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REMOVAL OF REACTIVE RED 45 USING ATERMIT FACTORY SOLID WASTES BY ADSORPTION

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ABSTRACT

This study, atermit factory solid wastes were used as an adsorbent to remove Reactive Red 45 (RR45) from aqueous solution by batch method. Effects of pH, initial dye concentration and time were studied. It was found that the removal of RR45 increased with increasing initial dye concentration Adsorption isotherms were analyzed by Langmuir and Freundlich models. Moreover, kinetic of adsorption were studied. Pseudo second order is the best model for the removal of RR45 from aqueous solution. Thermodynamic parameters were also studied. Gibbs free energy value was found to be -5.320 kJ/mol and indicating the spontaneity of the system. Atermit factory solid wastes were characterized by SEM. As a result, atermit factory wastes could be employed as no-cost and effective adsorbent for the removal of RR45 from aqueous solution.

KEYWORDS:
Adsorption, RR45, environment, SEM, thermodynamic, isotherm.

INTRODUCTION

Today, studies have been conducted to investigate the use conditions of waste materials for different purposes in order to ensure the availability of natural resources more efficiently. For this reason, reuse of waste is of great importance in terms of environmental and economic values. It is important to carry out studies to characterize of wastes from industrial facilities as raw material for another industry. In this study, the efficiency of solid wastes of the atermit production plant in adsorption of dyestuffs in the textile industry wastewater has been investigated.

Atermit is a roofing material produced using cement containing asbestos [1]. The use of asbestos in the production of roofing materials is forbidden after the adverse health effects have been demonstrated. Atermit first factory in Turkey was established in 1956. After that, the roofing materials were named as the aterit with the same name as the founding firm [2]. Turkey is completely prohibited the use of asbestos in the Official Gazette published the law on 2010, 31 December [3]. After this date, all Atermit producer companies are closed except Atermit firm which was changed their technology. In the new technology, raw cellulose and waste cardboard packaging, which provide a flexible feature to the final product instead of asbestos, are used in the production of atermit [4, 5, 6]. In the production of atermit; the main raw materials (cement and unbleached cellulose fibers) and auxiliary raw materials (waste cardboard packaging, antifoam and flocculants) are used [7, 8, 9, 10, 11]. Unbleached cellulose fibers are made into paper clay by the help of hot water. Unbleached cellulose fibers are made into paper clay with the help of hot water and then sent to the production band by adding other raw materials. The wastewaters formed during the atermit production are collected in the sedimentation basin. The water formed after precipitation is reused in the system and the sediment is stored as non-hazardous waste in the municipal landfill [10, 11].

The textile industry is one of the most important industries in the world. Textile dyes produced by natural and synthetic routes that form a large market all over the world are one of the most important raw materials of this industry. The textile paint industry, which has an economic volume of $ 5,625 billion in 2017, is expected to reach $ 7.982 billion by 2020. Textile dyes are used to color textile products such as fibers, yarns and fabrics [12]. Generally, 125-150 L of water is consumed in the dyeing of 1 kg fabric [13]. Textile wastewaters have high chemical oxygen demand (COD) due to dense color, suspended solids, cellulose fibers, dyes and solvents [14]. The wastewater of this industry is responsible for the coloring of the water, the inhibition of photosynthesis, affect the lifespan of living things due to toxic content and the aesthetic worry in the receiving environment [15]. The dyestuff Reactive Red 45 (RR45) is a commonly used in the textile industry. Since it has a potential to cause pollution in the water environment, it must be purified before discharged [16]. Azo dyes constitute about 70% of reactive dyes [17]. Reactive azo dyes are produced to resist biodegradation [18]. For this reason, biological treatment methods do not provide

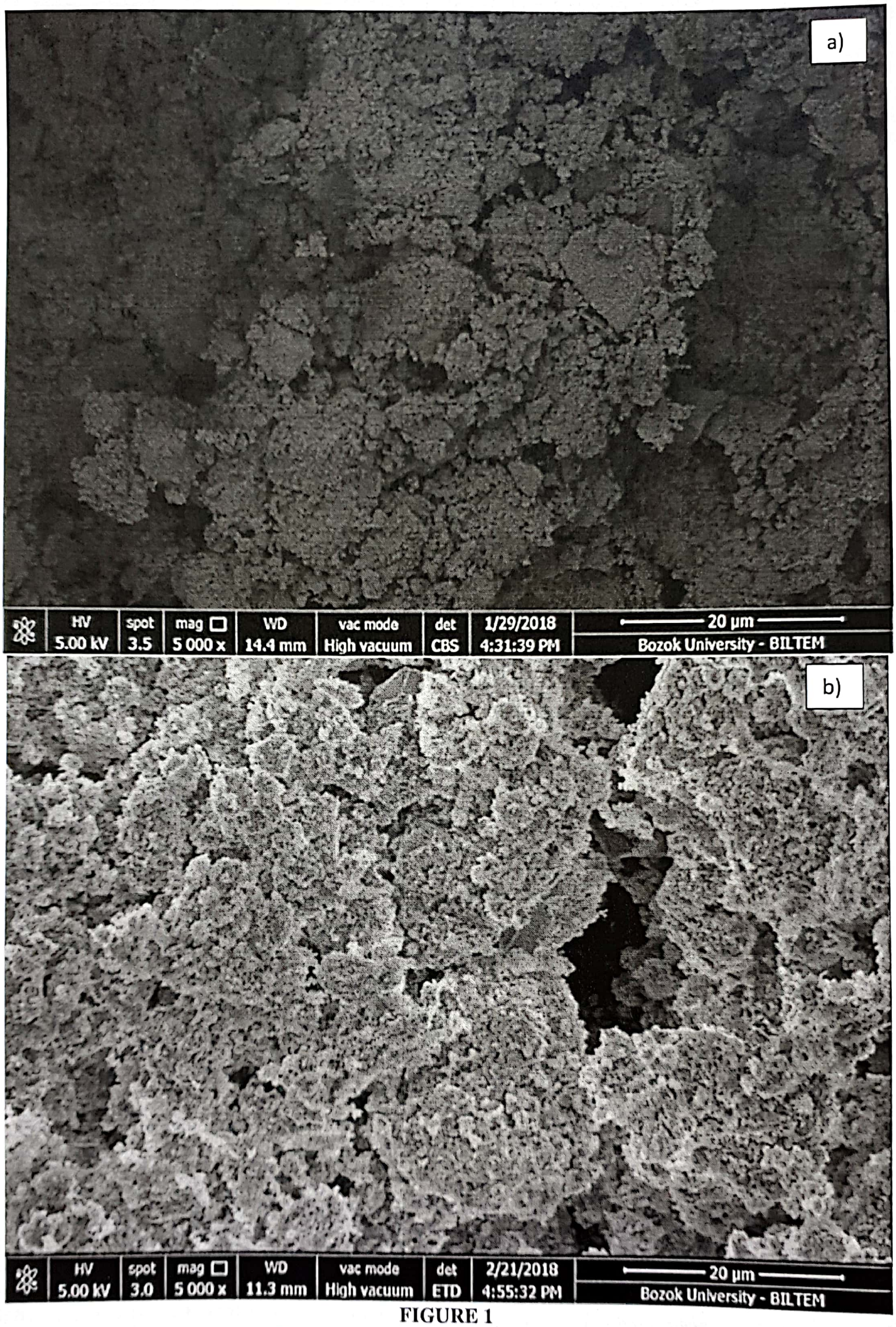


FIGURE 1
Sem image without dye (a) with dye (b)

the desired efficiency in the treatment of such contaminated water.

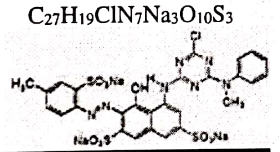
Adsorption is one of the advanced treatment techniques used in waste water treatment. In recent years, studies have been made to use solid wastes such as olive [19] and plastic industries [20] and also egg shells [21], plastic bottle [22], bentonite [23-24], peanut husk [25] as adsorbents.

In this study, atermit factory solid wastes were utilized as an adsorbent to remove Reactive Red 45 (RR45) from aqueous solution by batch method. Also, effects of pH, initial dye concentration and time were studied. Surface of atermit factory solid wastes characterized by SEM.

MATERIALS AND METHODS

Preparation of RR45. Reactive dye, RR45, was obtained from Merck and used without further purification. pH values of the medium were adjusted by addition of 0.1 M HCl or NaOH. Properties of RR45 described Table 1.

TABLE 1
Properties of RR45 [26]

	RR45
Molecular weight (g/mol)	802.10
Color	Red
λmax (nm)	505
Dye purity	<90%
Chemical formula	$C_{27}H_{19}ClN_7Na_3O_{10}S_3$
Structure	

Preparation of Atermit Factory solid wastes. Firstly, atermit factory solid wastes were washed pure water, secondly dried oven at 100 °C for two days and finally screen (100 mesh) before using.

Experiments. Experiments were performed in 750 mL erlenmeyer flasks including 1,5 g of atermit factory wastes with 150 mL of RR45 solution. All the adsorption experiments were performed at room temperature (25 °C) via batch method and four set (25 mg/L, 50 mg/L, 75 mg/L and 100 mg/L). The solution was shaken by a mechanical shaker (Edmund Bühler GmbH) at the constant agitation time (100 rpm) during 120 min. Then the supernatant was centrifuged at 6000 rpm and 10 minutes in a centrifuge (Hettich Zentrifugen) after the batch tests. The absorbance of RR45 was measured at maximum wavelength (λ_{max}: 505 nm) by UV–VIS Spectrophotometer (T 90). The incubation time was tested in a time from 5 to 120 min. All experiments were repeated three times. The removal efficiency of Malachite Green dye was calculated as follows, Eq. 1:

$$\text{Dye Removal (\%)} = \frac{C_o - C_t}{C_o} x100 \qquad (1)$$

C_o is the initial dye concentration (mg/L) whereas C_t is the dye concentration after sorption time t (mg/L) [27].

RESULTS AND DISCUSSION

Sem Images. Sem photo of atermit factory solid wastes presented Figure 1. The atermit factory solid wastes have rough structure. After adsorption, waste surfaces loaded dye.

FTIR Spectrum. FTIR spectrum of atermit factory solid wastes presented Figure 2. After adsorption there are appear new peak in the spectra Fig 2 (b). These findings implied that RR45 is adsorbed by atermit factory solid wastes.

Effect of Contact Time on RR45. First of all, adsorption experiments were done for different contact time (10, 20, 30, 60, 90, 120, 150, 180 minutes) and different conditions (600, 700, 800, 900, 1000 mg/L). Figure 3 is shown the effect of contact time on RR45.

Effect of Initial Dye Concentration. The effects of initial concentration on the removal of RR45 by atermit factory solid wastes were studied at room temperature (20 °C) and pH 6.0 at equilibrium times, and the results were graphed in Figure 3. According to Figure 4 the equilibrium sorption capacities of the sorbents increase with an increase in initial dye concentration and then stable. Huang et al., (2017) studied adsorption of Rhodamine B (RhB) and Acid red 1 by bentonite [28]. They found that similar results. At first, both the initial dye concentration from 50 to 300 mg/L to increased and amount of adsorbent increased. After that, the initial dyes concentration were 300 to 350 mg/L, adsorption process reached steady state.

Effect of pH. The pH is the one of the most important parameters to the adsorption because of the charge of sorbent surface. Figure 5 is shown that effect of pH for RR45. The removal of the RR45 increases with increasing initial pH from 4 to 6. The maximum dye removal shows pH 6.

Adsorption Isotherm. Langmuir model which describes the monolayer adsorption of dye molecules on a homogenous surface with a limited number of identical sites is given by Eq. 2 [29]:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + (\frac{a_L}{K_L})C_e \qquad (2)$$

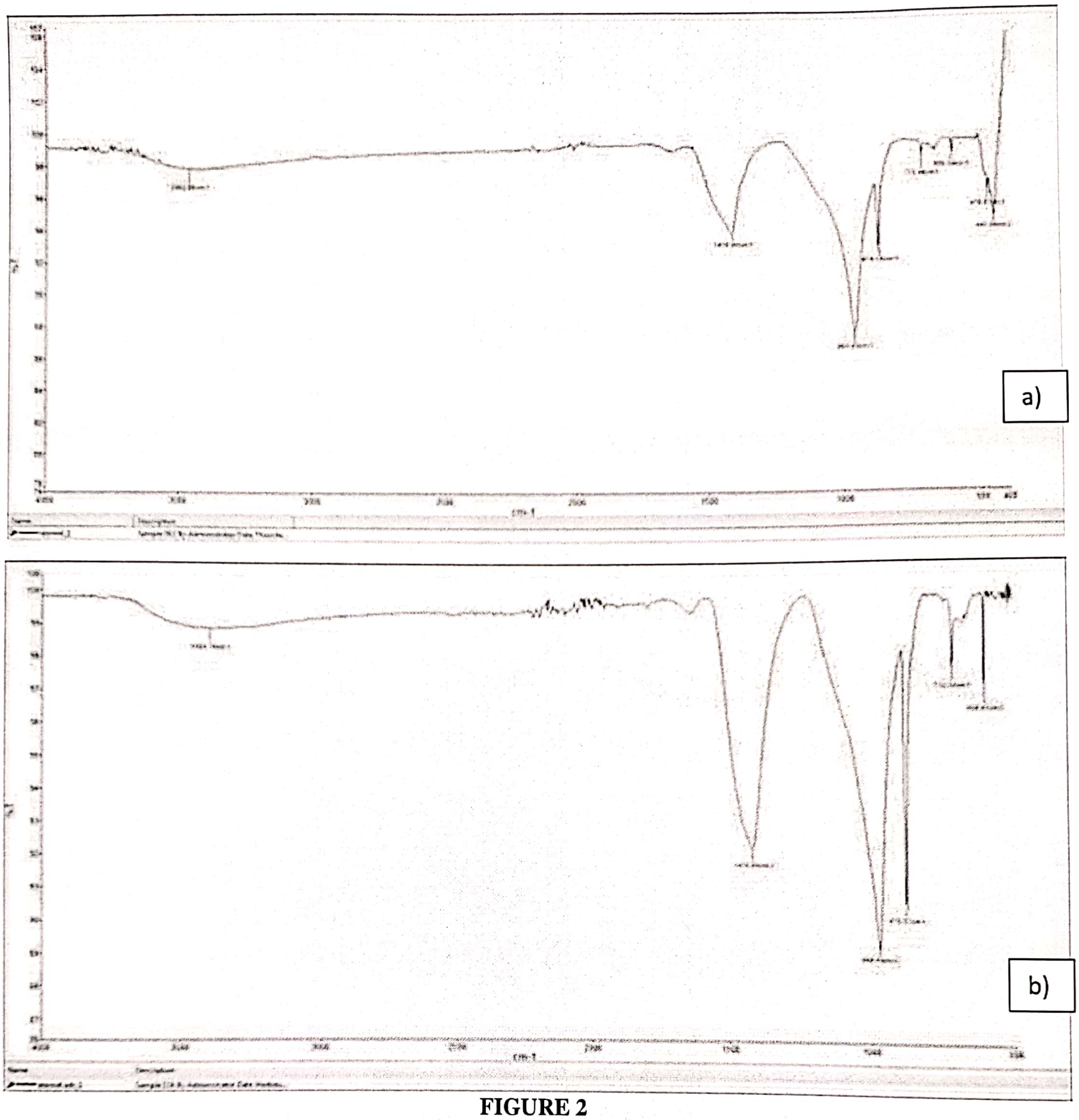


FIGURE 2
FTIR Spectrum Without dye (a) With dye (b)

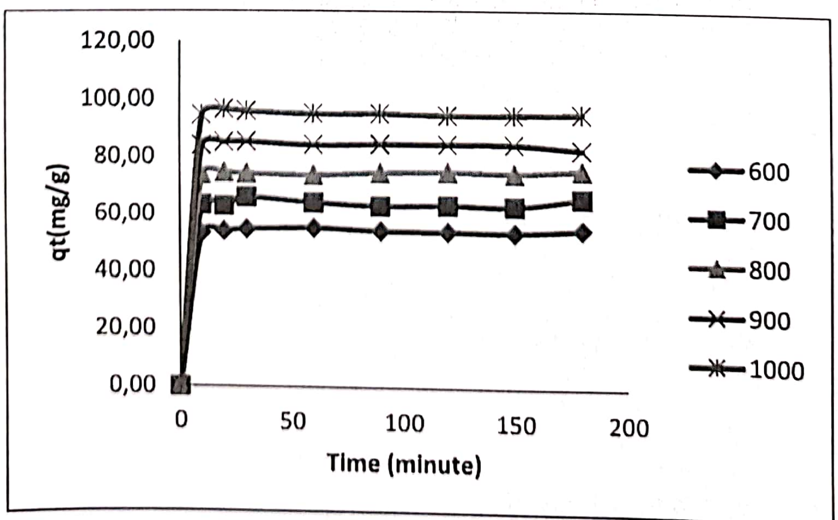


FIGURE 3
Effect of contact time on RR45

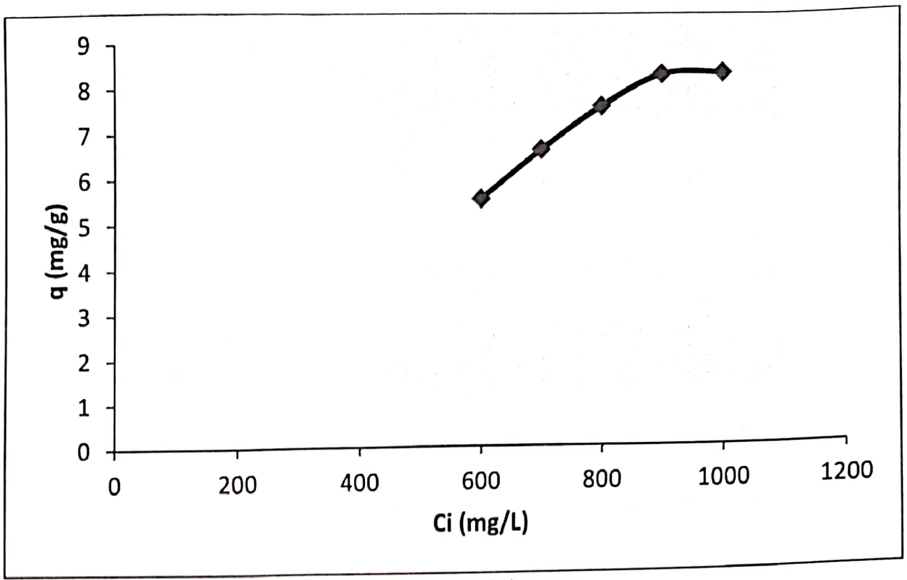


FIGURE 4
Effect of initial dye concentration

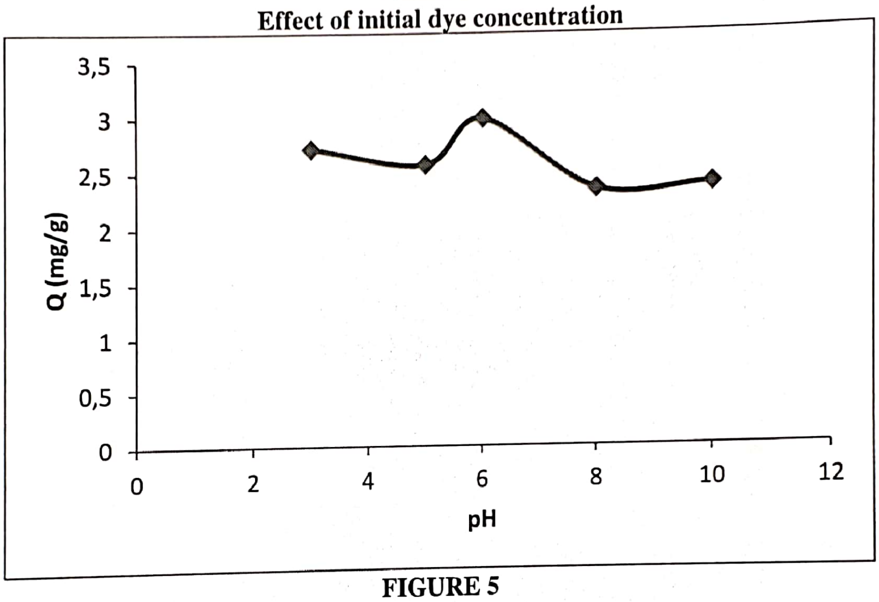


FIGURE 5
Effect of pH for Reactive Red 45

where; C_e is the equilibrium concentration of adsorbate in solution after adsorption (mg/L), q_e is the equilibrium solid phase concentration (mg/g), as well as K_L (L/g) and a_L (L/mg) are the Langmuir constants.

However, the Freundlich isotherm supposes a heterogeneous surface with a nonuniform distribution and can be expressed by Eq. 3:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

where K_F (L/g) iş the adsorption capacity at unit concentration and 1/n is adsorption intensity.

Isotherm models also studied for adsorption of RR45. Langmuir and Freundlich isotherm models applied for removal of RR45 by adsorption. Freundlich isotherm is better than Langmuir isotherm. Because of high correlation coefficient (R^2= 0.9335). Table 2 demonstrates isotherm constants.

Kinetic Study. Second order rate equation can be written as:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad [30]\ (4)$$

k (g/mg•min): The rate constant for second order

q_e and q_t are the amount of adsorbed on the atermit factory solid wastes (mg/g) at equilibrium and at time t (min), respectively, and $k_{2,ad}$ (1/min) is the rate constant of pseudo-second-order kinetics.

Dye concentration values were in the range of 600-1000 mg/L. For understand the reaction mechanism, kinetic models are applied kinetic data. The pseudo first order and pseudo second order kinetic models are explained the adsorption kinetic. The results of the pseudo second order kinetic experiments graphics were given in Figure 6. Moreover, the data fitted to pseudo second order kinetic model (Table 3).

TABLE 2
Isotherm parameters for the adsorption of RR45 onto atermit factory wastes

Isotherm constants	RR45
Langmuir	
q_{max} (mg/g)	35.771
K_L (L/mg)	0.0125
R^2	0.464
Freundlich	
K_f (L/g)	0.0315
n	1.211
R^2	0.9335

TABLE 3
Comparison of adsorption capacity of RR45 on atermit factory solid wastes in literature

Adsorbent	Dye	Q max (mg/g)	References
Si-APTES-BP	Reactive blue 19	37.45	[35]
	Reactive yellow 84	32.36	
Humin immobilize silica	Reactive Orange 16	19.45	[36]
	Reactive Red 120	2.29	
Clinoptilolite	Reactive Blue 21	9.652	[37]
	Reactive Red 195	3.186	
Industrial Sludge	Remazol Brilliant Blue R	33.47	[38]
Activated red mud	Reactive black 5	35.58	[39]
Atermit factory solid wastes	Reactive Red 45	35.771	This study

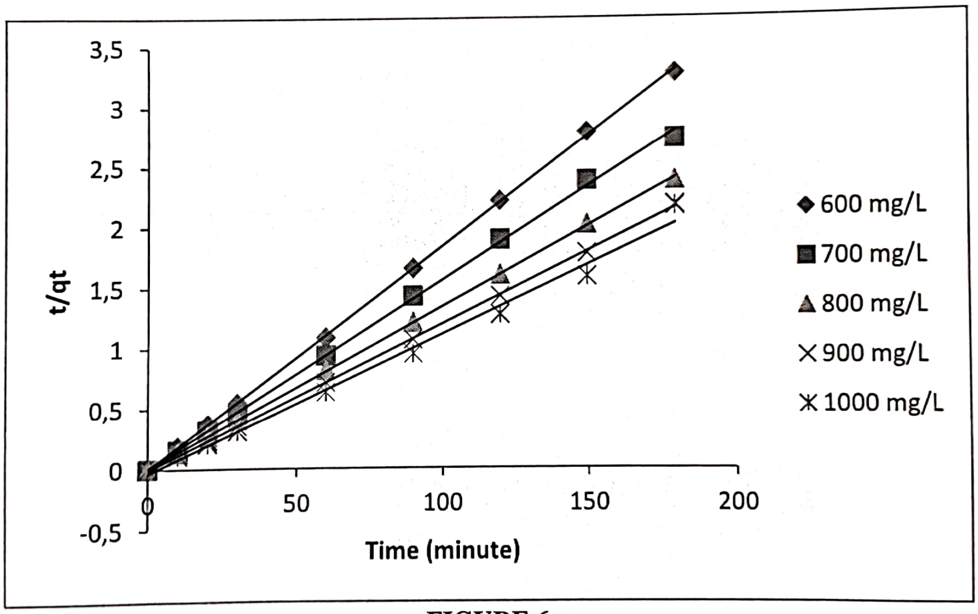


FIGURE 6
Pseudo Second Order Kinetic

TABLE 3
Values of Pseudo Second Order Kinetic Model

Initial Dye Concentration (mg/L)	qe	k_{2ad}	R^2
600	54.644	0.30400	0.999
700	64.516	0.02890	0.999
800	75.187	0.02940	0.999
900	83.333	0.02570	0.999
1000	87.719	0.00386	0.999

TABLE 4
Gibbs Free Energy Values For Systems

Sorbent	Dye	ΔG° (kJ/mol)	T (K)	References
Atermit Factory Solid Wastes	RR45	-5.320	298	This work
Banana peel powder	RB5	−0.198	298	[31]
Prawn shells	Reactive Red	- 2.5616	303	[32]
Crystal Violet	Bentonite	-17.46	303	[33]
Ash	Reactive blue	-2.979	293	[34]

Thermodynamic Studies. The thermodynamic parameters for the adsorption process of RR45 onto the atermit factory solid wastes can be determined using the experimental data in the following equations Eq. 5-7: Gibbs free energy values are shown in Table 4.

$$\Delta G = -RT\ln K_C^O \quad , (K_c=C_a/C_e) \quad (5)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

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

ΔS: The changes of entropy
ΔH: the changes of enthalpy
ΔG: Gibbs free energy
K_c: The equilibrium constant
T: Temperature (K)
R: The ideal gas constant (8.314 J/(mol K)).
Ca: The solid phase concentration in equilibrium (mg/L).

CONCLUSION

In this study, atermit factory wastes were used as an adsorbent to remove Reactive Red 45 (RR45) from aqueous solution by adsorption. Isotherm and kinetic parameters were studied for the adsorption. Freundlich isotherm model is more suitable than Langmuir model. Because of high correlation coefficient (R^2=0.9335). Adsorption kinetics also studied. The data fitted to pseudo second order kinetic model. Thermodynamic parameters were also studied. Gibbs free energy value was found to be -5.320 kJ/mol and indicating the spontaneity of the system. Properties of surface characterized by SEM. As a result, atermit factory wastes could be employed as no-cost and effective adsorbent for the removal of RR45 from aqueous solution.

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