Graphene quantum dots based on maltose as a high yield photocatalyst for efficient photodegradation of imipramine in wastewater samples

Raheleh Hatefi¹ · Ali Mashinchian-Moradi¹ · Habibollah Younesi² · Saeed Nojavan³

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Abstract

Purpose In this work, for the first time, graphene quantum dots (GQDs) based on maltose were fabricated as a new photocatalytic material to the photodegradation of imipramine (as a persistence organic pollutant) under light irradiation.

Methods The synthesized GQDs were characterized by different instrumentation approaches such as X-ray diffraction (XRD), Fourier transform-infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), nitrogen adsorption/desorption, and transmission electron microscopy (TEM). A Box–Behnken design (BBD) and the response surface methodology (RSM) were applied for the optimization of different factors that affect the overall photocatalytic yield.

Results Under the optimized conditions (pH of the sample solution: 2.0; photocatalyst dosage: 0.1 mg mL⁻¹; UV exposure time: 80 min), the highest achievable reduction efficiency was obtained about 80%. The stability and reusability of the synthesized photocatalytic material were investigated in four reaction cycles (80 min), which showed only a 15% photo-activity loss after the fourth photocatalytic runs.

Conclusions The proposed method was successfully applied to degrade the mentioned drug in the real wastewater samples by about 70%. Regarding the mentioned advantages by the proposed method, this new kind of photocatalytic material possesses a strong potential for photodegradation of pollutants in industrial wastewater samples.

Keywords Graphene quantum dot · Imipramine · Maltose · Photocatalyst · Photodegradation · Wastewater treatment

Introduction

These days great consideration has been paid to the presence of emerging contaminants in the environmental samples. Persistent organic pollutants (POPs) belong to one of the pollutant groups in the wastewater, exhibiting harmful effects on the water quality, human health, and ecosystems in a long time

[1, 2]. Nowadays, many POPs have been detected in surface water, groundwater, and urban wastewater plants, as reported in different works, done around the world [3–5]. Mostly, POPs are antibiotics, analgesics, steroids, antidepressants, antipyretics, fragrances, and cosmetics [1, 6]. According to the World Health Organization (WHO), they can be attended as main contributors toward a global health crisis [7]. Besides, the rise in POPs can impose enormous costs on society and government shortly [7].

As for the effective treatment of POPs can be unwieldy done by using conventional techniques. The removal of low concentrations of POPs is, therefore, highly difficult and emergency. As published in different studies, advanced oxidation processes (AOPs) could oxidize such pharmaceuticals to safe products (water, carbon dioxide, and inorganic salts) in the water media [8]. It is related to the generation of reactive oxygen species (ROS) such as hydroxyl radicals OH[•], applied semiconductors as a photocatalyst. Photo-excited holes (h⁺) and electrons (e⁻) are produced under the irradiation in the

✉ Ali Mashinchian-Moradi
mashinchian@gmail.com

¹ Department of Environmental Science, Faculty of Natural Resources, Science and Research Branch, Islamic Azad University (IAU), P.O. Box 14515-775, Tehran, Iran

² Department of Environmental Science, Faculty of Natural Resources, Tarbiat Modares University, P.O. Box 64414-356, Noor, Iran

³ Department of Analytical Chemistry and Pollutants, Shahid Beheshti University, P.O. Box 19839-4716, Tehran, Iran

valence band (VB) and the conduction band (CB), respectively, if energy is greater than or equal to the energy gap of semiconductors [9]. They could cause the redox reaction by forming radicals ($\text{OH}^\cdot$, O^{2-} , etc.) when they shift to the semiconductor surface [10].

Nowadays, introducing novel photocatalytic materials for photodegradation of pollutants under irradiation is still a challenging task [11]. Recently, graphene quantum dots (GQDs) have gained attention as a new generation of photocatalytic reagents [12]. GQDs prepared by hydrothermal protocols usually include many functional groups, such as carboxyl and hydroxyl groups. The GQDs have a size of few nanometers, which is typically below 10 nm and of spherical morphology [13]. Some typical characteristics of GQDs are quantum size-effect, low toxicity, large surface area, excellent biocompatibility, and specific optical-electric properties. These make them suitable photocatalysts allowing for biological sensing and bio-imaging [14, 15]. Also, their functional groups could increase the photocatalytic activity by enhancing the adsorption capacity [16]. Thus, GQDs are high environmentally friendly compared with commonly used semiconductor quantum dots. Recently, different techniques have been extended to GQDs synthesis and further use utilizing two approaches. The first involves bottom-up methods such as chemical solution-based, microwave-based, and ultrasonic-based methods. The latter one includes top-down methods include such as hydrothermal-based and electrochemical-based setups [17]. Up to now, several studies have also been attempted to modification of GQDs to improve their efficiencies for the degradation of target analytes [18, 19]. However, most of these approaches applied GQDs as photocatalyst with metal loading [19–21], which is toxic to the environment.

For addressing this issue, in the current work, maltose as a green and safe material was used for the fabrication of GQDs nanoparticles with a high active photocatalytic a via one-step hydrothermal technique. To the best of our knowledge, maltose has not been previously applied for photodegradation in water samples. In the current work, for the first time, maltose as a low cost, environmentally friendly, and widely available material was used for the fabrication of GQDs. So, a high active photocatalyst was synthesized via a one-step hydrothermal technique. The proposed approach is green, fast, high-yield, low-cost. Moreover, the prepared GQDs have excellent biocompatibility, which is more convenient for environmental usages. Also, the treatment efficiency of the prepared GQD nanoparticles photocatalytic activity was investigated in the batch photo-reactor. A Box–Behnken design (BBD) under response surface methodology (RSM) was used for optimization of the effective variables in the photocatalytic treatment of the wastewater in the batch mode study.

Material and method

Chemicals

Maltose ($360.32 \text{ g mol}^{-1}$) and hydrochloric acid (37%) were purchased from Merck (Germany) and were in analytical grade. The double-distilled water was used for the preparation of reagents in this study. Imipramine was received from Aminpharma Company (Tehran, Iran). Clomipramine was obtained from Tofigh Daru (Tehran, Iran) and used as an internal standard (IS).

Preparation of graphene quantum dot (GQD)

GQDs were synthesized by the hydrothermal method in one step, and high efficiency. Materials used as precursors were included, such as maltose, hydrochloric acid, and deionized water. The 0.008 mmol of maltose was dissolved in 10 mL deionized water. Then, the 10 mL HCl (37%) was poured into the mixture. The solution was transferred in Teflon-lined autoclave and placed at 200 °C for three h. The solution was neutralized with sodium hydroxide until $\text{pH} \approx 7$ and washed with distilled water three times. Thus, the product was separated from the solution by centrifuging and dried under the air temperature conditions.

Characterization analysis

The crystal structure of GQD nanoparticles was determined by a PW 8 Philips X'Pert X-ray diffractometer (XRD) using Cu K α as radiation. The X-ray wavelength was derived from a copper anode (CuK α) with $\lambda = 1.54 \text{ \AA}$ and in the range of 10–80° (2 θ) at 30 mA and 40 kV. The Fourier transform infrared (FT-IR) was estimated by FT-IR spectrophotometer (Shimadzu, FTIR1650, Japan) with a wavenumber range of 400–4000 cm^{-1} . The field emission scanning electron microscopy (FESEM, ZEISS, SIGMA VP, operated at 30 Kv and Oxford Instrument for EDS and Mapping) was performed for assaying the morphology of the nanoparticle. The nanoparticle size and morphology was recorded by a transmission electron microscope TEM (TEM, Zeiss-EM10C-100 KV).

UV-Vis absorption spectra of materials were measured by a V/650 spectrophotometer (Thermo, Japan) with a wavelength range from 200 to 1000 nm. Raman spectra were carried out by DPSS Nd: YAG with the wavelength range of 530–700 cm^{-1} and Raman shift range of 0–4400 cm^{-1} . The nitrogen adsorption/desorption isotherms were examined at 77 K using a conventional volumetric apparatus (BET, Bel Japan, Inc.).

Gas chromatography

Gas chromatography (GC) was employed to determine the removal percentage of imipramine. To obtain this object, after photodegradation, the samples were centrifuged to remove GQD particles, and then, the sample solution was analyzed by GC. The characteristic of system equipment was Varian CP-3800 GC-FID with a capillary column (CP-SIL 8CB, 25 m × 0.32 mm × 0.25 μm, Chrompack, USA). The initial oven temperature was set at 150 °C and then increased with ramp 15 °C min⁻¹ to 300 °C and held for 1 min. The temperature of the injection port and FID were 280 °C and 300 °C, respectively. The splitless mode of injection was used for 1 min, and then, the split valve was opened at the split ratio of 5:1.

Experimental condition

The experimental photo-decomposition was performed in a batch reactor with a cylindrical shape. At first, distilled water with a determined value of imipramine (200 mg L⁻¹), was poured into it. The optimum conditions included: proper GQDs content (0.1 gL⁻¹), pH adjusted solution (2) and, the required time of UV irradiation (80 min). These were estimated by an ANOVA analysis to enhance the photocatalytic activity. A mercury-vapor lamp (Philips, 9 W, Nederland) was located in the center inside of a quartz sleeve using a source of UV irradiation. The efficiency of photocatalytic degradation of the compound was calculated via the difference in the initial (*C*₀) and the equilibrium (*C*_t) concentrations using the following equation:

$$\text{Photocatalytic removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Experimental design and modeling

The experimental design matrix and data analysis were carried out by the Statgraphics Plus Package (version 5.1; Statistical Graphics, Manugistics, USA) [22]. The RSM was applied to the determination of the interaction process between variables and responses. Preliminary experiments were carried out for indicating the independent variables and their experimental ranges to design the experimental runs. Based on our initial results, the three most critical affecting variables on the photocatalytic efficacy, including pH of the sample, photocatalyst dose, and UV irradiation time were chosen. The examined levels of independent variables are displayed in Table 1.

Table 1 The experimental variables and levels of the BBD

Variable	Key	Level		
		Low	Central	Upper
pH	A	2.0	4.5	7.0
Amount of Photocatalyst (gL ⁻¹)	B	0.1	4.5	0.8
Contact time (min)	C	20	70	120

Results

Characterization study

Figure 1a presents the XRD spectrum of the GQDs, which show a broad diffraction peak (002) at around 2θ = 21.5° and amorphous carbon [23]. The synthesized GQDs reveal interlayer spacing about 0.407 nm which is wider than graphite [24] and is related to interlayer spacing ranges of GQD structure [25]. This corresponds with other reported interlayer spacing values of GQDs synthesized in different ways (0.340–0.481 nm) [26]. The different *d* spacing of graphite and GQDs is proceeded to O-H, C-H, and C-O-R at the edges of the GQDs [27]. The crystal size of GQD was evaluated by Scherrer's equation corresponded with XRD peaks at 2θ = 21.5.

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

where *D* shows the crystal size (nm), λ is the wavelength of the X-ray radiation (Cu Kα 0.154 nm), *k* reveals the Scherrer constant (0.89), β is the full width at the half-maximum of the (002) plane of GQD and θ is the diffraction angle. The crystallite size estimates about 0.88 nm in GQD nanoparticles.

The Raman spectrum of the GQDs is shown in Fig. 1b where typical D and G-band can be seen in the sample. The G peak is located at 1573.6 cm⁻¹, which determines the good crystallinity of GQDs [28] and attributes to the sp² in-plane vibration of carbon [29]. The D peak at 1380.7 cm⁻¹, is related to the numerous edges because of the defect states in the GQDs [30]. It corresponds with the hydrothermal method that causes very functional groups as surface defects [28]. The D/G ratio is 0.46, which confirms edge defects produced by hydrothermal methods [28].

Figure 1c shows the UV–visible absorption spectra of GQDs in aqueous solution. Two absorption peaks are placed at 216 and 263 nm, which corresponds to the electron transitions from π → π* of C=C and π → π* of C=O, respectively [31].

The absorption peak at 263 nm is due to the electron transition of sp² carbon structures. This peak shows the formation

Fig. 1 a) XRD spectra, and b) raman spectra, c) UV-Vis absorption spectra, d) FT-IR pattern e) TGA pattern, and f) the N₂ adsorption/desorption isotherm and the pore size distribution curve

of C=O, which corresponds to the electron transitions from $\pi \rightarrow \pi^*$. The absorption peak at 216 nm is attributed to the $\pi \rightarrow \pi^*$ transition of C=C bonds because the $\pi \rightarrow \pi^*$ transition of C=C in GQDs usually occurs at 200–270 nm wavelength [32].

FTIR results were carried out to confirm materials interaction and functional groups in GQD. Figure 1d displays the result of GQD with some vibration peaks which correlate with others [27, 28].

The most substantial peak is located at 1585 cm^{-1} , which is due to the C=C stretching mode. Other absorption peaks exhibit the presence of C-H (1376 cm^{-1} and 2976 cm^{-1}), C-O (1206 cm^{-1}), and O-H (3400 cm^{-1}) peaks of H₂O.

The result of TGA is shown in Fig. 1e, which displays the study of nanoparticle stability properties. TGA diagram of GQD particles reveals great lose weight and is not thermally stable. Constant loss weight is located until 400 °C for the carbon dots [33].

Nitrogen adsorption/desorption isotherm of GQDs (Fig. 1f) shows the type IV isotherm curve with a hysteresis loop and characteristic of mesoporous solids [34], for the hysteresis loop beginning at $P/P_0 \approx 0.45$ is an H_2 type mainly because adsorption and desorption branches are parallel. Regarding the IUPAC classification of adsorption isotherms, the nanoparticles group is categorized as mesoporous substance (mesoporous in IUPAC: pore size 2–50 nm) [34, 35].

FESEM image of photocatalyst shows the spherical morphology of synthesized particles with agglomeration, as depicted in Fig. 2a. The distribution size of particles is differently measured by FESEM from 76 to 118 nm because of agglomeration, while SEM does not enough belong among accurate tools for the estimating size. Energy dispersive X-ray (EDX) spectroscopy analysis (Fig. 2b) indicates sharp C and O signals. It proves successful in forming GQD particles. SEM mapping emphasizes the elemental composition obtained by FESEM (Fig. 2b) and proves the existence of C element and result of EDX.

Transmission electron microscopy (TEM) illustrates the morphology and distribution size of GQDs (Fig. 2c). TEM image of GQD crystals is sufficient, and the diameter of the particle size is about 1–3 nm. Also, it indicates spherical shape of GQDs synthesized, which is comparable with 0.88 nm for

the size of nanoparticle bulk substances calculated by applying the Scherrer's equation from the XRD spectrum. The image of high-resolution TEM (HRTEM) presents the d spacing lattice parameter with 0.24 nm (Fig. 2d), which corresponds to the graphene layers [36] and proves the graphitic structure of the GQDs [37]. Also, prepared GQDs are comparable to semi-crystalline of Yang [38].

Discussion

Photocatalytic degradation of imipramine

Preliminary experiments were performed before running the final experimental design. These experiments were accomplished to estimate the effect of UV irradiation on the photodecomposition and adsorption of imipramine. They were carried out in the presence of UV light and dark condition for a time period of 60 min. The results presented about 50% removal under UV irradiation with 1 g L^{-1} of photocatalyst concentration and neutral pH while around 5% removal in the absence of light source. The proposed experiment was carried out in the presence of light and the lack of photocatalyst under the same conditions obtaining zero

Fig. 2 Images of a) FESEM, b) mapping and EDX, c) TEM, and d) HRTEM of prepared GQD photocatalyst

removal. These results determined that photocatalyst plays the most crucial role in UV light and adsorption process. Thus photocatalyst and light irradiation are required for efficient treatment of imipramine.

RSM approach for optimized treatment of imipramine

The variables were attended as independent ones. The removal efficiency (%) was computed as the process response. The number of experiments (N) can be calculated by the following equation:

$$N = 2k(k-1) + C_o \quad (3)$$

Thus the experimental design consists of 15 operations for the modeling of three factors (k) such as pH, dose of nanoparticles, and time, with three center points allowing for the calculation of the response function at intermediate levels. It also enables estimation of the system performance at any experimental point within the studied range.

The non-linear computer-generated quadratic model employed in the response surface for the design of the experimental conditions are presented in Table 2 and estimated as follow:

$$Y(X) = \beta_o + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i=1}^3 \sum_{j=1}^3 \beta_{ij} X_i X_j \quad (4)$$

where $Y_{(x)}$ is the response, β_o presents an intercept, β_i and β_{ij} show the model's constant regression coefficients, and X_i , X_j ($i = 1, 3$; $j = 1, 3$ and $i \neq j$) are the levels of an independent factor. Regression analysis was utilized to fit the response function of experimental results and to optimize the appropriate model conditions. The value of R^2 , which is a measure of

the amount of variation around the mean according to the model and adjusted R^2 was evaluated as 0.95 and 0.90, respectively, which means that the obtained equation has good adequacy for correlating the experimental results. The second order polynomial model with the most reasonable statistics, i.e., higher F- and R-values and lower lack of fit were considered as the satisfactory response surface model to fit the experimental data (Table 3).

The experimental matrix and results of design for photocatalytic degradation of imipramine using GQDs, are shown in Table 2. Based on obtained results, the best removal efficiency was attributed to runs 1, 2, 3, and 4, referring to 81%, 76%, 77%, and 83%, respectively.

Figure 3 presents the ANOVA results, which created the Pareto plot of significant and interaction variables. The standard effect was obtained for calculating the t-statistic for any outcomes. The vertical line indicates the statistically significant results at 95% confidence amount. Moreover, either a negative or positive impact can be either increased or decreased by changing the specific parameter, is shown as a blue or pink (color) response. Regarding Fig. 5, pH reveals a negative effect on the removal efficiency while the contact time and nanoparticle concentration show a positive impact. It refers to the increase in removal efficiency at lower pH.

The RSM was employed to examine simultaneous variables of pH of the sample, photocatalyst dose, and exposure time on the response (Fig. 4).

Figure 4a and b display the interaction between the pH of the solution and photocatalyst dose and photocatalyst dose and irradiation time on efficiency removal. As a result, the maximum efficiency removal was achieved at a photocatalyst concentration of 0.1 g L^{-1} and reduced with an increase in both variables. Increasing the catalyst loading is led to a decrease in imipramine removal (%). It can be related to increasing the turbidity, lower the light penetration, and the

Table 2 Experimental design matrix in the BBD used in this study

Run	pH	Dose (g L^{-1})	Time (min)	Removal (%)
1	2.0	0.8	70	60.0
2	4.5	0.8	120	68.3
3	2.0	0.45	120	83.4
4	2.0	0.1	70	89.7
5	4.5	0.8	20	8.85
6	4.5	0.45	70	56.2
7	4.5	0.45	70	57.0
8	7.0	0.1	70	71.1
9	7.0	0.8	70	66.7
10	4.5	0.1	20	41.0
11	4.5	0.45	70	56.1
12	7.0	0.45	120	74.1
13	4.5	0.1	120	64.04
14	2.0	0.45	20	44.4
15	7.0	0.45	20	11.2

Table 3 Results of ANOVA for the fitted model

Source	Sum of Squares	Df	Mean Square	F-Ratio	P Value
A:pH	1104.63	1	1104.63	17.74	0.05
B:Dose	14.06	1	14.06	0.23	0.68
C:Time	3771.58	1	3771.58	60.58	0.02
AA	24.85	1	24.85	0.40	0.59
AB	12.62	1	12.62	0.20	0.70
AC	378	1	378	6.07	0.13
BB	244.12	1	244.12	3.92	0.19
BC	25.39	1	25.39	0.41	0.59
CC	723.25	1	723.25	11.62	0.08
Lack-of-fit	145.48	3	48.49	0.78	0.60
Pure error	124.51	2	62.26		
Total (corr.)	6648.33	14			

Fig. 3 Pareto chart of the main effects in the BBD

suspension of the photo-activated level while the availability of active sites increases with catalyst loading. Similar studies have given different organic pollutants [39]. On the other hand, the agglomeration enhances in high photocatalyst concentrations, which is due to reduce the available active sites and surface area for light penetration. Hence, the photocatalytic decomposition efficiency reduces [40]. Another reason can be affected by total light absorption by photocatalyst nanoparticles at an optimum concentration [40]. Thus, the maximum level of absorption photons occurs in the photo-reactor.

pH of the sample has a significant effect on photocatalyst surface charge, mechanism, and the rate of hydroxyl radical generation as well [41, 42]. Electrostatic interaction between

organic pollutants with photocatalyst surface, is intensively dependent on the pH of media [43]. According to previous studies, different organic substances show various activities in the photocatalytic process [22]. Some pollutants prefer acidic conditions to degrade, while others decompose better at basic pH. Thus, determination of the optimum pH is necessary for photocatalytic removal [44]. Figure 4a and c show the interaction effects between pH and photocatalyst dose and pH and UV exposure time on the removal efficiency, respectively. At the same time, the other variable was constant at the average value. According to them, pH shows an inverse effect on the response, so the degradation efficiency improves with reducing the pH value, photocatalyst level, and increase of UV exposure time. Briefly, the effect of pH on the photocatalytic degradation is strongly dependent to the point of zero charge of GQD nanoparticles [44] and the adsorption of the analytes on the surface of the photocatalyst in various pH [45]. Nanoparticles show a negative charge when the pH of the solution is higher than that of pH_{pzc} and is positive when the solution pH is lower than pH_{pzc} [46]. Also, removal efficiency depends on the adsorption of the pollutants on the photocatalyst in different pH values [45]. According to the literature, pH_{pzc} of GQDs can be about 3–4. It seems corresponding to the experimental results, which pKa of imipramine is 9.4 [47]. In other words, the solution shows a negative charge in $pH > pH_{pzc}$, and analyte has a positive charge that is favorable for photocatalytic interaction.

According to the overall results of the optimization step, the following optimal conditions were chosen: pH of sample, 2.0; photocatalyst dose, 0.1 g L^{-1} and UV irradiation time, 80 min that the removal percent was achieved about 80%, equal to 43 mg/L. In order to verification the synthesis GQDs, four different batch were experimented under optimum operating conditions for imipramine removal. The results showed an error less than 5% and $RSD \sim 7.5\%$. Therefore, the repeatability was acceptable. Also, GQDs based on maltose showed great photocatalytic property so that it was comparable with the degradation efficiency of imipramine in presence of TiO_2 and H_2O_2 (Calza et al., 2008). Table 4 presented the experimental conditions and removal efficiency of both studies.

Fig. 4 RSM plot of the main effects in the BBD

Table 4 The comparison between the removal efficiency of GQDs based on maltose and TiO₂

Nanoparticle	TiO ₂ + H ₂ O ₂	GQD based on maltose
light type	Visible	UVA
Lamp Power (W)	1500	8
Dose of photocatalyst	200	100
Imipramine Con.	15	200
T (°C)	20	30
t (min)	45	90
Removal (%)	93	80
Reference	Calza et al. (2008)	This work

Table 5 Physicochemical properties of wastewater sample of Parsian Pharmaceutical Co.

Parameter	Level
pH ^a	7.36
Soluble COD ^b	850
Total BOD (TBOD) ^b	640
Total dissolved Solids (TDS) ^b	1570
EC ^c	2019
Salt ^b	1010
Turbidity ^d	84.93

^a = none dimension, ^b = (mg per liter),
^c = $\mu\text{S}/\text{cm}$, ^d = NTU, 25 °C

Stability and recyclability of GQDs

The stability of a photocatalyst is the main factor for using a long time with high efficiency in photodegradation. Therefore, the stability of GQDs photocatalysts was examined four times as recycling tests under optimum conditions. At the end of each cycle, the photocatalyst was gathered *via* centrifugation. Then, the deposition photocatalyst was reused without any further treatment, as shown in Fig. 5. The removal percentage reveals a reduction which is probably related to the setting of potential by-product in the pores and on the surface of the photocatalyst because of the adsorption of pollutants, and decreasing the photocatalyst activity [48]. Also, a dark situation (without irradiation) was applied at the optimum condition, presenting only 16 mg/L about 10% removal (Fig. 5).

Real sample analysis

The real sample represented by pharmaceutical wastewater was examined to evaluate and assess the application of synthesized photocatalyst at the optimal condition. Wastewater

Fig. 5 The removal percentage recycling as a photocatalyst efficiency of GQD in optimum condition: pH of 2, photocatalyst concentration of 0.1 g L⁻¹ after 80 min

sample is received from effluent of Parsian pharmaceutical Co. Following the collection, sample was transported on ice,

Fig. 6 The GC chromatograms of the wastewater; a) before, and b) after the photocatalytic treatment under optimum conditions and UV light

stored at 4 °C, and examined after spike imipramine (lab fortified with 200 mg/L prior test) because not being the target analyte in the real wastewater within 72 h of collection. Table 5 showed the physico-chemical characteristic of this wastewater. After treatment process, 200 mg/L clomipramine was spiked as the internal standard for reducing fault. Figure 6 presents the GC chromatograms before and after irradiation, which indicates the efficiency of treatments considered under UV. The concentration of imipramine reduced to 58 mg/L after irradiation. Thus, it is assumed that the synthesized GQDs are capable of decomposing imipramine from real industrial wastewater up to 70% as a pharmaceutical pollutant under UV light.

The advantage of photocatalytic degradation is the lack of organic pollutant selectivity, which is proven by about 60% reduction in COD compared to the pre-treatment sample. Thus, the COD of wastewater decreased to 345 mg/L after irradiation.

Conclusion

In this study, for the first time, the GQD nanoparticles based on maltose were successfully applied for photodegradation of imipramine as a model persistence organic pollutant. The characterization of the prepared photocatalysts was determined using different analytical techniques such as XRD, Raman, FESEM, EDX, TEM, UV-vis, and BET. A considerable enhancement was achieved in the photo-treatment efficiency of imipramine under UV irradiation by using GQDs photocatalysts (Removal = 80%). It can be attributed due to the mesoporous structure of nanoparticles with a high specific surface area and photo-activity. The stability and recyclability were examined four times, showing almost the same results with a little reduction in fourth time that may be due to penetrating the by-product in the pores and on the surface of nanoparticles. Finally, the proposed method showed an industrial interest so that it was able to degrade real industrial wastewater up to 70%. Regarding outcomes mentioned above, this new type of photocatalytic material opens new horizons in the photodegradation area, especially for removing drugs in industrial wastewater samples.

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Compliance with ethical standards

Conflict of 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.

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