Removal of Phenol Dye by CoFe$_2$O$_4$-CdFe$_2$O$_4$ Nanocomposites

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Abstract.
This work includes the study of adsorption of phenol red dye by using spinel Co$_{1-x}$Cd$_x$Fe$_2$O$_4$ was prepare by Co-precipitation method at different ratios of (0.2:0.8, 0.5:0.5, 0.8:0.2) and calcinations at temperature 600 °C for three hours. The conclusion showed that (0.5:0.5) percentage has high activity than other ratio at different temperature. The prepared powder was differentiated by X-ray diffraction, Fourier Transform Technique (FT-IR), UV-Visible Spectroscopy, Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), Atomic Force Microscope (AFM), high performance liquid chromatography (HPLC).

Keywords: Adsorption Photodegradation, Freundlich & Langmuir Equation, Co-precipitation Method, Nanocomposites Co$_{1-x}$Cd$_x$Fe$_2$O$_4$, Phenol red dye.

1. Introduction.

Metal Oxide-based semiconductor photo catalysis is considered as one of the most promising green technologies for environmental remediation due to its potential utilization of solar energy for purification of water and air\textsuperscript{(1,2)}. It is the facile, cheap and non-toxic natural light-induced catalytic method for decontamination of inorganic and organic pollutants from wastewater. The process involves the complete mineralization of the contaminant molecules into carbon dioxide, water and mineral acids. The contaminant molecules reduced through redox reactions and include generation of electron-hole pairs on the surface of a metal oxide photo catalyst by the absorption of photons from a light source and its subsequent loss to an adsorbed molecule. Unlike other methods, this technique does not result the formation of secondary contaminants\textsuperscript{(3)}. Utilization of renewable UV energy and development of efficient visible light-driven photo catalyst has become one of the most significant topics of research recently. A large number of reports are there on the photocatalytic degradation of organic contaminants/dyes under UV light irradiation by using various metal oxide photo catalysts such as: Fe$_2$O$_3$\textsuperscript{(4)} and so on.
However, the photocatalytic efficiency is suppressed by the rapid recombination rate and long migration distance of the photo-generated charge carriers. Therefore, designing and exploring photo catalysts with higher efficiency has attracted recent research efforts in the field of photocatalysis (5). Use of heterogeneous/composite semiconductors can reduce the recombination rate of photo-generated electrons and holes and can be widely employed for improved photocatalytic efficiency. The formation of p-n heterojunctions in hetero nanostructures can separate the photo generated electron–hole pairs. This is mainly because of the inherent establishment of the internal electric field directed from the n-type to p-type semiconductor (6). We emphasize on the development of novel low-cost solar light sensitive photo catalyst with excellent photo-degradation ability and universality for decomposing various organic pollutants. Among all other metal oxides, iron oxides are considered technologically important catalytic materials, sorbents, pigments, flocculants, coatings, gas sensors and ion exchangers. Iron oxide-based catalysts have been found to be good candidates as cheap and efficient catalysts, especially in environmental catalysis (7). Similarly, cobalt oxide (CoO) is a low cost, low toxicity and highly available metal oxide with band gap energy near visible light (8).

2. Materials and Methods

2.1. Chemicals Used

The following chemicals were used for the synthesis of Metal oxide nanostructures and dye adsorption experiments. Fe(NO₃)₃·9H₂O, Co(NO₃)₂, Cd(NO₃)₂, and NaOH.

2.2. Synthesis of Co₁₋ₓCdₓFe₂O₄ Nanocomposite

Co₁₋ₓCdₓFe₂O₄ nanocomposite were synthesized by a simple Co-precipitation method with ratio (X= 0.0, 0.2, 0.5 and 0.8). All the metal nitrates were weighed in desired stoichiometric proportions and dissolved separately in amount of distilled water. After the complete dissolution, the metal nitrates were mixed. Afterward, entire solution was kept with constant stirring at 80 °C on a magnetic stirrer for 1 hour to assure removal of NaNO₃ from the powder. The produced precipitate was washed 10 times with hot deionized water to maintain the pH of the solution to about 7 (9, 10). Due to the continuous evaporation of water, the solution becomes viscous. The sample was put at the ignition temperature of 120 °C to form a fluffy mass. These masses were crushed, and the resultant material was annealed at 600 °C in a muffle furnace for 3 hours.
3. Adsorption isotherm

We have studied the adsorption isotherms to describe the interaction of molecules of adsorbate (dye) with adsorbent surface. The isotherm provides a relationship between the concentration of dye in solution and the amount of dye adsorbed on the adsorbent when both phases are in equilibrium. The analysis of the isotherm data is of great importance by fitting them to different isotherm models to optimize the adsorption system. Several adsorption isotherms models are available, but in the present study, we have followed the most widely used Langmuir and Freundlich isotherm models.

3.1. Langmuir Isotherm.

The Langmuir isotherm model assumes monolayer coverage of adsorbate on a homogeneous adsorbent surface. This model does not consider surface heterogeneity of the sorbent. It assumes that adsorption will take place only at specific site on the adsorbent. The Langmuir equation is given as (11):
$q_e = \frac{K_L q_{\text{max}} C_e}{1+C_e K_L}$

where $K_L$ is the Langmuir constant related to the energy of adsorption, $q_{\text{max}}$ is the maximum adsorption capacity corresponding to complete monolayer coverage (mg g$^{-1}$), which depends upon the number of adsorption sites.

### 3.2. Freundlich isotherm.

The Freundlich isotherm model describes the surface heterogeneity of the sorbent and considers multilayer adsorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. The Freundlich equation is given by

$q_e = K_F C_e^{1/n}$

where $C_e$ is the equilibrium concentration (mg L$^{-1}$), $q_e$ is the amount adsorbed at equilibrium (mg g$^{-1}$) and $K_F$ and $n$ are Freundlich constants, related to the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively.

The adsorption equilibrium data obtained from adsorption of phenol red dye by Co$_{1-x}$Cd$_x$Fe$_2$O$_4$ were non-linearly fitted to the Langmuir and Freundlich isotherms. The parameters and correlation coefficients calculated from the models are listed in (table 1.1). It can be seen that the least-squares correlation coefficient ($R^2$) value of the Langmuir model is significantly higher than that of the Freundlich model for both the cases of adsorbents, indicating that the Langmuir model should better describe the phenol red adsorption on Co$_{1-x}$Cd$_x$Fe$_2$O$_4$. The Langmuir and Freundlich adsorption isotherm plots for removal of phenol red by Co$_{1-x}$Cd$_x$Fe$_2$O$_4$ are given in figure 1.2a and 1.2b, respectively. This result indicates that the adsorption capacities of Co$_{1-x}$Cd$_x$Fe$_2$O$_4$ for adsorption of phenol red are 81.6 % of Cd spinel.

| Adsorbent | Langmuir isotherm model | Freundlich isotherm model |
|-----------|-------------------------|---------------------------|
|           | $q_{\text{max}}$ (mg g$^{-1}$) | $K_L$ (L g$^{-1}$) | $R_L^2$ | $K_F$ | $n$ | $r_F^2$ |
| CoFe$_2$O$_4$ | 147.5 | 0.053 | 0.933 | 26.66 | 2.99 | 0.92 |
| CdFe$_2$O$_4$ | 191 | 0.351 | 0.948 | 70.78 | 3.75 | 0.93 |

Table 1: Langmuir and Freundlich Constants for the Adsorption of Phenol Red.
4. Characterization of Adsorbent

4.1. X-ray diffraction patterns (XRD)

X-ray diffraction (XRD) measurements of the mesoporous materials were carried out using Cu Kα radiation. The characterization of spinel Co1-xCdxF2O4 at ratio 0.5:0.5 by using X-ray diffraction radiation (λ = 1.54 Å) were characterization after treatment in the alike condition of preparing catalyst that calcination at 600 °C for three hours from figure 2.1. Find dissimilar peaks apparent in the figure of the spectrum represent 2θ (17.44) back for spinel material.
4.2. Fourier Transition for Infrared Analysis (FT-IR).

The FTIR patterns of prepared \( \text{Co}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4 \) nanomaterials are presented in Figure 1.5. Peaks at 3700-3300 cm\(^{-1}\) are corresponding to the O–H stretching mode of hydroxyl groups present on the surface due to moisture. A broad band at 1560–1400 cm\(^{-1}\) in each pattern corresponds to \( \text{Co}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4 \) stretching vibrations. Peaks at 600–700 cm\(^{-1}\) corresponds to \( v_1 \) and \( v_2 \) stretching vibrations of metal oxygen bond. The major peaks in the range of 440-690 cm\(^{-1}\) are due to \( \text{Co}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4 \) stretching vibrations.

![Figure 4: FTIR Spectrum for spinel Co\(_{1-x}\)Cd\(_x\)Fe\(_2\)O\(_4\).](image)

4.3. Atomic Force Microscopy (AFM)

Atomic Force Microscope is a technique used to analyze the morphology of surface. AFM is used to characterize the surface of catalyst by determining the force between tip and surface of catalyst.

![Figure 5: AFM 2-D, 3-D images of spinel Co\(_{0.5}\)Cd\(_{0.5}\)Fe\(_2\)O\(_4\).](image)

4.4. Scanning Electron Microscopy (SEM)

Figure 2.4 represent the SEM images of \( \text{Co}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4 \) nanomaterials synthesized by precipitation method. The images suggest the formation of smooth and randomly arranged rod shaped nanomaterials with average diameters around 77-80 nm.

![Figure 2.4: SEM images of Co\(_{1-x}\)Cd\(_x\)Fe\(_2\)O\(_4\).](image)
This technique was used to study the structures of the prepared photocatalysts from the aspect of the morphology of crystals of the semiconductors using the SEM. Microscopy techniques help us to analyze the particle size distribution and the nanocrystalline size distribution. The prepared photocatalysts spinel Co_{0.5}Cd_{0.5}Fe_{2}O_{4}. All the results are showed in Figure (2.4).

**Figure 6: SEM images of Co_{1-x}Cd_{x}Fe_{2}O_{4} Nano-ferrites.**

4.5. *Energy Dispersive Spectroscopy (EDS) of Spinels Co_{1-x}Cd_{x}Fe_{2}O_{4}*

The EDS for coated Fe_{2}O_{4} and from spinel Co_{1-x}Cd_{x}Fe_{2}O_{4} were done. The EDS results are shown in Fig.7 the EDS give the type and weight percent of each element present in the selected point of sample at SEM micrographs. According to the definition of Fe_{2}O_{4}, it consists of Fe and O. Same results were obtained from EDS analysis. We can notice the differences between EDS analysis of coated Fe_{2}O_{4} and CoCdFe_{2}O_{4}.

**Figures.7. EDS images of Co_{1-x}Cd_{x}Fe_{2}O_{4} Nano-ferrites for X=0.0, 0.2, 0.5 and 0.8**

4.6. *HPLC Chromatographic Analysis of Spinels Co_{1-x}Cd_{x}Fe_{2}O_{4}*

Figure7 Shows the HPLC chromatogram for spinel Co_{1-x}Cd_{x}Fe_{2}O_{4} before irradiation 0 min and after 15, 30, 60 min irradiation. Before irradiation the HPLC chromatogram shows the absorbance, peak appeared at retention time of (3.757) min and after irradiation the intensity of this peak is gradually decreased with irradiation time. A new absorbance peaks starts to appear after 15 min and this is located at (3.698) and after 30 min appeared peak R_t= (3.590). After 60 min of irradiation the phenol red peak continues to decrease and becomes R_t= (3.432). These results are in a good agreement with that
obtained for the UV-Visible spectral changers results, and that again proves that the photolytic product is phenol red which in turn is photo mineralized to inorganic species.

Figure 7: HPLC phenol red solution a:0 min, b:15 min, c:30 min, d:60 min for Co$_{1-x}$Cd$_x$Fe$_2$O$_4$.

5. Removal of Phenol Red Dye from Aqueous Media

5.1: Effect of Adsorbent Dose on Removal of Spinel Co$_{1-x}$Cd$_x$Fe$_2$O$_4$

The study of adsorbent dosage provides knowledge of the effectiveness of the adsorbent and also shows the ability of dye to be adsorbed. The effect of adsorbent doses on the adsorption of phenol red dye onto surface was studied at pH=9 using 20 ml of 100 mg/L phenol red dye solution for 30 min contact time. The result obtained is represented in figure 2.5. From the figure, it is observed that, with an increase in adsorption dose from 0.01 to 0.05 g, the percentage of removal of phenol red dye increased up to a maximum value of 99.9%. This may be due to an increase in number of active sites of the adsorbent material with increasing amount of the adsorbent. After that further 94 increase in the amount of the adsorbent, no considerable change in the adsorption was observed. Hence, 0.5 g of each adsorbent was chosen as the optimum amount in future studies.

Figure 8: effect of dose Cd
5.2: Effect of pH on removal of Phenol red

pH is an important parameter for adsorption as it affects both the chemistry of the dye and the adsorbent materials and also plays an important role in the whole adsorption process and for determination of maximum absorption capacity (13). Figure 2.6 shows the influence of the initial solution pH from 2 to 12 on the adsorption of phenol red dye. The pH of the test solutions was adjusted by using HCl and NaOH solutions. 0.5 g of each adsorbent was used in 20 ml of 100 mg/L phenol red dye solution at different pH value with 30 min agitation time. The adsorptive removal percentage of phenol red dye was observed to be increased with increase in pH 2-9. From pH 9-12, there was no significant change in percentage of adsorption was observed. The results may be attributed to the following reasons. At lower pH, for cationic dye (phenol red) the lower adsorption values is probable due the presence of excess H⁺ ions competing with the cationic group on the dye for adsorption site. The increased adsorption at higher pH is mainly due to enhanced 93 association of the cationic dye with surface hydroxyl groups. It is related to the electrostatic force of attraction of the dye with the deprotonated hydroxyl group of adsorbents. Increase in the pH of the solution increases the electrostatic attraction between the positively charges dye and the surface of the adsorbent, which results increase in adsorption of phenol red dye. At high pH, OH⁻ on the surface of the adsorbent favors the adsorption of cationic dye molecules (14) have also reported a similar type of observation for the influence of pH on adsorption of phenol red. Therefore, further studies were carried out with pH 9 of dye solution. Application of higher pH in the wastewater treatment is also an advantage because the following reason. Practically in wastewater treatment, high pH’s also promote the precipitation of the toxic metal ions (if present in the wastewater) as hydroxides. The metal hydroxide precipitates out from the solution and will not interfere with the competing ions of dye molecules. Therefore, the dye molecules can be adsorbed more easily on the adsorbent surface.

![Figure 9: effect of pH Cd](image)

5.3: Effect of initial dye concentration on adsorption.

The effect of initial concentration of phenol red dye on degradation was examined using 100 mL of 5-25 mg/L of phenol red using 0.1 g of CdFe₂O₄-Fe₂O₃ photocatalyst for 120 min
irradiation time. It is observed from figure 2.5.2 that the degradation efficiency was gradually decreased with increase in dye concentration and around 97% degradation was occurred within 120 min for 25 mg/L phenol red dye. The primary factor controlling the degradation of phenol red dye is the formation of hydroxyl radicals on catalyst surface and interaction of such radicals with dye species. With increasing initial concentration, much more dye molecules are adsorbed on catalyst surface, and hence the generation of hydroxyl radicals would be reduced. As a result, the photodegradation efficiency decreased. Again, due to a high concentration of dye a shielding effect for light passing into solution is attained, which reduced the absorption of photons by catalyst, and thus the hydroxyl radicals formed on catalyst surface would decrease (15).

5.4: Effect of Temperature of Spinel

Adsorption process were performed in the same manner as mentioned in the above paragraph at temperature (20, 25, 30, 45, 50) °C to estimate the thermodynamic behavior of adsorption process, this depends if the adsorption decreases with increasing temperature then the process is exothermic and vice versa.
5.5: Effect of recovery of spinel.

Desorption of dyes from adsorbent and re-generation of the adsorbent is an important issue in view of re-usability of the adsorbent. With rising prices of raw materials and wastewater treatment processes, the attractiveness of product recovery processes has increased significantly. The main objective of the regeneration process is to restore the adsorption capacity of exhausted adsorbent and to recover valuable components present in the adsorbed phase. Desorption study was performed by mixing (0.15 Co and 0.1 Cd) g phenol red loaded CoCdFe₂O₄ (Fe: Cd = 0.5: 0.5) nanocomposite with 100 ml of phenol red solution and desorption was carried out for 1 hours.

Then the concentration of eluted phenol red was measured to calculate the amount of phenol red desorbed. For regeneration studies, successive adsorption–desorption processes were carried out for three consecutive cycles which is shown in figure 2.6. The figure shows that about 99 and 91 % phenol red effectively removed on the first cycle and the second cycle, respectively. After that, the removal capacity of the adsorbent decreases as the number of cycles increases.

Conclusion.

We have synthesized CoFe₂O₄-Fe₂O₃ composite nanostructures by precipitation and reflux methods and CdFe₂O₄ nanostructure by Co-precipitation method. XRD suggests the well crystalline nature of the nanomaterials with appropriate phase. FESEM images suggest that the CoFe₂O₄-Fe₂O₃ nanocomposites prepared by precipitation method contains very smooth nanoparticles with average diameters around 20-40 nm. However, the CoFe₂O₄-Fe₂O₃ nanocomposite prepared by reflux method contains both uniform microspheres and flower-like hierarchical nanostructures. The CdFe₂O₄ nanomaterials synthesized by hydrothermal method contains irregular shaped nanoparticles with diameter around 60-100 nm. These prepared nanomaterials were used as photo catalysts for degradation of Methylene blue under solar light irradiation. It was observed that the CoFe₂O₄-Fe₂O₃ nanocomposites prepared by precipitation method shows enhanced photocatalytic activity compared to the other prepared photo catalysts.

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