Sonochemical activation-assisted biosynthesis of Au/Fe₃O₄ nanoparticles and sonocatalytic degradation of methyl orange

Álvaro de Jesús Ruíz-Baltazar

CONACyT-Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México, Boulevard Juriquilla 3001, Santiago de Querétaro, Qro 76230, Mexico

ARTICLE INFO

Keywords:
Biosynthesis of Au/Fe₃O₄ nanoparticles
Sonocatalytic degradation
Spectroscopy

ABSTRACT

In this research, a sonochemical activation-assisted biosynthesis of Au/Fe₃O₄ nanoparticles is proposed. The proposed synthesis methodology incorporates the use of Piper auritum (an endemic plant) as reducing agent and in a complementary way, an ultrasonication process to promote the synthesis of the plasmonic/magnetic nanoparticles (Au/Fe₃O₄). The synergistic effect of the green and sonochemical synthesis favors the well-dispersion of precursor salts and the subsequent growth of the Au/Fe₃O₄ nanoparticles.

The hybrid green/sonochemical process generates an economical, ecological and simplified alternative to synthesizing Au/Fe₃O₄ nanoparticles with enhanced catalytic activity, pronounced magnetic properties. The morphological, chemical and structural characterization was carried out by high-resolution Scanning electron microscopy (HR-SEM), Energy Dispersive X-Ray Spectroscopy (EDS) and X-Ray diffraction (XRD), respectively. Ultraviolet–visible (UV–vis) and X-ray photoelectron (XPS) spectroscopy confirm the Au/Fe₃O₄ nanoparticles formation. The magnetic properties were evaluated by a vibrating sample magnetometer (VSM). Superparamagnetic behavior of the Au/Fe₃O₄ nanoparticles was observed ($M_s = 51$ emu/g and $H_c = 30$ Oe at 300 K).

Finally, the catalytic activity was evaluated by sonocatalytic degradation of methyl orange (MO). In this stage, it was possible to achieve a removal percentage of 91.2% at 15 min of the sonocatalytic process (160 W/42 kHz). The initial concentration of the MO was 20 mg L⁻¹, and the Fe₃O₄-Au dosage was 0.075 g L⁻¹. The MO degradation process was described mathematically by four kinetic adsorption models: Pseudo-first order model, Pseudo-second order model, Elovich and intraparticle diffusion model.

1. Introduction

In recent years, the magnetic-plasmonic materials have been widely studied due to their applications as bifunctional nanomaterials in several areas, including biology, biomedicine, bio-labelling, optics, electronics and catalysis [1-3]. Generally, the magnetic-plasmonic materials are composed in their magnetic part by superparamagnetic iron oxides nanoparticles (SPION), which are employed in wastewater treatment, heterogeneous catalysis, drug delivery, cancer treatment, magnetic resonance imaging (MRI), biological separation, photocatalysis and hyperthermia [4-6]. Regarding the plasmonic part, are composed of a noble metal such as Au. In whose case has been employed in electrochemical sensors, biocompatible systems, as antibacterial material and advanced oxidation process (AOPs) [7-11]. Recently, the AOPs has reported a high efficiency in wastewater treatment and pollutant degradation due to the AOPs promote the formation of highly reactive hydroxyl radicals, which exhibits a significant oxidation potential [12-14]. Some AOPs such as sonolysis, sonocatalysis, sonophotocatalysis, electro-Coagulation, electro-peroxene and Fenton process, among others, has been employed in the degradation of Methylene Blue, Methyl Orange, Acid Orange 7 (AO7), Basic Violet 10 (BV10), diclofenac, ciprofloxacin, moxifloxacin, Arsenate, Auramine-O (AO, acid blue 129, Chromium, nitrophenol [13,15-18].

Nonetheless, the properties of the magnetic-plasmonic materials depend in great measure of the morphology and particle size distribution [19]. In this sense, the implementation and study of new methodologies to synthesize magnetic plasmonic materials are focused on the green chemical and the use of the physico-chemical procedures that reduce or eliminate the use of toxic chemical reagents [20-23].

In recent years, sonochemistry has been widely studied due that offers a great quantity of application in many fields of knowledge. Nonetheless, the potential sonochemistry applications have not been exploited in deep [20,21]. Specifically, in the sonochemical synthesis of nanomaterials, the use of ultrasound in chemical reactions, favors the
The sonochemical synthesis has been generally employed to obtain well-dispersed and core–shell type nanoparticles [1].

On the other hand, the employ of the green chemistry in the synthesis of metallic and bimetallic nanoparticles has covered a preponderant role due to the green chemistry reduce or eliminate the use and/or generation of hazardous substances [7,24,25]. In this sense, the great quantity of organic and biocompatible components presents in the plant extracts (antioxidants, phenolic compounds, flavonoids, also known as secondary metabolites, which including the flavones, flavanols, isoflavones, flavanones and anthocyanidins), have promoted the use of plant extracts as reducing or stabilizing agents in the synthesis of nanomaterials, due to these organic components are directly involved in the reduction of metallic ions of the precursors [26,27].

The use of the endemic plant species such as Cynara cardunculus, Silybum marianum, Lonicera japonica, Melissa officinalis, Artemisia absinthium, Anthemis nobilis, Lonicera japonica, Melissa officinalis, Artemisia absinthium, Absinthium, Anthemis nobilis, Thymus kotschyanus, Moringa oleifera flower, Cricus Benedictus and Justicia spicigera were reported in the obtention of Au and Fe3O4 NP’s [28-32]. Nonetheless, the Piper auritum extract, has not been employed for the magnetic plasmonic nanoparticles of Au/Fe3O4 composition. The Piper auritum is an endemic and medicinal plant that grows in the tropical area of Central America. The Piper auritum, offers antimicrobial properties due to the great quantity of phytoalexins in their composition, which are compound of low molecular weight in the Piper auritum as result of the biotic and abiotic stresses [33-35]. In this sense, this work proposes the green synthesis of Au/Fe3O4 nanoparticles by Piper auritum extract and sonochemical activation. The synergic effect of the green synthesis and the sonochemical synthesis offers a functional methodology to the obtention of Au/Fe3O4 nanoparticles with significant catalytic and magnetic properties. Complementary, the sonocatalytic degradation of methyl orange is also studied, being possible to achieve a removal percentage of 91.2% at 15 min of the sonocatalytic process (160 W/42 kHz). Is important to mentioning that result obtained were highly competitive in relation to those reported in the literature, considering the simplification and economy of the catalyst synthesis route, as well as the low power of the ultrasound equipment and mainly the short period of time in which the sonocatalytic degradation was carried out.

2. Experimental section

2.1. Sonochemical activation-assisted green synthesis of Au/Fe3O4 nanoparticles

The proposed synthesis of Au/Fe3O4 nanoparticles, is based on the precursor salts reduction method by Piper auritum extract.

In the first stage of the process, The Piper auritum extract was obtained from the mixture of 200 ml of deionized water with 15 g of Piper auritum leaves (previously dried). The mixture obtained was heated at 100 °C for 10 min. In parallel form, a HAuCl4⋅3H2O solution at 50 mM was prepared. The Piper auritum extract and the HAuCl4⋅3H2O solution were mixed and ultrasonicated at 42 kHz for 15 min. Finally, a solution of salt precursors of de FeCl3⋅6H2O and FeCl2⋅4H2O was incorporated into the reaction in a ratio Fe (III)/Fe (II) = 2 under ultrasonic agitation for 60 min. The ultrasonic bath was operated at 42 kHz of frequency and 160 W (Digital Ultrasonic Cleaner, Brand: Kendall, Model: CD-4820; 9.5 × 5.9 × 3.0 in.) in all phases of the synthesis. The water volume employed in the ultrasonic bath was 1750 ml. The Ph reaction was adjusted to 11 by NaOH solution. The Au@Fe3O4 nanoparticles were washed with isopropl alcohol and lyophilized for their characterization. Fig. 1 shows the green synthesis of Au@Fe3O4 by Sonochemical activation.

Table 1

| Model                  | Equation                        | Integrated form                      |
|------------------------|---------------------------------|--------------------------------------|
| Pseudo-First Order     | $\frac{dq}{dt} = k_1(q_e - q_t)$ | $\ln(q_e - q_t) = \ln q_e - k_1 t$  |
| Pseudo-Second Order    | $\frac{dq}{dt} = k_2(q_e - q_t)^2$ | $\frac{1}{q_t} = \frac{1}{k_2 q_t^2} + \frac{1}{q_e t}$ |
| Elovich                | $\frac{dq}{dt} = \alpha e^{-q_t}$ | $q_t = \frac{1}{p} \ln(\alpha t) + \frac{1}{p} t^2$ |
| Intraparticle diffusion | $q_t = k_4 \sqrt{t} + C_1$        |                                       |

Fig. 1. Illustrative scheme of the sonochemical activation-assisted biosynthesis of Au/Fe3O4 nanoparticles.
2.2. Sonocatalytic degradation of Methylene orange (MO)

The Sonocatalytic degradation process of MO was carried out using an ultrasonic bath at 42 kHz. The initial MO concentration (pollutant) was 20 mgL⁻¹. Posteriorly, three solutions of Au/Fe₃O₄/MO at 25, 50 and 75 mgL⁻¹ were prepared. The solutions were placed in the ultrasonic bath. Aliquots of the Au/Fe₃O₄/MO solutions were collected, and the absorbance was measured by UV–vis in intervals of 1 min until the minimum surface plasmon resonance (SPR) value was observed. All experiments were performed in the dark at room temperature to nullify the photocatalytic reaction. The adsorption kinetic of the MO degradation was described by four models showed in Table 1 [36-39].

3. Results and Discussion.

3.1. Scanning electron microscopy (SEM)

Fig. 2 (a) Shows the morphology of the Au/Fe₃O₄ nano-alloys obtained by the hybrid green/sonochemical synthesis. In this image, a spherical morphology is appreciated. The observed agglomeration in the sample can be associated presumably with the stearic effect of the Au/Fe₃O₄ nanoparticles, whose effect is produced by the magnetic interaction between the individual particles. A size distribution particle size approximately of 35 nm can be observed. However, by subsequent analysis of X-ray diffraction (XRD), the crystallite size will be calculated.

Fig. 2 (b). Shows the Energy Dispersive X-Ray Spectroscopy (EDS)
analysis of the Au/Fe$_3$O$_4$ nano-alloys. The main elements identified were Fe, O and Au. Confirming the chemical composition of the Au/Fe$_3$O$_4$ nanostructures. In complementary form, Fig. 2 (c) reveals an SEM image of the Au/Fe$_3$O$_4$ nanostructures obtained by detection of secondary electrons (SE) at high magnification (220 kX). In this figure is possible to appreciate in detail the morphology, size distribution and structure of the Au/Fe$_3$O$_4$ nano-alloys. To identify the location of each element, Fig. 2 (d)-(e), shows an elemental mapping of the sample obtained by EDS. In both images, is possible to identify the Au as a core of the nanostructure, while the Fe and O are situated on the Au surface. This fact indicates presumably, the core–shell type structure formation.

Fig. 3 (a)-(c) display an additional EDS mapping of the Au/Fe$_3$O$_4$ nanostructures, while Fig. 3 (d)-(e) show Composition profile obtained by EDS line-scan across the sample, confirming the arrangement of the Au, Fe and O elements, gold in the core and Fe/O on the Au surface.

3.2. X-Ray diffraction analysis

Fig. 4 (a) shows the XRD pattern of the Au/Fe$_3$O$_4$ nanostructures obtained by sonochemical activation and (b)-(c) the intensities associated to the planes (Fe$_3$O$_4$-220) and (Au-111) of the Au/Fe$_3$O$_4$ nanoparticles.

| $2\theta$  | d-spacing  | hkl      | Area     | FWHM  | Shape factor | Max Height |
|----------|------------|----------|----------|-------|--------------|------------|
| 17.78723 | 4.8219     | Fe$_3$O$_4$ (1 1 1) | 1190.06465 | 8.6247 | 1.77498      | 55.46122   |
| 30.21173 | 2.9571     | Fe$_3$O$_4$ (2 2 0) | 239.20025  | 0.64835 | 0.44965      | 296.35886  |
| 35.58971 | 2.5185     | Fe$_3$O$_4$ (3 1 1) | 864.21665  | 0.639  | 0.70339      | 982.47862  |
| 38.16011 | 2.3515     | Fe$_3$O$_4$ (4 0 0) | 346.19008  | 0.80786 | 1.04958      | 266.37591  |
| 43.30779 | 2.0925     | Fe$_3$O$_4$ (5 1 1) | 216.97002  | 0.67555 | 0.84157      | 211.79379  |
| 44.39807 | 2.0365     | Fe$_3$O$_4$ (4 2 2) | 86.93023   | 0.22669 | 2.11608      | 114.52376  |
| 53.67608 | 1.7061     | Fe$_3$O$_4$ (4 4 0) | 490.96835  | 2.9535  | 1.84485      | 63.29905   |
| 57.27823 | 1.6102     | Fe$_3$O$_4$ (5 3 3) | 155.36929  | 0.73323 | -0.16396     | 209.58352  |
| 62.91244 | 1.4802     | Fe$_3$O$_4$ (4 4 0) | 289.67727  | 0.7049  | 0.5022       | 325.56291  |
| 64.46336 | 1.44       | Au (2 2 0)     | 195.38711  | 2.07424 | 1.28117      | 51.94736   |
| 74.32472 | 1.2588     | Fe$_3$O$_4$ (5 3 3) | 671.28478  | 3.76323 | 2.11375      | 53.39942   |
| 77.77532 | 1.2281     | Au (3 1 1)     | 58.67757   | 1.03287 | 3.21387      | 15.93292   |

Vp(x) = nL(x) − [(1 − n)G(x)]

(2)
where \( L(x) \) is the Gaussian curve which are described mathematically as:

\[
L(x) = \frac{1}{1 + \left( \frac{x - x_0}{\sigma} \right)^2}
\]

And \( G(x) \) is the Gaussian curve represented as:

\[
G(x) = \exp\left[-\frac{(x-x_0)^2}{2\sigma^2}\right]
\]

Fig. 4 (b)–(c) displays the intensities associated with the planes \((\text{Fe}_3\text{O}_4\cdot220)\)- and \((\text{Au} \cdot 111)\) respectively. In both figures the Gaussian and Lorentzian part of the Pseudo-Voight function is displayed.

The equation that governs the Williamson-Hall method described as follows:

\[
\frac{\beta \cos \theta}{\lambda} = \frac{1}{D_V} + 2\varepsilon \left( \frac{2 \sin \theta}{\lambda} \right)
\]

Graphically, the terms \( \frac{\beta \cos \theta}{\lambda} \) and \( 2 \sin \theta/\lambda \), denotes the microstrain and domain size, which are calculated from the slope and intercepts values, respectively [44]. Fig. 5 show the graphically the results of the Williamson-Hall analysis. The crystallite size calculated from this method is 24.44 nm. Which are in good agreement to the particle size observed by SEM.

3.3. X-ray photoelectron spectroscopy (XPS) analysis.

The valence state or electron structures of the \(\text{Au}/\text{Fe}_3\text{O}_4\) nanoparticles obtained by green/sonochemical synthesis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
nanoparticles obtained was studied by X-ray photoelectron spectroscopy (XPS). Fig. 6 (a) reveals a XPS survey spectra of Au/Fe$_3$O$_4$ nanoparticles. In this figure, the Fe 2p, O 1s and Au 4f signals were fully identified. This result confirms the Au/Fe$_3$O$_4$ nanoparticles formation and support the structural morphological, chemical and structural characterization presented previously.

Fig. 6 (b) presents the HR-XPS spectrum corresponding to the Fe2(p) orbital. The binding energies located at 724.8 and 711.2 eV, are associated to the Fe 2(p)\(^{1/2}\) and Fe 2 (p)\(^{3/2}\) spin orbitals of magnetite, respectively. Specifically, the energy separation between Fe 2 (p)\(^{1/2}\) and Fe 2p\(^{3/2}\), exhibits a typical value (13.6 eV) attributed the core level signal of Fe$_3$O$_4$[45].

Fig. 6 (c) displays the orbitals of Au (f)\(^{3/2}\) and Au (f)\(^{7/2}\), which were located at 87.8 and 84.1 eV, respectively [4,5]. Finally, Fig. 6 (d) shows the HR-XPS spectrum of the O 1(s) orbital, presumably associated to the Fe$_3$O$_4$ phase of the sample. The binding energy observed at 530.3 eV corresponds to the O 1(s) orbital. The XPS analysis corroborate and support the Au/Fe$_3$O$_4$ nanoparticles obtention through the proposed green/sonochemical method.

### Table 3
Capacitance specific for each cycle of the cyclic voltammetry of the Au/Fe$_3$O$_4$ nanoparticles (m = 0.001 g, scan rate = 50 mVs$^{-1}$ and (V2-V1) = 2.1 V).

| Cycle | Area (V*mA) | Cp (F/g) |
|-------|-------------|----------|
| 1     | 0.047       | 0.222    |
| 2     | 0.047       | 0.225    |
| 3     | 0.048       | 0.229    |
| 4     | 0.049       | 0.234    |
| 5     | 0.050       | 0.239    |
| 6     | 0.051       | 0.242    |
| 7     | 0.051       | 0.245    |
| 8     | 0.053       | 0.250    |
| 9     | 0.054       | 0.256    |

Fig. 7. Cyclic voltammograms of the Au/Fe$_3$O$_4$ nanoparticles in acid media and scan rate of 50 mAV$^{-1}$.

**3.4. Electrochemical characterization of the Au/Fe$_3$O$_4$ nanoparticles by cyclic voltammetry**

Fig. 7 shows the cyclic voltammetry profile of the Au/Fe$_3$O$_4$ nanoparticles, obtained from the –0.6 to 1.5 V at scan rate of 50 mVs$^{-1}$. The cathodic scan shows a reduction peak located at 0.3 V, which can be correlated with Au structure [46,47]. While a oxidation peak is observed at 0.62 V during the anodic stage, which can be also associated to the Au structure [48].

Is important to mentioning, that an oxidation or reduction peak associated to the Fe is not observe. This result indicates presumable, the Au interaction is predominant in the electrochemical behavior of the Au/Fe$_3$O$_4$ nanoparticles synthesized by green methodology. On the other hand, the stability of the sample is pronounced, due that after 9
cycles, the cyclic voltammetry does not exhibit significant variations in potential or current. With the results obtained, the specific capacitance of the material was calculated (Table 3) from the following equation [46].

$$C_P = \frac{Q}{mV}$$  \hspace{1cm} (5)

where:

- $C_P$ is the specific capacitance.
- $Q$ is the average charge during the charging and discharging process.
- $m$ is the mass of the active materials.
- $V$ is the potential window.

Regarding to the optical characteristics of the Au/Fe$_3$O$_4$ nanoalloy, Fig. 8 (a) shows a UV–vis spectrum of the Fe$_3$O$_4$ and Au/Fe$_3$O$_4$ nanoparticles. The typical intensity attributed to the surface plasmonic resonance (SPR) of the gold was observed at 535 nm. This fact corroborates the plasmonic nature of the nanoparticles synthesized by sonochemical activation-assisted biosynthesis of Au/Fe$_3$O$_4$ nanoparticles. Fig. 8 (b) display the band gap energy ($E_g$) which was determined according to the Tauc plot. The values of band gap for the Fe$_3$O$_4$ and Au/Fe$_3$O$_4$ were 2.64 and 2.77 eV, respectively. Based in these calculations, is possible to affirm that the presence of the Au, increase the band gap value of the material, and consequently, best catalytic properties.

### 3.5. Magnetic properties of Au/Fe$_3$O$_4$ nanoparticles

Fig. 9 display the magnetic hysteresis loops at 10, 100 and 300 K. The magnetic coercivity is nearly zero in the tree temperatures and consequently, a superparamagnetic behavior can be considered. The hysteresis loop at 300 K exhibits a mostly pronounced superparamagnetic behavior [49]. The saturation magnetization observed for the Au/Fe$_3$O$_4$ nanoparticles are in the range of 51 to 58 emu/g, whose value is inside the average values reported anteriorly. Moreover, the variations in the coercive field as a temperature function can be attributed to the crystallite size or interaction effects between the nanoparticles and/or canted spins at the surface and magnetic anisotropy [13,50]. However, the variations temperature dependence of the coercive field in the samples at 100 and 300 K it was minimums, in contrast with the sample evaluated at 10 K. Hence, the temperature dependence of the coercive in this case can be attributed to the temperature of the sample.

This result suggests that a spin freezing phenomenon is carried out, considering that the particles possess two phases, Au and Fe$_3$O$_4$ and the interaction between the interface of the species (Au/Fe$_3$O$_4$) generate different regions aligned in the spins located the interface and particle surface [3,49]. Fig. 9 show a ZFC-FC curve (insert) of the Au/Fe$_3$O$_4$ nanoparticles, indicate that the blocking temperature appreciate around 340 K. Hence, at low temperature the disorder of the spin most pronounced. Consequently, at 10 K, coercive field is mayor. The magnetic parameters of the Au/Fe$_3$O$_4$ nanoparticles are insert in the Fig. 9.

### 3.6. Methyl orange sonocatalytic degradation process

In order to determine the behavior of the Au/Fe$_3$O$_4$ nanostructures in the MO Sonocatalytic degradation process, four kinetic adsorption model were employed to describe and calculate the kinetic parameter of the organic dye. Fig. 10 (a)-(d) shows the Pseudo First order, Pseudo Second Order, Elovich and Intraparticle diffusion models plotted from the experimental data collected in MO Sonocatalytic degradation process.

Table 4. Show the kinetic parameters calculated in the sonochemical degradation of methyl orange and correlation factors ($R^2$) obtained from the experimental data obtained in the MO Sonocatalytic degradation process. Based on the results obtained, the best-fitting of the correlation...
factor $R^2$, is presented for the PSO model associated to the concentration of 25 mg L$^{-1}$ of Au/Fe$_3$O$_4$ nanoparticles. In this sense, is possible to affirm that the Pseudo second order model at lower concentration, describe the MO Sonocatalytic degradation phenomena. In general form, the PSO model suggests an exchange ionic between the adsorbent and the adsorbate and implicitly, a chemisorption process [51,52].

On the one hand, this result suggests that the positive partial charges of the Au/Fe$_3$O$_4$ nanostructures promote the ionic exchange with the MO. The significant interaction between the MO molecule and the Au/Fe$_3$O$_4$ nanoparticles promotes the chemisorption process. On the other hand, the Sonocatalytic degradation process also favor the MO degradation, due that the ultrasonic waves present in the reaction (aqueous solution) generates reactive radical species such as $\cdot$OH, which contribute to the degradation of the MO molecule [53,54]. It is to say, the MO degradation rate increase due to the generation of more hydroxyl radicals. The reaction to generate of hydroxyl radicals from the dissociation of water molecules can described by the follows equations [53,54,54-57]:

\[
\begin{align*}
H_2O + &&\rightarrow &&\cdotOH + H \\
O_2 + &&\rightarrow &&2O^- \\
O^- + H_2O &&\rightarrow &&2\cdotOH
\end{align*}
\]

Fig. 10. Experimental data and kinetics models of the Au/Fe$_3$O$_4$ nanoparticles evaluated on the sonocatalytic degradation of MO, (a) Pseudo-first order, (b) Pseudo-second order, (c) Elovich and (d) Intraparticle diffusion model.

Table 4
Kinetic parameters calculated in the sonochemical degradation of methyl orange.

| Au/Fe$_3$O$_4$ NP’s Concentration | Kinetic Model | 25 mg L$^{-1}$ | 50 mg L$^{-1}$ | 75 mg L$^{-1}$ |
|-----------------------------------|--------------|----------------|----------------|----------------|
| Lagrén First-Order $K_1$ (min$^{-1}$) | $K_1$ | 0.0737 | 0.3682 | 0.6082 | 0.9412 |
| Pseudo-second Order [K2] (g⋅mg$^{-1}$⋅min$^{-1}$) | $K_2$ | 20.2574 | 0.5383 | 0.9661 | 0.6724 | 0.1244 | 0.8991 | 0.6724 | 0.1244 | 0.8991 | 0.6724 | 0.1244 | 0.8991 | 0.6724 | 0.1244 | 0.8991 |
| Intraparticle Diffusion $K_i$ (mg$^{-1}$⋅min$^{-0.5}$) | $C_i$ | 0.1854 | 0.0465 | 0.3517 | 0.0079 | 0.1160 | 0.0059 | 0.0504 | 0.9110 |
| Elovich $\alpha$ (mg$^{-1}$⋅min$^{-1}$) $\beta$ (g⋅mg$^{-1}$) | $\alpha$ | 1.1571 | 16.0963 | 0.4642 | 0.2912 | 10.9552 | 0.8959 | 0.1130 | 21.4716 | 0.7221 |
The mechanism sonocatalytic of MO degradation, can be proposed from the follow way. In a first stage, the light and heat produced by the ultrasonic cavitation of the system, produce an excitation in the catalyst, consequently, electron-hole (e– and h+) pairs are formed on the on the Au/Fe3O4 surface. Posteriorly, the interaction of the electrons on the Au/Fe3O4 surface whit the oxygen molecules produce some active species as •OH, O2•− and H2O2 from a series of reactions described in general form as:

\[ \text{Catalyst} + \text{MO} \rightarrow \text{Catalyst} (e^- + h^+) \]  
\[ [\text{Fe}_3\text{O}_4/\text{Au}] + \text{MO} \rightarrow [\text{Fe}_3\text{O}_4/\text{Au}] (e^- + h^+) \]  
\[ h^+ + H_2O \rightarrow \text{OH} + H^+ \]  
\[ h^+ + OH^- \rightarrow \text{OH}^+ \]  
\[ e^- + O_2 \rightarrow O_2^- \]  
\[ O_2^- + H_2O \rightarrow HO_2^- + OH^- \]  

Finally, the reactive species or hydroxyl groups, promotes the MO degradation molecule, contributing to the decomposition of the –N = N– bonding, given as result the disappearance of orange color in the solution [58,59]. In others words, the hydroxyl radical interact directly with the –N = N– bond of the MO, given as result the decomposition of the MO in some intermediate products such as N,N-dimethyl-p-phenylenediamine and N,N-dimethyl-benzenamine. In the final stage of the process, is possible to obtain sulfanilic acid, carbon dioxide and water. In this sense, the MO sonocatalytic degradation process carried out in the present work, is in concordance with the previous reports [59]. Fig. 11 describe the proposed sonocatalytic mechanism and possible pathway for degradation of methyl orange by Au/Fe3O4 nanoparticles.

It is important to mentioning that by the employ of the Au/Fe3O4 nanoparticles in the sonocatalytic process with the experimental conditions proposed, was possible to achieve a removal percentage of 91.2% at 15 min of the sonocatalytic process (160 W/42 kHz). Is important to mentioning that result obtained were highly competitive in relation to those reported in the literature, considering the simplification and economy of the catalyst synthesis route, as well as the low power of the ultrasound equipment and mainly the short period of time in which the sonocatalytic degradation was carried out. Table 5 shows a comparative table of various catalysts evaluated in different advanced oxidation processes (AOPs). In this sense is possible to affirm, in conclusive form, that the proposed methodology offer the possibility to obtain Au/Fe3O4 nanoparticles whit notable magnetic and catalytic properties and consequently, with potential applications and several fields. This fact, represent the main scientific achievement of this work, taking in a count the efficiency of degradation of the material and the simplicity of the synthesis methodology.

4. Conclusions

The synthesis route proposed offers a greener alternative for the obtention of Au/Fe3O4 nanoparticles with significant magnetic and photocatalytic properties. The synthesis based on Piper auritum as reducing agent and assisted by sonication exhibits many advantages under the traditional methodologies. The main advantages of the method are their simple procedure, low or null toxicity, and a low cost. Taking into count the enhanced photocatalytic activity and pronounced magnetic properties of the Au/Fe3O4 nanoparticles. On the other hand, the reduction capacity of the antioxidants species present in the Piper auritum, make possible the reduction of the metallics salts of Au and Fe. Likewise, the incorporation of ultrasound waves, complementing and favor the reaction due to the generation of reactive radical species during the collapsing of the microbubbles process. Additionally, the ultrasound waves incorporation favors the dissociation of metallic ions in the aqueous solution of the reaction. Given as result obtained, is possible to affirm that the catalytic and magnetic properties of the Au/Fe3O4 nanoparticles, can be the starter point for
futures studies and application of the Au/Fe3O4 nanoparticles obtained by the proposed green sonochemical route. Finally, the ultrasound waves present sono catalytic degradation generates reactive radical species such as *OH, which contribute to the degradation of the MO molecule. It is to say, the MO degradation rate increase due to the generation of more hydroxyl radicals.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The author of this work, make manifest their gratitude to the “Cathedras CONACYT” program and the Center of Applied Physics and Advanced Technology belonging to the National Autonomous University of Mexico (CFATA-UNAM) as well as the to the National Materials Characterization Laboratory (LaNCaM).

References

[1] M.A. Dheyab, A.A. Azza, M.S. Jameel, P.M. Khanibadi, B. Mehrdel, Mechanisms of effective gold shell on Fe3O4 core nanoparticles formation using sonochemistry method, Ultrason. Sonochem. 64 (2020) 104865, https://doi.org/10.1016/j.ultsonch.2019.104865.
[2] E. Fantechi, A.G. Roca, B. Sepúlveda, P. Torruella, S. Estrada, F. Pérez, E. Coy, S. Jurga, N.G. Bastos, J. Nogues, V. Puntes, Seeded Growth Synthesis of Au@Fe3O4 Heterostructured Nanocrystals: Rational Design and Mechanistic Insights, Chem. Mater. 29 (9) (2017) 4022–4035, https://doi.org/10.1021/acs.chemmater.7b00608.
[3] F.-J. Lin, B.-a. Dong, Catalytic Nanoreactors of Au@Fe3O4 Yolk-Shell Nanoparticles in the voltammetric detection of heavy metals: A review, TrAC - Trends Anal. Chem. 131 (2019) 1–8, https://doi.org/10.1016/j.trac.2019.04.034.
[4] R.-B. Song, S. Zhao, D. Gao, P. Li, L.-P. Jiang, J.-R. Zhang, X. Wu, J.-J. Zhu, Core/Satellite Structured Fe3O4/Au Nanocomposites Incorporated with Three-Dimensional Macroporous Graphene Foam as a High-Performance Anode for Microbial Fuel Cells, ACS Sustain. Chem. Eng. 8 (2) (2020) 1311–1318, https://doi.org/10.1021/acssuschemeng.9b07055.
[5] S. Szwedan, R. Minafo, A. Errochid, N. Jaffrezic-Renault, Metal and metal oxide nanoparticles in the voltammetric detection of heavy metals: A review, TRAC - Trends Anal. Chem. 131 (2020) 116014, https://doi.org/10.1016/j.trac.2020.116014.
[6] C. Vijilvani, M.B. Bindhu, F.C. Frincy, M.S. AlSalihi, S. Sabitha, K. Saravanakumar, S. Devanesan, M. Umadevi, M.J. Aljaafreh, M. Atif, Antimicrobial and catalytic activities of biosynthesized gold, silver and palladium nanoparticles from Solanum nigrum leaves, J. Photochem. Photobiol. B Biol. 202 (2020), 111713, https://doi. org/10.1016/j.jphotobiol.2019.111713.
[7] J.A. Fuentes-García, J. Santoyo-Salazar, E. Rangel-Cortes, G.F. Goya, V. Cardozo-Mata, J.A. Pescador-Rojas, Effect of ultrasonic irradiation power on sonochemical synthesis of gold nanoparticles, Ultrason. Sonochem. 70 (2021) 105274, https://doi.org/10.1016/j.ultsonch.2020.105274.
Fe3O4/PAN nanofibers, Mater. Res. Express. 7 (5) (2020) 055001, https://doi.org/10.1088/2053-1591/abb8bc.

[51] M.Y. Akram, S. Ahmed, L. Li, N. Akhtar, S. Ali, G. Muhydin, X.-Q. Zha, J. Nie, N-doped reduced graphene oxide decorated with Fe 3 O 4 composite: Stable and magnetically separable adsorbent solution for high performance phosphate removal, J. Environ. Chem. Eng. 7 (3) (2019) 103137, https://doi.org/10.1016/j.jece.2019.103137.

[52] T. Wen, J. Wang, X. Li, S. Huang, Z. Chen, S. Wang, T. Hayat, A. Ahsadi, X. Wang, Production of a generic magnetic Fe3O4 nanoparticles decorated tea waste composites for highly efficient sorption of Cu(II) and Zn(II), J. Environ. Chem. Eng. 5 (4) (2017) 3656–3666, https://doi.org/10.1016/j.jece.2017.07.022.

[53] Sonocatalytic degradation 1 EXCELENTE 7.pdf, (n.d.).

[54] Sonocatalytic degradation 1 EXCELENTE equations 5.pdf, (n.d.).

[55] Sonocatalytic degradation 1 EXCELENTE equations 5.pdf, (n.d.).

[56] Sonocatalytic degradation 1 EXCELENTE 6.pdf, (n.d.).

[57] S. Chong, G. Zhang, Z. Wei, N. Zhang, T. Huang, Y. Liu, Sonocatalytic degradation of diclofenac with FeCeOx particles in water, Ultrason. Sonochem. 34 (2017) 418–425, https://doi.org/10.1016/j.ultsonch.2016.06.023.

[58] C.H. Nguyen, C.C. Fu, R.S. Juang, Degradation of methylene blue and methyl orange by palladium-doped TiO2 photocatalysts for water reuse: Efficiency and degradation pathways, J. Clean. Prod. 202 (2018) 413–427, https://doi.org/10.1016/j.jclepro.2018.08.110.

[59] S. Xie, P. Huang, J.J. Kruzic, X. Zeng, H. Qian, A highly efficient degradation mechanism of methyl orange using Fe-based metallic glass powders, Sci. Rep. 6 (2016) 1–10, https://doi.org/10.1038/srep21947.

[60] A. Khataee, P. Eghbali, M.H. Irani-Nezhad, A. Hassani, Sonocatalytic synthesis of WS2 nanosheets and its application in sonocatalytic removal of organic dyes from water solution, Ultrason. Sonochem. 48 (2018) 229–239, https://doi.org/10.1016/j.ultsonch.2018.06.003.

[61] A. Hassani, G. Celelavdag, P. Eghbali, M. Sevim, S. Karaca, O. Metin, Heterogeneous sono-Fenton-like process using magnetic cobalt ferrite-reduced graphene oxide (CoFe2O4-rGO) nanocomposite for the removal of organic dyes from aqueous solution, Ultrason. Sonochem. 40 (2018) 841–852, https://doi.org/10.1016/j.ultsonch.2017.08.026.

[62] A. Hassani, A. Khataee, S. Karaca, C. Karaca, P. Gholami, Sonocatalytic degradation of ciprofloxacin using synthesized TiO2 nanoparticles on montmorillonite, Ultrason. Sonochem. 35 (2017) 251–262, https://doi.org/10.1016/j.ultsonch.2016.09.027.

[63] L. Song, S. Zhang, X. Wu, Q. Wei, Synthesis of porous and trigonal TiO2 nanoflake, its high activity for sonocatalytic degradation of rhodamine B and kinetic analysis, Ultrason. Sonochem. 19 (6) (2012) 1169–1173, https://doi.org/10.1016/j.ultsonch.2012.03.011.

[64] M. Karaca, M. Kirançan, S. Karaca, A. Khataee, A. Karimi, Sonocatalytic removal of naproxen by synthesized zinc oxide nanoparticles on montmorillonite, Ultrason. Sonochem. 31 (2016) 250–256, https://doi.org/10.1016/j.ultsonch.2016.01.009.

[65] L.L. He, X.P. Liu, Y.X. Wang, Z.X. Wang, Y.J. Yang, Y.P. Gao, B. Liu, X. Wang, Sonocatalytic degradation of methyl orange in the presence of Bi2WO6: Effect of operating parameters and the generated reactive oxygen species, Ultrason. Sonochem. 33 (2016) 90–98, https://doi.org/10.1016/j.ultsonch.2016.04.028.

[66] F. Siadatnasab, S. Farhadi, A. Khataee, Sonocatalytic performance of magnetically separable CuS/CoFe2O4 nanohybrid for efficient degradation of organic dyes, Ultrason. Sonochem. 44 (2018) 359–367, https://doi.org/10.1016/j.ultsonch.2018.02.051.