RESEARCH ARTICLE

KINETIC, EQUILIBRIUM AND THERMODYNAMIC MODELING OF DISPERSE DYE ADSORPTION ONTO FLY ASH.

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Manuscript Info	*Abstract*

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Fly ash has been employed as adsorbent for the removal of an azo dye; disperse blue 79 from aqueous solution. The fly ash has been characterized by means of X-ray diffraction and Fourier transform infrared spectroscopy. Adsorption studies were performed at different temperatures, adsorbent doses, pH's and dye initial concentrations. It was found that increasing temperature increases the adsorption process thereby indicating an endothermic process, as for the pH, it had no significant influence on the dye adsorption onto the fly ash. Increasing dye concentration leaded to a decrease in the adsorption removal percentage. The Langmuir and Freundlich isotherm models were utilized to understand the nature of the adsorption process; the results suggested that Langmuir model fitted the adsorption data better than the Freundlich isotherm model. Further, the kinetic data were better correlated with the pseudo second order model than the pseudo first model. The thermodynamic parameters such as the free energy, enthalpy and entropies of adsorption of the dye-fly ash system were also evaluated; the negative value of ΔS^0 suggested that the system exhibits random behavior, the value of $\Delta G°$ is negative, which indicates that the adsorption process is spontaneous and feasible on the fly ash.

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Introduction:-

Extensive amounts of textile wastewater are being produced; previous papers have reported that the textile industry discharges nearly 100 tons of dyes per year into the waste streams [Wong et al., 2003]. Dyes and pigments represent one of the problematic groups; they are discharged into wastewaters from various industrial branches, mainly from the dye manufacturing and textile finishing [Hameed et al., 2007], since some of the dyes and their degradation products may be highly carcinogenic, toxic and can alter the aquatic life, their removal is of major concern among environmentalists. [Zolgharnein et al., 2015]. Adsorption process gives an attractive alternative for the treatment of contaminated waters, it remains an innovative and effective alternative treatment for dye removal from wastewater in terms of efficiency and simplicity [Rehman et al.,2013] especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application. [Palomo et al., 1999 .Shaobin et al., 2005] Fly ash, one of the industrial wastes originating from burning biomass and coal [Umesh et al., 2017] and the fact that coal is used as a fuel in most industries causes fly ash to be produced in higher amounts, and this, in turn, causes many

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concerns [Javadian et al., 2015] .It has proven its and suitability as sorbents to eliminate heavy metals and dyes from water [Pengthamkeerati et al., 2010]. The current study examines the disperse blue 79 dye removal from aqueous solutions onto Moroccan fly ash ,adsorption performance was used to question the effect of the initial dye concentration, contact time, pH and temperature, and empirical adsorption models were applied for describing the adsorption behavior of dye removal.

Materials and methods:-

1.1 Adsorption experiments:-

The fly ash (FA) used in this study was obtained from coal combustion in the thermal power station located in the city of El Jadida, Morocco; it mainly contains SiO_2, Al_2O_3, Fe_2O_3, CaO and other oxides such K_2O and MgO. FA was characterized using FTIR and DRX spectroscopy. Prior to its use, the adsorbent was oven-dried at 105°C for 2 hours to eliminate traces of moisture. Disperse blue 79 was purchased from sigma-Aldrich the (product number is 12239-34-8); its chemical structure is shown in figure1.
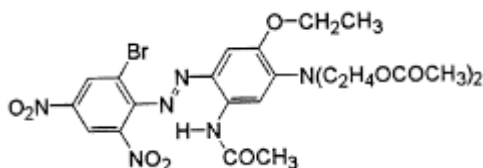

Figure 1:- disperse blue 79 molecule

The synthetic wastewater was prepared by dissolving the dye in distilled water to produce a stock solution of 100 $mg\ l^{-1}$. Batch experiments were carried out to measure the adsorption characteristics of disperse dye on fly ash (FA). Specific amount of the fly ash sample was added to 100 ml of dye solution of varying concentrations (20 to $100 mgl^{-1}$). The mixture was stirred with magnetic agitator to determine the equilibrium time at 293 K. After stirring, the suspensions were separated by centrifugation at 4600 rpm. The determination of dye residual concentration was done spectrophotometrically on a JASCO V-630 UV Visible spectrometer by measuring absorbance at λmax of 537 nm. The removal percentage of DB79 (%R) and the adsorption capacity values at equilibrium q_e $(mg.g^{-1})$ were calculated using the equations:

$\%R = \frac{C_0 - C_e}{C_e} * 100$ (1)

$q_e = \frac{C_0 - C_e}{w} * V$ (2)

C_0 $(mg.L^{-1})$ is the initial dye concentration, C_e is the dye concentration at equilibrium, V is the volume of the solution and W (g) is the amount of the adsorbent in the solution.

To scrutinize the effect of pH on adsorption, a series of dye solutions was prepared by adjusting pH over a range of 4–10 using dilute HCl (0,1N) or NaOH (0,1N) solutions. The solutions pH was measured with a pH meter (pH 700 EUTECH instruments). Other parameters were also put to the test such as adsorbent dosage (0.5 to 1.5 g/L), temperature (20 to 60°C) and initial dye concentration (10 to 50 $mg.L^{-1}$). For kinetic studies, Lagergren first-order and pseudo-second-order kinetic models were used to examine the controlling mechanism. Langmuir and Freundlich isotherm models were applied to evaluate the adsorption capacity. All adsorption data reported in this paper were the average values of three runs.

Results and discussions:-
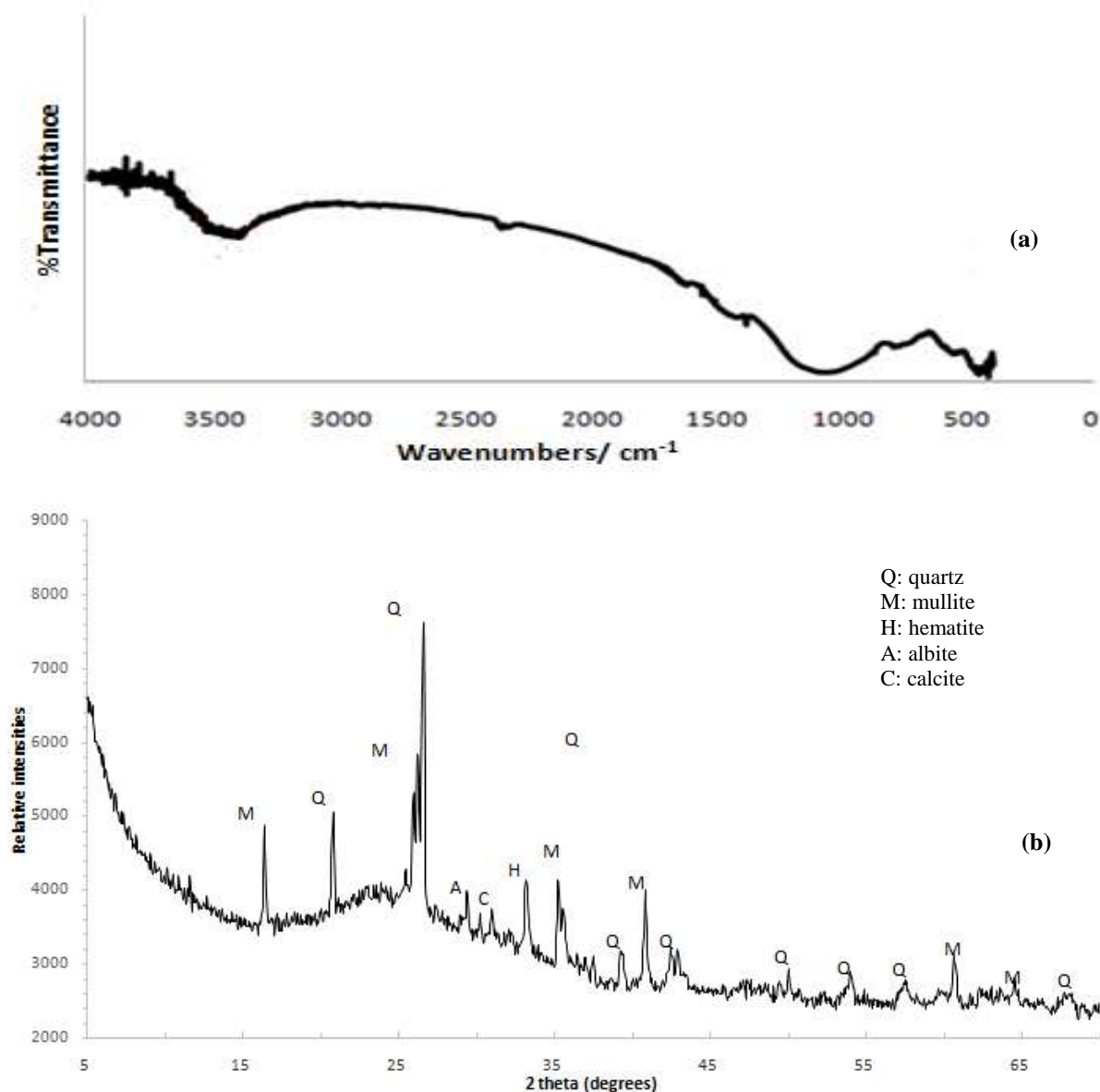### 2.1 characterization of the adsorbent

Figure 2:- FTIR (a) and XRD (b) patterns of fly ash

The fly ash was characterized by FTIR using Perkin-Elmer 1720-x spectrometer over the range of 400-4000 cm^{-1} and the results are given in figure (2.a), it shows an intense band at 1100-1000 cm^{-1} which corresponds to the –Si-O-group stretching variation [Silverstein et al.,2010], Bands at 554, 469, 540 and 875 cm^{-1} were attributed to ν (O–Si–O) bending modes of SiO$_4$tetrahedra [Ahmaruzzaman et al., 2010].

The X-ray spectrum of the FA (fig 2.b) shows that the FA mainly constituted of a major vitreous phases registered between 2θ=20° and 2θ=30° attributed to quartz and mullite, with minor hematite and magnetite [Zengqing, S. and Vollpracht,A , 2018]. pH$_{pzc}$ of FA was also determined and it was found to be 12, the overall surface charge is positive for pH solutions below this value and negative when the pH is above pH$_{PZC}$.

2.2 Effect of pH:

pH of solution is a key factor controlling the adsorption efficiency by influencing the surface charge of the adsorbent, the variation of disperse blue 79 adsorption on fly ash was inspected over a broad range of pH going from 4 to 10 as shown in figure 4. A slight decrease in the adsorption capacity was noticed in pH> 6 , this is maybe be due to the decomposition of the azo group in disperse dye molecules because the azo group is unstable in higher pH [Hallas et al.,1999].
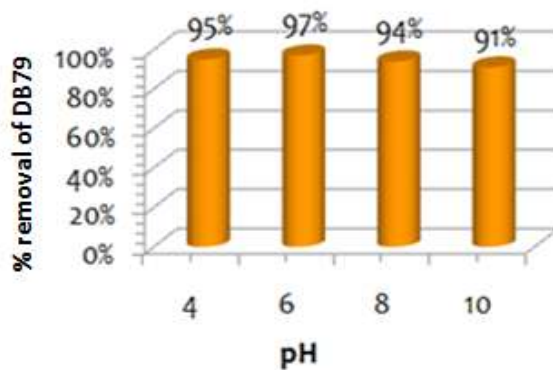

Figure 4:- effect of pH on the removal of DB79 on fly ash, initial dye concentration 20mg.L^{-1}, temperature 20°C, adsorbent dose 1g/L

2.3. Effect of adsorbent dose

Figure 5 shows the effect of dose variation of FA on the removal of DB79. Various amounts of FA were added to the solutions containing 20 mg/l of DB 79 while other parameters were kept constant. The percentage removal of the disperse dye increased with increasing the FA dose from 0.5 to 1.5 g/L due to the availability of more active sites on the surface of the adsorbent. After reaching maximum adsorption percentage at 1g/L, any further increase in the adsorption dose had no effect on the percentage removal of DB79, This may be due to the overlapping of adsorbent active sites because of the overcrowding of adsorbent particles [Namasivayam et al., 1998]. Therefore 1g/l was chosen as optimal dose for further adsorption experiments.
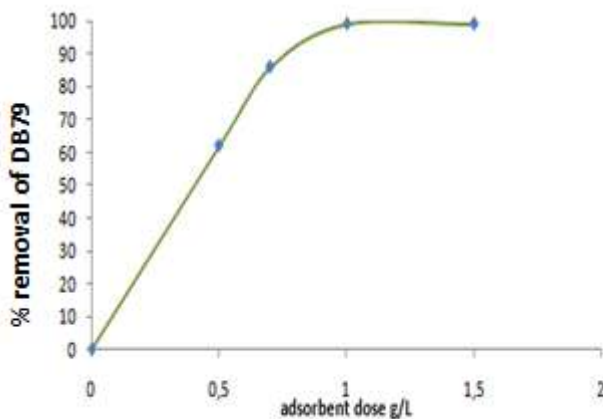

Figure 5:- effect of adsorbent dose on the adsorption removal percentage of DB79, initial dye concentration 20mg.L^{-1}, temperature 20°C, pH=6

2.4. Effect of initial concentration and contact time

The adsorption of Disperse blue 79 by fly ash at various initial dye concentrations was studied as function of contact time in order to optimize the equilibration time. The plot reveals that maximum removal of the dye reached 99% after only 45min of agitation. The rate of removal is higher in the beginning due to larger available surface area of the adsorbent. After adsorption, the rate of dye uptake is controlled by the rate of dye transported from the exterior to the interior sites of the adsorbent particles [Rahchamani et al., 2011].
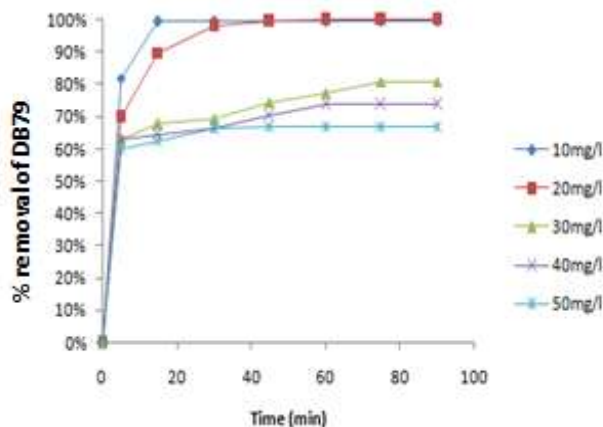
Figure 6:- effect of contact time for the adsorption of DB79 onto dry flyash, temperature 20°C, pH=6, adsorbent dose=1g/L.

2.5 Effect of temperature
The adsorption tests were conducted at different temperatures ranging from 20°C to 60°C. It was found that the adsorption increased with increasing temperature, which shows that the removal of DB79 is favored at high temperatures; this may be a result of increasing mobility of the dye with the increase temperature [Bouberka et al., 2005]. Thus the removal process is endothermic.
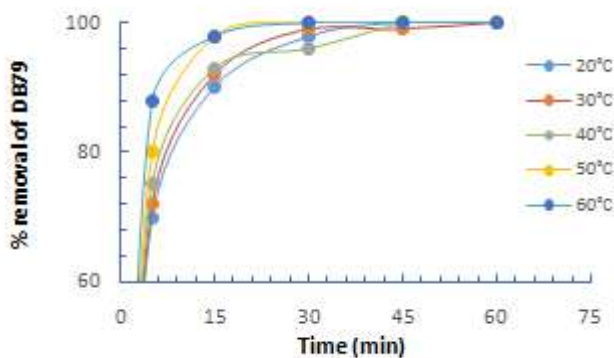

Figure 7:- effect of temperature on the removal of DB79 onto FA, initial DB79 concentration 20mg.L^{-1}, adsorbent dose=1 g/L, pH=6, temperature 20°C

2.6 Adsorption isotherms
Two adsorption models were tested to define the adsorption nature of DB79 onto fly ash; Langmuir and Freundlich. The Langmuir model assumes that surface of the adsorbent contains homogeneous binding sites with similar sorption energies and no interactions with the adsorbed molecules [Maneerung et al., 2016]. It can be described by following equation [Langmuir 1918].

$$\frac{C_e}{q_e} = \frac{1}{k_L + Q_{max}} + \frac{C_e}{Q_{max}} \quad (3)$$

where q_e is the solid phase adsorbate concentration in equilibrium (mg.g^{-1}), q_{max} the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg.g^{-1}), C_e the concentration of adsorbate at equilibrium (mg L^{-1}) and K_L is the Langmuir constant (L/mg). The constants can be evaluated from the intercepts and the slopes of the linear plots of Ce/qe versus Ce (fig8).
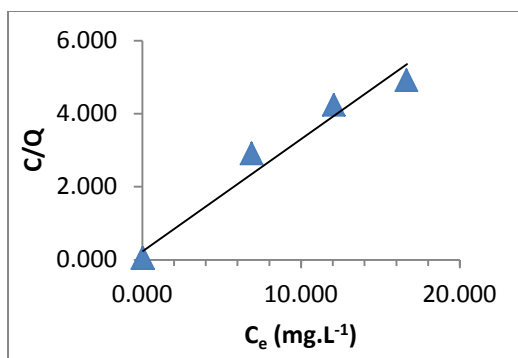
Figure 8:- Langmuir plots for the adsorption of Disperse blue 79 onto fly ash
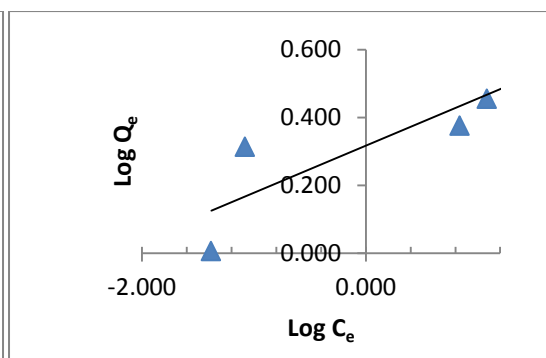
Figure 9:-Freundlich plots for the adsorption of disperse blue 79 onto fly ash

The Freundlich isotherm, which is empirical for heterogeneous surface energy [Walker et al., 2001], is written as:

$$q_e = KC_e^{\frac{1}{n}} \quad (4)$$

Where K $(1g^{-1})$ is the extent of the adsorption and n is the degree of nonlinearity between dye concentration and adsorption, where n (dimensionless) is the heterogeneity factor which has a lower value for more heterogeneous surfaces, the linearized form of freundlich isotherm is expressed by the following equation (5):

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

Where K_F and n are Freundlich isotherm constants related to the adsorption capacity of the adsorbent (mg/g) and the adsorption intensity, respectively. The values of K_F and n can be calculated from the intercept and slope of the plot log C_e versus log q_e.

Langmuir				Freundlich		
Qm	K	RL	R^2	n	K	R^2
3,26	1,364	0,04	0,946	3,155	1,37	0,662

Table 1:- Langmuir and Freundlich isotherm constants for DB79 adsorption

Results from the Freundlich and Langmuir analysis shown in Table 1 indicate that the Freundlich correlation coefficient is significantly less than the Langmuir coefficient in describing the adsorption process, therefore, the disperse blue 79 azo dye is homogeneously adsorbed on the surface of fly ash.

2.7 Kinetic study
Kinetic study was carried out varying the initial dye concentration to determine the specific rate constants of FA-BD79 system. Kinetic models used are;
Lagergren first-order, and pseudo-second-order and the Lagergren first-order model is given by equation (6): [Lagergren, 1898, Ho et al 2000]

$$\log (q_e - q_t) = log q_e - \frac{K_1 t}{2.303} \quad (6)$$

Where qe and qt are the adsorption capacities at equilibrium and at time t, k_1 is the adsorption rate constant. The values of adsorption capacity and rate constant were determined from the slope and intercept of the plot log $(q_e - q_t)$ versus t.
The pseudo-second-order model is given by Eq. (7)

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

where k_2 is the pseudo-second-order rate constant. The values of adsorption capacity and rate constant were derived by the intercept and slope of the plot t/q_t versus t.
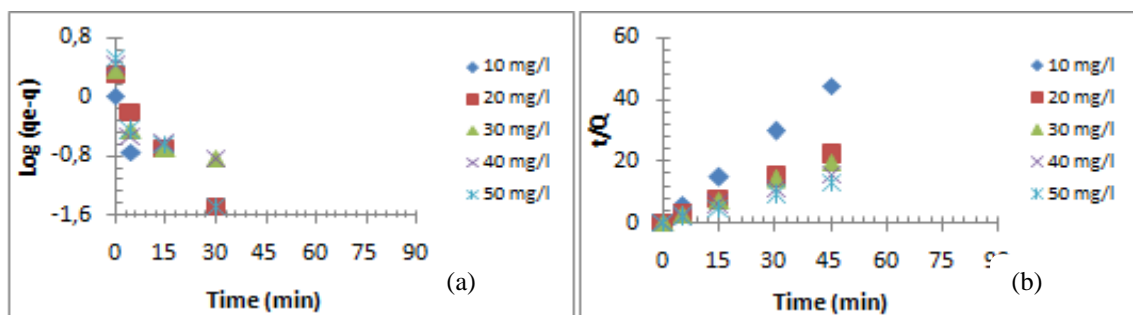
Figure 10:- Pseudo first order (a) and pseudo second order (b) plots for the adsorption of disperse blue 79 onto fly ash

Figure 10 presents the plots for Lagergren-first-order and pseudo-second-order kinetic models and table 2 represents values of the adsorption rate constants calculated from the slops and intercepts of both models.

Table 2:-Comparison of kinetic parameters for the adsorption of disperse blue 79 onto fly ash at various concentrations, at pH =6 and at 20°C

C (mg.L^{-1})	Q exp	pseudo-First ordre			pseudo-secondeordre		
		Q cal	K$_1$	R^2	Q cal	K$_2$	R^2
10	1,01	1,01	0,67	0,174	1,02	2,28	0,999
20	2,05	1,02	0,42	0,101	2,10	0,36	0,997
30	2,28	1,01	0,52	0,035	2,28	0,52	0,997
40	2,85	0,99	0,45	0,040	2,84	0,53	0,998
50	3,39	0,87	0,50	0,878	3,42	0,55	0,999

As shown in table 2, the result showed that pseudo-first-order rate expression is not fully valid for the present adsorption system due to low correlation coefficients. A good agreement of the experimental data with the pseudo-second-order kinetic model (Fig. 10, b) was observed. The theoretical qe values agree perfectly with the experimental qe values (Table 2) indicating that the adsorption of disperse blue 79 azo dye fits the pseudo-second-order kinetic model.

2.8 Thermodynamic studies
The adsorption experiments of DB79 on FA were also tested at different temperatures varying from 20°C to 60°C (figure 7) and showed an endothermic adsorption process due to an increase in the removal percentages at higher temperatures. The thermodynamic parameters; free energy (ΔG^0), enthalpy (ΔH^0); and entropy (ΔS^0), were calculated using the following equations [Ozturk et al., 2005]:

$\Delta G^0 = -RT \ln(K)$ (8)

According to the van't Hoff equation:

$$\ln K_L = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (9)$$

Where R (8.314 J mol-1 K^{-1}) is the gas constant, T (K) is the absolute temperature, and K$_L$ (L.mol^{-1}) is the constant calculated from the Langmuir isotherm model , ΔS^0 and ΔH^0 are change in entropy and enthalpy of adsorption, respectively. A plot of lnK versus 1/T is linear was drawn to determine the values of ΔH^0 and ΔS^0 were evaluated from the slope and intercept of Van't Hoff plots (Table 3). The positive values of ΔH^0 confirm the endothermic nature of adsorption [Acemioglu 2004]. The negative value of ΔS^0 suggests the system exhibits random behavior, the value of $\Delta G°$ is negative, which indicates that the adsorption process is spontaneous feasible on the fly ash [Wang et al., 2017].

Table 3:- Thermodynamic parameters for the adsorption of DB79 onto FA

C°	K°	ΔG° KJ/mol	ΔH° KJ/mol	ΔS°J mol-1 K-1
20	293	-32,83	398,830894	-26,67
30	303	-31,12		
40	313	-30,66		

50	323	-31,21		
60	333	-31,62		

Conclusion:-

Moroccan Fly ash waste material has been investigated in this study for the removal of disperse 79 azo dye in aqueous solution and has proven its efficiency in maximum removal of 99% at pH=6 , temperature 20°C, an initial disperse blue 79 concentration of 20mg.g^{-1} and 1g/L as optimum adsorbent dose. The adsorption was found to be endothermic in nature. Equilibrium adsorption data followed Langmuir isotherm for fly ash, the batch adsorption capacity was found 3.23 mg/g. The pseudo-second-order equation gives a best fit to the equilibrium data.

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