Adsorptive Removal of Acid Fuchsin Dye Using By-Product Silica Fume and Laccase-Modified Silica Fume

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ABSTRACT: *Silica fume, also known as micro silica, is a by-product of the reduction of high-purity quartz with coal in electric furnaces in the production of silicon and ferrosilicon alloys. This material and laccase-modified silica fume used as alternative low-cost adsorbent materials for dye removal from aqueous solutions. The silica fume was modified to maximize its adsorption capacity. For this purpose, the laccase enzyme was purified and immobilized on silica fume. Batch adsorption experiments have been performed as a function of pH, contact time, temperature, and adsorbent dosage. The equilibrium data were analyzed using Langmuir and Freundlich adsorption isotherms. The Langmuir adsorption model provided a better fit to the data. The kinetic data were evaluated with pseudo-first-order and pseudo-second-order kinetic models. The adsorption process undergoes pseudo-second-order kinetic as proved by the high value of R^2. The thermodynamic parameters such as free energy, enthalpy, and entropy were also determined. These parameters indicated that the adsorption of Acid Fuchsin dye onto silica fume and laccase-modified silica fume was a spontaneous, endothermic, and entropy-driven process. The results show that both of them, especially laccase-modified silica fume, can be used as alternative low-cost adsorbents for dye removal from aqueous colored solutions or effluents.*

KEYWORDS: *Acid Fuchsin dye; Silica fume; Dye removal; Adsorption isotherms; Adsorption kinetics Thermodynamic parameters.*

INTRODUCTION

The conventional treatment methods for dye removal, such as chemical coagulation, activated sludge, biodegradation, oxidation, membrane separation, adsorption, and photodegradation, have been extensively explored [13]. Among the physical and chemical processes, the adsorption the procedure is effective in producing high-quality effluent without the formation of harmful substances [14,15]. Ideal adsorbents should be highly efficient in the adsorption of pollutants, biodegradable and inexpensive. Untreated agricultural and industrial waste materials, which are

largely available and low in cost, have been used as adsorbents. Industrial wastes, such as metal hydroxide sludge [16], fly ash [17], bottom ash [18], silica fume (SF) [19], blast furnace slag [20] and red mud [21,22] have been utilized to remove reactive dyes from effluent [15].

One type of solid waste material, SF is a by-product of a silicon material or silicon alloy metal factories. Currently, it is widely used in concrete or mortar as an admixture [23,24]. The investigations show that SF waste material can be successfully used in geotechnical applications. The SF was modified with laccase prepared from Russulaceae (*Lactarius volemus*). The laccase is an enzyme and belongs to those enzymes, which have innate properties of reactive radical production. It uses oxygen and produces water as a by- product. It can degrade a range of compounds including phenolic and non-phenolic compounds. It also has the ability to detoxify a range of environmental pollutants [25].

The objective of this work is to explore the potentials of SF and LM-SF as low cost adsorbents for the removal of dye from aqueous solutions. The influences of adsorption parameters such as solution pH, contact time, temperature, and adsorbent dosage on the adsorption performance of SF and LM-SF were investigated. Adsorption isotherm, kinetic, and thermodynamic studies have been performed to describe the adsorption process.

EXPERIMENTAL SECTION
AFD dye material

Dye material AFD used in this study or 2-amino-5-[(4-amino-3-sulfophenyl)(4-amino-3-sulfo-2,5-cyclohexadiene-1-ylidene)-   methyl]   -3-methylbenzenesulfonic acid, is an organic dye. It was purchased from Biokim Co. Ltd. (Erzurum, Turkey). Its molecular structure and some characteristics are summarized in Table 1. This organic dye is also called as Acid Violet 19, Fuchsin Acid, or Rubin S and is widely used for staining procedures [26,27] and other purposes [28,29].

SF by-product

SF, also known as micro silica, is a by-product of the reduction of high-purity quartz with coal in electric furnaces in the production of silicon and ferrosilicon alloys. It is also collected as a by-product in the production of other silicon alloys such as ferrochromium, ferromanganese, ferromagnesium, and calcium silicon. SF has been obtained from a Ferro-Chromate Factory in Antalya (Turkey). The photograph of SF powder, the SEM of SF, and the XRD pattern of SF are shown in Fig. 1. Its physical properties and chemical components [30,31] are given in Table 2.

Laccase enzyme material

Lactarius volemus, a species of mushroom in the family Russulaceae, 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, *Lactarius volemus* has antioxidant, antiradical, and antimicrobial activities [32,33].

Material characterization

In this study, the Fourier Transform Infrared (FT-IR) Spectroscopy analyses were carried out to identify functional groups and molecular structures in the SF and LM-SF adsorbents. The FT-IR spectra were recorded on a Perkin-a Perkin-Elmer GX2000 FTIR spectrometer. The spectrum of the adsorbent was measured within the wave number range of 4000 and 400 cm^{-1}. In addition, a Scanning Electron Microscope (SEM) was used to examine the surface of the adsorbents before and after the adsorption process. Images were magnified 5000 times by a JEOL JSM-6400 model SEM.

Preparation of laccase enzyme

For the preparation of the laccase enzyme, the *Lactarius volemus* (20 g) were ground in liquid N_2 and then homogenized in a blender with 50 mL of 1M KCl by shaking and centrifuged at 5000 rpm for 60 min. For the purification of the laccase enzyme, the enzyme was partially purified by precipitation in $(NH_4)_2SO_4$ and then ion-exchange chromatography on diethylamino ethyl cellulose (DEAE)-Sephadex was used. Solid $(NH_4)_2SO_4$ was added to the supernatant to increase the concentration of $(NH_4)_2SO_4$ from 40% the fraction to 60%. After mixing in an ice-bath for 1 h with magnetic stirring, it was centrifuged (10000 rpm, 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

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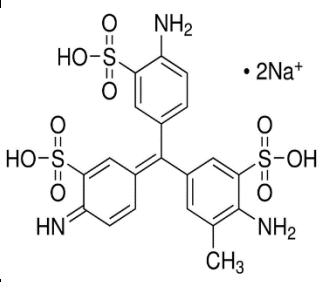***Table 1: The structure and some characteristics of dyeused in experimental study.***

Dye name	Chemical Structure	Empirical formula	Molecular Weight	Color Index Number	λ_{max}
AFD		$C_{20}H_{17}N_3Na_2O_9S_3$	585,54 g mol^{-1}	42685	545 nm

Table 2: Physical properties and chemical constituents of SF.

Properties	Value	Constituents	Value
Particle size (typical) (μm)	<1	SiO_2(%)	85-97
Density (Mg/m3)	2-2.5	Al_2O_3 (%)	1-3
Specific gravity	2.22	Fe_2O_3 (%)	0.5-1
Specific surface area (m^2/g)	3.05	CaO(%)	0.8-1.2
		MgO(%)	1-2
		Ignition (%)	8.44
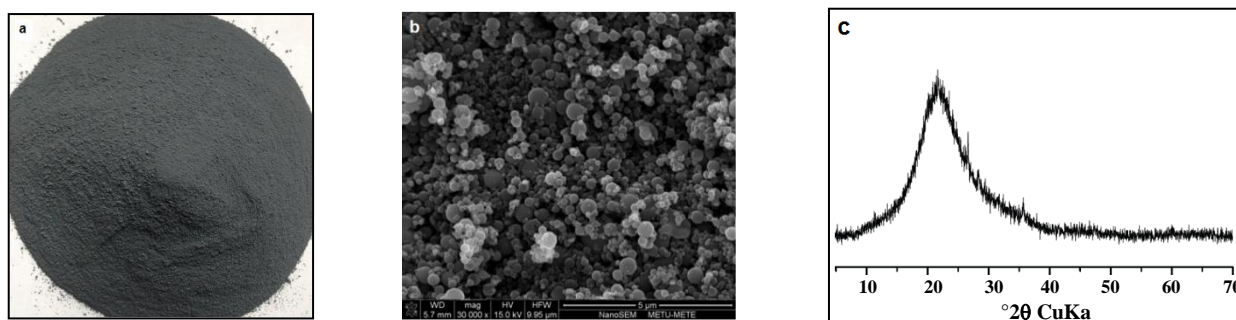
Fig. 1: The SF image (a), the SEM image of SF (b) and the XRD pattern of SF (c).

against the same buffer [34]. After the ammonium sulfate precipitation, the dialyzed suspension was subjected to anion-exchange chromatography on a DEAE-Sephadex fast flow column pre-equilibrated with 0.02 M acetate buffer with a pH of 5.0. The activity was measured by using ABTS as the assay substrate. The active fractions from each peak were pooled and stored at 4°C. To determine of laccase enzyme activity, the reagent 2,2´azino-di-[3-ethyl-benzothiazolin-sulfonate] (ABTS) was used as a substrate for the spectrophotometric determination of laccase activity [35,36]. After the purification of the enzyme, SDS polyacrylamide gel electrophoresis was performed, carried out in 3 and 10% acrylamide concentrations for the stacking and running gels [37]. Gels were stained in 0.1% Coomassie Brilliant Blue R-250 in 50% methanol, 10% acetic acid, and 40% distilled water for 1.5 h. It was de-stained by washing with 50% methanol, 10% acetic acid, and 40% distilled water several times. The standard protein solution was added to the column equilibrated with the buffer (0.05M Na$_2$HPO4,

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1mM dithioerythritol, pH: 7) until the absorbance was zero at 280 nm. The purified laccase enzyme was added into the column separately and then eluted under the same conditions. The flow rate through the column was 20 mL/h.

Modification of SF with laccase

To obtain LM-SF adsorbent material, the laccase enzyme obtained from Russulaceae (*Lactarius volemus)* was purified by using saturated precipitate $(NH_4)_2 SO_4$, DEAE-cellulose and immobilized on SF. The SF, thoroughly washed with distilled water until it became neutral, was wet sieved through a 200-mesh screen. The solid fraction was washed five times with distilled water following the sequence of mixing, settling, and decanting. The last suspension was filtered, and the residual solid was then dried at 105 °C, ground in a mortar, and sieved through a 200-mesh sieve. 1 gram of SF sample was shaken with 10 mL (5 mg protein/mL) laccase from Russulaceae (*Lactarius volemus)* solution for approximately 1 h, and then, the separated particles were stored. The LM-SF obtained was used for the study of AFD adsorption from aqueous solution.

Modification of SF with laccase

0-40 $ngmL^{-1}$ of AFD according to the general procedure. The amount of dyes adsorbed at equilibrium was calculated from the following mass balance equation [21]:

$$Q_e = \frac{(C_0 - C_e) V}{m} \tag{1}$$

Where Q_e (mg g^{-1}) is the amount of dye adsorbed per gram of adsorbent at equilibrium, C_0 (mg/L) is the initial concentration of dye in the solution, C_e (mg/L) is the concentration of dye at equilibrium, V (L) is the volume of the solution, and m (g) is the mass of the adsorbent used.

Adsorption isotherms

The studies of adsorption isotherms can describe how the adsorbates interact with adsorbents, which is the most important parameter for designing the desired adsorption system. In the current study, Freundlich and Langmuir isotherm models were used to describe the adsorption process [38]. The Langmuir isotherm is derived on the assumption that adsorption occurs at specific homogenous sites within the adsorbent [39]. 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 [40,41]. These models are described by the following equations;

Langmuir isotherm model:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}} + \frac{1}{Q_{max} K_L} \tag{2}$$

Freundlich isotherm model:

$$\ln Q_e = \ln K_F + b_F \ln C_e \tag{3}$$

where Q_{max} (mg g^{-1}) is the maximum adsorption capacity of the adsorbent, K_L (L mg^{-1}) is the Langmuir adsorption constant, K_F is the Freundlich constant and b_F is a constant depicting the adsorption intensity.

Adsorption kinetics

In this study, two well-known kinetic models were used to fit the adsorption date, namely pseudo-first-order and pseudo-second-order models [38, 42] to study the time dependence of the adsorption process and further investigate the adsorption mechanisms.

Pseudo-first-order equation:

$$\ln (Q_e - Q_t) = \ln Q_e + k_1 t \tag{4}$$

Pseudo-second-order equation:

$$\frac{t}{Q_t} = \left(\frac{1}{k_2 Q_e^2} \right) + \frac{t}{Q_e} \tag{5}$$

where Q_t (mgg^{-1}) is the amount of dye adsorbed at the

time t (min), k_1 (min^{-1}) is the pseudo-first-order rate constant, k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order rate constant.

Adsorption thermodynamics

Considerations of the thermodynamic properties of the adsorption process is necessary to conclude whether the process is spontaneous or not [43]. The aim of thermodynamic study is to establish the thermodynamic parameters that can characterize the adsorption process of AFD onto the SF and LM-SF. In this study, the adsorption capacity increased with an increase in the temperature of the system from 293-303 K. Thermodynamic parameters such as change in free energy ($\Delta G°$) kJ/mol, enthalpy ($\Delta H°$) kJ/mol, and entropy ($\Delta S°$) J/kmol were determined using the following equations [44]:

$$K_L = \frac{C_s}{C_e} \tag{6}$$

$$\Delta G° = -RT \ln K_L \tag{7}$$

$$\ln K_L = \left(\frac{\Delta S°}{R}\right) + \left(\frac{\Delta H°}{RT}\right) \tag{8}$$

where K_L is the equilibrium constant, C_s is the solid phase concentration at equilibrium (mg/L, C_e is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin, and R is the gas constant.

RESULTS AND DISCUSSION
Characterization study
FT-IR study

The FT-IR spectrums of SF and LM-SF adsorbents were illustrated in Figs. 2a and 2b. The peaks observed around the 470, 610, 864, 1100, and 1630 cm^{-1} wavelengths form characteristic peaks of SF. The asymmetric vibrations belonging to the Si-O structure in SF is appearing around the 470, 610, and 864 cm^{-1} wavelengths. The Si-O-Si structure is observed as a board peak in the form of asymmetric tension vibrations and at the 1109 cm^{-1} wavelength. The water adsorbed by SF is in the O-H-O structure, at a wavelength around 1613-1630 cm^{-1} and in the form of a bending vibration. Also, the water connected to the hydrogen bridge and SF structure was determined with a peak around the 3442 cm^{-1} wavelength [45,46]. It is shown that there is no significant change in the functional groups of SF and LM-SF after adsorption

of AFD on the adsorbents when AFD were treated with SF and LM-SF. It was concluded that AFD did not damage the functional groups of the adsorbents.

After adsorption of AFD to the surface of the LM-SF, the presence of various functional groups of azo dye, such as amine and alkene, was determined from the bands at 1213 and 1016 cm^{-1} of the FTIR spectrum. In addition, the C-H and O-H bonds were determined at 1280 and 3420 cm^{-1} wavelength respectively.

SEM study

The SEM is widely used to study morphological features and surface characteristics, and is also useful for determining particle shape, porosity, and appropriate size distribution of adsorbent materials [47,48]. Fig. 3 shows the SEM images of SF (Fig 3a), the AFD adsorbed SF (Fig. 3b), and the AFD adsorbed LM-SF (Fig. 3c). After AFD adsorption, a significant change is observed in the structure of the adsorbent, and it is clear that SF and LM-SF both have rough surfaces with heterogeneous pores and cavities [49]. This indicates that there is a good possibility for the AFD to be trapped and adsorbed onto the surface of the SF and LM-SF adsorbents [50].

Adsorption study
Effect of pH on AFD removal

The pH of an aqueous solution is an important parameter during the adsorption process, since it can affect the surface properties of adsorbents. In addition, the dissociation degree of ionic dyes in an aqueous solution is related to the solution's pH, which in turn affects the degree of dye adsorption onto adsorbents [51,52]. The effect of the initial pH on the removal of the AFD onto SF and LM-SF is shown in Fig. 4a. The optimum pH, at which the maximum removal occurred, was obtained at pH 4 and pH 5 for SF and LM-SF, respectively. The observed relatively low adsorption rate of the dye on SF and LM-SF at acidic pH values may be because the surface charge became positively charged, thus making (H$^+$) ions compete effectively with dye molecules causing a decrease in the amount of dye adsorbed. As the pH of the adsorption solution was increased, the negative charges on the surface increased. This attracted the positively charged functional groups located on the dye. Acid fuchsin in the structure of sulfate and amine groups in the unconsolidated electrons in acidic environment protonated AFD surface is bonded
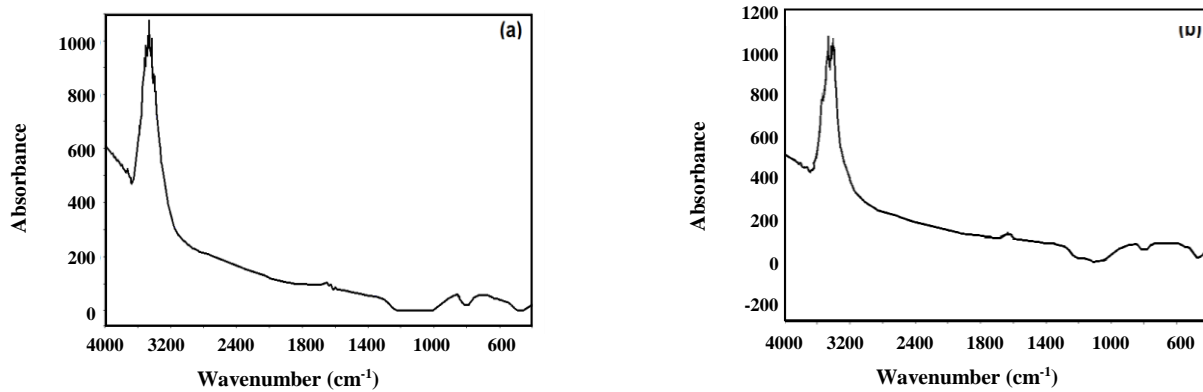
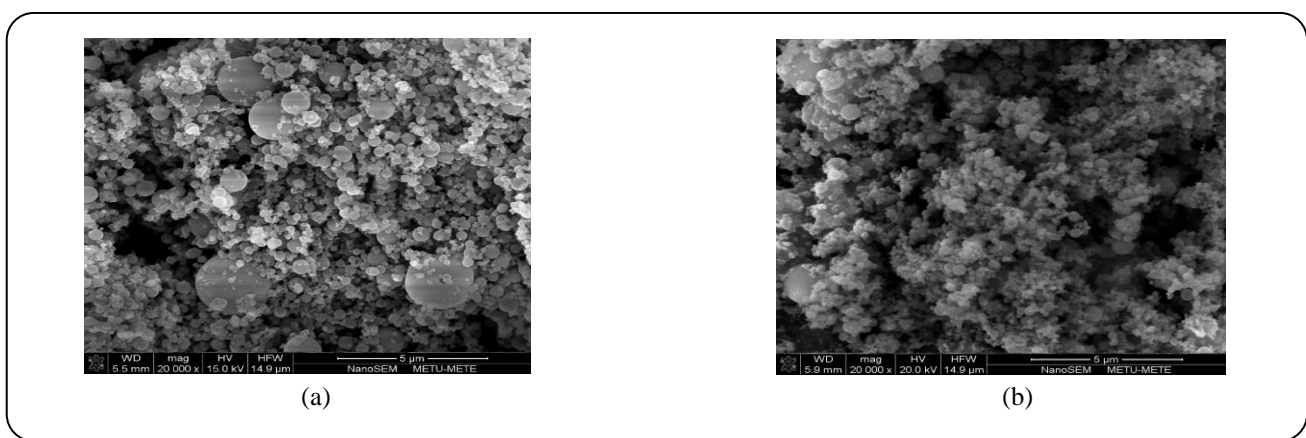*Fig. 2: FT-IR spectrums of SF (a) and LM-SF (b) adsorbents.*

Fig. 3: The SEM images of SF (a) and AFD loaded SF (b) and AFD loaded LM-SF.

with hydrogen bonds. They are also bound to the $-SO_3^-$ groups on the surface of the AFD by the (+) groups on the LM-SF surface in acidic medium [53,54]. It was determined that the surface of AFD SF and LM-SF was maximally adsorbed at pH 5. However, it has been determined that it is adsorbed on the surface of LM-SF with pH change and dosing differentiation.

Effect of contact time on AFD removal

The contact time between adsorbent and adsorbate species plays a significant role in the removal of pollutants from water and wastewater by means of adsorption at a particular temperature and pH. A rapid removal of dye pollutant and establishment of equilibrium in a short period of time signifies the efficiency of the adsorbent for its use in wastewater treatment [55]. In this study, the effect of contact time on the removal of AFD onto SF and LM-SF was investigated, and results were illustrated

in Fig. 4b. As can be seen from Fig. 4b, AFD adsorption was very fast initially and then slowly reached the adsorption equilibrium. This can be the consequence of the fact that a large number of free surface sites are available for adsorption during the initial stage and, afterwards, the remaining free surface sites resistant to occupation because of repulsive forces between the phases [56]. The rapid absorption and equilibrium establishment in a short period of time are related to the efficacy of the adsorbent, especially for wastewater treatment [57,58]. The rapid removal of the dye pollutant has significant practical importance as it facilitates smaller reactor volumes ensuring efficiency and economy [21, 59].

Effect of temperature on the AFD removal

The temperature of the adsorption process is another factor influencing the efficacy of the adsorption systems. It known to have a profound effect on various chemical
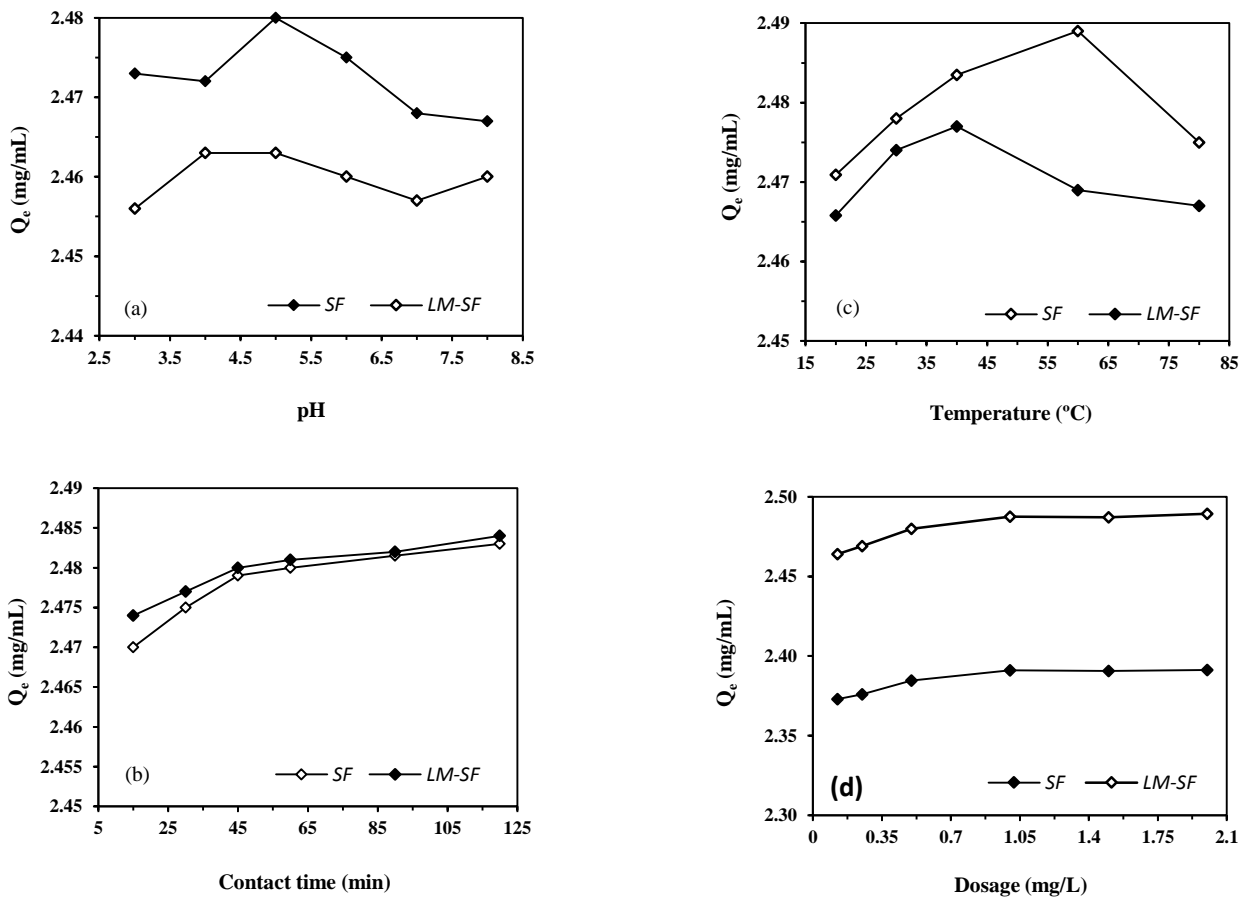
Fig. 4: Effect of pH (a), contact time (b), temperature (c) and dosage (d) on the removal of AFD onto SF and LM-SF (pH:5.0; 45 min; 40 °C temperature and 1mg/L dosage).

processes is one of the most important controlling parameters in adsorption. It affects the adsorption rate by altering molecular interactions and solubility of adsorbate [60,61]. In this research, the effect of temperature on AFD adsorption onto SF and LM-SF adsorbents was studied in the temperature range 20 to 80ºC and the results were illustrated in Fig. 4c. As shown in Fig. 4c, increasing of temperature from 20 to 40ºC and 20 to 60ºC lead to elevation of adsorbed AFD from 2.465 to 2.477mg/mL for SF and LM-SF, respectively. However, temperature increase from 40 to 80ºC and 60 to 80ºC causes the decreasing of Q_e to 2.467and 2.475 mg/mL for SF and LM-SF, respectively. These results show that, although the enhancing effects of temperature on AFD adsorption is not important, inhibition effects of the higher temperatures are significant and should be considered as an operational parameter in economical equipment's [62].

Effect of adsorbent dosage on the AFD removal

Adsorbent dosage is a parameter that needs to be optimized to maximize the interactions between dye molecules and adsorption sites of adsorbents in the solution, as well as being important for an economical wastewater treatment process [52]. The effect of the adsorbent dosage was studied by varying the adsorbent amounts from 0.125 to 2.0 mgmL[-1]. The effect of SF and LM-SF dosage on amount of AFD adsorbed was shown in Fig. 4d. As can be seen from Fig. 4d, AFD adsorption is very fast initially and then slowly reached the sorption equilibrium. The maximum amount of AFD removal was 2,388 and 2,486 mg/mL for AFD attained for an adsorbent dose of 1 mg/L for SF and LM-SF, respectively. As it can be seen, adsorption of AFD increased with increasing the amount of mesoporous adsorbent and remained almost constant after increasing up to a certain limit.

This can be attributed to increased adsorbent surface area and availability of more adsorption sites [55, 63,64].

Adsorption performance

The SF and LM-SF were explored as adsorbents for the removal of AFD from aqueous solution. The adsorption characteristics of these adsorbents were displayed in Fig. 5. For the adsorption study, 1 g SF and LM-SF adsorbents were added to the AFD solution (50 mg/L) and then exposed to the adsorption process for 60 min. Fig. 5 includes the photographs of AFD solution (50 mg/L) before adsorption (a) and after adsorption with SF (b) and LM-SF (c), respectively. The experimental results show that the AFD concentration of samples decreased from 50.00 to 21.20 mg/mL and from 50.00 to 15.89 mg/mL in the AFD solutions, respectively. It was also determined that LM-SF is a more effective material for AFD adsorption (Fig. 5). It is clearly shown that the AFD solution becomes almost clear after the adsorption process. This indicates that SF and LM-SF are effective adsorbent materials. Compared with the SF modified-AFD solution, the LM-SF modified-AFD better represents the colorless of the AFD adsorption.

Adsorption isotherms

The values of Q_{max} and K_L were calculated from the slope and intercept of the Langmuir plot of C_e versus C_e/q_e from Fig. 6 and the Langmuir parameters were presented in Table 3. The isotherm was found to be linear entire concentration range studied with good linear correlation coefficients (R^2= 0.9831 and 0.9885) for SF and LM-SF, showing that data correctly fit the Langmuir model in both cases.

Similarly, the value of $\ln Q_e$ against $\ln C_e$ according to the experimental isotherm data was shown in the inset of Fig. 6. The calculated values of Freundlich parameters were illustrated in Table 3. The corresponding R^2 for adsorption of AFD onto SF and LM-SF adsorbents were 0.9785 and 0.9844, respectively. Compared with the Freundlich isotherm model, the Langmuir isotherm model better represents the equilibrium adsorption of AFD onto SF and LM-SF, suggesting that the adsorption process is the monolayer coverage of the dye on the surface of SF and LM-SF adsorbent [38].

Adsorption kinetics

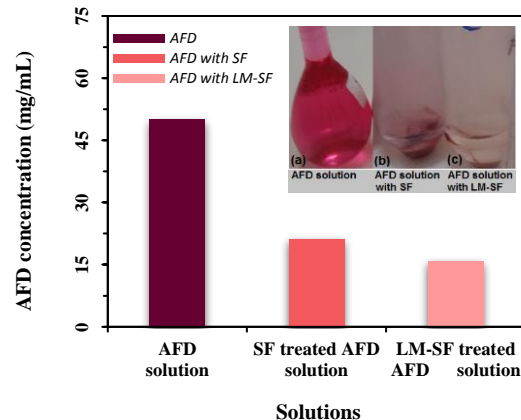At different concentrations such as 5, 25 and 50 mg/L,

Fig. 5: The effect of SF and LM-SF on the AFD concentration with the photographs of ADF solution (a) SF treated AFD solution (b) and LM-SF treated AFD solution (c).
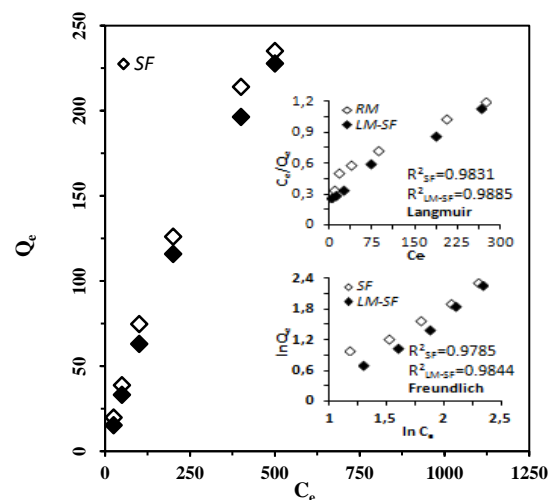

Fig. 6: Adsorption isotherms for the adsorption of AFD onto SF and LM-SF. The inserts: the values of $\ln Q_e$ against $\ln C_e$ based on the Freundlich isotherm model and the linear dependence of C_e/Q_e on C_e based on the Langmuir isotherm model.

the correlation coefficients and k_1 were calculated from the linear plots of $\ln(Q_e-Q_t)$ vs. t for SF and LM-SF adsorbents (Fig. 7). For pseudo-first-order model, the correlation coefficients (R^2) for SF and LM-SF adsorbents range from 0.9572 to 0.9901 and from 0.9597 to 0.9978 (Table 4), respectively. The high correlation coefficients suggest that this model is a suitable model for the AFD removal by SF and LM-SF adsorbents.

In similarly, for the pseudo-second-order models, linear plots of t/Q_t against t give high R^2 values range from 0.9663 to 0.9951 and from 0.9939 to 0.9997 for SF and

Table 3: Values of the Langmuir and the Freundlich adsorption isotherm models

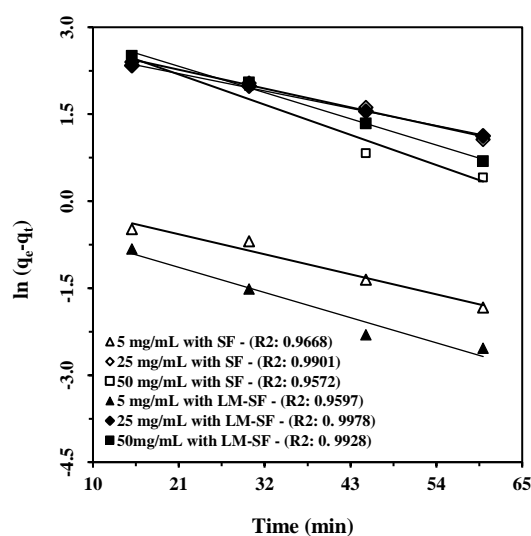| Langmuir adsorption model			Freundlich adsorption model		
Langmuir constants	SF	LM-SF	Freundlich constants	SF	LM-SF
Q_{max}	500	333,33	K_F	0,258	0,38
K_L	216,50	90,33	b_F	0,802	0,630
R^2	0,9831	0,9885	R^2	0,9785	0,9844

Fig. 7: Pseudo-first-order reaction for AFD adsorbed onto SF and LM-SF at different concentrations.
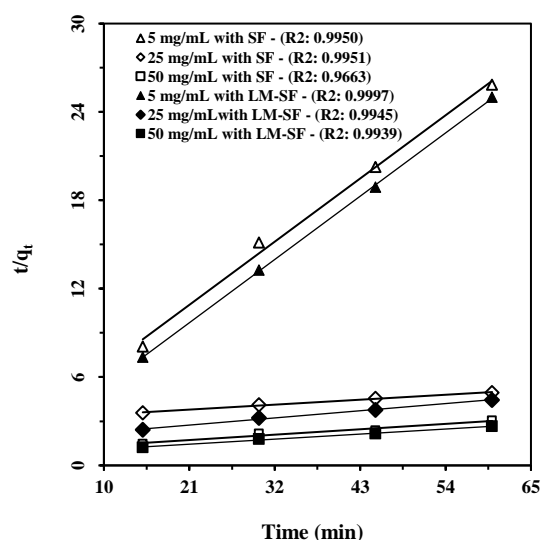

Fig. 8: Pseudo-second-order reaction for AFD adsorbed onto SF and LM-SF at different concentrations.

LM-SF adsorbents (Fig. 8, Table 4), respectively. The very high correlation coefficients suggest that the pseudo-second-order model is a suitable model for the dye removal by SF and LM-SF adsorbents, respectively.

Compared with for the pseudo-first-order model, the pseudo-second-order model is closer to unity and the calculated Q_e values computed from pseudo-second-order equation show very good agreement with experimental values. This indicates that the pseudo-second-order kinetic model is more applicable for the adsorption of AFD onto SF and LM-SF adsorbents.

Adsorption thermodynamics

The ΔG^o change indicates the degree of spontaneity of the adsorption process. For significant adsorption to occur, the free energy changes ΔG^o of adsorption must be negative [65]. In this study, the aim of the thermodynamic study is to establish the thermodynamic parameters that can characterize the adsorption process of the AFD onto SF and LM-SF adsorbent materials. The influence

of temperature on thermodynamic behavior of AFD adsorption by SF and LM-SF adsorbents was illustrated in Fig. 9 and the observed values of the thermodynamic parameters were given in Table 5.

It is seen from Table 5 that the $\Delta G°$ has negative values whereas the $\Delta H°$ and the $\Delta S°$ have positive values. The negative values of the $\Delta G°$ indicate that the adsorption is favorable and spontaneous. The positive values of the $\Delta H°$ further confirm the endothermic nature of the adsorption process. The positive values of the $\Delta S°$ indicate good affinity of the anion exchangers for AFD molecules and show an increase in the degree of freedom for the adsorbed species [66,67]. The positive value of the $\Delta S°$ suggests increased randomness at the solid/solution interface occurs in the internal structure of the adsorption of the AFD onto the SF and LM-SF adsorbents [67].

CONCLUSIONS

In this study, the SF and LM-SF were used as low-cost absorbent materials and the suitability of the adsorption

Table 4: Kinetic parameters for the adsorption of AFD onto SF and LM-SF.

Initial AFD concentration (mg/L)	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
SF absorbent							
5	2,48	0,0314	1,094	0,9668	0,41	2,56	0,9950
25	15,0	0,03	17,95	0,9901	$2,5*10^{-3}$	32,79	0,9951
50	21,1	0,047	24,05	0,9578	$1,09*10^{-3}$	30,12	0,9663
LM-SF absorbent							
5	2,48	0,039	0,732	0,9590	0,226	2,56	0,9997
25	16,6	0,027	15,96	0,9972	$3,55*10^{-3}$	22,57	0,9945
50	24,6	0,041	24,29	0,9927	$7,7*10^{-4}$	32,05	0,9939

Table 5: Thermodynamic parameters for the AFD dye adsorption by SF and LM-SF.

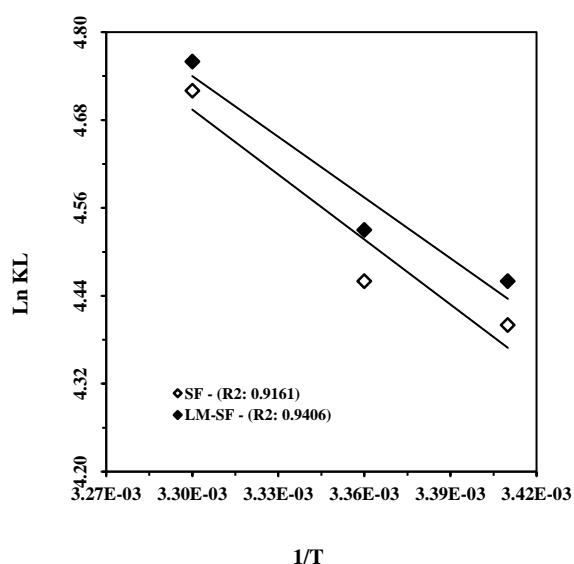| Temperature (K)	Thermodynamic parameters		
	ΔG^o (kJmol^{-1})	ΔH^o (kJmol^{-1})	ΔS^o (Jmol^{-1})
SF absorbent			
293	-43231,3		
298	-43970,2	32,470	147,66
303	-44708,5		
LM-SF absorbent			
293	-51067,4		
298	-51939,4	40,697	174,43
303	-52811,6		

Fig. 9: Influence of temperature on thermodynamic behavior of AFD adsorption by SF and LM-SF adsorbents.

of AFD molecules from aqueous solutions was investigated. The results of different experiments showed that SF being by-product of the silicon and ferrosilicon alloy production and LM-SF modified with laccase prepared from Russulaceae (*Lactarius volemus)* have the ability to absorb the AFD from aqueous solutions. The findings obtained from the batch adsorption experiments show that different variables such as pH, contact time, temperature and adsorbent dose influenced the adsorptive quantity. It is seen that the adsorption process is to be pH dependent and the optimum pH is < 5. The adsorption process has nearly reached equilibrium in 40 and 60 min for SF and LM-SF adsorbents, respectively. The optimum adsorbent dose is 1 mg/mL for both adsorbents. The Langmuir adsorption isotherm model is found to have the highest value of R^2 compared with the Freundlich model. The adsorption kinetics of AFD adsorption onto the SF and LM-SF indicate that the pseudo-second-order chemical reaction

kinetics is more suitable for the adsorption process. Thermodynamic parameters such as $\Delta G°$, $\Delta H°$, and $\Delta S°$ indicate feasible, spontaneous, and endothermic AFD adsorption from aqueous solutions. Based on the results, SF and LM-SF can be used as a relatively efficient and low-cost adsorbent for the removal of AFD from aqueous solutions.

Acknowledgments

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