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Green Removal of phenolic azo dye from aqueous solutions using rice straw fly ash

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Abstract

The present adsorption of phenolic azo dye onto rice straw fly ash (RSFA) from aqueous solutions was investigated, in which the influence of solution pH, contact time, concentration of adsorbate, adsorbent dosage and temperature were investigated. More than 85 % removal efficiency was obtained within 50 min. at an adsorbent dose of 0.05 g for initial dye concentration of 30-100mg/L at pH 2. The experimental equilibrium data were analyzed using two common adsorption models: Langmuir and Freundlich. The results revealed that Freundlich isotherm fits the experimental results well.Kinetic analysis was conducted using pseudo-first-order and pseudo-second-order models. The activation energy of adsorption was also evaluated and found to be +17.68 kJ.mol^{-1} indicating that the adsorption is physisorption. All ΔG^o values were negative; the $\Delta H^o$and ΔS^o values of RSFA were -19.78 kJ.mol^{-1} and 0.039 J.mol^{-1}.K^{-1}, respectively, indicating that the adsorption was feasible, spontaneous and exothermic process in nature.

Keywords: Adsorption, Phenolic azo dye, Rice straw fly ash,Thermodynamics

1. Introduction

The colored materials and dyes toconstitute the focus of many environmental concerns because of their non-biodegradable and polluting nature. Dyes are an important class of pollutants which came in large amounts from textile, dyeing, paper and pulp, tannery and paint industries [1]. Therefore, these industrial effluents must be treated before discharge. Currently, much attention has been paid to the removal of dyes from industrial wastewater [2]. Various treatment methods, including physical, chemical and biological schemes have been developed to remove dyes from wastewater [3]. Some of the applied techniques for the treatment of dye contaminated wastewaters are flocculation, coagulation, precipitation, adsorption, membrane filtration, electrochemical techniques, ozonation and fungal decolorization [4-6]. Among them, adsorption has been recognized as a promising technique due to its high efficiency, simplicity of design, ease of operation as well as the wide suitability for diverse types of dyes [7]. Many studies have been conducted about the sorption of phenolic compounds by polymeric adsorbents [8-11]. The Egyptian Environmental Protection Agency regarded rice straw fly ash adsorption as the best available technology for the removal of organic contaminants limited in the environmental regulations. In Egypt, rice straw is an easily available agricultural waste material, produced in large quantities as a by-product of rice milling and create potential environmental problems. The waste products which are the main contributors to biomass burning is wheat residue and rice straw. The disposal of rice straw by open-field burning frequently causes serious air pollution, hence new economic technologies for rice straw disposal and utilization must be developed [12-14]. In this study phenolic azo dye was selected a model pollutant onto rice straw fly ash as a waste adsorbent. Effects of different parameters such as initial adsorbate concentration, adsorbent dosage, contact time, solution pH and temperature were studied. Both Langmuir and Freundlich adsorption isotherms were applied to the experimental results and thermodynamic parameters were also calculated.

2. **Experimental**

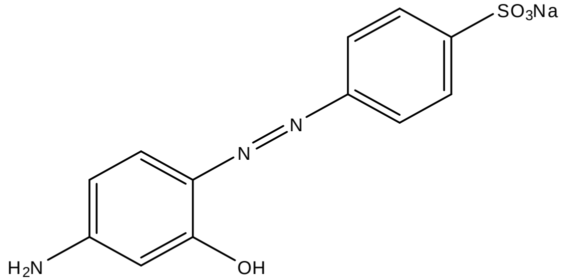
2.1. *Physical measurements*

IR spectrum of rice straw fly ash (KBr discs, 4000-400 cm^{-1}) by Jasco-4100 spectrophotometer was obtained. The SEM results of the RSFA sample before and after the adsorption processes were obtained using (JEOL-JSM-6510 LV) scanning microscope to observe surface modification. UV-visible spectrophotometer (Perkin-Elmer AA800 Model AAS) was employed for absorbance measurements of samples. An Orion 900S2 model digital pH meter and a Gallenkamp Orbital Incubator were used for pH adjustment and shaking, respectively. N_2 adsorption/desorption isotherm on RSFA at 77 K was measured on a Quantachrome Nova Instruments version 10, from which the Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore volume were calculated.

2.2.Phenolic azo dye

Phenolic azo dye used in this study was prepared by the same method described previously [15]. The dye information was presented in Table 1. A stock solution of 1000 mg/L was prepared by dissolving accurately weighed amounts of phenolic azo dye in separate doses. The desirable experimental concentrations of solutions were prepared [14] by diluting the stock solution with bidistilled water when necessary.

Table 1. Properties of the adsorbate (phenolic azo dye) used in the study

Parameter	**Characteristic**
Characteristic	Phenolic azo dye
Type color	Anionic
Chemical formula	$C_{12}H_{10}N_3NaO_4S$
Molecular weight (g/mol)	315.28
Wavelength of maximum absorption (nm)	437
Molar extinction coefficient, ε595 (M^{-1} cm^{-1})	29900
Chemical structure of color	

2.3. *Preparation of rice straw fly ash*

Rice straw fly ash (RSFA)as adsorbent was collected from Tammy Amdid, Dakahlia, EgyptBio Gas Factory[14]. The concept is based on the burning of waste rice straw in a special incinerator at the temperature of 1000-1200 °C. During the burning process the hydrocarbons are converted to carbon oxides, hydrogen, methane, propane and other gases. The carbon waste was left to cool down. In our laboratory, the fly ash made from rice straw (RSFA) was crushed, ground and sieved through a 170 µm sieve and washed several times with bidistilled water. The adsorbent sample was dried at 120°C for 48 h. Preserved in the desiccators over anhydrous $CaCl_2$ for further use. FT-IR adsorption peaks are: IR (KBr) (ν cm^{-1}): 3397 (-SiOH or -OH), 1585 (C=O), 1195 (Si-O-Si) and 792 (Si-H) cm^{-1}[16].

2.4.Adsorption experiments

Batch adsorption studies were carried out by shaking 100 ml conical flasks containing 0.05 g of (RSFA) and 25 mL of dye solution of the desired concentration with adjusted pH on an orbital shaker machine at 200 rpm at 25 ^{o}C. The solution pH was adjusted with 0.1 mol/L HCl and 0.1 mol/L NaOH solutions. At the end of the adsorption period, the supernatant solution was separated by centrifugation at 200 rpm for 10 min. Then the concentration of the residual dye was determined spectrophotometrically by monitoring the absorbance at 437 nm for dye using UV–Vis spectrophotometer. Percentage of phenolic azo dye removal was calculated using eq. (1):

$$R = 100\,(C_0 - C_t) / C_0 \qquad (1)$$

where C_0 (mg/L) and C_t (mg/L) are dye concentration initially and at time t, respectively. For adsorption isotherms, dye solutions different concentrations (30–100 mg/L) were agitated with known amounts of adsorbents until the equilibrium was achieved. Equilibrium adsorption capacity, q_e (mg dye per g adsorbent) was calculated from the following eq. (2):

$$q_e = V\,(C_0 - C_t) / W \qquad (2)$$

where C_t (mg/L) is the dye concentration at equilibrium, V (L) is the volume of solution and W (g) is the weight of adsorbent.

The procedures of kinetic experiments were identical with those of equilibrium tests. At predetermined moments, aqueous samples (5 mL) were taken from the solution, the liquid was separated from the adsorbent and concentration of dye in solution was determined spectrophotometrically at a wavelength of 437 nm. The amount of dye adsorbed at time t, q_t (mg/g) was calculated by following eq. (3):

$$q_t = V\,(C_0 - C_t) / m \qquad (3)$$

where C_0 (mg/L) is the initial dye concentration, C_t (mg/L) the dye concentration at any time t, V (L) the volume of the solution and m (g) is the mass of the adsorbent.

In an adsorption study, it is necessary to fit the equilibrium adsorption data using different adsorption isotherm models and kinetic equations in order to analyze and design an adsorption process [13].

3. Results and discussion

3.1. Brunauer-Emmett-Teller (BET) surface area.

The TheBrunauer-Emmett-Teller (BET) [17] surface area and Barrett-Joyner-Halenda (BJH) pore size of RSFA have been investigated using N_2 adsorption/desorption measurements at 77 K. The BET surface area of RSFA was obtained as 67.4 m^2g^{-1} can supply more surface active sites, leading to an enhancement of adsorption performance. It is suggested that the pore structure of the adsorbent RSFA consists of macropores, mesopores and micropores. The total pore volume (V_p) at $P/P_o = 0.959$ was obtained as 0.134 cm^3g^{-1}, which indicating that RSFA has a mesoporous structure and makes it easy for phenolic azo dye to penetrate into the mesopores of RSFA.

3.2. SEM analysis

Scanning electron microscopy (SEM) has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent surface. It is useful for determining the particle shape, porosity and appropriate size distribution of the adsorbent. Scanning electron micrographs of raw RSFA mainly constituted of hollowed spheres of different size and some unshaped fragments ascribed to unburned rice straw. It might also be seen in the micrograph where some of the smaller size particles were adhered on bigger size particles. After adsorption of phenolic azo dye, very distinguished dark spots which can be taken as a sign of effective adsorption of phenolic azo dye molecules in the cavities and pores of this adsorbent.

3.3. Effect of pH

One of the most important parameters that affect the adsorption of dye molecules is pH of the solution. The removal of phenolic azo dye by RSFA at different pH values was studied at initial concentrations of 100 mg/L of the dye, 25 ^{o}C and 0.05 g/L adsorbent dosage. RSFA has proved to be an effective adsorbent for the removal of the dye, which was achieved via adsorption from an aqueous solution at pH 2was achieved (Fig. 1). It shows that the adsorption capacity of testing dye onto RSFA increases significantly with decreasing pH. The maximum removals for contact time 50 min were carried out at pH 2. In acidic solutions, the surface of RSFA has apositive charge due to the increase in the H^+ ions in the solution, which leads to strong electrostatic adsorption between the positive charge of the carbon surface and anions of the dye molecule and increase the adsorption rate. At high pH levels, hydroxyl ions compete with the dye anions for the adsorption sites [18,19].

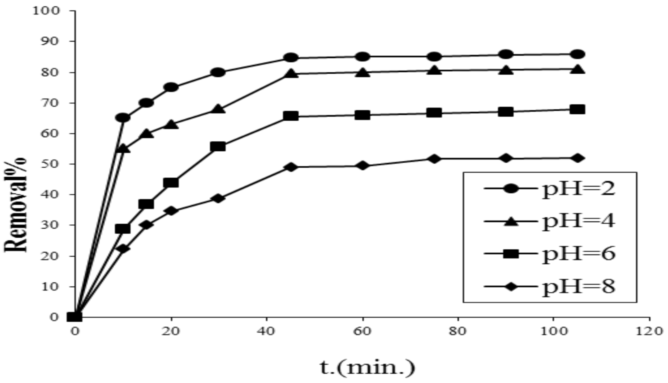


Fig. 1 . Effect of pH on adsorption of phenolic azo dye onto RSFA at dosage 0.05 g/l and temperature 25 ºC.

3.4. Effect of dye concentrations

The removal of phenolic azo dye by adsorption on the adsorbent (RSFA)was shown to increase with time and attained a maximum value at about 50 min, and thereafter, it remained almost constant (Fig.2). On changing the initial concentration of dye solution from 30 to 100 mg/L at 25 ºC, pH 2 and 0.05 g/L adsorbent dosage the amount of removed dyes was decreased. It was clear that the removal of the dye was dependent on the initial concentration of the dye because the decrease in the initial dye concentration increased the amount of dye adsorbed. This is very clear because, for a fixed adsorbent dose, the number of active adsorption sites to accommodate adsorbate ions remains unchanged but with increasing adsorbate concentration, the adsorbate ions to be accommodated increase and hence the percentage of adsorption goes down.

3.5. Effect of adsorbent dosage

The adsorbent dose is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of dye solution. The uptake of phenolic azo dyewith change in adsorbent dosage (0.01–0.05g) at adsorbate concentrations of 100 mg/L at 25 ^{o}C and pH 2 is presented at (Fig.3).
Adsorption of dye shows that the uptake of dye per gram of adsorbent increases with increasing adsorbent dosage from 0.01 to 0.05 g. This is because a higher dose of adsorbent, led to increased surface area and more adsorption sites are available causing higher removal of the dye. Increasing the RSFA dose increases the probability of the RSFA entanglement in the solution, causing adsorption in the interlayer space and a decrease in the aggregation of phenolic azo dye at the external surface. Accordingly, the adsorption capacity declined as the RSFA dosage increased. Moreover, the high RSFA dosage may influence the physical characteristics of the solid-liquid suspensions, such as by increasing the viscosity and inhibiting the diffusion of phenolic azo dye molecules to the surface of RSFA.

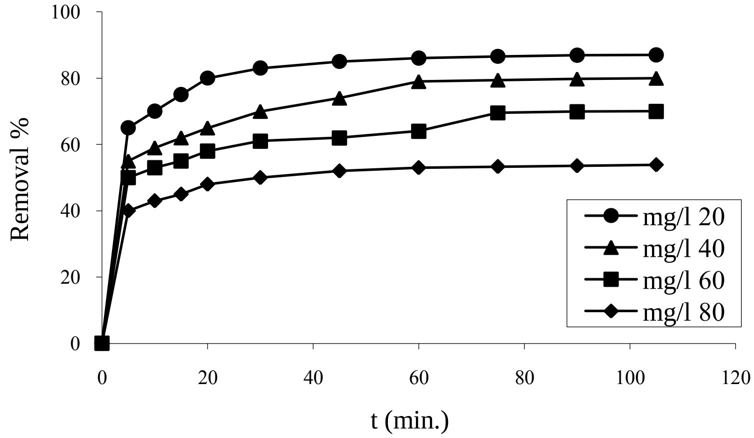


Fig. 2. Effect of intial azorhodanine dye concentratios on adsorption of phenolic azo dye onto RSFA, dosage 0.05 g/l, pH=2 and 25 °C.

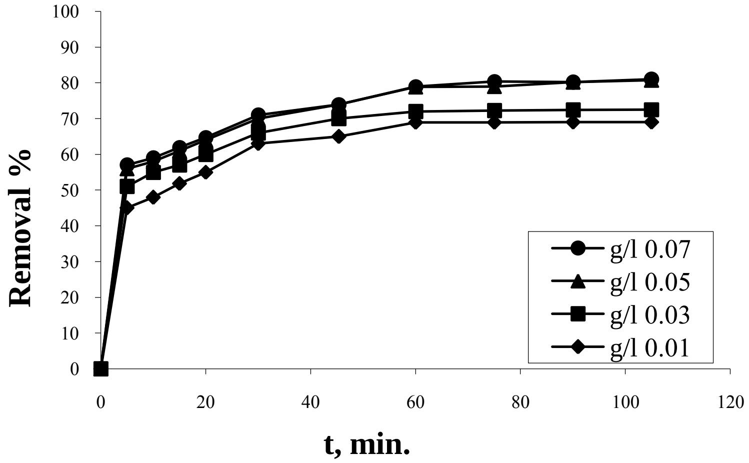


Fig. 3. Effect of dosage on the adsorption of phenolic azo dye at concentration 100 mg/l, pH=2 and 25 °C.

3.6. Effect of temperature

Temperature is an important parameter in the adsorption process (Fig. 4) which explain the relation between theremoval of dye ratio and time at different temperatures (25, 40, 50 and 60 ^{o}C) onto RSFA. In our case the experimental data obtained at pH 2, adsorbent dosage 0.05 g/L, and initial concentration of 100 mg/L show that increase in the adsorption capacity at temperatures from 25 to 60 ^{o}C. This may be attributed to the fact that at high temperature, the mobility and diffusion rate of dye molecules increased, while the solution viscosity decreasedwhich is due to the existence of available empty surfaces during the early stages of adsorption.

3.7. Equilibrium isotherms

Equilibrium data, generally known as adsorption isotherms, are important in the basic design of adsorption systems, and are critical in optimizing the use of adsorbents. To optimize the design of an adsorption system for removing phenolic azo dye from solutions, it is essential to establish the most appropriate correlation for the equilibrium curves [20-22]. Several isotherm equations are available and two important isotherms are applied to fit the equilibrium data in this study; Langmuir and Freundlich isotherms are listed in Table 2.

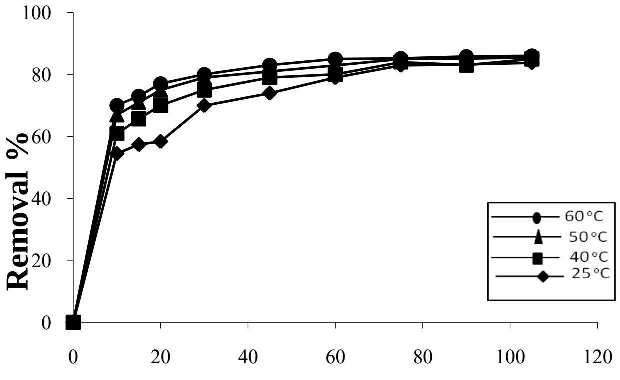


Fig. 4. Effect of temprature on the adsorption of phenolic azo dye onto RSFA, dosage 0.05 g/l, pH=2 and 25 °C

Table 2. Langmuir and Freundlich parameters for the adsorption of phenolic azo dye onto RSFA.

Temperature (^oC)	Langmuir isotherm			Freundlich isotherm		
	q_{max} (mg/g)	K_L (L/gm)	r_L^2	K_F (mg/g)	n	r_F^2
25	38.24	0.2199	0.997	0.927	1.160	0.997
40	105.69	0.0620	0.993	0.951	1.158	0.995
50	208.19	0.0329	0.995	0.950	1.157	0.996
60	221.12	0.0320	0.994	0.864	1.160	0.998

Langmuir adsorption isotherm assumes monolayer adsorption of adsorbate over a homogeneous adsorbent surface with a finite number of identical sites, which are energetically equivalent and negligible interaction between the adsorbed molecules. Theoretically, the sorbet has a finite capacity for the sorbate. Therefore, a saturation value is reached beyond which no further sorption can occur. The Langmuir adsorption isotherm in the linear form is expressed as the following equation [23-27],

$$C_e / q_e = 1/ (q_{max}K_L) + C_e / q_{max} \qquad (4)$$

where C_e is the equilibrium dye concentration (mg/L), q_e is the equilibrium amount of adsorbed dye per unit weight of adsorbent (mg/g), q_{max} is the maximum amount of adsorbed dye per unit weight of adsorbent to form a complete monolayer coverage (mg/g) and K_L is the Langmuir adsorption constant (L/mg).Therefore, a plot of C_e/q_e*vs*. C_e (Fig.5), gives a straight line of slope $1/q_{max}$ and the intercept $1/(q_{max}K_L)$. The Langmuir equation is applicable to homogeneous sorption, where the sorption of each sorbet molecule onto the surface is equal to the sorption activation energy.

The Freundlich adsorption isotherm assumes multilayer adsorption and it is applicable to adsorption on heterogeneous surfaces with interaction between the adsorbed molecules. The Freundlich isotherm [26-28] is expressed as the following equation:

$$q_e = K_F \,.\, C_e^{1/n} \qquad (5)$$

where q_e is the equilibrium dye concentration on adsorbent (mg/g), C_e is the equilibrium dye concentration in solution (mg/L), K_F is the Freundlich adsorption constant (L/g) and 1/n is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking logarithms of the equation

$$\log q_e = \log K_F + 1/n \,.\, \log C_e \qquad (6)$$

Therefore, a plot of log q_e*vs*. log C_e for the adsorption of testing dye onto RSFA (Fig. 6) was employed to generate the intercept value of K_F and the slope of 1/n.

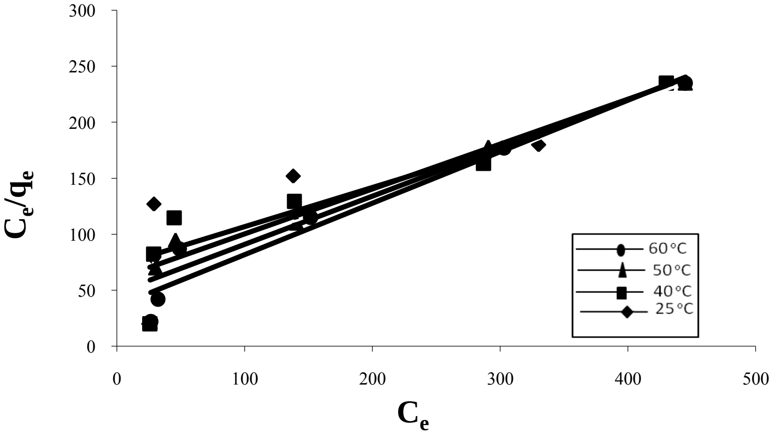


Fig. 5. Langmuir plot for the adsorption of phenolic azo dye onto RSFA at different temperatures.

The model parameters and correlation coefficients for Langmuir (r_L^2) and for Freundlich (r_F^2) values are compared in Table 2. From the values of the correlation coefficient in Table 2, it is clear that the adsorption curves fit better to the Freundlich isotherm than Langmuir isotherm, indicating that the adsorption of phenolic azo dye onto RSFA adsorbent is multilayer covered. Furthermore, the surface of (RSFA) is mostly made up of heterogeneous adsorption batches. The highest value of n at equilibrium is 1.76 (Table 2), which would seem to suggest that the adsorption is physical, which is referred the adsorption bond which becomes weak [29,30] and conducted with Van der Waals forces.

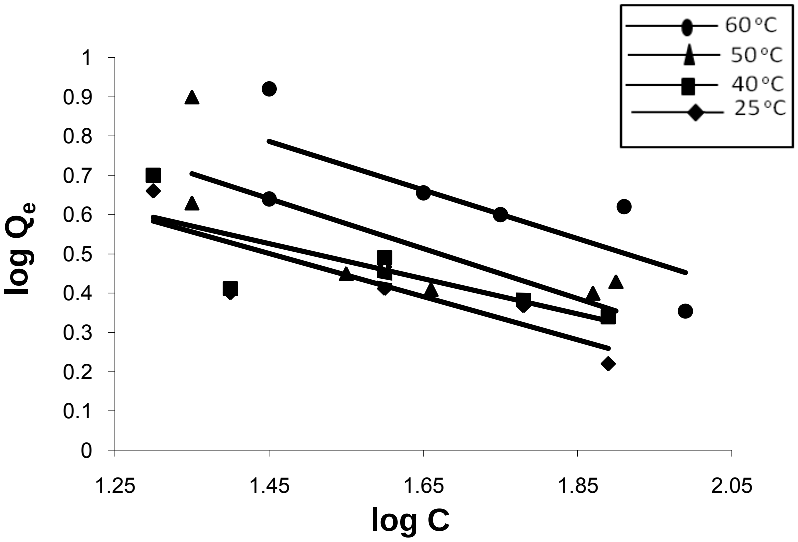


Fig. 6. Freundlich plots isotherm for the adsorption of phenolic azo dye onto RSFA at different temperatures.

3.8. Adsorption kinetics

Kinetic models not only allows estimation of adsorption rates, but also leads to suitable rate expressions characteristic of possible reaction mechanisms. In this respect, two kinetic models including the pseudo-first-order and pseudo-second-order equations were investigated to fit the experimental data [31,32]. The rate of removal of phenolic azo dye by adsorption was rapid initially and then slowed gradually until it attained an

equilibrium beyond which there was a significant increase in the rate of removal. The maximum adsorption was observed at 50min. and it is thus fixed at the equilibrium time.
The pseudo-first-order rate expression of Lagergren [31,32] is given as:

$$\log (q_e - q_t) = \log q_e - k_1 t \qquad (7)$$

The pseudo-second-order kinetic model [32] is expressed as:

$$t/q_t = 1/k_2 q_2^2 + 1/q^2\, t \qquad (8)$$

where q_t is the amount of dye adsorbed (mg/g) at various times t, q_e is the maximum adsorption capacity (mg/g) for pseudo-first-order adsorption, k_1 is the pseudo-first-order rate constant for the adsorption process (min^{-1}), q^2 is the maximum adsorption capacity (mg/g) for the pseudo-second-order adsorption, k_2 is the rate constant of pseudo-second-order adsorption ($g.mg^{-1}.min^{-1}$). The straight-line plots of log ($q_e - q_t$) versus t for the pseudo-first-order reaction and t/q_t *vs.* t for the pseudo-second-order reaction (Figs.7 and 8) for the adsorption of phenolic azo dye onto RSFA have also been tested to obtain the rate parameters.

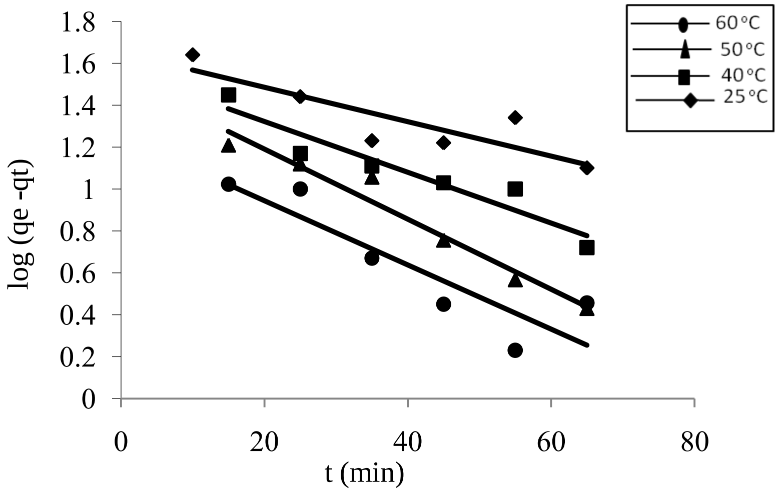


Fig. 7. Pseudo-first-order kinetic plot for the adsorption at different temperatures.

The k_1, k_2, q_e, q_2, and correlation coefficients, r_1^2 and r_2^2 for the dye under different temperatures were calculated from these plots and are given in Table 3. As shown, the kinetics of phenolic azo dye removal by RSFA followed the pseudo-second-order kinetic equation with correlation coefficients (r_2^2) > 0.996.

3.9. *Thermodynamic parameters*

In any adsorption process, both energy and entropy considerations must be taken into account in order to determine what process will occur spontaneously. Values of thermodynamic parameters are the actual indicators for practical application of a process. The amount of phenolic azo dye adsorbed onto RSFA at equilibrium and at different temperatures 25, 40, 50,60 ^{o}C, has been examined to obtain thermodynamic parameters for the adsorption system. The pseudo-second-order rate constant of testing dye adsorption is expressed as a function of temperature by the following Arrhenius type relationship [33]:

$$\ln k_2 = \ln A - E_a/RT \qquad (9)$$

where E_a is the Arrhenius activation energy of adsorption, A is the Arrhenius factor, R is the gas constant and is equal to 8.314 $J.mol^{-1}.K^{-1}$ and T is the operated temperature. A linear plot of $\ln k_2$ *vs.* 1/T for the adsorption (Fig. 9) was constructed to generate the activation energy from the slope ($-E_a/R$).

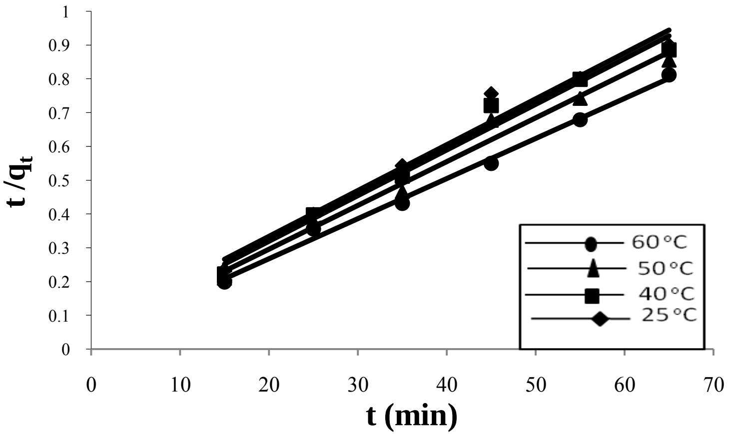


Fig. 8. Pseudo-fsecond-order kinetic plot for the adsorption at different temperatures.

Table 3. Pseudo-first-order and Pseudo-second-order for the adsorption of phenolic azo dye ontoRSFA.

	Pseudo-first-order			Pseudo-second-order		
Temperature (^oC)	q_e(mg/g)	k_1(min^{-1})	r_1^2	q_2(mg/g)	k_2($g.mg^{-1}min^{-1}$)	r_2^2
25	0.951	4.181	0.996	149.33	0.192	0.996
40	0.926	4.141	0.981	145.98	0.371	0.995
50	0.951	3.215	0.868	145.19	0.569	0.995
60	0.945	3.240	0.986	144.33	0.647	0.996

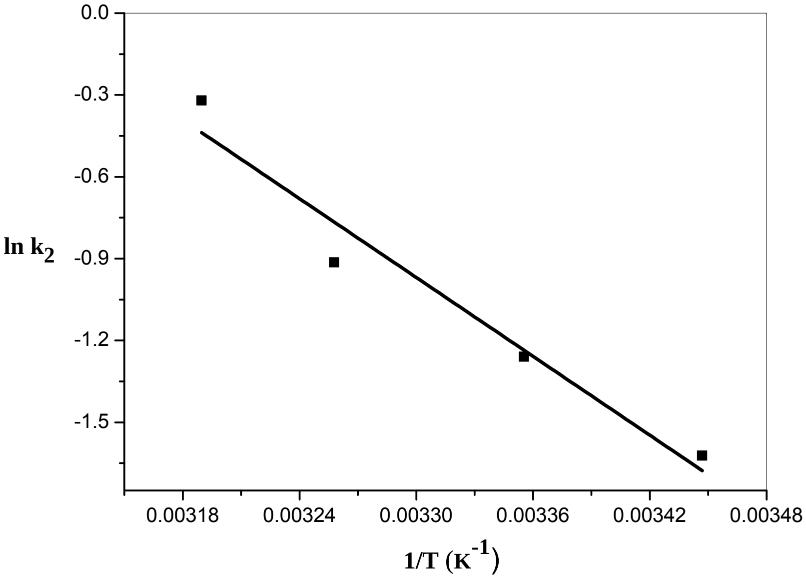


Fig. 9. Arrhenius plot of the adsorption of phenolic azo dye onto RSFA.

The chemical (chemisorption) or physical (physisorption) adsorption mechanism isoften an important indicator to describe the type of interactions between phenolic azo dye and RSFA. The magnitude of activation energy gives an idea about the type of adsorption which is mainly physical or chemical. Low activation energies (5–40 kJ/mol) are characteristics for physisorption, while higher activation energies (40–800 kJ/mol) suggest chemisorption [34]. The result obtained is +17.68 kJ/mol (Table 4) for the adsorption of phenolic azo dye onto RSFA, indicating that the adsorption has a low potential barrier and corresponding to a physisorption.

Table 4. Thermodynamic parameters calculated with the pseudo-second rate constant for phenolic azo dye onto RSFA.

Temperature(°C)	K_c	E_a (kJ mol^{-1})	ΔG^O (kJ mol^{-1})	ΔH^O (kJ mol^{-1})	ΔS^O (J.mol^{-1}.K^{-1})
25	87.44	17.68	-30.35	-19.78	0.039
40	147.34		-30.57		
50	222.21		-30.89		
60	202.95		-31.23		

The other thermodynamic parameters, change in the standard free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) were determined by using following equations:

$K_C = C_A/C_S$ (10)

$\Delta G^o = -RT \ln K_C$ (11)

$\ln K_C = \Delta S^o/R - \Delta H^o/RT$ (12)

where K_C is the equilibrium constant, C_A is the amount of phenolic azo dye adsorbed on RSFA of the solution at equilibrium (mg/L), and C_S is the equilibrium concentration of the dye in the solution (mg/L). The q^2 of the pseudo-second-order model in Table 3 was used to obtain C_A and C_S. T is the solution temperature (K) and R is the gas constant. ΔH^o and ΔS^o were calculated from the slope and the intercept of Van't Hoff plots of ln K_C*vs.* 1/T (Fig. 10). The results are given in Table 4.

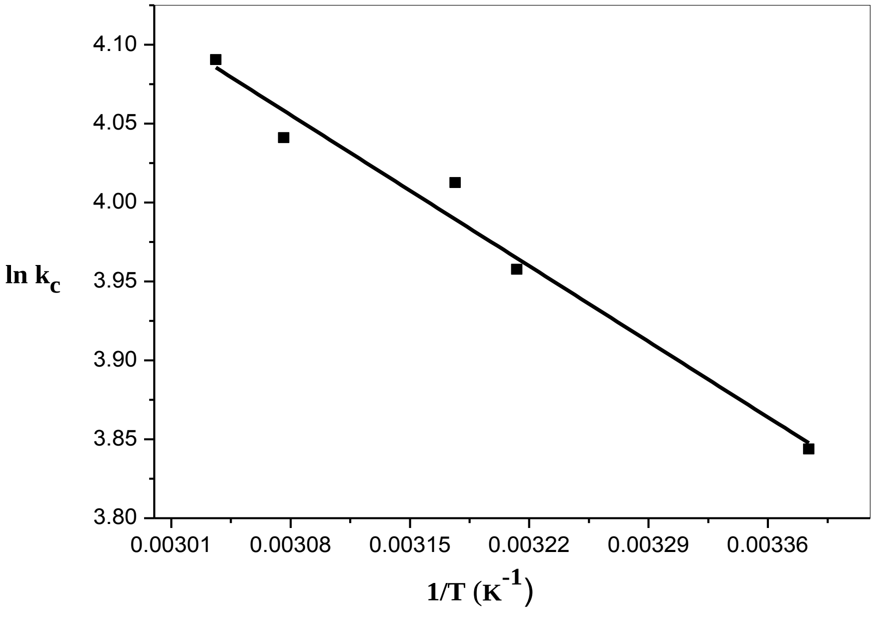


Fig. 10. Van't Hoff plot for determination of thermodynamic parameters for the adsorption.

The values of adsorption thermodynamic parameters are listed in Table 4. The negative value of the change of free energy (ΔG^o) confirms the feasibility of the adsorption process and also indicates spontaneous adsorption of phenolic azo dye onto RSFA in the temperature range studied [35]. The small negative value of the standard enthalpy change (ΔH^o) which is (–19.78 kJ/mol) indicates that the adsorption is physical in nature involving weak forces of attraction and is also exothermic, thereby demonstrating that the process is stable energetically [36,37].

Conclusions

From the present study which clearly demonstrated that rice straw fly ash (RSFA) are an effective adsorbent for the removal of phenolic azo dye from an aqueous solution and polluted water. The high adsorption capacity of phenolic azo dye onto RSFA in highly acidic solutions (pH 2) is due to the strong electrostatic interactions between its adsorption site and dye anion. The Brunauer-Emmett-Teller (BET) surface area and Barrett-Joyner-Halenda (BJH) pore volume were calculated and found to be 67.4 m^2g^{-1} and 0.134 cm^3g^{-1}, respectively. SEM images show well defined and characterized morphological images that are evident for the effective adsorption of phenolic azo dye molecules on the cavities and pores of RSFA. For the application of Langmuir and Freundlich equations, the experimental results show that the Freundlich model was the best. The highest value of n at equilibrium is 1.16 suggested that the adsorption is physical. The kinetic data tend to fit very well in the pseudo-second-order kinetics model with high correlation coefficients. The calculated values of different thermodynamic parameters clearly indicate that the ongoing adsorption process is feasible, spontaneous, favorable and exothermic in nature and a physical adsorption. Finally, the adsorbent RSFA displayed the main advantages of excellent dispersion in an aqueous solution, separation convenience and high adsorption capacity, which implied their application potentials for effective removal of other dye pollutants from an aqueous solution.

References

1. Guzel F., Saygili H., Saygili G.A., and Koyuncu F., *J. Mol. Liq.* 194 (2014) 130.
2. Fu J., Z. Chen, Wang M., Liu S., Zhang J., Zhang J., Han R., Xu Q., *J. Chem. Eng.* 259 (2015) 53.
3. Ma T.T., Chang P.R., Zheng P.W., Zhao F., Ma X.F., *J. Chem. Eng*. 240 (2014) 595.
4. Saleh T.A., Gupta,V.K., *Environ. Sci. Poll. Res.*19 (2012) 1224.
5. El-Bindary A.A., Hussien M.A., Diab M.A., Eessa A.M., *J. Mol. Liq.*197 (2014) 236.
6. El-Bindary A.A., Diab M.A., Hussien M.A., El-Sonbati A.Z., Eessa A.M., *Spectrochim. Acta A* 124(2014) 70.
7. El-Bindary A.A., El-Sonbati A.Z., Al-Sarawy A.A., Mohamed K.S., Farid M.A., *J. Mol. Liq.* 199(2014) 71.
8. Sobiesiak M. , Podkos´cielna B., Podkos´cielny P., *Adsorption* 22 (2016) 653.
9. Mergola L., Scorrano S., Bloise E., Bello M. P. D., Catalano M., Vasapollo G. , Sole R. D., *Polym. J*. 48 (2016) 73.
10. Misra P., Chitanda J. M., Dalai A. K., Adjaye J., *Chem. Eng. J*. 295 (2016) 109.
11. Anbia M., Amirmahmoodi S., *Scien. Iran. C* 18 (2011) 446.
12. Sun D., Zhang X., Wu Y., Liu X., *J. Hazard. Mater.* 18(2010) 335.
13. El-Bindary A.A., El-Sonbati A.Z., Al-Sarawy A.A., Mohamed K.S., Farid M.A., *J. Mater. Environ. Sci.* 6 (2015) 1.
14. El-Bindary A.A., El-Sonbati A.Z., Al-Sarawy A.A., Mohamed K.S., Farid, M.A., *Spectrochim. Acta A* 136 (2015) 1842.
15. El-Bindary A.A., Hussein M.A., El-Boz R.A.,*J. Mol.Liq.*211 (2015) 256.
16. Daffalla S.B., Mukhtar H., Shaharun M.S.,*J.Appl. Sci.*10(2010) 1060.
17. Brunauer S., Emmett P.H., Teller E.,*J. Am. Chem. Soc.* 60(2002) 309.

18. Alkan M., Demirbas O., Celikcapa S., Dogan M., *J. Hazard. Mater.* 116(2010) 135.
19. Khan M.R., RayM., Guha,A.K., *Bio. Resource Technol.* 102 (2011) 2394.
20. Guendy H.R.,*J. Appl. Sci. Res.* 6(2010)964.
21. Kiran I., AkarT., OzcanA.S., OzcanA., Tunali S., *Bio. chem. Eng. J.*, 31(2006) 197.
22. Yavuz M., GodeF., PehlivanE., OzmertS., SharmaY.C.,*Chem. Eng. J.*, 137 (2008) 453.
23. Langmuir I., *J. Am.Chem. Soc.* 38 (1916) 31.
24. Langmuir I., *J. Am.Chem. Soc*. 39(1917) 1848.
25. Langmuir I., *J. Am.Chem. Soc*. 40 (1918) 1361.
26. Alley A.R. *Water quality control handbook. McGraw-Hill Education*: *Europe: London*, 2000.
27. Woodard F. *Industrial waste treatment handbook. Butterworth-Heinemann: Boston*, 2001.
28. FreundlichH.M.F., *Z. Phys. Chem. (Leipzig)* 57A(1906)385.
29. Tunali S., OzcanA.S., OzcanA., GedikbeyT., *J. Hazard. Mater.*135 (2006)141.
30. Jiang J.O., CooperC., OukiS.,*Chemosphere* 47(2002) 711.
31. Lagergren S.,*Handlingar* 241(898) 1.
32. Kumar K.V., Ramamurthi V., Sivanesan S., *J. Coll. Interf. Sci*. 284 (2005) 14.
33. Elwakeel K.Z., El-Bindary A.A., Ismail A., Morshidy A.M., RSC Adv. 6(27) (2016) 22395.
34. Nollet H., RoelsM., LutgenP., Van der MeerenP., VerstraeteW.,Chemosphere 53 (2003) 655.
35. El-Bindary A.A., Abd El-Kawi M.A., Hafez A.M., Rashed I.G.A., Aboelnaga E.E., *J. Mater. Env. Sci.* 7(3) (2016) 1023.
36. Elwakeel K.Z., El-Bindary A.A., El-Sonbati A.Z., Hawas A.R., *RSC Adv.* 6(4) (2016) 3350.
37. Ghaedi M., Nasiri K.S., *Spectrochim. Acta A* 136 (2015) 141.

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