Research article

Nano-catalytic behavior of highly efficient and regenerable mussel-inspired Fe₃O₄@CFR@GO and Fe₃O₄@CFR@TiO₂ magnetic nanospheres in the reduction of Evans blue dye

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ABSTRACT

Fe₃O₄@catechol formaldehyde resin coated @Graphene Oxide nanocomposite (Fe₃O₄@CFR@GO) and Fe₃O₄@catechol formaldehyde resin coated @TiO₂ (Fe₃O₄@CFR@TiO₂) nanocomposites were fabricated by hydrothermal method. Particularly, catechol bunches on the highest layer of nanospheres to play a mussel-inspired chemistry to assist combined with graphene oxide (GO) to wrap the Fe₃O₄@ coated nanosphere. The prepared catalyst was proven to be very efficient with less than a minute and very less dosage (15–17 mg) in the adsorptive degradation of Evans blue dye. The adsorptive degradation of Evans blue dye with Fe₃O₄@CFR@GO and Fe₃O₄@CFR@TiO₂ nanocomposites are studied by several variables like the dye concentration, dosage, pH, contact time and temperature. It shows maximum adsorption capacity of 0.1435 mg/g (Fe₃O₄@CFR@GO) and 9.345 mg/g (Fe₃O₄@CFR@TiO₂) nanocomposites. The equilibrium concentration and the adsorption capacity were evaluated using three different isothermal models. The kinetic study determined that Evans blue dye adsorption was in good analogy with the pseudo-first-order kinetic model.

1. Introduction

Historically, human population and industrial activities have led to an increase in water pollution. Synthetic chemical compounds and dyes form a new class of toxic waste in the water source. Their presence in water or biosphere is generally related to pollutants that have no control or whose effects are unknown and are known to affect the environment [1]. The presence of increasing toxic and foreign matter in ground/surface water resources used for drinking leads to a serious problem. Among the pollutants, Evans Blue dye (direct blue-S3 dye or T-1824), a synthetic bis azo dye has retained a long history which is used directly on fibers and textiles (Figure 1). The Evans blue is classified as toxic dye, which has chronic health effect, affecting the lung function, liver, kidney, skin irritation, and intestine. It also irritates the skin when applied in heavy doses and also known to be carcinogenic and genotoxic [2]. Removal of such dyes is an important part of wastewater management before being released to environment [3].

The use of Graphene Oxide (GO) has shown good adsorption properties due to improved charge separation, porous, stability in addition to its adsorption attributes [4]. It is well known that 2D structural GO has a very high surface area and 2D morphology [5]. Earlier literature manifests that GO has more oxygenated functionalities that can be used as sites to form a contact with materials like metal oxides and polymers etc [6]. Since the graphene oxide has affinity to metal particles to form composites due to oxygen functional groups [7]. In addition, graphene-supported metal/metal oxide composite materials are better catalyst with better catalytic efficiency compared to the other traditional catalysts formed from the stable metal oxide particles [8, 9, 10, 11].

Lately, the catechol and its derivatives have received much more attention due to the use as functional adhesives through mussel-inspired chemistry [12, 13], which coats on the nano-metal oxides which can be

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used for highly efficient adsorptive degradation of dyes. Better catalytic activity can be obtained if the catechol groups on the nanospheres are mixed with metal nanoparticles and GO catalysts since the GO interacts very strongly with aromatic compounds through the π-π stacking effect [14]. Further, Fe3O4 nanoparticle can be used for dye degradation application. On the other hand, catechol formaldehyde resin cannot be used dye degradation application. Moreover, TiO2 can also be used for photocatalytic dye degradation application. Therefore, using catechol groups is very important for many applications in catalysis, energy related applications, biomedical aspects, sensors and water treatment [15, 16]. In this article, we report coated Fe3O4 core-shell magnetic nanosphere by catechol-formaldehyde (CFR) resin by hydrothermal method and combined with GO and TiO2 to form GO and TiO2 nanocomposites. As a result, we prepared two nanocomposites and applied for the study of adsorptive degradation of Evans blue dye.

2. Material and methods

2.1. Experimental

2.1.1. Synthesis of graphene oxide (GO)

Graphene oxide (GO), Catechol (C6H6O2), potassium permanganate (KMnO4), Titanium Oxide (TiO2), Ferro ferric oxide (FeO.Fe3O4), Sodium Borohydride (NaBH4), Evans blue dye (C34H24N6Na4O14S4), Formaldehyde (CH2O), Anhydrous ammonia (NH3), Hydrogen Peroxide (H2O2), Hydrochloric acid (HCl), o-phosphoric acid (H3PO4), Sulphuric acid (H2SO4), Tris-aminomethane (C4H11NO3) and Ethanol (C2H5OH) are used. KMnO4 (18 g) is gradually mixed and is heated to 50 °C with constant stirring in the ice bath (approximately -10 °C) for about 24 h. KMnO4 (18 g) is gradually mixed and is heated to 50 °C with nonstop stirring for 20 h. This is diluted in cold water with H2O2 at normal temperature and allowed to settle for 3 h. The solution is washed with HCl till its pH value becomes neutral. The product is dried in oven at 60 °C.

2.1.2. Synthesis of Fe3O4@CFR core-shell nanospheres

Natural graphite powder (3 g) was made to react with a homogeneous acidic mixture of H2SO4 and o-H3PO4 (9:1 ratio and 360:40 ml each) each with constant stirring in the ice bath (approximately -10 °C) for about 24 h. KMnO4 (18 g) is gradually mixed and is heated to 50 °C with nonstop stirring for 20 h. This is diluted in cold water with H2O2 at normal temperature and allowed to settle for 3 h. The solution is washed with HCl till its pH value becomes neutral. The product is dried in oven at 60 °C.

2.1.3. Synthesis of Fe3O4@CFR-decorated on GO hybrid nanocomposite (Fe3O4@CFR@GO)

15 mg of GO powder and the 50 mg of above nanospheres are distributed in 75 ml tris-aminomethane solution under ultra-sonication for 40 min. To the above aqueous suspension, GO suspension was added dropwise within 20 min in ultrasonic bath, and then allowed to stir for 24 h at 25 °C. Unadhered GO powder are removed by washing and the material obtained was dried in a vacuum for 12 h (Figure 2) [17].

2.1.4. Synthesis of Fe3O4@CFR-decorated on TiO2 hybrid nanocomposite (Fe3O4@CFR@TiO2)

50 mg of Fe3O4@CFR core-shell nanospheres were distributed with magnetic stirring in 50 ml of absolute ethanol for 30 min. Thus obtained black suspension was combined with 3.7 ml of TiO2 solution (0.1 M) for 1 h with ultra-sonication. Above solution is stirred at room temperature for 24 h. The product was collected through a magnet, unloaded TiO2 was removed and dried in vacuum for 12 h (Figure 2) [18].

2.1.5. Performance of nanocomposites for the reduction of Evans blue dye

The fresh NaBH4 solution (1 ml, 0.5 M) and Evans blue solution (2 ml, 5 mg L−1) are mixed and shaken up for 30 s. Catalytic amount of GO nanocomposite (0.015 mg L−1) and TiO2 nanocomposite (0.017 mg L−1) were gradually added to the above mixture and allowed to undergo catalytic reaction, and is supervised using UV-Vis spectrophotometer. Since the catalyst is magnetically active after the experiments, the samples were separated by a magnetic bar. After the experiment, nanocomposites were recollected by the magnet from the solution and rinsed with water and ethanol to check the reusability of the material. We have found from our experiments that the same catalytic material can be reused for six to seven times.

3. Results and discussion

3.1. Characterization of GO and TiO2 nanocomposites

Magnetic Fe3O4@CFR core-shell nanospheres are prepared by polycondensation of C6H6O2 and FeO.Fe3O4 (Ferro ferric oxide) catalyzed by NH3 and formaldehyde (CH2O) also using magnetic Fe3O4 nanoparticles as the seeds under the autoclave condition. The outside part of magnetic Fe3O4 nanocomposite formed has irregular surface. It can be seen that the coated nanosphere shells onto the Fe3O4 nanoparticles, there is a strong different elemental interaction between 2–OH groups of catechol and

Figure 1. Structural representation of Evans Blue.
Fe–O moieties. The circular structure leads to surface energy reduction on the coated nanosphere shell grown on the surface of Fe₃O₄-nanoparticles.

Further, we studied the effect of different conditions and reactant ratios on coating thickness and shape of above said nanospheres [17]. The coating thickness depends on the quantity of reactants of formaldehyde and Catechol. GO nanocomposites are in the form of sheets, and TiO₂ nanocomposites are spherical in shape. Inquiry on the structural behavior of samples was accomplished through XRD method. Diffraction patterns of GO and TiO₂ nanocomposites are shown in Figure 3. It is observed that the XRD pattern (JCPDS: 98-009-6946 and 98-018-5863) showed that the GO nanocomposite is more crystalline than TiO₂ nanocomposite. A number of characteristic diffraction peaks are reported at 62.8, 57.1, 53.8 and 36.5° and are indexed to different Fe₃O₄ planes. After the Fe₃O₄ NPs are coated with CFR polymers the XRD pattern reveals a broad peak at 2θ = 20–30°, referring to amorphous polymers.

The morphology of the as-prepared nanocomposites were studied using SEM micrographs (Figure 4), which showed that nanocomposite of TiO₂ were in the range of 44–54 nm and for the GO, 55–77.5 nm in diameter. The morphology of the nanospheres did not change on attaching TiO₂ nanoparticles on them. However, the TiO₂ nanoparticles agglomerated together on Fe₃O₄ with strong interaction with catechol groups compared with GO nanocomposite as shown, which in turn indicated that the catechol group on the nanospheres immobilized on the surface of GO lead to relatively weak interaction [11].

As shown in Figure 5, Fe–O bonds of Fe₃O₄@CFR@GO and Fe₃O₄@CFR@TiO₂ nanocomposites are given as the characteristic absorption bands at 592 cm⁻¹. Bands of the 1460-1600 cm⁻¹ and 3100 cm⁻¹ belong to benzene rings and OH group. The 1270 cm⁻¹ band is for aromatic C–O vibration for catechol groups. A 3,200 cm⁻¹ broad absorption band is an OH stretching vibration on the graphene oxides (GO) surface and confirms GO's presence around CFR shell for Fe₃O₄@CFR@GO.

3.2. Selection and optimization of catalyst

The catalytic activity of newly synthesized GO and TiO₂ nanocomposites were tested by deciding the reduction reaction of Evans blue. While studying reaction kinetics, it is observed that, the blue solution will turn to colorless when 0.017 mgL⁻¹ of TiO₂ nanocomposite and 0.015 mgL⁻¹ of GO nanocomposite are used.

In the Figure 6, the comparison of UV-Visible spectra for Evans blue catalyzed by GO and TiO₂ nanocomposites as catalysts, respectively is depicted. It is clear from the graph that characteristic absorption maxima of Evan blue at 622 nm gradually drops during catalytic reaction. This is accompanied by change in the absorption peaks at 568 nm and at 622 nm indicating the reduction of Evans blue on the basis of color change from blue to colorless. Absorbance as a function of reaction time (t) for the catalysts were also studied. As observed in Figure 7a, b, reaction rate of GO nanocomposite is much faster than TiO₂ nanocomposite.

High catalytic activity can be related to the interaction of nanocatalysts with the Evans blue dye substrate and reduced due to the adsorption of dye molecules in vacant surface sites of the catalyst. Since the surface area of GO nanocomposite is more than TiO₂ nanocomposite, the reaction is faster in case of GO nanocomposite. Due to the vacant surface sites which are exhausted by the dye molecules, which leads to a
decrease in the rate of adsorption at later stages. The removal curves are simple, smooth and continuous, suggesting a single layer of dye coverage on the adsorbent surface. Evans blue molecules have a positive charge, while the coated nanosphere shell or GO layers on the catalytic surface have a negative charge over them, and that is the reason for increased adsorption capacity as with pH values [19].

The electrostatic attraction between the Evans blue and the coated nanospheres results in a rapid movement of the Evans blue molecule towards the surfaces of the catalyst, forming a nearby concentrated layer around the catalyst. Further, a reduction reaction happens through an electron transfer system that generates an intermediate redox potential between the acceptor and donor on the surface of both catalysts [19]. Results in Figure 8 have shown that the adsorption capacity has improved with the higher concentration of dye and pH. Area with –OH and –NH2 groups of the Evans blue dye depending on the pH of the solution can attach on the heterogeneous surface of the adsorbent mixed oxide Fe3O4@CFR decorated with GO nanosheets and TiO2 nanospheres. Also, it is observed that increase in the dye concentration leads to the equilibrium state over the period of time. This increase in adsorption capacity is mainly due to the existence of concentration gradient by transferring the molecules in between liquid solution and solid catalyst [20].

We observed that, Fe3O4@CFR decorated with GO showed more adsorptive degradation (96.9%) compared to that of TiO2 nano-composite (81.7%) (Figure 9). Due to high surface area of GO, Van der waals forces and π-π interactions, the catalytic reduction is faster in case of GO nanocomposite compared to TiO2 nanocomposite.

The experiment is repeated thrice in order to check the consistency and reproducibility. A highly efficient catalytic reaction of Evans blue dye with a low dosage of Fe3O4@CFR@GO (15 mg) and Fe3O4@CFR@TiO2 (17 mg) catalyst in the duration less than one minute. This can be observed with mussel inspired coating [19].

3.3. Adsorption isotherms

We used Langmuir (L), Freundlich (F) and Tempkin (T) isotherms [21] as shown in Figure 10a–c and Table 1 to determine the relationship between the concentration of adsorbate on the solution and the adsorbent surface. It can be observed that the correlation coefficient (R²) in Freundlich (F) and Langmuir (L) isotherms is high. However, the adsorption power of Langmuir (L) (0.999) is greater than Freundlich (F) (0.986) indicating that Langmuir fits better. The development of a multi-layer is formed in the GO nanocomposite ((Langmuir (L) (0.9992) is almost similar to Freundlich (F) (0.986)). Since both R² are near to one it is expected to form multi-layer [22]. While monolayer in TiO2 nano-composite is expected as only Langmuir fits better. (Langmuir (L) (0.986) and Freundlich (F) (0.199)). So it has also taken place through the adsorption process [23]. It shows maximum adsorption capacity of 331.2 mg/g.

3.4. Kinetics study

In order to achieve the best fit model for the experimental data gathered, two renowned kinetic models are examined [24].
following pseudo first-order rate equation was used for treating the kinetic information.

\[
\log(q_e - q_t) = \log q_e - k_1 t / 2.303
\]

where \(q_t\) and \(q_e\) are the amount adsorbed at time \(t\) and at equilibrium (mg/g) and pseudo first-order rate constant is the \(k_1\) for the adsorption process (min \(^{-1}\)). The pseudo second-order model can be written in the below form:

\[
t/q_t = 1/k_2 q_e^2 + (1/q_e)t
\]

where the pseudo second order rate constant is \(k_2\) (g/mg min). The plots of \(\ln (q_e - q_t)\) versus \(t\) and the plots of \(t/q_t\) versus \(t\) are shown in, respectively.

**Figure 11(a) and (b) shows the pseudo 1\(^{st}\) and 2\(^{nd}\) order of Evans blue.**

Compatibility of chemical adsorption process with pseudo 1\(^{st}\) order is \(R^2 = 0.94\) and 2\(^{nd}\) order, \(R^2 = 0.85\), respectively (Table 2). The results show that the adsorption process is physisorption.

### 3.5. Mechanism of adsorption

Stronger adsorption ability is one of the characteristics of organic dye, and it is easily adsorbing on the large specific surface area of Graphene Oxide (GO). Three steps are involved in the removal of dye by Fe\(_3\)O\(_4\)@CFR@GO nanocomposite. In the first step, the Evans blue dye molecules migrated from the liquid phase to the outer surface of adsorbent particles. In the second step, the Evans blue dye molecules moved within the pores of adsorbent particles. In the third step, the adsorption of Evans blue dye molecules by Fe\(_3\)O\(_4\)@CFR@GO nanocomposite took place on the surface. In this process, the cationic dyes displayed a high affinity to be adsorbed on Fe3O4@CFR@GO, which could be due to the electrostatic interactions between GO’s π-electrons and the positively
Figure 10. The (a) Langmuir, (b) Freundlich and (c) Tempkin isotherms of Evans blue.

Table 1. Correlation Coeficient for the Adsorption of Evans blue on GO and TiO2 nanocomposite.

| Isotherm       | R²       | GO nanocomposite | TiO2 nanocomposite | GO nanocomposite | TiO2 nanocomposite |
|----------------|----------|------------------|--------------------|------------------|-------------------|
| Langmuir       |          | 0.999            | 0.959              | 0.00317          | 0.0017            |
| Freundlich     |          | 0.986            | 0.199              | 0.417            | 0.66              |
| Tempkin        |          | 0.891            | 0.151              | 0.3              | 0.31              |

Figure 11. Pseudo (a) First order and (b) Second order plots of adsorption of Evans blue dye.

Table 2. Kinetic parameter of Evans blue dye on GO and TiO2 nanocomposite.

| Kinetic Study | GO nanocomposite | TiO2 nanocomposite | qe = V(Co−Cf)/m | GO nanocomposite | TiO2 nanocomposite |
|---------------|------------------|--------------------|-----------------|------------------|-------------------|
| pseudo 1st order | R² = 0.94 | R² = 0.63          | GO nanocomposite | TiO2 nanocomposite | k₁ x 10⁻³ (min⁻¹) | k₂ x 10⁻³ (mg/g min⁻¹) |
| pseudo 2nd order | R² = 0.85 | R² = 0.75          | 331.2 mg/g       | 165.63 mg/g      | 0.181             | 0.0537            |
charged cationic dyes. The phenomenon is referred as the π-π electron-donor (GO)/acceptor (cationic dyes) interaction (Figure 12). Evans blue is a preferably planar molecule and can thus be readily adsorbed by π-π interactions between the aromatic backbone of the dyes and the GO. Thus Fe3O4@CFR@GO nanocomposite could thus play a potential usefulness in organic pollutant treatment.

![Figure 12. The possible mechanism of interaction between Fe3O4@CFR@GO and Evans blue dye (Blue dashed line indicates Hydrogen bond; Red line indicates π-π interaction, Black line indicates Electrostatic interaction).](image)

![Figure 13. Plot of lnK0 against 1/T for the adsorption of Evans blue.](image)

| Temp (K) | GO nanocomposite | | TiO2 nanocomposite | |
|---|---|---|---|---|---|
| | ΔH° (kJ/mol) | ΔS° (J/molK) | ΔG° (kJ/mol) | R² | | ΔH° (kJ/mol) | ΔS° (J/molK) | ΔG° (kJ/mol) | R² |
| 225 | 183.6 | 1.641 | -4.3241 | 0.85 | | 350 | 2.64 | -2.31153 | 0.98 |
| 228 | -4.3572 | -2.29858 | | | 236 | -4.2962 | -2.2664 | | |
| 240 | -4.2689 | | | | |

Table 3. Thermodynamic parameters of the adsorption of Evans blue.
3.6. Effect of temperature

Temperature plays a significant role in the adsorptive degradation of dye on catalysts. Figure 13 indicates an improvement in the adsorption potential of dye (50 μmol/L) with an increase in temperature. This suggests that the process is endothermic. It is enhanced by raising the temperature due to the rate of diffusion of the dye molecules across the outer boundary layer and in the inside pores of the catalyst increased and consequently the adsorption increased [26, 27]. Thermodynamic parameters of the adsorption is given by Van’t Hoff equation from Eqs. (1), (2), and (3).

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

(1)

\[
\ln K_d = \frac{q_d}{C_e}
\]  

(2)

\[
\Delta G^o = R T \ln K_d
\]  

(3)

where R is gas constant, KD is the distribution coefficient for adsorption in g/L, \( \Delta S^o \) and \( \Delta H^o \) are standard entropy and standard enthalpy changes, \( \Delta G^o \) is standard Gibbs free energy change. A straight line is plotted between \( \ln K_d \) and \( \frac{1}{T} \) as shown in Figure 13.

Table 3 specifies the value of the thermodynamic parameters. Due to the + ve value and the higher \( \Delta H^o \) value, the process can be seen in physisorption and endothermic. The value of \( \Delta S^o \) shows the high order of reaction during adsorption. –ve \( \Delta G^o \) implies a random process and the value increased at a higher temperature, which corresponds to the adsorption cycle, is ideally at an elevated temperature.

4. Conclusion

In summary, magnetic core-shell nanospheres covered in mussel inspired stable coatings have been fabricated effectively with a convenient and effective path. The as prepared Fe₃O₄@catechol coated magnetic nanospheres @TiO₂ NPs and Fe₃O₄@catechol coated magnetic nanosheets @GO have shown an extremely efficient catalytic property with low dosage and less than minute time for the adsorptive degradation of Evans blue dye. Thus, we conclude that the Fe₃O₄@CFR@TiO₂ nanocomposites and as an efficient material for the removal of Evans blue dye from aqueous environment. It shows maximum adsorption capacity of 0.1435 mg/g (Fe₃O₄@CFR@TiO₂) and 9.345 mg/g (Fe₃O₄@CFR@TiO₂) nanocomposites. The synthesized material remains stable even after six consecutive reaction runs and exhibited high reusability potential, which shows the use in practical applications.

Declarations

Author contribution statement

Jithendra Kumara K S: Conceived and designed the experiments. Usha Jinendra: Performed the experiments. Dinesh Bilecha, Shiva Prasad Kollur: Analyzed and interpreted the data; Wrote the paper.

B. M. Nagabhushana: Contributed reagents, materials, analysis tools or data.

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Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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