7.5 at 108 h [6]. Axelsson et al. investigated decolourization of Reactive Red 2 and Reactive Blue 4 using *Bjerkandera* sp. strain BOL 13 in a batch and a continuous rotating biological contactor reactor [7]. Dye removal efficiency was almost 96% at the end of 7 days for both dyes (50 mg/L) in the batch system. Decolourization (80-95% for [6]; 96% for [7]) was successful, but the dye removal time (4-5 days for [6]; 7 days for [7]) was very long. Furthermore, Gözmen et al. achieved oxidative degradation of Reactive Blue 4 by different advanced oxidation methods such as wet air oxidation (WAO), wet peroxide oxidation (WPO), photocatalytic oxidation, and electro-fenton (EF) [8]. They found that the most efficient method for the mineralization of Reactive Blue 4 was WPO. Almost complete degradation was achieved in 1-2 minutes by WPO. However, all these techniques are expensive. Bayramoğlu et al. investigated the biosorption of Reactive Blue 4 by native and treated fungus *Phanerocheate chrysosporium*. The dye uptake capacities of the biosorbents at 600 mg/L dye concentration were reported to be 132.5, 156.9, 147.6, and 81.1 mg/g for the native and heat-, acid-, and base-treated dry fungal preparations, respectively [9].

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The most common process for dye removal is through adsorption by activated carbon; although it is highly effective, running costs are high, with regeneration required after each sorption cycle [10]. Chitosan is used for this purpose as well. Chiou et al. applied a batch system to study the adsorption of four reactive dyes (RB-2, RR-2, RY-2, and RY-86), three acid dyes (AO-12, AR-14, and AO-7), and one direct dye (DR-81) from aqueous solutions by cross-linked chitosan beads [11]. The adsorption capacities for all dyes had very large values of 1911-2498 mg/g at pH 3-4 and 30°C by cross-linked chitosan beads. However, the acidic treatment (pH 3-4) is not suitable environmentally. The utilization of waste materials is increasingly becoming of vital concern because these wastes represent unused resources and, in many cases, present serious disposal problems.

In the literature, many researchers have performed textile wastewater treatment using different solid wastes: waste red mud [12], sugar-industry mud [13], blast furnace dust, sludge, and slag from steel plants and carbon slurry from the fertilizer industry [14], formaldehyde-treated and sulphuric acid-treated sawdust [1], orange peel [15], beer brewery waste [16], sugar beet pulp [4], waste from a soda ash plant [3], and cotton plant waste [17]. Moreover, studies using waste metal hydroxide sludge as potential adsorbents have been reported in the literature. Netpradit et al. found that metal hydroxide sludge (including various insoluble metal hydroxide compounds) is an effective adsorbent for azo reactive dyes (RR-2, RR-120, and RR-141) [18]. Only 0.2% (w/v) of powdered sludge (<75 µm) achieved colour removal from 30 mg/L reactive dye solutions (RR-2, RR-120, and RR-141) within 5 min without pH adjustment. The larger the charge amount of the dyes, the greater the adsorption (>90%) on the metal hydroxide sludge. The maximum adsorption capacity for reactive dyes was 42–66 mg dye/g adsorbent [18,19]. Santos and Vilar reported that the maximum adsorption capacities varied between 275 mg/g (at 25°C and pH 4) and 21.9 mg/g (at 25°C and pH 10) for the removal of Remazol Blue reactive dye in aqueous solution by waste metal hydroxide sludge [2].

The aim of the present study was the removal of Reactive Red 2 and Reactive Blue 4 by adsorption from aqueous solutions using poppy bagasse, sugar beet bagasse, aluminium hydroxide sludge, phosphogypsum, ferrochromium plant waste, and orange peel. The adsorption capacity of each solid waste was determined and the solid waste with the maximum adsorption capacity was selected. The effects on adsorption of contact time, initial pH of solution, initial concentration of adsorbent and stirring rate were investigated. At different temperatures, the Langmuir and Freundlich isotherm models were tested for their applicability. Pseudo-first- and pseudo-second-order kinetic models were applied to the kinetics of adsorption. Various thermodynamic parameters, such as  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ , were calculated.

## Materials and Methods

### Adsorbents

Poppy bagasse, sugar beet bagasse, aluminium hydroxide sludge, phosphogypsum, ferrochromium plant waste, and orange peel were used as adsorbents for the removal of Reactive Red 2 and Reactive Blue 4. The wastes were obtained from the Turkish Grain Board Opium Alkaloid Plant (Afyon, Turkey), Afyon Sugar Mill (Afyon, Turkey), Fenis Aluminium Co. Inc. (Kocaeli, Turkey), TUGSAS Samsun Fertilizer Plant (Samsun, Turkey), Eti Chrome Inc. (Elazığ, Turkey), and the Antalya region (Turkey), respectively.

Before drying, the orange peel was ground with a kitchen-type

grinder (Moulinex). Then the orange peel, sugar beet bagasse, poppy bagasse, and aluminium hydroxide sludge were dried in an oven at 105°C for approximately 8 hours, separately. After drying, the aluminium hydroxide sludge was ground using a mill (Retsch ZM 200). All wastes were sieved and the part of 355-500 µm particle size was used in the experiments.

### Dyes

Reactive Red 2 and Reactive Blue 4 were purchased from Sigma-Aldrich Co. In the preparation of the dye solutions, distilled water was used. The pHs of dye solutions were adjusted with diluted  $H_2SO_4$  and NaOH solutions.

### Sorption studies

**Adsorption experiments:** Removal experiments were carried out in 250 mL screw cap glass bottles with 100 mL solution volume. Adsorption tests were performed using an orbital shaker (Labcon 5081U). Samples were centrifuged at the temperature of 25°C and the rate of 4000 rpm for 10 minutes (Hettich Zentrifugen Rotina 35 R). In the first step of the runs, the effects on adsorption of adsorbent type, contact time (1-5 days), initial pH of solution (2, 7, 10), adsorbent concentration (2, 10, 20, 30 g/L) and stirring rate (100, 150, 200 rpm) were investigated at the initial dye concentration of 100 mg/L. Then adsorption isotherms were drawn, kinetic models were tested, and thermodynamic parameters were calculated.

The percentage of removal of dye after adsorption was calculated from:

$$Removal\% = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

In this equation,  $C_0$  and  $C_t$  are the initial and equilibrium dye concentrations (mg/L), respectively.

**Desorption experiments:** The desorption experiments were carried out at the conditions of the temperature of 25°C, the stirring rate of 150 rpm and the adsorbent concentration of 10 g/L through 2 days.

The percentage of removal of dye after desorption was calculated from:

$$Removal\% = \frac{(q_{t(\text{afteradsorption})} - q_{q(\text{afterdesorption})})}{q_{t(\text{afteradsorption})}} \times 100 \quad (2)$$

In this equation,  $q_t$ , amount of dye adsorbed onto 1 g solid at time  $t$  (mg dye/g solid)

### Analysis

The concentrations of the dyes in their solutions were determined with a Shimadzu UV 1601 UV spectrophotometer. The wavelengths of maximum absorbance ( $\lambda_{max}$ ) were 536 nm and 598.5 nm for RR-2 and RB-4, respectively.

## Results and Discussion

### Effect of adsorbent type

To determine the effects of adsorbent type on adsorption of RR-2 and RB-4, six different solid wastes were used Figure 1. shows changes in the concentration in the dye solutions with contact time. Based on concentration values at the end of 24 h, the solid waste with the highest adsorption capacity was selected.

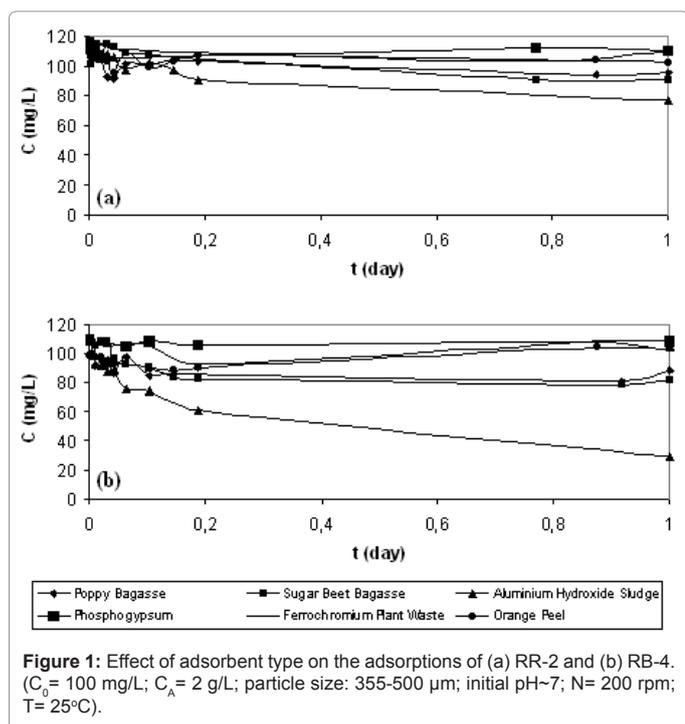
The best adsorption capacity was obtained with aluminium hydroxide sludge for both dyes, i.e. 14.92 mg/g and 31.80 mg/g for RR-2 and RB-4, respectively (Table 1). Thus, it was decided to use aluminium hydroxide sludge as the adsorbent in the experiments.

Anionic dyes contain sulfonate ions ( $\text{SO}_3^-$ ) [20] and positively charged adsorbents can mostly adsorb these dyes well. Metal hydroxide sludges, which are a waste produced by the electrocoating industry, are suitable adsorbents for textile wastewaters containing anionic dyes. Aluminium hydroxide sludge is a waste that forms by coagulation of aluminium ions in the water used for the anodized coating process in aluminum factories [21-23]. This sludge provides active surfaces for the adsorption of the polluting species such as the textile dyes. During the anodized coating process, the electrolytic dissolution of the aluminum anode produces the cationic monomeric species such as  $\text{Al}^{3+}$ ,  $\text{AlOH}^{2+}$  and  $\text{Al}(\text{OH})_2^+$  at low pH. At appropriate pH values, they are transformed into  $\text{Al}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_4^-$ ,  $\text{Al}_2(\text{OH})_2^{+4}$  according to the some hydrolyze reactions [24,25]. A chemical affinity forms between this positive charge (in aluminum hydroxide sludge) and negative charges in the structures of RR2 and RB4. As a result of this chemical affinity, the resistance of the boundary layer surrounding the adsorbent weakens. Thus, adsorption occurs very easily.

High molecular weight dyes were more strongly adsorbed on the metal hydroxide sludge than the others, because they have a higher negative charge and their solubility is lower than the others [18]. It was observed that the adsorption capacity of RB4 (MW: 637 g/mol) on the aluminium hydroxide sludge was 2-fold higher than that of RR2 (MW: 615 g/mol).

### Effect of contact time

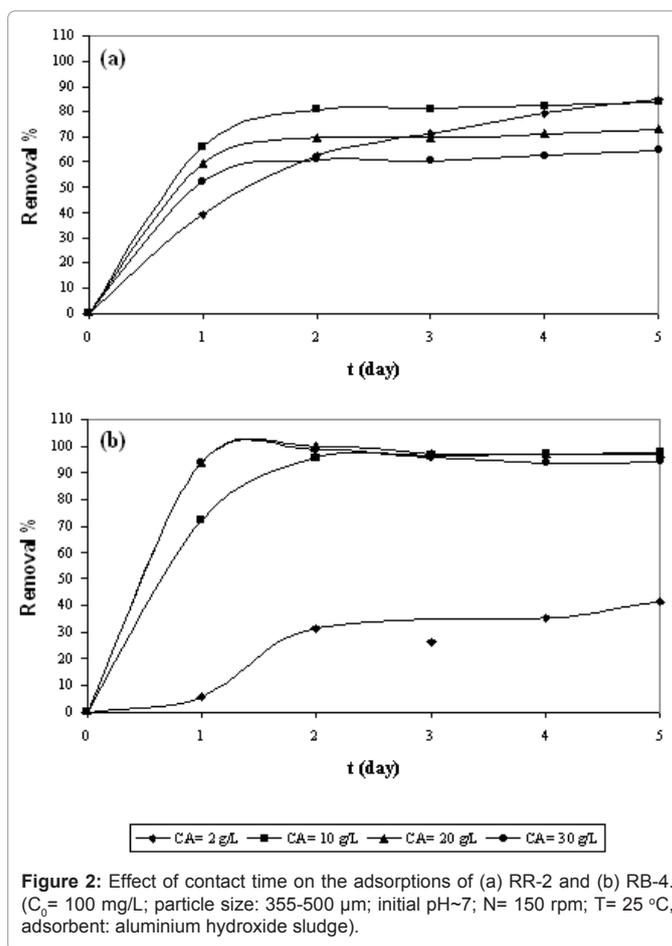
In this section, the experiments were carried out at the four different adsorbent concentrations over 5 days with sampling every 24 hours. Figure 2. shows the changes in dye removal with contact time. It was observed that there was no remarkable change in dye removal after the second day for all adsorbent concentrations. Therefore, the equilibrium time was accepted as 2 days.



**Figure 1:** Effect of adsorbent type on the adsorptions of (a) RR-2 and (b) RB-4. ( $C_0 = 100 \text{ mg/L}$ ;  $C_A = 2 \text{ g/L}$ ; particle size: 355-500  $\mu\text{m}$ ; initial pH~7;  $N = 200 \text{ rpm}$ ;  $T = 25^\circ\text{C}$ ).

Adsorbent Type	RR-2		RB-4	
	$q_t$ (mg dye/g solid)	Removal (%)	$q_t$ (mg dye/g solid)	Removal (%)
Poppy Bagasse	6.75	13.69	9.49	19.35
Sugar Beet Bagasse	11.06	21.18	12.31	25.37
<b>Aluminium Hydroxide Sludge</b>	<b>14.92</b>	<b>30.19</b>	<b>31.80</b>	<b>70.90</b>
Phosphogypsum	1.96	3.76	0.21	0.43
Ferrochromium Plant Waste	2.47	4.68	3.13	6.45
Orange Peel	3.98	8.08	2.50	5.16

**Table 1:** Comparison of removal percentages and adsorption capacities obtained with different solid wastes ( $C_0 = 100 \text{ mg/L}$ ;  $C_A = 2 \text{ g/L}$ ; particle size: 355-500  $\mu\text{m}$ ; initial pH~7;  $N = 200 \text{ rpm}$ ;  $T = 25^\circ\text{C}$ ,  $t = 1 \text{ day}$ ).



**Figure 2:** Effect of contact time on the adsorptions of (a) RR-2 and (b) RB-4. ( $C_0 = 100 \text{ mg/L}$ ; particle size: 355-500  $\mu\text{m}$ ; initial pH~7;  $N = 150 \text{ rpm}$ ;  $T = 25^\circ\text{C}$ , adsorbent: aluminium hydroxide sludge).

### Effect of initial pH

Three different initial pH levels were studied, i.e. acidic (pH: 2), neutral (pH: 7), and basic (pH: 10), for both dyes by sampling at particular times over 2 days Figure 3. Shows changes in the dye concentrations with contact time for the three initial pH levels. The removal percentages achieved at the end of 48 h are given in Table 2. The maximum removal percentages were 48.37% and 95.65% at the pH of 7 for RR-2 and RB-4, respectively. The difference between the removal percentage of RB-4 for pH 7 and pH 10 is small. Metal hydroxides generally have an amphoteric character. Therefore, the

adsorption capacity may decrease because of the increasing solubility of the metal hydroxides in the strong acidic or basic medium. The existence of excessive acid or base in the solution decreases the adsorption effectiveness of metal hydroxide sludges [18]. It is thought that the removal operation must be carried out at natural pH.

### Effects of adsorbent concentration and stirring rate

With the aim of investigating the adsorbent concentration and stirring rate effects on removal by adsorption from their aqueous solutions of RR-2 and RB-4, experiments were carried out at four different adsorbent concentrations and three different stirring rates. The removal percentages are shown in Figure 4.

It was found that the maximum removal percentage for RR-2 was 80.75% at the adsorbent concentration of 10 g/L and the stirring rate of 150 rpm (Figure 4). Adsorption of RR-2 increased to a certain value with increasing adsorbent concentration (10 g/L). A similar phenomenon was reported in a study that investigated malachite green adsorption on to agro-industry waste [1]. However, the excessive increase reduced the removal percentage to the level obtained at the low adsorbent concentration. This may be attributed to overlapping or aggregation of adsorption sites, resulting in a decrease in total adsorbent surface area available to reactive dyes. The maximum removal percentage for RB-4 was 99.74% at the adsorbent concentration of 20 g/L and the stirring rate of 150 rpm (Figure 4). The increase in adsorbent concentration

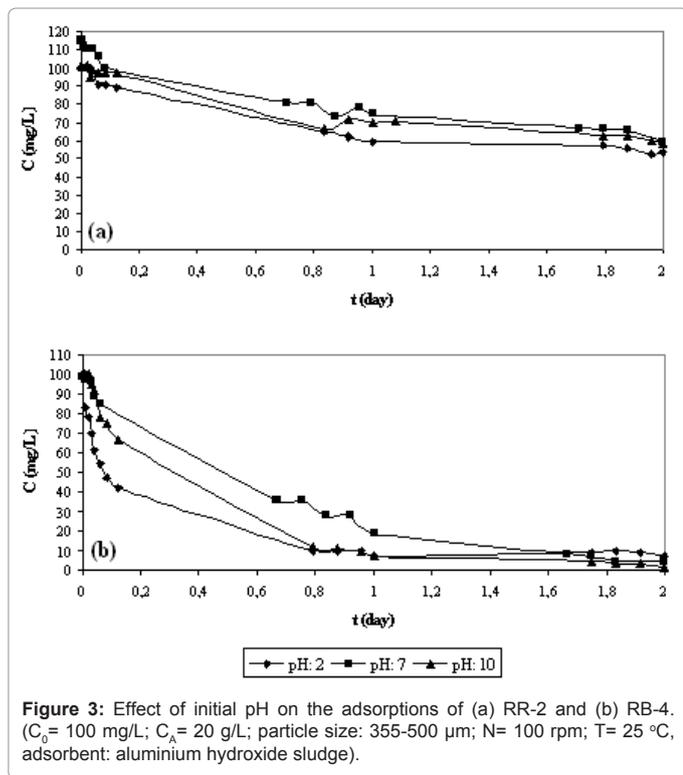


Figure 3: Effect of initial pH on the adsorptions of (a) RR-2 and (b) RB-4. ( $C_0 = 100$  mg/L;  $C_A = 20$  g/L; particle size: 355-500  $\mu$ m;  $N = 100$  rpm;  $T = 25^\circ$  C, adsorbent: aluminium hydroxide sludge).

pH	Removal (%)	
	RR-2	RB-4
2	46.44	93.07
7	48.37	95.65
10	42.08	98.50

Table 2: Effect of initial pH ( $C_0 = 100$  mg/L;  $C_A = 20$  g/L; particle size: 355-500  $\mu$ m;  $N = 100$  rpm;  $T = 25^\circ$  C, time: 48 h).

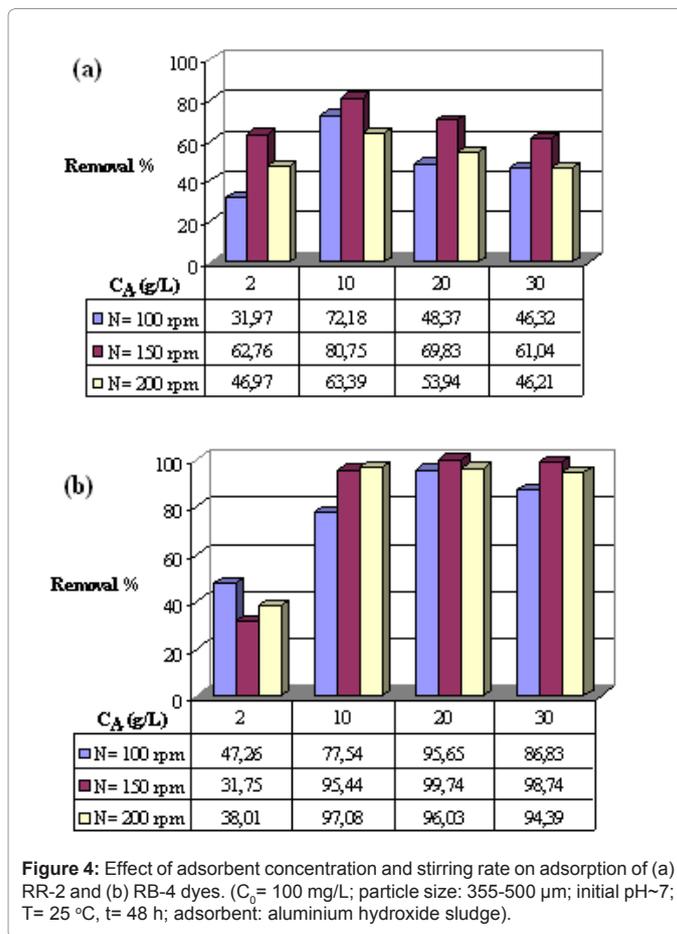


Figure 4: Effect of adsorbent concentration and stirring rate on adsorption of (a) RR-2 and (b) RB-4 dyes. ( $C_0 = 100$  mg/L; particle size: 355-500  $\mu$ m; initial pH~7;  $T = 25^\circ$  C,  $t = 48$  h; adsorbent: aluminium hydroxide sludge).

caused an increase in removal percentage. The mass transfer condition that yielded the highest removal percentage was 150 rpm for both dyes among the examined stirring rates.

### Equilibrium of adsorption

The adsorption isotherms which are the relationships between the amount of dye adsorbed per unit mass of adsorbent ( $q_e$ ) and the equilibrium concentration ( $C_e$ ) for RR-2/aluminium hydroxide sludge and RB-4/aluminium hydroxide sludge binary systems at the three temperatures were given in Figure 5(a,b). The experiments were carried out for the five different initial dye concentrations at the temperatures of 25, 35, and 45 $^\circ$ C. Besides the experimental values, the theoretical values determined by Langmuir and Freundlich models which are expressed the interaction between adsorbent with dye molecules were also shown in Figure 5(a,b). The Langmuir model is given by Eq. (3).

$$q_e = Q^0 K C_e / (1 + K C_e) \tag{3}$$

where  $Q^0$  and  $K$  are the Langmuir constants related to maximum adsorption capacity and bonding energy of adsorption, respectively. The Freundlich model is given Eq. (4).

$$q_e = K_F C_e^{1/n} \tag{4}$$

where  $K_F$  and  $n$  are indicators of sorption capacity and sorption intensity which are the Freundlich constants belong to the system, respectively.

As can be seen in Figure 5(a,b), the adsorption capacity increased

with increasing temperature. This result showed that the process was endothermic. The increase in temperature may cause easy diffusion of the dye to the pores because of increases in the molecule's kinetic energy.

The linear plots of the Langmuir ( $C_e/q_e$  vs  $C_e$ ) and Freundlich ( $\log q_e$  vs  $\log C_e$ ) models were given Figure 6(a,b). The maximum adsorption capacities ( $Q^0$ ) and the  $K$  constants were calculated from the slope and interception of the Langmuir plots, respectively, by using Equation (5) [18].

$$\frac{C_e}{q_e} = \frac{1}{Q^0 K} + \frac{C_e}{Q^0} \quad (5)$$

The Freundlich constants of  $n$  and  $K_F$  were calculated from the slope and interception of the Freundlich plots, respectively, by using Equation (6) [18].

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

Langmuir and Freundlich constants for both dyes at the three temperatures examined are given in Table 3. The Langmuir constants for RR-2 were negative values. Since the mono layer capacity ( $Q^0$ ) and

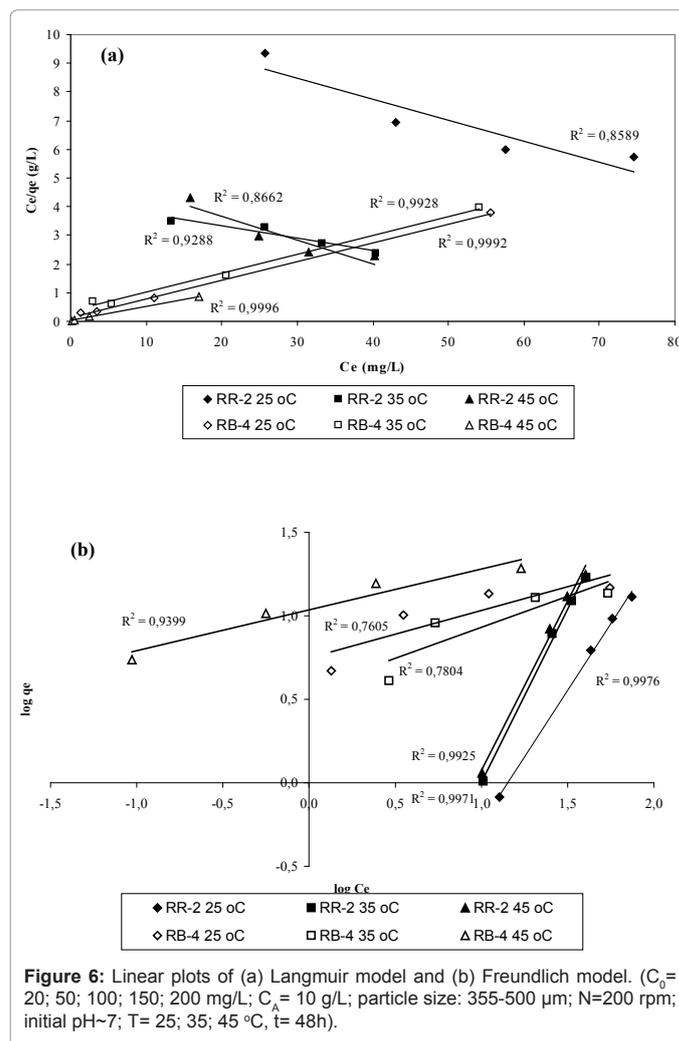
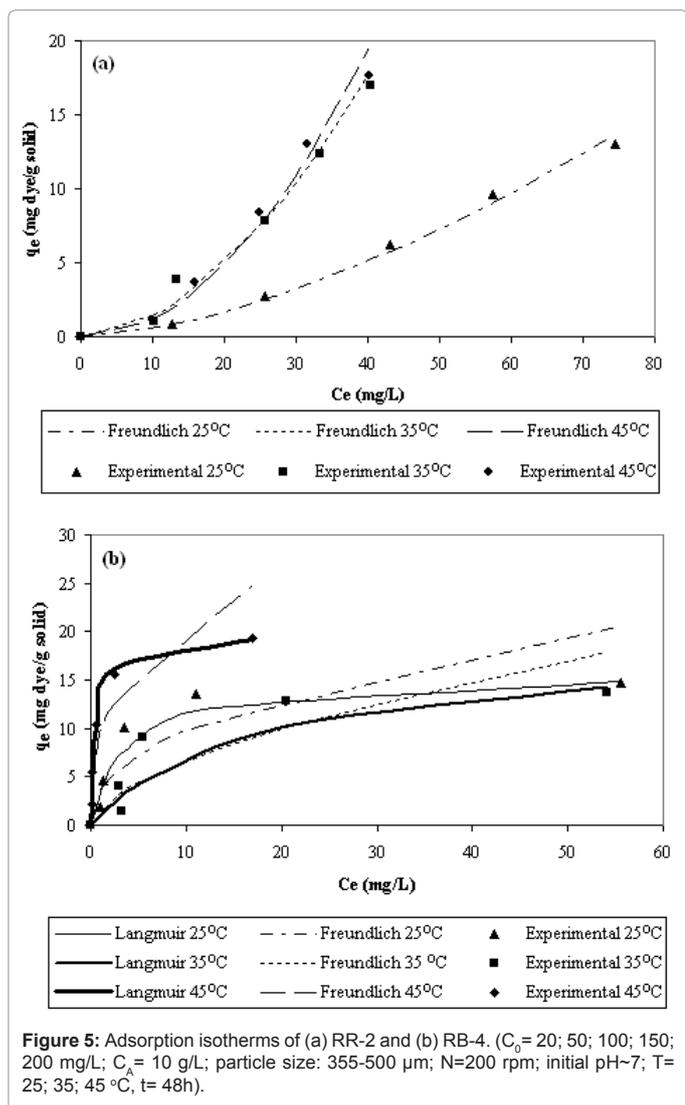


Figure 6: Linear plots of (a) Langmuir model and (b) Freundlich model. ( $C_0 = 20; 50; 100; 150; 200$  mg/L;  $C_A = 10$  g/L; particle size: 355-500  $\mu$ m; N=200 rpm; initial pH~7; T= 25; 35; 45  $^{\circ}$ C, t= 48h).

Dye	T ( $^{\circ}$ C)	Langmuir Constants			Freundlich Constants		
		$Q^0$ (mg/g)	$K$ (L/mg)	$R^2$	$K_F$	$1/n$	$R^2$
RR-2	25	-	-	-	0.015	1.5802	0.9970
	35	-	-	-	0.021	1.8254	0.9308
	45	-	-	-	0.013	1.9794	0.9871
RB-4	25	15.823	0.268	0.9905	3.503	0.4418	0.7104
	35	18.762	0.058	0.7183	1.712	0.5881	0.6123
	45	19.881	1.809	0.9992	9.101	0.3549	0.7742

Table 3: Langmuir and Freundlich adsorption isotherm constants for the adsorptions of RR-2 and RB-4 onto aluminium hydroxide sludge ( $C_0 = 20; 50; 100; 150; 200$  mg/L;  $C_A = 10$  g/L; particle size: 355-500  $\mu$ m; initial pH~7; N= 200 rpm; time= 48 h).

the adsorption equilibrium constant ( $K$ ) were never negative values, the adsorption isotherms of RR-2/aluminium hydroxide sludge binary system could be said to be inconsistent with the Langmuir adsorption equation. However, they were consistent with the Freundlich adsorption equation by the high regression coefficient. Freundlich isotherms explain the adsorption in heterogeneous surfaces, which are not homogeneous in terms of energy and its functional groups are not specific [3]. The low value of the Freundlich constant ( $K_F$ ) for RR-2 showed that the capacity of the adsorbent is very sensitive to increase in the dye concentration [18].

The adsorption of RB-4 onto aluminium hydroxide sludge was

consistent with the Langmuir adsorption equation, but not the Freundlich equation. The Langmuir equation defines the adsorption on strong homogeneous surfaces [3]. Increases in the values of  $Q^0$ ,  $K$ , and  $K_F$  with increasing temperature show that the process is endothermic. The value between 0 and 1 of the  $1/n$  constant in the Freundlich equation ( $0 < (1/n) < 1$ ) indicated that the adsorption was suitable [18].

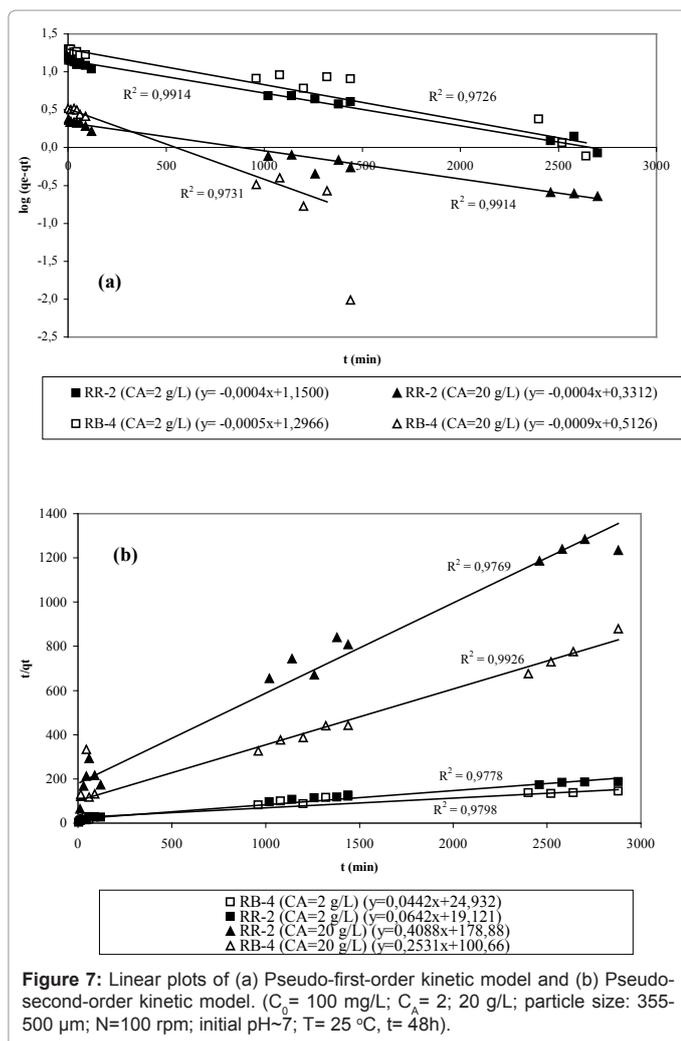
### Kinetics of adsorption

In this section, for the determination of the adsorption kinetics that agreed with the rate equation dye/aluminium hydroxide sludge binary systems and the calculation of adsorption rate constants, experiments were carried out at the adsorbent concentrations of 20 g/L by periodically sampling and analysis over 2 days.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2,303} t \quad \text{Pseudo-first-order kinetic model (Lagergren equation)} \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Pseudo-second-order kinetic model (Ho equation)} \quad (8)$$

The rate constants  $k_1$  and  $q_e$  of a pseudo-first-order kinetic model were calculated from the slope and interception of the Lagergren equation [26], respectively, by using Equation. (7) and Figure 7(a).



**Figure 7:** Linear plots of (a) Pseudo-first-order kinetic model and (b) Pseudo-second-order kinetic model. ( $C_0 = 100$  mg/L;  $C_A = 2; 20$  g/L; particle size: 355-500  $\mu\text{m}$ ;  $N=100$  rpm; initial pH=7;  $T = 25$   $^\circ\text{C}$ ,  $t = 48$ h).

Dye	$q_{e,exp.}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		$k_1$ ( $\text{min}^{-1}$ )	$q_{e,cal.}$ (mg/g)	$R^2$	$k_2$ (g/mg/min)	$q_{e,cal.}$ (mg/g)	$R^2$
RR-2	2.33	0.0009	2.14	0.9914	0.0009	2.45	0.9769
RB-4	3.27	0.0021	3.26	0.9731	0.0006	3.95	0.9926

**Table 4:** The rate constants of pseudo-first-order kinetic model and pseudo-second-order kinetic model and correlation constants for RR-2 and RB-4 ( $C_0 = 100$  mg/L;  $C_A = 20$  g/L; particle size: 355-500  $\mu\text{m}$ ; initial pH=7;  $N = 100$  rpm;  $T = 25$   $^\circ\text{C}$ , contact time: 48 h).

The rate constants  $q_e$  and  $k_2$  of a pseudo-second-order kinetic model were calculated from the slope and interception of the Ho equation [27], respectively, by using Equation. (8) and Figure 7(b). The constants obtained for both of dyes are given in Table 4.

The adsorption of RR-2 on aluminium hydroxide sludge agreed better with the pseudo-first-order kinetic model than the others. It was found that the experimental  $q_e$  values were very close to  $q_{e,cal.}$  determined by the pseudo-first-order kinetic model.

The adsorption of RB-4 on aluminium hydroxide sludge agreed better with the pseudo-second-order kinetic model than the others. It was found that the experimental  $q_e$  values were very close to  $q_{e,cal.}$  determined by the pseudo-second-order kinetic model.

### Thermodynamic parameters

To determine of the changes in Gibbs free energy ( $\Delta G^0$ ), adsorption enthalpy ( $\Delta H^0$ ) and adsorption entropy ( $\Delta S^0$ ), the following equations [3,28] were used:

$$\Delta G^0 = -RT \ln K \quad (9)$$

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (10)$$

$$\Delta H^0 = \Delta G^0 + T\Delta S^0 \quad (11)$$

Since the adsorption of RR-2 on the aluminium hydroxide sludge was not consistent with the Langmuir adsorption equation, the  $K$  constant, which is the Langmuir coefficient related to adsorption energy, was found to be a negative value. For this reason, thermodynamic parameters could not be determined.

For RB-4, firstly,  $K$  values were obtained by the Langmuir adsorption equation at different temperatures. Then  $\Delta G^0$  values were determined by putting  $K$  values in Eq. (9). The values of  $\Delta H^0$  and  $\Delta S^0$  were calculated from the slope and intercept of a Van't Hoff linear plot of  $\ln K$  versus  $1/T$  (Eq.(10)). The results are given in Table 5.

The negative value of  $\Delta G^0$  (-1.567 kJ/mol) at 45 $^\circ\text{C}$  shows that the adsorption was self-induced at this temperature. The positive values of  $\Delta G^0$  (3.263 and 7.291 kJ/mol) at the temperatures of 25 and 35 $^\circ\text{C}$  show that this spontaneous does not occur at low temperatures. A similar phenomenon was reported in a study that investigated Congo Red adsorption onto activated carbon prepared from coir pith [29]. The fact that  $\Delta H^0$  was a positive value (73.078 kJ/mol) and higher than 40 kJ/mol shows that the adsorption process is chemical and endothermic [30]. Moreover, many researchers have reported that the adsorption of reactive dyes on to different type adsorbents was endothermic [12,29,31]. In this state, the bonds formed are very strong. The fact that  $\Delta S^0$  was a positive value (0.228 J/mol/K) shows that the disturbance increases at the solid-solvent interface. Similarly,  $\Delta S^0$  was found to be a positive value (23.549 J/mol/K) in the study mentioned above that investigated Congo Red adsorption [29].

T (°C)	K (L/mg)	$\Delta G^{\circ}$ (kJ/mol)	$\Delta H^{\circ}$ (kJ/mol)	$\Delta S^{\circ}$ (J/mol/K)
25	0.268	3.263	73.078	0.228
35	0.058	7.291		
45	1.809	-1.567		

**Table 5:** Thermodynamic parameters for adsorption of RB-4 onto aluminium hydroxide sludge.

### Stability of the dye-adsorbent

To understand the stability of the dye-adsorbent, the desorption experiments were carried out at the conditions of the temperature of 25°C, the stirring rate of 150 rpm and the adsorbent concentration of 10 g/L through 2 days. In these conditions, desorption yields are obtained 0.56 % and 0 % for RR2 and RB4, respectively. It was found that RR2 and RB4 did hardly ever desorb from the solid. Thus, it could be said that adsorption of RR2 or RB4 onto aluminum hydroxide sludge is chemical adsorption.

### Conclusion

Adsorption of the textile dyes Reactive Red 2 (RR-2) and Reactive Blue 4 (RB-4) onto six different solid wastes was examined. Aluminium hydroxide sludge was the solid waste with the highest adsorption capacity for both dyes. The equilibrium time was two days using aluminium hydroxide sludge for both dyes. For RR-2, the removal percentages were 46.44%, 48.37%, and 42.08% at pH values of 2, 7, and 10, respectively. For RB-4, the removal percentages were 93.07%, 95.65%, and 98.50% at pH values of 2, 7, and 10, respectively. It was decided that the initial pH mostly did not affect the removal of either dye. When the wastewater is discharged after its treatment, it is important that it is at the natural pH in terms of protecting the environment. For this reason, the natural pH was used in this study.

The maximum removal was 80.75% and 99.74% ( $q_e = 7.99$  mg/g and 4.48 mg/g) for RR-2 and RB-4, respectively, in the conditions of  $C_0 = 100$  mg/L, initial pH: 7,  $N = 150$  rpm,  $T = 25^{\circ}\text{C}$ ,  $t = 2$  days. Aluminium hydroxide sludge is a suitable adsorbent that ensures high removal of both RR-2 and RB-4. It was observed that RB-4 was more adsorbed than RR-2 onto aluminium hydroxide sludge. High molecular weight dyes were more strongly adsorbed on the metal hydroxide sludge than the others.

It was observed that the adsorption capacity increased with increasing temperature (25-45°C). This shows that the process is endothermic. The adsorption of RR-2 onto aluminium hydroxide sludge is consistent with the Freundlich adsorption equation while the adsorption of RB-4 is consistent with the Langmuir adsorption equation. For the adsorption of RR-2, the dynamic behaviour agrees well with the pseudo-first-order kinetic model. Furthermore, for the adsorption of RB-4, the dynamic behaviour agrees well with the pseudo-second-order kinetic model. The  $q_e$  values calculated by the suitable kinetic model were very close to the experimental  $q_e$  values for both dyes. It was observed for RB-4 that the adsorption occurred spontaneously ( $\Delta G^{\circ} = -1.567$  kJ/mol) at high temperature (45°C) but energy was required ( $\Delta G^{\circ} = 3.263$  kJ/mol at 25°C and 7.291 kJ/mol at 35°C) for adsorption to occur at low temperature. Moreover, it was seen that the adsorption process is endothermic ( $\Delta H^{\circ} = 73.078$  kJ/mol) and chemical ( $\Delta H^{\circ} > 40$  kJ/mol). The positive  $\Delta S^{\circ}$  value ( $\Delta S^{\circ} = 0.228$  J/mol/K) shows that the disturbance increases at the solid-solvent interface.

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