Saima Noreen, Safa Ismail, Sobhy M. Ibrahim, Heri S. Kusuma, Arif Nazir, Muhammad Yaseen, Muhammad I. Khan and Munawar Iqbal*

ZnO, CuO and Fe$_2$O$_3$ green synthesis for the adsorptive removal of direct golden yellow dye adsorption: kinetics, equilibrium and thermodynamics studies

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Abstract: In the present investigation, ZnO, CuO and Fe$_2$O$_3$ were prepared via green route and utilized for the sequestration of DGY (Direct Golden Yellow) dye. Affecting variables i.e., temperature, contact time, adsorbent dose and pH were optimized for maximum sequestration of dye from aqueous medium. The pH 2, adsorbent dose 0.1 g/50 mL dye solution, temperature 30 °C and 50 mg/L dye initial concentration were best levels for efficient dye adsorption and equilibrium was attained in 30 min reaction time. The dye sequestration on to ZnO, CuO and Fe$_2$O$_3$ was an exothermic process. Freundlich and Temkin adsorption isotherms explained well the dye adsorption onto nanoadsorbents and dye adsorption followed pseudo first order kinetic model. Effect of electrolytes and heavy metal ions was also investigated and both affected the adsorption process significantly. In the presences of surfactant/detergent, the removal of dye was reduced and 0.5 N NaOH efficiently desorbed the dye from nanoadsorbents. Findings depicted that the nanoadsorbents are effectual for the sequestration of DGY dye, which can be employed for the remediation of textile effluents.

*Corresponding author: Munawar Iqbal, Department of Chemistry, The University of Lahore, Lahore, Pakistan, E-mail: bosalvee@yahoo.com
Saima Noreen and Safa Ismail, Department of Chemistry, University of Agriculture, Faisalabad, Pakistan
Sobhy M. Ibrahim, Department of Biochemistry, College of Science, King Saud University, P.O. Box: 2455, Riyadh 11451, Saudi Arabia
Heri S. Kusuma, Department of Chemical Education, Analytical Chemistry Research Group, Faculty of Education and Teachers Training, University of Nusa Cendana, Kupang, Indonesia
Arif Nazir, Department of Chemistry, The University of Lahore, Lahore, Pakistan
Muhammad Yaseen, Department of Physics, University of Agriculture, Faisalabad, Pakistan
Muhammad I. Khan, Department of Physics, The University of Lahore, Lahore, Pakistan

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1 Introduction

The pollution due to dyes has increased many folds in recent decade, hence, public health and environment pollution is emerged as a one of major issues worldwide. So far, the chemical pollutant control is one of challenging issue for the researchers. It is important to design and create a suitable method for the remediation of dyes [1–4]. Dyes are the foremost sources of wastewater, which are widely used in leather, paint, fabric, textile, paper and food industries [5, 6]. Synthetic dyes discharged from the industries cause the harmful and carcinogenic effect on aquatic life as well as human beings. Textile industry use huge amount of fresh water in the production and processing, which is discharged into the environment without treatment and is responsible for environmental degradation [7–11] Research has been progressed in the last two decades on advanced wastewater treatment techniques. The conventional techniques like oxidation, coagulation-flocculation, membrane separation, electro-precipitation, ion exchange are insufficient to deal with the wastewater treatment due to cost and secondary pollution issues [12–27]. The adsorption is a proficient to treat the wastewater versus other methods employed for wastewater treatment [28–32].

Nowadays, advanced and green materials have been prepared for the treatment of wastewater and nanomaterials are performing better in this regard [33, 34]. Several types of nanomaterial have been prepared via green techniques, which involved the fabrication of nanoadsorbents using plant extracts. The plants extracts act as a reducing, capping and stabilizing agents [35–45]. More recently, the nanoadsorbents have been prepared via green routes since plant produce primary and secondary metabolites as bioactive agents [32, 46–51] and this nanoadsorbents prepared are used successfully for the removal of pollutant from wastewater (Table 1), which shows the nanocomposites and their applications for the removal of different types of pollutants from wastewater [6, 52–54].

In the present study, three types of nanoadsorbent were synthesized (ZnO, CuO and Fe$_2$O$_3$) via green route and their adsorption efficiencies were evaluated for Direct Golden Yellow (DGY) dye (Figure 1). The impacts of various variables, i.e., nanoadsorbent dose, pH, contact time, dye initial conc., temperature, presence of electrolytes and surfactants have been evaluated. Adsorption isotherms, kinetics and thermodynamics were also analyzed.
## 2 Material and methods

### 2.1 Plant material

The leaves of *Cassia Fistula* were obtained from Botanical Garden, University of Agriculture, Pakistan. Dust particles were removed by washing with water. Washed biomasses were dried overnight at 60 °C. By using grinder mixture (Moulinex, France), dry biomass was grounded and sieved using OCT-DIGITAL 4527-01 at size of 300 μm.

### Table 1: Application of nanocomposites efficiency for the sequestration of dyes.

| Types of wastewater       | Types of nanocomposites                  | Optimizing conditions                                                                 | Removal Efficiency | References |
|---------------------------|------------------------------------------|---------------------------------------------------------------------------------------|--------------------|------------|
| Malachite green dye Wastewater | Polyacrylic acid nanoclay nanocomposite | pH 7.0                                                                                | 68%                | [55]       |
| Crystal violet dye        | TiO$_2$/adsorbent nanocomposite          | Concentration (2.0 M) 20 °C                                                           |                    | [56]       |
| Crystal violet dye        | MnFe$_2$O$_4$/clay composite             | pH 8, 30 min, dose 0.05 mg/L, 35 °C, 100 mg/L dye conc.                               | 49.74%             | [57]       |
| Reactive dyes             | Starch/polyaniline nanocomposite         | pH 3                                                                                  | 99%                | [58, 59]   |
| Rhodamine B               | Nanocomposites                           | 703 K                                                                                 | 90%                | [60]       |
| Reactive dyes             | Fe$_3$O$_4$ composite with gum ghatti    | Dose 0.8 g/L, pH 7.0                                                                   | 65.5%              | [61]       |
| Industrial water          | Thin film nanocomposites                 | 20 min, 120 °C                                                                         | 70–80%             | [62]       |
| Industrial dye waste water | TiO$_2$–zeolite nanocomposite            | 37 °C, 4 h                                                                             | 60%                | [63]       |
| Wastewater                | Carboxymethyl cellulose based nanocomposite | pH 2–10, 100 mg/L, 20 65 °C                                                       | 97%                | [64]       |
| R123 and DSB dyes removal | FeO and gold                             | pH 4.0                                                                                | 100 %              | [65]       |
| Wastewater                | Prussian red and poly-pyrrole composite  | 80 min and neutral pH                                                                  | 80%                | [66]       |
| Rhodamine B               | γ-Fe2O3- ZnO-biochar                     | 10 min, 120 °C                                                                         | 70%                | [67]       |
| Methyl orange dye         | Bimetal nanocomposite                    | 45 min, dose 5.0 mg, pH 6, 35 °C                                                      | 95%                | [68]       |
| Methylene blue dye        | Polyaniline zirconium (IV) silicophosphate nanocomposite | 0–1 pH, 240 min, 250 mg, 9.6 mg/L, 35–85 °C                                           | 99.9%              | [69]       |
2.2 Synthesis procedure

2.2.1 Preparation of leaf extract: A 20 g of fine cut and washed dry leaves of *Cassia Fistula* was taken with deionized water of 100 mL and then, boiled for 20 min till the color of suspension turns into yellow. The extract is cool down at room temperature. The suspension is then filtered with filter paper for further use.

2.2.2 Preparation of NPs: For ZnO NPs, 50 mL extract is boiled at 60–80 °C on stirrer heater by operating magnetic stirrer. Cooled down to 60 °C, then 5 g of Zn(NO₃)₂ is added to the solution. This mixture is heated until the suspension color turn into deep yellow. This mixture was collected in 100 mL crucible and place into oven for 400 °C. White yellow powder is obtained which is collected for further characterization [70]. For CuO, 10 mM of aqueous solution of copper nitrate was added to the 5 mL of *Cassia Fistula* solution. Heated with constant stirrer by using magnetic stirrer at temperature of 100 °C and mixture is observed until the blue color is turn into colorless, then bright red to flaming red on continuously stirring for 24 h. Then, the solution is centrifuge for 10 min at 10,000 rpm. The CuO NPs was filtered and dried [71]. Same procedure was adopted for Fe₂O₃ NPs preparation using 0.01 M FeSO₄. The salt solution to the extract ratio was 2:1. The black color indicates the reduction of Fe⁺ ions.

2.2.3 Preparation of nanocomposites: CF-ZnO NPs (1 g) was mixed to deionized water (100 mL) and 10 g of finely grinded powdered egg shell was mixed in it. Then, placed in orbital shaker incubator for 3 h at 120 rpm and for CuO NPs, 1 g NPs was added into 100 mL of distilled water and 10 g finely grinded powdered egg shell. Then, place in orbital shaking incubator for 3 h at 120 rpm 1 g of NP of Fe₂O₃ was mixed with 100 mL of deionized water and 10 g of finely powdered of egg shell were mixed in it. Then, it was placed in orbital shaker incubator for 3 h at 120 rpm, dried, ground and used for adsorption purpose.

2.3 Batch adsorption experiments

For the comparison of biosorption efficiency, contact time, pH, dye initial conc., nanoabsorbent dose and temperature were optimized. A 50 mL of dye was taken in 250 mL flask at different pH, adsorbent dose and dye concentration was set in in orbital shaker incubator at 120 rpm. Except the addition of adsorbent blank solution were also run under same conditions. Adding 0.1 M HCL and NaOH solution was used for pH of the solution adjustment. After stipulated time period, the catalyst was separated and absorbance was monitored (CE Cecil 7200, UK) and Eq. (1) was used for dye uptake \( (q_e \text{ mg/g}) \) estimation.

![Figure 1: Structure of direct golden yellow.](image-url)
\[ q_e = \frac{(C_o - C_e)V}{W} \]  \hspace{1cm} (1)

where, \( C_o, C_e, V \) and \( W \) are representing initial dye conc. (mg/L), dye conc. at equilibrium (mg/L), volume (L) and mass of nanocomposites (g).

2.4 Adsorption equilibrium, kinetics and thermodynamic studies

For dye adsorption mechanism different models of were applied. The isotherm models include [72–75]. To explain the biosorption data, pseudo first order, pseudo second order and intraparticle were computed [76]. In the thermodynamic, \( \Delta G \), \( \Delta H \) and \( \Delta S \) were calculated [77, 78].

3 Results and discussion

3.1 Effect of pH

The solutions pH affects surface charges due to H\(^+\) and OH\(^-\) ions. The charge development on surface is characterized by a point of zero charge (pzc) [78]. By knowing that which point charge is on the biosorbent is helpful for the determination of biosorption mechanism. The pH\(_{PZC}\) is very important to indicate the biosorbent exterior that is presumption that it carries negative charge or positive [77]. For the biosorption of cations pH \( > \) pH\(_{PZC}\) is favorable, while for the

![Figure 2: Point of zero charge; (A) CF-CuO, (B) CF-ZnO, (C) CF-FeO and (D) CF.](image-url)
biosorption anions pH < pH_{pzc} is favorable and boost the biosorption of anion (Figure 2). The pH_{pzc} of CF-CuO, CF-ZnO, CF-Fe_{2}O_{3} and CF was observed to be 5, 5, 3.2 and 5.3, respectively. This is because of presences of positive charge on the surface, which favored pH < pH_{pzc}. Also, \cite{77, 78} determines pH_{pzc} of nano-composites and similar trend was reported. Because on biosorbent surface formation of more than one positive charge in acidic condition that increase the electrostatic forces between dye anions and surface. The pH effect for DGY dye is observed in the range of 2–11 (Figure 3). Results showed that the pH in acidic range was suitable for dye removal. With the increase in pH from 2–11 the dye biosorbent amount is decreased. At pH 11 lowest biosorbent of dye is occurred and at pH 2 maximum biosorbent was observed. At basic pH more anionic species are form due to the ionization of carboxylic group. These anionic species such as carboxylic and hydroxyl ions compete with binding site of dye anions and hence, biosorption was decreased \cite{77}.

### 3.2 Effect of dye initial concentration

The initial concentration of dye has a very important role in adsorption phenomena. A 10–300 (mg/L) range was studied and output is depicted in Figure 4. The trend showed that by increasing the dye concentration, the adsorption of DGY dye increased and maximum adsorption capacities were as; CF was (47.95), CF-CuO (50.94), CF-ZnO (59.42) and CF-FeO (63.56). The results showed that the resistant is reduced due to concentration between two phases. So far, by increasing the initial dye concentration, the biosorption capacity is also increased. Same trend was observed for polyaniline chitosan, polypyrrole, and starch biocomposite with...
bagasse for the sequestration of Acid Black dye [77]. At the beginning, the dye molecule absorbed and the rate of biosorption was rapid. When the adsorbent surface become saturated, the dye adsorption slowed down [78].

3.3 Effect of contact time

For selection of adsorbent, the equilibrium time is a significant parameter [79–81]. The contact time (5–150 min) effect on the biosorption of efficiency of nano-adsorbents (CF-CuO, CF-FeO, CF-ZnO) for DGY dye was observed at optimum pH 2, dose 0.1, 120 rpm, and 30 °C. The results show that adsorption increases rapidly up to 45 min and then, it was slowed down and equilibrium was attained after 60 min.
The maximum values for dye adsorption were as; CF-CuO (57.32 mg/g), CF-ZnO (57.11 mg/g), CF-FeO (60.18 mg/g) and CF (44.92 mg/g). It was noticed that with increase in time biosorption is increased and equilibrium was reached after 60 min. A positive charge on composite make the anionic dye more interactive [82]. Similar trend was found for equilibrium time was observed for polypyrrole, polyaniline and sodium alginate biocomposites, which was due to high efficiency of the biocomposites [78].

3.4 Effect of temperature

In biosorption process, temperature is an important parameter. The temperature was studied in the range of 30–70 °C (Figure 6). The capacity of biosorption of different nanoadsorbents for the removal of DGY dye was higher at low temperature. Results showed that the adsorption capacity decreased from 57.29 to 9.4 mg/g for CF-FeO, 53.42 to 7.3 mg/g for CF-ZnO, 50.12 to 5.3 mg/g for CF-CuO and 45.92 to 1.2 for CF by increasing the temperature from 30 to 70 °C. It is due to break down of bond among binding groups and the dye anions present on the surface of the biosorbent [83]. Which causes the weakening of the force by increasing the temperature reduces and similar trend was found for polyaniline, sodium alginate and polypyrrole composites, which indicate the exothermic nature of dye adsorption on to nanoadsorbents [78].

![Figure 6: Adsorptive removal of Direct Golden Yellow dye using nanoadsorbents as a function of temperature.](image-url)
3.5 Effect of nanoadsorbent dose

The dose effect was studied in the range 0.05–0.5 g on the biosorption of DGY dye and response thus observed are shown in Figure 7. The biosorption of dye decreased from 57.34 to 11.57 mg/g for CF-FeO, 53.34 to 8.19 mg/g for CF-ZnO, 50.34 to 1.92 mg/g for CF-Cuo and 41.22 to 1.24 for CF as the dose was increased from 0.1 to 0.5 g. The result indicate that all the nanocomposite shows the maximum biosorption at 0.1 g. The decrease in biosorption is due to accumulation of dye ions at surface and aggregates formation of adsorbent dose at higher dose [84]. Also, [78] reported similar result that by increasing the dose the biosorption efficacy was decreased of the biocomposites.

3.6 Adsorption isotherms

The biosorption systems showed the interaction between dye and adsorbent molecule [85]. On the adsorbent surface, at equilibrium constant temperature, the relationship between dye concentration that adsorbed and the dye concentration in aqueous solution is studied using isotherm [20]. By using the different isotherms, the biosorption data can be examined, which express surface properties and affinity of the adsorbent. Four important isotherm models namely Langmuir, Freundlich, Temkin and Harkin Jura were applied. The adsorption behavior in
adsorption process can be described by the Langmuir model. According to the Langmuir model, the surface of the adsorbent contains a fixed number of active sites for adsorbate to form a monolayer. After the formation of a monolayer, no further adsorption can occur on the surface. The Langmuir model is shown in Eq. (2) [73]. Where, \( C_e \) is the conc. and \( q_e \) is the adsorption value and \( b \) (L/mg) is a constant. The linear form of the Freundlich isotherm is shown in Eq. (3). Where, \( k_f \) shows the Freundlich constant, \( 1/n \) shows the biosorption intensity that depends on the biosorbent heterogeneous nature. The Eq. (4) represents the linear form of the Temkin equation. Where, \( B = RT/b \) (KJ/Mol) represents the Temkin constant, \( R \) known as the universal gas constant (8.314 J mol\(^{-1}\) per kelvin), \( B \) shows the heat of adsorption (J/mol) and \( A \) is the Temkin constant. The creation of many layers of dye molecule on the porous heterogeneous adsorbent surface is explained by the Harkins Jura model (Eq. (5)). Results mention in Table 2 indicate the fitness of models using different nanocomposites for the removal of dye, which shows that the most appropriate was Freundlich and Temkin with \( R^2 \) readings 0.999–0.918 and \( q_e \) values was also found to be close to the experimental value [86, 87].

**Table 2:** Isotherms parameters for the removal of dye using nanoadsorbents.

| Isotherm models              | CF-CuO       | CF-ZnO       | CF-FeO       | CF            |
|-----------------------------|--------------|--------------|--------------|---------------|
| **Langmuir model**          |              |              |              |               |
| \( q_m \) \( \text{Cal} \) (mg/g) | 21.31        | 70.43        | 80.44        | 76.32         |
| \( q_m \) \( \text{Exp} \) (mg/g) | 44.701       | 50.053       | 45.576       | 43.42         |
| \( B \)                     | 11.136       | 10.789       | 19.65        | 20.65         |
| \( R_L \)                   | 0.321        | 0.45678      | 0.12345      | 0.2134        |
| \( R^2 \)                   | 0.139        | 0.057        | 0.612        | 0.127         |
| **Freundlich model**        |              |              |              |               |
| \( q_m \) \( \text{Cal} \) (milligram/gram) | 53           | 30.28        | 39.12        | 40.32         |
| \( K_F \)                   | 3.6812       | 15.4534      | 3.5809       | 4.4567        |
| \( n \)                     | 0.92         | 1.037        | 2.323        | 1.9654        |
| \( R^2 \)                   | 0.976        | 0.999        | 0.976        | 0.963         |
| **Temkin model**            |              |              |              |               |
| \( q_m \) \( \text{Cal} \) (mg/g) | 41           | 47           | 33           | 42            |
| \( A \)                     | 2.564        | 3.02615      | 9            | 4.567         |
| \( B \)                     | 9.225        | 10.11        | 4.637        | 7.3656        |
| \( R^2 \)                   | 0.918        | 0.942        | 0.934        | 0.999         |
| **Harkins-Jura model**      |              |              |              |               |
| \( q_m \) \( \text{Cal} \) (mg/g) | 2            | -1           | 0            | 3             |
| \( A \)                     | 1            | 0.929        | 0.23         | 0.986         |
| \( B \)                     | 0.21         | 0.289        | 1            | 0.432         |
| \( R^2 \)                   | 0.01         | 0.009        | 0.016        | 0.032         |
\[ \frac{C_e}{q_e} = \frac{1}{q_m} + \frac{C_e}{q_m} \]  

(2)

\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]  

(3)

\[ q_e = B \ln A + B \ln C_e \]  

(4)

\[ \frac{1}{q^2} = \left( \frac{B}{A} \right) - \left( \frac{1}{A} \right) \log C_e \]  

(5)

### 3.7 Kinetics studies

Kinetic models are used to establish the potential rate controlling step and the kinetic data from the batch process is analyzed by intraparticle diffusion, pseudo-first and pseudo-second-order kinetic models. The equation of the pseudo first order is shown in Eq. (6) [88].

\[ \log(q_e - q_t) = \log q_e - k_1 \cdot \frac{t}{2303} \]  

(6)

where, \( q_e, q_t, t \) and \( k_1 \) are representing adsorption capacity, adsorption at time \( t \), contact time, and constant, respectively. The values of \( R^2, k_1 \), adsorption capacities (cal and exp) of DGY dye using different types of nanosorbents are listed in Table 3.

| Kinetic model               | CT-CuO   | CT-ZnO   | CT-FeO   | CF         |
|-----------------------------|----------|----------|----------|------------|
| Pseudo first order          |          |          |          |            |
| \( K_1 \) (L/min)           | 0.039    | 0.029    | 0.034    | 0.029      |
| \( q_{exp} \) (mg/g)        | 43       | 47       | 53       | 49         |
| \( q_{cal} \) (mg/g)        | 46       | 36       | 41       | 42         |
| \( R^2 \)                   | 0.999    | 0.995    | 0.997    | 0.993      |
| Pseudo second order         |          |          |          |            |
| \( K_2 \) (g/mg.min)        | 0.02411  | 0.000977 | 0.000322 | 0.000378   |
| \( q_{exp} \) (mg/g)        | 43       | 47       | 53       | 42         |
| \( q_{cal} \) (mg/g)        | 39.41    | 56.62    | 45.169   | 43.47      |
| \( R^2 \)                   | 0.95     | 0.995    | 0.987    | 0.994      |
| Intraparticle diffusion     |          |          |          |            |
| \( K_{pi} \) (mg/g.min^{1/2}) | 4.682    | 1.396    | 0.206    | 0.185      |
| \( C_f \)                   | 0.387    | 0.223    | 1.804    | 1.733      |
| \( R^2 \)                   | 0.92     | 0.96     | 0.945    | 0.983      |
The pseudo-second-order shows the surface assimilation nature of biosorption process. The linear form of pseudo-second-order is shown in Eq. (7) [76].

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]  (7)

where, \(k_2\) is pseudo-second-order constant and the \(q_e\) (mg/g), determined from intercept and slope against \(t/q_t\) against \(t\). The values are for the removal of DGY dye by using distinct types of nanosorbents are shown in Table 3. Data revealed that pseudo first order fitted well to the dye adsorption on the nanoadsorbents with \(R^2\) values for all adsorbent 0.99. Many steps involved in dye adsorption on biosorbent surface from aqueous solution. The following Eq. (8) shows the intraparticle diffusion.

\[
q_t = K_{pi} t^{1/2} + C_i
\]  (8)

where, \(C_i\) and \(K_{pi}\) (mg/g min\(^{1/2}\)) are the boundary layer thickness and diffusion rate constant. The graph was plotted between \(q_t\) against \(t^{1/2}\) and \(C_i\) and \(K_{pi}\) were calculated from intercept and slope, respectively and responses are represented in Table 3, which also showed satisfactory fitness to the dye adsorption on to nanoadsorbents [83, 89, 90].

### 3.8 Thermodynamic study

Standard enthalpy change (\(\Delta H^o\)), Gibbs free energy (\(\Delta G^o\)), enthalpy change (\(\Delta S^o\)) were calculated. Thermodynamic is used to examine the nature of biosorption condition (exothermic or endothermic nature) for the adsorption process. It supports the spontaneity and reaction feasibility. It is non-spontaneous in nature if the value is positive, while spontaneous nature if value is negative. The biosorption condition of the \(\Delta G^o\) can be calculated using Eqs. (9) and (10).

\[
\Delta G^o = \Delta H^o - T \Delta S^o
\]  (9)

\[
\Delta G^o = -RT \ln K_d
\]  (10)

where, \(\Delta G^o\) is Gibbs free energy, \(\Delta S^o\) is enthalpy change, \(\Delta H^o\) is standard enthalpy change, \(R\) is rate constant, \(T\) is temperature, \(K_d\) is a constant. By plotting a graph between \(\ln K_d\) and \(\frac{1}{T}\) the intercept and slope were calculated as shown in Eq. (11).

\[
\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}
\]  (11)

The thermodynamic data is given in Table 4. The negative value of \(\Delta H^o\) for nanoadsorbents of the DGY dye showed the spontaneous nature of adsorption
process. Decrease in order on solid liquid is representing by $\Delta S^\circ$ during the removal of dye. By increasing the temperature, the reduction in biosorption capacity takes place, which revealed the exothermic nature of dye adsorption on to nanoadsorbents [83, 90].

### 3.9 Effect of detergent/surfactant on dye adsorptive

Different detergents are used in industries, which may influence the adsorption efficiency of biosorbent. Different surfactant such as SDS, Triton X-100, CTAB and detergent (Arial and surfactant) effect was studied at 1% concentration on Cf, CF-CuO, CF-ZnO, CF-FeO adsorptive efficiency for the elimination of dye and responses are shown in Figure 8. Adsorption capacity decreased in the presence of detergent/surfactant, which was due to the coverage of active binding sites and dye adsorption was decreased and this trend is inline with previous studies [77, 78].

| Thermodynamic | Temperature |
|---------------|-------------|
|               | 303 | 311 | 319 | 327 | 335 | 343 |
| CF-CuO $\Delta G$ (kJ/mol) | 2.98 | 3.56 | 4.33 | 5.7 | 5.19 | 7.62 |
| $\Delta S$ (J/mol.K) | -139.6 | -139.6 | -139.6 | -139.6 | -139.6 | -139.6 |
| $\Delta H$ (kJ/mol) | -83.32 | -83.32 | -83.32 | -83.32 | -83.32 | -83.32 |
| CF-ZnO $\Delta G$ (kJ/mol) | -0.35 | 2.09 | 3.45 | 5.12 | 1.32 | 2.93 |
| $\Delta S$ (J/mol.K) | -159.31 | -159.31 | -159.31 | -159.31 | -159.31 | -159.31 |
| $\Delta H$ (kJ/mol) | -90.1 | -90.1 | -90.1 | -90.1 | -90.1 | -90.1 |
| CF $\Delta G$ (kJ/mol) | 1.24 | 1.43 | 2.46 | 1.23 | 1.34 | 9.67 |
| $\Delta S$ (J/mol.K) | -160.45 | -160.45 | -160.45 | -160.45 | -160.45 | -160.45 |
| $\Delta H$ (kJ/mol) | -53.23 | -53.23 | -53.23 | -53.23 | -53.23 | -53.23 |
| CF-FeO $\Delta G$ (kJ/mol) | 3.05 | 2.22 | 4.97 | 0.3 | 1.87 | 2.65 |
| $\Delta S$ (J/mol.K) | -199.08 | -199.08 | -199.08 | -199.08 | -199.08 | -199.08 |
| $\Delta H$ (kJ/mol) | -64.56 | -64.56 | -64.56 | -64.56 | -64.56 | -64.56 |
3.10 Effect of electrolyte on dye adsorption

Large amount of salt are consumed by the textile industry during the dyeing process and this is one of the important factor which controls the electrostatic boning or non-electrostatic interaction among dye molecule or absorbent surface which influence the sorption capacity [77, 78]. To study the electrolyte effect, different electrolyte (NaCl, MgSO₄) in concentration range (0.1–0.5 g) was studied on the adsorption efficiency of nanoadsorbents (CF-CuO, CF-ZnO, CF-Fe₂O₃). The results showed that the electrolyte affected the dye adsorption significantly (Figure 9). These may either increase or decrease the adsorption capacity of nanocomposites. NaCl increased the adsorption capacity of nano-adsorbents, while MgSO₄ reduced the sorption capacity of dye using nano-adsorbents. At higher concentration of salt, the interaction between adsorbent and anionic dye was decreased due to change in solubility [77, 78]. In the presence of salts, force of attraction between the positively charged dye ions and the functional group on adsorbent surface was decreased and resultantly, the adsorption was also decreased. The results revealed that nanoadsorbents (ZnO, CuO and Fe₂O₃) proved to be efficient adsorbents for the removal of DGY dye and under the current scenario of environmental pollution [9, 91–98], there is a need to utilize efficient materials to mitigate the pollution issue and nanoadsorbents are efficient in this regard.

Figure 8: Adsorptive removal of Direct Golden Yellow dye using nanoadsorbents in the presence of various surfactant and detergents.
3.11 Desorption study

Choosing of any biosorbent is also based on its regeneration for reuse and desorption was studied for this purpose. The maximum adsorption was at pH due to the electrostatic interaction between the dye molecule and adsorbent surface. By changing the pH, desorption can be achieved and NaOH of different concentration (0.1–0.5 M) were used (Figure 10). Maximum desorption was achieved using 0.2 M NaOH, which was 84%. This observation is also in line with previous studies that the biocomposite can efficiently desorbed in basic pH, that was studied for chitosan, starch, polyaniline and polypyrrole biocomposite and polypyrrole, polyaniline and sodium alginate biocomposites [77, 78].

Figure 9: Adsorptive removal of Direct Golden Yellow dye using nanoadsorbents in the presence of electrolytes (A) NaCl (B) MgSO₄.
3.12 FTIR analysis

FT-IR is a technique which is used to identify the functional groups responsible for adsorption of adsorbate on to adsorbent surface. A spectrum is formed which indicates the peak of functional groups, which identify the type of bonding and interaction between the dye and functional group of adsorbent. The FTIR response are shown in Figures 11 and 12. In unloaded adsorbents, peaks were recorded at 2978.0, 1636.3, 1653.1, 1507.7, 1457.4, 1395.9, 1034.3, 1058.6, 872.2 and 711.9 (cm$^{-1}$) and these peaks have been changed/shifted in loaded CF-CuO, which is an indication of involvement of different functional groups for the binding of dye onto the surface of CF-CuO (Figure 11). A broad peak at 3850.2 cm$^{-1}$ of CF-CuO loaded indicates the -OH functional group and after loading with dye, the intensity of band changed, which indicates interaction of functional group with dye anion. Similar peak 3410.5 cm$^{-1}$ was observed for CF-Fe$_2$O$_3$. A3282.6 cm$^{-1}$ peak in CF-ZnO indicates the OH functional group, which also changed after interacting with dye. At 2967.0 cm$^{-1}$ shows the carbon hydrogen bonding. At peak 2500 cm$^{-1}$ in unloaded CF-FeO shows the presence of –CH stretching. These bands have low intensity when dye was loaded. In CF-ZnO peak from 1600–1525 cm$^{-1}$ shows the nitrogen double bond. The peak at 1036.09 cm$^{-1}$ indicated the carbon oxygen bond in CF-CuO and the intensity of peak changed after adsorption. The decrease in peak intensities, shifting and appearance of the peaks in loaded adsorbent indicates the adsorption of dye onto the nano-adsorbents.

Figure 10: Desorption of Direct Golden Yellow dye using NaOH from nanoadsorbents.
Figure 11: FTIR analysis; (A) unloaded CF-CuO and (B) loaded CF-CuO.

Figure 12: FTIR analysis (A) unloaded CF-FeO and (B) loaded CF-FeO.
4 Conclusion

Nanoadsorbents, i.e., ZnO, CuO and Fe₂O₃ were successfully prepared via green route and used for the removal of DGY dye and maximum adsorption was achieved at pH 2, 0.1 g/50 mL adsorbent dose, temperature 30 °C, 50 mg/L initial dye concentration and equilibrium was achieved within 30 min of contact time. The dye adsorption on to nanoadsorbents was an exothermic process. Freundlich and Temkin adsorption isotherms fitted well to the dye adsorption data. The adsorption kinetics followed the pseudo first order kinetic model. Electrolyte and surfactant/detergent affected the adsorption process negatively. Results revealed that the nanoadsorbents prepared via green route are efficient adsorbents for the removal of dye and could possibly be used for the remediation of dyes in textile wastewater.

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