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Synthesis of $CuCo_2O_4$ spinel composite as an adsorbent surface for removal of celestine blue B dye

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***Abstract*---**This study included a synthesis of $CuCo_2O_4$ spinel composite, which was prepared by the co-precipitation method from their aqueous nitrates as starting materials, the prepared spinel composite was characterized by using XRD, FTIR, UV-Visible, AFM, and FESEM spectroscopies. The particles size of the prepared adsorbent surface was found to range from 25-75 nm. As it has been applied in removing toxic organic dyes from textile industry wastewater. This study showed the best optimal conditions for removal of dye was 30 minutes of adsorption time 0.005g of the surface adsorbent, 50 $mg.L^{-1}$ for Celestine Blue B dye concentration, pH value 5, at a temperature of 298K, gave a high removal of 97%, also found that the negative free energy ΔG and heat of reaction ΔH values, indicating that the reaction is spontaneous and exothermic, while the entropy value ΔS was positive, indicate that the occurrence of disturbance of water molecules around the dyes.

***Keywords*---**Organic dye, Celestine blue B, CBB, adsorption, Catalysis.

Introduction

Pollution is a dangerous phenomenon resulting from the rapid and increasing human activity in agriculture and industry to meet the needs of people. In addition to the lack of good planning for these activities [1]. Pollution is found in

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the three main environments of air, soil, and water. Because of the importance of water in agriculture and industry, it has become subject to pollution in large and dangerous quantities. One of the most dangerous water pollutants is dyes, which have wide applications in the industries of textile dyeing, dyes, and paper inks. These industries release non-degradable and toxic compounds in the form of pollutants in river water [2,3]. The danger of dyes is that they contain homogeneous or heterogeneous aromatic structures that are not subject to disintegration and biodegradation, in addition to being carcinogenic and causing diseases and genetic mutations[4.] It produces more than $1x10^5$ types with an estimated amount of 700 thousand tons annually to cover the requirements of the textile industry [5], which is the most important economic source, which causes 2-20% of it to be dumped into the wastewater, which causes pollution to the aquatic environment[6] The danger of dyes increases because they block the passage of light in the aquatic environment and a deficiency in the BOD and also COD, which required finding solutions to remove these dyes from the aquatic environment as they are very dangerous pollutants. [7]. One of the examples of organic dyes belonging to the oxazine group is a heterocyclic ring containing nitrogen and an oxygen elements and is a toxic and carcinogenic group present. Celestine blue B (CBB) dye, the molecular weight of the dye 363.80 $g.mol^{-1}$, chemical formula ($C_{17}H_{18}ClN_3O_4$), and its maximum length λ 645 nm[8]. There are many techniques for removing pollutants under three main sections, chemical, biological and physical techniques such as adsorption[9].

Adsorption technology is considered the most efficient technology in treating and purifying water from pollutants up to 99%, in addition to wide adsorption applications, ease of work and low cost. The basis of the action of adsorption is the deposition or adhesion of particles of pollutant components on the surface or interface between a solid substance called the adsorbent surface. Affected by the time factor, the amount of surface adsorbed, the temperature and the acidity of the medium, the addition of materials and other impurities [10,11].

The current study suggested the synthesis of a new surface from oxides of copper, cobalt due to the characteristics of the surfaces of these materials from effective sites and high surface area[12], their raw materials are low cost and highly efficient in removing pollutants, in addition to the stability of the removal technique and the study of the best conditions.

Experimental

Material of Chemicals

The following chemicals were used in this study: Celestine blue B (CBB), $Co(NO_3)_2.6H_2O$, $Cu(NO_3)_2.3H_2O$, Na_2CO_3, NaCl, KCl, $MgCl_2$, $CaCl_2.2H_2O$, NaOH, and HCl All materials are of very high purity and from BHD, HIMEDIA and SIGMA companies.

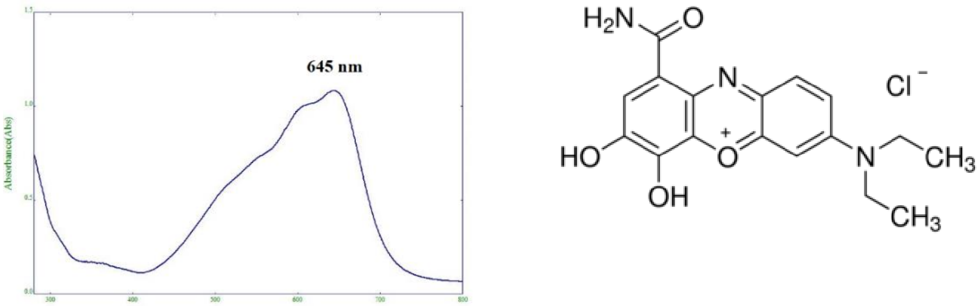
Preparation of Absorbance Surface

The equivalent weights of composite ratios 40%, and 60% of copper, cobalt, and magnesium nitrates, respectively, were dissolved in 400 ml of distilled water in an 1L glass beaker capacity. The mixture solution was heated to the temperature of

70-75°C with constant stirring using a magnetic stirrer, then add 0.1 M sodium carbonate as a precipitating agent drop by drop until reaching to pH9, in which the precipitation was completed. After that, the mixture is left with heating and stirring for 2 hrs. The solution was filtered to obtain the precipitate and washed by hot distilled water several times until the of filtrate water reached to pH7. Then dried the precipitate at 120°C and crushed. Then burned at 600°C for 4 hours. .[13-14,] and Characterized by using UV. Vis, FT-IR , XRD , AFM , and FESEM techniques.

Preparation of dye solution:

The Stoke solution of 100 ppm was prepared to dissolve 0.1 g of CBB dye in 1 liter to distilled water, then prepare a series of 10 - 80 ppm of the Stoke solution by dilution as a calibration curve. The UV. Visible spectra of Celestin blue B dye showed that, the maximum absorption at λmax = 645 as shown in fig. 1a.



a. **b.**

Figr.1 a. the UV. visible spectra of CBB dye showed that, the maximum absorption at λmax=645, b Chemical structure of CBB dye.

Study of the optimization conditions

The effect of equilibrium time, adsorbent surface weight, acidity of the solution and ionic strength on efficiency of the adsorption process (the efficiency of dye removal from its aqueous solutions) in addition to temperature was studied by adding the mass of the adsorbent surface to 30 ml of a 50 ppm dye solution in 50 mL conical flask and shaking the mixture in a water shaker, then the mixture was centrifuged to separate the solid adsorbent and measured the absorbance of the supernatant at the maximum wavelength of the dye.

$$\text{Re\%} = \frac{C_o - C_e}{C_o} X100\% \qquad (1)$$

Whereas:
Re% = Removal efficiency of dye.
C_o dye concentration before adsorption.
C_e the equilibrium concentration of the dye (after the adsorption process) can be extracted from the titration curve equation.

Adsorption Isotherm

To obtain the Celestine blue dye isotherms adsorbed on the surface of $CuCo_2O_4$ spinel composite, a series of different dye concentrations, C_o (initial concentrations) were prepared before adsorption (10, 20,30,40,50,60,70,80 and 90) mig.L^{-1}, 0.005 g of the adsorbent surface was added to 30 mL from each dye concentration in 50 mL conical flask at different temperatures (298, 308,318,328 and 338 K) at a shaking speed of 150 for 30 minutes, according to the isotherm of dye adsorption on the surface and its comparison with Giles's classification by drawing between the adsorption capacity Q_e and the concentration of dye at equilibrium C_e

$$Qe = \frac{(C_o - C_e)V}{m} \qquad (2)$$

Whereas:
Q_e = The quantity of the absorbances to the quantity of the adsorbent, its unit is mg per g and is called the adsorption capacity
C_e= the equilibrium concentration of the adsorbent solution in units of (mg.L^{-1})
C_o = the initial concentration of the adsorbent solution in units of (mg.L^{-1})
V = total volume of the adsorbent solution in units (L)
m = weight of the adsorbent in units of (g).

Result and Discussion
Characterization of $CuCo_2O_4$ spinel composite (adsorbent surface)

The FT-IR spectra in Fig.2 showed the absorption in the fingerprint region between 667.39 - 572.88 cm-1 for the prepared CuCo2O4 adsorbent surface and our matching with the stretching vibrations of the bonds of tetrahedral $Co^{+3} – O^{-2}$ and $Cu^{+2} - O^{-2}$ octahedral complexes, respectively. These resultant values are attributed to the fingerprint, infrared material of CuCo2O4, with most metal oxides showing peaks below 1000 cm^{-1}. This indicates that the spinal type catalyst is not $CuCo_2O_4$ [15].

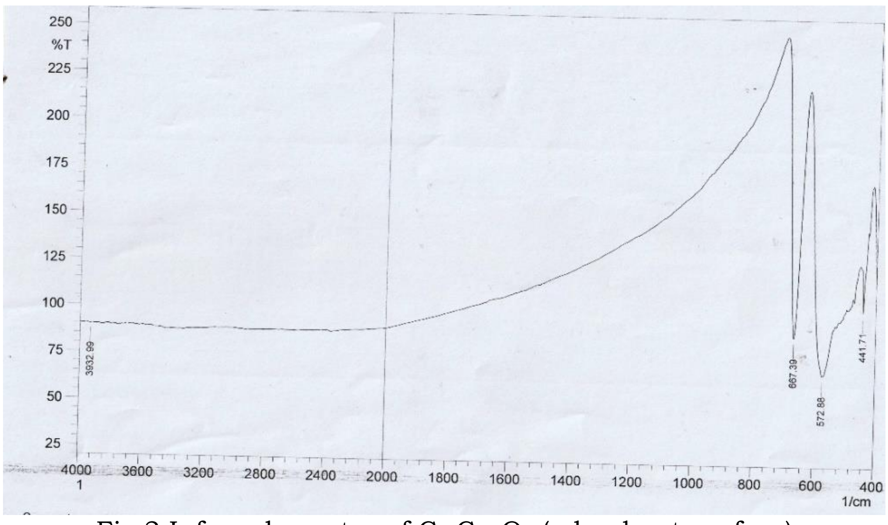


Fig.2 Infrared spectra of $CuCo_2O_4$ (adsorbent surface)

Fig.3, showed the X-ray patterns of the surface of the adsorbent spinel composite at angles of 2θ, 19.06°,31.33° , 36.91°, 38.79 , 44.87, 48.79 , 59 ,45 and 68.13° have relative intensity I% of 11.8 , 38.97, 100, 93,66 , 21.33 , 20.85 , 21.73 and 10.75, and respectively, It also matched with planes of 111, 220 , 311 , 222 , 400 , 331, 511 , and 531 respectively compared to JCPDS 00-001-1155 and 01-087-2177 corresponding to the $CuCo_2O_3$ spinel [16, 17].

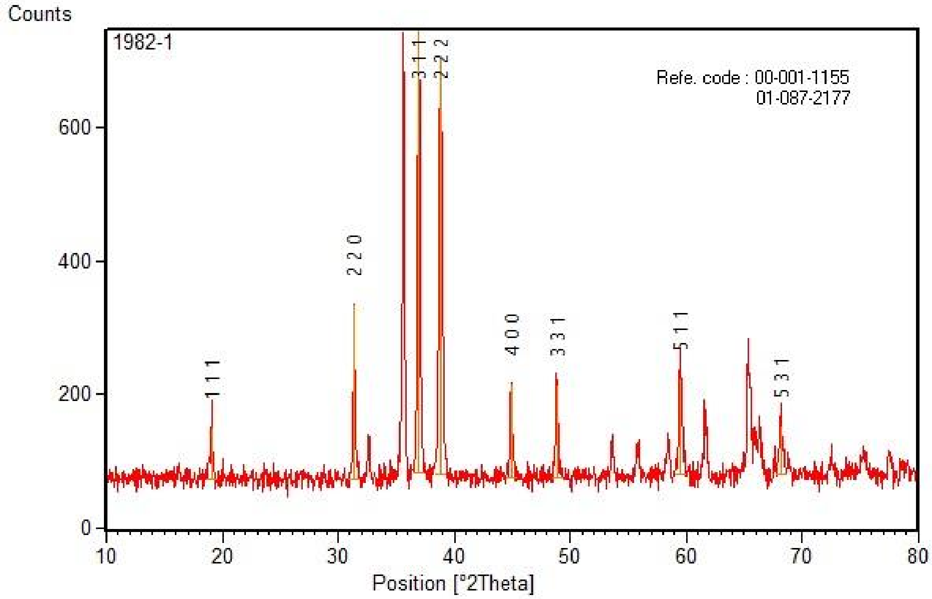


Fig.3 the X-ray diffraction diagram of $CuCo_2O_4$. the prepared adsorbent surface

The AFM technique explains the particles size of the extent of surface homogeneity as shown in Fig.4. The size of the particles of the catalyst (adsorbent surface) $CuCo_2O_4$ ranges between 20-28 nm with a high homogeneity ratio, which increases the active sites of the catalyst due to increase in the surface area, while the FESEM technique diagnosed the size and morphology of the prepared $CuCo_2O_4$ particles (adsorbent surface) and the interlayers, their spherical size ranged from 31-364 nm and good interfacial distances were found as shown in fig.5.

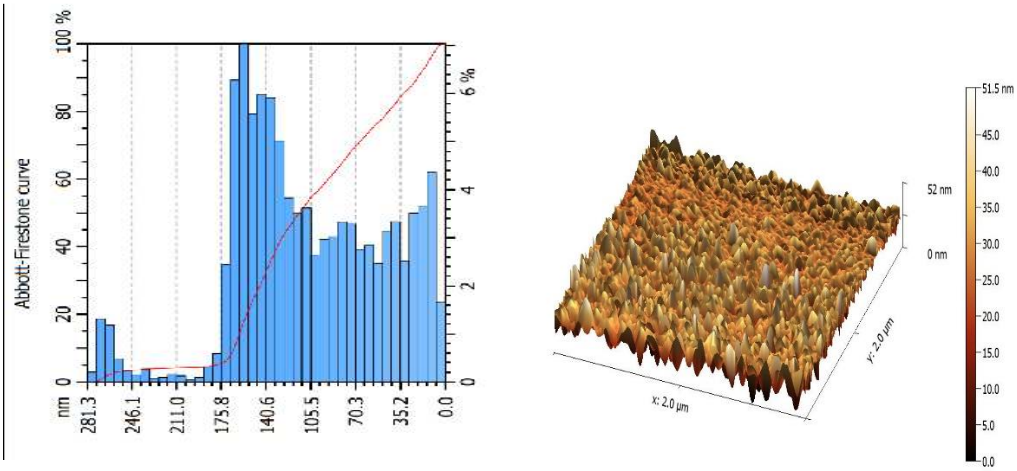


Fig.4 AFM diagram of $CuCo_2O_4$. the prepared adsorbent surface

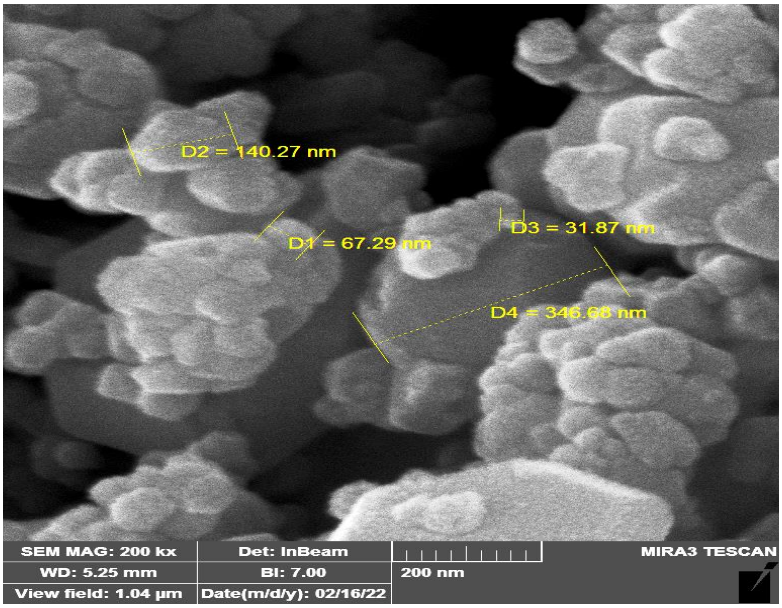


Fig.5: FESEM of $CuCo_2O_4$ particles (adsorbent surface)

Study of the optimum conditions for removing CBB
Equilibrium Time of Adsorption System

The most important factors affecting the adsorption process and determining the adsorption capacity and surface efficiency of the adsorbent is the time required to achieve a balance between the surface of adsorbent and the adsorption dye called the equilibrium time, which is an important step in its use in subsequent experiments. Different equilibrium times (5,10, ..., 120) minutes at absolute temperature of 298 K showed that Re% increased abruptly in the first 20 minutes, after which a very slight increase lasted from 30 to 120 minutes as in the fig. 6, This indicates the great affinity between the active sites present in the surface of the spinel compound and the dye, an appropriate time of 30 minutes was appropriate [18].

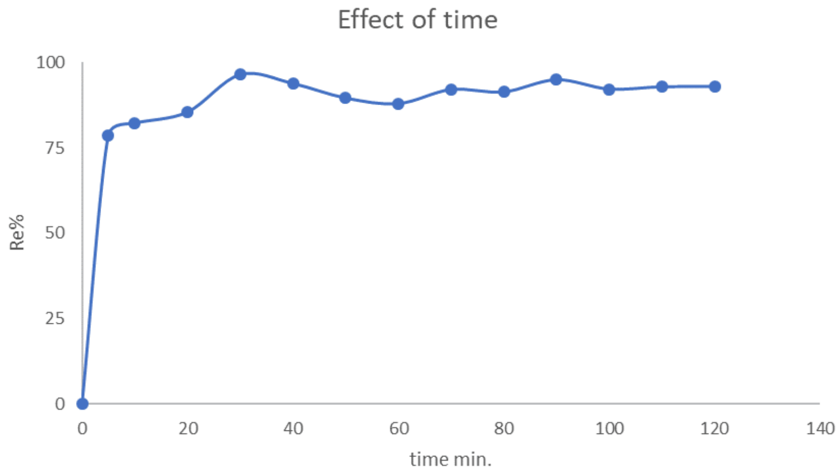


Fig.6 the Effect of equilibrium time for removal efficiency of CBB dye by using $CuCo_2O_4$ spinel composite at 298 K

Effect of the mass of Surface Adsorbent

The amount of absorbent material had an effect on the adsorption capacity and the adsorption process (removal efficiency), where a series of doses of the prepared adsorbent surface were carried out from (0.005 - 0.08) g . It was found that there is an increase in the removal ratio with the increase in the amount of surface adsorbents due to the increase of the active sites on the adsorbent surface that is directly proportional to the amount of the adsorbent surface and its correlation with the adsorbent as shown in Figure 7, the slight increase in the removal percentage compared to the increase in the weight of the surface admirable. The best absorbent surface mass of 0.05 g was chosen because most of the active sites were bound to 88% of the active sites of the dye.[19]

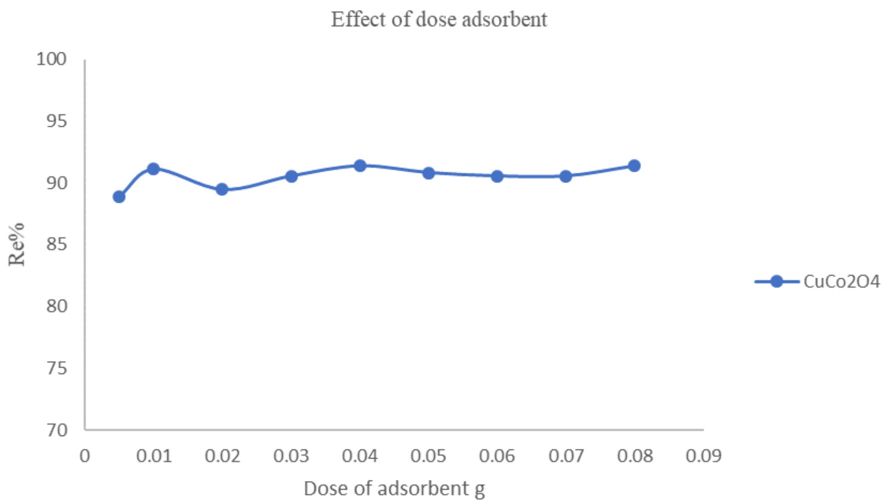


Fig.7 Effect of the weight of $CuCo_2O_4$ (adsorbent surface) on the efficiency of CBB dye removal at a time of 30 minutes and a temperature of 298 K.

The effect pH

Fig.9 showed the effect of pH (2,4,6,8,10, and 12) on the removal efficiency of CBB dye (absorbances) with the adsorbent surface. While we observe a significant decrease with increasing pH as well as in the basic medium due to competition of H^+ and hydroxyl dye for their active site on the surface. Therefore, the best pH of 4-6 was chosen with the concentration of 50 $mg.L^{-1}$ and a mass of 0.005 g $CuCo_2O_4$ at and 30 minutes.

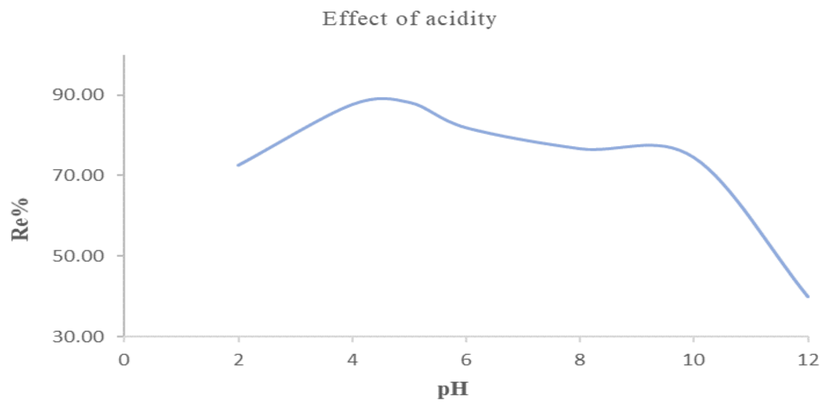


Fig.9 Effect of pH on the efficiency of CBB dye removal using $CuCo_2O_4$ at time of 30 minutes and a mass of 0.005 g from the adsorbent surface

The effect of ionic strength

The effect of the ionic strength on the adsorption process by adding 0.02, 0.05, and 0.07 M of ionic salts (Na^+, K^+, Mg^{+2}, and Ca^{+2}) on the adsorption process, as in Figure 8, showed a decrease in the dye removal efficiency with an increase in the charge and size of the ion due to the ionic salts of the dye compete with the active sites on the adsorbent surface. The lower the solubility, the more affinity with the adsorbent surface.

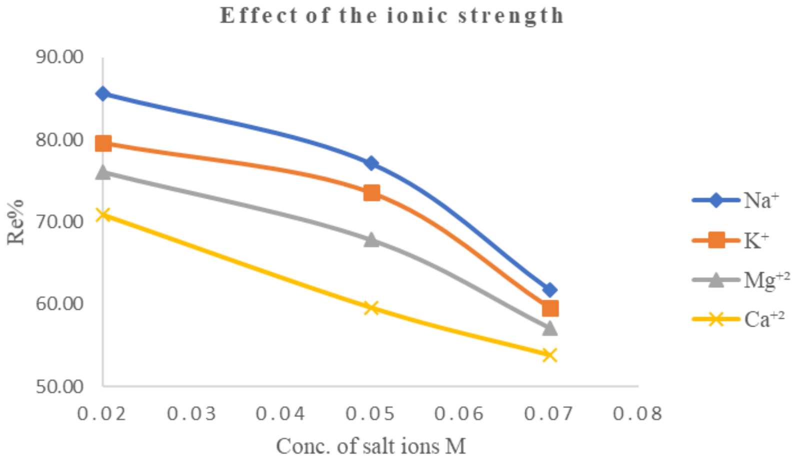


Fig. 8 Effect of the ionic strength of salt ions of different charges, sizes, and concentrations on the efficiency of removing CBB dye using Co_2CuO_4.

Adsorption isotherms

The relationship between amount of absorbent material on the surface of adsorbent at equilibrium Qe and the concentration of the absorbent material in a solution at equilibrium at a certain temperature is called the adsorption isotherm. Fi 9 showed the values of the Qe adsorption capacity from Equation 2 and the concentration of Ce adsorbents at the different concentrations (10, 20 .... and 90 mg L^{-1}) before adsorption and at different temperatures (298-338) K . It was found according to the classification of Giles S4. It was found that there is a high affinity between the adsorbent materials and the adsorbent surface and it corresponds to the classification according to the classification of the Giles at all temperatures. Addition of its conformity with models. Langmuir, Freundlich and Temkin Isotherms.[20]

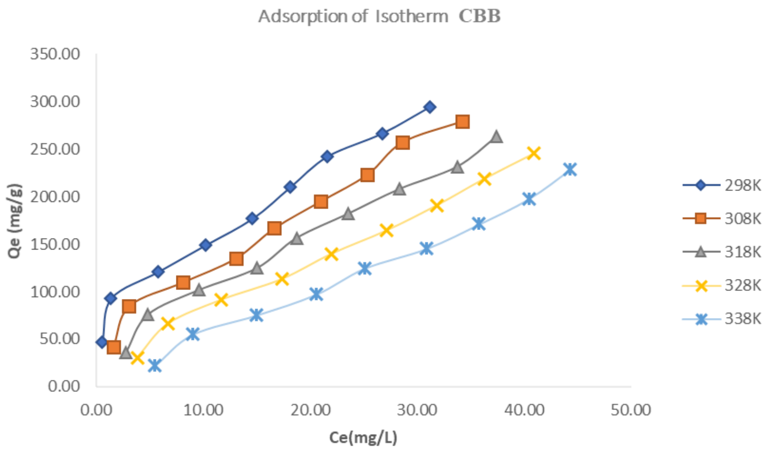


Fig.9 The relationship between the adsorption capacity Q_e mg. g^{-1} and equilibrium concentration C_e mg. L^{-1} of CBB dye at different temperatures (298–338K) on the adsorbent surface $CuCo_2O_4$.

Models of the adsorption process

The scientist **Langmuir** suggested that the adsorption process occurs on one layer, while **Freundlich** and **Temkin** made a modification to the equation of **Langmuir** and suggested the adsorption process occurs on more than one layer.

$$Qe = \frac{a\,b\,Ce}{1+b\,Ce} \qquad (3) \qquad \text{Langmuir}$$

$$Q_e = K_f\,Ce^{1/n} \qquad (4) \qquad \text{Freundlich}$$

$$Q_e = RT(LnK_tC_e)\,/b_T \qquad (5) \qquad \text{Tekmin}$$

A linear **Langmuir** equation was drawn between C_e / Q_e and C_e, While the **Freundlich** equation $\log C_e$ and $\log Q_e$, and Temkin equation between LnCe and Q_e. The finding the extent of the adsorption process of CBB dye from its aqueous solutions at optimal conditions in fig10,11, and 12respectively [21]. It was found that the Langmuir equation does not apply to it in contrast to the **Freundlich** and **Tekmin** equations as according to their coefficients and correlation values for each adsorption equation as shown in Table1.

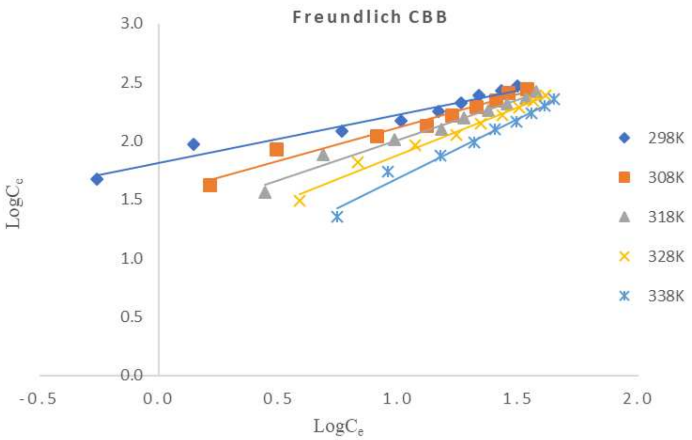


Fig. 10 The Freundlich isotherm between log Q_e and Log C_e to CBB dye at different temperatures (298 - 338 K) on the adsorbent surface $CuCo_2O_4$.

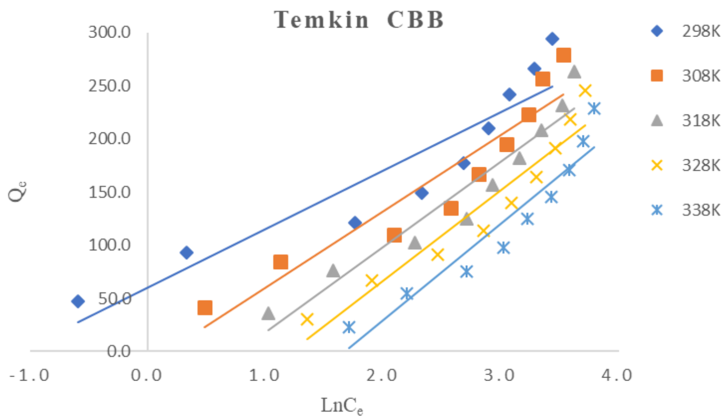


Fig.11 Temkin isothermal model between between Q_e and LnC_e to CBB dye at different temperatures (298 - 338 K) on the adsorbent surface $CuCo_2O_4$.

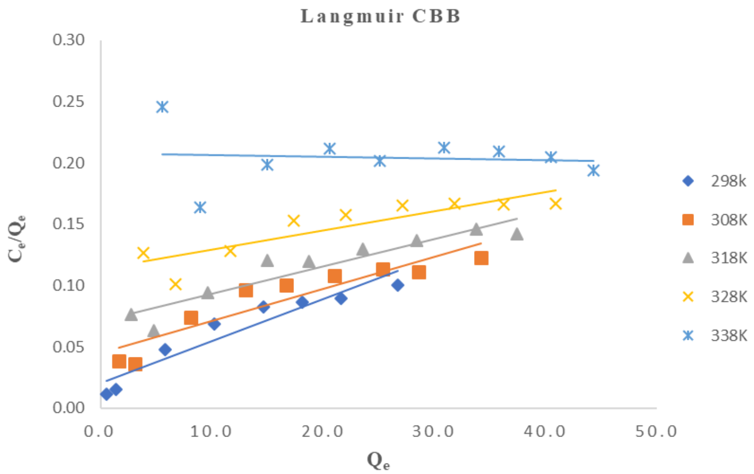


Fig. 12 The linear relationship between the Langmuir isotherm between between C_e/Q_e and C_e to CBB dye at different temperatures (298 - 338 K) on the adsorbent surface $CuCo_2O_4$.

Table 1 The values of Langmuir, Freundlich, and Temkin constants, enablement, and correlation coefficient of CBB dye adsorbed on $CuCo_2O_4$

CBB										
Temp. K	Langmuir isotherm				Freundlich isotherm			Temkin isotherm		
	a (mg. g^{-1})	b (mg. L^{-1})	(R^2)	RL 1+bC_e	(Kf)	(n)	(R^2)	b_T	K_T	R^2
298	294.1	0.1667	0.9054	0.1	65.22	2.44	0.9608	60.37	2.997	0.8667
308	384.6	0.0579	0.8594	0.3	35.38	1.76	0.9678	-52.78	0.851	0.8885
318	454.5	0.0309	0.8823	0.4	20.70	1.44	0.9764	-62	0.462	0.9266
328	625.0	0.0141	0.698	0.6	11.70	1.23	0.9821	-103.21	0.297	0.921
338	-10000.0	-0.0005	0.0083	1.0	4.70	0.99	0.979	-103.2	0.187	0.9095

To understand the adsorption process, he studied the effect of temperature and calculate the values of thermodynamic functions (free energy, ΔG, enthalpy ΔH, entropy ΔS) for the importance of these functions in explaining the behavior of the adsorption process and determining the type of reaction, spontaneous or not, emitting or endothermic. The values of free energy ΔG can be calculated using equation (6-10), the relationship between the equilibrium constant LnK_{qe} and 1/T shown in fig. 13 and table2 [22].

$\Delta G = -R\, K_{eq}\, T$ (6)

$K_{eq} = \frac{Qe\, m}{Ce\, V}$ (7) Sub. equ. 2 in equ. 7

$K_{eq} = \frac{(C_o - C_e)}{C_e}$ (8)

$LnK_{eq} = -R\Delta H/T + con$ (9)

Slope = -RΔH (10)
ΔS= (ΔH- ΔG)/T (11)

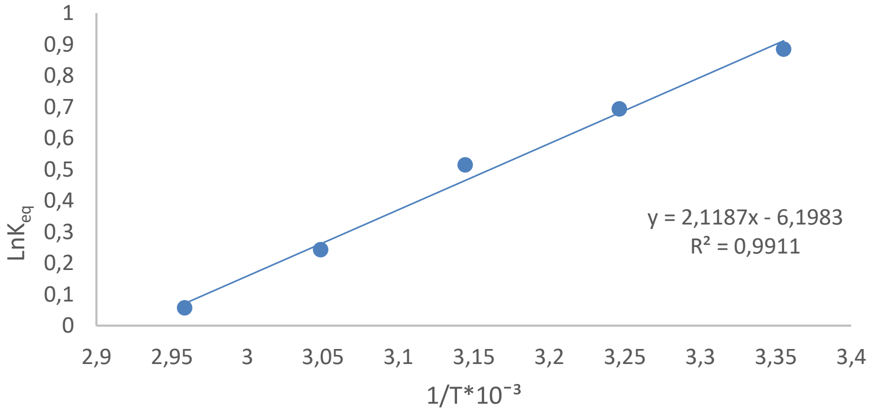


Fig.13 The relationship between the equilibrium constant LnK_{qe} and 1/T

Table 2 The values of thermodynamic functions and equilibrium constant Kqe adsorption process of CBB dye on $CuCo_2O_4$ at 298 – 338 K

T	C_e	$K_{eq} = \frac{(C_o - C_e)}{C_e}$	1/T*10^{-3}	LnK_{eq}	ΔG KJ.mol^{-1}. K^{-1}	ΔH KJ.mol^{-1}. K^{-1}	ΔS KJ.mol^{-1}. K^{-1}
298	14.6233	2.419201	3.355705	0.8834	-5.99	-17.614	-38.99
308	16.6644	2.000408	3.246753	0.6933	-5.12	-17.614	-40.55
318	18.71918	1.671057	3.144654	0.5134	-4.41	-17.614	-41.49
328	22.00132	1.272591	3.04878	0.2410	-3.47	-17.614	-43.12
338	24.3041	1.057266	2.95858	0.0556	-2.97	-17.614	-43.32

From table 2 and fig. 13, we can observe that, the effect of absolute temperature on the adsorption process and that the values of free energy are negative indicating that the adsorption process is spontaneous and does not need energy, while the value of the heat of reaction is negative for an exothermic process. While the change in entropy showed a negative value at 298-338K, indicating a decrease in the randomness and uniformity of the surface due to the fullness of the active sites on it.

Conclusions

The Spectroscopic studies give excellent evidence for obtained of $CuCo_2O_4$-MgO spinel composite, which gave the highest removal efficacy of Celestin blue B dye, with the optimal conditions; dyes concentration of 50 mg. L^{-1}, the weight of adsorbent surface, 0.005 gm, pH4-6 and time of adsorption, 30 minutes at a temperature of 298K.

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