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Remove of hazardous heterocyclic dyes from aqueous solutions with CuO adsorbent

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Abstract**-** In this study , Copper oxide as a good and inexpensive adsorbent has been introduced and used for the removal of erythrosine and red carmoisine dyes from several water solutions successfully. The effect of various parameters such as pH, dye concentration, amount of adsorbent, contact time and temperature on removal processing was investigated. Adsorption isothermal data could be interpreted by the Langmuir and Freundlich, isotherm models.

Keyword: Copper oxide, Erythrosine, Red carmoisine, Absorption.

Introduction

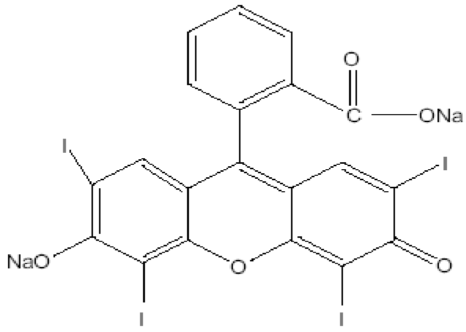
Dyes from the effluent of textile, paper, leather, food, cosmetic, plastic and pharmaceutical industries, are the major source of water contamination [1]. Over 10000 dyes with an annual world wide production of over 7×10^5 tons are commercially available, about 50% of which are azo dyes and 10-15% of dyes produced world wide has been reported to be discharged in to the water streams[2]. These dyes are not only aesthetically displeasing, also, reduces light penetration and hinders photosynthesis in aquatic plants[3].some dyes and their degradation products in surface water are reported to be highly carcinogenic, however many organic dyes are harmful to human being and toxic to microorganisms. Therefore effective removal of color from dye effluents are environmentally important. Most dyes are recalcitrant molecules, which are resistant to aerobic digestion. They are also stable in light, heat and oxidizing agent[4]. Numerous treatments, such as biological treatment, coagulation or flocculation, ozon treatment, chemical oxidation, membrane filtration, photocatalytic degradation and adsorption, have been developed. Adsorption methods are relatively simple, easy to operate, more effective and less expensive than other technologies[5].

Erythrosine or acid Red 51(C.I.45430, $C_{20}H_6I_4Na_2O_5$,M.W: 879.86) is a xanthene class and water soluble synthetic dye that often used as a food colorant(Scheme 1). When excessively consumed it can cause sensitivity to light, affecting thyroid hormone levels and lead to hyperthyroidism in some cases. The maximum allowed level of erythrosine is 200mg/kg in some food stuffs [6].

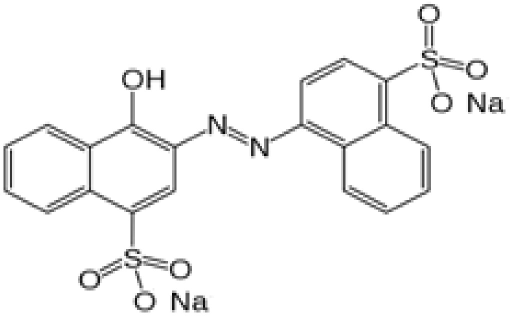
Red carmoisine or acid red 14 (C.I.14720 , $C_{20}H_{12}N_2Na_2O_7S_2$, MW: 502.44) is synthetic azo dye commercially used for the purpose where the food is heat – treated after fermentation(Scheme 2). Synthetic azo dyes have found broad industrial application due to the non-expensive production and the wide spectrum of colors that can be produced when compared to natural colorants. The massive everyday consumption of synthetic dyes by humans has increased the interest on finding their toxicity properties. In this century, it has been found that some of these dyes can be harmful to people's health, and in some cases they could even provoke cancer and infant birth deformation depending on the ingested levels [7]. These findings have increased the interest for developing reliable sensitive quantitative methodologies for the determination of these synthetic dyes and derived metabolites in food products and human fluids.

Metal oxides have potential applications in water treatment due to their high surface area added to low production and regeneration[8].

In this work, we utilized ZnO as adsorbent for the removal of red carmoisine and erythrosine from water.



Scheme 1. The molecular structure of Erythrosine



Scheme 2. The molecular structure of Red Carmoisine

2. Experimental

2.1. Adsorbents

In this study, ZnO was used as adsorbent for Erythrosine and red carmoisine dye removal from textile wastewater in laboratory scale.

2.2. Dye

A commercial red carmoisine azo-dye and erythrosine was supplied from Aldrich Chemical Co. Inc (St. Louis, Mo. USA), and was used without further purification. A solution of the carmoisine azo-dye and erythrosine was prepared in deionized water.

Other chemicals were all of analytical grade from Merck Chemical Company. Distilled deionized water was used for preparation of all solutions. pH adjustments were done using dilute hydrochloric acid and sodium hydroxide solutions[9]. The pH measurements were made by a pH meter (Metrohm-827). The agitation process for mixed adsorbent and dye solutions was carried out using shaker (model-Orbital L) and also dyes was determined by a double beam UV-Vis spectrophotometer (Model UV mini 1240).

2.3. Batch adsorption

The effect of variables such as pH, amount of adsorbent, contact time, initial dye concentration and temperature on the adsorptive removal of Erythrosine and Red Carmoisine was investigated.

In each adsorption experiment, 150 ml of dye solution of known concentration and pH was added to 700 mg of adsorbent. This was done at a at fixed control temperature. The mixtures were then stirred on centrifuge at 4000 rpm for 10 min.

Therefore, samples were withdrawn from the shaker every 15 or 30 minutes and the adsorbent was separated from the solution by centrifugation at 4000 rpm for 6 times. In order to determine the residual dye concentration, the absorbance value of the supernatant solution was measured before and after the treatment, with Shimadzu UV Visible spectrophotometer (Model UV mini 1240).

The obtained experimental data at various times, temperatures and concentrations were fitted to different models to calculate the isotherm parameters of adsorption process at optimum values of all variables were investigated. The pH was adjusted by addition of dilute aqueous solutions of

HCl and/or NaOH (1.0Mand 0.1M). The removal percentage of Erythrosine and Red Carmoisine was calculated using the following relationship

$$q_e = \frac{(C_0 - C_e).V}{w} \qquad (1)$$

where C_0 and Ce (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (L) and W is the mass of sorbent used (g)[10].

3. Results and discussion

3. 1. Calibration of Erythrosine and Red Carmoisine

In order to calculate the concentration of the sample from each experiment, a calibration curve of Erythrosine and Red Carmoisine dyes was obtained. Beers law was obeyed wih in the experimental initial concentrations of dyes. Therefore, the concentration of dye samples could be calculated from related maximum absorbance values. Construction of calibration curves shown in Fig 1 and Fig 2.

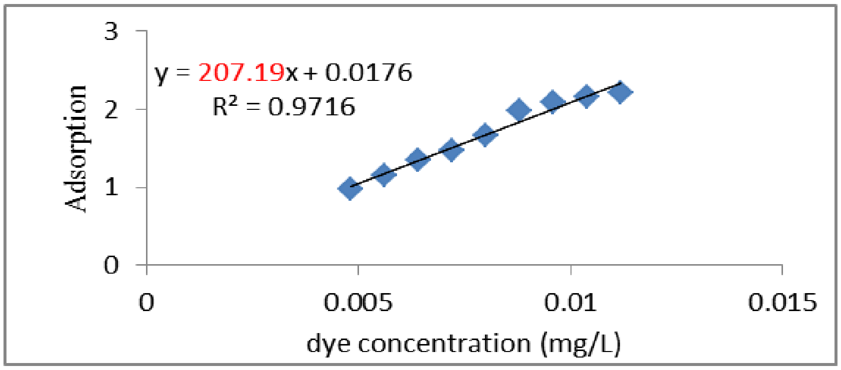


Fig1 . Calibration Curve of Red Carmoisine

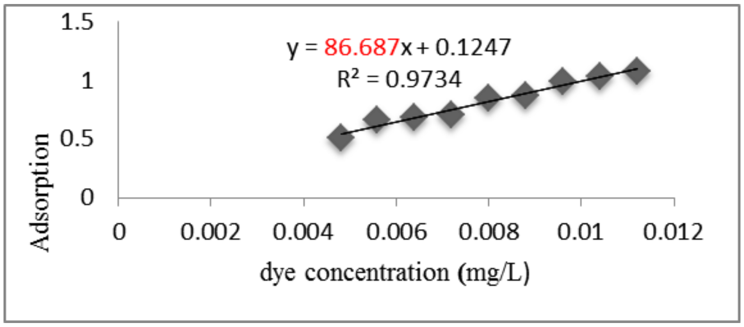


Fig 2. Calibration Curve of Erythrosine

3.2. Effect of pH

In order to study the effect of pH on Erythrosine and Red Carmoisine dyes adsorption on ZnO, experiments were carried out at 8mg/L initial dye concentration with 700 mg/150 ml adsorbent mass at room temperature of 25±1oC for 90 minute equilibrium time. Results are presented in Figure 3, Fig 4.

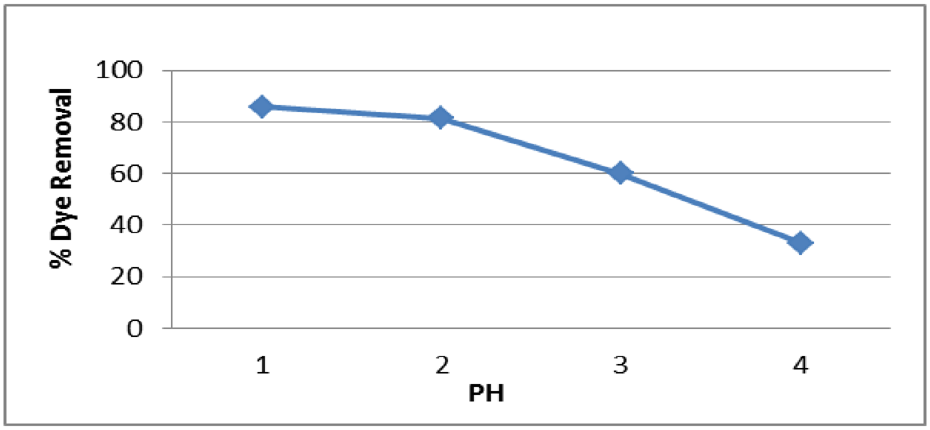


Fig 3. Effect of pH on the removal of erythrosine 25 ºC, agitation rate of 1800rpm 0.733 gr adsorbent in 100 ml of 8 mg L^{-1} dye solution

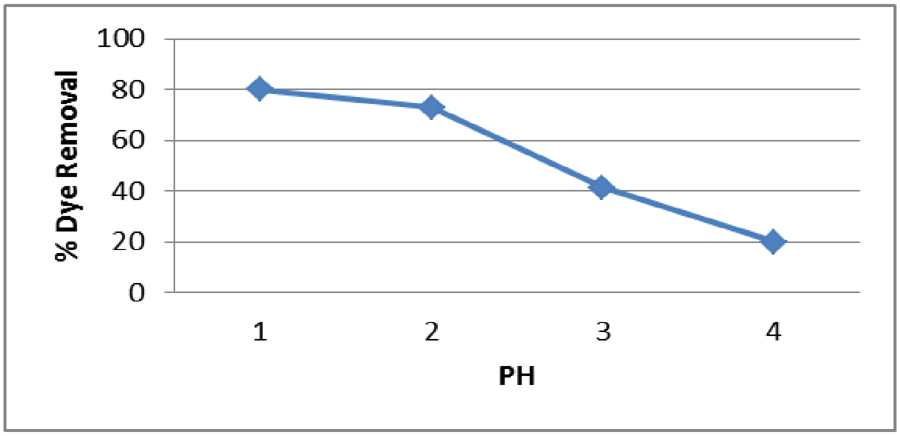


Fig 4. Effect of pH on the removal of red carmoisine 25 ºC, agitation rate of 180rpm 0.733gr adsorbent in 150 ml of 8 mg L^{-1} dye solution

The effect of pH in the range 4-12 on the removal of Red carmoisine and erythrosine was investigated using 0.01 mol L^{-1} HCl or NaOH solutions for pH adjustment, with the initial dyes concentration fixed at 8 mg.L^{-1}. As Fig. 3 and Fig. 4 show, the percent adsorption increased by decreasing pH and reached maximum at pH 4 and then decreased at higher pHs. At higher pHs, the high negatively charged adsorbent surface sites did not favor the adsorption of deprotonated CR due to electrostatic repulsion[11-14].

3.3. Effect of contact time

Recognizing equilibrium contact time is essential for absorption process design and rapid sorption is among desirable parameters. Results of effect of contact time on erythrosine and red carmoisine dyes removal in different concentrations are shown in Fig. 5 and Fig 6. Based on results, as contact time increases, the dye removal efficiency increases too. In initial minutes of experiment, dye was quickly removed and high quantity of dye concentrations were removed in few minutes and then the dye removal was increased constantly with increasing contact time up to reach to 83.52 , 60.2% in 90 min for Erythrosine and Red Carmoisine respectively. According to results, 90 min was obtained as equilibrium contact time; at this time, due to saturation of absorption sites on absorbent, dye removal efficiency won't have any changes[8].

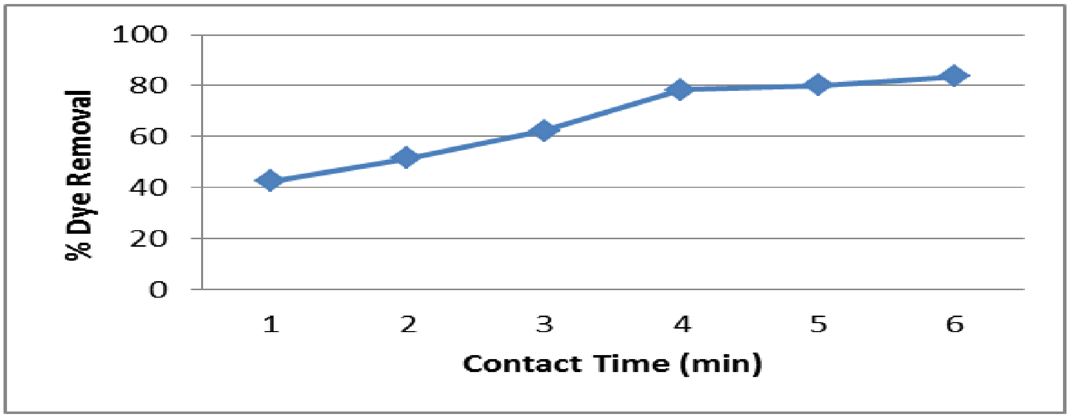


Fig. 5. Effect of contact time for 8 ppm erythrosine concentrations; pH 4, 25 ºC, agitation rate of 180 rpm and 0.733 g adsorbent in 150 ml of dye solution.

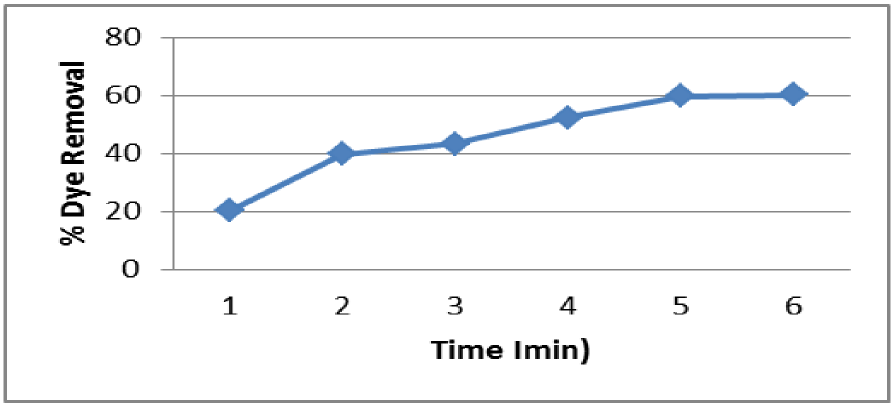


Fig. 6. Effect of contact time for 8 ppm red carmoisine concentrations; pH 4, 25 ºC, agitation rate of 180 rpm and 0.733 g adsorbent in 150 ml of dye solution.

3.4. Effect of different concentrations on dye removal

The equilibrium condition was achieved within 90 min for 4, 8 and 12 mg L^{-1} dye concentrations. The effect of initial dye concentration on the ability of ZnO to adsorb dyes from solution suggested that the percentage color removal of Erythrosine and Red Carmoisine decreased when the initial dye concentration increased.

. In the present study, the adsorption experiments are performed to study the effect of dye initial concentration by varying it from 4 to 12 mg L^{-1}, while maintaining the ZnO amount 0.733 g and obtained results are presented in Fig. 7. and Fig. 8. The results showed that with increase of dye concentration from 4 to 12 mg L^{-1}, the removal efficiency decreases from 89.1 % to 78.84%. and 81.33% to 52.4% for erythrosine and red carmoisine respectively. The decrease in removal efficiency can be explained by the fact that all the adsorbents had a limited number of active sites, which would have become saturated above a certain concentration[9].

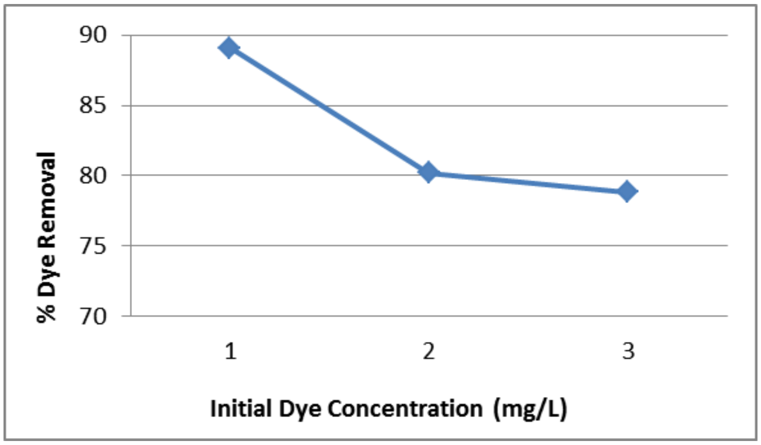


Fig (7): Effect of different Erythrosine concentrations pH 4, 25 ºC, agitation rate of 180 rpm and 0.733 g adsorbent in 150 ml of dye solution.

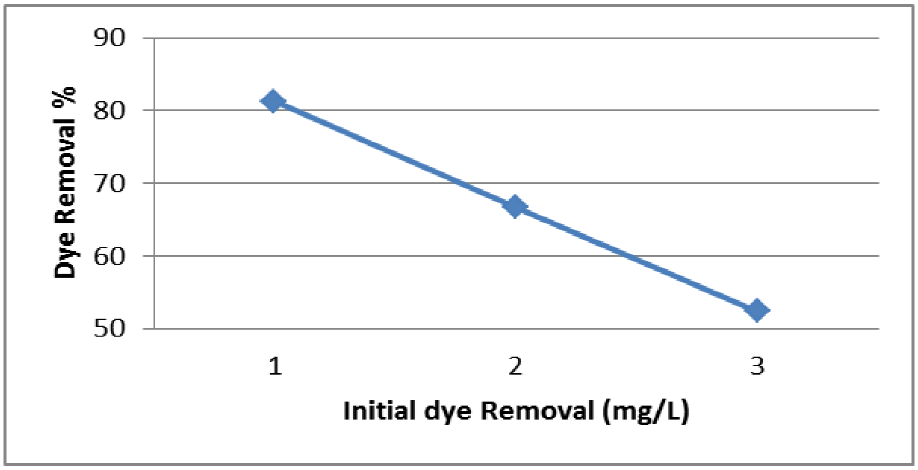


Fig (8): Effect of different Red Carmoisine concentrations pH 4, 25 ºC, agitation rate of180 rpm and 0.733 g adsorbent in 150 ml of dye solution

3.5. Effect of adsorbent dose on dye removal

The adsorption of dye on absorbent were studied by changing the quantity of adsorbent (0.5, 0.7 and 0.9g/100 ml) in the test solution while keeping the initial dye concentration (8 mg/L), temperature (25±1oC) and pH (4.0) constant. Experiments were carried out at different contact times for 90 mins. As shown in Fig9 and Fig10 the percent adsorption increased and equilibrium time decreased with increasing adsorbent doses. As the ZnO dose was increased from 0.5 g to 0.9 g/100 ml the adsorption increased from 69.47 to 83.6%, and 56.22 to 73. 27% for Erythrosine and Red Carmoine at equilibrium time (90 min) respectively. Increase in the adsorption with adsorbent dose can be attributed to the increase in adsorbent surface area and availability of more adsorption sites.

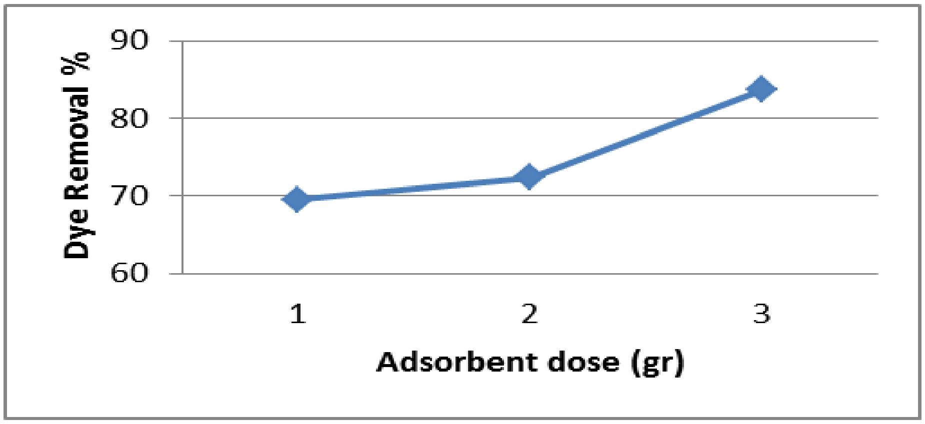


Fig (9): Effect of different copper oxide dose pH 4, 25 ºC, agitation rate of 180 rpm and initial dye concentration8mg L^{-1} in 150 ml of Erythrosine dye solution.

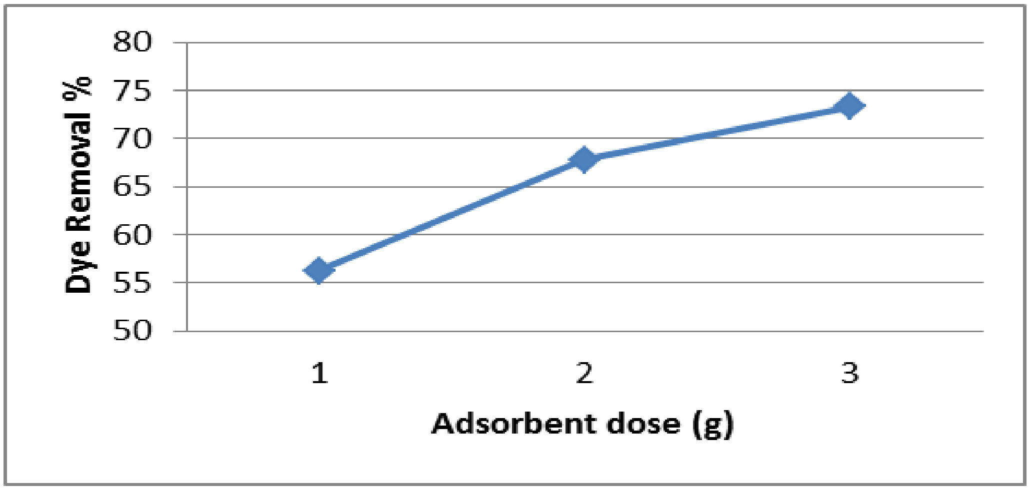


Fig (10): Effect of different copper oxide dose pH 4, 25 ºC, agitation rate of 180 rpm and initial dye concentration8mg L^{-1} in 150 ml of Red Carmoisine dye solution.

3.6. Effect of temperature on dye removal

To study the effect of temperature, the experiments were carried out for adsorbent at temperature varying from 20 to 40 ^{0}C. It was observed that ZnO removed 72.8to 74.048.5% of Erythrosine, However, in case of Red Carmoisine, the removal of dye was 72.4 to 76.59% . The result have been shown in Fig 9 and Fig10. All the experiments were carried out for 90 min. The equilibrium was obtain at 40 ^{0}Cfor both dyes when treated with ZnO adsorbent .

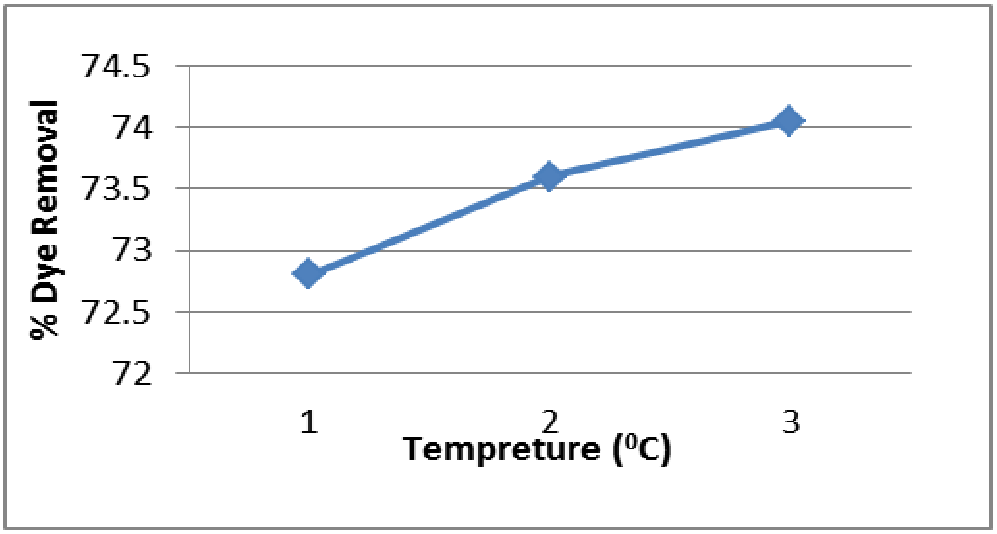


Fig (11): Effect of different temperature on removal of erythrosine pH 4, 25 ºC, agitation rate of 180 rpm and initial dye concentration 8 mg L^{-1} in 150 ml of dye solution.

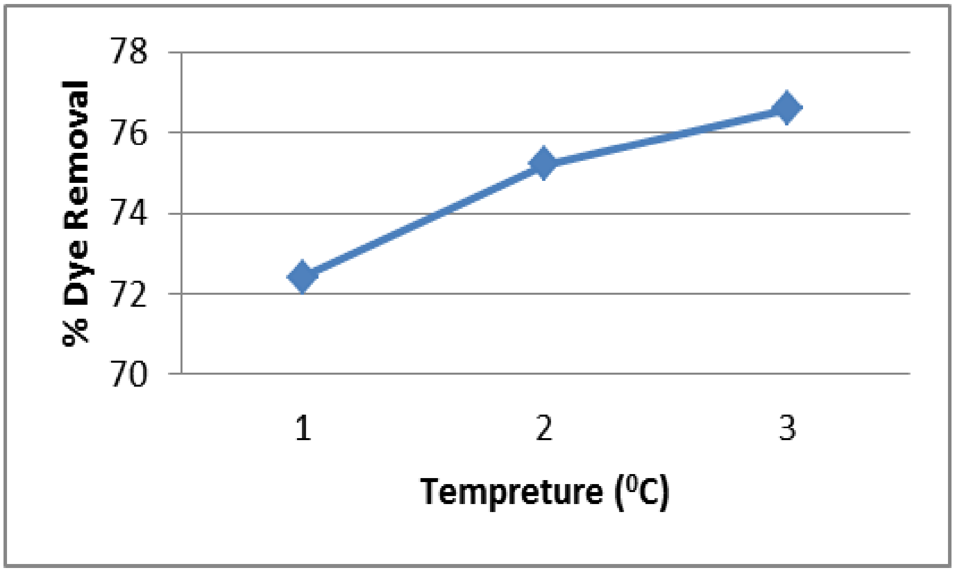


Fig (12): Effect of different temperature on removal of red carmosi pH 4, 25 ºC, agitation rate of 180 rpm and initial dye concentration 8 mg L^{-1} in 150 ml of dye solution.

3.7. Adsorption Isotherm.

The study of isotherm data is important to find out the adsorption capacity of various adsorbents. In order to investigate the adsorption isotherm, two equilibrium isotherms were analyzed: Langmuir and Freundlich isotherms are used for fitting the experimental data in adsorption studies to understand the extent and degree of favorability of adsorption.

3.7.1. Langmuir Isotherm.

Langmuir theory presumes that adsorption is limited to the formation of monolayer coverage of adsorbate on homogeneous adsorbent surface. The linearized Langmuir equation is given below:

$$C_e / q_e = 1/k_a V_m + C_e / V_m$$

Where, q_e is the amount adsorbed per mass of adsorbent (mg/g), C_e is the concentration of the dye solution at equilibrium (mg/L), K and V_m are Langmuir constants. V_m and K_a is Langmuir constants related to the capacity and energy of sorption respectively. The values V_m and k_a shown in table ()were determined from slops and intercepts of the plot of (Fig). The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter RL that is defined by the following equation

$$RL=1/(1+K_aC_o)$$

RL indicates isotherm shape and whether it is favorable or not as per the criteria given below

RL values	Adsorption
RL>1	Unfavorable
RL=1	Linear
0<RL<1	favorable
RL=0	Irreversible

The value of the correlation coefficient $R^2 = 0.9998$ and $R^2 = 0.8474$ for Erythrosine and Red Carmoisine obtained from Langmuir expression indicates that Langmuir expression provided a good linearity [15-20].

3.6.2. Freundlich Isotherm.

The Freundlich model is based on the assumption that multilayer adsorption occurs on a heterogeneous adsorption surface containing unequally available sites of different adsorption energies and is given by the relation

A linear form of the Freundlich expression will yield the constants K and n hence:

$$\log q_e = \log K + 1/n \log C_e$$

Where, q_e is the amount adsorbed per mass of adsorbent (mg/g), C_e is the concentration of the dye solution at equilibrium (mg/L), K_f and 1/n are Freudlich constants related to adsorption capacity and adsorption intensity of the sorbent respectively. The values of K_f and 1/n were calculated from the intercept and slope respectively and are given in table (1). The result shows that the value of n is greater than unity n=2.6075 and n=2.940 indicating that the both dyes are favorably adsorbed on.

This is in great agreement with the findings regarding to RL value[16].

Table 1: Equations and results of isotherms calculations

Isotherm	Parameter	Amount for Erythrosine	Amount for Red carmoisine
Langmuir: $C_e/q_e = (1/K_aV_m) + C_e/V_m$ $C/q=1/bqm+C/qm$	R^2	0.9998	0.8474
	b(L/mg)	1.06054	0.02415
	V_m(mg/g)	1.9546	1.5918
	R_L	0.29149	0.5668
Freundlich: $\ln q_e = \ln K_F + (1/n) \ln C_e$	R^2	0.9812	0.9557
	K_f(mg/g)	43.103	10.162
	n	2.6075	2.940

The higher value of K 43.103 and 10.162 mg/g for Erythrosine and Red Carmoisine indicates that Copper Oxide have greater affinity for dyes compared with other adsorbents. The adsorption intention n is found to 2.6075and 2.940for Erythrosine and Red Carmoisine , it is observed that the ZnO adsorbent satisfy the condition of heterogeneity, i.e., $1<n<10$. From the table *1*, the higher value of b 1.06054 indicates that the amount of erythrosine per unit weight of copper oxide seem to significantly higher than Red carmoisine. However, the correlation coefficient for the Freundlich isotherm is higher than that for Langmuir, suggesting higher probably of multilayer adsorption than monolayer adsorption.

Conclusion

The following conclusion may be drawn from the present investigation. ZnO adsorbent, with the special characteristics such as availability, inexpensiveness and large area, is used for the removal of dyes such as Erythrosine and Red Carmoisine from its aqueous solution. The experimental data were in line with the Freundlich adsorption isotherms. Results show that the adsorbent employed has considerable potential as an adsorbent for the removal of dye.

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