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The performance of Cement Kiln Dust in Removal of Some Dyes from Aqueous Solutions

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ABSTRACT

The adsorption of Murexide, Eosin yellowish and Bromo cresol green (BCG) dyes by CKD was carried out by varying the parameters such as contact time, dye concentration, adsorbent dose, pH and temperature. Adsorption isotherm equations were tested for all of Langmuir, Freundlich, Temkin, Modified Frumkin, Dobinin-Radushvich, Harkins-Jura and Elovich. The equilibrium adsorption data were fitted between Freundlich and Temkin isotherms for Murexide, D-R isotherm for Eosin yellowish and Freundlich for BCG. Adsorption followed pseudo-second-order rate kinetics. The high percentage removal was found $\approx 80.2\%$ at 333K, pH 6; $\approx 42\%$ at 303K, pH 6; and $\approx 50\%$ at 303K, pH 5 of Murexide, Eosin yellowish and BCG respectively. Thermodynamic parameters ΔG , ΔH , ΔS and E_a were computed, and showed that the adsorption process onto CKD was endothermic and spontaneous in Murexide adsorption process, while in Eosin yellowish and BCG adsorption was exothermic and spontaneous. Also adsorption studies suggest that physisorption might be the major mode of adsorption and CKD expressed as low affinity for removal of Eosin yellowish and BCG and in general the adsorption process was less affected by temperature.

Keywords: Adsorption isotherms; Cement Kiln Dust; dyes; Kinetic studies; Thermodynamic studies

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INTRODUCTION

The adsorption phenomenon underlies a number of extremely important processes of utilitarian significance its practical applications in; industry ,environmental protection, methods of separation of mixture, purification of water, ion exchange and so on. Moreover the adsorption of substrates is the first stage in many catalytic process¹ . Cement kiln dust (CKD) as industrial by product is a fine powdery material which is created in the kiln during the production of cement clinker. The dust is a particulate mixture of partially calcined and unreacted raw feed, clinker dust and ash, enriched with alkali sulfates, halides and

other volatiles. These particulates are captured by the exhaust gases and collected in particulate matter control devices such as cyclones, baghouses and electrostatic precipitators². Several factors influence the physical and chemical characteristics of CKD depend on raw materials, type of kiln operation, dust collection systems and fuel type used in cement clinker production³. Many researchers have been working several studies on economic and efficient methods to use this dust in a number of applications such as , industrial waste water treatment , soil stabilization, cement production , agricultural fertilizers and etc⁴⁻⁹.

In this study batch adsorption experiments were performed at temperature range from 30°C to 60°C using UV- Visible spectrophotometer. The objective of this study was to to extent the previous works⁵⁻¹⁵ of adsorption onto some agriculture wastes or natural kaoline for removal dyes ,drugs and some organic compounds from aqueous solutions, its thermodynamic and kinetic parameters.

MATERIALS AND METHOD

Characterization of CKD

Table: 1 The Chemical composition (wt. %) of cement kiln dust of Al-kufa cement factories, Iraq.

Components	Weight (%)
SiO ₂	15.46
Al ₂ O ₃	3.91
Fe ₂ O ₃	4.05
CaO	43.4
MgO	2.98
SO ₃	6.34
N ₂	1.42
K ₂ O	2.44
Cl	0.92
L.O.I	19.08

These values are in the range with those reported in the literature¹⁶⁻¹⁹ .

The byproduct cement kiln dust (CKD) is generated in a large quantities in Al-kufa Portland cement factory in Al-kufa city, Iraq it was Collected and prepared by the method which described elsewhere² to be used in the adsorption experiments. Table 1 shows the Chemical composition (wt. %) of cement kiln dust.

MATERIALS AND METHOD

All reagents Murexide, Eosin yellowish and BCG were used of analytical grade chemicals and purchased from Sigma-Aldrich company (USA) while hydrochloric acid and ammonia from Merck company (Germany) was used to adjust the pH of the solutions. Stock solution (100ppm) was prepared by dissolving 0.1g of each dyes in 1000 ml volumetric flask contains distilled water for Murexide and Eosin yellowish while for BCG dissolved in ethanol. Solutions of different concentrations were prepared from stock solution by serial dilutions ranging from 10 to 50 ppm for Murexide and BCG, from 2 to 20 ppm for Eosin.

Instruments

For measuring the absorbance of each dye concentrations a UV- Visible spectrophotometer (Shimadzu UV 4000, Japan) was employed. HANA model (China) pH meter for applied pH measurements. A thermostat shaker water bath at model GCA, Percision scientific Chicago, U.S.A, was used to stirred the solutions at 160 rpm. The centrifuge of model Magafuge1.0, Herouse sepatech at 3000.rpm, was used to centerifugate the dyes solutions.

Equilibrium Adsorption Experiment

In order to calculate the kinetic and thermodynamic parameters, batch technique was used in adsorption studies by adding the best amount of CKD to a series of 50 ml sealed conical flasks filled with 15 ml of known initial concentration of Murexide, Eosin yellowish and BCG at 303K, pH was adjusted by using HCl and NH₄OH solutions. The flasks were put in a thermostat shaker water bath in a speed 160 rpm the best equilibrium time, then was removed and the solution was filtered at appropriate time interval, centrifuged at 3000 rpm for 10 min. after that CKD and dyes were separated by filtration. The residual dye concentration was estimated spectrophotometrically at the λ_{max} corresponding to maximum absorbance; 511nm for Murexide and 515 nm for Eosin yellowish and 422nm for BCG. The extent of dye adsorption at equilibrium q_e (mgg⁻¹) onto CKD was determined from the following equation⁽²⁰⁾:

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

Where C_o and C_e in (mgL⁻¹) are the concentrations of dye at initial and equilibrium respectively, V

in (L) is the volume of the solution, and m in (g) is the weight of CKD. The removal efficiency was calculated by using equation²¹ :

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} \times 100 \quad \dots\dots\dots(2)$$

Optimization of contact time of Dye

To identify the required time for equilibrium sorption, the batch adsorption experiments were performed at 303K . 25 ml of dye solutions of initial concentration 40, 15 and 50 mg/L for Murexide, Eosin yellowish and BCG respectively were put in to 50 ml stoppered conical flasks and shaken with 0.1 g of CKD in a thermostat shaker water bath was setting at 303K. Initial pH was adjusted at the optimum pH obtained from the first set of experiments (pH value of 6 for Murexide, Eosin and 5 for BCG) , the percentage of dye uptake was measured at time intervals from 10 minutes to 100 minutes . After each 10 min. flasks were removed from the shaker water bath, then the solution was filtered, centrifuged at 165 rpm for 15 min. and CKD and dyes were separated by filtration through filter paper. The dye concentration was analyzed using spectrophotometer Biochrom Ltd, combridge CBU at the λ_{max} for Murexide, Eosin yellowish and BCG.

Optimization of Adsorbent Dosage

To determine the optimum adsorbent dosage, experiments were carried out by adding different weights of the CKD from 0.05 to 0.45 g to 15 ml of desired concentration of these dyes in conical flask at pH 6 and temperature 303K , then agitated til to attain equilibrium time for each dyes. 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 dyes were determined also spectrophotometry at those lambdas,

RESULTS AND DISCUSSION

Effect of contact time of Dyes

Figure 1 shows that the equilibrium time was found to be 30 min. for Murexide and Eosin yellowish and BCG was found 20 min with the percentage removal reaching nearly 70 ,40 and 60 % for Murexide ,Eosin and BCG respectively.

Effect of Adsorbent Dosage

The results of percentage removal of dyes with respect to CKD dosage are shown in figure 2. The extent of adsorption at equilibrium showed that the best weights is 0.15g for Murexide, 0.05g for

Eosin yellowish and 0.1 for BCG respectively were required to achieve adsorption process onto CKD surface .

Effect of Initial Dye concentration

Figures 3 ,4 and 5 show the effect of initial Murexide, Eosin and Bromo cresol green concentrations on the adsorption capacity by CKD in the concentrations range from 5 to 50 ppm (for Murexide , BCG and 2-20 for yellowish Eosin) at 303K,160 rpm agitation speed and solution pH was ranging from 2 to 12, the experimental results showed that the adsorption capacity increased with increasing Concentration.

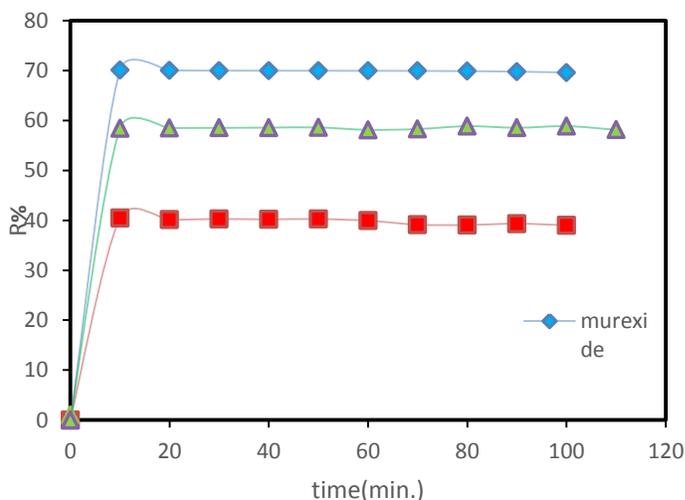


Figure. 1: Variation of contact time on percent removal of Murexide, Eosin yellowish and BCG from aqueous solution onto 0.1g CKD at temperature = 303K ; $C_0 = 40$ ppm, pH 6 for Murexide and 15ppm,pH 6 for Eosin yellowis And 50 ppm for BCG at pH 5.

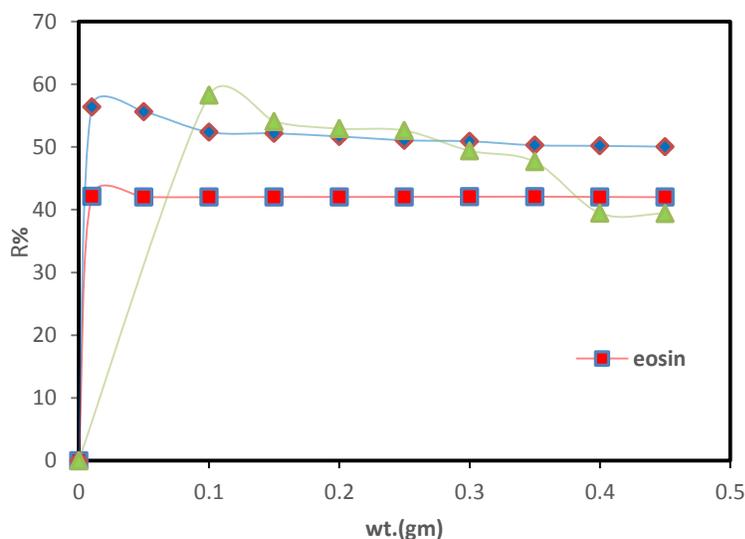


Figure 2: Variation of CKD dosage on Murexide , Eosin yellowish and BCG adsorption from aqueous solution at temperature = 303K ; $C_0 = 40$ ppm pH 6 for Murexide and

15ppm,pH 6 for Eosin yellowish and 50 ppm for BCG at pH 5 and experimental contact time.

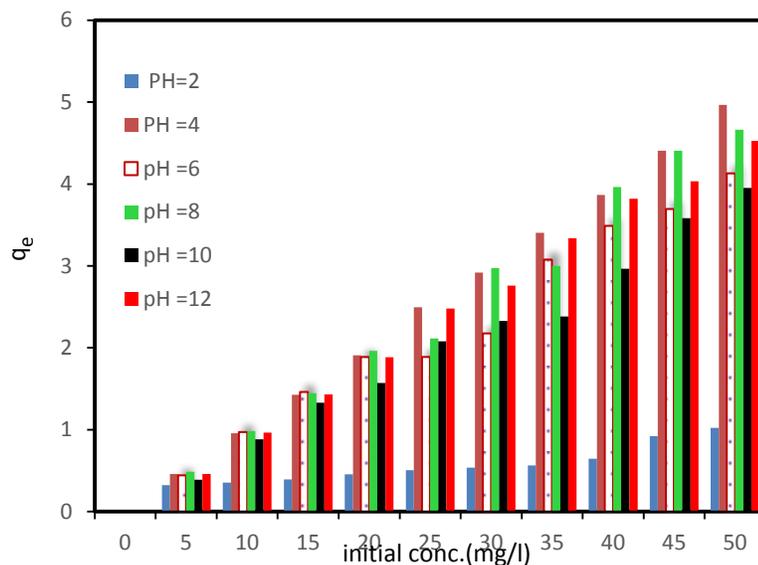


Figure 3: Effect of initial concentration of Murexide on adsorption capacity onto the CKD surface in the pH range 2-12 and at temperature 303K.

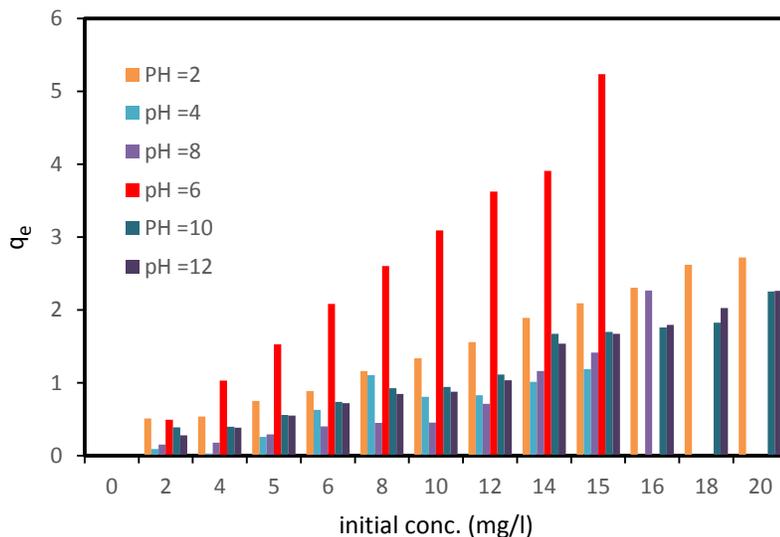


Figure 4: Effect of initial concentration of Eosin yellowish on adsorption capacity onto the CKD surface at the pH range 2-12 and at temperature 303K.

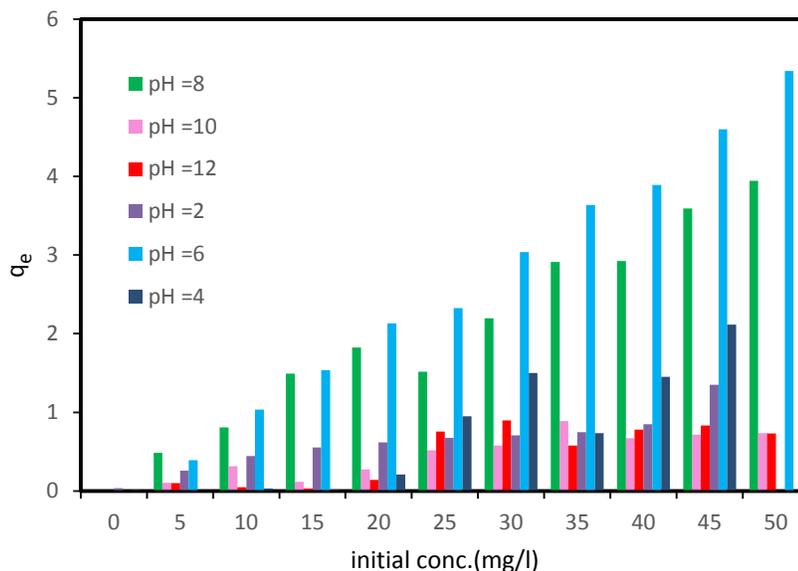


Figure 5: Effect of initial concentration of BCG on adsorption capacity onto the CKD surface at the pH range 2-12 and at temperature 303K.

Determination of pH of Zero Charge (pH_{pzc})

In adsorption studies it is very important to know the surface charge of the material in the aqueous media. The pH at which the sorbent surface charge takes a zero value is defined as point of zero charge (pH_{pzc}). Several methods have been used for the determination of pH_{pzc} of oxides, hydroxides, soils and other heterogeneous solid materials²².

To determine the pH_{pzc} we can use pH drift method²³, in this method suspensions of 0.15g/ 50 ml of CKD were put into contact with 0.01M of NaCl solutions at pH in the range of 2-12. The suspensions were agitated at room temperature for 48 h in a shaker water bath at 160 rpm until an equilibrium pH value was reached, after that these solutions are filtered and the final pH during equilibration was measured. The pH_{pzc} was determined by plotting the final pH versus initial pH. The point on the at which initial pH is equal to final pH is pH_{pzc}. Figure 6 show the value of pH_{pzc} of CKD is about 10, it also indicates that the surface charge on the CKD surface is neutral at pH \approx 10, when the pH is lower than 10 that means the water donates protons than hydroxide ions so the CKD surface is positively charged, while the pH above 10 the CKD surface is negatively charged.

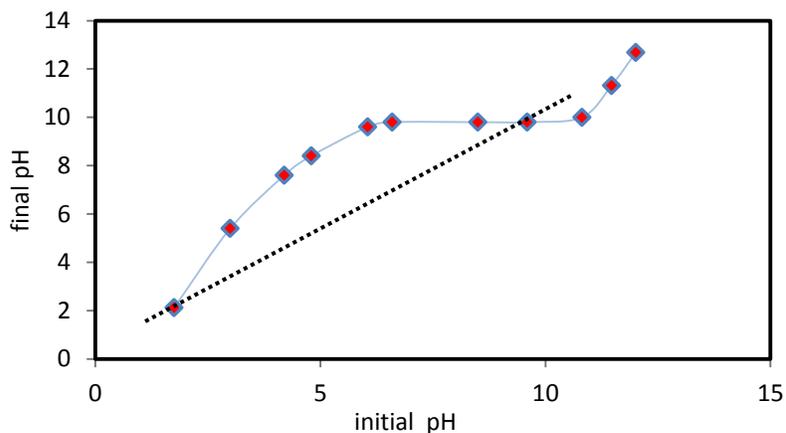


Figure 6: pH drift method to determine the pH_{pzc} of CKD surface

Effect of Initial pH.

Batch equilibrium method was used in order to determine the sorption amount of dyes by CKD at various pH values ranging 2-12, initial concentrations 45ppm for Murexide and Bromocresol green while 15 ppm for Eosin at temperature 303K. The pH of Al- Kufa plant CKD samples were 11.2 (in general, the pH of CKD leachates using standard EPA leachate procedures falls between 11 and 13)⁽²⁴⁾. The variation of solution pH value is influenced the degree of ionization of the dyes as well as the surface binding sites of the adsorbent²¹

Figures 7,8 and 9 showed the maximum adsorption of dyes, Murexide at pH 4 while Eosin yellowish and BCG the maximum adsorption at pH 6 the reason can be explained by considering the pH_{pzc} of CKD surface which had positively charged at pH below 10 (the $\text{pH}_{\text{zpc}} \approx 10$) and the molecular nature of Murexide, Eosin Yellowish and BCG. It was also reported in literature that below pH 7, a significantly high electrostatic attraction exists between the positively charged surface of the adsorbent and anionic dye. As the pH of the system is increased, the number of negatively charged sites increased and the number of positively charged sites decreased. Also lower adsorption of anionic dye molecules at pH greater than pH_{pzc} is due to the presence of excess OH^- ions which compete with the anionic dyes, the same results are reported in the literature^{2,18,25-28}.

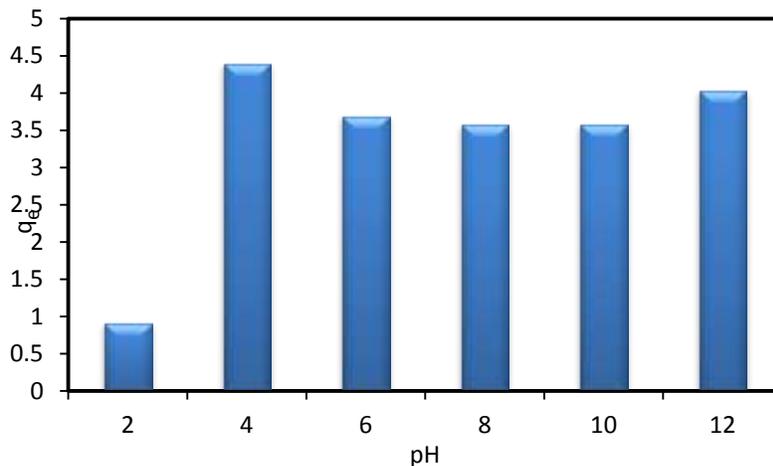


Figure 7: variation of pH value on Murexide adsorption onto CKD Surface, initial concentration 40 ppm, CKD dosage 0.15 g and temperature = 303 K.

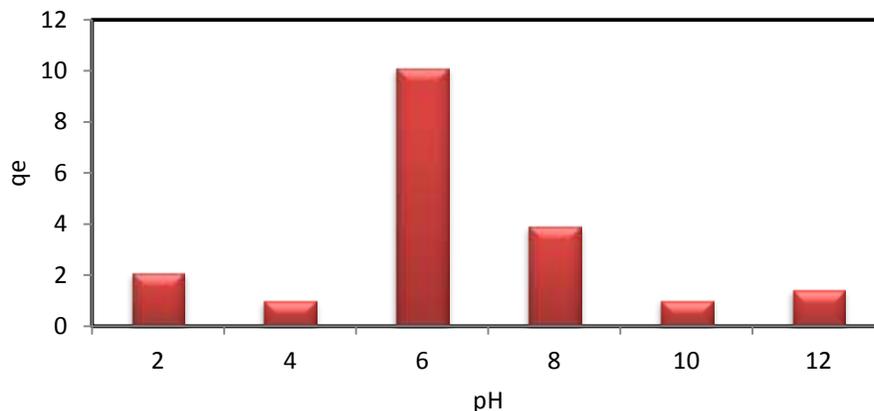


Figure 8: variation of pH value on Eosin yellowish adsorption onto CKD surface, initial concentration 15 ppm, CKD dosage 0.05 g and Temperature 303 K.

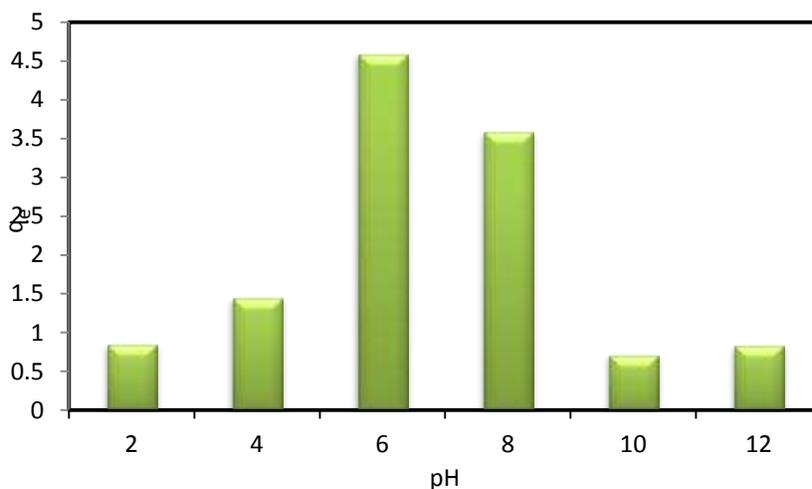


Figure 9: variation of pH value on BCG adsorption onto CKD surface, initial concentration 45 ppm, CKD dosage 0.1 g and Temperature = 303 K.

Adsorption Equilibrium and Adsorption Isotherms Models

In order to understand the adsorptive behaviour for solid - liquid adsorption system, it is important to find the most appropriate correlation for the equilibrium curve, the applicability of the type isotherm models to the adsorption study have been compared by the correlation coefficients, R^2 values. In this research various isotherm models have been tested for explaining the adsorption processes such as; Langmuir, Freundlich, Temkin, Frumkin, Dubinin – Radushkevich (D-R), Elovich and Harkins- Jura isotherms²⁷⁻³². Tables 2, 3, 4 and Figures 10, 11, 12 have been shown the isotherm constants, correlation coefficients, the total sorption capacity and the isotherm models. From these tables and figures, correlation coefficients of Freundlich and Temkins isotherms models were the good fitting for Murexide adsorption at temperature 313K, that means the adsorption sites increase exponentially with adsorption and the heat of adsorption of all molecules in the layer would decrease linearly with coverage^{2,33} The correlation coefficient of D-R isotherm model was the best fitting for Eosin adsorption at temperature 313K, also for Langmuir model the values of q_m were negative which reflects the inadequacy of this model for explaining the adsorption process, although shows a good linearity³³. For BCG the correlation coefficients Freundlich isotherm models were the best fitting at temperature 313K, that means the adsorption on heterogeneous surfaces are multilayer adsorption with an exponential distribution of site energy the same results were reported in literature^{21,27}.

Kinetics Investigation of Adsorption

Pseudo –first-order, Pseudo-second-order, Elovich and Intra-particle diffusion were using as a kinetics models to explain the adsorption mechanism. The values of correlation coefficients (R^2) showed that. Tables 5,6 and 7 showed the kinetic models equations and the kinetic constants for Murexide, Eosin and BCG adsorption onto CKD. From these tables it is clear that the pseudo – second – order kinetic model is the best fitting to the experimental data better than than the other models (R^2 values are the higher for all dyes and some time was attained to (0.9900) as shown in Figures 13, 14, 15, that means the kinetics of these dyes adsorption is followed pseudo- second-order model mechanism.

Temperature dependence on dye adsorption

The adsorption of Murexide, Eosin yellowish and BCG dyes on CKD from aqueous solution was studied at temperatures of 303, 313, 323, 333 K and 160 rpm agitation speed,(at pH 6, initial concentration 45ppm, 0.15 g CKD dosage and 20 min. contact time for Murexide ; for Yollowish Eosin at pH 6 , initial concentration 15ppm, 0.05g CKD dosage and 40 min. contact

time while for BCG pH 5, initial concentration 30 ppm, 0.1g CKD dosage and 40 min. contact time for). As shown in Figure 17 the percentage removal of Murexide increased at higher temperatures which indicates that adsorption process is endothermic (the temperature accelerates penetration of Murexide molecules inside pores of CKD with interaction between oxide ion and cationic groups of the dye molecule at higher temperature). Same results have been reported²⁷ in literature. Also figures 18 and 19 show the effect of temperature on percentage removal of Eosin yellowish and BCG, percentage the removal decreased with increasing temperature from 303 to 333K, that means the adsorption process was an exothermic.

Table 2 : Comparison of the isotherm equations constants and correlation coefficients for Murexide Adsorption onto CKD at pH= 6 , initial concentration ppm 40, contact time 30min., CKD dosage 0.15 g and the temperature range 303-333K.

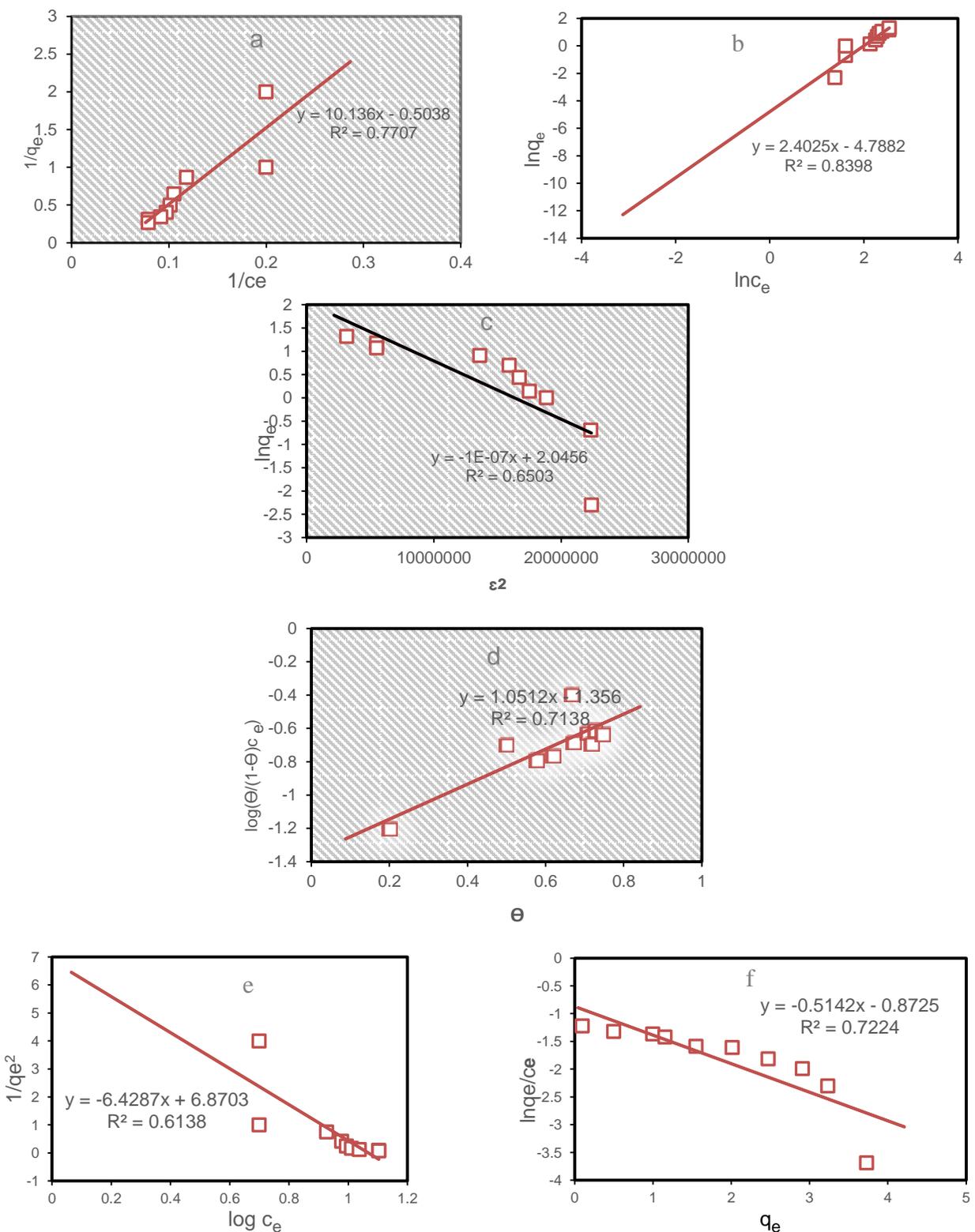
Dye	Linear equation of isotherm model	Parameters	Temperature			
			303	313	323	333
Murexide	Langmuir $\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	K (L /mg) q _m (mg /g) R ²	1.199 15.385 0.7183	0.863 15.244 0.7707	1.585 10.764 0.6963	-0.105 -0.907 0.9908
	Freundlich $\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	n K _f (L /mg) R ²	3.6036 0.7810 0.7504	0.4162 0.0083 0.8398	0.4043 0.0107 0.8324	0.2713 0.0020 0.8305
	Dubinin-Radushkevich $\ln q_e = \ln q_s - K_{DR} \epsilon$ $E = 1 / (2K_{RD})^{1/2}$	q _m (mg /g) k E (kJ /mol) R ²	7.086 7 x10 ⁻² 0.4483	7.693 7 x10 ⁻² 0.6503	7.268 7 x10 ⁻² 0.7116	10.939 7 x10 ⁻³ 0.6331
	Elovich $\ln \frac{q_e}{C_e} = \ln K q_m - \frac{1}{q_m} q_e$	qm(mg /g) K R ²	1.471 0.410 0.6873	1.945 0.418 0.7224	2.153 0.499 0.7721	1.888 0.412 0.7389
	Harkins-Jura $\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A} \log C_e$	A B R ²	0.596 1.224 0.7369	0.156 1.069 0.6138	0.775 1.102 0.7958	0.009 0.844 0.3587
	Modified Frumkin $\ln \left[\frac{\theta}{C(1-\theta)} \right] = 2a\theta + \log K$	a K R ²	0.745 0.0193 0.814	0.525 0.0441 0.713	0.468 0.0664 0.746	0.726 0.0403 0.761
	Temkin $q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$	K (L /mg) B (J /mol) R ²	1.676 8061.2 0.7742	1.566 8214.3 0.8411	1.559 9134.1 0.8990	1.991 14648.4 0.8930

Table 3 :Comparison of the isotherm equations constants and correlation coefficients for Eosin adsorption onto CKD at pH= 6, initial concentration 15 ppm , contact time 40min., CKD dosage 0.05 g and the temperature range 303-333K.

Dye	Linear equation of isotherm model	Parameters	Temperature			
			303	313	323	333
Eosin	Langmuir $\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	K (L /mg) q _m (mg /g) R ²	0.0293 3.278 0.8749	-0.0141 -8.511 0.9514	-0.141 -8.511 0.807	-0.027 -1.838 0.6363
	Freundlich $\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	1/n K _f (L /mg) R ²	0.8880 0.0730 0.8239	0.5365 0.0240 0.7354	0.4033 0.0032 0.8862	0.3507 0.0013 0.9364
	Dubinin-Radushkevich $\ln q_e = \ln q_s - K_{DR} E$ E = 1/ (2K _{RD}) ^{1/2}	q _m (mg /g) k x10 ⁻ E (kJ /mol) R ²	0.7450 7x10 ⁻³ 0.4685	1.569 7x10 ⁻⁷ 0.9549	1.196 7x10 ⁻⁷ 0.8324	1.298 7x10 ⁻⁸ 0.8553
	Elovich $\ln \frac{q_e}{c_e} = \ln K q_m - \frac{1}{q_m} q_e$	qm(mg /g) K R ²	1.898 0.135 0.6873	0.918 0.277 0.7251	0.646 0.135 0.9397	0.5663 0.117 0.9025
	Harkins-Jura $\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A} \log C_e$	A B R ²	0.023 0.9938 0.8745	0.091 1.021 0.821	0.029 1.089 0.772	0.011 1.033 0.8967
	Modified Frumkin $] = 2a\theta + \log K \log \left[\frac{\theta}{c(1-\theta)} \right]$	A K R ²	0.845 0.0023 0.1407	1.091 0.0144 0.6821	1.198 0.0110 0.6023	1.515 0.0069 0.6844
	Temkin $q_t = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$	K (L /mg) B (J /mol) R ²	0.577 3621.5 0.460	0.108 3050.0 0.790	0.662 3783.3 0.570	0.722 3979.5 0.550

Table 4 : Comparison of the isotherm equations constants and correlation coefficients for BCG adsorption onto CKD at pH= 5, initial concentration 45 ppm , contact time 40 min., CKD dosage 0.1 g and the temperature range 303-333K.

Dye	Linear equation of isotherm model	Parameters	Temperature			
			303	313	323	333
BCG	Langmuir $\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	K (L /mg)	0.113	0.052	0.0033	0.060
		q _m (mg /g)	2.380	4.103	5.131	2.798
		R ²	0.7294	0.7261	0.8920	0.9286
	Freundlich $\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	1/n	1.433	1.023	0.908	1.1568
		K _f (L /mg)	0.1925	0.1099	0.0739	0.1081
		R ²	0.5658	0.9651	0.9604	0.7705
	Dubinin-Radushkevich $\ln q_e = \ln q_s - K_{DR} \epsilon$ $E = 1 / (2K_{RD})^{1/2}$	q _m (mg /g)	2.028	2.513	2.552	1.903
		k	0.060	0.006	0.006	0.11
E (kJ /mol)						
R ²		0.8307	0.8781	0.8010	0.7372	
Elovich $\ln \frac{q_e}{C_e} = \ln K q_m - \frac{1}{q_m} q_e$	qm(mg /g)	1.167	1.908	1.980	2.641	
	K	0.3254	0.2510	0.2249	0.1280	
	R ²	0.8214	0.8700	0.8975	0.8409	
Harkins-Jura $\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A} \log C_e$	A	2.348	0.6727	0.4170	2.3724	
	B	2.2073	1.1341	1.449	3.8200	
	R ²	0.8313	0.8942	0.7744	0.8717	
Modified Frumkin $J = 2a\theta + \log K \log \left[\frac{\theta}{C(1-\theta)} \right]$	a	1.566	1.200	1.256	1.656	
	K	0.0027	0.0054	0.0047	0.0024	
	R ²	0.7484	0.5162	0.6831	0.8206	
Temkin $q_t = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$	K (L /mg)	0.8534	0.3673	0.3243	0.3906	
	B (J /mol)	3882.1	2402.6	2273.2	3759.5	
	R ²	0.8103	0.8826	0.7161	0.9151	



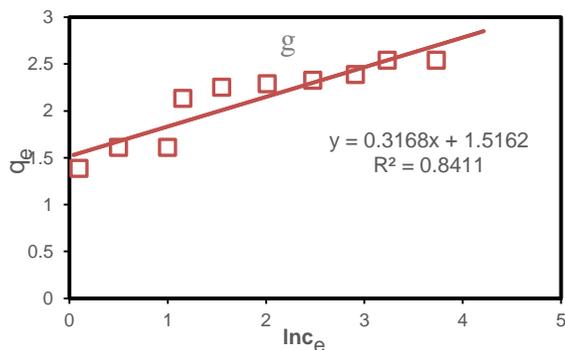
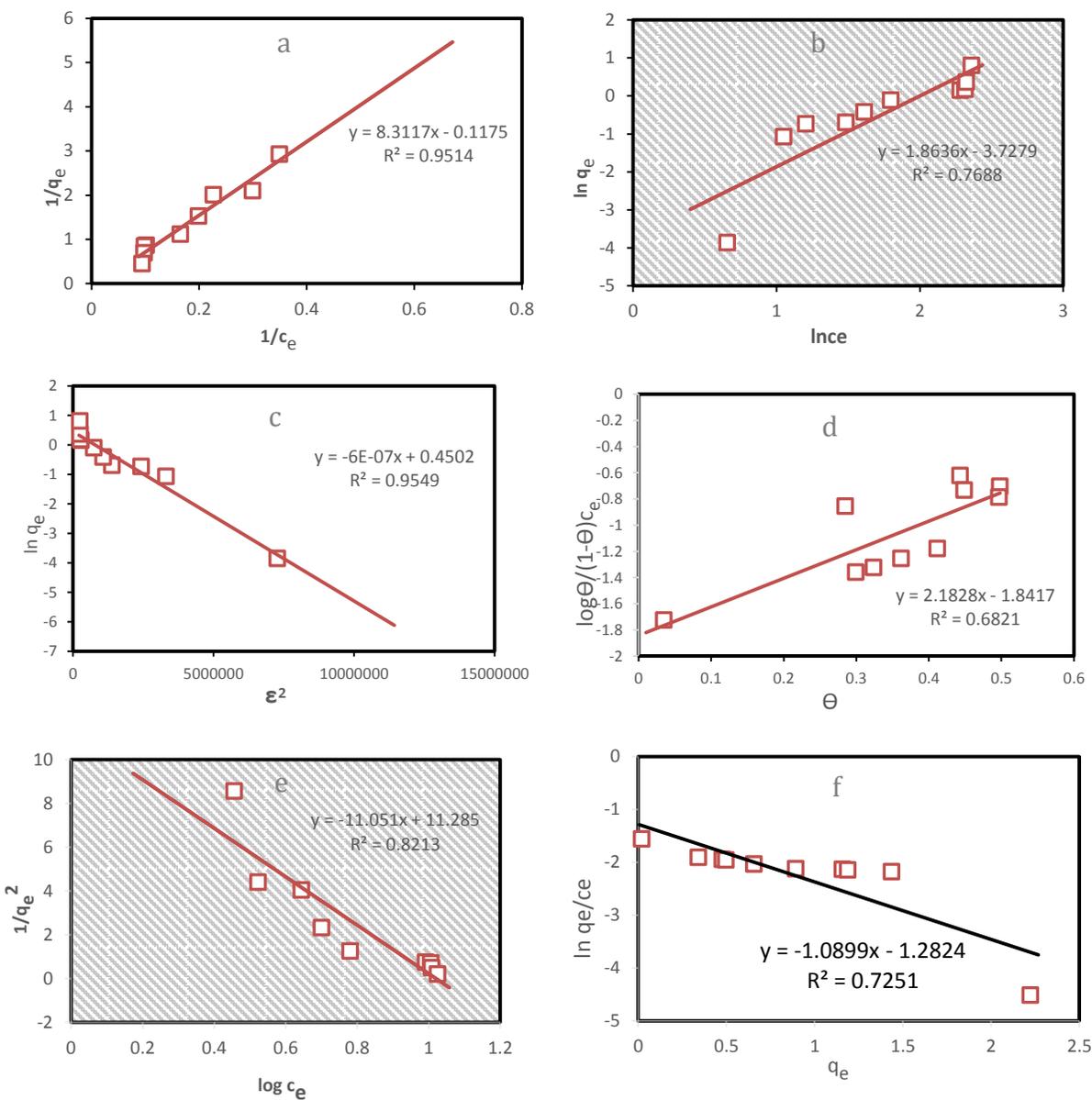


Figure 10 : (a) Langmuir isotherm (b) Freundlich isotherm (c)D-R isotherm (d)Frumkin isotherm (e) Harkins-Jura isotherm (F) Elovich isotherm(g) Temkin plots for different initial concentrations ranging 5-50 ppm of the Murexide adsorption by CKD at 313K.



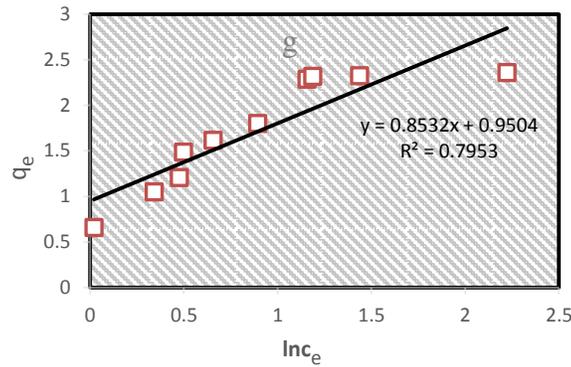
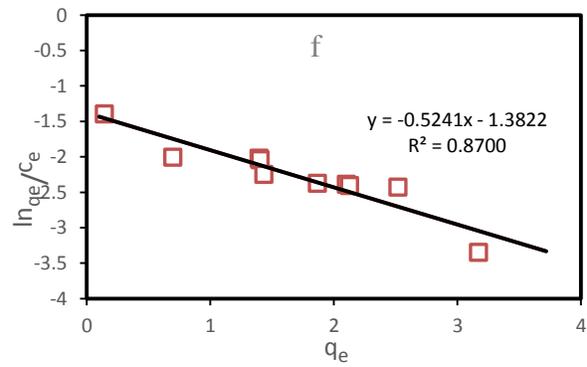
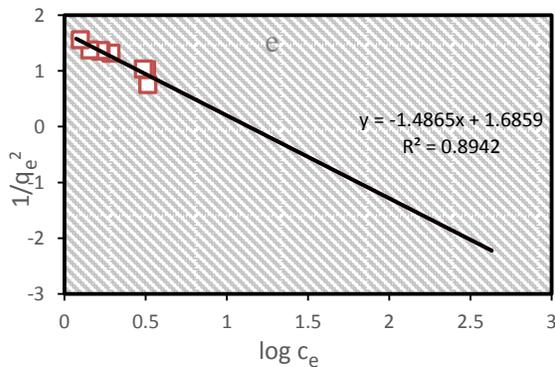
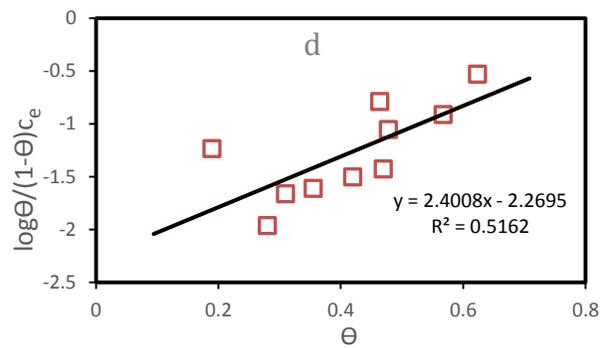
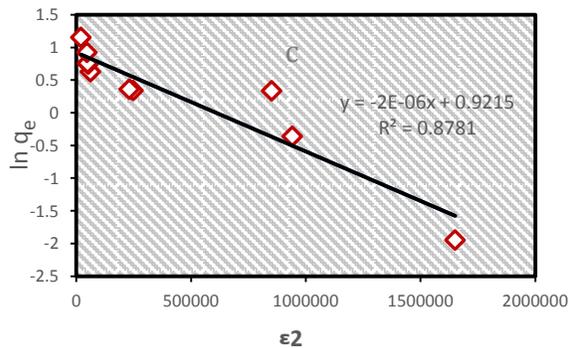
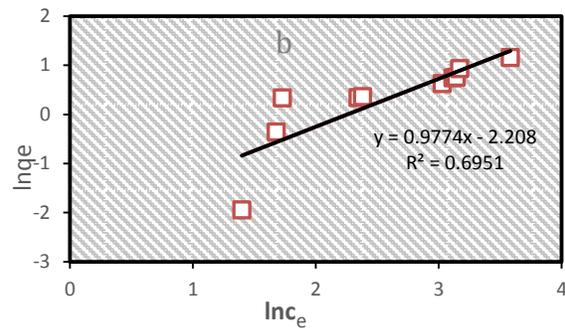
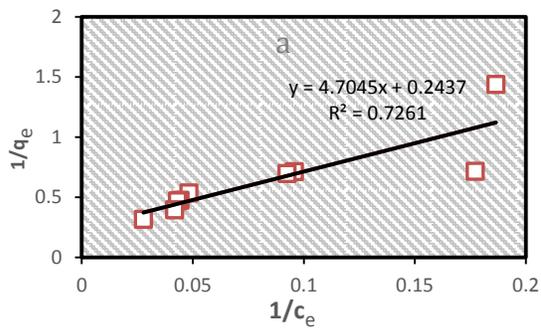


Figure 11: (a) Freundlich isotherm (b) Langmuir isotherm (c) Frumkin isotherm (d) D-R isotherm (e) Harkins-Jura isotherm (F) Elovich isotherm (g) Temkin plots for different initial concentrations ranging 2-20 ppm of the Eosin yellowish adsorption by CKD at 313K.



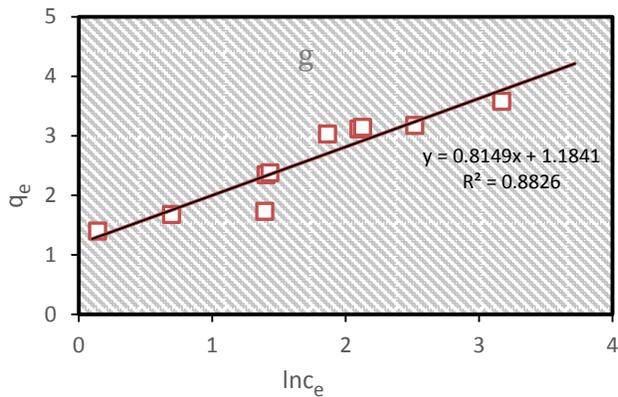


Figure 12 : (a) Langmuir isotherm (b) Freundlich isotherm(c)Frumkin isotherm(d)D-R isotherm (e) Harkins-Jura isotherm (F) Elovich isotherm(g) Temkin plots for different initial concentrations ranging 5-50ppm of the BCG adsorption by CKD at 313K.

Table 5 : Rate constants and correlation coefficients for Murexide adsorption onto CKD at pH=6 , initial concentration 40ppm, contact time 30 min. , CKD dosage 0.15g at the temperature range303-333K.

Dye	Linear equation of Kinetic model	Parameters	Temperature			
			303	313	323	333
Murexide	Pseudo-first- order $\ln(q_e - q_t) = \ln q_e - Kt$	$K \text{ (min}^{-1}\text{)}$ R^2	-0.0108 0.6619	-0.0102 0.7778	-0.010 0.8360	-0.0096 0.8167
	Pseudo-second- order $\frac{t}{q_t} = \frac{1}{K q_e^2} + \frac{1}{q_e} t$	$K \text{ ((mg /g min}^{-1}\text{)}$ R^2	0.006653 0.83210	0.006653 0.9889	0.0711 0.9999	0.0176 0.9994
	Elovich $q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t$	$\alpha \text{ (mg g}^{-1}\text{min}^{-1}\text{)}$ $\beta \text{ (g mg}^{-1}\text{)}$ R^2	0.7286 2.7473 0.4130	0.7799 0.3203 0.6836	0.3547 9.4162 0.9719	0.3495 2.0773 0.8972
	Intra – partical - diffusion $= k_{diff} t^{1/2} + c q_t$	$(K \text{ (mgg}^{-1}\text{Min.}^{-1/2}\text{)})$ R^2	0.0773 0.5215	17.719 0.7859	0.0198 0.9464	36.216 0.9399

Table 6 : Rate constants and correlation coefficients for Eosin adsorption onto CKD at pH= 6, initial concentration 15ppm, contact time 30 min. , CKD dosage0.05g at the temperature range 303-333K.

Dye	Linear equation of Kinetic model	Parameters	Temperature			
			303	313	323	333
Eosin	Pseudo-first- order $\ln(q_e - q_t) = \ln q_e - Kt$	$K \text{ (min}^{-1}\text{)}$ R^2	0.0107 0.9743	0.0081 0.7322	0.0067 0.9095	0.0252 0.9560
	Pseudo-second- order $\frac{t}{q_t} = \frac{1}{K q_e^2} + \frac{1}{q_e} t$	$K \text{ ((mg /g min}^{-1}\text{)}$ R^2	0,0884 0.9973	0.0575 0.9930	0.0245 0.9913	0.0005 0.8661
	Elovich $q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t$	$\alpha \text{ (mg g}^{-1}\text{min}^{-1}\text{)}$ $\beta \text{ (g mg}^{-1}\text{)}$ R^2	0.1447 7.8186 0.8746	0.1698 8.9954 0.8359	0.2157 6.1425 0.7168	0.0161 2.1168 0.7284
	Intra – partical - diffusion $= k_{diff} t^{1/2} + c q_t$	$(K \text{ (mgg}^{-1}\text{Min.}^{-1/2}\text{)})$ R^2	0.0267 0.5542	0.0217 0.962	0.0342 0.9361	0.0934 0.8800

Table 7 : Rate constants and correlation coefficients for BCG adsorption onto CKD at pH= 5 ,initial concentration 50 ppm, contact time 20 min., CKD dosage 0.1g and the temperature range 303-333K.

Dye	Linear equation of Kinetic model	Parameters	Temperature			
			303	313	323	333
BCG	Pseudo-first- order	K (min ⁻¹)	-0.0033	-0.0094	-0.0097	-0.0099
	$\ln(q_e - q_t) = \ln q_e - Kt$	R ²	0.1066	0.7526	0.5533	0.7291
	Pseudo-second- order	K ((mg /g min ⁻¹)	0.071	0.184	0.105	0.091
	$\frac{t}{q_t} = \frac{1}{K q_e^2} + \frac{1}{q_e} t$	R ²	0.9843	0.9933	0.9951	0.9774
	Elovich	α (mg g ⁻¹ min ⁻¹)	0.051	0.298	0.069	0.611
	$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t$	B (g mg ⁻¹) R ²	0.821 0.668	2.994 0.776	2.134 0.728	2.744 0.616
Intra – partical - diffusion	(K(mgg ⁻¹ Min. ^{-1/2})	0.2719	0.0743	0,1123	0.0905	
$= k_{diff} t^{1/2} + c q_t$	R ²	0.79810	0.6730	0.7798	0.8301	

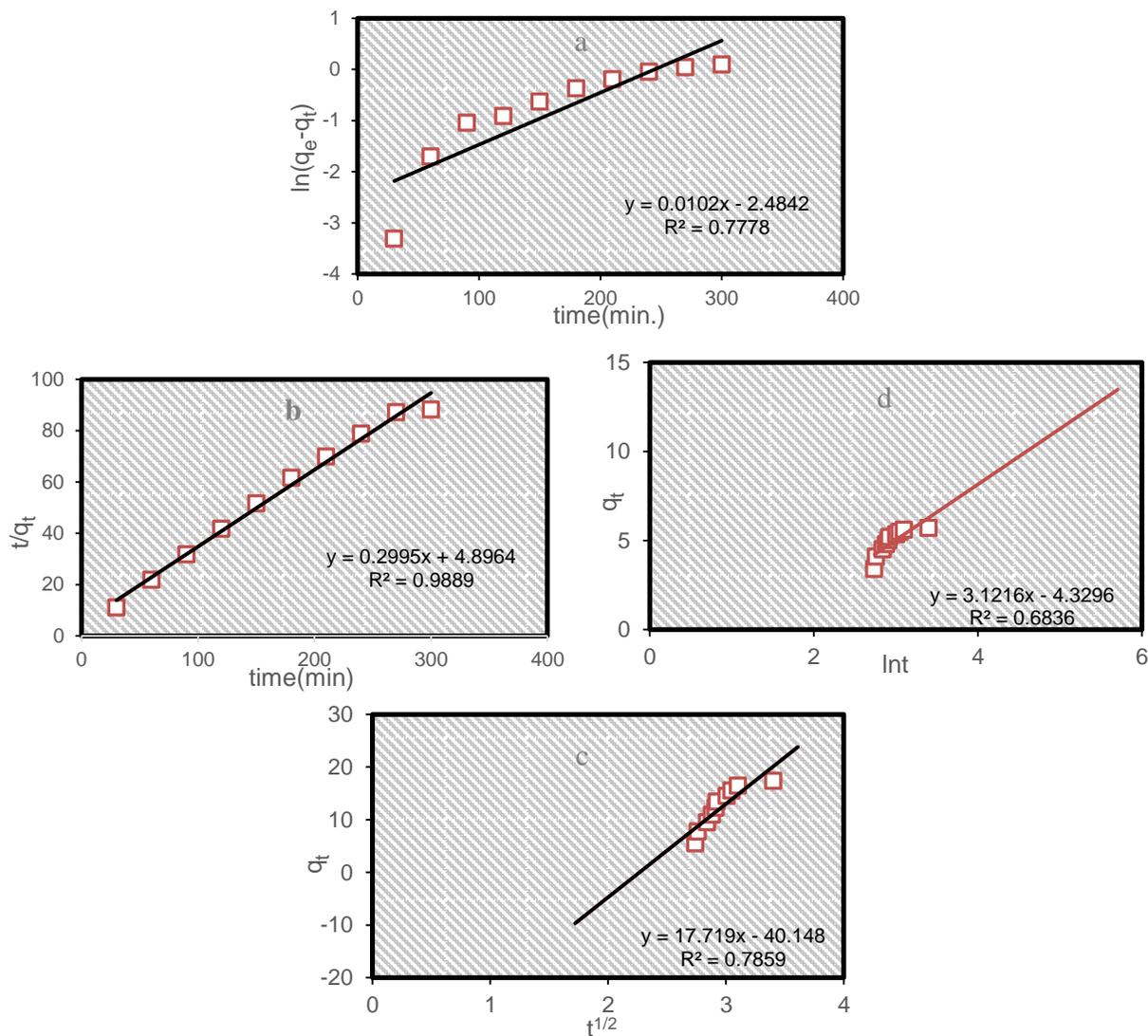
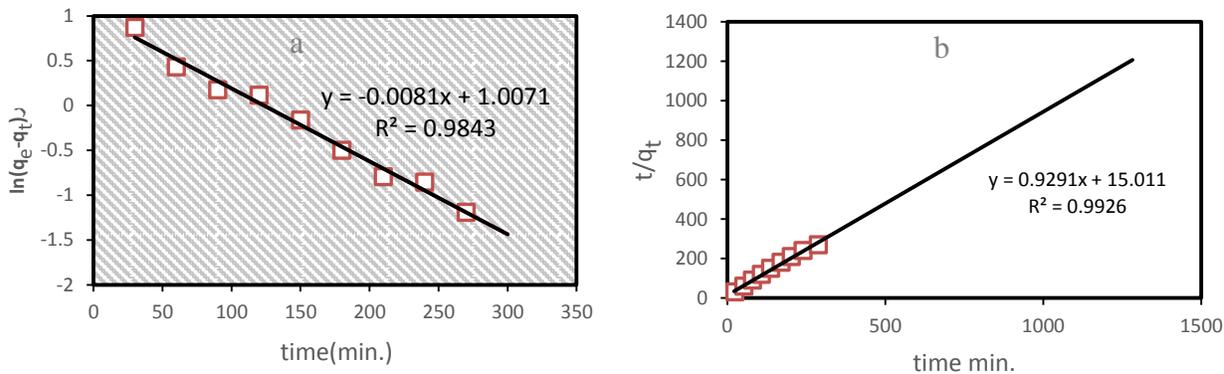


Figure 13 (a) pseudo – first – order (b) pseudo –second – order (c) intra partical diffusion (d)elovich, kinetic plots for adsorption of Murexide onto CKD at 313K.



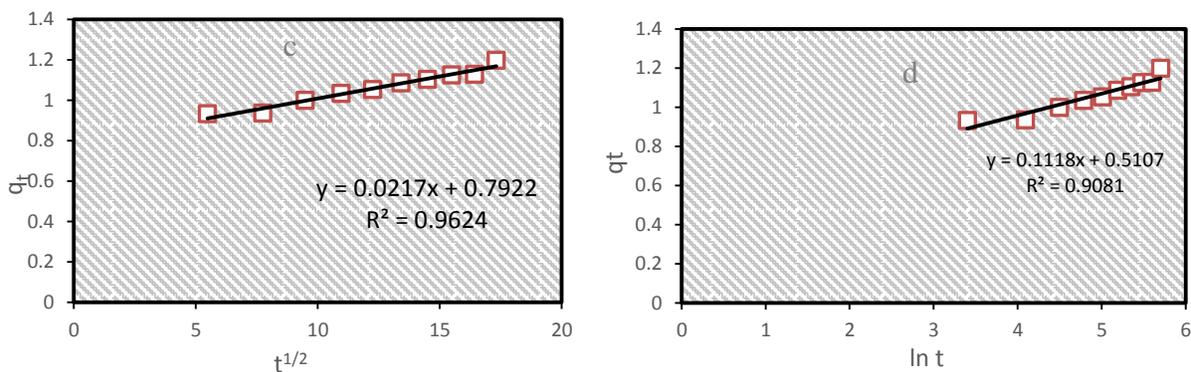


Figure 14 (a) pseudo – first – order (b) pseudo –second – order (c) intra partical diffusion (d) elovich, kinetic plots for adsorption of Eosin yellowish onto CKD at temperature 313K.

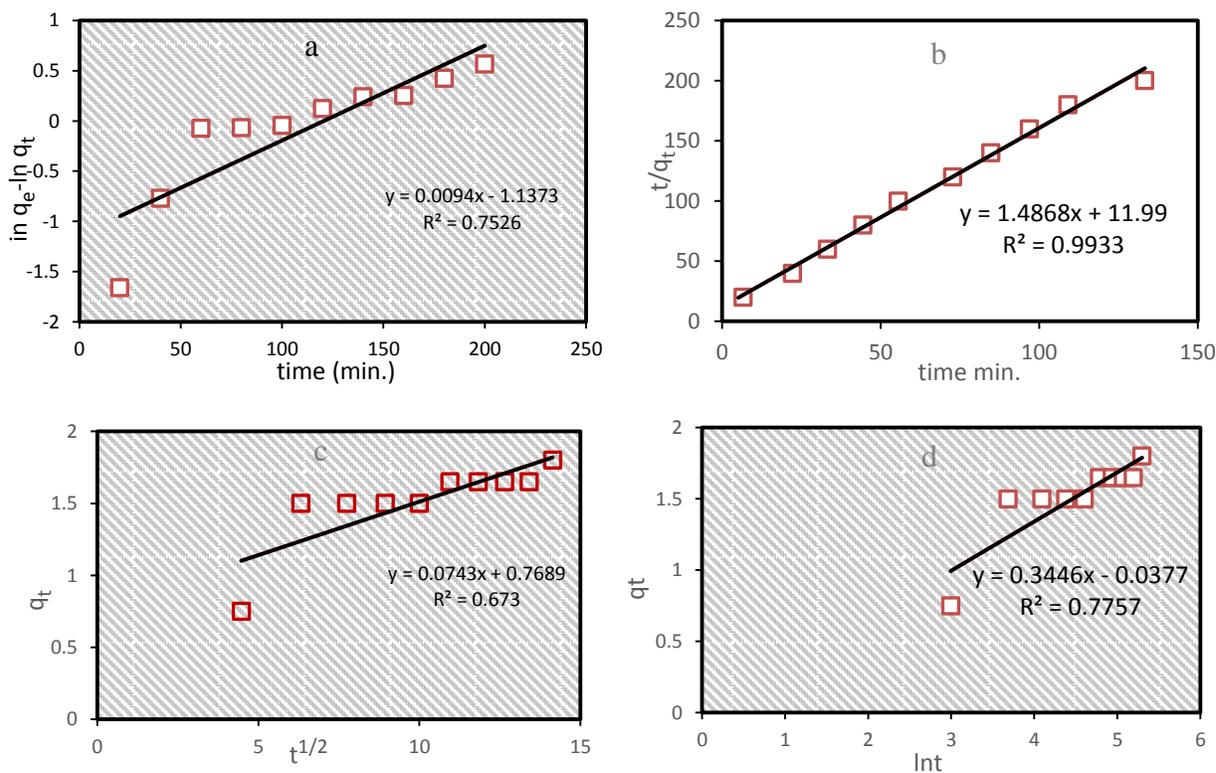


Figure 15: (a) pseudo – first – order (b) pseudo –second – order (c) intra particle diffusion (d) elovich, kinetic plots for adsorption of BCG onto CKD at 313K.

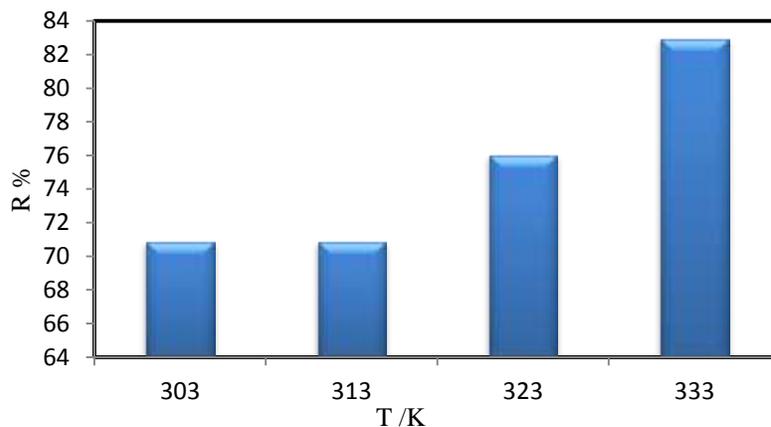


Figure 16 : Effect of temperature on Murexide dye removal onto CKD ;initial dye concentration 45ppm , adsorbent dosage 0.15 g, agitation speed160 rpm, solution pH= 6 and 20 min. contact time.

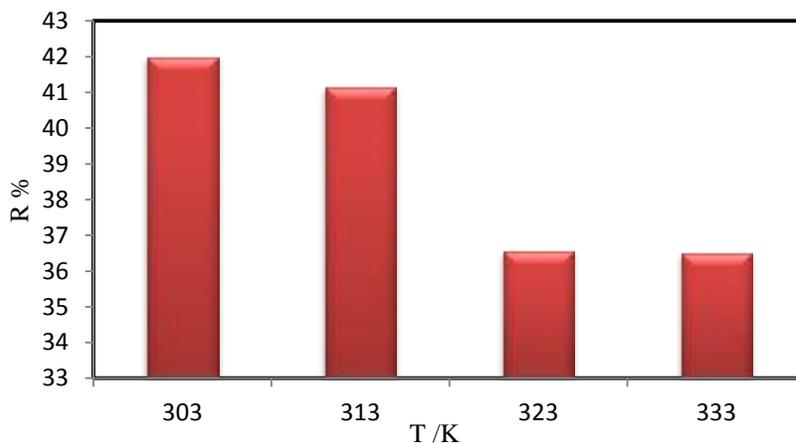


Figure 17 : Effect of temperature on Eosin yellowish dye adsorption onto CKD ; initial dye concentration 15ppm , adsorbent dosage 0.05g, agitation speed 160 rpm, solution pH= 6 and 30 min. contact time.

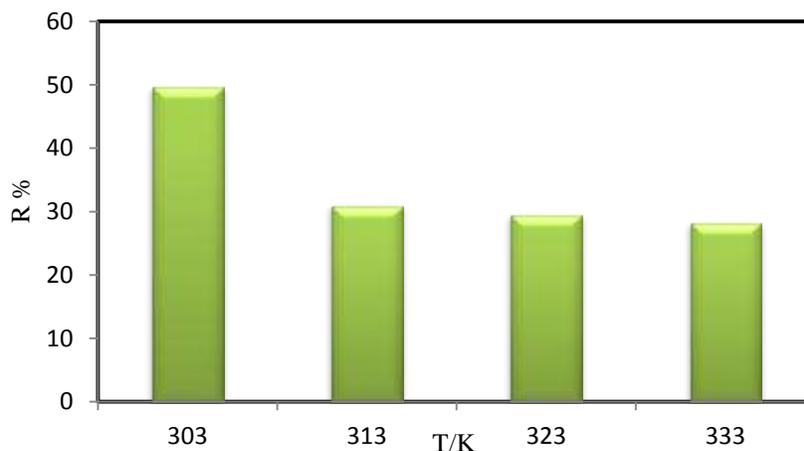


Figure 18 : Effect of temperature on BCG dye adsorption on CKD ; initial dye concentration 30ppm , adsorbent dosage 0.1g, agitation speed 160 rpm, solution pH= 5 and 30min. contact time.

Thermodynamic parameters

Thermodynamic parameters, the enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) changes were determined to evaluate the thermodynamic feasibility and spontaneously nature of the adsorption process and they were calculated using the following equations⁽³⁴⁻⁴⁶⁾:

$$K_{eq} = q_e / c_e \quad \dots\dots\dots(3)$$

where K_{eq} is the equilibrium constant, q_e is the amount of dyes adsorbed at equilibrium and C_e is the equilibrium concentrations of dyes in solution. Values of K_{eq} was calculated from the intercept of the plots of $\ln(q_e / c_e)$ vs. q_e at different temperature. The changes in ΔH and ΔS were calculated from the Van't-Hoff equation :

$$\ln K_{eq} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad \dots\dots\dots(4)$$

A plot of $\ln K_{eq}$ vs. $1/T$ (Figure 19) gives a straight line with slope $-(\Delta H/R)$ and extrapolated intercept $(\Delta S/R)$. The change in ΔG was calculated using equation:

$$\Delta G = \Delta H - T\Delta S \quad \dots\dots\dots(5)$$

The observed thermodynamic parameters are listed in Table 9 . The negative values of ΔG indicates the adsorption process is favorable and spontaneous, while positive values indicate the unfavorable adsorption process at the experimental conditions. The negative values of ΔH confirm the exothermic nature of adsorption, while the positive value of ΔH indicate that the the endothermic nature. The negative value of entropy change indicated that the mobility of the adsorbed dyes on the surface of CKD was restricted and could be conformational changes. Negative values of ΔS were also observed for adsorbed dyes during other studies^{2,25} . Also the

activation energy of adsorption process which gives an information of the type of adsorption was computed from the following equation³⁷.

$$E_a = \Delta H + RT \quad \dots\dots\dots(6)$$

The positive value of E_a indicates that the adsorption process is endothermic with a diffusion controlled - process mechanism, while the negative values of E_a indicates that the adsorption process is exothermic which suggested that the rise in the solution temperature did not favour Eosin yellowish and BCG adsorption onto CKD, that means the Eosin yellowish and BCG molecules moving much faster than Murexide molecules to diffuse into CKD³⁸, also the activation energy gives an idea whether adsorption process is physical or chemical, low activation energy(0 - 88kJ mol⁻¹) suggests physisorption and a high activation energy (88- 400 kJ mol⁻¹) suggests chemisorption³⁹.

Table 9: Thermodynamic parameters of Murexide, Eosin and BCG for dyes adsorption onto CKD at the temperature range 303-333K.

Dye	ΔG kJmol ⁻¹				$H\Delta$ kJmol ⁻¹	$S\Delta$ Jmol ⁻¹ K ⁻¹	E_a / kJ mol ⁻¹			
	303	313	323	333			303	313	323	333
Murexide	8.71	7.91	7.10	6.30	33.02	-80.22	35.53	35.75	35.70	35.87
Eosin	-	116.95	-	-	-54.57	-199.03	-	-	-	-
BCG	114.96	-	118.94	120.94	-	-	52.05	51.98	51.89	51.81
BCG	-26.30	-26.83	-27.36	-27.89	-10.21	-53.09	-7.68	-7.61	-7.53	-7.45

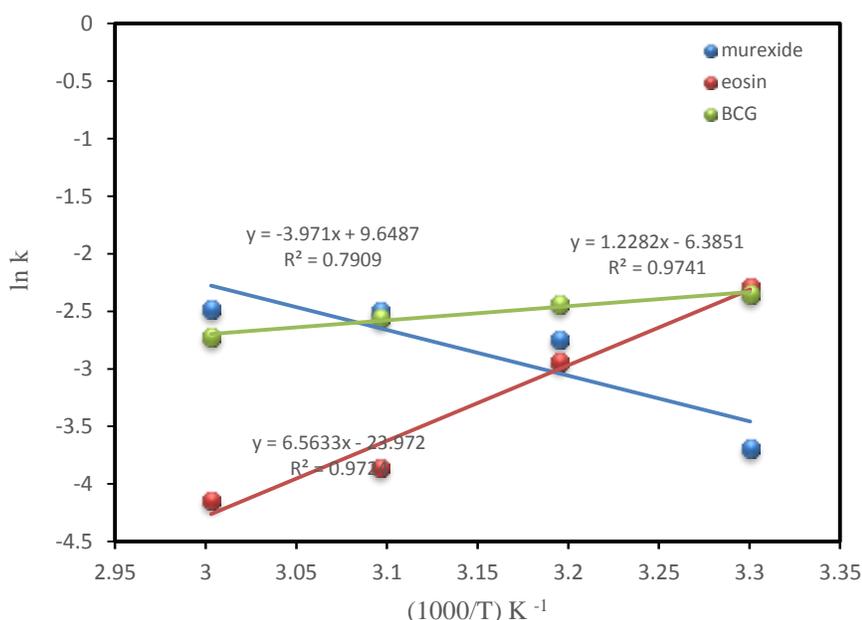


Figure 19: plots of lnK versus 1/T for adsorption of (a) Murexide(b)Eosin (c) BCG on CKD at the temperature range 303-333K.

CONCLUSION

From the experiment results for adsorption of Murexide, Eosin and BCG onto the CKD, the important findings are summarized :

1. The study shows that CKD has an basic character on its surface.
2. The optimum dosage of CKD are 0.1,0.05 and 0.15g were shown.
3. .The knowledge of point of zero charge of the studied materials provides information about the possible attraction and repulsion between sorbent and sorbate.
4. The high percentage removal was found to be $\approx 80.2\%$ at 333K , pH 6.5 ; $\approx 42\%$ at 303K, pH 6.5 ; and $\approx 50\%$ at 303K, pH 5.5 of Murexide ,Eosin yellowish and BCG Respectively.
5. The equilibrium adsorption data were fitted between Freundlich and Temkin isotherms for Murexide, D-R isotherm for Eosin yellowish and Freundlich for BCG.
6. Four adsorption kinetic models were applied and the most fitting is Pseudo-second-order For all dyes.
7. From the thermodynamic data. ΔH , ΔG , ΔS .The results indicate that the adsorption process of dyes onto CKD is spontaneous and had a negative values of entropy changes which indicated that the mobility of the adsorbed dyes on the surface of CKD was restricted and could be conformational changes, while the enthalpy changes was positive (endothermic) for adsorption of Murexide and negative (exothermic) for adsorption of Eosin and BCG.
8. The values of activation energy for adsorption of Murexide, Eosin and BCG onto CKD were + 35.35, - 52.05 and $- 7.68 \text{ kJmol}^{-1}$ respectively, the positive value of E_a indicates that the adsorption process is endothermic, while the negative values of E_a indicates that the adsorption process is exothermic and that suggests the physisorption process occurs.

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