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Efficiency of sono-nano-catalytic process of magnesium oxide nano particle in removal of penicillin G from aqueous solution

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ABSTRACT

Antibiotics act as an ecological factor in the environment that could potentially affect microbial communities. The aim of this study is to evaluate the applicability of magnesium oxide nano-particles (MgO-NPs) for the removal of penicillin G (PG) from aqueous solution using sono-nano-catalytic process. The structural properties of the MgO -NPs were established using transmission electron microscopy (TEM) and Fourier transform infrared (FTIR) techniques. Effects of independent variables such as pH, catalyst dose, contact time, and initial concentrations of PG on the removal efficiency of PG were examined. Pseudo-first-order and pseudo-second-order kinetic models were applied at optimum condition to study the PG disintegration kinetics. All experiments were performed under ultrasonic irradiation in ultrasonic bath at a frequency of 60 kHz. Optimum conditions of pH 3, nano-particle concentration of 1.5 g/L, reaction time of 60 min, and initial concentration of 80 mg/l were obtained for the PG removal using sono-nano-catalytic process, which gave removal efficiency of 81.14%. The sono-nano-catalytic experimental data was found to fit the pseudo-first-order kinetic model (R^2 = 0.9140) than the pseudo-second-order model (R^2 = 0.7766). The results of this study showed that the sono-nano- catalytic process using MgO-NPs is very effective and can be used for removal of PG antibiotics from aqueous solutions.

Keywords: Penicillin G; Sono-nano-catalytic; MgO nano-particle; Aqueous solution

1. Introduction

In pharmacology, a pharmaceutical drug, also called a medication or medicine, is a chemical substance used to treat, cure, prevent, or diagnose a disease [1]. Drugs are used in the treatment and prevention of bacterial infections [2,3]. They may either kill or inhibit the growth of bacteria [2]. Unused therapeutic drugs are sometimes disposed into the sewage system. If the drugs are not degraded or eliminated during sewage treatment, in soil or in other environmental compartments, they will reach the surface water and ground water, and, potentially, drinking water [3]. Benzyl penicillin, also known as penicillin G (PG), is an antibiotic used to treat a number of bacterial infections. This antibiotic consists of beta lactam (B-lactam) and is very sensitive to the pH, heat, and beta-lactam enzyme [2,4]. Antibiotics cause increased bacterial resistance, thus removing these antibiotics from the wastewater before being discharged into aqueous systems is essential [1]. Several treatments methods have been proposed for the removal of PG from contaminated waters, which include photo decomposition [5], electrolysis [6] adsorption [1,2], oxidation [2,6], biodegradation [2], and other processes, involving advanced technologies to destroy the PG structure. The adsorption method is widely used due to simplicity, low cost and adsorption recovery to remove pollutant [1,7]. Adsorbents in nano scale with greater size and mass form have more adsorbing capacity in pollutant elimination, in comparison with the aforesaid adsorbents

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[1,8]. However, these treatment methods cannot be widely applied because they are expensive and time consuming thus; there is a need for developing technologies to rapidly remove PG from wastewater [9,10]. Advanced oxidation process (AOP) is known as one the effective method in decomposing and removing the dangerous organic, resistive and biological irresolvable pollutants [10]. The main mechanism of this process is based on hydroxyl radical production [11]. The radicals are able to oxidize the organic compounds very fast and non-selectively. Hydroxyls are produced in aqueous environment by using H_2O_2/Fe, UV/ZnO, UV/ H_2O_2 and US/H_2O_2 [10,12]. Among different oxidation processes, sono-nano-catalytic process is a novel technology in which toxic materials and resistant organic contaminants are completely degraded and converted to carbon dioxide [13]. Ultrasound waves have attracted attention owing to being environmentally friendly, low cost, and lack of sludge production. The main mechanism behind ultrasonic process in oxidation of contaminants is based on developing pore or very tiny micro bubbles resulting from acoustic cavitation in water [14]. The pores developed in water have a temperature of 500 K and pressure of 1000 atmosphere, which eventually results in formation of OH and OOH free radicals and thus oxidation of organic compounds in aqueous environments [15]. The use of ultrasonic process alone for removing contaminants is time-consuming and consumes a great deal of electric energy. Therefore, nano particles such as magnesium can be used to reduce energy [16,17]. So, Magnesium oxide nano particles (MgO-NPs) as a catalyst were applied in this process, since it provided high catalytic activity, non-toxicity and stability in aqueous solution [18]. In order to disintegrate and remove the pollutants that showed low biodegradability, sono-nano-catalytic process in the presence of catalyst (MgO-NPs) compared to other advanced oxidation process is new in aqueous solutions. This process, which provided high catalytic capacity could be applied as an effective method of treatment [19]. This study aims to investigate the sono-nano-catalytic process using MgO-NPs in advanced oxidation process to disintegrate and remove the PG from aqueous solution.

2. Materials and methods

2.1. Materials

Benzyl penicillin or penicillin G (PG) (purity100%) with molecular weight 372.48 g/mol was supplied by Sigma–Aldrich. Its pK_a value is 2.75. The structure of the PG (chemical molecular formulae: $C_{16}H_{17}KN_2O_4S$) is as shown in Fig. 1.

2.2. Pilot ultrasonic

Reactor of determined surface area which contains a digital ultrasonic (Elma CD-Germany, 4820) appliance made of plexiglas with volumes of 3.7 L, input energy per unit 2.5 w/cm^2, and input power 500 w with 100 ml samples in bath with US waves. It is schematically shown in Fig. 2.

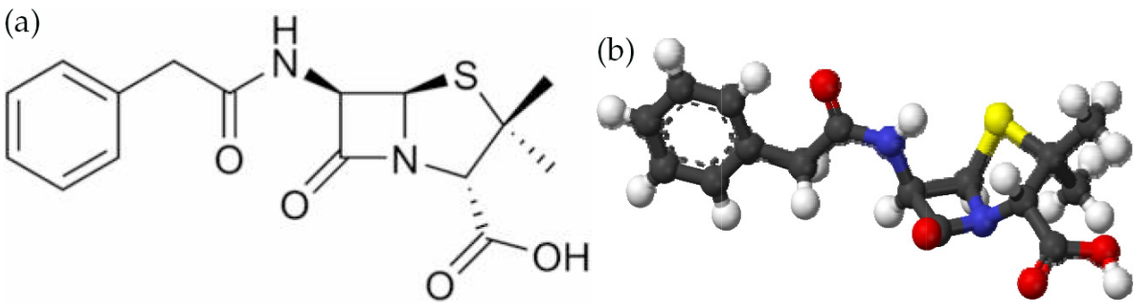

Fig. 1. The chemical structure of PG.

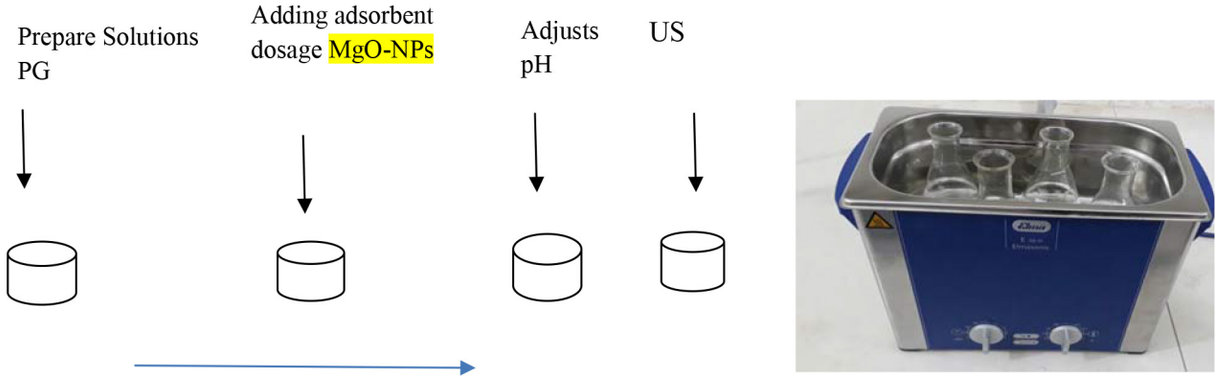

Fig. 2. The schematic illustration of sono chemical process.

2.3. Structure characterization of MgO-NPs

Magnesium oxide nano particles (MgO-NPs) were purchased from Sigma Co. (US) with diameter of less than 50 nm and purity of 98%. Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum) was employed in order to determine the functional groups present in the MgO-NPs, .TEM (FEI Tecnai G2 20 S-TWIN) was used to measure the diameter of nano particles.

2.4. Experimental methods

Stock solution of PG was prepared with a concentration of 1000 ppm in double distilled water. The water sample pH was adjusted by adding 0.1 N HCl (hydrochloric acid) or 0.1 N NaOH (sodium hydroxide) solutions in each bottle. Four process variables have been studied in this study which includes the initial pH of solution (3–11), concentration of nano particles (0.3–2.3 g/L), contact time (20–150 min), and initial concentration of PG (50–200 mg/L). The final pH of the water sample was measured using a MIT 65 pH meter. The prepared PG solution was poured intothe Erlenmeyer flask and MgO-NPs added. The Erlenmeyer flask with its contents was placed inside the ultrasonic apparatus under ultrasound waves (60 KHz) according to the set different times were refined. The residual concentrations were measured usinga UV visible spectrophotometer (Shimadzu Model: CE-1021-UK). The readings were taken at 248 nm with spectro photometer. The removal efficiency; *R* (%) was calculated based on the formula [20,21]:

$$\%R = \frac{(C_o - C_f)}{C_o}100 \quad (1)$$

where C_0 and C_e is the initial and equilibrium liquid phase concentration of PG (mg/L), respectively.

3. Result and discussion

3.1. Determination of Point of Zero Charge (pH_{zpc})

To determine the pH_{zpc}, 50 mL nitrite potassium (0.01 M) was added to glass plates and the pH was adjusted to 2–14 using HCl and NaOH. Then 0.2 g magnesium oxide nano particles (MgO-NPs) was added and mixed in shaker with velocity of 180 rpm. After 24 h, the final pH was measured. The graph of $pH_{i\ (initial)}$ against $pH_{f\ (final)}$ was drawn, and the intersection point is the isoelectric pH (Fig. 3). pH_{zpc} for MgO-NPs was found to be 12.4.

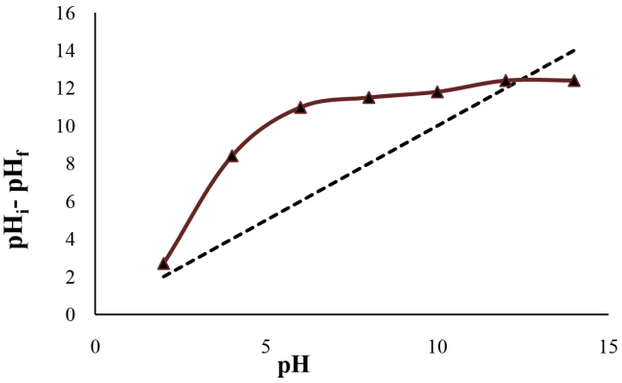

Fig. 3. Determination of the point of zero charges of MgO-NPs.

3.2. FT-IR and TEM analysis on MgO-NPs

Transmission electron microscopy (TEM) (Fig. 4a) shows that the sizes of MgO-NPs are 50 ± 10 nm length or width and about 20 nm thicknesses, which confirms that the MgO-NPs is in nanometer. Fourier transform infrared (FT-IR) analysis was carried out the dictate the functional groups taking part in the sono-nano-catalytic process for PG degradation. The FTIR spectrum (Fig. 4b) indicates the presence of alkynes with C–H bend (679.60 cm^{-1}), C–O stretch of alcohols (1090.82 cm^{-1}), C–H rock of alkanes (1384.59 cm^{-1}), and N–H bend of 1° amines (1615.99 cm^{-1}). O–H stretch, H–bonded of alcohols (3418.90 and 3700.56 cm^{-1}), which are very strong and broad bonds were also observed. O–H stretches, H–bonded of alcohols are very significant sites for a catalytic process. The effect of O–H stretch is more felt because of the H–bonding with other hydroxyl bonds.

3.3. Effect of pH

The effect of different pH (3 to 11) on the removal of PG using sono-nano-catalytic process at contact time of 60 min, initial concentration of 100 mg/L, and frequency of 60 KHz is shown in Fig. 5. pH played a significant role in disintegrating and removing the antibiotics [22]. PG pH_{zpc} of 2.75 and MgO-NPs pH_{zpc} of 12.4 were obtained. In the pH less than pH_{zpc}, the catalyst had positive charge [10,22]. In this study sono-nano-catalytic process, an increase in pH resulted in the decrease in efficiency because of the reduction in the hydroxyl radicals. The reason for high efficiency in acidic pH can be assigned to the ability of the reactions to take place in the acidic environment [Eqs. (2)–(5)] [23].

$$2HO_2^{\ 0} \rightarrow O_2 + H_2O_2 \quad (2)$$

$$H_2O_2 + O_2^{\ 0-} \rightarrow OH^0 + OH^- + O_2 \quad (3)$$

$$e^- + O_2 \rightarrow O_2^{\ 0-} \quad (4)$$

$$O_2^{\ 0-} + H^+ \rightarrow HO_2^{\ 0} \quad (5)$$

Degradation of organic compounds by ultrasonic process is slightly greater in acidic media than in alkaline environments due to the production of hydroxide radical [24]. At higher pHs, H_2O_2 is rapidly degraded into molecular oxygen and H_2O, and thus hydroxide radical is reduced at higher pHs. Furthermore, at alkaline pH, sequestration of MgO-NPs occurs. This sequestration occupies superficial active sites on the nano particles [25]. Also, their stability is greater, which is in line with the research by Zarrabi [26].

3.4. Effect of MgO-NPs concentration

The effect of MgO-NPs concentration on the sono-nano-catalytic process for the removal of PG was studied by

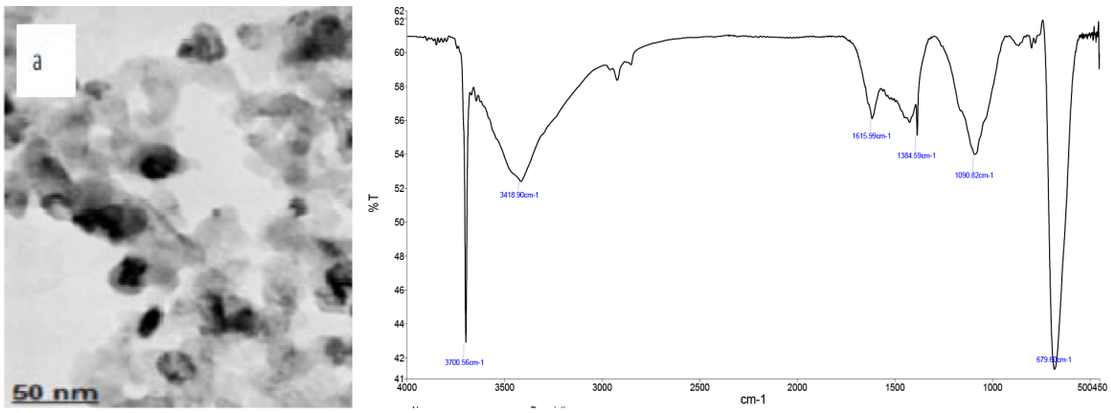

Fig. 4. TEM (a) and FT-TR (b) image of the MgO-NPs.

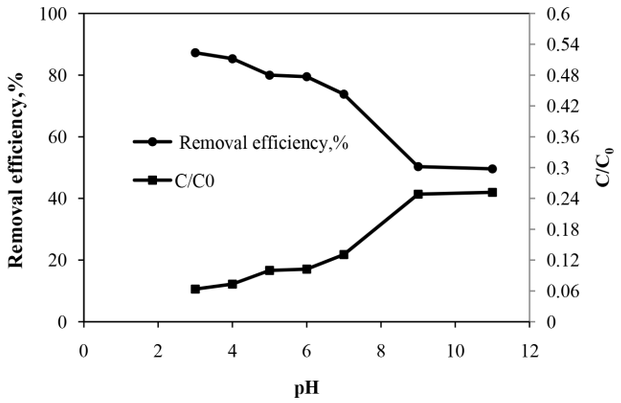

Fig. 5. Effect of pH on removal efficiency of PG. (Time: 60 min, MgO-NPs dosage: 0.3 g/L, PG initial concentration: 100 mg/L, frequency: 60 KHz).

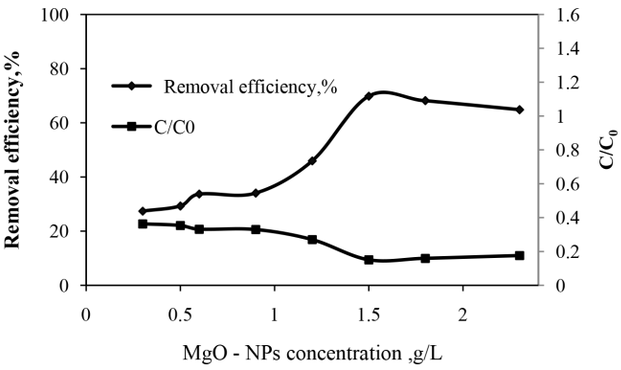

Fig. 6. Effect of MgO-NPs concentration on removal efficiency of PG (Time: 60 min, pH: 3, PG initial concentration: 100 mg/L, frequency: 60 KHz).

varying the concentrations from 0.3 to 2.3 g/L (Fig. 6). In sono-nano-catalytic process, the reason for the increased efficiency with elevation of the nano particle concentration is that the presence of MgO-NP$_s$ in the sono-nano-catalytic process generates extra kernels, which in turn increases the number of bubbles and radicals. In addition, the cavitation threshold may drop due to the vapors and gases in the pores of the nano particles. In other words, nano particles provide extra surfaces for cavitation [27].

3.5. Effect of time and concentration

To determine the effect of initial PG concentration on the sono-nano-catalytic process (Fig. 7), the initial concentration of PG was varied from 50 to 150 mg/L at pH 3, 2.3 g/L MgO-NPs, and time of reaction 60 min. Fig. 8 shows the effect of contact time on the removal efficiency of PG using sono-nano-catalytic process (at optimum pH 3, initial PG concentration of 80 mg/l, and MgO-NPs concentration of 1.5 g/l).The results indicated that with increased contact time and reduction of initial concentration, with constancy of the other conditions, the removal efficiency increases, such that the greatest extent of removal (81.14%) was obtained at 60 min, and temperature of 298 K (Fig. 8).Over the time, more hydroxyl radicals are produced, which are expended for the oxidation of PG molecules, thereby reducing PG concentration [28]. At low PG concentration, prolongation of the process causes continued production of hydroxyl radicals and more contact of these radicals with antibiotics, and greater degradation of PG [29]. Over time, the active sites for antibiotic adsorption change and the number of products obtained from MgO-NPs reaction in the aqueous environment increases, thus enhancing the removal efficiency with prolonged retention time [30,31]. The result obtained is similar or even better than those reported by other authors (Table 1).

3.6. Kinetics of sono-nano-catalytic degradation

The sono-nano-catalytic degradation of PG can be well explained by a pseudo-first-order and pseudo-second-order reaction. Linear form of the equations used for analyzing the sono nano-catalytic degradation data are shown in Table 2.

The slope of the plot of In and versus time gives the value of the rate constant K (min^{-1}). Here, C_o denotes

the initial concentration in milligrams per liter, and C is the concentration value in milligrams per liter at time t. The test was applied at optimum condition to study the disintegration kinetics (pH 3, contact time of 60 min, and MgO-NPs concentration of 2.3 g/L).The estimated sono-nano-catalytic disintegration kinetic parameters are presented in Table 3. The sono-nano-catalytic experimental data was found to conform to the pseudo-first-order kinetic model (R^2 = 0.9140) than the pseudo-second-order model (R^2 = 0.7766).

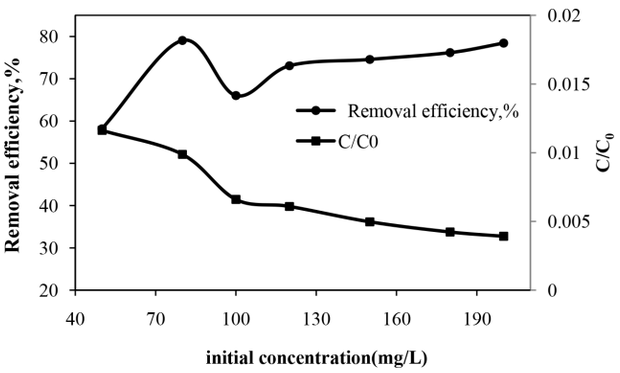

Fig. 7. Effect of initial concentration on removal efficiency of PG (MgO-NPs dose: 1.5 g/l, pH: 3, time: 60 min, frequency: 60 KHz).

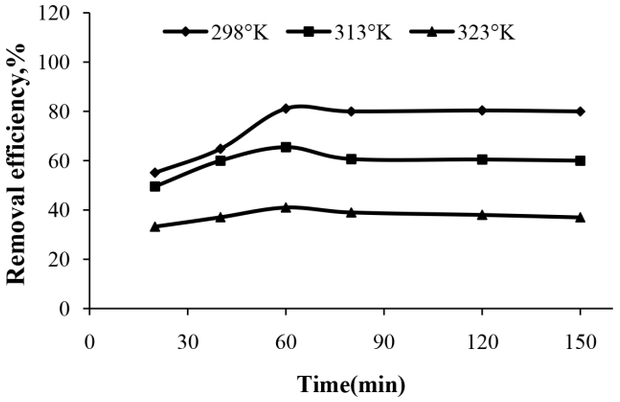

Fig. 8. Effect of contact time on removal efficiency of PG (MgO-NPs dose: 1.5 g/l, pH: 3, initial concentration: 80 mg/L, frequency: 60 KHz).

4. Conclusion

The applicability of magnesium oxide nano-particles (MgO-NPs) for the removal of Penicillin G (PG) from aqueous solution using sono-nano-catalytic process. The effect of variables such as pH (3–11), catalyst dose (0.3–2.3 g/L), contact time (20–150 min), and initial concentrations of PG (50–200 mg/L) on the removal efficiency of PG were examined at 60 kHz. The pseudo-first-order and pseudo-second-order kinetic models were applied to study the PG disintegration kinetics. Optimum conditions of pH 3, nano-particle concentration of 1.5 g/L, reaction time of 60 min, and initial concentration of 80 mg/l were obtained for the PG removal using

Table 2
Kinetics model equations applied for the PG degradation processes

Model	Equations	Reference
Pseudo-first-order	$\ln(c) = -K_t + \ln(C_0)$	[34]
Pseudo-second-order	$\frac{1}{((c))} = \frac{1}{((C_0))} + K_t$	[35]

Table 3
Kinetics parameters for the PG degradation process

Kinetic model	R^2	k (min^{-1})	C_0 (mg/l)
Pseudo-first-order	0.914	0.009	80
Pseudo-second-order	0.7766	9E-05	80

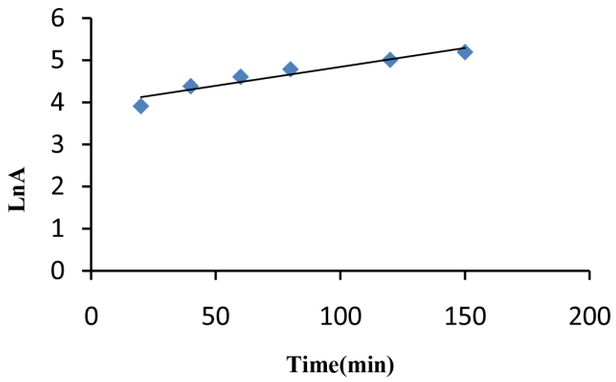

Fig. 9. Pseudo-second-order plot of PG degradation process.

Table 1
Removal percentages of antibiotics reported by different authors with time of reaction, catalyst type, and antibiotics concentrations

Catalysts	Concentration of antibiotics (mg/L)	Time (min)	Dosage catalysts (g/L)	Removal (%)	Reference
TiO_2	Erythromycin: 50	85.5	0.4	98.5	[32]
Fe_2O_3	Penicilin:10	53	0.3	95.5	[33]
TiO_2	Tetracycline:250	60	0.25	94.3	[23]

sono-nano-catalytic process, which gave removal efficiency of 81.14%. The sono-nano-catalytic experimental data was found to fit the pseudo-first-order kinetic model (R^2 = 0.9140) than the pseudo-second-order model (R^2 = 0.7766). In the current study, sono-catalytic process accelerated in the presence of MgO-NPs enhanced the removal of PG.

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