

Antibacterial applications and Comparative Study for Adsorption Phenol Red Dye Using Spinel $\text{Co}_{1-x}\text{M}_x\text{Fe}_2\text{O}_4$ Nano Composites (M= Cd, Ag)

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Abstract

This work concerned with the study of adsorption of phenol red dye by using spinel $\text{Co}_{1-x}\text{M}_x\text{Fe}_2\text{O}_4$ was prepared by Co-precipitation method at different ratios of (0.2:0.8, 0.5:0.5, 0.8:0.2) and calcinations at temperature $600\text{ }^\circ\text{C}$ 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) were also studied for all spinel. X-ray and Electron Microscopy studies showed the average size of the granules prepared for the composite in this manner (17.44 for Cd and 37.55 for Ag).

Keywords: Adsorption, Freundlich & Langmuir Equation, photocatalytic degradation, Co-precipitation method, nanocomposites $\text{Co}_{1-x}\text{M}_x\text{Fe}_2\text{O}_4$, phenol red dye.

Introduction

The expanding enthusiasm for nanotechnology is expected to the nanostructured material with measurements for example grain estimate, layer thickness or shapes beneath 100 nm ¹. The bizarre properties of nanomaterials are explicit to the Nano-measurements. Nanomaterials are the materials having something like one measurement under². In the previous two decades, overall endeavors in both the hypothesis and the exploratory examination of development, portrayal and utilizations of inorganic nanostructures including metal oxides, earthenware production and composites have brought about a develop, multidisciplinary field. Nanostructured materials are noted for their security, green science and find assorted specialized application³. Late research concentrated on the utilization of nanomaterials to tackle natural issues and to clean the earth for what's to come. Nano-sized materials are new useful materials, which offer high explicit surface region to volume proportion and surface-dynamic locales, accordingly, can be utilized as compelling adsorbents. Besides, nanomaterials have been utilized in different natural applications, for example, in green

science, photograph synergist debasement of natural color, remediation of dirtied water, toxin detecting and discovery, antibacterial action, etc. The got nanomaterials and their composites have been utilized in natural applications, for example, adsorption investigations of poisonous metal particles, expulsion of natural color from fluid arrangement and antibacterial applications. In this investigation, we have concentrated on iron oxide and Cd and Ag nanomaterials and furthermore about iron oxide-cadmium and silver blended nanocomposite. Cadmium or silver and iron oxide are the most vital clay materials. Compact disc and Ag demonstrates countless substance and physical properties. It is broadly utilized as an electrical protector, displaying extraordinarily high protection from substance specialists, just as giving superb execution as an impetus for some compound responses, in microelectronics, layer applications, and wastewater treatment. In addition, press oxide assumes an essential job in natural and organic procedures and is additionally broadly utilized in various mechanical applications.

Experimental part.

Preparation of solution.

Chemical materials used in this work were prepared by the Co-precipitation method with ratio (X= 0.0, 0.2, 0.5 and 0.8). During the synthesis, Fe(NO₃)₃·9H₂O, Co(NO₃)₂, Cd(NO₃)₂, Ag(NO₃)₂ and NaOH were used as the oxidizing agent. 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 together. Afterward, entire solution was kept with constant stirring at 80 C⁰ on a magnetic stirrer for 1 hour to assure removal of NaNO₃ from the powder⁴.

The produced precipitate was washed 10 times with hot deionized water to maintain the PH of the solution to about 7 (4-5). Due to the continuous evaporation of water, the solution becomes viscous. The sample was put at the ignition temperature of 120 C⁰ to form a fluffy mass. These masses were crushed and the resultant material was annealed at 600 C⁰ in a muffle furnace for 3 h For the pellet formation.

Adsorption studies.

To decide equilibrium relationship of sum adsorbed by a unit load of adsorbent (q_e) with the grouping of adsorbent staying in the medium at balance (C_e), investigations of different adsorption isotherm models is required, which can enhance the plan of a sorption framework. There is different sort of adsorption models grew, for example, Freundlich, Langmuir isothermal models, etc⁶. The most widely recognized models, for example, Freundlich and Langmuir conditions are utilized to examination of this investigation. The underlying color focuses were differed from 5 to 70 mg/L utilizing (0.15 Cd and 0.1 Ag) g of every adsorbent in 100 ml of phenol red arrangement (normal pH) with fomentation time 60 min.

Adsorption Isotherms.

Adsorption tests were led utilizing 50 ml stoppered conical flasks at room temperature 25 C⁰. (0.15 Cd and 0.1 Ag) mg of adsorbent was added to every flagon which comprised of 10ml phenol red arrangement of different beginning focuses from color. All flagons were shaken at 6000rpm in a thermostated shaker for (120min). After decantation and filtration, the color focus was broke

down by utilizing UV-obvious spectrophotometer the measure of color adsorbed was determined from the accompanying condition.

Langmuir Isotherm.

The Langmuir isotherm show expect monolayer inclusion of adsorbate on a homogeneous adsorbent surface. This model does not think about surface heterogeneity of the sorbent. It accept adsorption will happen just at specific site on the adsorbent⁷⁻⁸The Langmuir condition is given as:

$$\frac{q_e a_L}{K_L} = \frac{K_L C_e}{(1 + K_L C_e)}$$

The linear form of the Langmuir isotherm is:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + C_e / q_{max}$$

where a_L (Lmg⁻¹) and K_L (Lg⁻¹) are the Langmuir constants, q_{max}(=K_L/a_L) is the most extreme adsorption limit comparing to finish monolayer inclusion (mg g⁻¹), which relies on the quantity of adsorption locales⁹. The values of q_{max} and K_L are calculated from the slopes and intercepts of the straight lines of plot of C_e/q_e versus C_e.

Freundlich isotherm.

The Freundlich isotherm demonstrate is an observational condition that depicts the surface heterogeneity of the sorbent. It considers multilayer adsorption with a heterogeneous enthusiastic circulation of dynamic destinations, joined by communications between adsorbed atoms¹⁰. The Freundlich isotherm equation is given as¹¹:

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

The linear form of the Freundlich isotherm is:

$$\ln q_e = \ln K_F + 1/n \ln C_e$$

where C_e is the balance fixation (mg L⁻¹), q_e is the sum adsorbed at harmony (mg g⁻¹) and K_F and n are Freundlich constants, identified with the degree of

the adsorption and the level of nonlinearity between arrangement focus and adsorption, separately. KF and (1/n) can be resolved from the direct plot of ln qe versus ln Ce.

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter (RL) that is defined by the following equation^(7, 12-13):

$$R_L = \frac{1}{1 + a_L C_0}$$

where aL and C0 are the parameters as characterized beforehand. The estimation of RL determined from the above articulation. The idea of the adsorption procedure to be either ominous (RL > 1), direct (RL = 1), great (0 < RL < 1) or irreversible (RL = 0) (Lian et al., 2009). Here RL values acquired are recorded in table 3.2. The direct Langmuir and Freundlich plots for the adsorption of CR onto the three nanorod adsorbents are gotten by plotting Ce/qe versus Ce and ln qe versus ln Ce, separately (given in figure 3.8). The isotherm constants and connection coefficients were determined and recorded in table 3.2. By looking at the connection coefficients rL 2, it tends to be found that the exploratory harmony adsorption information are all around depicted by both the Langmuir and Freundlich models, however the Langmuir show is progressively appropriate.

Table 1. Adsorption isotherm constants for adsorption of phenol red dye in 25 0C Temp.

	Adsorbent	Qm	KL	R2
Langmuir	Co0.5Cd0.5Fe2O4	4.4207	0.174	0.9659
	Co0.5Ag0.5Fe2O4	4.9008	0.557	0.8817
Freundlich	Adsorbent	Kf	n	R2
	Co0.5Cd0.5Fe2O4	0.186	1.333	0.9969
	Co0.5Ag0.5Fe2O4	0.016	0.557	0.9292

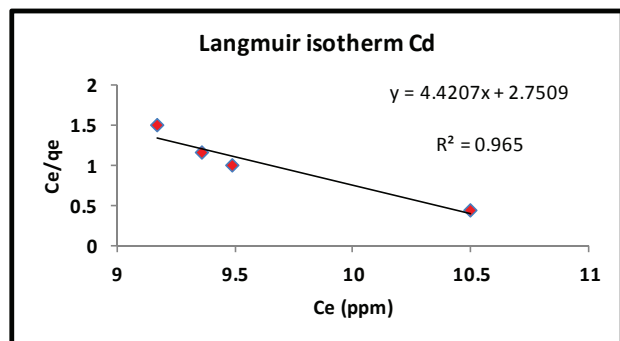


Fig 1. Langmuir isotherm for adsorption of Cd²⁺

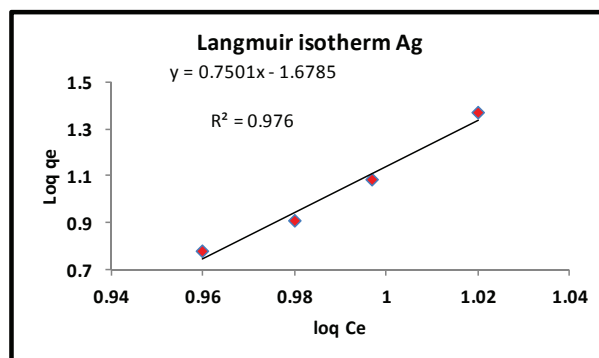


Fig 2. Freundlich isotherm for adsorption of Cd²⁺

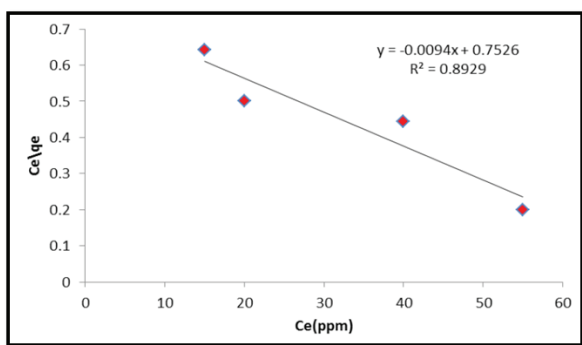


Fig 3. Langmuir isotherm for adsorption of Ag²⁺

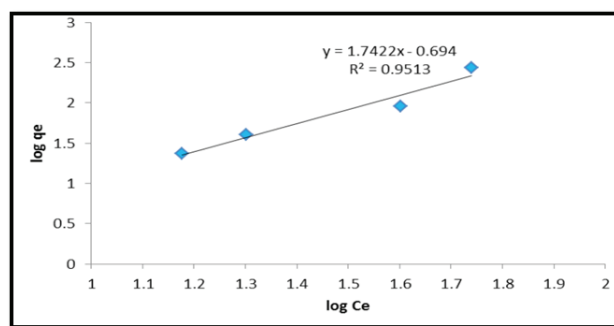


Fig 4. Freundlich isotherm for adsorption of Ag²⁺

Result and Discussion

X-ray diffraction patterns.

Solid semiconductor at crystalline state was studied by using XRD technique. In this work, X – Ray diffraction was used to study Co_{1-x}M_xFe₂O₄Table 3.2 illustrations the spinel of Co_{1-x}Cd_xFe₂O₄; the best from spinel Co_{1-x}Ag_xFe₂O₄ in photocatalytic degradation. The characterization of spinel Co_{1-x}M_xFe₂O₄at ratio 0.5:0.5 by using x-ray diffraction radiation ($\lambda = 1.54 \text{ \AA}$) were characterization after treatment in the alike condition of preparing catalyst that calcination at 600 °C for four hours from fig. 3.1. Find dissimilar peaks apparent in the figure of the spectrum represent 2θ (17.44) back for spinel material.

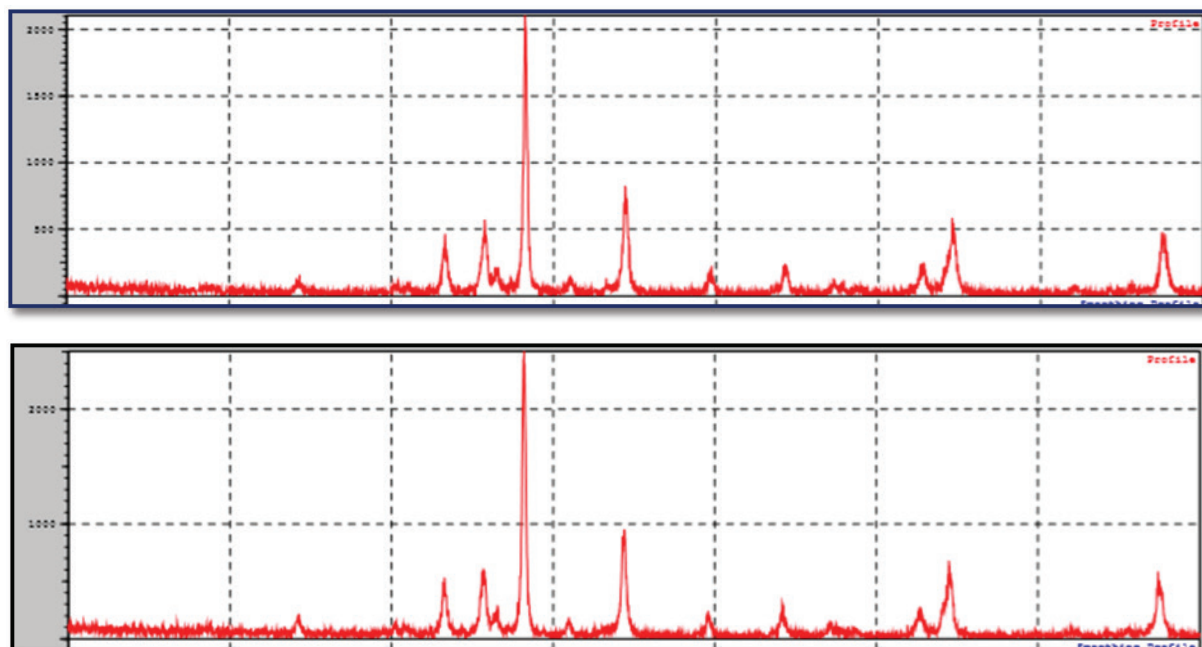


Fig 5. X-ray diffraction spectrum of spinel.

Fourier Transition for Infrared spectrum (FT-IR).

A study of the double prepared catalyst was achieved by using Fourier Transform Infrared (FTIR).

All spectra were recorded at the wavenumber ranged from 400-4000 cm⁻¹. Fig. 3.2. is characteristic of the sample Co_{1-x}M_xFe₂O₄that appearance the peaks at (1506.46–1651.12) cm⁻¹ and (412.78 – 667.39) cm⁻¹, respectively. In the range of 800 – 400 cm⁻¹, two main

absorption bands with very low intensity are observed around 412.78 and 667.39 cm^{-1} and may be caused by metal oxygen vibration in the octahedral side.

2.4.3. Atomic Force Microscopy.

Atomic Force Microscope (AFM) 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.

Fig.7 AFM 2-D, 3-D images of a:Co_{0.5}Cd_{0.5}Fe₂O₄, b:Co_{0.5}Ag_{0.5}Fe₂O₄.

Scanning Electron Microscopy

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}M_{0.5}Fe₂O₄.

Factors influencing Adsorption process.

Effect of adsorbent dose.

Adsorbent measurements is a standout amongst the most vital parameter that has been considered to decide the ideal condition for the execution of adsorption. Basically, insufficient measurement or overdosing would result in the poor execution in adsorption. Accordingly, it is significant to decide the ideal measurements so as to limit the dosing cost and slime development and furthermore to acquire the ideal execution in treatment. The impact of adsorbent portions on the expulsion of phenol red utilizing Co_{0.5}Cd_{0.5}Fe₂O₄ and Co_{0.5}Ag_{0.5}Fe₂O₄ was performed by blending the examples of various load to 100 ml of phenol red color, looking after pH=7 (pH at ordinary condition) for 60 min contact time.

The heaviness of the adsorbents was shifted in the range 0.01-0.3 g. demonstrates the UV-vis retention spectra of phenol red arrangements in the wake of being treated with various doses of the readied spinel adsorbents utilizing an underlying color convergence of 100 mg L⁻¹. It is seen there is a ceaseless expulsion of phenol red with increment in adsorbent portion up to (0.15 for Cd and 0.1 for Ag) g.

This may be due to an increase in number of active sites of the adsorbent material with increasing amount of the adsorbent. Further increase in the amount of the adsorbent does not bring any considerable change in the adsorption i.e. approximately straight line is obtained. Therefore (0.15 Cd and 0.1 Ag) g was chosen as the optimum amount for all studies of the adsorbents.

Effect of pH of phenol red solution.

Impact of pH of phenol red arrangement pH influences both watery science and surface restricting locales of the adsorbents. To examine the impact of pH on the adsorption of phenol red color the pH extend 3– 11 was picked. The pH of the test arrangements was balanced by utilizing HCl and NaOH arrangements. (0.15 Cd or 0.1 Ag) g of every adsorbent utilized in 100 ml of phenol red arrangement of every pH esteem with 60 min disturbance time. From figure 3. it is discovered that, for Co_{0.5}M_{0.5}Fe₂O₄, there is no huge change in the rate adsorption by expanding pH from 3-9 and achieved most extreme at pH = 9 and after that marginally diminished at higher pH. This is expected to for higher pH arrangement; the high adversely charged adsorbent surface locales did not support the adsorption of deprotonated CR because of electrostatic repugnance ¹².

Effect of initial dye concentration on adsorption.

The underlying focus gives essential data that defeats the mass exchange opposition of all atoms between the watery and strong phases¹⁴. The adsorption is incredibly influenced by the centralization of the arrangement, as the adsorptive responses are specifically relative to the convergence of the solute⁶. In this segment, (0.15 Cd and 0.1 Ag) g of every adsorbent utilized every 100 ml of phenol red arrangement (common pH) with fixation going from 5ppm to 70ppm and the unsettling time was kept 60 min. It is discovered that with the expansion in beginning color fixation, rate adsorption diminishes while the harmony adsorption limit of the adsorbent for phenol red increments with expanding starting color focus for example the more focused the color arrangement, the higher the adsorption limit. This is most likely because of a high main impetus for mass move in high color focus.

D) Effect of temperature of spinel.

Adsorption process were performed in indistinguishable way from referenced in the above passage at temperature (20, 25, 30, 45, 50) C0 to appraise the thermodynamic conduct of adsorption process, this depends in the event that the adsorption diminishes with expanding temperature, the procedure is exothermic and the other way around.

A) Effect of recovery of spinel.

Desorption of colors from adsorbent and re-age of the adsorbent is a critical issue in perspective of re-use of the adsorbent. With rising costs of crude materials and wastewater treatment forms, the appeal of item recuperation forms has expanded essentially. The fundamental target of the recovery procedure is to reestablish the adsorption limit of depleted adsorbent and to recoup profitable parts present in the adsorbed stage. Desorption think about was performed by blending (0.15 Cd and 0.1 Ag) g phenol red stacked CoMFe₂O₄(Fe: Cd or Ag = 0.5: 0.5) nanocomposite with 100 ml of phenol red arrangement and desorption was completed for 1 hours. At that point the centralization of eluted phenol red was estimated to figure the measure of phenol red desorbed. For recovery considers, progressive adsorption– desorption forms were done for three back to back cycle. The figure demonstrates that about 84.2% of Cd and 75.2% of Ag phenol red viably expelled on the primary cycle. From that point forward, the expulsion limit of the adsorbent reductions as the quantity of cycles increases 15.

Conclusion

The primary object of the present work is to investigate the likelihood of utilizing spinel Co_{1-x}M_xFe₂O₄ as adsorbents. The procedure is unconstrained and exothermic the impact of different working parameters, for example, pH, adsorbent dose and temperature was assessed. The thermodynamic capacities are exceptionally valuable if the present outcomes are to be used on huge scale.

Financial Disclosure: There is no financial disclosure.

Conflict of Interest: None to declare.

Ethical Clearance: All experimental protocols were approved under the Babylon Education Directorate, Ministry of Education, Hilla-Iraq and all experiments were carried out in accordance with approved guidelines.

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