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RESEARCH ARTICLE

Adsorption of 1- (2⁻-Hydroxy - 4⁻-Nitrophenyl azo)-2- Napthol Dye onto the Cement Kiln Dust (CKD)

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Abstract

The adsorption of 1-(2⁻- Hydroxy-4⁻-nitrophenyl azo) -2-naphthol dye onto the Cement Kiln Dust (CKD) was studied in the temperature range 298-328K. The sorption process was examined in terms of its equilibria and kinetics. Batch adsorption experiments were conducted to evaluate the percentage removal of 1-(2⁻-Hydroxy -4⁻ - nitrophenyl azo)-2-napthol onto CKD waste at operation conditions of sorbate concentration, pH, contact time, sorbent dose. Time-dependent experiments for the removal efficiency required a shortest contact time, i.e , binding to the CKD was rapid and occurred within 25 min. Adsorption isotherms equations were tested for all of Langmuir, Freundlich, Temkin,3 Dobinin-Radushvich, and Elovich. The equilibrium adsorption data were fitted to Freundlich and Temkin isotherms at 298K. Adsorption followed Intra – partical - diffusion rate kinetics. Thermodynamic parameters ΔG^*, ΔH^*, ΔS^* and Ea were computed, and showed that the adsorption process onto CKD was exothermic and non-spontaneous. Also adsorption studies suggest that physisorption might be the major mode of adsorption and CKD expressed as low affinity for removal of 1-(2⁻- Hydroxy-4⁻-nitrophenyl azo) -2-naphthol Dye onto the Cement Kiln Dust that the high percentage removal was found ≈50% at 298K , pH=6.

Keywords: *Cement Kiln Dust; Azo dyes; Adsorption isotherms; Kinetic study; Thermodynamic study.*

Introduction

Dyes are colored compounds which are widely used in various industries, such as cosmetics, food, paper, colouring, leather, pharmaceutical, dyeing, printing etc. Which generating a large amount of colored waste water and release these dye pollutants into environment as waste water effluents. Some of dyes are highly toxic and even carcinogenic, stable to light and not biologically degradable; hence these are needed to remove from the water effluents before they are released into water bodies) [1].

Cement Kiln Dust (CKD) are wastes and pollutants which. has been reported as a potentially important sorbent due to the high specific surface area, high amount of alkali oxides, excellent thermal resistance. It was indicated that CKD can effectively remove heavy metal and dye ions from wastewater [2]. The cement industry in Iraq applies wet and dry processes in cement manufacture and releases a large amount of by-pass cement kiln dust (CKD) , is both a waste and a pollutant therefore, it was desired to make use of this waste and to save the environment. CKD generated in large quantities in Al-Kufa portoland cement factory, the production of CKD, which is about 477 ton/day for 9000 ton/day of cement.

In this company 205 ton of the total CKD produced may be recycled to the wet process but the residual amount is discharged in the desert. Some materials have been investigated as effective sorbent in previous works , including agriculture and industrial wastes or natural kaoline for removal dyes ,drugs and some organic compounds from aqueous solutions[3-9]. The present work has been carried out to investigate the interaction of CKD with 1-(2⁻-Hydroxy -4⁻ - nitrophynol azo)-2- napthol dye by adsorption technique, due to their good solubility, toxic, carcinogenic and this poses a serious hazard to aquatic living organisms [10].

Experimental Section

Preparation of CKD Waste

CKD were collected from Al-najaf-Al-Ashraf governorate, Iraq, preparation of these wastes have been described elsewhere [11.

Preparation Solution of 1-(2ˉ- Hydroxy-4ˉ-nitrophenyl azo) -2-naphthol

1-(2ˉ- Hydroxy- 4ˉ-nitrophenyl azo) -2-naphthol used as adsorbate, Table (1) showed some physical and chemical properties. A stock solution of 100 mgl^{-1} was prepared by adding appropriate amount of 1-(2ˉ- Hydroxy-4ˉ-nitrophenyl azo) -2-naphthol with 500ml distilled ethanol in volumetric flask ,different concentrations were prepared by dilution of the stock solution to the initial concentrations ranging from 2 - 20 mgL^{-1}. All reagents used were of analytical grade and were supplied from B. D. H, England

Equilibrium Studies

Batch adsorption experiments were investigated at 298K .15ml of 1-(2ˉ- Hydroxy-4ˉ-nitrophenyl azo) -2-naphthol was taken at concentrations ranging (2-20 mgL^{-1}) and placed in a 50ml conical flasks containing 0.1 g of adsorbent. Shacking was provided at 150 rpm for 20 min (equilibrium contact time). The concentration of dye after and before adsorption was determined using spectrophotometer (shimadzu UV 4000, Japan) at λ_{max} of 521 nm.

The amount of dye adsorption q_e mgg^{-1}) at equilibrium was determined using the following equation [12:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

Where, C_0 and C_e (in mgl^{-1}) are the initial and equilibr ium dye concentrations and q_e

Is the adsorption capacity mgg^{-1} at equilibrium?

Adsorption Isothrems

The adsorption isotherm of the dye was obtained by preparing 10-12 different concentrations of dye within the range (2-20 mgl^{-1}) in volumetric flasks (100ml) at 298K. The different concentration was taken and placed in contact with a certain weight of adsorbent in a conical flask capacity (50ml) and then placed in a temperature controlled shaking water bath for 20min. And the solutions pH was adjusted to the required value by adding either HCl or Na OH solution.

Kinetic Studies

Experiments were carried out at temperature range from 298 to 328 K, a certain dye concentration was taken with a required weight of adsorbent and then placed in a temperature controlled shaking water bath for contact time (20min.) at pH=7. Samples were analysis at different times.

Thermodynamics Studies

The effect of temperature on the adsorption process was studied with in the temperature range (298-328K). The thermodynamic parameters were calculated to evaluate the feasibility of the adsorption process.

Results and Discussion

Effect of Contact Time

The effect of contact time on the adsorption of dye was carried out at 15 mgl^{-1} dye concentration and 0.15g of adsorbent. It can be seen from Fig.1, that the removal of dye was found to be rapid at the initial period of contact time and remain constant after equilibrium time (40min.).The reason is due to the Vander Waals forces and electrostatic attraction between the dye molecules and CKD.

Effect of Doses

To determine the optimum adsorbent dosage, experiments were carried out by adding different weights of the CKD from 0.05 to 0.5 g to 15 ml of desired concentration of the dye in conical flask at pH 6 and temperature 303K , then agitated til to attain equilibrium time for each dye. After that 15 ml was removed from the shaking water bath, then the solution was filtered, centrifuged at 3000 rpm for 10 min. after that CKD and dyes were separated by filtration through filter paper, aliquots concentration of dye was determined also spectrophotometry .The best weight of the surface was 0.15gm as showed in the Fig 2.

Adsorption Isotherm Models

Adsorption isotherms are basic requirements for the design adsorption systems [13]. In addition, the experimental adsorption isotherms were modeled to the Langmuir, Freundlich, Temkin, Elovich and the Dubinin- Radushkevich (D-R) models[14-18]

(Figs.,4,5,6,7,8), these equations are listed in table1 .The results (table 1) and the linear plots(Figs.3-7) shows that the adsorption process were fitting Freundlich and Temkin adsorption isotherm models at 298K ,the correlation coefficients R^2 are 0.9768 and 0.9304 respectively. The values of Freundlich constants (n is greater than unity n= 1.4493 and K_f = 0.0780) indicate that the dye adsorption favorable and easy uptake from aqueous solution, considering that Freundlich isotherm assumes a multi layers forming on the CKD surface. The same results was reported for adsorption of onto CKD surface [11].The Table 1 shows the comparison of the values of the adsorption equations of isotherm and the correlation coefficients for adsorption of the dye on the surface of the CKD at a weight of 0.15 g and the equilirium weight of 25min within the thermal range 298 to 328 K.

Kinetics Models

To describe the adsorption mechanism Pseudo–first-order, Pseudo-second-order, Elovich and Intra-particle diffusion [19-22] were tested as a kinetics models for the adsorption of dye on CKD. Figs. (8-11) showed the plots of kinetic model equations at different dye concentrations. Table2 listed the kinetic models equations and the rate constants and correlation coefficients for the dye adsorption onto CKD.

From Table 2 it was clear that Intra-particle diffusion shows high R^2 value at all temperature range (R^2= 0.9997) , thus it seems that the kinetic of 1-(2¯- Hydroxy-4¯-nitrophenyl azo) -2-naphthol adsorption is well explained by intra-particle diffusion model (the diffusion of the dye molecules inside the adsorbent is the rate-determing step i.e. :it can identify the diffusion mechanisms of the adsorption process) [23] .

Temperature Effect

The effect of temperature on the adsorption process of dye has been studied at the temperature range (298-328K). Fig.12 showed that the removal decreases with increasing temperature due to the decrease of the rate of diffusion of dye molecules across internal pores of CKD particles, indicating the adsorption process is exothermic. Also activation energy can be calculated from the temperature dependence of the adsorption rate constant

According to Arrhenius equation [24]:

$$\text{Log } k_{diff} = \log A - \frac{Ea}{2.303RT}$$

Where Ea activation energy (kJmol-1), A, Arrhenius constant and R,gas constant (8.314kJmol^{-1}K^{-1}). Fig.13 shows a plot of logk_{diff} versus 1/T giving a straight line with slope $-\frac{Ea}{2.303R}$ and intercept logA. A lower value of activation energy 28 kJmol^{-1} (table3) suggests that the transfer of adsorbate from the aqueous phase to the CKD surface easily occurs and passes through physisorption [25-26] process.

Thermodynamics Parameters

Thermodynamic parameters of activation (ΔH^*, ΔS^*, ΔG^*) for the adsorption of of 1-(2¯-Hydroxy-4¯-nitrophenyl azo) -2-naphthol dye onto CKD at different temperatures were calculated to evaluate the thermodynamic feasibility and spontaneity nature of the adsorption process using Erying equation [27]:

$$\text{Log}\frac{k_{diff}}{T} = [\log\frac{k_B}{h} + \frac{\Delta S^*}{R}] - \frac{\Delta H^*}{2.303RT}$$

Where, $k_B$and h are the Boltzmann, and Planck constants. A plot of log$\frac{k_2}{T}$against $\frac{1}{T}$ gives a straight line with slope [$-\frac{\Delta H^*}{2.303R}$]and intercept [log $\frac{k_B}{h}$ + $\frac{\Delta S^*}{R}$] (Fig. 14). The activation Gibbs free energy was calculated from the equation:

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

The enthalpy (ΔH^*) entropy (ΔS^*) and the Gibbs free energy (ΔG^*) are listed in Table3. The results showed that the reaction was physical and the enthalpy was negative indicating that the reaction is exothermic, also the negative values of ΔS^* and positive ΔG^* indicating the spontaneous formation of activated complex.

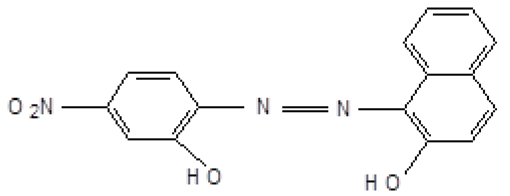
Conclusion

Some of the important conclosions from the experimental results for adsorption of 1-(2¯-Hydroxy- 4¯-nitrophenyl azo) -2-naphthol dye onto the Cement Kiln Dust (CKD) surface, are summarized as follows

- The study shows that CKD has a basic character and the optimum dosage of CKD are 0.15g was shown and the percentage removal was found to be ≈50.2% at 298,308K at pH = 6.5.

- The equilibrium data were tested using Langmuir, Freundlich, Temkin, Dobinin- R and Elvich isotherms .Correlation coefficients indicated that the best fitting are Freundlich and Temkin at 298K.
- Kinetic models were also applied using pseudo-first-order, pseudo-second-order, Elovich and and intra partical diffusion. The best conformity of 1-(2^{-}- Hydroxy-4-nitrophenyl azo) -2-naphthol adsorption is with intra partical diffusion model.
- The results of thermodynamic activation data ΔG^*, ΔS^* and ΔH^* indicates that the adsorption process is non spontaneous. The negative ΔS^* value indicates that randomness decreases at the interface during the adsorption of 1-(2^{-}- Hydroxy-4^{-}-nitrophenyl azo) -2-naphthol dye by CKD .Negative ΔH^* value confirm the exothermic process of the adsorption process.
- The value of activation energy for adsorption of dye onto CKD was 28kJmol^{-1} that suggests the physisorption process occurs and the positive value of Ea indicates that the adsorption process is endothermic.

Table 1: Properties of 1-(2^{-}- Hydroxy-4^{-}-nitrophenyl azo) -2-naphthol (HNPAN)

Specification sheet		Structure
Empirical formula	$C_{16}H_{11}N_3O_4$	
Molar mass	309 g/mol	
Melting point	263-264	
Soluibility	Ethanol	
λ_{max}	521 nm	
Appearance	red crystalline	

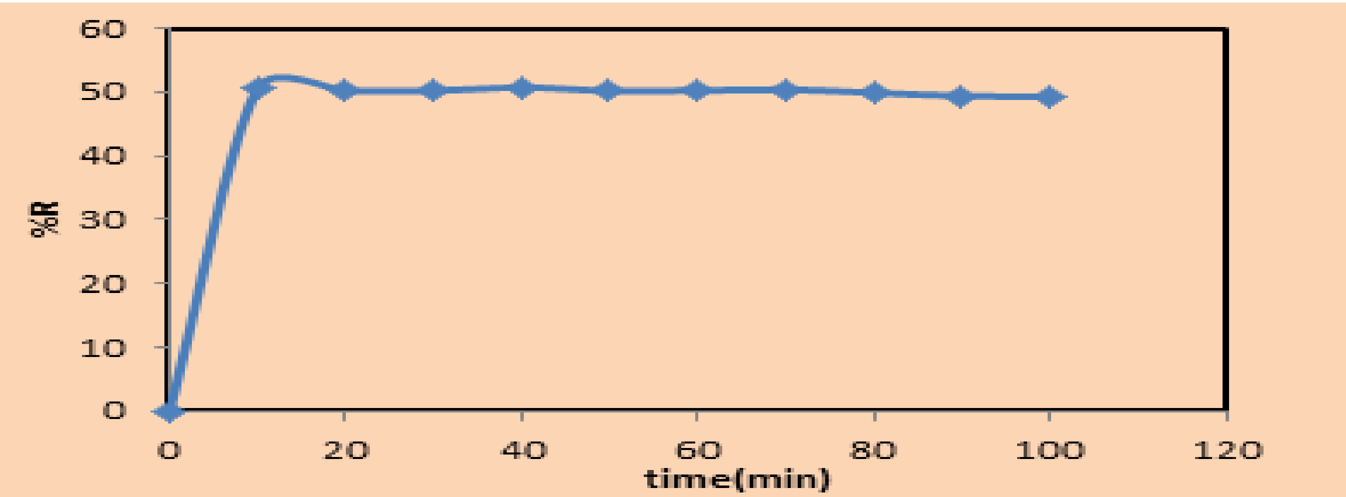


Fig 1: Effect of contact time on the removal of dye onto CKD (temperature 303K, pH = 5-6, dye concentration15mg /l, adsorbent dose =0.15g and agitation speed 150rpm)

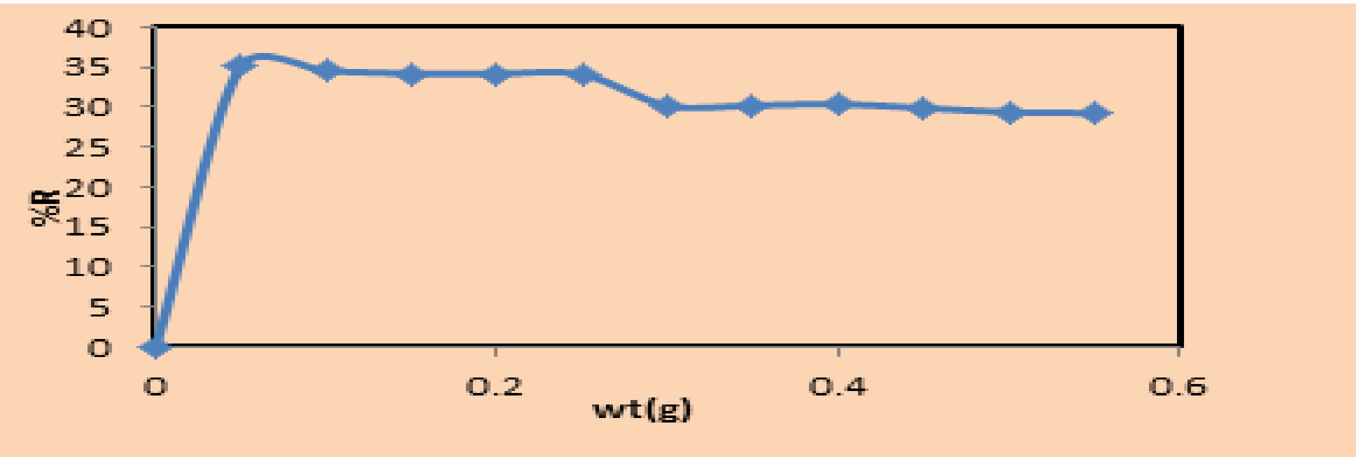


Fig 2: The effect of adsorbent weight on adsorption of dye onto CKD (temperature 303K, pH = 5-6, dye concentration15mg /l, contact time 40min. and agitation speed150rpm

Table 1: values of the adsorption equations isotherms and the correlation coefficients for adsorption of the dye onto the surface of the CKD, weight of CKD 0.15 g and the equilirium time of 25min. within the temperature range 298 to 328 K

Isotherm equation	temperature 298K	308K	318K	328K
Langmuir				
$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$				
q_m	0.0884	0.0688	0.0403	0.0229
K_L	5.9020	4.9787	9.8657	22.6895
R^2	0.8826	0.6052	0.3504	0.1152
Freundlich				
$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$				
n	1.4493	1.3122	1.0649	1.1340
K_f	0.0780	0.0527	0.0214	0.0338
R^2	0.9768	0.8545	0.8485	0.8460
Temkin				
$q_e = B \ln K_T + B \ln C_e$				
q_m	0.7279	0.1622	0.3537	0.1734
K_E	0.5915	4.2767	2.9534	4.2469
R^2	0.9304	0.8024	0.7994	0.7327
Elovich				
$\ln \frac{q_e}{c_e} = \ln K q_m - \frac{1}{q_m} q_e$				
q_m	0.4253	0.3299	0.2797	0.2435
K_E	0.0568	0.4504	0.4240	0.0793
R^2	0.7548	0.7340	0.7458	0.7030
Dubinin–Radushkevich(D-R)				
$\ln q_e = \ln q_s - K_{D-R} \varepsilon^2$				
K_{D-R}	2.2219	1.8235	2.5871	3.0733
R^2	0.5100	0.6781	0.7365	0.7660

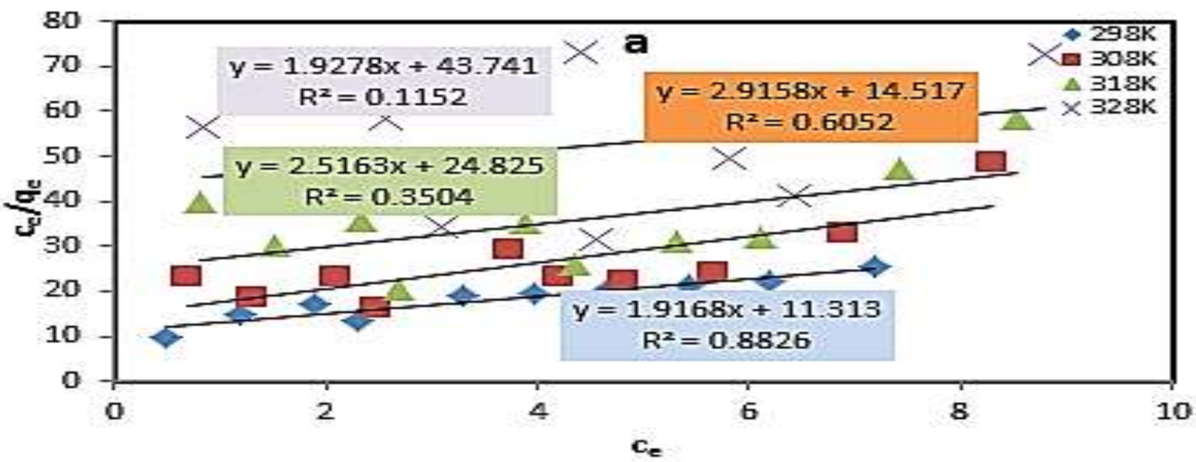


Fig 3: Langmuir isotherm plots for different initial concentrations ranging 2-20ppm of the dye adsorption onto CKD at298- 328K

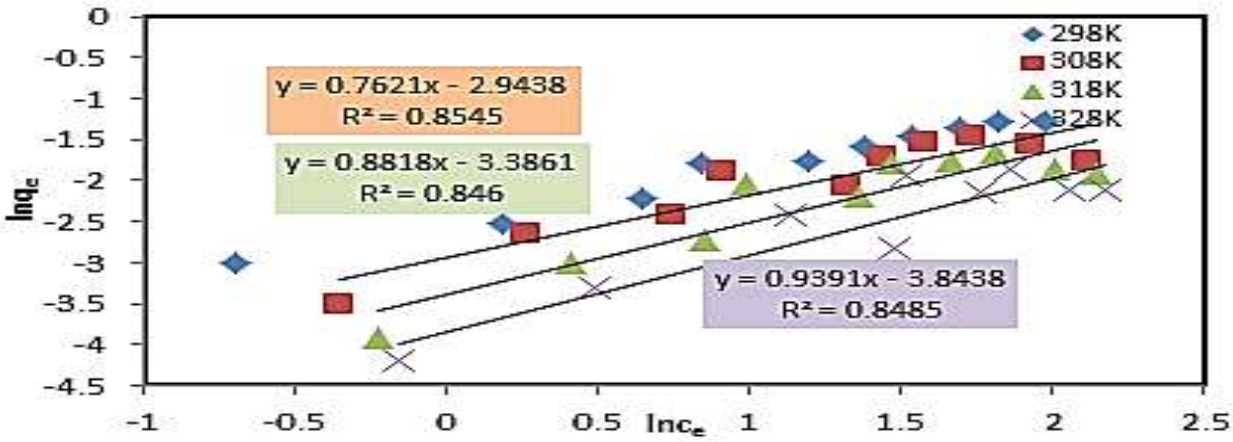


Fig 4: Freundlich isotherm plots for different initial concentrations ranging 2-20ppm of the dye adsorption onto CKD at298- 328K

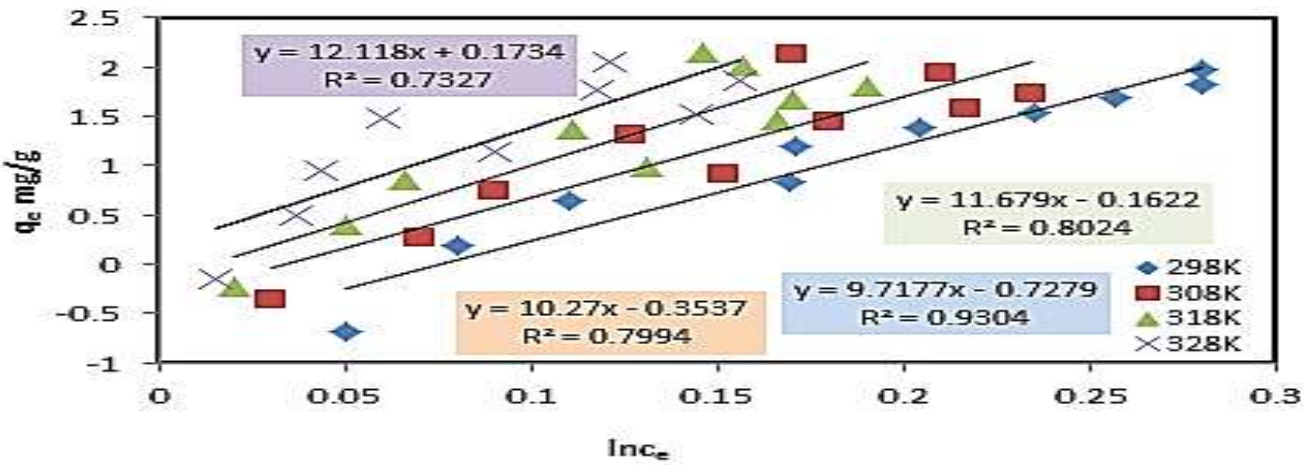


Fig 5: Temkin isotherm plots for different initial concentrations ranging 2-20ppm of the dye adsorption onto CKD at298- 328K

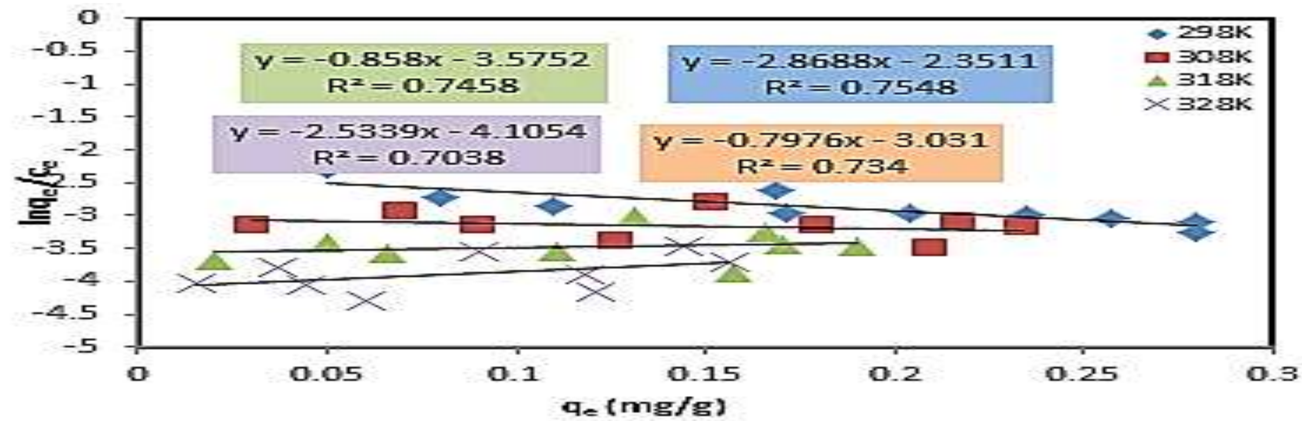


Fig 6: Elovich isotherm plots for different initial concentrations ranging 2-20ppm of the dye adsorption onto CKD at298- 328K

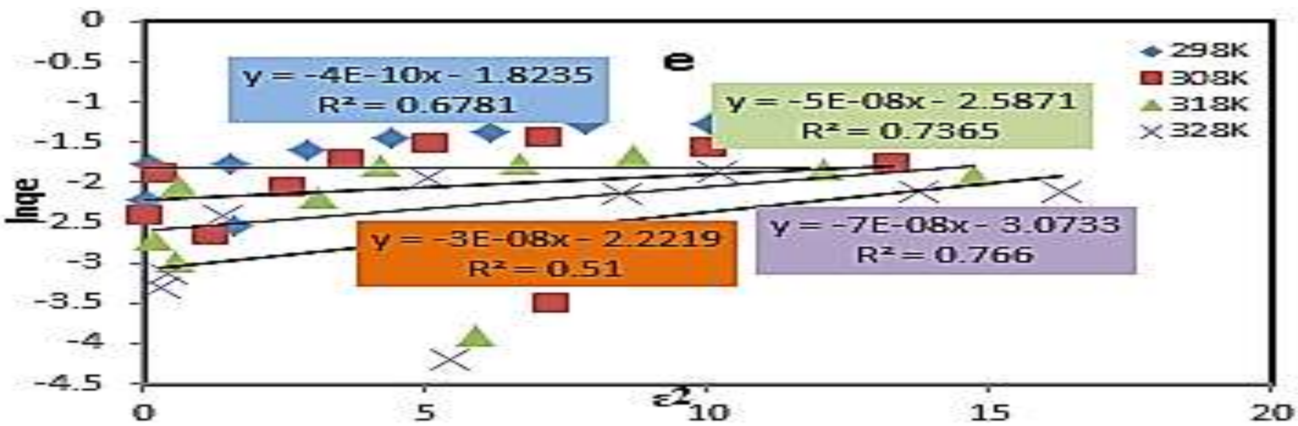


Fig 7: D-R isotherm plots for different initial concentrations ranging 2-20ppm of the dye adsorption by CKD at298-328K.

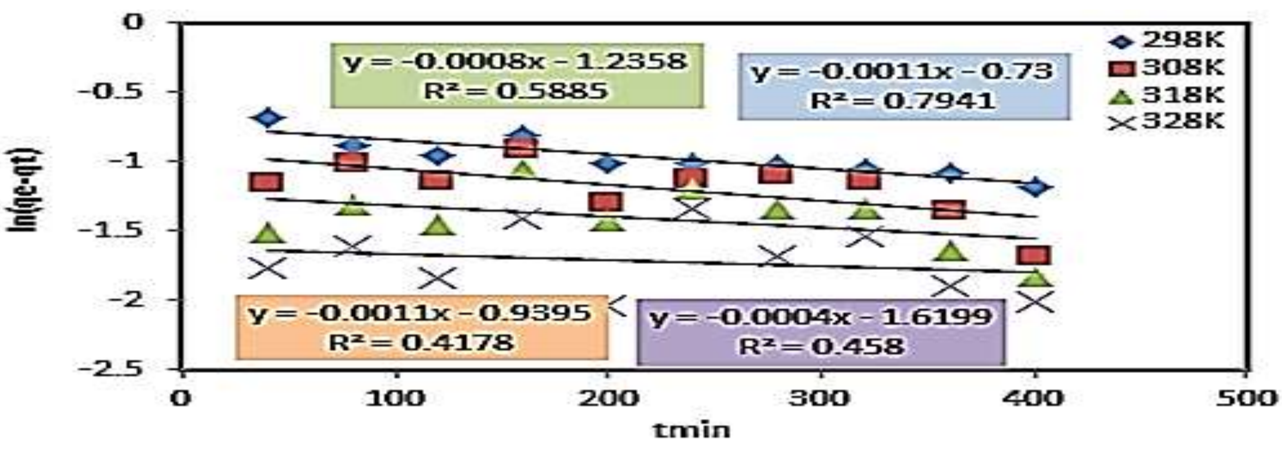


Fig 8: pseudo – first – order kinetic plots for adsorption of dye onto CKD at the temperature range 298-328K

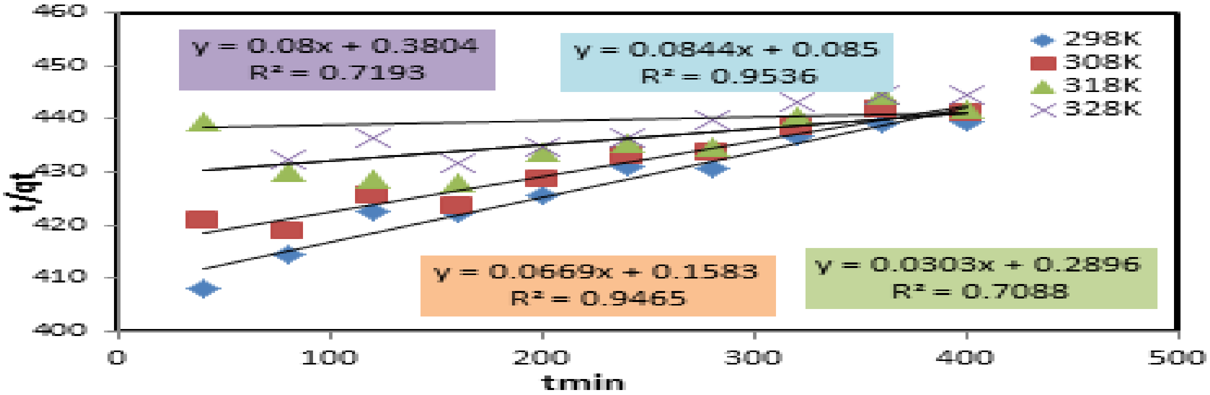


Fig 9: pseudo – second – order kinetic plots for adsorption of dye onto CKD at the temperature range 298-328K

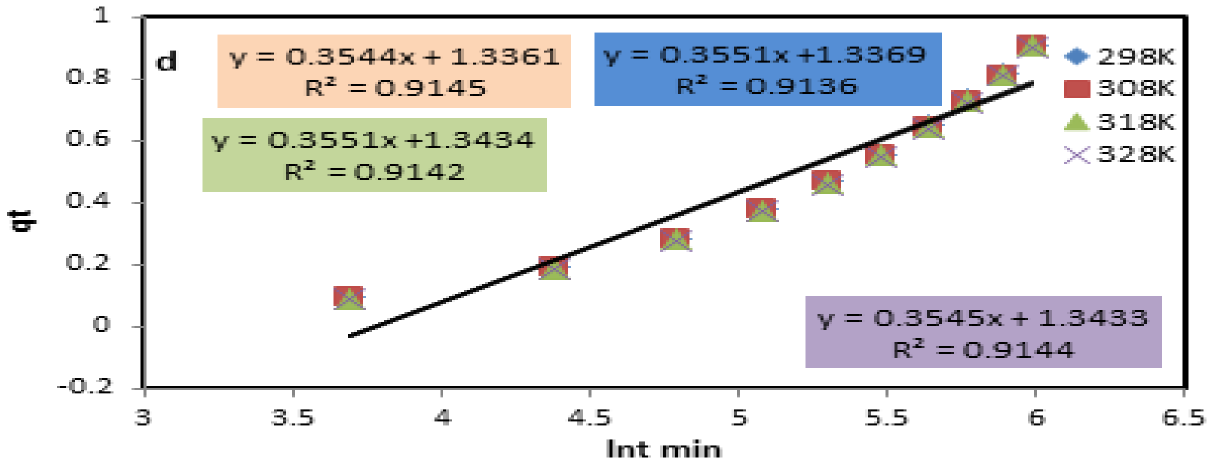


Fig 10: Elovich kinetic plots for adsorption of dye onto CKD at the temperature range 298-328K

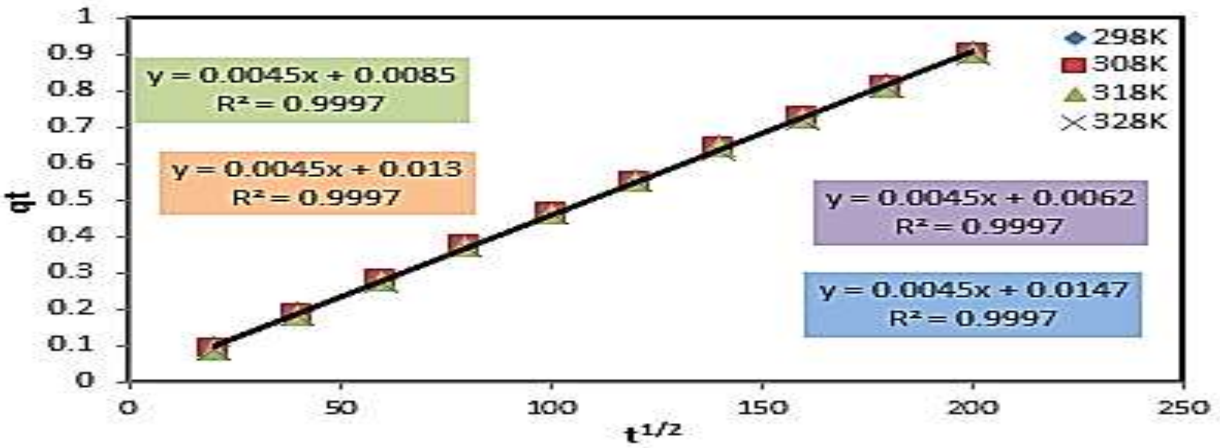


Fig 11: Intra partical diffusion kinetic plots for adsorption of dye onto CKD at the temperature range 298-328K

Table 2: Rate constants and correlation coefficients for dye adsorption onto CKD at pH=6 , initial concentration 15ppm, contact time 25 min. , CKD dosage 0.15g at the temperature range298-328K

linear equation of kinetic model		temperature 298K	308K	318K	328K
Pseudo- first- order $\ln(q_e - q_t) = \ln q_e - kt$	k (min⁻¹)	0.7300	0.9395	1.2358	1.6199
	R^2	0.7941	0.4178	0.5885	0.4580
Pseudo-second-order $\frac{t}{qt} == \frac{1}{kq2} + \frac{1}{qe} t$	k(mg /g min⁻¹)	0.0856	0.3745	2.7679	8.6196
	R^2	0.9536	0.9465	0.7088	0.7193
Elovich $qt = \frac{1}{\beta}\ln(\propto \beta) + \frac{1}{\beta}\ln t$	∝ (mg g⁻¹min⁻¹)	1.3981	1.4250	1.4263	1.4254
	β (g mg⁻¹)	0.7480	0.8150	0.7443	0.7443
	R^2	0.9136	0.9145	0.9144	0.9142
Intra – partical – diffusion $q_t = K_{diff}\, t^{1/2}$	K_{diff} (mgg⁻¹min.⁻¹ᐟ²)	0.0147	0.0130	0.0085	0.0062
	R^2	0.9997	0.9997	0.9997	0.9997

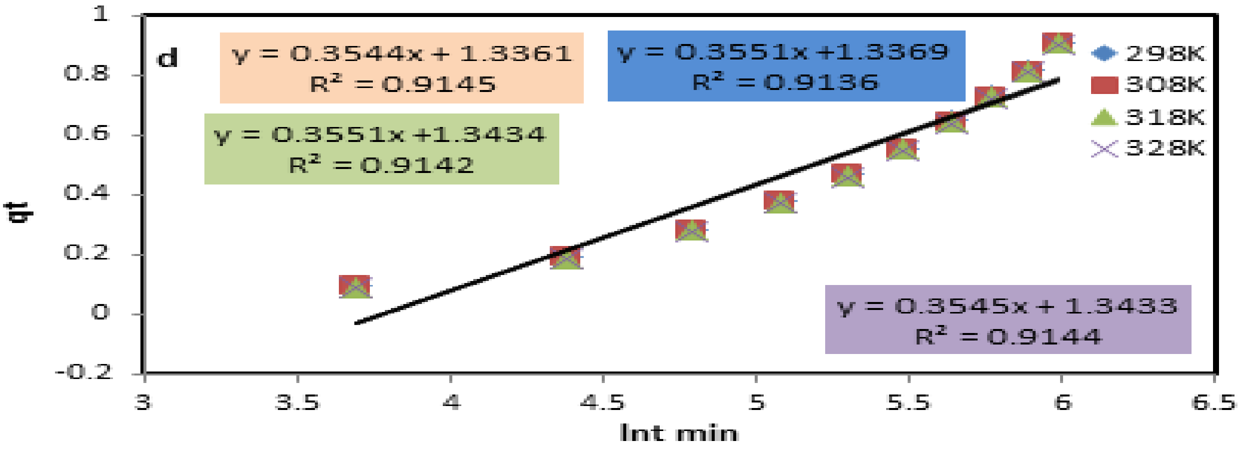


Fig 12: Effect of temperature on the adsorption of dye onto CKD (dye concentration mgl-1, contact time 40min..PH=6.5adsorbent dose 0.15g and agitation speed=150 rpm)

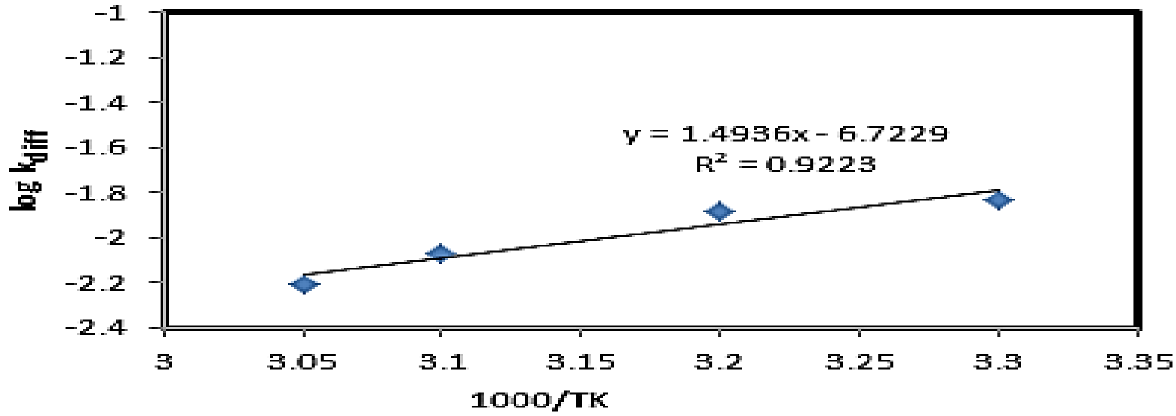


Fig 13: Arrhenius plots for adsorption of dye on CKD at the temperature range 298-328K

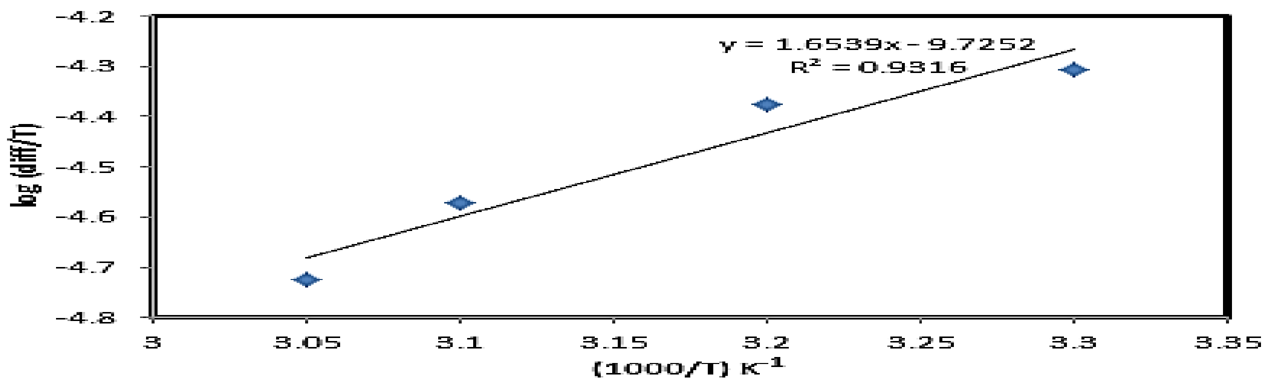


Fig 14: plots of log$\frac{k_{diff}}{T}$ versus $\frac{1}{T}$ for adsorption of dye on CKD at the temperature range 298-328K

Table 3: Thermodynamic parameters for dye sadsorption onto CKD at the temperature range 298-328K

ΔG^* $kJmol^{-1}$				ΔS^* $Jmol^{-1}K^{-1}$	ΔH^* $kJmol^{-1}$	E_a $kJmol^{-1}K^{-1}$
298K	308K	318K	328K			
17.991	91.657	21.323	22.990	-31.670	-166.646	-28.644

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