The Synthesis and Characterization of Nano Composites of CdO and Its Applications for the Treatment of Simulated Dye Wastewater

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

Original Research Article

ABSTRACT

The current study emphasizes the fabrications of Cadmium Oxide by extremity up approach adopting co-precipitation procedure. The surface morphology of fabricated Nano composites cadmium oxide was analyzed by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microcopy (SEM) techniques.

The treatment of simulated dyes wastewater was carried out by adsorption method using CdO Nano composites. In addition Malachite Green Oxalate (MGO) was selected as a model replicated system of dye wastewater, to explore the potential practicability for the elimination of the toxic dye. The adsorption experiments were heralded under the optimized conditions like adsorbent dosage, dye concentration and temperature. The acceptability of adsorption progression was estimated by proceeding adsorption models like Freundlich, Langmuir and D-R (Dubinin–Radushkevich). The values of R^2 show that Freundlich model is the best fitted model. The thermodynamic study was conducted to determine the values of free energy ($\Delta G°$), entropy ($\Delta S°$) and enthalpy ($\Delta H°$) change of the system. Adsorption Kinetic was also studied by Boyd's model. The results demonstrated that adsorption efficiency was found to be 93% for Cadmium Oxide- dye-Nano composites systems. The present model system can be employed on industrial scale as a single step process for the removal of dye pollutants and thus it could provide a new raised area for waste minimization.

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1. INTRODUCTION

Nanotechnology, is the statistics and sculpture of deploying matter at the Nano scale (1-100 nm), offers the potential of unique nanomaterial's for the comportment of surface water, groundwater and wastewater tainted by toxic metal ions, organic and inorganic solutes and microorganisms [1]. Due to their inimitable activity toward contaminants many Nano materials are under active research and advancement for use in the treatment of water [2]. Environmental pollution is one of the scorching issues of the today's world [3]. Pollution not only causes environmental vagaries but also causes dissimilar illnesses. Textile seepage is a major contributor of water pollution [4]. The dumping of dyes into getting water reasons reimbursements to the atmosphere and effect bionetwork [5].

Dyes are festooned, ionizing and aromatic organic composites which spectacle and attraction towards the substrate to which it is being pragmatic. Their erections have aryl rings which delocalized electron system. These arrangements are said to be accountable for the absorption of electromagnetic radiation that has unsettled wavelengths, based upon the energy of the electron clouds [6]. The amputations of dyes have been conceded out by different methods: coagulation, chemical oxidation, membrane separation, electrochemical, biological and adsorption processes [7]. In the present studies adsorption was implemented by using Nano particles which are interim as active adsorbent [8].

In the contemporaneous study CdO was synthesized by cadmium chloride by implementing sol gel method. They have high surface reactivity and adsorption capacity to remove dyes from the simulated waste water system [9]. The exclusion of Malachite green dye (MGO) dyes was carried out using CdO nanoparticles by implementing adsorption method. Adsorption experiments were heralded at the optimized amount of adsorbent, contact time, concentration of adsorbate and temperature. Experimental data showed that CdO nanoparticles can effectively remove more than 93% of the dye from the aqueous solution. The adsorption isotherms like Langmiur, Freundich and Dubinin-Radushkevich were employed and the values of respective constants were calculated to estimate the adsorption characteristics [10]. Various thermodynamic parameters such as the Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) change were also studied. Pseudo-second order models were used to describe the kinetics of dyes adsorption [11].

The surface morphology of adsorbent and adsorbate was determined by Fourier Transform Spectroscopy (FTIR) and Scanning Electron Microscope (SEM) techniques. The measurement was studied to explore the potential achievability for the removal of (MGO) dye [12].

2. MATERIALS AND METHODS

The removal of dye was carried out by developing simulated dye system for this purpose MGO was used for the removal studies. The cadmium chloride [$CdCl_2.6H_2O$] and sodium hydroxide were selected to prepare their Nano particles and utilized for the removal of respective dyes. All chemicals were analytical grade and customs without further purification. The solutions were prepared with deionize distilled water. Malachite green oxalate (MGO) (C.I. # 42000) was used with molecular weight 927.02gm/mol and molar extinction coefficient is found to be 148900 $M^{-1}cm^{-1}$ [13].

2.1 Preparation of Dye Solutions

The 500 mg/L solution of MGO dye was prepared and its λ_{max} was recorded by UV-visible spectrophotometer (T80 UV/VIS Spectrophotometer). The working standards were prepared by diluting stock solution to the desired concentrations [14].

2.2 Preparation of Nanoparticles

CdO nanoparticles were prepared by dissolving 100 gm of $CdCl_2.5H_2O$ in 500 ml distilled water. The prepared solution was added to 1 M NaOH. Both solutions were mixed and the mixture was stirred for 8 hours on shaking incubator at 200 rpm at temperature 30°C then suspended slurry was primed. The resulting solution was evaporated to parchedness by adopting evaporation method after that the content were

oven dried at 500°C and CdO particles were prepared and they stored in desiccators for further use.

3. SURFACE MORPHOLOGY OF CADMIUM OXIDE NANO PARTICLES

The surface morphology of synthesized Nano composite was inspected by FTIR and SEM techniques.

3.1 FTIR Analysis

The presence of strong FTIR interactions are confirmed by the FTIR spectrum in the wavelength region of 389-390 nm cm^{-1} for the synthesized CdO nanoparticle is accessible in the mentioned Fig. 1. The broad FTIR absorption band at 3457 cm^{-1} is assigned to stretching vibrations of hydroxyl group (O–H) of water molecules [15].

3.2 Scanning Electron Microscopy (SEM) Analysis

The surface morphology of synthesized CdO Nano composites was studied by SEM technique. It was observed that the sizes were about 500 nm range.

The empty sites present on the surface of CdO provide active sites for the adsorption of dye molecules. After adsorption empty spaces were filled by dye molecules that were adsorbed on the surface of CdO which appears as shown in the Fig. 2 [16].

3.3 Batch Adsorption Experiments

Adsorption studies were accompanied by the batch technique. Batch experiments were carried out to determine the adsorption isotherms. The flasks were traumatized at a perpetual rate, permitting sufficient time for adsorption equilibrium. It was expected that the functional shaking speed allows all the surface area to come in contact with the dye over the progression of the tests. All experiments were approved out in duplicate and the average value was used for additional calculation. The possessions of various parameters on the rate of adsorption process were perceived by varying contact time, adsorbent concentration and temperature of the solution. The solution volume was kept constant.

3.4 Effect of Amount of Adsorbent

The % removal of dye onto the adsorbent as a function of adsorbent dosage is shown in Fig. 3. It was observed that the adsorption efficiency increased from 35 - 93% for CdO. As the adsorbent dose increases from 0.1 to 0.8 g the amount of adsorbent was increase due to the availability of active sites. Hence percentage removal was also upturns [17].
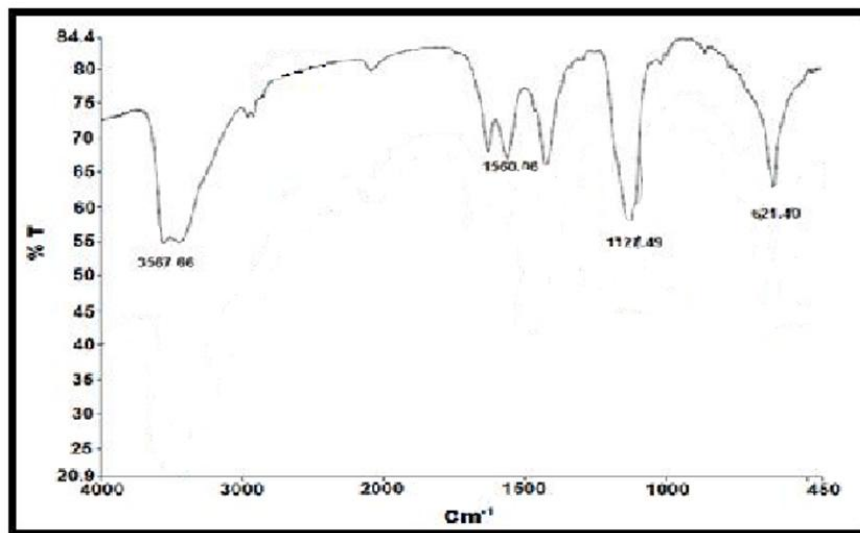

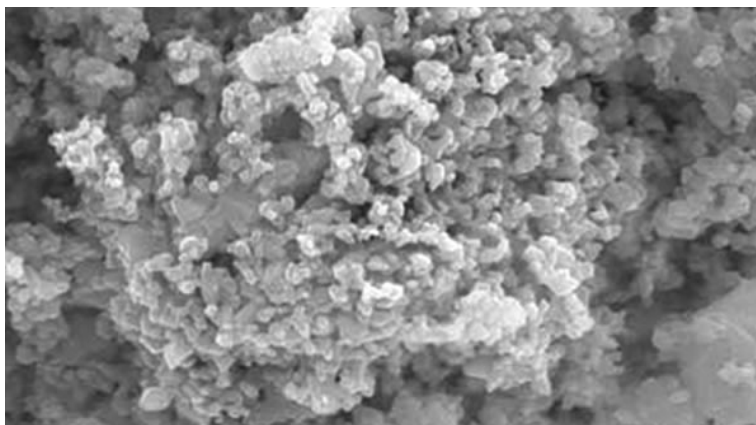**Fig. 1. FTIR spectrum of CdO nanoparticles**

Fig. 2. SEM image of CdO Nano composite after adsorption

3.5 Effect of Contact Time

Adsorption equilibrium was achieved after certain time interlude. The process adsorption of dye on the surface of adsorbent was increased by the intensification in contact time and removal effectiveness reached to an optimum value when the equilibrium between both adsorbate and adsorbent was achieved [18]. The maximum adsorption capacity of MGO for CdO was found to be 91.40% at 80min as shown in Fig. 4.

3.6 Adsorption Isotherms

The study of equilibrium parameters between adsorbate and adsorbent is identified as adsorption isotherm. These isotherms express us about the effectiveness of adsorbent as well adsorption mechanism. Hence, enable to make a correlate the equilibrium data by using theoretical or empirical equation which was helpful for the prediction and interpretation of adsorption mechanism [19]. There are several isotherm equations available for analyzing experimental adsorption mechanism, the most common being Langmuir, Freundlich and Dubini Radushkevich (D-R) models. These models were thus commissioned to fit our investigational data [20].

3.7 Freundlich Adsorption Isotherms

The empirical equation used to describe heterogeneous system is given by the Freundlich isotherm. It is articulated as:

$$Log \, ^X/_m \; = Log \, K \; + \, ^1/_n \, Log \, Ce$$

Where X/m is the amount adsorbed per unit mass of the adsorbent, Ce is the equilibrium concentration and 1/n and K are Freundlich

constants. These parameters give a measure of adsorption capacity of the adsorbent and intensity of adsorption, respectively [21]. It is observed that the process of adsorption is less favorable at high temperatures because the decreasing value of K with the rise in temperature indicates that adsorption affinity of dye decreases with the rise in temperature.

3.8 Langmuir Adsorption Isotherm

A finite number of active sites which are homogeneously distributed over the surface of the adsorbent were the basis of the Langmuir isotherm model. This model also states that, there is no interaction between adsorbed molecules and have the same affinity for adsorption of a mono layer adsorption process [22]. The Langmuir isotherm is expressed as

$$\left(^{Ce}/_{X/m}\right) = \left(^1/_{KVm}\right) + \left(^{Ce}/_{Vm}\right)$$

3.9 D-R adsorption Isotherm

The adsorption data were applied on Dubinin-Radushkevich (D-R) isotherm equation, which is represented in the linear form as:

$$Ln \, ^X/_m \; = \ln Xm \, - K\varepsilon^2$$

Where, X_m is the monolayer capacity of adsorbent, K is a constant related to adsorption energy; ε is adsorption potential, which can be calculated as:

$$\varepsilon = RT \, Ln\left(1 + ^1/_{Ce}\right)$$

Where R is a gas constant, T is absolute temperature; X/m and C_e have usual meaning as described in the above mentioned equation. The

D-R plots of ln (X_m) Vs ε^2 were obtained at various temperatures and the values of K and X_m are given in Table 1. It reveals that the K was decreases with the rise in temperature due to strengthening of the adsorbate-adsorbent interaction for all systems [23-26].

Table 1. Optimization of amount for the removal of MGO dye by using CdO nanoparticles

Sl_no.	Amount(gm)	Ce (M) (10^5)	Removal (%)	KD (ml/gm)
1	0.1	3.44	35.87	179.45
2	0.2	4.75	49.43	123.46
3	0.3	5.70	59.40	99.01
4	0.4	6.78	70.60	88.25
5	0.5	7.19	74.87	74.87
6	0.6	7.49	78.06	65.05
7	0.7	7.95	82.79	59.13
8	0.8	8.97	93.45	58.41
9	0.9	8.46	88.12	48.95
10	1.0	8.77	91.32	45.66
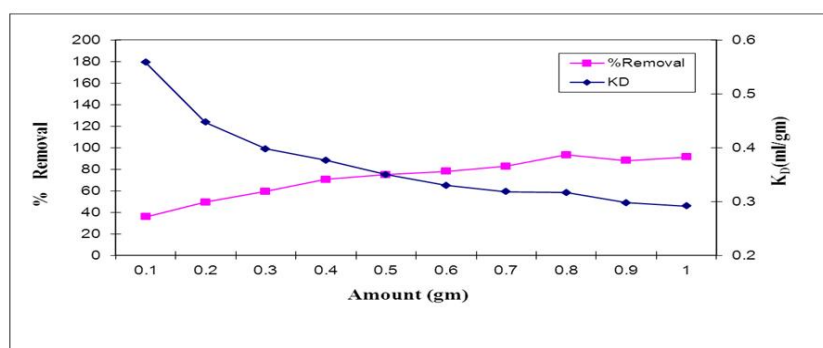
Fig. 3. Optimization of amount of MGO-CdO system

Table 2. Optimization of stay time for the removal of MGO dye by using CdO nanoparticles

Sl_no.	Time (min)	Ce (M) (10^5)	Removal (%)	KD (ml/gm)
1	10	8.34	86.84	54.27
2	20	8.54	88.93	55.59
3	30	8.17	85.01	53.17
4	40	8.51	88.66	55.41
5	50	8.61	89.72	56.07
6	60	8.75	91.14	56.95
7	80	8.78	91.40	57.14
8	100	8.62	89.74	56.09
9	120	8.39	87.40	54.61

Table 3. % Removal of MGO by using CdO nps at different temperatures

Dyes	Ci (M) (10^5)	% Removal			
		298K	303K	308K	313K
MGO	7.68	75.89	92.48	92.81	70.07
	8.64	75.61	91.91	93.53	72.03
	9.60	77.08	92.56	94.05	71.05
	10.5	86.09	90.99	93.61	67.42
	11.5	70.12	90.48	94.76	61.71
	12.4	72.98	93.27	80.57	56.48

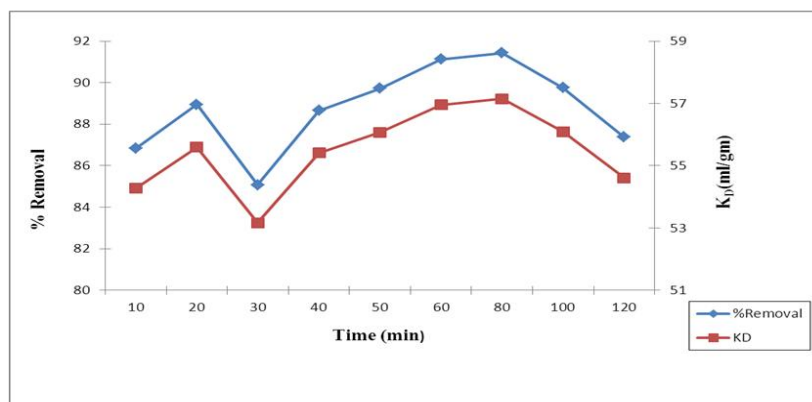**Fig. 4. Optimization of time for removal of MGO by using CdO nanoparticles**

Table 4. Langmiur parameters of adsorption of MGO Dye on CdO nps

Dyes	Temperature (K)	Constant K (10^{-4})	Constant V_m (10^3)	R^2 J/mol.K
MGO	298	6.68	1.66	0.129
	303	0.0579	9.80	0.005
	308	0.0735	6.82	0.001
	313	-0.9638	-1.47	0.321

Table 5. Freundlich parameters of adsorption of MGO Dyes on CdO nps

Sl_no.	Temperature (K)	Constant K (10^3)	Constant N	R^2 J/mol.K
MGO	298	204	1.917	0.077
	303	6903	0.975	0.628
	308	26977	0.703	0.147
	313	110.1539	0.4298	0.554

Table 6. Dubinin Radushkevich (DR) parameters for MGO dye on CdO nps

Dyes	Temperature (K)	Constant X_m (10^3)	Sorption free energy ε_s (Kj/mol) (10^{-3})	R2 J/mol.K
MGO	298	408.12	7.0710	0.323
	303	45.543	7.9051	0.626
	308	226.91	7.0712	0.133
	313	198145.20	5.01	0.565

3.10 Thermodynamic Parameter

The values of thermodynamic parameters ∆G°, ∆H° and ∆S° were calculated from the distribution constant K_D. They were calculated from the plot of ln K_D with the reciprocal of temperature (1/T) by using the following equations

$$\Delta G = -RTlnK_D$$

$$lnK_D = \Delta S°/R - \Delta H°/RT$$
$$\Delta G° = \Delta H° - T\Delta S°$$

The values of ∆G° are negative at different temperatures showing the spontaneous performance of the system. The values of ∆H° are negative show exothermic behavior and the values of ∆S° are positive [27].

3.11 Adsorption Kinetics

The study of adsorption kinetics provides the information regarding the rate of adsorption and feasibility of adsorption process. The experimental data were applied to examine the kinetics by Lagergren's pseudo first order and

Ho-Mckay's pseudo-second order models [28] as represented:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

The values of rate constant and R^2 for the MGO sorption on CdO systems are represented in above table. The results show that the system follows the pseudo second order kinetics.

Where k_{id} is the intra-particle diffusion rate constant which was obtained from the slope of the linearized plot of qt verses $t_{1/2}$. The intercept gives an idea of the thickness of the boundary layer i.e. the larger the intercept; the greater will be the boundary layer effect .The positive values of slope shows controlled adsorption process [29].
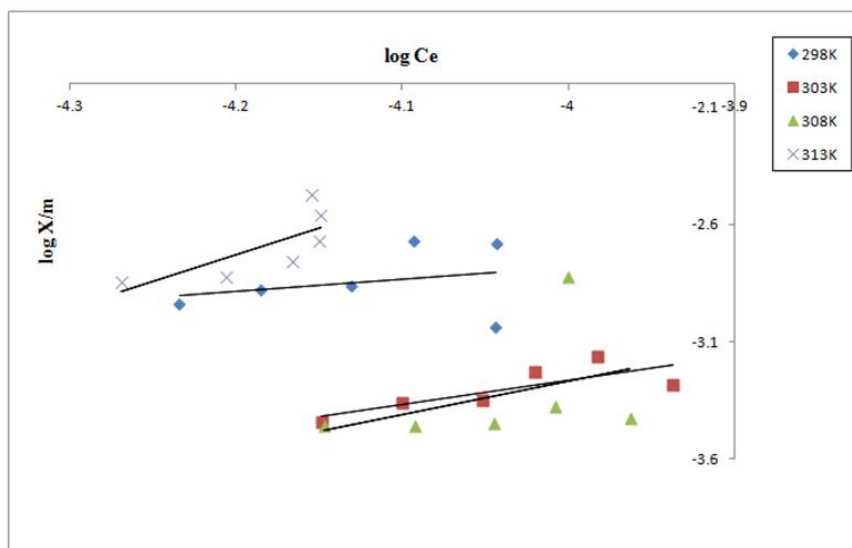

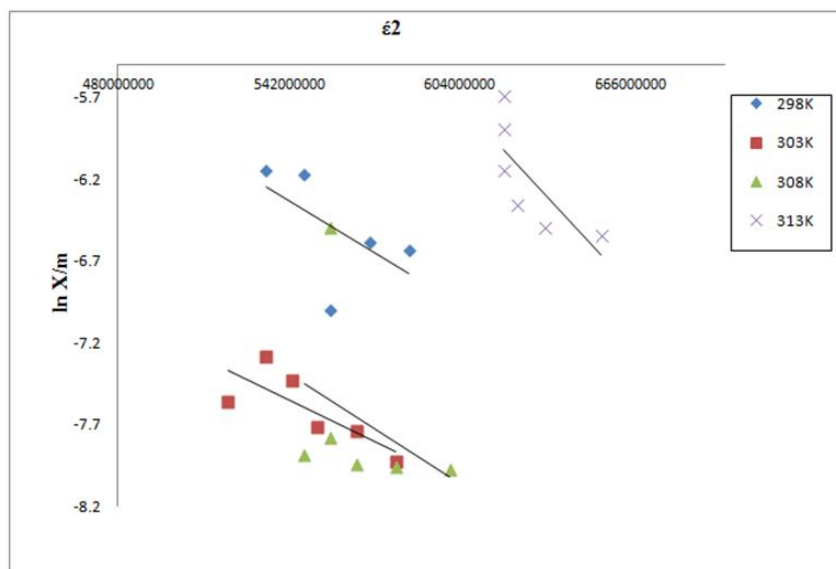**Fig. 5. Freundlich isotherm plots of CdO nanoparticles- MGO system**

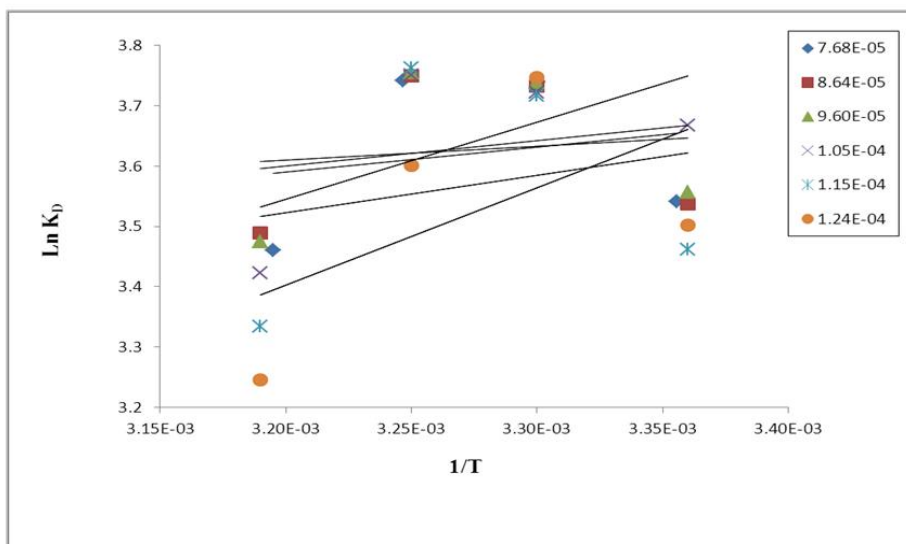**Fig. 6. D-R isotherm plots of CdO nanoparticles- MGO system**

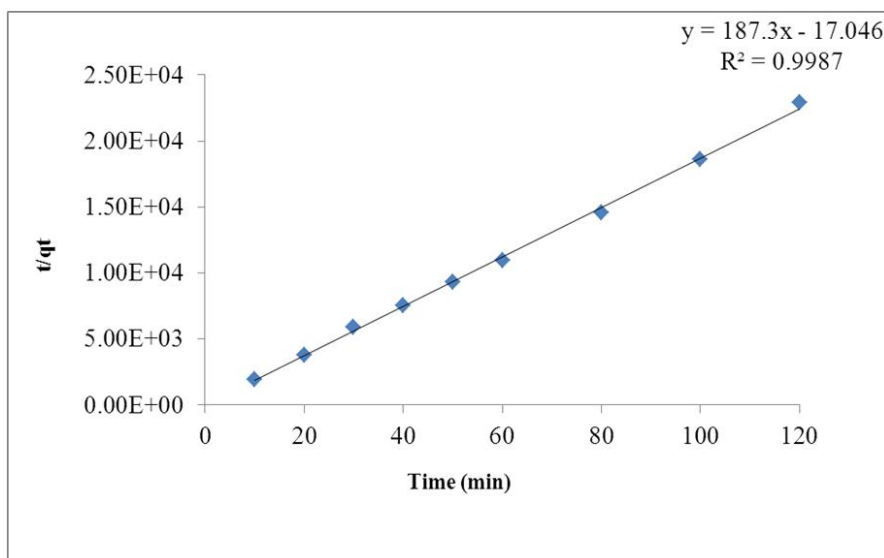**Fig. 7. Plot Ln K_D vs 1/T CdO nanoparticles- MGO system**

Fig. 8. Pseudo-second order adsorption kinetics of MGO onto CdO nanoparticles

Table 7. Thermodynamic Parameters for the Adsorption of MGO on CdO nps

	Concentration (mol/dm^3) (10^5)	ΔH^o (J/mol)	ΔS^o (J/mol.K)	ΔG^o (J/mol)			
MGO				**298K**	**303K**	**308K**	**313K**
	7.68	-3420.38	18.898	-9051.9	-9149.27	-9268	-9207
	8.64	-1957.12	23.737	-9030.58	-917.73	-9229.70	-9150.77
	9.60	-3457.79	18.865	-9079.4	-952.36	-9086.67	-8813.2
	10.5	-10625.3	-4.531	-9275.02	-9022.57	-8887.57	-9207.05
	11.5	-5138.05	12.820	-8958.47	-8961.93	-9086.67	-8813.2
	12.4	-13468.7	-14.874	-9036.3	-8961.93	-8887.57	8813.2

4. RESULTS AND DISCUSSION

In the contemporaneous study, CdO was used as an easily prepared and most nominal adsorbent for the removal of reactive dye including Malachite green oxalate dye (MGO) dye. CdO nanoparticles was synthesized by adopting sol-gel method, CdO nps have high surface area, hygroscopic in nature, porous and amorphous powder. Adsorption, thermodynamic and kinetics studies were proceeded to determine the validity of progression. The adsorption experiments were run under the optimized conditions of amount of adsorbent, stay time, initial concentration and at different temperatures. The adsorption models like: Freundlich, D-R and Langmuir adsorption isotherm models were applied for the mathematical description of the adsorption equilibrium data. Adsorption of (MGO) dye on CdO nps follows Freundlich isotherm mode. Thermodynamic parameters, Gibbs free energy, enthalpy and entropy changes shows that the adsorption of Malachite green Oxalate (MGO) dye onto CdO was spontaneous and exothermic process. The kinetic data showed that the adsorption of (MGO) dye onto CdO nps followed the pseudo second order.

5. CONCLUSION

It was estimated that inexpensive, easily prepared and effective CdO nps could be used in place of commercial adsorbents for the elimination of dyes from aqueous solution. Minute amount of CdO nps obligatory for the removal of dyes, Unquestionably CdO adsorbents offer a lot of promising benefits in the prospect.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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