Adsorption of Congo Red on Nano MgO Particles Prepared by Molten Salt Method

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Abstract

Nano-substances show many surface properties due to their high activity and high surface area. This study concentrates on the possibility of using nano-MgO (NMO) for removing Congo red (CR) dye from wastewater. The effects of equilibrium time, pH, dye concentration and temperature have been investigated. Isotherm studies revealed the favorability of the adsorption process and the energy of adsorption ($10.38<E<11.60$ kJ/mol) suggest a mechanism controlled by chemical processes. The overall process was spontaneous and endothermic in nature with a maximum adsorption capacity of 1100 mg/g at 40^{o}C as estimated from Langmuir isotherm. The adsorption kinetics was found to follow pseudo second-order rate equations.

Keywords: Magnesium oxide, nanoparticles, Congo red, adsorption.

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امتزاز الكونغو الحمراء على اوكسيد المغنيسيوم النانوي المحضر بطريقة الصهر الملحي

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الخلاصة

اظهرت المواد النانوية خواص سطحيه مختلفه وذلك لمساحتها السطحيه وفاعلية المواقع السطحيه. هذه الدراسه تضمنت امكانية استخدام اوكسيد المغنيسيوم النانوي لازالة صبغة الكونغو الحمراء من المياه الملوثه. تمت دراسة تاثير زمن الاسقرار،دالة الحامضيه، تركيز الصبغه ودرجة الحرارة. اظهرت دراسة الآيزوثرم افضلية عملية الامتزاز وكانت طاقة الامتزاز بين 10.38 - 11.60 kJ/mol وهذا يعني ان آلية الامتزاز تمر بعمليات كيميائيه. اجمالا كانت عملية الامتزاز تلقائيه وماصه للحراره مع اقصى سعه استيعابيه تصل الى 1100 mg/g عند درجة حراره 40° C كما حسبت بموجب معادلة لانكماير.اما حركية الامتزاز فكانت من المرتبه الثانيه الكاذبه.

كلمات مفتاحيه :اوكسيد المغنيسيوم، دقائق نانويه، الكونغو الاحمر، الامتزاز.

Introduction

Nano magnesium oxide has a wide range of applications in different fields of science and technology; this is because the physical properties of nano-materials are completely different from the bulk material that makes the nano-material more applicable [1]. Surface properties like porosity, morphology and size of the particles define the specific surface area and adsorption capacity of the nano-material. On the other hand, the surface properties are controlled by the preparation method and preparation conditions of the nanomaterial [2]. Due to the large surface area of nanoparticles, they have been used as adsorbent widely. In the gaseous phase, nano- metal oxides were used efficiently as adsorbents and destruction of hazardous chemicals [1]. Nanomaterials have also shown an excellent efficiency in removing heavy metal ions from aqueous solutions [3]. One of the polluting industrial wastes is dye effluents from textile, rubber, plastics [4]. The concentrations of dye stuff in waste effluents are in the range (10-200 mg/L). Beside inhibition of sunlight diffusion and reducing photosynthesis, most of these dyes (especially synthetic dyes) are toxic, mutagenic and

carcinogenic [5] and most of these synthetic dyes are non-biodegradable [6]. Benzidine, a human carcinogen, is a product of Congo red (CR) metabolism. Due to the significant impact of CR as an industrial dye waste on aquatic system and human health, it has to be treated before discharge [7]. Among all physical, chemical and biological treating strategies, adsorption still remains the most simple, low cost and efficient treating method for dye effluents [8]. Recently, researchers found that nano-metal oxides are selective sorbents against heavy metal ions with high sorption capacity [9]. Furthermore, nano crystalline MgO [5,10] and MgO nano-composites [11] have been used in removing dyes from waste water effectively. In the present study, a simple method (molten salt) was used to synthesis nano-MgO, and the nano-product was examined for its efficiency as an adsorbent to remove Congo red from aqueous solutions. Optimization of some key factors, like contact time, initial pH, initial concentration of dye and temperature were performed as well. Kinetics and isotherm studies are necessary for proposing the possible mechanism of the adsorption process which is important in transferring the current study to a large scale.

Materials and Methods

Materials used in this research were all of analytical reagent grade and used without further purification. Congo red (CR) was obtained from Fluka- Guaranties. The stock solution of CR 2000 mg/L ($C_{32}H_{22}N_6Na_2O_6S_2$) was prepared with distilled water, and the desired experimental concentrations of CR solutions were prepared by consecutive dilutions of the stock solution. In a previous work of the authors, molten salt method was used for the synthesis of NMO particles and the product was well characterized using XRD and SEM [12].

Adsorption Studies

Batch method was used in adsorption measurements to obtain kinetics and equilibrium data. Adsorption experiments were performed at temperature 30 °C and initial CR solution pH 4.3, exclude those of which the effects of pH and temperature were investigated. Adsorption experiments were carried out in a series of polyethylene bottle containing 0.1 g of MgO adsorbent and 50 ml of CR solution of desired concentration in a water bath shaker for 150 minutes shaking. At the end of the adsorption period, the suspensions were separated by centrifugation at a rate of 3500 rpm for 12 minutes. The amount of CR adsorbed on NMO was

determined by using spectrophotometer (TU-1800S UV-VIS spectrophotometer) at λ= 497 nm. The adsorbed amount of CR on NMO was computed from Eq. (1)

$$Q_e = \frac{C_o - C_e}{m}.\mathrm{V} \qquad (1)$$

Where V (L) is the volume of solution, m (g) is the mass of adsorbent, C_o and C_e (mg/L) are initial and equilibrium concentrations of the CR dye in the solution.

Equilibrium time and kinetic studies was performed in batch adsorption experiments using a serial of 50ml of dye solutions contacted with 0.1g of NMO. At premeasured contact times (5, 10, 15, 30, 60, 90,120,180, 240,300,360, 420 and 1440 minute), a sample bottle was withdrawn from the water bath shaker for analysis. pH effect was examined in the range of pH 2.5–12 using 50ml of 2000 mg/L dye solutions (a sample bottle for each pH). The pH of the solutions were controlled with approximately 0.1MHCl and 0.1M NaOH solution as per required. Effect of initial dye concentrations on kinetic measurements were examined using 250, 500, 100 and 2000 ppm CR concentration.

Dye solutions at a concentration range 50 to 2000 mg/L were mixed with 0.1 g NMO and shacked for 150 minutes at constant temperature in isotherm studies.

The effect of temperature on adsorption was done by operating the adsorption process at various temperatures; 298, 303, 313, and 318.

Results and Discussion

1. Equilibrium Time and Initial Dye Concentration Study

The equilibrium time is a function of initial dye concentration [13]. Figure 1 shows the equilibrium time study using different initial concentrations of Congo red adsorbent. The figure demonstrates that equilibration was reached after 120 minutes; therefore, a period of 150 minutes of equilibration was selected for the next studies to ensure complete equilibration.

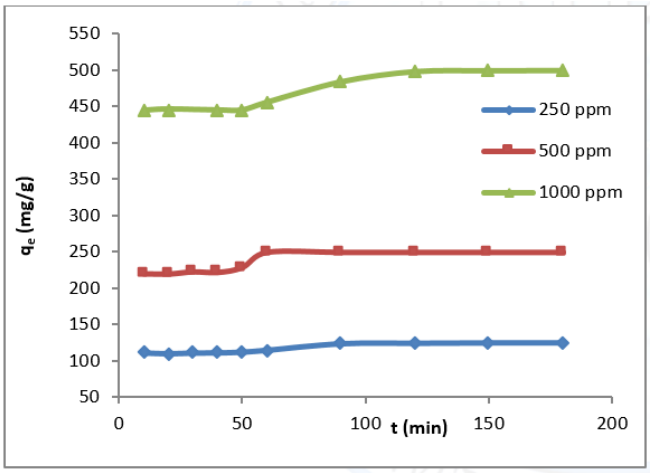

Figure 1: Equilibrium time study at different initial concentrations of CR

2. Effect of Initial pH

The initial pH of the dye solution can significantly affect the adsorption capacity of the dye because it affects the charge distribution of the surface of the adsorbent (NMO) as well as the adsorbate (the dye molecules). Fig. 2 shows that in acidic medium the adsorption capacity is maximum till pH=6, after which the adsorption capacity decreased slightly with the increase of initial pH of CR solution. This result is agreed with literature for the adsorption of CR on various materials like red mud [14], zeolite and kaolin [15] and anilinepropylsilicaxerogel [16].

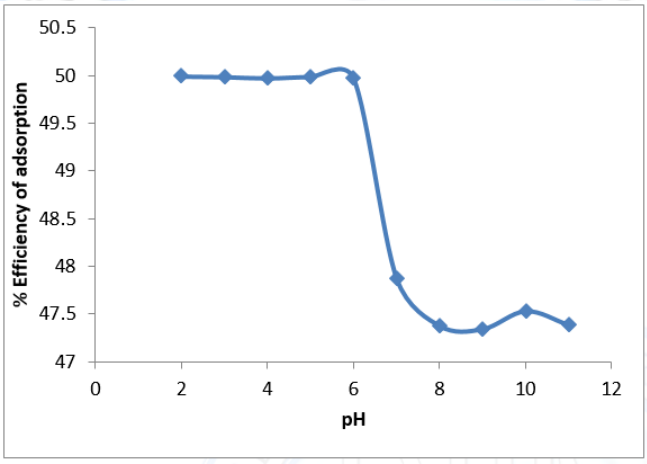

Figure 2: Effect of initial pH of dye solution (500 ppm initial concentration) on the adsorption of CR on NMO

3. Adsorption Isotherm

The benefit behind the sorption isotherms is to explore the relation between the adsorbate concentration in the bulk (at equilibrium) and the amount adsorbed at the surface.Five commonly used isotherm models (Langmuir, the Freundlich, the Temkin, the Dubinin–Kaganer–Radushkevich and BET) were applied to the experimental data to explain the dye-NMO interaction. The linear forms of the isotherms are presented below:

For monolayer adsorption, Langmuir isotherm is the most important model:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (2)$$

Where *C*e is the equilibrium concentration of CR (mg/L), q_m the monolayer maximum adsorption capacity of the adsorbent (mg/g) and K_L is the Langmuir adsorption constant (L/mg) [17]. The problem of Langmuir isotherm is assuming a homogeneous surface with identical adsorptions sites and their binding energies and neglecting any interactions between adsorbed ions, atoms or molecules [18]. From the intercept and slope of the plots in Fig. 3, the Langmuir constants q_m and K_L were calculated at different temperatures and are presented in Table 1. A dimensionless constant separation factor of Langmuir isotherm (R_L) is used to determine the favorability of adsorption for Langmuir type process which is defined as:

$$R_L = \frac{1}{1+K_L C_o} \qquad (3)$$

C_o is the initial concentration of Congo Red solution (mg/L) and K_L(L/mg) is the Langmuir adsorption constant given in table 1. The values of $R_L$were in the range $0<R_L<1$ which indicate that Langmuir adsorption is favorable. Figure 4 shows the variation of R_L with C_o at 25°C and 45°C.

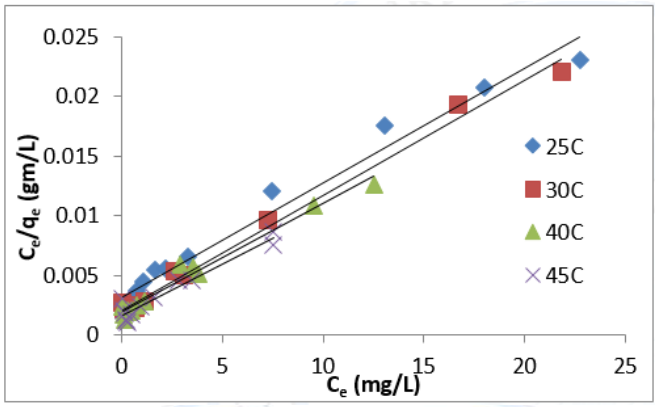

Figure 3: Langmuir adsorption isotherm of CR sorption on NMO at different temperatures

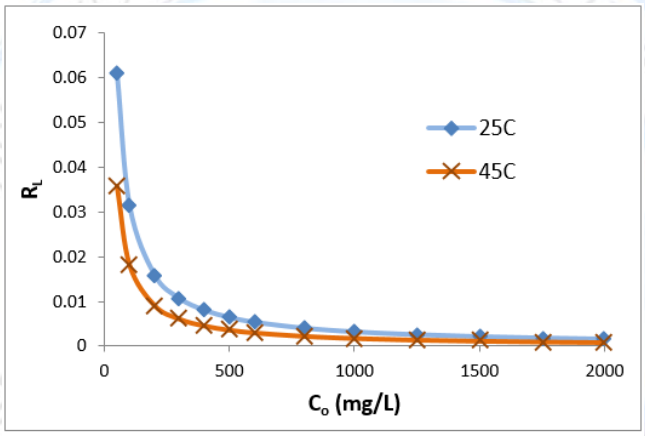

Figure 4: Variation of R_L with initial concentration

For multilayer adsorption and adsorption on heterogeneous surfaces, Freundlich isotherm was formulated [19]. The linear form of the isotherm is given below:

$$log\ q_e = \log K_f + \frac{1}{n}\log C_e \qquad (4)$$

Where K_f (mg g^{-1} (mg $L^{-1})^{-1/n}$) and n are representing adsorption capacity and nonlinearity coefficients respectively. Fig. 5 shows Freundlich adsorption isotherms of CR adsorption on NMO at different temperatures and the isotherm parameters are listed in table 1.

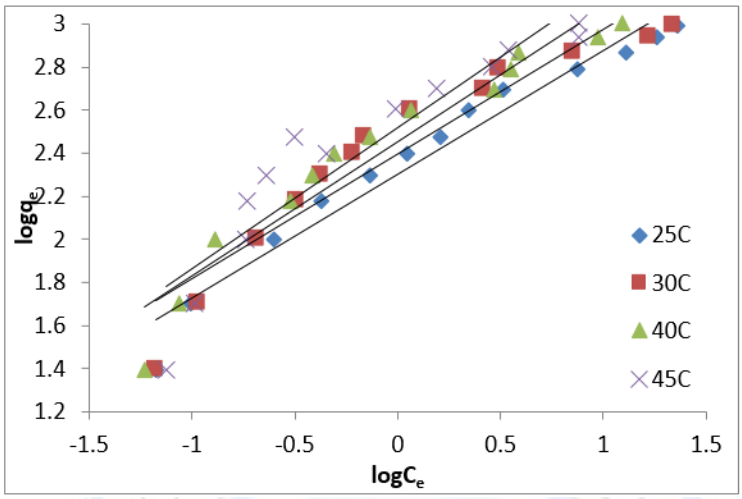

Figure 5: Freundlich adsorption isotherm of CR adsorption on NMO at different temperatures

On the bases of the interactions between adsorbate molecules on the surface, Temkin suggested a linear decrease of heat of adsorption with the coverage of the surface with all adsorbate molecules [20]. The Temkin isotherm in the linear form has been used as the following:

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \qquad (5)$$

And the simplified equation as:

$q_e = B \ln A + B \ln C_e$ (6)

Where $B = RT/b_T$, b_T is related to heat of adsorption (J/mol), A is the Temkin isotherm constant (L/g), R is the gas constant (8.314 J/mol K). Both isotherm constants A and B are calculated (as shown in table 1) from the intercept and the slope of the curve between $\ln C_e$ and q_e as in fig. 6.

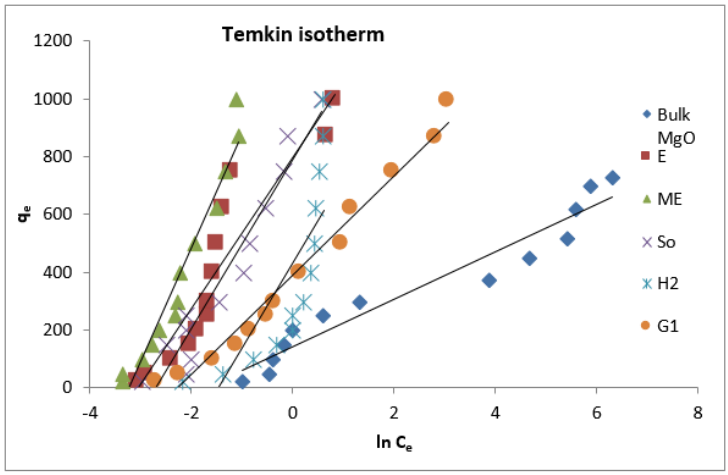

Figure 6: Temkin adsorption isotherm for the adsorption of CR on NMO at different temperatures.

A more common isotherm than Langmuir is D-R isotherm was proposed by Dubinin which does not assume a homogenous surface of sorbent. It is applied to determine the adsorption mechanism (physical or chemical). The linear form of D-R isotherm can be expressed as follows [21].

$$\ln q_e = \ln q_D - B_D \varepsilon^2 \qquad (7)$$

q_D is the maximum adsorption capacity (mg/g), B_D is the adsorption energy constant (mol^2/J^2),ε is the Polani potential defined as:

$$\varepsilon = RTln\,(1 + \frac{1}{C_e}) \qquad (8)$$

Prognostication of the adsorption mechanism (physical or chemical sorption) can be done by calculating the value of the mean sorption energy, E (J/mol) from the relation below:

$$E = -\frac{1}{\sqrt{2B_D}} \qquad (9)$$

If the values of E were less than 8 kJ/mol, the mechanism maybe a physical adsorption, while E values between 8-16 kJ/mol assumes the adsorption to be controlled by ion exchange and E greater than 16kJ/mol presume a particle diffusion mechanism (chemical process). From the slope and intercept of the plots of ε^2 versus $\ln q_e$ of the linear expression of D-R isotherms, the

values of q_D (mol/g), B_D (mol^2/J^2)and E (J/mol) were calculated as shown in Fig. 7according to Eq. (7 and 9). The above isotherm parameters are listed in Table 1.

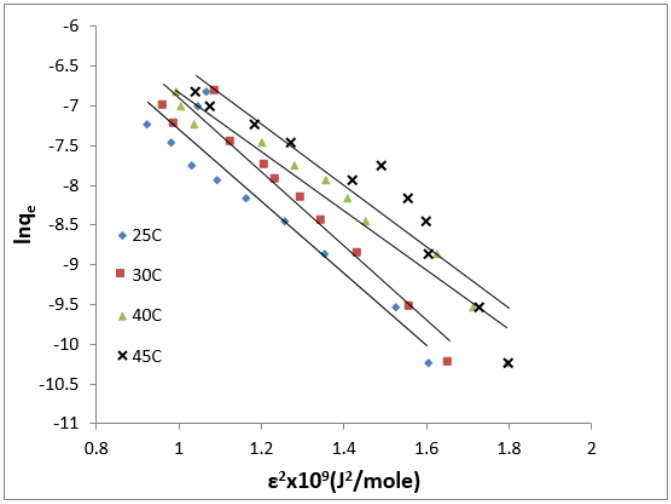

Figure 7: D-R adsorption isotherm for the adsorption of CR on NMO at different temperatures.

Table 1: The calculated adsorption parameters of the four used isotherms

Temp. °C	Freundlich			Langmuir			Temkin			D-R			
	$K_{mg.g^{-1}(mgL^{-1})^{-1/n}}$	n	r^2	K_L(L/mg)	q_m(mg/g)	r^2	A(L/g)	B	r^2	B_D(Mol^2/J^2)	q_m(mol/g)	E(kJ/mol)	r^2
25	3.765	1.737	0.959	0.3074	1039.50	0.972	7.7706	160.9	0.927	$4.52x10^{-9}$	0.0628	10.51	0.895
30	3.808	1.722	0.900	0.4636	1037.02	0.993	9.6281	171.9	0.975	$4.64x10^{-9}$	0.1031	10.38	0.948
40	4.188	1.608	0.932	0.4819	1100.84	0.968	10.8507	178.8	0.943	$3.71x10^{-9}$	0.0443	11.60	0.955
45	4.54	1.522	0.871	0.5391	1152.07	0.941	11.0555	198.3	0.966	$3.87x10^{-9}$	0.0749	11.37	0.879

Freundlich constants (***n***) at all temperatures were greater than one, pointing to the favorability of the adsorption. Langmuir constants (q_m and K_L) were found to increase slightly with temperature and the results were close to that reported for adsorption of toxic dyes on nano-MgO. Flower like nano-MgO [22] showed 1500 mg/g adsorption capacity for Cd(II)[3].

The adsorption energies (*E*) calculated from Dubinin isotherm were found to be (10.38<*E*<11.60 kJ/mol) which presumes a mechanism controlled by chemical process [23,24].

4. Thermodynamic Study

Table 1 show that the maximum adsorption capacity calculated from Langmuir isotherm increases with increasing temperature, this can be used to determine the thermodynamic parameters. The thermodynamic equilibrium constants (K_c) at different temperatures for the adsorption of CR on g1 NMO adsorbent were calculated from the intercept of the plots of $\ln(q_e/C_e)$ versus q_e by extrapolating to $q_e = 0$ (Khan plot) [25] as shown in Fig. 8.

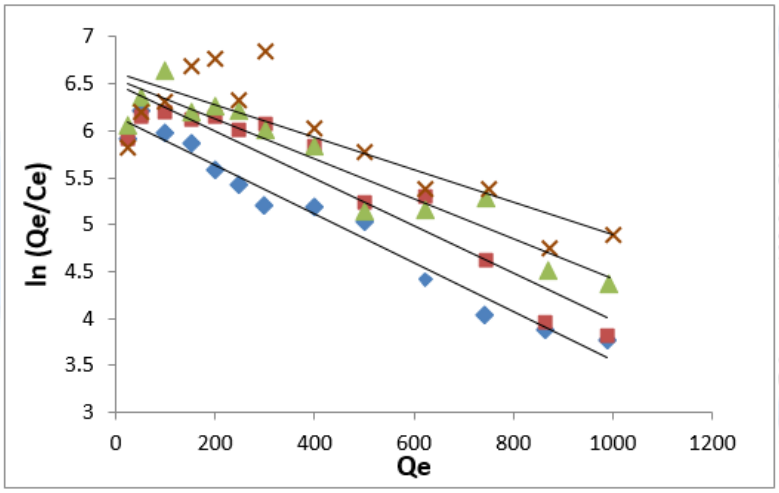

Figure 8: Khan plots for the adsorption of CR on nano-MgO at different temperatures

The adsorption thermodynamic parameters, i.e., the standard Gibbs free energy ΔG^o, enthalpy ΔH^o and entropy ΔS^o, were calculated according to the equations (10 and 11).

$$\Delta G^o = -RT \ln K_c \qquad (10)$$

$$lnK_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (11)$$

The plots of $\ln K_c$ versus 1/T were used to determine the ΔH^o and ΔS^o values. Table 2 lists the thermodynamic parameters.

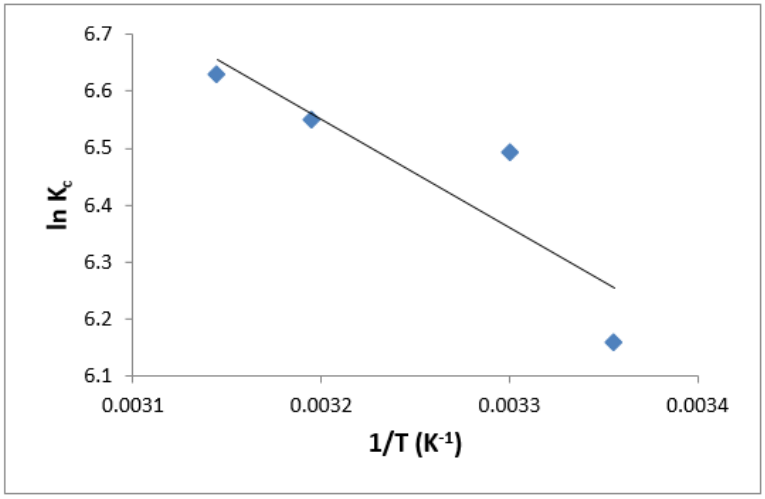

Figure 9: Van't Hoff plot of adsorption of CR on nano-MgO

Table 2: Thermodynamic parameters for adsorption of CR on NMO

Temp. °C	(kJ/mol)ΔH^o	(J/mol K)ΔS^o	(kJ/mol)ΔG^o
25	15.812	105.06	- 15.495
30			-16.021
40			-17.071
45			-17.597

The free energy of the adsorption process at the studied temperature range were negative and changed with the rise in temperature, this imply that the adsorption was spontaneous and thermodynamically favorable. The positive ΔHº value indicates the endothermic of the adsorption process in nature. The positive value of ΔSº show increased randomness at the solid/solution interface and an affinity of the nano-MgO toward Congo red dye. Mi-Hwa found analogous results for the adsorption of Malachite green onto degreased coffee bean [11].

5. Adsorption Kinetics

In order to assess the rate of the adsorption for CR, experiments were carried out for different initial concentrations (250, 500, 1000 and 2000 ppm). Both pseudo first order and pseudo second order kinetics were applied to the adsorption data. Pseudo first order (Lagergren) rate equation [26] given as:

$$\mathrm{Ln}(q_e - q_t) = Lnq_e - k_1 t \qquad (12)$$

Where q_e and q_t (mg.g^{-1}) are the amounts of dye adsorbed at equilibrium and at time t respectively, $k_1$is the pseudo-first order rate constant (min^{-1}). The pseudo second order equation (Ho and McKay) [27] expressed by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_o} \qquad (13)$$

Where k_2 (g/mg.min) is the pseudo second order rate constant.

The plots of the equations were examined for best fit by comparing their correlation coefficients. Fig. (10 and 11) are typical examples of pseudo first order and pseudo second order plots of the adsorption of CR on NMO at 30°C. The correlation coefficients of the linear curves of both kinetics shows that the process more likely follows a second order kinetics.

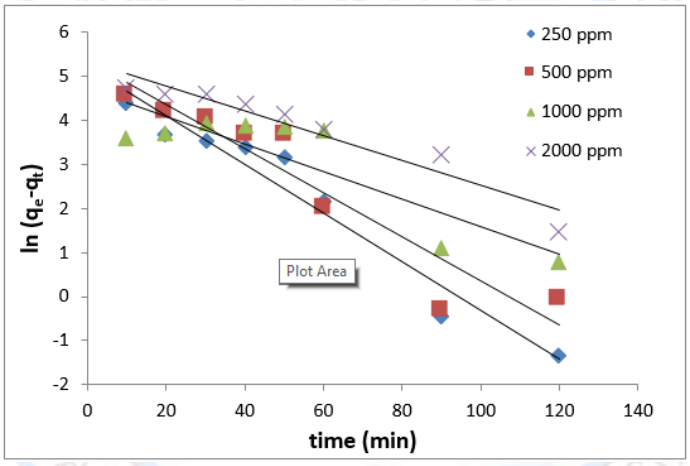

Figure 10: Pseudo first order plots at different initial CR concentrations

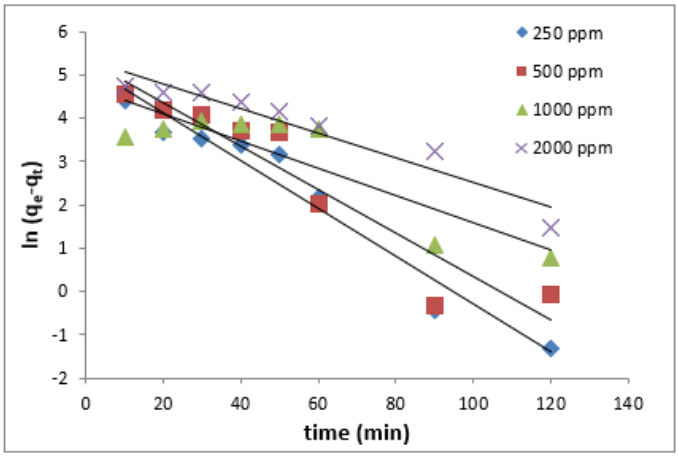

Figure 11: Pseudo second order plots at different initial CR concentrations

The effect of initial concentration of the CR dye was further explored by plotting both (k_2 and q_m) versus initial concentration of CR. Fig. 12 shows that q_m increases linearly with increasing initial concentration of the dye, while k_2 showed no regular pattern.

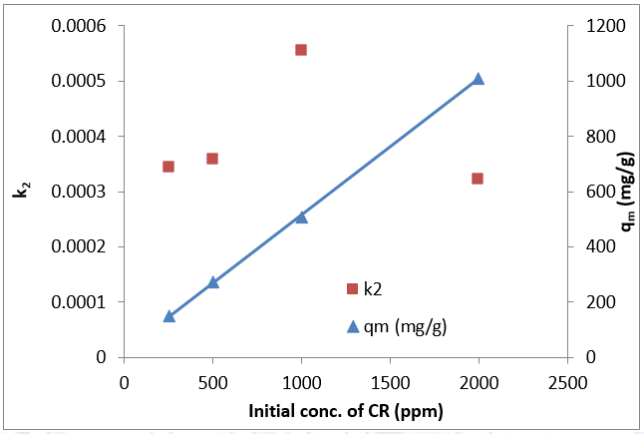

Figure 12: Effect of initial concentration of CR (ppm) on k_2 and q_m at 30°C

6. Effect of Temperature

Effect of temperature on the kinetics of the adsorption of CR on nano-MgO was studied with 500 ppm initial dye concentrations at different temperatures (25, 30, 40 and 45°C). Fig. 13 illustrates the effect of temperature on the adsorption capacity and time required to reach equilibrium.

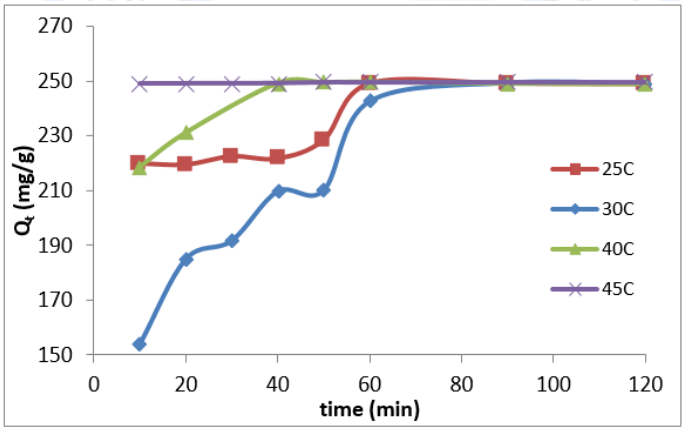

Figure 13: Effect of temperature on the adsorption kinetics of CR (500mg/L) on NMO

Results show that the equilibrium is reached at higher rates at elevated temperatures, while the maximum adsorption capacity remained almost unchanged which is consistent with the chemisorption mechanism of the process. Pseudo second order kinetic plots at different temperatures are presented in Fig. 14 from which the pseudo second order rate constant (k_2) and maximum adsorption capacity ($q_{calc.}$) were calculated and the results are presented in Table 3.

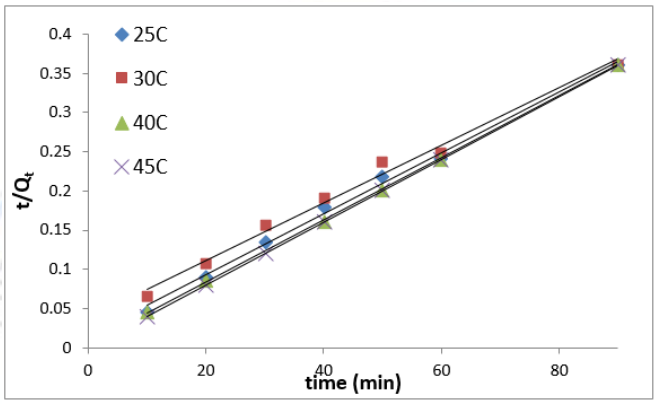

Figure 14: Effect of temperature on the pseudo second order kinetics of the adsorption of CR on nanoMgO

Table 3: Effect of temperature on the pseudo second order rate constant and adsorption capacity for the adsorption of 500 ppm CR onto NMO

Temp. °C	q_{exp} (mg/g)	k_1 (1/min)	$q_{calc.}$ (mg/g)	r^2	k_2 (g/mg min)	$q_{calc.}$ (mg/g)	r^2
25	248.89	0.0193	39.57	0.954	0.001003	257.07	0.999
30	249.28	0.0501	211.47	0.674	0.000358	271.74	0.995
40	249.21	0.0136	5.36	0.283	0.004798	250.56	0.995
45	249.66	0.0236	0.485	0.741	0.094118	250	1

In general, adsorption experiments with different temperatures are used for the evaluation of thermodynamic parameters of activation associated with adsorption, such as activation energy

E_a using Arrhenius equation and Gibbs energy ΔG^*, enthalpy ΔH^*, and entropy ΔS^* of activation using Eyring equation below:

$$k_2 = e^{-E_a/RT} \qquad \text{Arrhenius equation} \quad (14)$$

$$ln\frac{k_2 h}{k_b T} = \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \qquad \text{Eyring equation} \quad (15)$$

where k_b and h are Boltzmann's constant and Plank's constant respectively.

Plotting lnk_2 vs $1/T$ would give a straight line with slope equal to $\frac{-E_a}{R}$ as in Fig. 15 and plotting $ln\frac{k_2 h}{k_b T}$ vs $1/T$ should give a straight line with slope = $\frac{-\Delta H^*}{R}$ and intercept = $\frac{\Delta S^*}{R}$ as in Fig. 16.

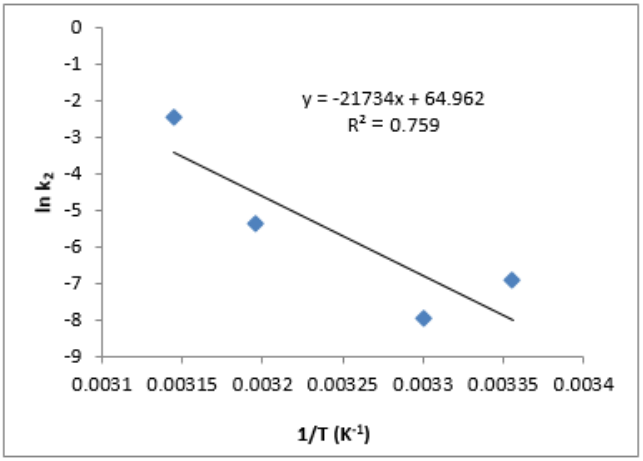

Figure 15: Arrhenius plot for the adsorption of CR on NMO

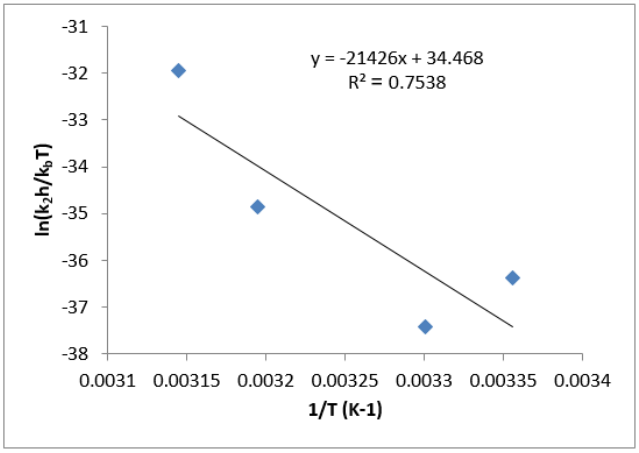

Figure 16: Eyring plot for the adsorption of CR on NMO

The calculated activation parameters are given in Table 4 below.

Table 4: Activation parameters of the adsorption of CR on NMO with an initial concentration of 500 ppm.

Temp. °C	E_a (kJ/mol)	(kJ/mol)ΔH^*	(J/mol K)ΔS^*	(kJ/mol)ΔG^*
25	180.7	178.1	286.6	95.29
30				93.86
40				90.99
45				89.56

The magnitude of E_a may give an indication of whether a physical or chemical adsorption process is involved. In physical adsorption (physisorption), the interaction is easily reversible, equilibrium is rapidly attained and its energy requirements are small and E_a is usually in the range of 5-40 kJ/mol, this because of weak intermolecular forces are involved. However, with chemical adsorption (chemisorption) much stronger bonding forces are involved and E_a range is from 40-800 kJ/mol. In the present study, the high value of E_a (175.77 kJ/mol) is consistent with the chemisorption mechanism for the adsorption process [11].

Conclusions

The results of the present work show that nano-MgO can be considered as an effective adsorbent for the treatment of CR from waste water. In batch experiments, the influence of initial dye concentration and temperature were shown to be effective, while initial pH effect was found to be insignificant on adsorption capacity. In the acidic medium, the efficiency of adsorption was maximum (≈50%) and decreased slightly in neutral and basic medium to (≈47.3%). Results of the thermodynamic studies indicated a spontaneous and endothermic adsorption.A pseudo second-order rate model might have followed by the adsorption process as supported by correlation coefficients of the linear plots, and also the $q_{calc.}$ Were very close to the q_{exp} for the pseudo second-order rate kinetics. The overall adsorption experiments above suggest that NMO can be considered as an effective adsorbent to remove CR from industrial waste water. As the adsorption process is the first step in catalytic photo-degradation, the prepared NMO might be useful as a photo-catalyst in degradation of CR after adsorption.

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