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Catalytic Properties of Graphene Oxide Synthesized by a “Green” Process for Efficient Abatement of Auramine-O Cationic Dye

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Abstract: The management of water pollution in the world is an important need and easy to implement methods are urgently needed for water purification. In this study, efforts were made to assess the efficiency of graphene oxide (GO) as a catalyst in the Fenton process to degrade water pollutants, using the Auramine-O (AM) dye as a model compound. GO was synthesized by the green and direct method using a muffle furnace and was used as a catalyst for dye degradation, along with hydrogen peroxide. The prepared GO was characterized in terms of crystalline properties, morphology and stability using various techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and thermogravimetric analysis (TGA). Dye degradation was monitored at pH 5. The effect of experimental conditions, i.e., pH, amount of GO, dye and H₂O₂ on dye degradation was determined. Further, studies were conducted on the reusability of the GO.

Key words: Graphene oxide, catalyst, wastewater, heterogeneous fenton process.

Introduction

Graphene is a 2D carbon material with unique features, such as a large surface area, thermal stability, electrical and mechanical properties, synthesized from naturally occurring graphite ¹⁻³. The oxidation of graphite results in the accumulation of oxygen functionalities such as hydroxyl, carbonyl and epoxy groups in the graphene layer to form GO ⁴. This material has a number of applications, such as sensors ⁵⁻⁶, adsorbent ⁷, catalysts ⁸, energy storage ⁹, antibacterial agent ¹⁰ and drug delivery ¹¹. It has a sp² hybridized carbon structure that is the base for 0D buckyball structures, 1D nanotubes and 3D graphite ¹². Even, among

all nanomaterials graphene based nanocomposites have inflamed worldwide researchers for dealing with various environmental issues, i.e., as photocatalyst for gaseous acetaldehyde degradation and water oxidation ¹³, for hydrogen production ¹⁴, dye degradation ¹⁵ etc.

There are various dry and wet methods available for GO synthesis. In terms of wet methods, firstly, graphite slurry was oxidized using potassium chlorate in fuming nitric acid ¹⁶. Next is Brodie's method was improved by adding sulfuric acid during oxidation process ¹⁷. Later on, a highly used process to prepare GO is by using KMnO₄ and nitric acid in concentrated sulfuric

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acid¹⁸. Nowadays, the Hummers method is modified and is commonly used¹⁹. Three basic principles are used for GO synthesis, i.e., first a mechanical method is used, followed by oxidation, second, exfoliation in aqueous medium takes place, through ultrasonic treatment, and third, exfoliation, followed by oxidation in strong acidic medium. A toxic gas ClO_2 is emitted when Brodie and Staudenmaier methods are used. The Hummers method is time consuming in terms of separation and purification process.

In the dry method, oxidation of graphite occurs at ultra-high vacuum conditions, avoiding the disadvantages of the wet methods. In the present study, we synthesized GO by a dry method, along with a “green” process, using sweet lime peels as a source of carbonaceous material. This process did not require the use of any toxic solvent, such as sulfuric acid, nitric acid or potassium chlorate, and no toxic gas was emitted.

The presence of dyes in aquatic systems adversely affects the lifecycle of aquatic animals and plants, by inhibiting sunlight from entering the water stream. Further, dyes are toxic and affect the natural color of the aquatic systems. These compounds are usually non-biodegradable and a lot of effort is needed to achieve their safe degradation²⁰⁻²⁵. Auramine-O ($\text{C}_{17}\text{H}_{22}\text{ClN}_3$, bis[4-(dimethylamino) phenyl] methaniminium chloride, AM), is a dye traditionally used for dyeing leather, silk, linen, cotton, bamboo and paper. The International Agency for Research on Cancer (IARC) included AM in the list of possible carcinogens due to its bio-transformation into reactive species in rat and human²⁶. Various methods have been reported for its removal²⁷⁻³².

Some previous research reported the use of heterogeneous catalyst to be the best route to mineralize pollutants in both day and night³³⁻³⁴. Graphene is often used as a metal-free catalyst for advanced oxidation process³⁵⁻³⁶. Very high surface area, superb adsorption efficiency and tunable structure of GO make it a more efficient catalyst compared to metal oxides³⁷. Advanced oxidation involves the transfer of electrons from the active sites of the catalyst to generate hydroxyl radicals and anions from hydrogen peroxide to degrade pollutants present in water³⁸⁻⁴⁰. Thus, the

design and development of non-toxic catalysts, capable to remove large amounts of hazardous dyes from wastewater in a short time, is crucial. Thus far, there are no studies on the potential removal of AM dye using GO prepared by “green”, cost effective and less time consuming route as a heterogeneous Fenton catalyst. Therefore, in the present investigation, we developed a “green” route for GO synthesis and used the material to catalyze AM degradation, using the Fenton process at pH 5, under ambient temperature conditions (25°C).

Materials and methods

Chemicals

Hydrogen peroxide (30 %), sodium sulfite, sodium hydroxide, sulfuric acid and ferrocene (99 %) were obtained from Merck, India. Double distilled water was used for all the reactions. Sweet lime peels were collected from the juice stalls of a local market. Auramine-O (S.D. Fine Chemicals) was used as model azo dye.

Synthesis of graphene oxide

Initially, sweet lime peels were washed with tap water and then rinsed 4 to 5 times with double distilled water; they were left to dry for the following 4 to 5 days and then ground in a mortar. Finally, 0.5 g of sweet lime peel powder were mixed with 0.3 g of ferrocene in a crucible and heated in a muffle furnace at 400°C, for 15-17 min. A black solid residue was collected after allowing the mixture to cool down naturally to room temperature. This product was subjected to further analysis.

Characterization

X-ray powder diffraction (XRD) patterns were recorded on a Bruker AXS D8 Advance instrument using Cu radiation ($\lambda = 0.1541 \text{ nm}$) and a Si (Li) PSD detector. The morphological features and particle size of the synthesized GO were characterized by scanning electron microscopy (SEM, JEOL Model JSM-6390LV) and high-resolution transmission electron microscopy (HR-TEM, JEOL/JEM 2100). Thermogravimetric analysis (TGA) was conducted on a Mettler Toledo DSC 822e instrument to assess the thermal stability of the synthesized GO.

Degradation studies

All the experiments were conducted in 100 mL beakers using UV-Visible spectroscopy to monitor the changes in the absorbance of the dye. Initially, the reaction mixture, consisting in GO and AM in aqueous medium, was allowed to react, while stirring in the dark for 30 min. After stabilization at the desired pH, the reaction was allowed to proceed. A calculated volume of hydrogen peroxide was poured after complete homogenization of the reaction mixture to completely mineralize the dye. This point was considered as starting time, $t=0$ min. Small aliquots were periodically withdrawn from the conical flask, and sodium sulfite was immediately added to the reaction mixture, in order to consume the residual H_2O_2 and to instantly stop the reaction. All these steps were repeated with water replacing hydrogen peroxide to calculate the adsorption efficiency of GO. The removal percentage (%R) of the dye was calculated using the following formula:

$$\% R = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Where C_0 (mg/L) is the initial concentration of the dye and C_t (mg/L) is the concentration after a given time t .

Results and discussion

Characterization of GO nanoparticles

XRD analysis

XRD is mainly used to determine the microstructural properties of the materials, such as crystal size, microstrain, d-spacing, dislocation density. The XRD diffractogram of GO shown in Figure 1, exhibits a diffraction peak at 12.218° corresponding to the (002) carbon plane. The particle size was calculated by the Debye Sherrer's equation, and Bragg's equation helped to find the d-spacing, while micro-strain was calculated by Stokes-Wilson, and the Williamson-Smallman's method to calculate dislocation density (Equation 2-5, Table 1)⁴⁰⁻⁴¹.

$$\% D = \frac{K\lambda}{\beta \cos\theta} \times 100 \quad (2)$$

$$n \lambda = 2 d \sin\theta \quad (2)$$

$$\epsilon \text{ str} = \frac{\beta}{4 \tan\theta} \quad (4)$$

$$\delta = \frac{1}{D^2} \text{ lines/m}^2 \quad (5)$$

Where, D is the size of the crystal, K is a constant (~ 0.89), λ represents wavelength (0.1541

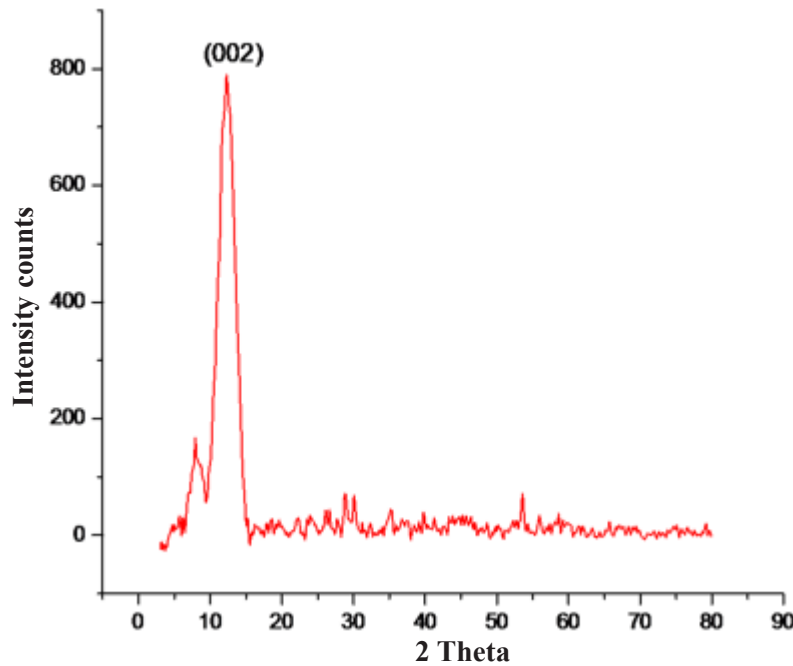


Figure 1. XRD diffractogram of synthesized GO

Table 1. Microstructural properties of GO obtained from XRD data

Crystal size, D (nm)	2.97
Interlayer spacing, d (nm)	0.72
Micro strain, ϵ	10.96×10^{-2}
Dislocation density, δ (lines/m ²)	11.33×10^{16}

nm), and β defines the full width at half maximum (FWHM) and interlayer spacing (d).

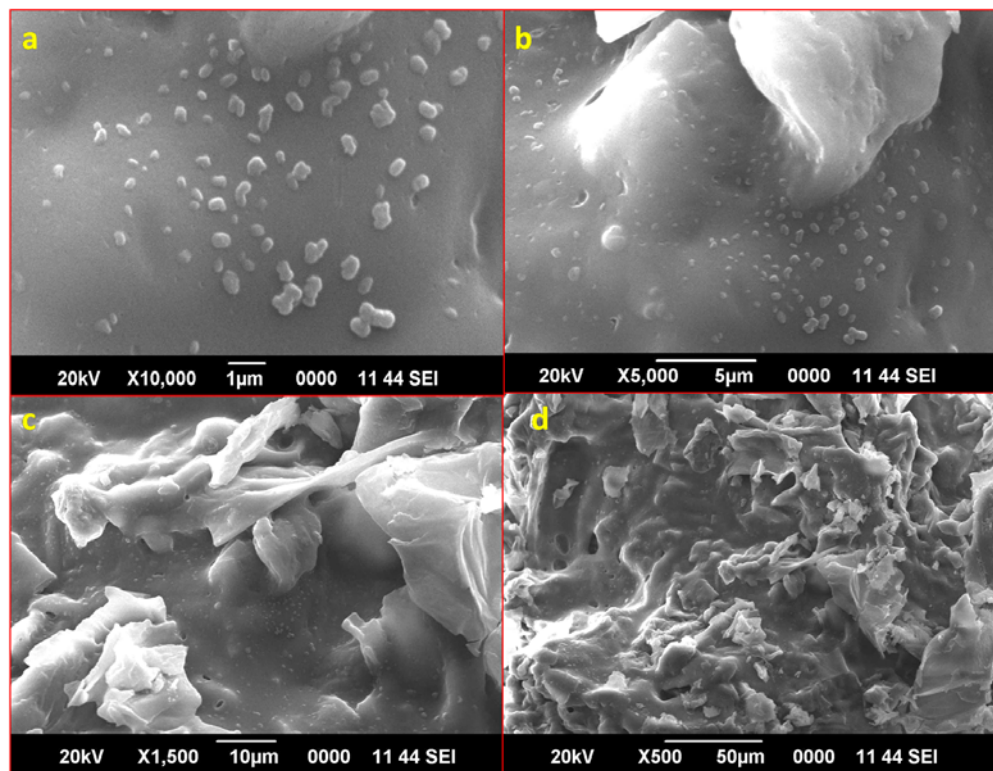
The surface morphology and structure of the as-synthesized GO were determined by SEM analysis. Images of exfoliated GO are shown in Figure 2, at different magnifications from 500 $\times$ to 5000 $\times$, in the scale range of 1 to 50 μ m.

HR-TEM was used to determine the average particle size of the as-synthesized GO, which was in the range of 24-30 nm. The HR-TEM image of GO synthesized from sweet lime shows particle agglomeration with porous morphology (Figures 3a). Selected area electron diffraction (SAED) analysis was employed to analyze the crystalline state of the sample, as shown in Figure 3b. The results indicated that GO has a polycrystalline nature.

TGA and differential thermal analysis (DTA)

were conducted to determine the thermal stability of GO. The GO sample was heated from 38.16 $^{\circ}$ C to 740 $^{\circ}$ C with an incremental rate of 20 $^{\circ}$ C/min in air. The obtained thermal patterns are presented in Figure 4.

The initial weight loss, from 10.298 mg to 9.777 mg, is attributed to moisture loss in the temperature range of 38.16 $^{\circ}$ C to 134.17 $^{\circ}$ C. Beyond this point, until 220 $^{\circ}$ C, the compound was very stable. In the temperature range of 250 $^{\circ}$ C to 510 $^{\circ}$ C, continuous and rapid weight loss occurred due to the decomposition of labile oxygen groups, such as carboxylates, anhydrides and lactone groups. In the temperature range of 510 $^{\circ}$ C to the end, up to 740 $^{\circ}$ C, high-temperature pyrolysis of the carbon skeleton occurred. No weight loss occurred beyond this point. When compared to the initial weight of the sample (10.298 mg), we were left

**Figure 2.** SEM images of the synthesized GO with a flaky structure

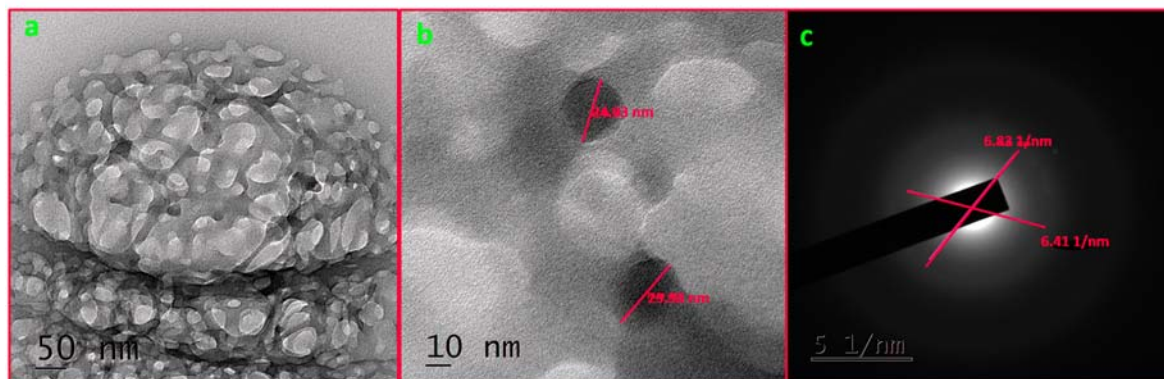


Figure 3. (a) HRTEM image (b) SAED patterns (c) particle size by HRTEM image of the synthesized GO nanoparticles

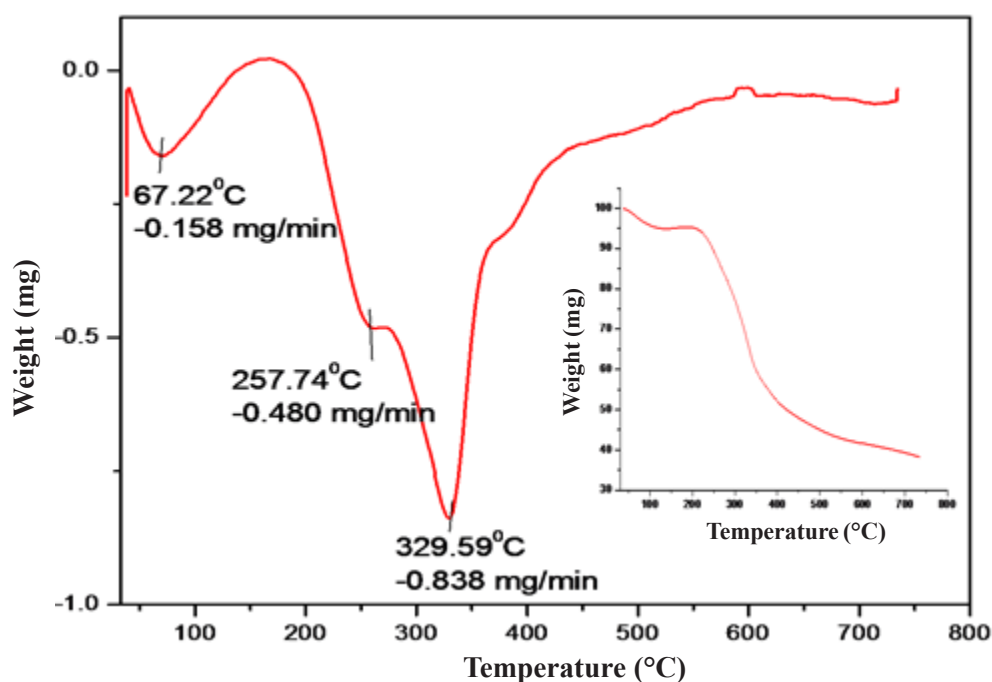


Figure 4. TGA curve. Inset: DTA curve of the synthesized of GO nanoparticles

with a residue of 3.942 mg, which indicated a weight loss of 61.72 %. DTA was used to measure the difference in the temperature of a sample with a reference, with temperature increase. The exothermic peak at 192.39°C in Figure 4 (inset) indicates a probable phase change in GO from amorphous to anatase. Further, three endothermic peaks were also observed at 67.22, 257.74, and 329.59°C.

Photo-degradation studies

AM degradation increases during the heterogeneous Fenton process ($\text{H}_2\text{O}_2 + \text{GO}$), because GO

transfers photo-generated electrons to H_2O_2 , to produce hydroxyl radicals for AM removal, and ultimately increases the degradation efficiency and provides more surface area to react with dyes. On the other hand, the uncatalyzed reaction (only with H_2O_2) is very slow, while the presence of the catalyst (GO) alone induced only a small dye removal (Figure 5).

Effect of pH

One of the most important parameters affecting AM removal is the pH. The classical Fenton reactions yield the best degradation results only

in the acidic pH range (3 to 4). Therefore, we studied the effect of pH for AM removal in the range of 3-11 (Figure 6). AM removal was almost completely within 120 min at pH=3-5, similarly to the classical Fenton process.

However, the removal efficiency decreased to 50 %, in alkaline medium (pH = 11). It can then be concluded that GO slightly broadened the effective pH limit for degradation to 3-5.

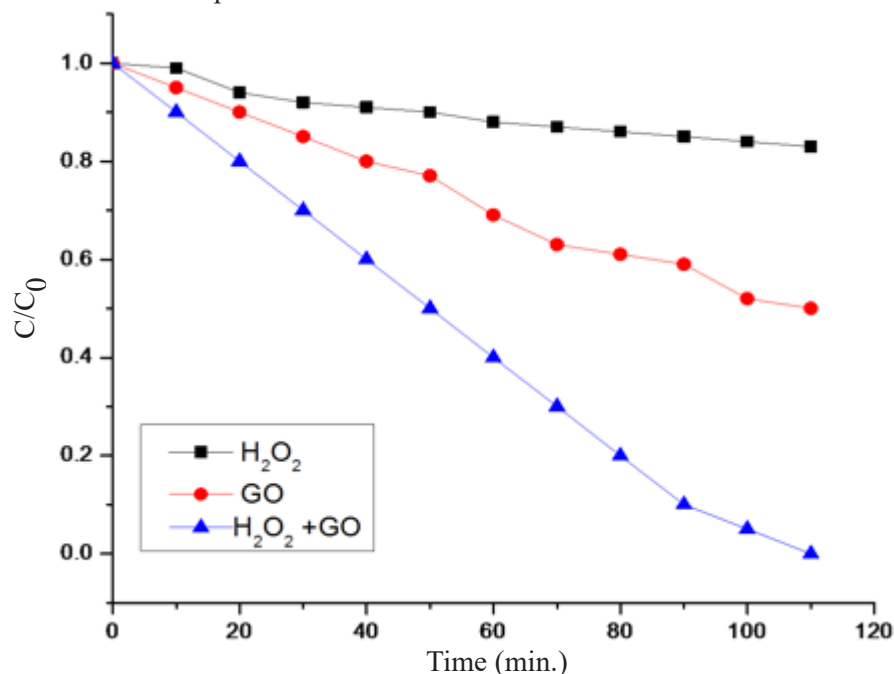


Figure 5. Kinetics of AM degradation in different conditions
[AM]=35 mg/L, $[H_2O_2]$ = 9 mmol/L, [GO]= 0.5 g/L, pH =5, room temperature

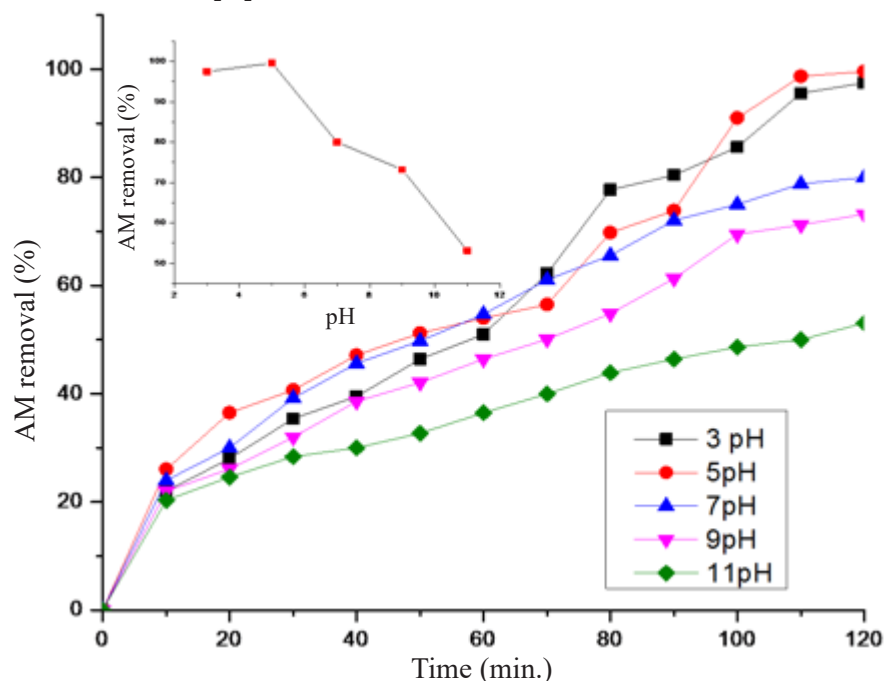


Figure 6. AM removal (%) with time at different pH values. Reaction conditions: [AM]=35 mg/L, $[H_2O_2]$ = 9 mmol/L, [GO]= 0.5 g/L, room temperature. Inset: AM (%) removal at pH 3-11

Effect of H_2O_2

The effect of H_2O_2 on AM removal was investigated in the concentration range of 3-15 mmol/L. Figure 7 shows that the dye removal efficiency increased upon increasing the concentration of hydrogen peroxide from 3 mmol/L to 15 mmol/L; however, after this concentration limit, the removal rate was not significantly affected because it acts as scavenger for hydroxyl radicals. At higher concentrations, perhaps hydrogen peroxide cannot generate a large number of hydroxyl radicals. Therefore, we used a hydrogen peroxide concentration of 9 mmol/L for the removal of AM, as a concentration higher than this would only increase the cost of the reaction.

Effect of catalyst dosage

The traditional Fenton process is limited by a narrow pH range. Research indicates that use of a heterogeneous catalyst may help in overcoming this problem. Using an adequately high quantity of catalyst is of great importance; therefore, in this study, we varied the catalyst concentration from 0.1 g/L to 2 g/L and studied its influence (Figure 8). The initial removal rate increased upon the catalyst concentration increase, as more active sites were formed, which in turn generated

a large number of hydroxyl radicals, that assisted in AM removal. When the catalyst concentration was 0.5, 1.0, and 2.0 g/L, the dye removal rate was almost 100 %. As the concentration of catalyst increases, active sites in catalyst also increases. This access of active sites sometimes slows down/stop further the removal process. So, in the present case, at initial concentrations, the catalyst easily generates hydroxyl radicals and may be at higher concentration and acts as hydroxyl radical scavenger. This indicates that an excess of the catalyst is not required. Thus, the catalyst concentration of 0.5 g/L is optimal for 100 % AM.

Effect of AM variation

To study the effect of AM dosage on the removal efficiency, AM concentration in the reaction mixture was varied from 15 to 55 mg/L (Figure 9). It was observed that, as the dye concentration increased, more time was required for total removal, as expected.

Reaction mechanism

We propose a mechanism for the effective removal of AM dyes from aqueous mixtures, using GO as catalyst in the modified Fenton process.

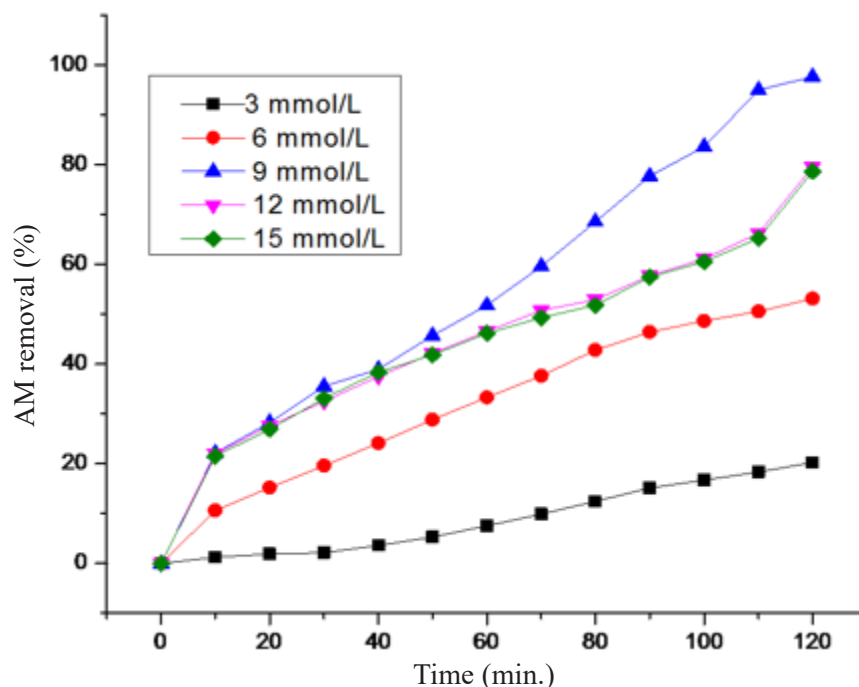


Figure 7. Effect of $[\text{H}_2\text{O}_2]$ on AM removal (%). Reaction conditions: $[\text{AM}] = 35 \text{ mg/L}$, $[\text{GO}] = 0.5 \text{ g/L}$, $\text{pH} = 5$, room temperature

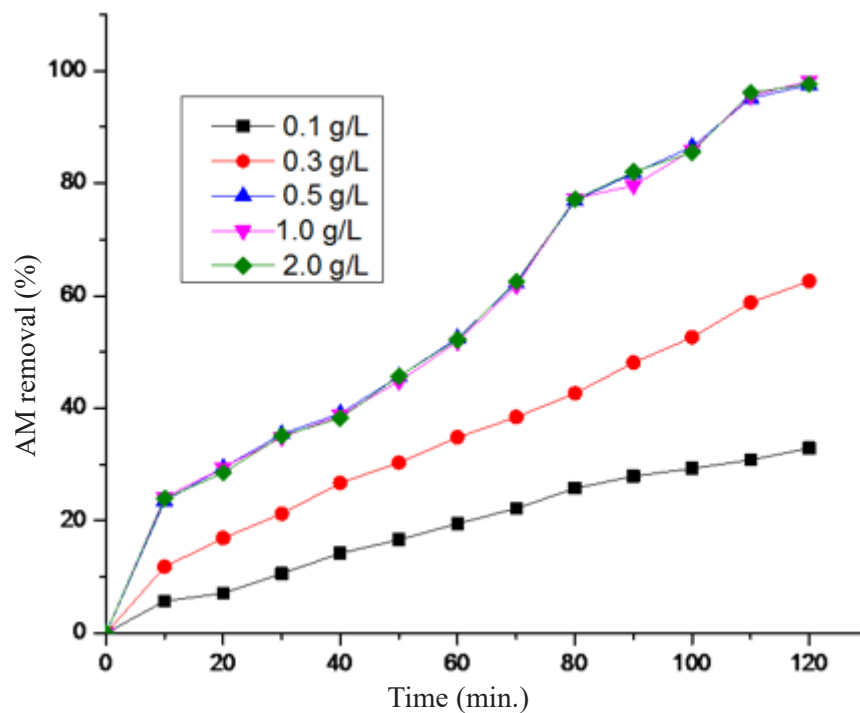


Figure 8. AM removal (%) at different GO concentrations. Reaction conditions: [AM]=35 mg/L, [H₂O₂] = 9 mmol/L, pH =5, room temperature.

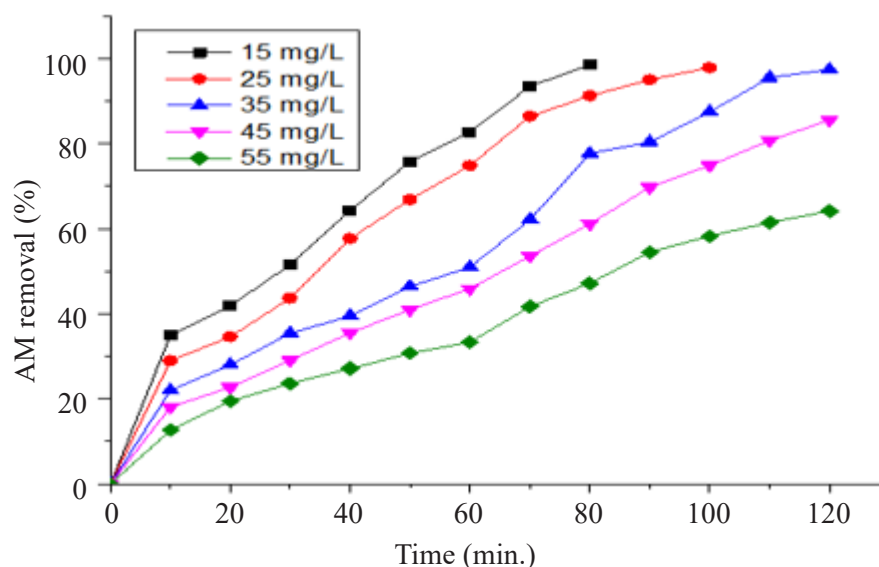


Figure 9. AM removal (%) at different AM concentrations. Reaction conditions: [H₂O₂] = 9 mmol/L, [GO]= 0.5 g/L, pH =5, room temperature

Initially, GO leads to the generation of a large number of hydroxyl radicals from hydrogen peroxide. GO generates an electron and a hole and this hole is generated in the valance band after the jump of electron to the conduction band. Later, the hydroxyl radical is generated when

hole reacts with an aqueous reaction mixture and superoxide radical anion ($\bullet\text{O}_2^-$), generated by the electrons from the conduction band, reacts with dissolved oxygen. If we go through the literature and compare the oxidation potential of superoxide radical anion and hydroxyl radical, the hy-

droxyl radical is more responsible for efficiently decolorizing the dye. In brief, AM is a cationic dye which behaves as an electrophile and radical generated during the Fenton process acts as a nucleophile. This nucleophile attacks on electrophile to break it into small molecules. These assist in the breakdown of AM into smaller molecules, such as Michler's ketone, 4-dimethylamino-benzoic acid, 4-hydroxy benzoic acid, hydroquinone, maleic acid, oxalic acid, and later into smaller molecules, i.e., CO_2 and H_2O , as shown in Scheme 1.

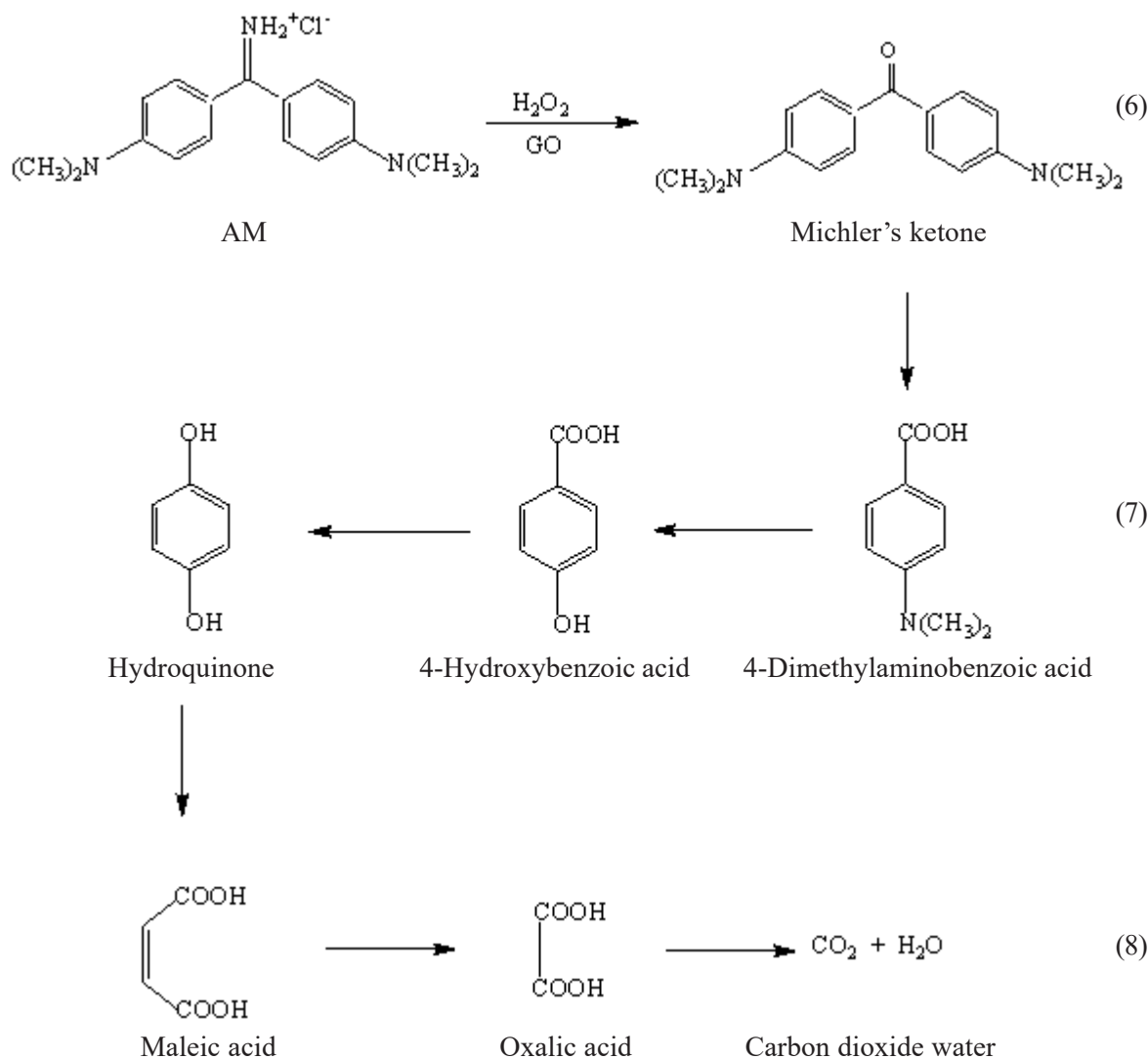
factor when considering its reuse. To evaluate the stability of GO in the modified Fenton process, we used it repeatedly for several consecutive AM removal cycles. The solid catalyst was separated from the reaction mixture each time, washed with ethanol, distilled water, and then vacuum dried. Figure 10 clearly demonstrates that GO retained 97 %-98.5 % of its catalytic activity after 8 cycles. The small decrease in its catalytic activity may be attributed to its incomplete removal during washing. In summary, GO exhibits high stability during AM removal from aqueous mixtures.

Catalyst reuse

The stability of a catalyst is the most important

Conclusions

GO was successfully synthesized in a "green"



Scheme 1. Overall pathway proposed for the degradation of AM in a heterogeneous Fenton process catalyzed by GO

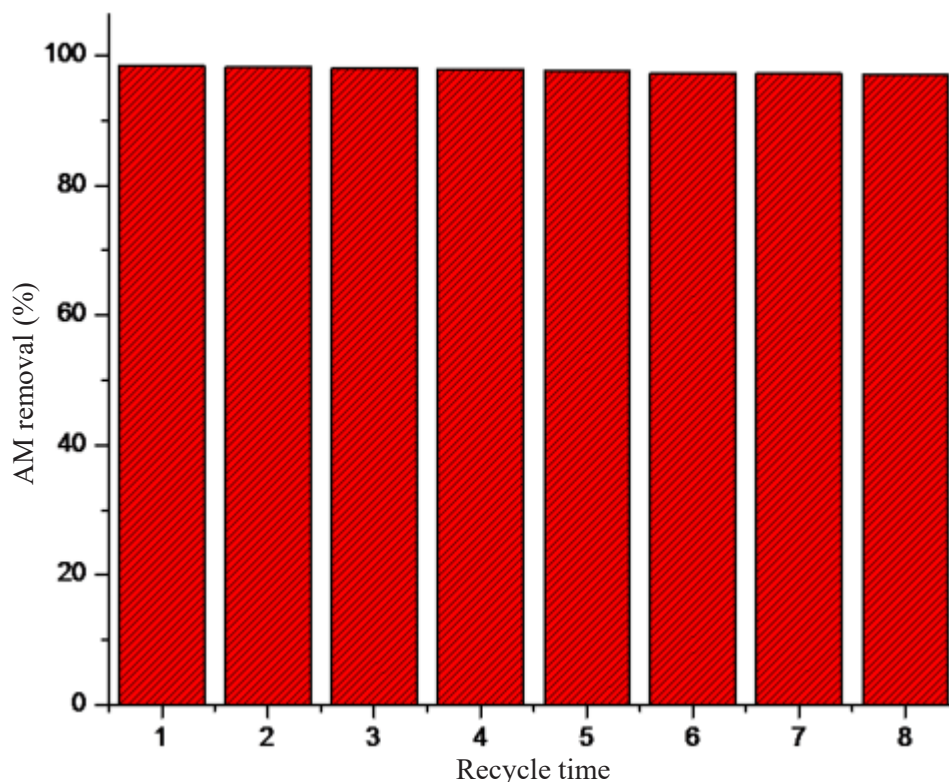


Figure 10. Reuse and stability of GO after several AM removal cycles. Reaction conditions: [AM]= 35 mg/L, [H₂O₂] = 9 mmol/L, [GO]= 0.5 g/L, pH =5, room temperature

and facile manner from sweet lime peel using ferrocene in a muffle furnace. The resulting GO nanoparticles exhibited excellent heterogeneous catalytic properties for AM removal from aqueous mixtures, according to the Fenton mechanism. The recovery properties of this catalyst indicate its good long-term stability, tested up to 8 cycles without much loss of activity. Furthermore, the use of such a heterogeneous catalyst helps in overcoming the limitations faced in a Fenton process with a homogeneous material. Therefore, the methodology proposed in this study is expected

to open up a new way to synthesize GO at a commercial scale and promote its use as heterogeneous catalyst in the Fenton process for industrial wastewater treatment.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

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