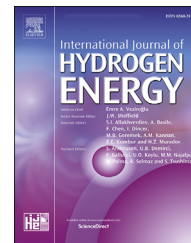


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Au nanoparticles decorated on magnetic nanocomposite (GO-Fe₃O₄/Dop/Au) as a recoverable catalyst for degradation of methylene blue and methyl orange in water

Neda Esmaeili ^{a,c}, Pourya Mohammadi ^{a,c}, Mehdi Abbaszadeh ^b, Hassan Sheibani ^{a,*}

^a Department of Chemistry, Shahid Bahonar University of Kerman, Kerman, 76169, Iran

^b Pharmaceutics Research Center, Institute of Neuropharmacology, Kerman University of Medical Sciences, Kerman, 76175493, Iran

^c Young Researchers Society, Shahid Bahonar University of Kerman, Kerman, 76169, Iran

HIGHLIGHTS

- Green synthesis of silver nanoparticles using *Acorus calamus* plant extract.
- Preparation and characterization of the GO-Fe₃O₄/Dop/Au nanocomposite as a recoverable magnetic nanocatalyst.
- Reduction of methylene blue and methyl orange in water at room temperature.
- Good catalytic activity after running 7 cycles without significant decreasing catalytic activity.

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ABSTRACT

In the present research, magnetically recyclable graphene oxide (GO)/dopamine hydrochloride/AuNPs nanocatalyst are prepared by a green path with *Acorus calamus* seeds extract as a stabilizing and reducing agent and its catalytic efficiency was used for the reduction of methylene blue (MB) and methyl orange (MO) in the presence of NaBH₄ as a reducing agent in the aqueous medium in the ambient conditions. The prepared nanocatalyst was characterized by X-ray diffraction (XRD), vibrating sample magnetometer (VSM), transmission electron microscopy (TEM), Fourier transformed infrared (FT-IR) spectroscopy, scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) and UV–Vis spectroscopy. The prepared nanocatalyst has good catalytic activity and can be regain by an external magnet and recycled several times without considerable loss of its catalytic activity in the process of reduction of organic dyes.

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* Corresponding author.

E-mail address: hsheibani@uk.ac.ir (H. Sheibani).

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Introduction

Graphene, the single layer graphite material, is now well known for its unusual electronic properties [1], high surface area [2], room temperature Hall [3], tunable band gap [4], excellent thermal [5], easy surface modification [6], and feasible applications in various research fields. useful and potential applications of graphene include electronics [7], energy storage [8], sensors [9], plasmonics [10], adsorption [11], electrochemical [12], meta-materials [13], drug delivery [14], catalyst [15] as well as various medical [16], and other industrial processes enhanced or provided by the use of new graphene materials. Among the new derivatives of graphene, graphene oxide (GO) has been much considered by researchers. When the exfoliated sheets contain only one or a few layers of carbon atoms like graphene, the achieved structures are named GO [17], which is applied in the fields of biology, absorption, catalyst, and separation [18]. The nanocatalysts are important substances in chemical processes and prevention of environmental pollution [19–39]. The green chemistry synthesized nanocatalysts have features such as high surface area, controllable shape and size, high selectivity, easy separation of reaction mixtures, and a variety of chemical modifications. Moreover, they are appropriate for solving environmental and industrial challenges [40–46]. The magnetic separation of the catalyst from the reaction mixture has been considered due to the less catalyst is wastes [47–49]. The composition of magnetic nanoparticles (Fe_3O_4 NPs) with GO as nanocatalyst has been extensively investigated [50]. The inimitable properties of GO-based magnetic Fe_3O_4 such as a high surface-to-volume ratio (s/v), good conductivity, inexpensive cost, and an environmentally benign temperment have opened options for useful applications [51]. Today, one of the global concern for the water environment is dye contamination wastewaters. In fact, the world bank calculations about 17–20% of industrial water contamination were released from textile dyeing and treatment processes [52]. As requirements become more accurate, the need for useful treatment of these contaminants is imperative prior to release into natural water bodies [53]. Due to their complex structures, are not easily biodegradable [54]. Methylene blue (MB) is the most common soluble dye in water that is generally applied for cotton, printing and tannin, medicinal purposes and dying leather [55]. Methyl Orange (MO) is an acidic dye that used in pharmaceutical, textile, and paper industries [56]. Therefore, reducing these dyes and turning them into harmless materials is great importance. With regard to our previous works on nanocatalysts to reduce organic dyes matter [57], the present study was conducted to synthesize $\text{GO}/\text{Fe}_3\text{O}_4@\text{Dop}/\text{Au}$ magnetic nanocatalyst by grafting the dopamine group on GO and accumulation of Au NPs. Also, its catalytic efficiency was evaluated on the organic dyes of MB and MO. Finally, the prepared nanocatalyst was easily separated by an external magnet and recovered from a reaction mixture and reused for the next reaction. The catalytic activity of nanocatalyst had reduced slightly after several time.

Experimental

Preparation of extract

Dried seeds of *Acorus calamus* plant (Fig. 1) were washed and dried. Then, 6 gr of powder dried seeds were extracted with 100 mL of the mixture of solvents ethanol/deionized water (1:1) at 100 °C using the soxhlet extractor for overnight. The precipitate was filtered at 25 °C and dried.

Synthesis of Au NPs using the aqueous extract seed of *Acorus calamus*

For the purpose, 6 mL of 1.5 mM HAuCl_4 solution was diluted and put in a round-bottom flask. Then, the prepared solution was stirred at 60 °C and subsequently, 1 mL of the plant extract with 2.5% (w/v) concentration was added to it. Finally, the UV–Vis spectra ($\lambda = 540$ nm) of the solution was done which shown the formation of Au nanoparticles.

Synthesis of magnetic Fe_3O_4 NPs

Typically, to prepare Fe_3O_4 nanoparticles, 1.37 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.5 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ with molar ratio (2/1) were dissolved in distilled water. The prepared solution under N_2 gas was heated at 60 °C for 45 min and next 11 mL of ammonia solution was added dropwise to the it. Subsequently, the process was continued for 60 min to ensure completion of the reaction. Finally, the prepared Fe_3O_4 nanoparticles were collected using an external magnet and then washed several times with H_2O , dried at room-temperature for overnight.

Synthesis of GO and GO-Cl

According to Humber modified method, graphene oxide was prepared from graphite. For the preparation of GO-Cl, 0.3 g of GO added to the 25 mL of thionyl chloride and was refluxed for 24 h and then and. Finally, the product was centrifuged and washed several times with dried dichloromethane (without water) and dried at roomtemperature for 24 h.



Fig. 1 – Plant of *Acorus calamus*.

Synthesis of $\text{Fe}_3\text{O}_4@\text{DOP}$

To prepare $\text{Fe}_3\text{O}_4@\text{DOP}$, 0.568 g dopamine hydrochloride and 0.12 g NaOH were mixed followed by adding 20 mL distilled water to the previous solution and stirred for 20 min. Next, 0.25 g of Fe_3O_4 NPs was dispersed in deionized water by an ultrasonic bathroom and then stirred at 40 °C for 6 h. The final product was washed several times with distilled H_2O and EtOH (1:1) and dried at room temperature.

Synthesis of $\text{GO}/\text{Fe}_3\text{O}_4@\text{Dop}$

About 0.33 g of $\text{Fe}_3\text{O}_4@\text{Dop}$ was dispersed to 40 mL of dried DMF. Then, the solution was sonicated at 50 °C for 10 min. Next, 0.025 g GO-Cl dispersed in 20 mL dried DMF and then was added to the resultant solution and then sonicated by ultrasonic bathroom for 15 min. After that, the component was refluxed at 70 °C and the mixture was centrifuged and washed with acetone. The collected precipitates were dried at room temperature for 24 h.

Synthesis of $\text{Fe}_3\text{O}_4@\text{Dop}/\text{GO}/\text{Au}$ nanocatalyst

Au NPs were supported on $\text{GO}/\text{Fe}_3\text{O}_4@\text{Dop}$ by using the in-situ method. A certain amount of $\text{GO}/\text{Fe}_3\text{O}_4@\text{Dop}$ was added to the 40 mL of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and vigorously stirred at 60 °C for 60 min and then, 5 mL of *Acorus calamus* plant extract slowly was added to the reaction mixture and stirred for 3 h at 60 °C. The product was separated by an external magnet and washed with distilled water and ethanol (1:1). Finally, the prepared magnetic nanocatalyst dried at room temperature for overnight.

Catalytic degradation of organic dyes using $\text{GO}/\text{Fe}_3\text{O}_4@\text{Dop}/\text{Au}$ NPs nanocatalyst

Catalytic degradation of MB and MO dyes were select as the model reaction. In a generic experiment, 2 mL of MO dye (3.05×10^{-5} M) or MB dye (3.12×10^{-5} M) aqueous solution and different amounts of nanocatalyst (1, 2, and 3 mg) were blended followed by the addition of 2 mL of prepared NaBH_4

aqueous solution (0.2 M) and was allowed to stir at room temperature. Next, the conversion reaction progress was considered by recording the time-dependent UV–vis absorption spectra of the reaction mixture using a spectrophotometer in the range of 300–600 nm. After the end of the reaction, the nanocatalyst was separated by using an external magnet, several times washed with ethanol and water (1:1), and then reused for the next reactions.

Results and discussion

XRD analysis

Fig. 2 presents the XRD pattern of the $\text{Fe}_3\text{O}_4@\text{Dop}/\text{GO}/\text{Au}$ NPs nanocatalyst. The peaks appeared at $2\theta = 76.5^\circ$, 4.64° , 5.44° , and $2/38^\circ$ related to miller coefficients of (111), (200), (220), and (311) nanoparticles gold with a cubic structure, which demonstrates the existence of gold with a cubic structure and also, the peaks are sharp that can be due to the ordered and crystalline phase of Au nanoparticles. The particle size of Au nanoparticles was obtained using the Debye-Scherrer equation ($D = (0.9\lambda)/(\beta \cos \theta)$, where λ (wavelength), θ (angle of diffraction), and β (full width half maximum intensity), and D (average crystal size). Hence, the average cubic crystal size of the Au nanoparticle is 64.1 nm. Also, the diffraction peaks of Fe_3O_4 NPs at $2\theta = 28.9^\circ$, 36.1° , 45.1° , 55.2° , 58.4° , 65.8° that related to the (220), (311), (400), (422), (511), (440) planes of Fe_3O_4 . Widely observed peaks can be due to poor crystallinity or small grains of nanoparticles.

TEM images of $\text{GO}/\text{Fe}_3\text{O}_4@\text{Dop}/\text{Au}$ NPs

TEM images of $\text{GO}/\text{Fe}_3\text{O}_4@\text{Dop}/\text{Au}$ NPs were shown in Fig. 3. The graphene sheets are shown in the images as gray sheets. These images showed which nanoparticles of Fe_3O_4 and Au in immobilized on GO are uniformly distributed on the surface of GO. The black grains in the images prove the presence of Fe_3O_4 and Au nanoparticles immobilized on the surface of GO.

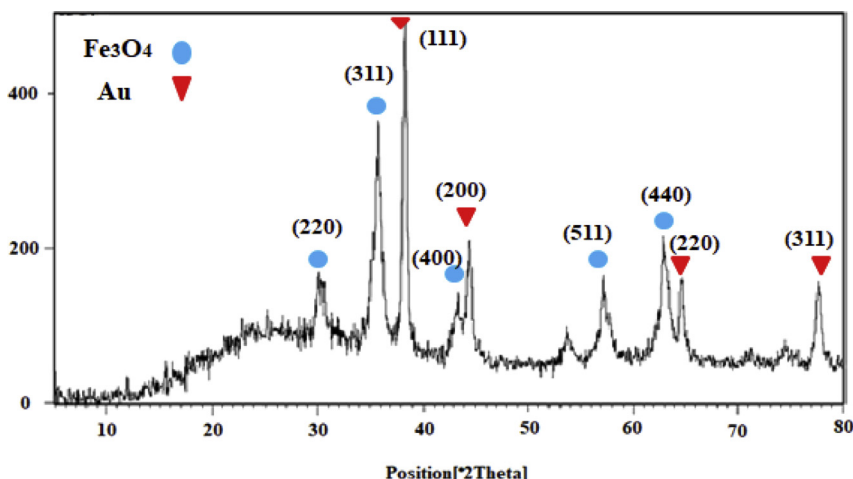


Fig. 2 – XRD pattern of $\text{GO}/\text{Fe}_3\text{O}_4@\text{DOP}/\text{Au}$ nanocatalyst.

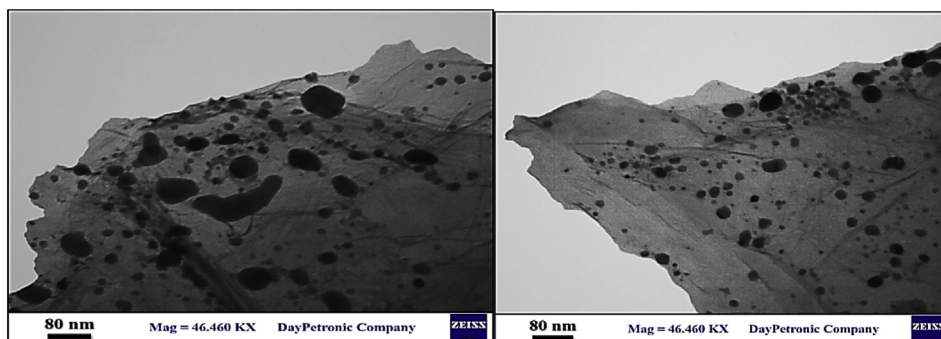
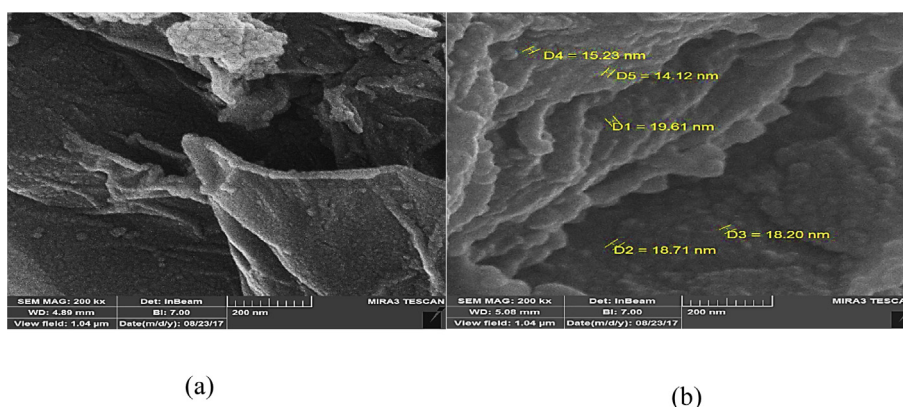


Fig. 3 – TEM images of GO/Fe₃O₄@DOP/Au.

SEM images and EDS of GO/Fe₃O₄@Dop/AuNPs

The morphology of the nanocatalysts prepared using the SEM was confirmed. Fig. 4a was shown the structure of the graphene oxide layer. Also, Fig. 4b shows uniform and homogeneous distributions of nanoparticles on the surface of GO and the size of nanoparticles ranged from 14.12 to 19.61 nm. On the other hand, graphene oxide crumbling in the final nanocatalyst can be attributed to the immobilization of Au

nanoparticles and its functionalization by dopamine. The EDS analysis of the GO/Fe₃O₄@Dop/AuNP_s sample is shown in Fig. 4c. As can be seen, the elements presence of Fe and Au which confirmed the presence of Fe₃O₄ and Au in the nanocatalyst. The existence of the peak of carbon in the EDS analysis because of the presence of graphene oxide. Also, the presence of oxygen in the prepared nanocatalyst is due to the modification with hydroxyl, epoxide and etc functional groups.



(c)

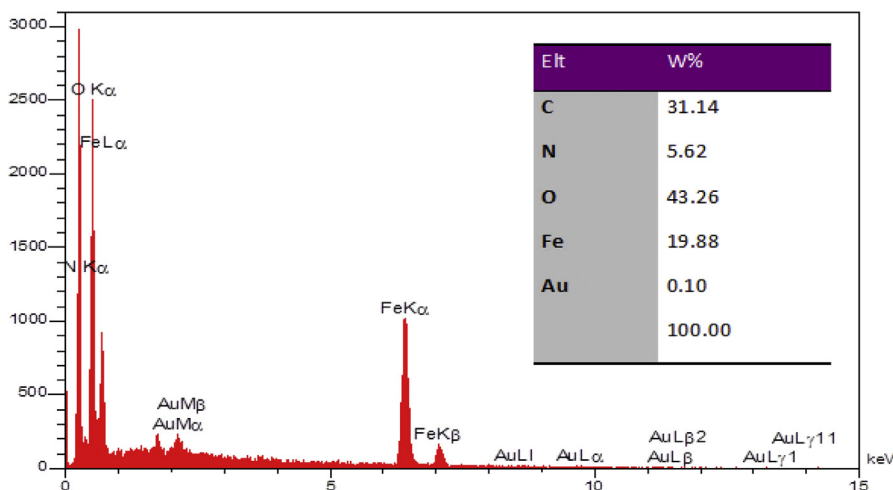


Fig. 4 – SEM of GO (a) and SEM of GO/Fe₃O₄@Dop/AuNPs (b) and EDS analysis of GO/Fe₃O₄@Dop/AuNPs(c).

VSM analysis

Fig. 5 exhibits the magnetic analysis of nanocatalyst $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}/\text{AuNPs}$. The amount of saturated magnetism for Fe_3O_4 , $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}$ composite and $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}/\text{AuNPs}$ nanocomposites were 69.90, 45.77 and 42.02 emu/g, respectively. This magnetic reduction due to the coating of magnetic nanoparticle with Dop groups and Au NPs. In addition, the VSM diagram of Fe_3O_4 NPs does not show a magnetic residue. Consequently, Fe_3O_4 NPs have a superparamagnetic structure. The results of VSM showed that the synthesized nanocatalyst has good magnetic properties for reducing pollutants.

FT-IR analysis

The prepared products were characterized by FT-IR spectra. Fig. 6a–c depict the FTIR spectra of $\text{Fe}_3\text{O}_4@/\text{Dop}$, $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}$, and $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}/\text{AuNPs}$ nanohybrids, respectively. As shown in Fig. 6a, the characteristic peak at 3425 cm^{-1} is credited to the existence of O–H and N–H stretching vibrations at the dopamine and Fe_3O_4 , respectively. The peak at 575 cm^{-1} related to the bending absorption of Fe–O stretches. Absorption bands at 1485 cm^{-1} belong to C=C stretching vibrations of benzene ring. As shown in $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}$ nanocomposites, the peak appeared at 1626 cm^{-1} is most related to the stretching vibration of C=O and the absorption band at 1121 cm^{-1} corresponds to the C–N bending vibration. Fig. 6c shows the FT-IR spectrum of $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}/\text{AuNPs}$. Since Au NPs do not have an absorption band in the FT-IR region, the FT-IR spectrum of $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}/\text{Au}$ nanoparticles is approximately the similar to $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}$ nanocomposites.

UV–vis analysis of *Acorus calamus* seed extract and green synthesized Au NPs

In this work, AuNPs were prepared using *Acorus calamus* seed extract. The UV–Vis spectrum of sample synthesized AuNPs using *Acorus calamus* seed extract is indicated in Fig. 7a and also the maximum absorption of UV–Vis of *Acorus calamus* seed extract is 292 nm and presented in this figure. When the $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution was added to the extract, the color of the solution turned to bright red, also was observed maximum

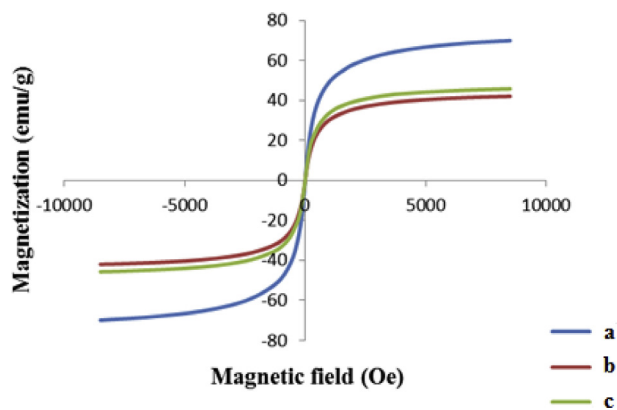


Fig. 5 – VSM analysis of a) Fe_3O_4 , b) $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}$ and c) $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}/\text{Au}$

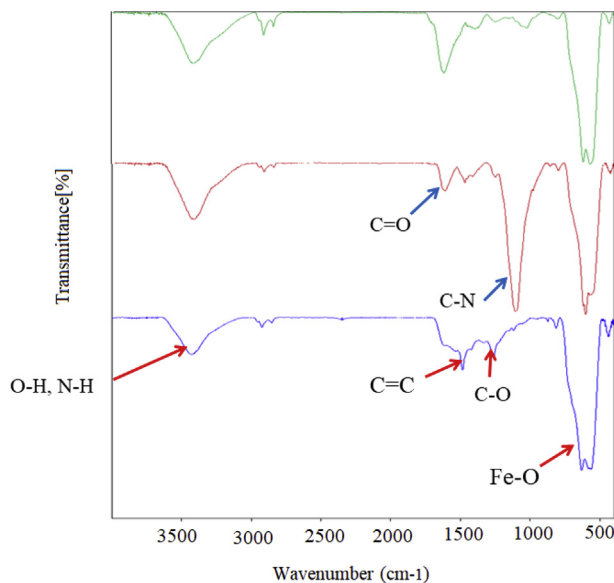
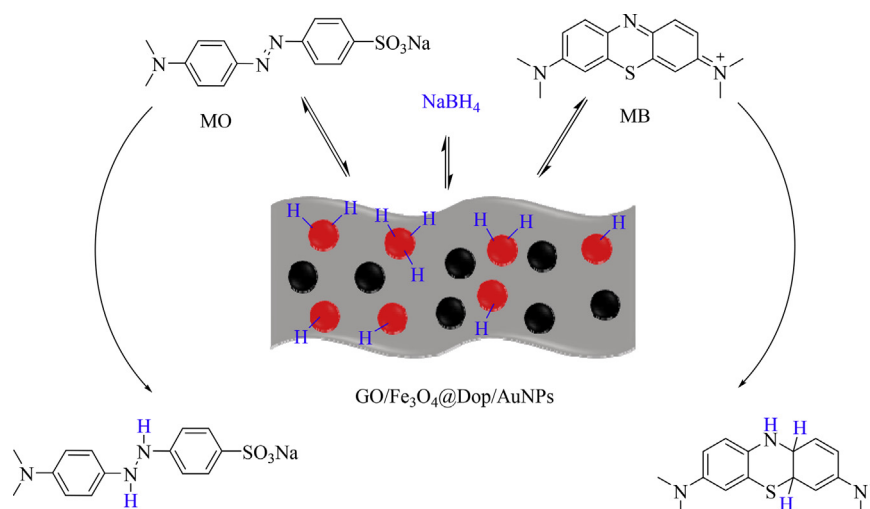


Fig. 6 – FTIR spectra of $\text{Fe}_3\text{O}_4@/\text{Dop}$ (a), $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}$ (b), $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}/\text{AuNPs}$ (c).

absorption of UV–Vis of Au NPs at 550 nm (Fig. 7b, S1), suggesting the forming of Au^0 from Au^{3+} ions.

Application of $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}/\text{AuNPs}$ for catalytic reduction of MB and MO

To consider the efficiency of the prepared $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}/\text{AuNPs}$ catalyst, the reduction reaction of the recognized dyes, MO and MB were considered using NaBH_4 . The progress of reduction reaction was done through the measurement of the absorption spectra maximum of the azo dyes (MO and MB) at consecutive times using UV–Vis spectroscopy (Figs. 8 and 9, S2 and S3). In Figs. 8 and 9 was shown degradation spectra of dyes MB and MO for 1, 2, and 3 mg. Also, UV–Vis spectra of MO and MB colorful aqueous solutions display maximum absorption peaks at 664 and 466 nm, respectively, which disappear in 120 (1 mg), 60 (2 mg) and 40 s (3 mg) as a result of MO degradation and 20 (1 mg), 15 (2 mg), and 5 s (3 mg) as result of MB degradation by $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}/\text{AuNPs}$ in the presence of NaBH_4 . However, the color of the solution was immediately changed from colorful to colorless after the addition of $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}/\text{AuNPs}$ catalyst into it and reduction reaction was completed at short times, for MB and MO. The mechanism of the reduction reaction of MB and MO in the attendance of $\text{GO}/\text{Fe}_3\text{O}_4@/\text{Dop}/\text{AuNPs}$ and NaBH_4 can be follow by the Langmuir–Hinshelwood model [56]. For as much as in the reaction the concentration of NaBH_4 is greater than the concentration of the MB and MO, this reaction can be considered as a pseudo-first order reaction. Accordingly, the dyes concentration during the reaction (C_t) were obtained from the absorbance of the dye at the λ_{max} of it. The rate of reduction reaction was considered with respect to time, based on a decrease in absorbance of the λ_{max} peak versus time. The ratio of absorbance of dye at the time of reduction (measured at time t) to A_0 (measured at $t = 0$) is equal to the



Scheme 1 – The reduction mechanism of MO, MB using NaBH₄ in the presence of GO/Fe₃O₄@Dop/AuNPs nanocatalyst.

concentration ratio C_t/C_0 of the dye at that the time. Therefore, for determination of the apparent rate constant (k_{app}) was used the following equation:

$$dC_t/dt = dA_t/dt = kC_t \text{ or } \ln(C_t/C_0) = \ln(A_t/A_0) = -kt.$$

Apparent rate constant for the MO degradation kinetics obtained from the slope of $\ln(A_t/A_0)$ versus time plot in Fig. 8b, d and f were obtained for 1, 2, and 3 mg of catalyst 0.0126, 0.0183, and 0.193 (s^{-1}), respectively. As well as can be concluded from Fig. 9, the rate constant obtained for MB for 1 and 2 mg catalyst is 0.088 and 0.147 (s^{-1}), respectively (Fig. 9b and d). Also, TON and TOF of catalyst were calculated which were obtained for MB (1 mg catalyst) 29.3 and 0.146 s^{-1} and MO (1 mg catalyst) 29 and 0.019 s^{-1} , respectively. This methodology for the removal of organic dyes was on basis of reduction reactions, on the other hand, various methods used on basis of photo-oxidation, that this method usually has a long time reaction, but chemical reactants less than reduction reaction method is used [58–61]. Also, was shown the reduction mechanism of MO, MB using NaBH₄ in the presence of GO/Fe₃O₄@Dop/AuNPs nanocatalyst (Scheme 1).

Recycle of the catalyst

In order to investigate recyclability and stability of GO/Fe₃O₄@Dop/AuNPs in the reduction reaction of the MB and MO, the catalyst after the end of the reaction can be separated with an external magnet, washed, and dried and finally used for the subsequent run of catalysis. This method was repeated 7 times and the time was recorded for completion of dyes reduction reaction. The activity of the GO/Fe₃O₄@Dop/AuNPs catalyst is not significantly reduced for neither of MB and MO dyes. The leaching test of the prepared catalyst was done. The results of ICP-AES analysis shown that this catalyst has good stability. (amount of Au decreased from 0.21 to 0.19 mmol.g⁻¹).

Conclusion

In this research, the AuNPs were synthesized using *Acorus calamus* seed extract as a stabilizing and reducing nontoxic agent. The synthesized nanocomposite can be used as a good efficiency catalyst for the reduction of azo dyes such as methylene blue (MB) and methyl orange (MO) and can be applied to the catalytic reduction of other reducible pollutants. Moreover, GO/Fe₃O₄@Dop/AuNPs prepared nanocatalyst is able to recovered several times by an external magnet and can be used again. Meanwhile, the synthesized nanocatalyst can be mentioned advantages such as easy separation, good catalytic activity and good stability.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2019.07.025>.

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