

# Adsorption Performance of Laccase Modified-Red Mud for Acid Fuchsin Dye Removal from Aqueous Solutions

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**Keywords** Acid Fuchsin dye removal; Red mud; Laccase from Russulaceae (*Lactariusvolemus*); Adsorption isotherms; Adsorption kinetics; Thermodynamic parameters

## Abstract

One of the powerful treatment processes for the removal of dyes from aqueous solutions is adsorption method. In this study, removal of Acid Fuchsin dye from aqueous solutions has been studied by using Red Mud (RM) waste material after its modification with laccase from Russulaceae (*Lactariusvolemus*). Laccase was purified by using saturated precipitate  $(\text{NH}_4)_2\text{SO}_4$ , DEAE-cellulose and immobilized on red mud. Batch adsorption experiments have been performed as a function of pH, contact time, temperature, and adsorbent dosage. The Freundlich equation was found to have the highest value of correlation coefficient compared with the Langmuir model. In addition, pseudo-first-order and pseudo-second order models were used to study the kinetics of Acid Fuchsin dye adsorption onto RM and laccase modified-RM. It was proved that adsorption process undergoes pseudo-second-order kinetic by the high value of correlation coefficient. Thermodynamic parameters including the Gibbs free energy, enthalpy and entropy changes indicated that the adsorption of Acid Fuchsin dye onto laccase modified-red mud was feasible, spontaneous and endothermic. The results show that the laccase-modified red mud can be used for the treatment of aqueous solutions as an alternative low cost adsorbent.

## Introduction

The conventional treatment methods for dye removal, such as chemical coagulation, activated sludge, biodegradation, oxidation, membrane separation, adsorption and photo degradation, have been extensively explored [1-3]. Among the physical and chemical processes, the adsorption procedure is effective in producing high-quality effluent without the formation of harmful substances [4-7]. However, low-cost adsorbents with high adsorption capacities are still being developed to reduce the adsorbent dose and minimize the problem of disposal. Significant attention has been directed toward various adsorbent materials, which may be obtained in significant quantities and are nontoxic to nature [8-9].

As an alternative low-cost adsorbent material, solid wastes are generally used as adsorbent for the removal of heavy metals and dyes from wastewater. One type of solid waste material, Red Mud (RM) is largely produced by the alumina industry. It emerges as a by-product of the caustic leaching of bauxite to produce alumina. The RM is principally composed of fine particles of silica, aluminum, iron, calcium, and titanium oxides and hydroxides, which are responsible for its high surface reactivity [10-12].

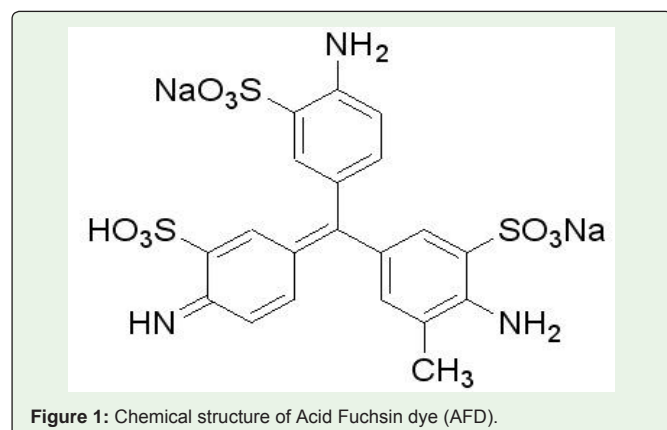
The RM waste material was used, as low-cost adsorbent material after its modification with laccase from Russulaceae (*Lactariusvolemus*). It is an enzyme and belongs to those enzymes, which have innate properties of reactive radical production. There are diverse sources of laccase producing organisms like bacteria, fungi and plants. Laccases use oxygen and produce water as by product. They can degrade a range of compounds including phenolic and non-phenolic compounds. They also have ability to detoxify a range of environmental pollutants [9].

This paper describes the use of RM and laccase modified-RM for removal of Acid Fuchsin Dye (AFD) from aqueous solutions. The adsorption of AFD has been investigated as a function of pH, contact time, temperature, and adsorbent dose. Adsorption isotherm, kinetic and thermodynamic studies have been performed to describe the adsorption process.

## Material and Methods

### Acid Fuchsin dye (AFD)

The AFD, 2-amino-5-[(4-amino-3-sulphophenyl) (4-imino-3-sulfo- 2,5-cyclohexadien-1-ylidene)-methyl]-3-methylbenzenesulfonic acid, is an organic dye (C.I. 42685) and has a formula,  $\text{C}_{20}\text{H}_{17}\text{N}_3\text{Na}_2\text{O}_9\text{S}_3$ . Its molecular structure is given in Figure 1. This organic dye is also called as Acid



Violet 19 or Fuchsin Acid or Rubin S and is widely used for staining procedures [13] and other purposes [14].

### Red mud

The red mud material emerges as unwanted by-products during alkaline-leaching of bauxite in Bayer process. The alkaline RM-water pump has been dumped annually into specially constructed dams around the Seydisehir Aluminum Plant, Konya (Turkey). RM used in this experimental study has been obtained from this plant. Its physical properties, chemical constituents and mineralogical composition are given in Table 1.

### Laccase enzyme

Laccase is an enzyme that has potential ability of oxidation. There are diverse sources of laccase producing organisms like bacteria, fungi and plants [9]. *Lactariusvolemus* is a species of mushroom in the family Russulaceae. It is widely distributed in Erzurum (Turkey). As a mycorrhizal fungus, its fruit bodies grow on the ground at the base of various species of trees in the summer and autumn in broad-leaved forests, either individually or in groups. It is valued as an edible mushroom and not toxic. Also, *Lactariusvolemus* has antioxidant, antiradical and antimicrobial activities [15].

### Purification of laccase enzyme

*Lactariusvolemus* (10 g) was ground in liquid N<sub>2</sub> and homogenized in a blender with 50 cm<sup>3</sup> of 1 M KCl by shaking, and centrifuged at 5.000xg for 60 min. The homogenates were centrifuged and precipitates were removed. For the purification of the laccase enzyme,

**Table 1:** Physical properties, chemical constituents and mineralogical composition of R.

Property	Value	Constituents	Value	Minerals	Value
Density (mg/m <sup>3</sup> )	28.5	Al <sub>2</sub> O <sub>3</sub> (%)	20.2	Sodalite(%)	32.2
Specific gravity	3.05	Fe <sub>2</sub> O <sub>3</sub> (%)	35.04	Cancrinite(%)	4.6
		CaO(%)	5.3	Hematite(%)	34.7
		MgO(%)	0.33	Diaspore(%)	2.6
		TiO <sub>2</sub> (%)	4	Rutile(%)	1.6
		Na <sub>2</sub> O(%)	9.4	Calcite(%)	1.3
		SiO <sub>2</sub> (%)	17.29		
		Ignition(%)	8.44		

the following procedure was implemented [15]. Laccase was purified from the supernatant in two steps. Firstly, it was partially purified by precipitation in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Secondly, ion exchange chromatography on DEAE-sephadex was used. The collapse of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was done from 0 to 90% in supernatant with the internals of 0-10, 10-20, 20-30, 30-40, 40-50, 50-60, 60-70, 70-80 and 80-90%. Significant activity was not observed below a range of 0-40% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The majority of activity was found in the 40-60% precipitate. Solid (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was added to the supernatant to increase the concentration of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> from 40% of the fraction to 60%. After, mixing it in an ice-bath for 1 h with magnetic stirring, it was centrifuged (10.000 x g, 30 min, and 4 °C). The supernatant was discarded and the precipitate was dissolved in 0.01 M acetate buffer (pH 5.0) and dialyzed against the same buffer [15-16].

### Adsorbent preparation for experimental study

The RM was thoroughly washed with distilled water until it became neutral. The suspension was wet sieved through a 200-mesh screen. A little amount of the suspension remained on the sieve and was discarded. The solid fraction was washed five times with distilled water following the sequence of mixing, settling, and decanting. The last portion of suspension was filtered, and the residual solid was then dried at 105°C, ground in a mortar, and sieved through a 200-mesh sieve. Laccase from Russulaceae (*Lactariusvolemus*) was purified by using precipitate of saturation (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, DEAE-cellulose and immobilized on RM. 1 g of RM sample was shaken with 10 cm<sup>3</sup> (5 mg protein/cm<sup>3</sup>) laccase from *Lactariusvolemus* solution for approximately 1 h, and then the separated particles were stored.

### Material characterization

The Scanning Electron Microscope (SEM) was used to examine the surface of the adsorbent. Images of native adsorbent and dye loaded adsorbent were magnified 5000 times by SEM modeled JEOL JSM-6400 SEM. In addition, the Fourier Transform Infrared Spectroscopy (FTIR) analyses were carried out to identify functional groups and molecular structure in the laccase-modified RM and AFD loaded laccase-modified RM. FTIR spectra were recorded on the on Perkin-a Perkin-Elmer GX2000 FTIR spectrometer. The spectrum of the adsorbent was measured within the range of 4000 and 700 cm<sup>-1</sup> wave number.

### Adsorption procedure

All studies were made in a 50 cm<sup>3</sup> stoppered Erlenmeyer flasks filled with AFD from 50 mg/dm<sup>3</sup>. The Red Mud was added to dye solution in the amount from 0.125 to 2 g red mud. The pH was adjusted to the desired value by using 0.1 M NaOH or 0.1 M HCl. Then, the glasses were placed in a shaker at the room temperature. The agitation was provided at 500rpm and 15 min to reach the equilibrium state. The samples were taken out from the flasks periodically by using a micropipette. Then the reaction mixtures were centrifuged at 5000 rpm for 10 min. Upper solution was filtered using 0.45 μm filters. The concentration of AFD was measured using a spectrophotometer set at 545 nm.

Calibration curves were established prior to the analysis. A calibration curve was prepared in the range 0-40 ng/cm<sup>3</sup> of AFD according to the general procedure. The obtained absorbance values from the samples were substituted in the equation of the calibration curve and the concentration of the dye in the samples was found.

The amounts of the dyes adsorbed onto adsorbent ( $q_e$  in mg/g) and the percentages of the dyes were calculated from the equations:

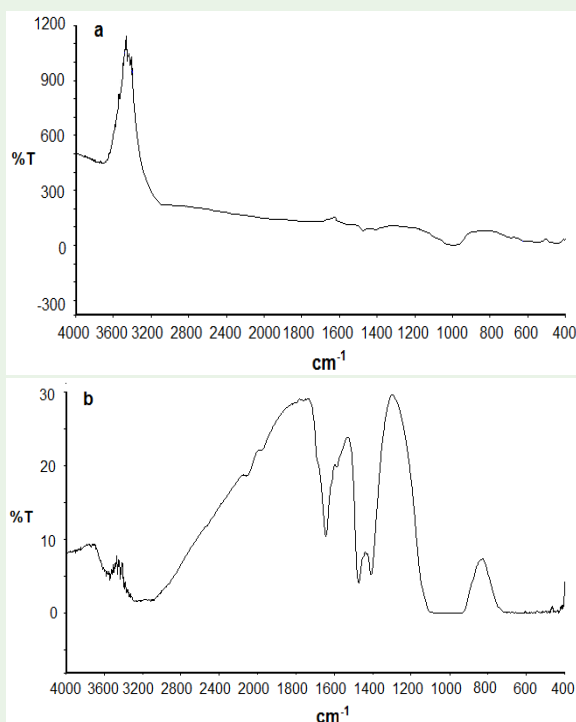
$$q_e = \frac{(C_o - C_e) * V}{m} \quad (1)$$

where  $C_o$  and  $C_e$  are the initial and equilibrium concentrations of AFD in solution (mg/dm<sup>3</sup>);  $V$  is the volume of solution (dm<sup>3</sup>) and  $m$  is the mass of adsorbent (g).

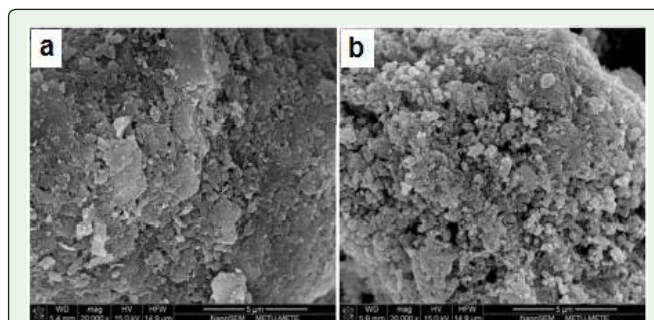
## Results and Discussion

### Red mud characteristics

**FT-IR spectra:** The functional groups and surface properties of the native adsorbent and after adsorption by FT-IR spectra were illustrated in the Figure 2 (a-b). The strong bands between 3270-3543 cm<sup>-1</sup> express hydroxyl-stretching region. This state has become more pronounced after AFD absorption and it express that there is water in RM. The peak around 1646.17 cm<sup>-1</sup> is attributed to water molecules absorbed into alumina silicate structure [17]. The absorption bands of carbonates incorporated in the main channel of can crinite were appeared between 1409.79-1473.51 cm<sup>-1</sup> regions in the samples. The peak around 1410 cm<sup>-1</sup> belongs to NO-group within can crinite and sodalite (Table 1). Another peak around 959.44 cm<sup>-1</sup> belongs to stretching vibrations of Si(Al)-O structure. To evaluate, through the FTIR technique, the interaction mechanisms between the AFD and RM, we focused our attention on a part of the mid infrared region, 629-644 cm<sup>-1</sup>, where bands associated with various AFD-O(H) stretching vibrations were found.



**Figure 2:** FT-IR spectrum of adsorbent (a) and adsorbent loaded with AFD (b).

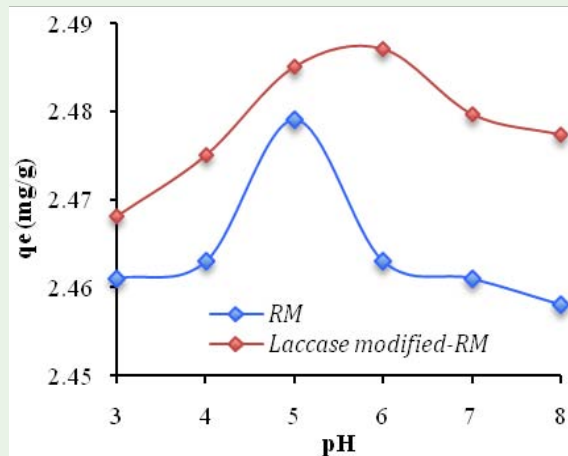


**Figure 3:** SEM images of RM (a) and AFD loaded laccase modified-RM (b).

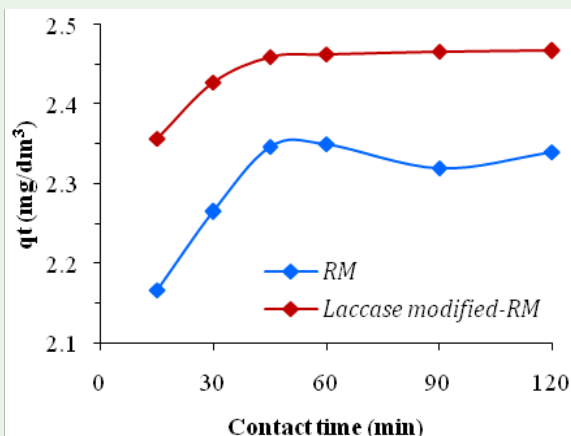
**SEM study:** The photography has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent surface. The SEM is useful for determining the particle shape, porosity and appropriate size distribution of the adsorbent [18]. The SEM images of modified-RM and AFD adsorbed laccase modified-RM are shown in Figure 3 (a-b). It is clear that, RM has considerable numbers of pores where, there is a good possibility for dyes to be trapped and adsorbed into these pores. Based on analysis of the images taken by SEM before and after the dye adsorption process, highly heterogeneous pores within RM particles were observed. After adsorption process, the pores were packed with AFD and this finding revealed the coverage of the modified natural material surface with molecular cloud of dye [18].

### Adsorption study

**Effect of pH:** The effect of initial pH on removal of the AFD onto RM and laccase modified-RM is shown in Figure 4. The optimum pH, at which the maximum removal occurred, was obtained at pH 6 and pH 5 for RM and laccase modified-RM, respectively. This is due to the surface complexation reactions, which are mostly influenced by the electrostatic force of attraction between AFD and the surface of the adsorbent. The acidity of the medium can affect the AFD ions' uptake amount of the RM and laccase modified-RM adsorbents because hydrogen ions in the solution could compete with AFD for active sites



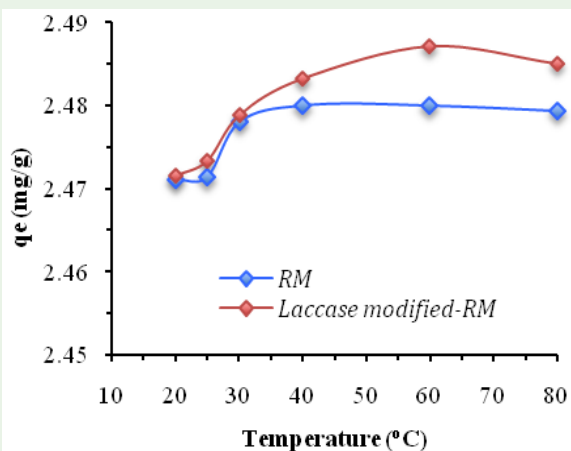
**Figure 4:** Effect of pH on the removal of AFD by RM and laccase modified-RM (initial AFD concentration: 50 mg/dm<sup>3</sup>, red mud dose: 1 g/ 50 cm<sup>3</sup>, agitation speed: 500 rpm and temperature: 30 ± 1°C).



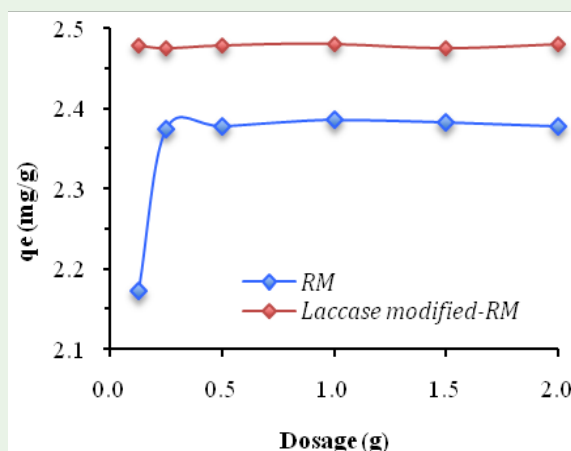
**Figure 5:** Effect of contact time on the AFD concentration ( $C_t$ ) after adsorption on RM and laccase modified-RM (pH: 5.0, initial AFM concentration: 50 mg/dm<sup>3</sup>, red mud dose: 1 g/50 cm<sup>3</sup>, agitation speed: 500 rpm and temperature: 30 ± 1°C).

on the adsorbent surface [19]. At lower pH values, the amount of dye adsorbed decreased due to repulsive force between positively charged surface and the positively charged dye molecules. When the pH of the solution is increased, the positive charge on the solution interface decreases and the adsorbent surface becomes negatively charged. Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites [20].

**Effect of contact time:** The effect of contact time on removal of the AFD onto RM and laccase-modified RM absorbents was shown in Figure 5. The removal of AFD increases with time in the first 45 min for laccase modified-RM. Basically, the removal of AFD was rapid at this time but it gradually increases with time until it reaches equilibrium. At the first 45 min of contact time, the concentration of AFD molecules in aqueous solution reached 2.35 mg/dm<sup>3</sup> and 2.46 mg/g was adsorbed by laccase-modified RM at the equilibrium state. Also, at 90<sup>th</sup> min of contact time, the adsorption rate was reached to 2.32 mg/g and 2.41 mg/g for RM and modified RM, respectively.



**Figure 6:** Effect of temperature on the removal of AFD by RM and laccase modified-RM (pH: 5.0, initial AFM concentration: 50 mg/dm<sup>3</sup>, red mud dose: 1 g/50 cm<sup>3</sup>, agitation speed: 500 rpm).



**Figure 7:** Effect of adsorbent dosage on the removal of AFD by RM and laccase modified-RM (pH: 5.0, initial AFM concentration: 50 mg/dm<sup>3</sup>, agitation speed: 500 rpm and temperature: 30 ± 1°C).

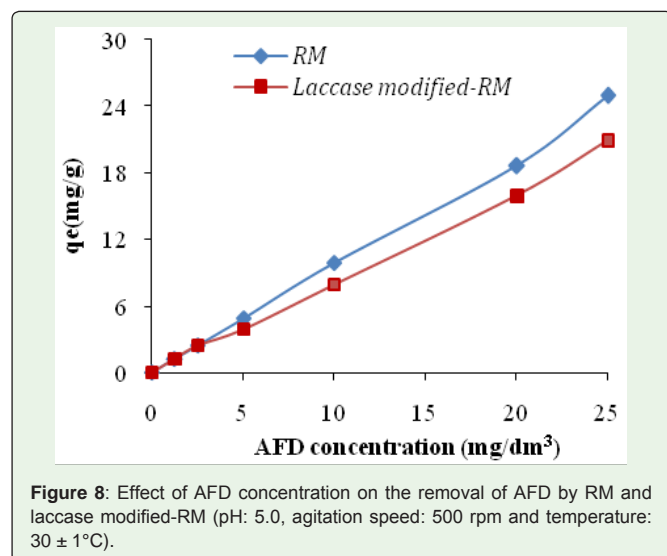
For the laccase-modified-RM adsorption, rapid adsorption and equilibrium in a short period of time is related to the efficacy of the adsorbent, especially for waste water treatment [21-22]. The rapid removal of the adsorbate has significant practical importance as it facilitates smaller reactor volumes ensuring efficiency and economy [19-23].

**Effect of temperature:** The effect of temperature on the adsorption of AFD by RM and laccase-modified RM absorbents was illustrated in Figure 6. The maximum removal amount of adsorbate was 2.480 mg/g for RM at 40°C and 2.487 mg/g for laccase modified-RM at 40°C. A temperature increase can lead to a rise in kinetic energy and mobility of dye molecules, and can also cause an increase in the intra-particle diffusion rate of the adsorbate. This increase also affects the solubility and chemical potential of the adsorbate, possibly becoming a factor that controls adsorption [24]. Since adsorption is an exothermic process, it would be expected that an increase in temperature of the adsorbate-adsorbent system would result in decreased adsorption capacity. Thus, the adsorption of AFD leads to a decrease in the residual forces on the surface of adsorbent and hence causing a decrease in the surface energy of the adsorbent [25].

**Effect of adsorbent dosage:** The effect of RM and laccase modified-RM dosage on amount of AFD adsorbed was shown in Figure 7. The maximum amount of AFD adsorbed was 23.85 and 24.80 mg/g for AFD attained for adsorbent dose of 1g/50 cm<sup>3</sup> for RM and laccase modified-RM, respectively. Increase in adsorbent dosage increased the amount of dye removal, which is due to the increase in contact surface area of the adsorbent [26]. Increase in adsorption efficiency with increase in adsorbent dosage is attributed to the increase of active sites for adsorption of dye molecules. At very low adsorbent concentration, the adsorbent surface becomes saturated with the dye and the residual dye concentration in the solution is too high [27].

**Effect of initial dye concentration:** The effect of initial dye concentration on the adsorption was also studied at different concentrations of dye (1.25, 2.5, 5, 10, 20 and 25 mg/dm<sup>3</sup>) at initial pH value 5.0 and temperature 30 ± 1°C. The Figure 8 shows the effect of initial dye concentration on the amount of dye adsorbed. The amount





adsorbed was greater for higher initial dye concentration for RM and laccase modified-RM. The amount of AFD adsorbed, in equilibrium state, increased from 1.23 to 20.94 for RM and from 1.24 to 24.94 mg/g for laccase modified-RM when the initial dye concentration increased from 1.25 to 25 mg/dm<sup>3</sup>, respectively.

At higher initial concentrations, the resistance to mass transfer between the solid and aqueous phase is more easily overcome due to the driving forces, moreover the number of collisions between dye molecules and adsorbent increases, increasing the adsorption [28].

### Adsorption isotherms

**Langmuir adsorption isotherm model:** The Langmuir isotherm is derived on the assumption that adsorption occurs at specific homogenous sites within the adsorbent. The linear form of the Langmuir isotherm equation is given as:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (2)$$

(Where  $q_{\max}$  (mg/g) and  $b$  (dm<sup>3</sup>/mg) are Langmuir constants which are indicators of the maximum adsorption capacity and the affinity of the binding sites, respectively. They can be determined from a linear form of Eq. 3 (by plotting the  $C_e/q_e$  versus  $C_e$ ), represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{b q_{\max}} + \frac{C_e}{q_{\max}} \quad (3)$$

The values of  $q_{\max}$  and  $b$  were calculated from the slope and intercept of the Langmuir plot of  $C_e/q_e$  versus  $C_e$  from Figure 9a. The empirical constants  $q_{\max}$  and  $b$  for laccase modified-RM were found to be 233.33 mg/g and 134.67 dm<sup>3</sup>/mg (Table 2) respectively. The applicability of the linear form of Langmuir model to RM and laccase modified-RM was proved by the high correlation coefficients  $R^2$  (0.9576 and 0.9608, respectively) > 0.95. These suggest that the Langmuir isotherm provides a good model of the sorption system.

**Table 2:** Values of the Langmuir and the Freundlich adsorption isotherm models.

Langmuir adsorption model			Freundlich adsorption model		
Langmuir constants	RM	Laccase modified-RM	Freundlich constants	RM	Laccase modified-RM
$q_{\max}$ (mg/g)	250	333.33	$K_F$ (mg/g)	0.052	0.052
$b$ (dm <sup>3</sup> /mg)	123.25	134.67	$n$	0.599	0.615
$R^2$	0.9576	0.9608	$R^2$	0.9945	0.9697

**Freundlich adsorption isotherm model:** The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. It is described by applying the following equation:

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

Where  $K_F$  and  $n$  are the Freundlich constants related to the sorption capacity of the adsorbent (mg/g) and the energy of adsorption, respectively. They can be calculated in the following linear form;

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

$K_F$  and  $n$  values were calculated from the intercept and slope of the plot (Figure 9b). In the literature, it is pointed out that the parameters,  $K_F$  and  $n$  affect the adsorption isotherm. For RM and laccase modified-RM, based on the high correlation coefficients  $R^2$  (0.9945 and 0.9697 respectively) > 0.95, it has been deduced that Freundlich model better fitted to the experimental data (Table 2).

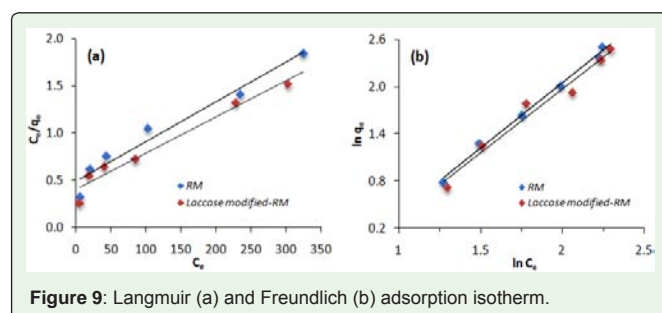
### Adsorption kinetic models

**The pseudo-first-order kinetic model:** The linearized form of pseudo-first-order kinetic model can be written as [29]:

$$\frac{1}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \quad (6)$$

Where  $k_1$  is the pseudo-first-order rate constant (min<sup>-1</sup>),  $q_t$  and  $q_e$  are the amounts of AFD adsorbed at time  $t$  and at equilibrium (mg/g). At different dye concentrations, the correlation coefficients and  $k_1$  were calculated for AFD adsorption from the linear plots of  $\log (q_e - q_t)$  versus  $t$  for RM and laccase modified-RM (Figure 10).

The results were presented in Table 3. The plots of Eq. 7 show lower correlation coefficient values and the  $q_e$ -cal values of pseudo-



**Table 3:** Kinetic parameters for the adsorption of AFD.

Initial AFD concentration (mg/dm <sup>3</sup> )	$q_e$ -exp (mg/g)	Pseudo-first-order rate equation			Pseudo-second-order rate equation		
		$k_1$	$q_e$ -cal (mg/g)	$R^2$	$k_2$	$q_e$ -cal (mg/g)	$R^2$
RM adsorbent 5 25 50	2.48	0.014	1.24	0.9265	0.82	2.19	0.9833
	14.2	0.033	13.67	0.9362	4.7*10 <sup>-3</sup>	19.49	0.9174
	19.4	0.038	13.65	0.9018	1.2*10 <sup>-3</sup>	21.37	0.9855
Laccase modified-RM adsorbent 5 25 50	2.48	0.034	1.66	0.8323	0.645	2.64	0.9636
	17.1	0.035	16.12	0.9573	2.7*10 <sup>-3</sup>	21.74	0.9404
	23.4	0.038	13.79	0.9476	5.72*10 <sup>-4</sup>	24.063	0.9927

first-order equation are found to be lower than the experimental one. This indicates that pseudo-first-order model is not suitable to describe kinetic data.

**The pseudo-second-order kinetic model:** The pseudo-second-order kinetics can be written as follows [22]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Where the equilibrium rate constant of pseudo-second-order model is  $k_2$  here (g mol<sup>-1</sup> min<sup>-1</sup>). This equation has been applied to the current study on AFD adsorption. At different dye concentrations, the correlation coefficients,  $q_e$  and  $k_2$  were calculated for AFD adsorption from the linear plots of  $t/q_t$  versus  $t$  for RM and laccase modified-RM (Figure 11). The results were presented in Table 3. The correlation coefficients of the pseudo-second order kinetic models are closer to unity and the calculated  $q_e$  values computed from pseudo-second-order equation show good agreement with experimental values. This indicates that the pseudo-second-order kinetic model is applicable for the adsorption of AFD onto RM and laccase modified-RM.

### Adsorption thermodynamics

The aim of thermodynamic study is to establish the thermodynamic parameters that can characterize the adsorption process of AFD onto the RM and laccase modified-RM. The adsorption capacity of laccase modified-RM adsorbent increased with increase in the temperature of the system from 293 to 303 K. Thermodynamic parameters such as change in free energy ( $\Delta G^\circ$ ) kJ/mol, enthalpy ( $\Delta H^\circ$ ) kJ/mol, and

**Table 4:** Thermodynamic parameters for the AFD adsorption.

Temperature (K)	Thermodynamic parameters		
	$\Delta G^\circ$ (kJmol <sup>-1</sup> )	$\Delta H^\circ$ (kJmol <sup>-1</sup> )	$\Delta S^\circ$ (Jmol <sup>-1</sup> )
RM adsorbent 293 298 303	-35150.1 -35750.3 -36350.6	24.58	120.05
Laccase modified-RM adsorbent 293 298 303	-33739.4 -34315.6 -34891.7	22.97	115.23

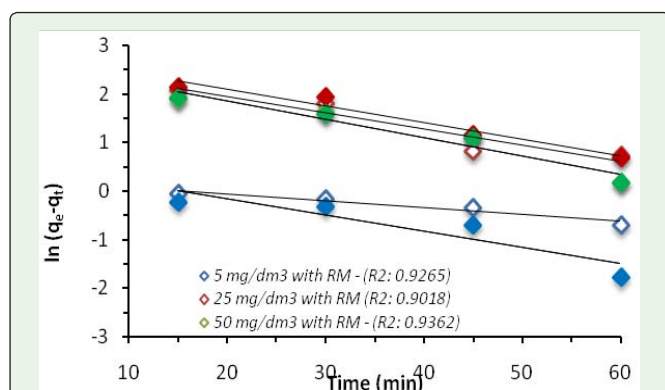
entropy ( $\Delta S^\circ$ ) J/Kmol were determined using the following equations [30]:

$$K_L = \frac{C_s}{C_e} \quad (8)$$

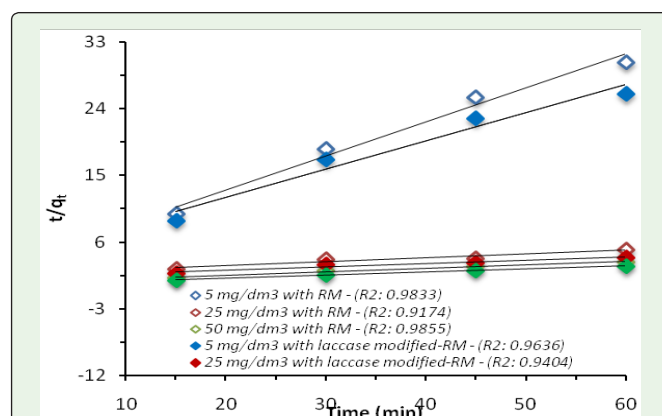
$$\Delta G^\circ = RT \ln K_L \quad (9)$$

$$\ln K_L = \left( \frac{\Delta S^\circ}{R} \right) - \left( \frac{\Delta H^\circ}{RT} \right) \quad (10)$$

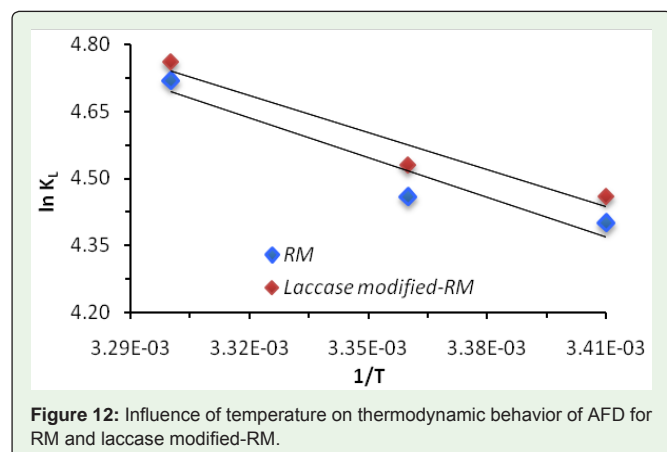
Where  $K_L$  is the equilibrium constant,  $C_s$  is the solid phase concentration at equilibrium (mg/dm<sup>3</sup>),  $C_e$  is the liquid phase concentration at equilibrium (mg/dm<sup>3</sup>),  $T$  is the temperature in Kelvin, and  $R$  is the gas constant.  $\Delta H^\circ$  and  $\Delta S^\circ$  values are obtained from the slope and intercept of plot  $\ln K_L$  against  $1/T$ . Van't Hoff plot of the temperature effect on adsorption of AFD onto the RM and laccase modified-RM was illustrate in Figure 12 and the observed thermodynamic values were summarized in Table 4.



**Figure 10:** Pseudo-first-order reaction for AFD adsorbed onto RM and laccase modified-RM adsorbents at different dye concentrations.



**Figure11:** Pseudo-first-order reaction for AFD adsorbed onto RM and laccase modified-RM adsorbents at different concentrations.



**Figure 12:** Influence of temperature on thermodynamic behavior of AFD for RM and laccase modified-RM.

The  $\Delta G^\circ$  values decrease with an increase in temperature, indicating an increased trend in the degree of spontaneity and feasibility of AFD adsorption. In the case of AFD adsorption onto RM and lacc(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>ase modified-RM, the values of Gibbs free energy of the process at all temperatures are negative. The negative value of  $\Delta G^\circ$  indicates the adsorption is favorable and spontaneous. The  $\Delta G^\circ$  values are found to decrease as the temperature increases in both dye-anion exchanger systems suggesting that higher temperatures make the adsorption easier [31]. For the RM and laccase modified-RM, the  $\Delta H^\circ$  and  $\Delta S^\circ$  have positive values. The positive values of  $\Delta H^\circ$  further confirm the endothermic nature of adsorption process. The positive values of  $\Delta S^\circ$  indicate good affinity of the anion exchangers for AFD molecules and show increase in the degree of freedom for the adsorbed species [32-35].

## Conclusion

In this study, red mud (RM) and laccase modified-RM were used as low-cost adsorbent materials and the suitability of the activated RM for adsorption of Acid Fuchsin dye (AFD) from aqueous solutions was investigated. The results indicate that RM and laccase modified-RM can be successfully used for the adsorption of AFD from aqueous solutions. The results showed that laccase modified-RM was more applicable for the AFD adsorption compared with RM. The pH, adsorbent dose, contact time and temperature affected the adsorption process. For the laccase modified-RM, the optimum values were obtained at pH 5, contact time of 45 min, temperature of 60°C and an adsorbent dose of 1 mg/dm<sup>3</sup>. The Freundlich equation was found to have the highest value of correlation coefficient compared with the Langmuir model. The kinetics of the adsorption of AFD reports to be pseudo second-order chemical reaction kinetics. Thermodynamic parameters including the Gibbs free energy, enthalpy and entropy changes indicated that the adsorption of AFD onto laccase modified-RM adsorbent was feasible, spontaneous and endothermic. Based on the results, RM and laccase modified-RM can be used as a relatively efficient and low cost adsorbent for the removal of AFD dye from aqueous solutions. However, the maximum adsorption capacity ( $q_{\max}$ ) values showed that laccase modified-RM was as a better adsorbent for remediation of AFD from aqueous solutions.

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