Removal of alizarin red-S from aqueous solution by adsorption on nanocrystalline Cu$_{0.5}$Zn$_{0.5}$Ce$_3$O$_5$

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ABSTRACT

In this work, the nanocrystalline mixed oxide Cu$_{0.5}$Zn$_{0.5}$Ce$_3$O$_5$ synthesized by combustion method. The characteristic studies were performed by XRD, SEM and TEM analysis to investigate particle size of oxide. It was then used as an adsorbent for alizarin red-S from aqueous solutions. The alizarin adsorption capacity of the nanocrystalline oxide was studied with various factors such as temperature, pH of dye solution, initial dye concentration & contact time. The adsorption isotherms were agreed with the Langmuir & Freundlich isotherm models. Freundlich isotherm was well analogous with experimental results. According to the experimental results about 83% alizarin red-S was removed from aqueous solutions at lower temperature.

INTRODUCTION

Pollution of surface and ground water with the industry effluents is a major problem to public health. Synthetic dyes, suspended solids, dissolved chemicals are the main carcinogenic pollutants found in textile and dying effluents [1, 2]. Such pollutants can alter the chemical and physical properties of water. The degradation of some dyes take place to produce toxic and hazards products [3]. In addition the coloured pollutants decrease light penetration & prevent photosynthesis [4]. Alizarin red-S dye is one of them produce ‘red and’ purple coloured solution depending on pH of water. Many conventional methods for the removal of dying effluents from aqueous solutions can be divided into three classes; physical biological and chemical treatments [5,6]. Physical adsorption is considered to be competitive & cost effective and efficient process for the removal of dyes. Moreover activated carbon is the most popular adsorbent and has been used for the adsorption of different chemicals from aqueous solutions. [7- 9]. Alizarin red-S is used in large quantities in dying industries & produces many environment problems. To find an appropriate & cost effective adsorbent is an important consideration for designing a suitable adsorption method to minimize water pollution. The objective of this study was to investigate the possibility of use of nanocrystalline Cu$_{0.5}$Zn$_{0.5}$Ce$_3$O$_5$ as a new adsorbent for the significant
removal of alizarin red-S from aqueous solution. The equilibrium study is investigated to observe the effects of various process parameters such as pH, contact time, initial dye concentration temperature & the sorbent dosage on the adsorption process.

In the present work we have synthesized nanocrystalline mixed oxide Cu$_{0.5}$Zn$_{0.5}$Ce$_3$O$_5$ exhibits excellent adsorption properties and used as adsorbent for the adsorption & removal of alizarin molecules from contaminated water [10].

**MATERIALS AND METHODS**

2.1 Materials:-
Alizarin red S (98%) was purchased from Loba Chem Co. Copper nitrate, Zinc nitrate & cerrick ammonium nitrate and urea were purchased from Merck Chemicals. Deionized water was obtained in the laboratory.

2.2 Preparation and Characterization of adsorbent:-
The nanocrystalline Cu$_{0.5}$Zn$_{0.5}$Ce$_3$O$_5$ oxide as adsorbent used in this study was synthesized by the combustion method was described in detail in our previous work [11-18]. The mixed oxide was then sintered at 600$^\circ$C for about 3 hours. The phase purity and crystalline size of the oxide were determined by powder x-ray diffraction (XRD) using Cu K$_\alpha$ ($\lambda=1.5405\text{Å})$ radiation.

The SEM micrographs were obtained using SEM model JEOL-JSM 6360. The grain size of crystal is 17 nm determined from XRD and SEM information.

2.3 Adsorption experiments.
The influence of contact time on alizarin adsorption on nanocrystalline Cu$_{0.5}$Zn$_{0.5}$Ce$_3$O$_5$ was studied based on the alizarin concentration in the range 10-100 mg/L. The adsorption experiments were carried out by mixing 0.2 gm of oxide samples with 100ml aqueous solution in a 250ml round bottom flask at temperature of 298K. Samples were shaken vigorously. After adsorption experiments, the dye solutions were centrifuged for 15 min. in centrifuge machine at 2000 rpm in order to separate the adsorbent from the solution and dye concentration was then determined. For the optimization of adsorbent dosage, a 15ml alizarin solution was contacted with different quantities of nanocrystalline mixed oxide adsorbent (50-500 mg/L) till equilibrium was attained & it was found to be 200 mg/L.

The adsorption isotherm experiments of alizarin on mixed oxide, as well as effects of PH of alizarin were studied with the help of batch experiments. A desired amount of mixed oxide 200 mg was placed in a 250 ml jar into which 50 ml of alizarin solution with varying concentrations was added. The adsorption experiments were carried in a temperature constant water bath the samples were shaken vigorously for 1 hour at a speed of 200 rpm. The residual concentration of alizarin was not changed with further contact time when the process reached equilibrium. Then after the solutions were centrifuged as explained above and analyzed for the remaining concentration of nanocrystalline mixed oxide adsorbent (50-500 mg/L) till equilibrium was attained & it was found to be 200 mg/L.

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Percentage Removal = $[S_1 - S_2] \times 100 / S_1$  \hspace{1cm} (I)

The adsorption capacity of adsorbent was calculated using the mass balance equation

$$Q_2 = \frac{(S_1 - S_2)}{V/W}$$  \hspace{1cm} (II)
Where, $Q_2$ mg/gm is the equilibrium capacity, $S_1$ and $S_2$ mg/L are the original and equilibrium concentrations of alizarin in solution. And $V$ is the volume of aqueous solution containing alizarin. $W$ gm is the weight of adsorbent. The experiments were carried three times and mean values were considered for calculations.

2.4 Analysis method
The residual dye concentrations in aqueous medium were determined using a uv/visible spectrophotometer corresponding to maximum wavelength 470 nm for alizarin dye. The chemical structure of alizarin red-S is shown in [Fig.1].

![Chemical structure of alizarin red-S](image1)

**RESULTS AND DISCUSSION**

Characterization of nanocrystalline $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Ce}_3\text{O}_5$ oxide powder x-ray diffraction patterns showing $2\theta$, intensity and hkl values of oxide are presented in [Fig.2]. Mixed oxides shows single phase cubic structure & only reacted constituents are present. Particle size calculated using Scherer’s equation was found to be 20 nm.

[Fig.3] showed the morphology of nanocrystalline oxide sample by TEM observations. It indicated that the oxide particles are cubic in shape with almost no amorphous constituents & weakly aggregated. The particle size of the oxide was distributed in the range of 20-60 nm. This was in consistent with the XRD data. The surface area of the $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Ce}_3\text{O}_5$ oxide measured by BET method was calculated to be 16.5 m$^2$/g.

![XRD pattern of nanocrystalline Cu$_{0.5}$Zn$_{0.5}$Ce$_3$O$_5$](image2)
Fig. 3 TEM images of nanocrystalline Cu$_{0.50}$Zn$_{0.50}$Ce$_3$O$_5$

![TEM images](image)

Fig. 3 TEM images of nanocrystalline Cu$_{0.50}$Zn$_{0.50}$Ce$_3$O$_5$

4. **Effect of adsorbent quantity and contact time on alizarin removal.**

The adsorption equilibrium state of alizarin was obtained within 5 min for the initial alizarin concentration of 10, 40 and 70 mg/L respectively. [Fig. 4] showed the influence of contact time on the adsorption of the alizarin on nanocrystalline Cu$_{0.50}$Zn$_{0.50}$Ce$_3$O$_5$ oxide. The average removal efficiency of alizarin dye reached about 83%, 80% and 62% from the initial concentrations of dye were 10, 40 and 70 mg/L respectively. It was observed that after equilibrium state no appreciable change in concentration of dye obtained. The rapid adsorption of dye on nanocrystalline oxide ensured that sufficient time was available for adsorption equilibrium to get at the usual operation condition of the adsorption. It was also found that the initial alizarin concentrations had small effect on the adsorption equilibrium time. The graphical [Fig. 4] showed
that the removal of alizarin dye at equilibrium decreased at higher initial dye concentration. It was confirmed that the limited number of adsorption sites available for the uptake of alizarin molecules at that particular adsorption dosage.

The effect of adsorbent quantities was studied with different adsorbent dosages (50-500 mg/L) and using 50ml dye solution at equilibrium time. Increase in adsorbent quantity enhances the percentage of removed alizarin. The alizarin removal efficiency increased up to 83%. It is evident that the number of available adsorption points increases at high adsorbent quantity & therefore leads to increase in the amount of removed alizarin molecules. In this work the optimized adsorbent dosage was fixed at 200 mg/L for the experiments.

4.1. Adsorption isotherms:-

The mass of adsorbate adsorbed per unit weight of adsorbent and liquid phase equilibrium concentration of adsorbate, generally represented by adsorption isotherms. The adsorption isotherms of alizarin on Cu_{0.5}Zn_{0.5}Ce_{3}O_{5} oxide at temperatures of 287K, 295K and 303K were shown in [Fig.5].

![Fig. 5] Adsorption isotherm of removal of alizarin red-s dye on mixed oxide at various temperatures at acidic pH.

It is observed that the adsorption of alizarin on adsorbent decreased with increased temperature, and it is fallen up to 50% removal at temperature 303K at an initial concentration of 100 mg/L The alizarin removal by adsorption on oxide favored at low temperature. Adsorption equilibrium data have been studied with Langmuir and Freundlich isotherms at different temperatures. The Langmuir [19] theory is valid for monolayer adsorption on a surface having a finite number of identical points & is well known isotherm curves due to its simplicity and its good result with experimental data. The Langmuir isotherm equation is expressed as

\[
\frac{1}{Q_2} = \frac{1}{Q_1} + \frac{1}{Q_1}K_LS_2
\]

Where \(Q_2\) = amount of adsorbed in mg/g at equilibrium \(S_2\) = equilibrium concentration of alizarin in mg/L in solution \(Q_1\) = in mg/g is the maximum monolayer adsorption capacity.
& $K_L$ is the constant in $L/mg$ related to the free energy of adsorption. The Freundlich [20-23] isotherm model is an imperial equation & it is fit for heterogeneous surfaces. It assumes that the adsorption process occurs on heterogeneous surfaces. The Freundlich equation is expressed as

$$lnQ_2 = lnK_F + \frac{1}{n} \ln S_2$$

Where $K_F =$ empirical constant of Freundlich isotherm in $[mg/g (L/mg)^{1/n}]$ & $S_2 =$ as explained above. $n=$ the empirical parameter related to the intensity of adsorption.

[Fig.6a & 6b] showed the plots of Langmuir and Freundlich adsorption isotherms of alizarin on nanocrystalline CuZnCe$_3$O$_5$ at 303 K. The constants of Langmuir and Freundlich isotherms obtained from the intercept & slope values of the plots of each isotherm at temperatures 287K, 295K and 303K. The different parameters showed that, the Freundlich isotherm was more suitable than the Langmuir model. All values of $1/n$ are less than one, indicating that the adsorption of alizarin on mixed oxide is physical process.

[Fig.6 (a)] The Langmuir isotherm plot for alizarin red-s adsorption on mixed oxide

[Fig.6 (b)] The Freundlich isotherm plot for alizarin adsorption on mixed oxide
4.2. Effect on pH on alizarin adsorption

Generally the pH of aqueous solutions affects the adsorbing capacity of the adsorbent. Hence to find out the effect of pH on adsorption capacity of nanocrystalline Cu$_{0.5}$Zn$_{0.5}$Ce$_3$O$_5$ oxide aqueous solutions of alizarin were prepared at different pH values ranging from 3.0 to 11.0 pH. The pH after adsorption was also measured and the results showed that the difference between the before & after experiment values was about 0.3 only. From the above various experimental results clearly showed that there was slight influence of pH values on adsorption capacity of nanocrystalline Cu$_{0.5}$Zn$_{0.5}$Ce$_3$O$_5$ mixed oxide.

CONCLUSION

Mixed oxide Cu$_{0.5}$Zn$_{0.5}$Ce$_3$O$_5$ has been synthesized successfully by combustion method. The average particle size of nanocrystalline mixed oxide determined by the studies of XRD and TEM is 17-23 nm. The experimental results showed that alizarin dye could be adsorbed on nanocrystalline mixed oxide quickly. The adsorption followed both Langmuir and Freundlich isotherms but better results fitted to Freundlich model. The removal of alizarin from aqueous solution appreciably depended on the absorbate concentration and temperature and less depended on the pH of solution. The results showed that adsorption of dye on mixed oxide are physisorption, spontaneous in nature. The adsorption of alizarin on mixed oxide was found to be 83%. The main advantages of nanocrystalline Cu$_{0.5}$Zn$_{0.5}$Ce$_3$O$_5$ oxide are easy preparation method & low cost.

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