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Sustainable Textile Dyes Pollution Control with Metal Doped Iron Oxide Nanoparticles

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ABSTRACT:
The discharge of dyes in aquatic system presents significant environmental and public health problems. This study examines the potential of gadolinium doped iron oxide nanoparticles (Gd-Fe_3O_4) as a sustainable adsorbent for dye removal from contaminated water. Gd-Fe_3O_4 nanoparticles were synthesized using a cost-effective co-precipitation method. The doping of gadolinium improved the surface properties of Fe_3O_4, making it more suitable for the adsorption removal of dyes from wastewater. The characterization of synthesized Nano particles was done using XRD, TEM techniques. The adsorption and removal efficiency of dyes on Gd-Fe_3O_4 were optimized by examining various parameters, including dye and adsorbent dosage, temperature, and pH using batch adsorption experiments. The results showed that increasing the dosage of Gd-Fe_3O_4 enhanced removal efficiency, with optimal performance observed at low pH levels. Langmuir and Freundlich adsorption isotherms were utilized to understand adsorption mechanism and removal capacity of Gd-Fe_3O_4 for the two textile dyes alizarin yellow (AY) and acid orange 10 (AO10). The findings demonstrate that Gd-Fe_3O_4 is highly effective in adsorbing dyes, making it a promising and sustainable option for mitigating dye pollution in aquatic environments.

1. Introduction

Water pollution from industrial dyes is a critical environmental issue, posing risks to ecosystems and public health due to the toxicity and persistence of these contaminants. Approximately 7,00,000 tons of synthetic dyes are produced each year for the global textile industry, with about 10 – 20 % of these dyes being released into the environment as wastewater after the dyeing and processing stages [1,2]. It is anticipated that dye production will rise in parallel with the projected growth in textile fibre production. Dyes are used extensively in various aspects of daily life, including clothing, cosmetics, paper and food processes [3, 4, 5]. They are inherently mutagenic and carcinogenic, which leads to severe health problems such as kidney dysfunction, liver complications, and central nervous system damage [6, 7, 8]. It is utmost important to remove these impurities from water. Historically, various methods have been employed to remove dyes from wastewater, including chemical, physical, and biological approaches [9, 10, 11 12, 13]. Among these, adsorption is considered to be practical and cost-effective technique for treating industrial wastewater. Common adsorbents used for this purpose include agricultural solid waste, fly ash activated carbon, zeolite, functionalized graphene, magnetic Nanoparticles. [14, 15, 16, 17, 18, 19, 20]. Iron oxide nanoparticles such as Fe_3O_4, Fe_2O_3, zero valent ions are commonly used adsorbents for removal of metal ions, dyes and other pollutants from waste water. [21, 22, 23]. The problem associated with iron oxide Nano panicles are reduced surface area due to clumping of particles and leaching of adsorbent in acidic medium. In this study we have tried to improve these limitations by doping the iron oxide with gadolinium and used it as

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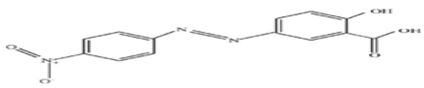
adsorbent to remove the anionic dyes from wastewater. Two dyes alizarin yellow (AY) and acid orange 10 (AO10), were used to study the removal of dyes. Table 1 exhibits the chemical structures of the under investigated dyes. The influence of initial concentration, temperature, and pH on the removal of dyes was also examined. Two models for the equilibrium data, the Langmuir and Freundlich isotherm equations, were employed.

Table 1. Chemical structure and Colour Index Number of Anion dyes Alizarin Yellow and Acid orange 10

Dye Name	Chemic
Alizarin Yellow (CI 14025)	 Alizarine Yellow
Acid Orange 10 (CI 16230)	

2. Experimentals

2.1. Reagents

All the chemicals used in the studies were of analytical grade purity and used without further purification. $Fe(NO_3)_3 .9H_2O$ (99%, pure) and $Gd(NO_3)_3.6\ H_2O$ (99%, pure) and were purchased from Sigma-Aldrich. Alizarin Yellow (AY) and Acid orange 10 (AO 10) were obtained from SD Fine Chemicals.

2.2. Synthesis of adsorbent

Gadolinium doped Fe_3O_4 nanoparticles were prepared via the co precipitation method. 25 ml of 0.2M Ferrous sulphate hepta hydrate ($FeSO_4.7H_2O$, 98% pure) is mixed with 25 ml of 0.1M Ferric nitrate nona hydrate ($Fe\ (NO_3)_3.9\ H_2O$, 98% pure) the mixture added. To this mixture 50 ml of 0.04 M gadolinium nitrate hexa hydrate ($Gd\ (NO_3)_3.6\ H_2O$, 98% pure) is added with constant stirring for 30 minutes. Then 25 % NaOH solution is added dropwise till the pH of solution is 11 under constant stirring for 2 hours in nitrogen environment. The precipitate obtained was washed several times with deionized water and dried at 500^0C in muffle furnace for 5 hours and stored and utilized as adsorbent.

2.3. Adsorption Study

A batch adsorption procedure was conducted to evaluate the effects of initial adsorbent dose, dye concentration, pH, temperature, and contact time. In this experiment, 0.02 g of adsorbent was mixed with 25 ml of dye solution in an Erlenmeyer flask at room temperature. To investigate the influence of each parameter, one parameter was varied while keeping the others constant at their optimal conditions: pH, agitation speed of 150 rpm, contact time of 120 minutes, and dye concentration of 150 mg/L. After adsorption, the solutions were centrifuged, and the absorbance of the supernatant was measured at the maximum wavelength (λmax) to determine the dye content. The amount of dye adsorbed (q) was calculated using a mass balance equation.

$q = (C_0 - Ce)\ v/m$

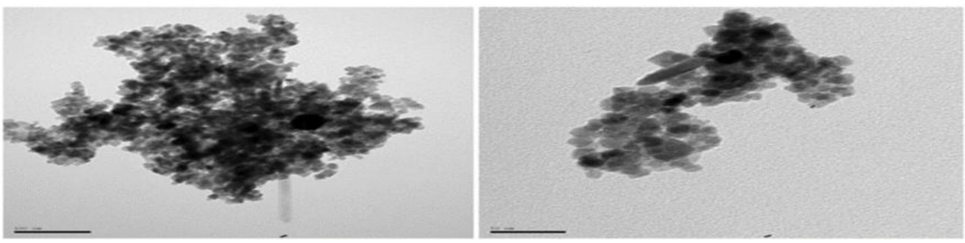


Figure 1. TEM micrograph of Gd-doped Fe_3O_4 nanoparticles

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$$\% \text{ Removal efficiency} = \frac{C_0 - Ce}{C_0} \times 100$$

Where C_0 and Ce is the initial and equilibrium concentration of dye in the solution respectively (mg/L), V is the volume of solution (L), m (g) is the mass of adsorbent used.

2.4 Characterization methods

X-ray diffraction was used to determine the crystalline structure and size of the nanoparticles. The XRD study was performed at IIT Bombay, SAIF facilities using Cu X ray tube with fixed anode. TEM (Tunnelling Electron Microscopy) was used to analyse surface characteristics of synthesized Gd-Fe_3O_4. HR-TEM 300 kV JEOL JEM 2100F at IIT Bombay, SAIF facilities was used to analyse the surface characteristics of synthesized nanoparticle. The zeta potential study of synthesized Gd-Fe_3O_4 were carried out

3. Results and Discussions:

3.1 Morphological and structural properties of Gd doped Fe_3O_4:

Various techniques are employed to characterize the Gd-doped Fe_3O_4 nanoparticles post-synthesis. The surface characterization of the Gd-doped Fe_3O_4 nanoparticles is done using TEM. Figure 1 shows a representative TEM image of the synthesized gadolinium-doped Fe_3O_4 nanoparticles with 50 nm scale bar. The TEM analysis revealed that the nanoparticles exhibit a spherical to nearly spherical morphology with a tendency to form aggregates this aggregation is due to magnetic interaction due to Fe_3O_4 materials. The particle size was determined to be in the range of 10 to 30 nm, which is consistent with the expected dimensions for nanoparticles synthesized using the co-precipitation method.

Figure 2 shows the powder X-ray diffraction patterns for the as-synthesized Gd-doped Fe_3O_4 nanoparticles. The XRD pattern reveals peaks at approximately 2θ values of 30.3°, 34.5°, 44.4°, 54.4°, 56.5°, and 63.5°, corresponding to the (220), (311), (400), (422), (511), and (440) planes, respectively. These peaks align well with the literature [24, 25]. The doping of gadolinium does not distort the observed 'd' values and peak intensities correspond to the crystalline spinel form of Fe_3O_4 nanoparticles (JCPDS Card No. 01-0629).

3.2 Adsorption studies on Gd doped Fe_3O_4

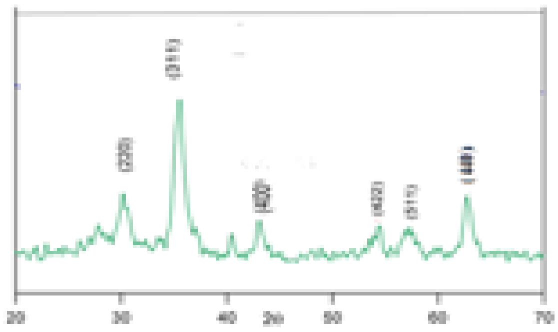

Figure 2. XRD of Gd-doped Fe3O4 nanoparticles

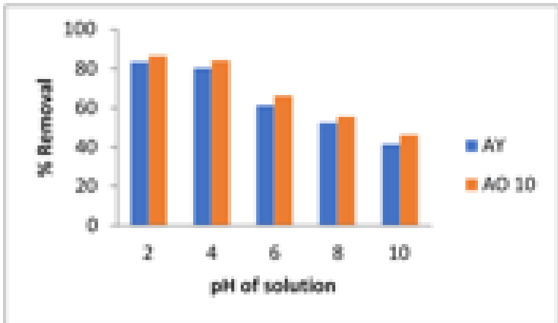

Figure 3. Effect of PH on % removal of dyes

The dyes from the polluted water were removed using Gd doped Fe_3O_4 as an adsorbent. This removal of dyes is based on three major effects.

3.2.1 Effect of pH

The pH of the solution is an important factor that affects the surface charge of adsorbent and ionization of dyes molecules. For carrying out the study to understand the effect of on removal of dyes 25 ml of 150 ppm of dye solution was equilibrated with 0.02 g of Gd doped Fe_3O_4 and pH of solution was varied from 2 to 10. Figure 3 shows the removal efficiency of dyes at various pH of the dyes solution. It can be seen that removal efficiency of AY and AO10 was maximum in acidic and then it falls gradually from pH 6 to pH 10. The point of zero charge for Gd doped Fe_3O_4 was found to be around 6.8 which were in agreement with previous reported work. Maximum removal in acidic condition can be explained by strong electrostatic attraction between positively charge adsorbent and negatively charge dyes molecule [24, 26]. The decrease in removal

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efficiency at higher pH is attributed to negative surface charge on Gd- Fe_3O_4.

3.3.2 Effect of Contact Time and amount of adsorbent

The study focused on assessing the influence of adsorbent quantity and contact time on the efficiency of dye removal. By adjusting the adsorbent concentrations at a solution pH of 4 and maintaining a temperature of 25°C, with an initial dye concentration of 150 ppm (as shown in Figure 4a), it was observed that increasing the adsorbent dose improved the dye removal efficiency due to the enhanced surface of adsorbent available for adsorption. Notably, the adsorption process reached its maximum efficiency at 0.02 g of adsorbent; further increases in adsorbent quantity did not significantly enhance dye removal, suggesting a saturation point where additional adsorbent no longer contributes to higher efficiency.

Moreover, the effect of contact time, depicted in Figure 4b, revealed that optimal dye removal was achieved within 90 minutes. Beyond this duration, no further increase in removal efficiency was observed. In fact, exceeding this threshold led to a decline in effectiveness due to the high mixing rate, which facilitated desorption and reduced the dye removal efficiency [27, 28]. This study introduces a nuanced understanding of the limits of adsorbent dosage and contact time, highlighting the importance of optimizing these parameters to maximize dye removal efficiency in nanoparticle-based adsorption processes.

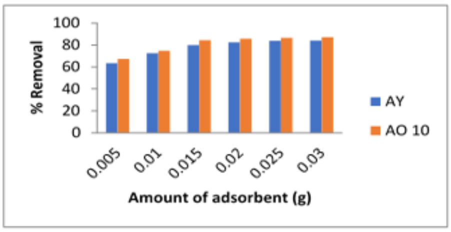

Figure 4 b Effect of amount of adsorbent

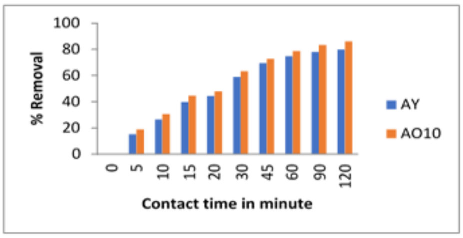

Figure 4 b. Effect of contact time on % Removal of dyes

3.3.3 Adsorption isotherms

Freundlich and Langmuir models were used to determine the adsorption efficiency, and to describe adsorption behaviour. The Langmuir isotherm model assumes that adsorption occurs as a monolayer on homogeneous surfaces, where each adsorption site is identical and has an equal affinity for the adsorbate. In contrast, the Freundlich isotherm is an empirical model that accounts for adsorption on heterogeneous surfaces, where adsorption sites have varying affinities for the adsorbate. The comparative linear forms of these two isotherms provide insights into the nature of the adsorption process and help in understanding the underlying mechanisms. This study introduces a novel approach by analysing the adsorption behaviour

using both models, offering a comprehensive evaluation of the adsorption process on nanoparticle surfaces. The linear representations of the isotherms are as follows:

Langmuir adsorption isotherm: Ce/Qe = Ce/Qmax +1/KL Qmax ------ (3)

Freundlich adsorption isotherm: InQe =In KF + 1/n InCe -------- (4)

Where Ce is the concentration of the dyes, Qe is the adsorption capacity, KL is the Langmuir constant, Qmax is the maximum adsorption capacity per unit mass of the adsorbent, Freundlich constant KF represents the adsorption capacity and 1/n, n represents the adsorption strength

The linear forms of the Langmuir and Freundlich isotherms were plotted, with the variables Ce and qe shown in Figure 5. The parameters for the Langmuir and Freundlich isotherms determined and summarized in Table 2. The maximum adsorption capacity (Qmax) determined by the Langmuir model is 102.04 mg/g and 117.45 for alizarin yellow and acid orange 10 respectively. However, the findings suggest that the Langmuir isotherm does not adequately describe the adsorption behaviour of alizarin yellow. The R^2 values for the Langmuir and Freundlich models for alizarin yellow were 0.9783 and 0.9932, respectively, indicating that the Freundlich isotherm provides a better fit for alizarin yellow adsorption on Gd- Fe_3O_4.

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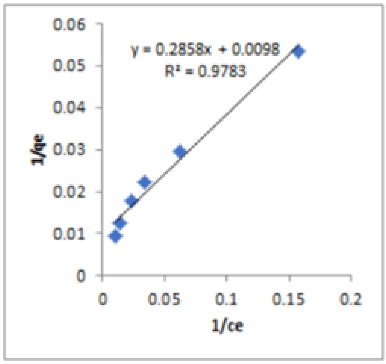

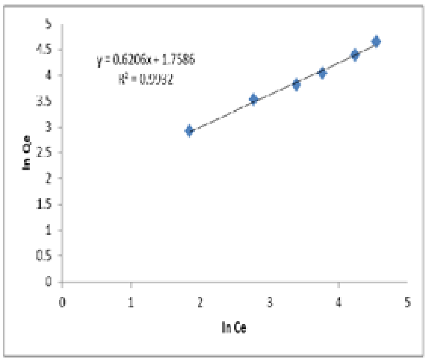

Figure 5. a Langmuir adsorption isotherm **Figure 5 b** Freundlich adsorption isotherm

For Alizarin Yellow on Gd-Fe_3O_4

Table 2. Langmuir and Freundlich adsorption isotherm constant

Langmuir Adsorption Constant	Alizarine Yellow	Acid Orange 10	Freundlich Adsorption Constant	Alizarine Yellow	Acid Orange 10
Q max	102.04	117.45	K_F	5.80	7.45
K_L	0.0342	0.0456	1/n	0.6206	0.74350
R^2	0.9783	0.9567	R^2	0.9932	0.9785

6. **Conclusion**

In this study, a novel gadolinium-doped Fe_3O_4 adsorbent was synthesized using an eco-friendly and cost-effective method, showing promise for large-scale production. The removal of harmful textile dyes from contaminated water using Gd-doped Fe_3O_4 nanoparticles demonstrates significant potential in dye clean-up processes. The dye removal efficiency was optimized by adjusting parameters such as pH, contact time, and the dosages of both adsorbent and adsorbate. The results indicated that the Gd-doped Fe_3O_4 nanoparticles are highly effective in dye removal. The adsorption capacity of gadolinium-doped Fe_3O_4 for alizarine yellow (AY) was determined to be 102.04 mg/g. The adsorption of AY dye on the doped Fe_3O_4 followed the Freundlich isotherm model, with an R^2 value of 0.9992, suggesting that this adsorbent is highly effective for removing the dyes from wastewater.

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