

ORIGINAL RESEARCH PAPER

Sonocatalyst efficiency of palladium-graphene nanocomposite for ibuprofen degradation from aqueous solution

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ABSTRACT

Worldwide studies on contamination levels of anti-inflammatory drugs such as ibuprofen (IBF) show that their concentration in water bodies is increasing. Graphene oxide/palladium nanoparticle (Pd NPs-GO) was synthesized via a simple solvothermal method. The characteristics of the as-prepared samples were examined using X-ray fluorescence, scanning electron microscopy, and Fourier transforms infrared spectroscopy. The performance of Pd NPs-GO nanocomposite as a sonocatalyst was evaluated for the degradation of IBF under ultrasonic irradiation (35 kHz), and compared with graphene (GO) and palladium nanoparticle (Pd NPs). Some influencing parameters such as IBF initial concentration, pH, catalyst dosage, and irradiation time were investigated. The findings showed that Pd NPs-GO nanocomposite exhibited higher sonocatalyst activity for IBF than other catalysts. A higher ibuprofen degradation efficiency was observed in lower pH (3), lower initial concentration (30 mg/L), higher catalyst dosage (2 g/L), and higher ultrasonic irradiation time (50 min). The kinetics of the degradation of IBF followed pseudo-first-order reaction kinetics.

Keywords: Catalysis; Ibuprofen; Nanocomposites; Palladium; Ultrasonics

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INTRODUCTION

Pharmaceutical and personal care products (PPCPs) include a diverse group of medicines used in veterinary medicine, agricultural activities, human health (e.g. such as analgesics, antibiotics, hormones) and personal care products (e.g. cosmetics, insecticides, and preservatives) [1]. These compounds are used to diagnose, prevent, and treat various types of human and livestock diseases. In a short period of time after being consumed, they are eliminated from the body. Because of their high polarity and low volatility, they can easily be entered and transported into water supplies [2, 3]. Many PPCPs are poisonous, stable and semi-sustained and resistant to biodegradation and have high bioaccumulation potential; therefore, they

can have harmful effects on human health and the environment, even at low concentrations [1].

Ibuprofen (2- [3- (2-methylpropyl) phenyl] propionic acid (C₁₃H₁₈O₂)) is classified as a Non-Steroidal anti-Inflammatory Drug (NSAIDs) [4]. This drug is one of the most widely used NSAIDs available for humans and animals [5, 6]. Worldwide surveys on contamination levels of anti-inflammatory drugs such as ibuprofen indicate that their concentration in water bodies is in the range of µg /L and higher concentrations were detected in municipal sewage [7]. Although the concentration of this drug in the environment is low, they have a potential danger to aquatic ecosystems due to their continuous evacuation into the media and its cumulative effect. Therefore, an

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effective purification system is needed to remove these compounds [8]. So far, various methods such as filtration, adsorption, coagulation-flocculation, flotation, and biological methods have been used for the removal of drug compounds [9], but these methods do not completely eliminate the pollutant and only transfer it from one phase to another [10]. Advanced oxidation processes (AOPs) are the most effective technique for the decomposition and removal of hazardous, resistant, and non-degradable organic pollutants from water and wastewater [11]. Among different AOPs, ultrasonic irradiation is an applied method for water purification which has the following advantages: the absence of any kind of cancer products, the lack of odor and taste, and the lack of need for the use and storage of dangerous chemicals, the need for a small space for the installation of ultrasonic units. The influence of ultrasound irradiation reactions is principally due to the cavitation of ultrasound. It can induce a large number of tiny bubbles at a certain frequencies and intensity of ultrasonic waves. Formation, oscillation, growth, and contraction to the collapse of the bubbles result in hot spots (areas with high temperature (up to 5000 K) and pressure (some 1000atm) in the very small space inside and around the cavitation. These conditions break down water molecules to produce H_2O_2 and $\cdot H$, $\cdot OH$ radicals with strong oxidative activity, which can degrade various organic compounds in solution [12, 13]. Moreover, the degradation of organic pollutants needs a large quantity of energy and its complete mineralization scarcely occurs by using sonolysis alone [14, 15].

Sonocatalytic process, which is a combination of catalysts with ultrasonic has widely considered overcoming obstacles. Besides, the so no catalytic performance to decompose organic compounds can be increased due to a synergistic influence of ultrasonic irradiation with a solid catalyst [16]. According to literature, various semiconductors have been utilized as effective sonocatalysts such as TiO_2 [17], ZnO [17], $CdSe$ [18], CO_3O_4 [19], Pd . To improve the sonocatalysis efficiency, it modified or doped with other elements, which leads to its immobilization on the different solid substrates [20]. Graphene is an outstanding solid material in the sonocatalysis field which supports dual or triple catalysts for the effective destruction of pollutants [21]. In previous researches, metal nanoparticles immobilized on graphene have been synthesized and the results indicated the improvement in catalytic properties through a synergistic effect [17,

18, 22-24].

To the best of our knowledge, there is no report that coated the Pd NPs on GO and its sonocatalyst efficiency for the degradation of IBF. In this study, GO-Pd nanocomposite sonocatalyst was prepared via a simple solvothermal method to acquire a synergistic effect on the efficient degradation of pharmaceutical pollutants. The structure and composition of synthesized Pd NPs-GO are characterized and the sonocatalyst activity toward IBF degradation is investigated. The effect of some main factors such as solution pH, initial concentration of IBF, ultrasonic irradiation time and sonocatalyst dosage were evaluated. Finally, the performance of Pd NPs, GO, and Pd NPs-GO sonocatalysts was compared.

MATERIAL AND METHOD

Material

For the green synthesis of palladium nanoparticle (Pd NPs), *Dictyota indica* was collected from the Oman Sea coasts in Chabahar, Iran. Graphene oxide (GO), palladium chloride ($PdCl_2$), ammonium hydroxide and ethanol were purchased from Merck Co. Ibuprofen powder was gotten from Sigma Co.

Synthesis of Pd NPs

The method for the preparation of Pd NPs was reported previously [25]. Briefly, to produce Pd NPs through the methodology of green synthesis, 100 mL of 1mM $PdCl_2$ solution was added to 20 mL of algae (*Dictyota indica*) extract. The resulting mixture was stirred for 2 h at 60 °C. At this time, the color of the solution changed from yellow to dark brown.

Synthesis of Graphene oxide – palladium nanoparticle

GO-palladium nanocomposite was prepared according to the method described by Hosseini et al [23]. Pd NPs (5 mg) was first dissolved in a concentrated hydrochloric acid solution and then diluted with 50 mL of deionized water. Next, 50 mg of GO was added to 50 mL of Pd NPs with ultrasonic for 2 h to form a solution in steady-state. The pH of the solution was adjusted by ammonium hydroxide at pH = 10 and again stirred for 30 min. Then it was heated at 200 °C for 12 h in the oven and cooled at room temperature. After this step, it was filtered and washed with ethanol and de-ionized water. Finally, the resulting product was dried at 50 °C for 12 h.

Characterization

The surface functional groups of GO and GO-Pd NPs was determined by a Fourier transform infrared spectroscopy (FTIR) (Nicolet Avatar, Thermo, USA) over the range of 400-4000 cm⁻¹ using KBr disk method. The crystal structure of the sonocatalysts was analyzed using X-ray Powder Diffraction (XRD) (PW 1730, Philips, Netherland). The morphology of Pd NPs was characterized by a Transmission Electron Microscope (TEM, CM120, Philips, Netherlands).

Adsorption analysis

According to the GO-Pd nanoparticles can act as an adsorbent; in the optimum conditions without ultraviolet radiation, the adsorption of ibuprofen was studied from aqueous solution. The result showed that adsorption of ibuprofen by GO-Pb nano-composite was complete in the 25 min contact time. Accordingly, after 25 min of exposure, the efficiency of ultraviolet radiation on the ibuprofen degradation was evaluated.

Degradation of ibuprofen

IBF stock solution was obtained by dissolving different amounts of its powder in a 10% methanol solution. Various concentrations (30, 50, 60, 70 and 80 mg/L) of IBF were prepared from the stock solution. The pH of the solution was adjusted using 0.01 molar of HCl and NaOH. Degradation experiments were performed in an Erlenmeyer using the ultrasonic device (35 kHz, PARSONIC

7500S, Iran). The effect of various parameters affecting the process including pH (3, 4, 5, 7 and 8), reaction time (10, 20, 30, 40 and 50 minutes), reaction temperature (20, 23, 25, 30, 35 and 40) °C and IBF concentrations (30, 50, 60, 70 and 80 mg/L) was studied. The concentration of IBF was measured using a UV-visible spectrophotometer with a wavelength of 222 nm. The efficacy of ibuprofen removal was calculated as follows:

$$\text{Removal efficiency} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

Where C_0 is the initial concentration of IBF and C_t is the concentration of IBF at any given time.

TOC analyzer (Analytik Jena AG, multi N/C® 3100, Germany) measured the concentration of total organic carbon in the solution. A schematic diagram of the experimental set-up is shown in Fig. 1.

RESULTS

Characterization of sonocatalytic catalysts

Pd NPs were successfully synthesized using *Dictyota indica* seaweed extract. Its properties were characterized and reported in detail in our previous study [25]. Fig. 2 showed the TEM images of Pd NPs. From this figure, it can be seen that the nanoparticles have a spherical shape with an average diameter of 19 nm.

Fig. 3 shows the XRD pattern of GO and GO/Pd NPs. As presented in Fig. 3, the peaks at around $2\theta = 39.5, 46,$ and 67.4 which could be allocated to

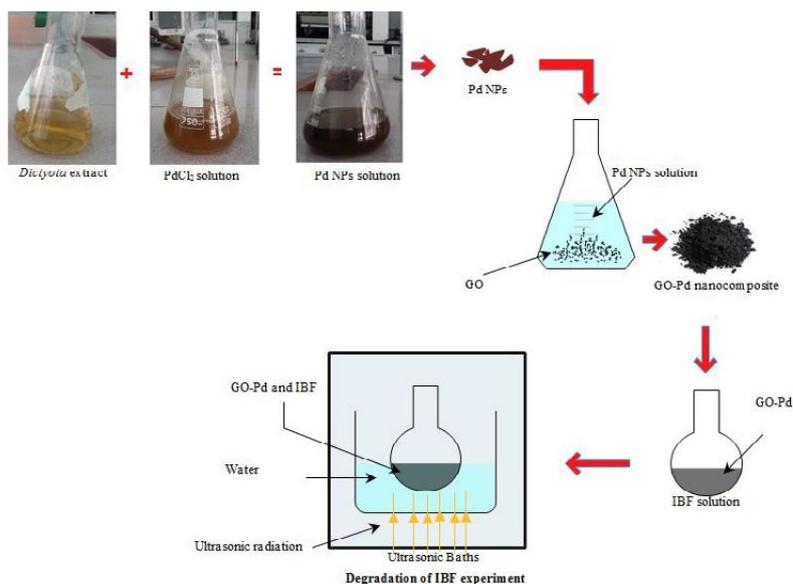


Fig. 1. A schematic diagram of the experimental set up.

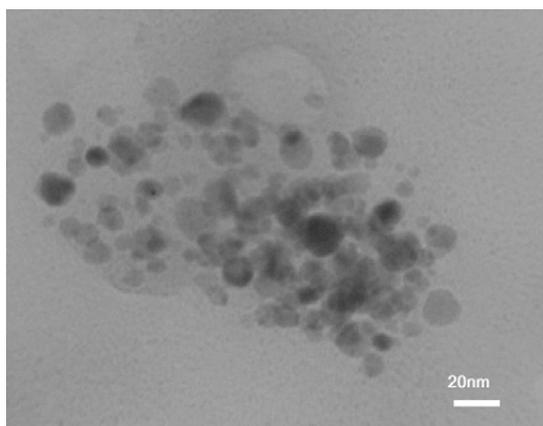


Fig. 2. TEM images of Pd NPs

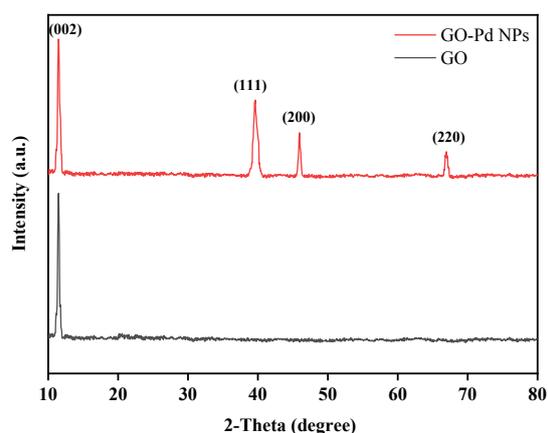


Fig. 3. XRD patterns of GO and GO-Pd NPs.

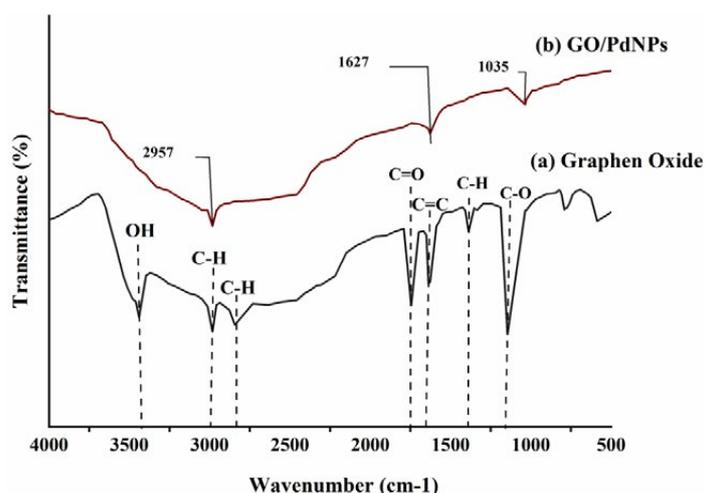


Fig. 4. FTIR spectra of GO (a) and GO-Pd NPs (b).

the (111), (200), (220) crystalline planes of the face-centered cubic (fcc) structured palladium (JCPDS No. 46-1043), respectively [26]. For graphene oxide, a peak was observed at $2\theta = 11.54^\circ$ corresponding to the (002) plane of graphene nanosheets (JCPDS 01-0646) [27]. In the GO-Pd NPs pattern, no diffraction peak of graphite was noticed. It implied that Pd NPs supported on graphene preserve it from restacking [28]. This result was in compliance with Wang et al [28] and Yang et al [26], which decorated Pd NPs on graphene oxide sheets.

Fig. 4 presents the FTIR spectra of GO and GO-Pd NPs. According to results, in the spectrum of GO, the peak at 1385 cm^{-1} , 2700 cm^{-1} , and 2900 cm^{-1} are attributed to C-H stretching vibrations. Given peaks at 1048 cm^{-1} , 1670 cm^{-1} , 1740 cm^{-1} are corresponding to C-O, C=C, and C=O bands, respectively [29, 30]. The peak located at 3400 cm^{-1}

is attributed to the O-H stretching vibrations [28, 31]. Besides, the peaks observed at 1035 cm^{-1} , 1627 cm^{-1} , and 2957 cm^{-1} in the spectrum of GO-Pd NPs, are ascribed to C-O, C=C, and C-H stretching vibrations [28].

Sonocatalytic degradation of IBF

Effect of solution pH

pH plays an important role in the degradation of organic pollutants in the sonolysis process. Effect of different pH (3, 4, 5, 7 and 8) on the degradation of IBF by Go-Pd NPs was investigated in a steady state of 50 mg/L, 0.8 g/L, 25°C and 20 min. As shown in Fig. 5. by increasing the pH from 3 to 8, the degradation efficiency of IBF is reduced from 68.9 to 41 %, respectively. In other word, acid conditions improved ibuprofen degradation efficiency. The reason for decreasing

the degradation removal in alkaline conditions may be due to the high concentration of OH recombine to H_2O_2 and do not interact with IBF [32]. A similar trend was observed by Guettaia et al [32] for the sonochemical elimination of IBF.

Effect of the initial concentration of IBF

The effect of the initial concentration of IBF on degradation efficiency by Go-Pd NPs was investigated at a concentration range from 30 mg/L to 80 mg/L under a pH of 3, the ultrasonic irradiation time of 30 min at 25 °C. It can be seen from Fig. 6 that by increasing initial concentration from 30 to 80 mg/L, the degradation efficiency percentage increased from 57.5 % to 90.2 %. This phenomenon can be explained in this way: with rising IBF concentration in solution, a number of its molecules enhanced, while the OH and O_2 concentrations were constant. It leads to insufficient oxidation of IBF and as a result low degradation efficiency [17, 33]. A similar trend was observed by

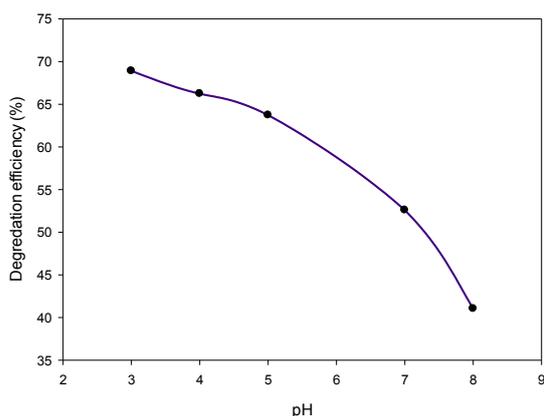


Fig. 5. The effect of solution pH on the Go-Pd NPs sonocatalytic degradation of IBF.

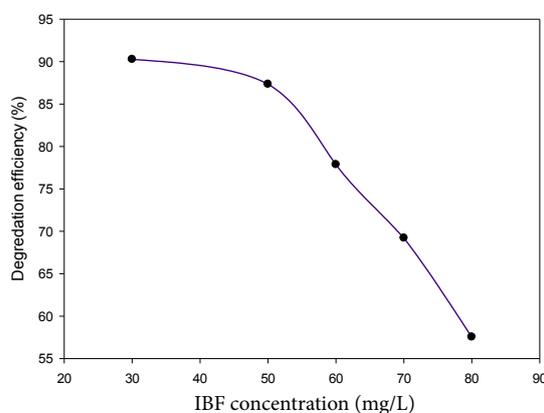


Fig. 6. The effect of initial concentration of IBF on degradation efficiency by the Go-Pd NPs

Madhavan et al for IBF on TiO_2 .

Effect of ultrasonic irradiation time

Sonolysis is an energy-intensive process, so, optimization the reaction time will save energy and cost. For this purpose, the effect of ultrasonic irradiation time was investigated at ranged from 0-50 min under 50 mg/L, 25 °C and pH of 3. As the results show in Fig. 7, with an increment of ultrasonic time to 30 min, the rate of IBF degradation efficiency was rapidly increased from 54.3 to 87 %, and then it reached to nearly steady state. The optimum degradation efficiency was chosen at 50 min. The mechanism of IBF degradation by the sonocatalyst can be explained in this way. In the presence of ultrasonic irradiation, the molecule of water is decomposed and forms the hydrogen and hydroxyl radicals. If the oxygen molecule is an exit, it also decomposes and forms oxygen atoms in the water cavitation bubbles. The oxygen atom reacts with the water molecule and creates a hydroxyl radical. Hydroxyl radicals in combination with Pd NPs-GO carry out IBF degradation. The degradation rate depends on the hydroxyl radical concentration and the concentration of IBF molecules at the interface of the cavitation bubble [32, 34]. Beside, Pd NPs-GO is stimulated by ultrasonic and generates electron-hole pairs via electrons transfer between these two catalysts. The electron-hole pairs lead to an increase in sonocatalyst activity [18].

Effect of catalyst dosage

The sonocatalyst activity of GO was investigated using IBF under the following optimum conditions; 50 mg/L, pH of 3, 25 °C and different adsorbent

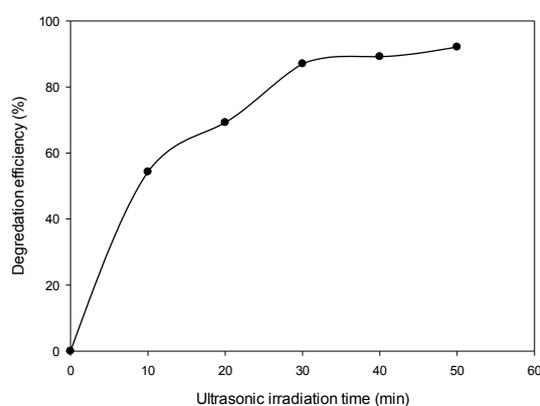


Fig. 7. The effect of ultrasonic irradiation time on degradation efficiency of IBF by the Go-Pd NPs

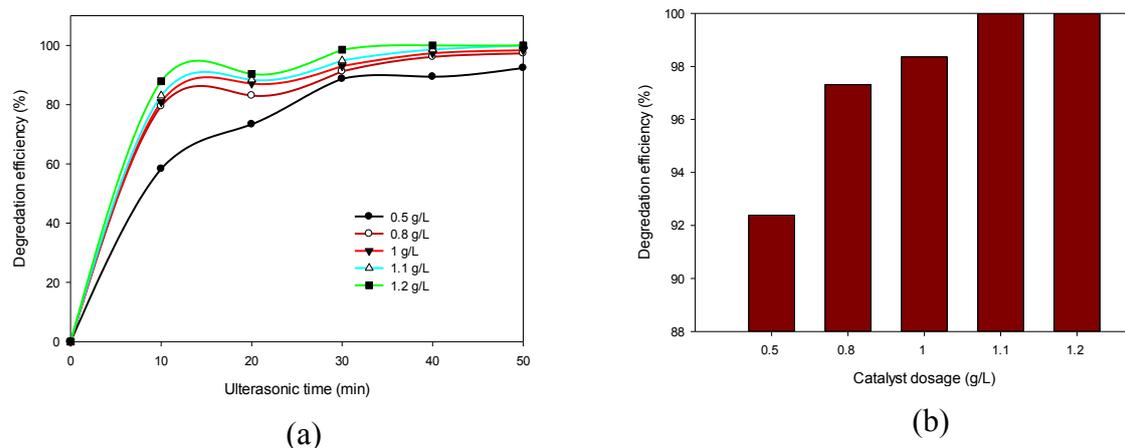


Fig. 8. The effect of Go dosage on IBF degradation.

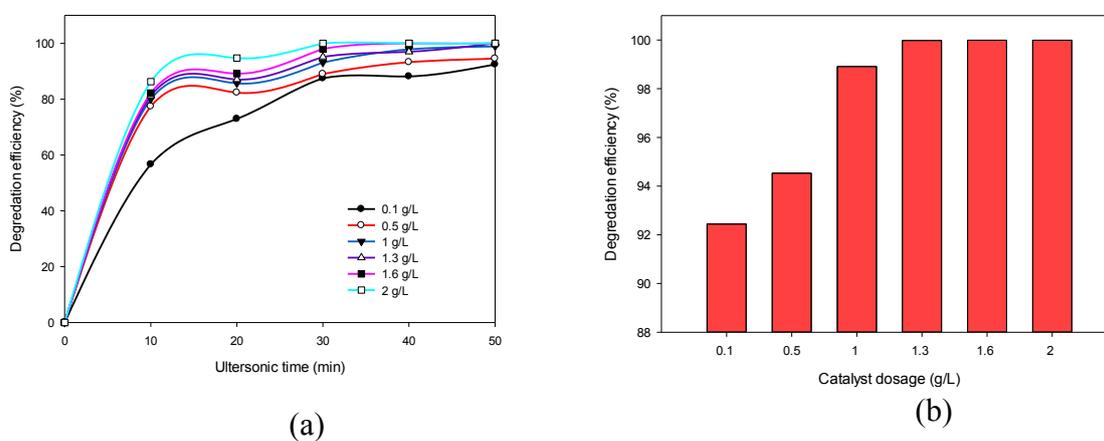


Fig. 9. The effect of Pd NPs dosage on IBF degradation.

dosage 0.5-1.2 g/L. Their results in Fig. 8a and b show that the increase in graphene dosage in the range of 0.5 g/L to 1.2 g/L, along with the increment in reaction time, enhanced IBF removal efficiency. There was not any different in removal efficiency of 1.1 g/L to 1.2 g/L (99.99 % - 99.99%) at 50 min. The reason for increasing IBF degradation by increasing the amount of graphene adsorbent may be ascribed to the expansion in the adsorptive surface area and availability of more active sites [24, 35]. With increasing in catalyst dosage, the degradation efficiency does not change due to the saturation. A similar trend was seen for the degradation of IBF on graphene oxide nanoplatelets [35].

Fig. 9 a and b presents the effect of various Pd NPs dosage in the range of 0.1 g/L to 2 g/L on the degradation efficiency of IBF. It can be seen from Fig. 9 b that the percent degradation of IBF increased (94.5-99.9 %) with increment in Pd NPs dosage (0.1-2 g/L) and there was no decrease in the

range of 1-2 g/L. Besides, as shown in Fig. 8 a, the increment dosage of Pd NPs led to the complete degradation time of IBF from 50 to 30 min. As mentioned in section 3.6.1, the improvement in removal efficiency can be attributed to high numbers of active sites on the Pd NPs by increasing its dosage [36, 37]. A similar trend was observed for the degradation of organic dye by Pd/Fe₃O₄-PEI-RGO nano hybrids [36].

The influence of the quantity of GO-Pd NPs over the degradation of IBF was evaluated as well. As can be seen in Fig. 10, for various GO-Pd NPs amounts, the degradation removal of IBF rises along with the increment of catalyst doses. After 10 min ultrasonic irradiation, the sonocatalyst degradation efficiency is more than 80 percent for all dosages. The removal efficiency of IBF rises very slowly after 20 min and higher than 98 percent of degradation obtained for all GO-Pd NPs amounts. Thus, 0.8 g/L sonocatalyst is selected as a proper dosage.

DISCUSSION

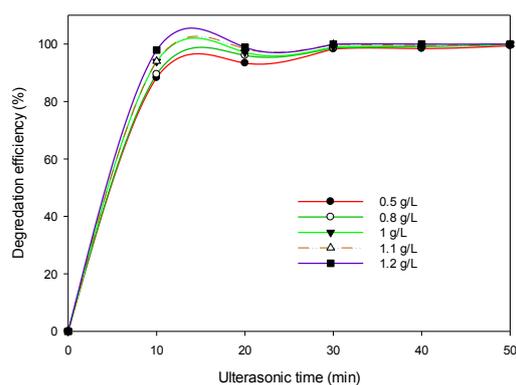
The performance of Pd NPs, GO, and Pd NPs-GO sonocatalysts were compared in the following optimal conditions; initial IBF concentration of 50 mg/L, catalyst dosage of 0.8 g/L, the ultrasonic irradiation time of 50 min and at 25 °C. From the findings presented in Fig. 10, it can be seen that the degradation ratio (C_t/C_0) of Pd NPs-GO is much more than other catalysts which represent more activity under ultrasonic irradiation. In fact, the large surface area of graphene has led to the more dispersion of Pd NPs in it and hence increasing absorption of ultrasonic irradiation, which makes more electron-hole pairs for IBF removal [17, 22]. The kinetics of the degradation of IBF can be stated as $-\ln(C_t/C_0)=k_{app}t$, where C_0 and C_t are the concentration (mg/L) of IBF at time 0 and t, and K_{app} is the reaction rate constant [38]. Fig. 11 shows the plot of $-\ln(C_t/C_0)$ versus t and the kinetic coefficient and R^2 are given in Table 1. The

order of sonocatalyst magnitude was as following; Pd NPs-GO > GO > Pd NPs. Among all, Pd NPs-GO indicated more sonocatalyst activity due to the synergic effect of two catalysts.

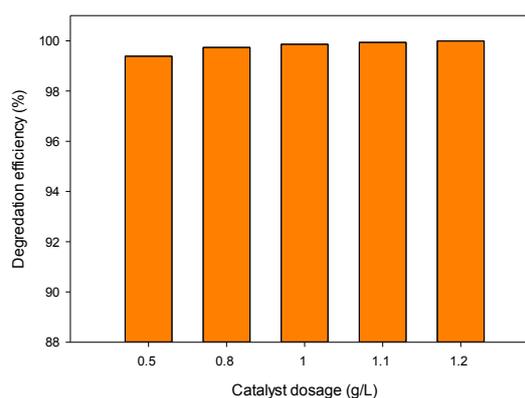
According to reports some of the intermediate products of a degradation process are more toxic and carcinogenic than the parent organic compounds [33]. Therefore, before discharging into the environment, the complete destruction of pollutants must be ensured. A comparison of total organic carbon (TOC) values done from the experiments sonocatalysis, and the obtained results are shown in Fig. 12. According to TOC data, we

Table 1. the kinetic parameters of degradation of IBF by sonocatalysts.

Sonocatalyst	Parameter	
	k_{app} (min^{-1})	R^2
Pd NPs- GO	0.1137	0.9387
GO	0.0875	0.9861
Pd NPs	0.0786	0.9700

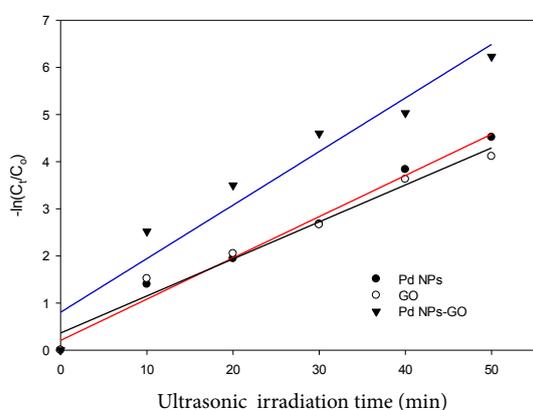


(a)

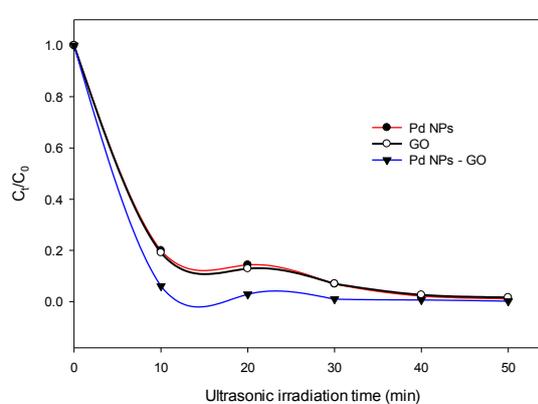


(b)

Fig. 10. The effect of GO-Pd NPs dosage on IBF degradation.



(a)



(b)

Fig. 11. The comparison of sonocatalyst degradation activity (a), Kinetic plots for the sonocatalyst degradation of IBF.

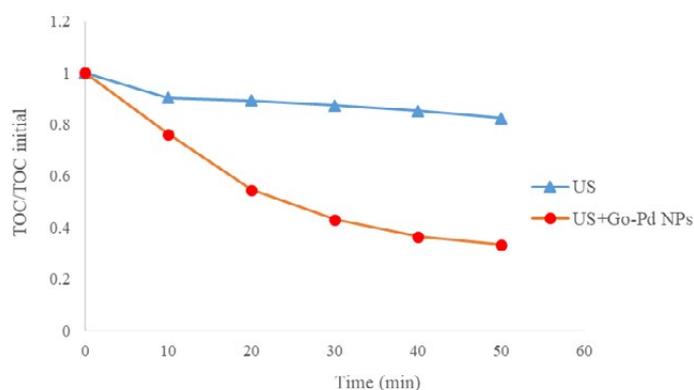
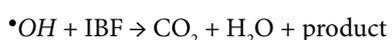
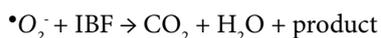
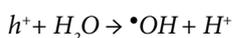
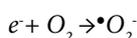
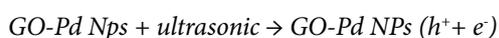


Fig. 12. Change in TOC as a function of time for different degradation processes in presence of Go-Pd NPs

can conclude the TOC removal rate was much less than that of the degradation process under the same experimental conditions; yet sonochemical reactions were quite efficient for the degradation of IBF, but complete mineralization was not achieved over the time range examined which may be due to the high polarity of the intermediate products [34].

The degradation of IBF from the actual hospital's wastewater was investigated. As revealed in this study, the effective parameters (pH of 3 and catalyst dosage 0.8 mg/L at 25°C) on the degradation of ibuprofen from wastewater were optimized. The initial concentrations of IBF in the wastewaters of 4 hospitals were 0.003, 0.011, 0.006 and 0.005 mg/L, respectively. The effect of ultrasonic irradiation time was investigated at ranged from 0-15 min. The 100 percentage (not detect) degradation of IBF was optioned at 5, 15, 10, 10 min respectively.

As shown in Equations (1-5), $\bullet O_2^-$ and $\bullet OH$ play a key role in the degradation process of IBF by ultrasonic technique. Previous research is designated that the existence of heterogeneous catalysts in the ultrasonic system can increase the oxidizing process [39].



Furthermore, the existence of heterogeneous catalysts provides additional cores which enhance the rate of formation of cavitation bubbles, which subsequently improve the generation of $\bullet OH$ by growing the pyrolysis degree of H_2O [40].

CONCLUSION

In this study, the Pd NPs coated GO was successfully synthesized by the solvothermal approach. The sonocatalyst activity of Pd NPs-GO nanocomposite presented better IBF degradation efficiency than Pd NPs and GO. The order of sonocatalyst magnitude was as following; Pd NPs-GO > GO > Pd NPs. The optimized amounts for key experimental parameters were specified as pH of 4, Pd NPs-GO dosage of 0.8 g/L, IBF initial concentration of 30 mg/L and ultrasonic irradiation time of 50 min. The IBF degradation efficiency considerably decreased with a decrease in pH, initial concentration and catalyst dosage. The kinetics of the degradation of IBF followed pseudo-first-order reaction kinetics.

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COMPETING INTERESTS

The authors declare that they have no competing interests.

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