Taguchi optimization approach for metronidazole removal from aqueous solutions by using graphene oxide functionalized $\beta$-cyclodextrin/Ag nanocomposite

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**ABSTRACT**

Metronidazole (MNZ) is a major threat to the ecosystems and human health, due to its toxicity and carcinogenic nature. The main aim of this study was to evaluate the efficiency of graphene oxide functionalized $\beta$-cyclodextrin/Ag nanocomposite (GO/$\beta$-CD/Ag) for MNZ removal from aqueous solution. The effect of operational parameters such as solution pH (2–5), adsorbent dosages (0.2–1 g/L), contact time (10–80 min), initial MNZ concentrations (0.25–10 mg/L) and ionic strength (0.001–0.1 mol/L) was studied using Taguchi experimental design. The maximum removal efficiency of 93.5% was observed for optimum conditions. The optimum values of contact time, the initial MNZ concentration, the ionic strength, the adsorbent dosage and solution pH were found to be 20 min, 0.25 ppm, 0.01 mol/L, 0.4 g/L and 2, respectively. Freundlich and Dubinin–Radushkevich isotherm models were best-fitted with experimental data. Pseudo-first order and type 1 pseudo-second order kinetic models showed the maximum correlation with the experimental data. Adsorption experiments with real samples indicated that the adsorptive removal of MNZ from a hospital wastewater was 72%. Desorption studies showed maximum recovery of GO/$\beta$-CD/Ag nanocomposite during three cycles. According to the obtained results, it can be concluded that the application of carbon adsorbents such as GO/$\beta$-CD/Ag can be considered an efficient method for final treatment of effluents containing antibiotics.

**Key words** | adsorption, Ag, $\beta$-cyclodextrin, graphene oxide, metronidazole

**INTRODUCTION**

Metronidazole (MNZ) is a common nitroimidazole antibiotic derivative that has antibacterial and anti-inflammatory properties (Ocampo-Pérez et al. 2015). MNZ has been used to treat infectious diseases caused by anaerobic bacteria and protozoans, including giardiasis and amoebiasis (Rivera-Utrilla et al. 2003; Ocampo-Pérez et al. 2015). MNZ is the only nitroimidazole that is contained in the WHO list of essential drugs (Ocampo-Pérez et al. 2013). Because of the toxicity, non-degradability, potential mutagenicity, and carcinogenicity of MNZ, it poses a major threat to the ecosystems and human health (Ahmed & Theydan 2013; Ocampo-Pérez et al. 2013). According to the International Agency for Research on Cancer, adequate evidence says that to consider MNZ as a potentially carcinogenic material (Ocampo-Pérez et al. 2013). A maximum concentration of MNZ of 9,400 ng/L in the effluents of a hospital and 127 ng/L in sewage treatment plant has been found (Dong et al. 2014). These characteristics make nitroimidazoles potentially dangerous compounds because they are prone to accumulation in aquatic and terrestrial organisms (Ahmed & Theydan 2013). Therefore, they are considered to be an emerging environmental problem and it is necessary to remove them from contaminated waters.

Several techniques such as electrochemical oxidation, chemical reduction, ozonation and adsorption have been suggested as separation methods for nitroimidazole
antibiotics (Ahmed & Theydan 2015). Among these methods, adsorption is the most widely used method, due to numerous advantages, including applicability at very low concentrations, ease of operation, possibility of regeneration and cost-effectiveness (Li et al. 2013). Thus, there is a strong desire to find a high-performance, low-cost, and easily regenerated adsorbent to remove MNZ from wastewater.

Graphene, a single layer of sp2 bonded carbon atoms in a two-dimensional hexagonal lattice, has attracted a great deal of scientific interest in recent years, because of its high conductivity (10^3–10^4 S/m), economical use and high surface areas (theoretical value 2,635 m^2/g) (Wang et al. 2013). Graphene oxides (GO), the oxidized form of graphene, have many oxygen-containing functional groups on the surface, including hydroxyl, epoxy and carboxylic acid groups. The functional groups make GO to be hydrophilic, easily chemically modified and suitable to be used as an adsorbent (Tang et al. 2015). Hence, it is considered that GOs can be used as a unique adsorbent for pollutant removal.

β-cyclodextrin (β-CD), is a doughnut-shaped structure cyclic oligosaccharide consisting of seven glucopyranose units with a hydrophilic outer surface and a lipophilic cavity (Badruddoza et al. 2010). Cyclodextrins (CDs) can form inclusion complexes with a wide variety of organic and inorganic compounds in solution or in the solid state within the hydrophobic cavity (Hu et al. 2013). Therefore, CD complexation is a method of choice for decontaminating techniques.

In the nanometre scale, silver nanoparticles due to their high surface area and also redox reaction production are highly reactive species (Tuan et al. 2011). So, they can be used to increase the pollutant removal efficiency.

Taguchi methods have been extensively used to optimize the reaction parameters by a minimum number of experiments. Taguchi experimental design reduces cost and improves process performance, yield, and productivity design of experiments. It is a useful method that can identify the key variables that affect the quality characteristics of the process (Huang et al. 2009).

The purpose of this experiment is determination of levels of controllable factors to achieve the highest efficiency. In the Taguchi method, an analysis of the signal-to-noise (S/N) ratio is needed to evaluate the experimental results. The S/N ratio is given by Equation (1) (Farzadkia et al. 2009).

\[
S/N = -10 \log \left( \frac{1/y_1^2 + 1/y_2^2 + \cdots + 1/y_n^2}{n} \right)
\]

where \( n \) is the number of repetitions under the same experimental conditions and \( y_i \) is the characteristic property.

Therefore, the Taguchi method was chosen for laying out this study.

Recently, several studies have focused on utilizing GO modified magnetite for the removal of tetracycline (Zhang et al. 2011), ZnSnO3/RGO nanocomposites for the removal of MNZ (Dong et al. 2014), and GO functionalized with magnetic cyclodextrin–chitosan for the removal of hydroquinone (Li et al. 2013) from aqueous solution under static conditions. However, although these adsorbents presented an excellent performance in removal of contaminants, some drawbacks such as high cost of silver and difficulties in separation of adsorbents caused some doubt in environmentalists.

In the present study, the clean method was used for preparation of GO functionalized β-cyclodextrin/Ag nanocomposite (GO/β-CD/Ag) through GO and AgNO3 under microwave conditions (Liu et al. 2013). The novelty of this study is the Taguchi optimization method for the removal of MNZ by GO/β-CD/Ag from aqueous solution.

In this study, the size, structure, surface properties and functional groups of GO/β-CD/Ag were characterized by using different analytical tools. Also, solution pH, ionic strength, contact time, initial MNZ concentrations and adsorbent dosages were studied as the controllable factors. Accordingly, the percentage contribution of each of the above experimental parameters to the process is determined using the Taguchi method. In addition, adsorption and desorption experiments with real samples were also carried out.

MATERIALS AND METHODS

Chemicals and reagents

Natural graphite, β-cyclodextrin and standards of MNZ were purchased from Sigma Aldrich, Co. AgNO3 and the other reagents used in this study were of analytical grade from Merck Co., Germany. Aqueous solutions were prepared with deionized water. Nitric acid (HNO3, 98%) and sodium hydroxide were used to control the solution pH. Moreover, different amounts of NaCl were used to study the effect of salt concentrations. In addition, acetone was used for desorption experiments.

Characterization

MNZ concentration was measured by high performance liquid chromatography (HPLC) (model: KNAUER). GO and GO/β-CD/Ag nanocomposite were characterized
using various techniques such as X-ray photoelectron spectroscopy (Model X’PertPro) using CuKα = 1.5. The diffractograms were recorded in the 2θ range of 5–80°. Field emission scanning electron microscopy (FESEM) (Model Mira 3-XMU) was also used. Fourier transform infrared (FT-IR) spectra were recorded using an FT-IR analyzer (Bruker, Vertex 70), and KBr served as a reference sample.

Preparation of adsorbents

GO/β-CD/Ag was prepared by a microwave heating method. GO was prepared using a natural graphite powder by the modified Hummers method (Cote et al. 2010) and the detailed synthesis of GO/β-CD/Ag was as follows: GO aqueous dispersion (0.25 mg/mL, 10 mL) and β-CD aqueous solution (2.5 mg/mL, 10 mL) were mixed together. The pH value of the mixed solution was regulated to 12.0 using NaOH solution. Then, 50 mL of 0.1 mol/L AgNO₃ solution was added. Then, the above-mentioned solution was heated for 4 min in a household microwave oven (Kenwood, power: 1,000 W, 60% of the power was used). The product was isolated by centrifugation for 15 min at 10,000 rpm, followed by consecutive washing/centrifugation cycles with deionized water. Finally, the collected product was dried by freeze-drying cycles (model Cryodos, Spain) (Liu et al. 2013).

Adsorption experiments

The experiments were conducted by shaking 16 series of 25 mL Erlenmeyer flasks based on the conditions reported in Table 2. To evaluate the effects of operational and environmental factors on the efficiency of antibiotic removal, the batch adsorption experiments were carried out at different solution pH (2–5), ionic strength (0.001–0.1 mol/L), adsorbent dosages (0.2–1 g/L), contact time (10–80 min) and different initial MNZ concentrations (0.25–10 ppm). All samples were prepared under the same conditions. After the adsorbent was removed, the residual concentration of antibiotic in the supernatant was measured by HPLC (model KNAUER) equipped with a C8 column (Eurospher 100-5 C8) and a UV detector at 319 nm. The mobile phase was 4:1 (v:v) of deionized water and methanol with a flow rate of 1 mL/min. The Chromatograms recorded for about twice the retention time of MNZ and measured the responses for the MNZ peak. The results are the mean of experimental data (U.S.P. 2011). The maximum adsorption capacity was obtained from the isotherm study. The PRE (pollutant removal efficiency, %) of MNZ (Zolfaghari et al. 2011) and the amount of MNZ adsorbed (Qₑ, mg/g) were calculated using the following equations:

\[
\text{PRE} = 100 \times \left( \frac{C_0 - C_e}{C_0} \right) \\
Q_e = \frac{(C_0 - C_e)V}{m}
\]

where \(C_0\) and \(C_e\) are the initial and equilibrium concentrations of pollutant (mg/L), respectively. \(V\) is the volume of the solution (L), and \(W\) is the mass of adsorbent (g).

Experimental design and procedure

In this study, the optimum levels of variables were optimized using Taguchi experimental (Qualitek-4 (Nutek Inc.)) design. Five controllable factors of solution pH, ionic strength, adsorbent dosages, contact time and initial MNZ concentrations were selected and the removal efficiency of aqueous solutions was studied for each factor at four levels (Table 1). Therefore, the orthogonal array of L₁₆ (4⁵) type was used, and the experimental conditions are represented in Table 2.

Desorption and reusability experiments

According to the optimum conditions, 0.4 g/L GO/β-CD/Ag was mixed with 25 mL of 0.25 mg/1 MNZ solution at pH 2.0. After adsorption, GO/β-CD/Ag adsorbents were separated from solution, and the supernatant was discarded and washed sequentially via acetone and deionized water. Then, the regenerated adsorbents were used for the next adsorption cycle.

Table 1 | The experimental factors and their levels

<table>
<thead>
<tr>
<th>Factors</th>
<th>Level 1</th>
<th>Level 2</th>
<th>Level 3</th>
<th>Level 4</th>
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<td>A: pH</td>
<td>2</td>
<td>3</td>
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<td>5</td>
</tr>
<tr>
<td>B: ionic strength (mol/L)</td>
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<tr>
<td>D: contact time (min)</td>
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</tr>
<tr>
<td>E: initial MNZ concentration (mg/L)</td>
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<td>10</td>
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</table>
Real experiments

To evaluate the effect of adsorbent on MNZ adsorption from a real sample, raw sewage samples were collected from a hospital. Then, after passing the real sample through a filter, the electrical conductivity, pH, total suspended solids and temperature were measured. According to the optimum conditions, 0.4 g/L GO/β-CD/Ag was mixed with 25 mL of 0.25 mg/L MNZ solution at pH 2.0. After adsorption, GO/β-CD/Ag adsorbents were separated from solution and the residual concentration of MNZ in solution was measured.

RESULTS AND DISCUSSION

Preparation and characterization of GO functionalized β-cyclodextrin/Ag nanocomposite

The FT-IR spectrum of GO is shown in Figure 1. In the FT-IR spectrum of GO, the adsorption peaks appearing at 3,578.3, 1,729.9, 1,621.11, 1,220.97, and 1,055.03 cm⁻¹ are attributed to OH stretching vibrations, stretching vibration of carbonyl groups C=O, stretching vibration of C=C, stretching peak C-OH, and epoxy C-O-C, respectively. Another adsorption peak is attributable to deformation vibrations of O-H groups of tertiary C-OH, at 1,384.59 cm⁻¹.

In the X-ray diffraction (XRD) patterns (Figure 2) of GO and GO/β-CD/Ag nanocomposite, the diffraction peak at 2θ = 9.8° corresponds to the typical diffraction peak of GO (Deng et al. 2015). For GO/β-CD/Ag, the peaks found at 2θ = 38.2, 44.2, 64.6, and 77.6° are assigned to the Ag (111) (200) (220) (311) (222) (400) faces, respectively (Liu et al. 2015).

The particle size and morphology information of GO and GO/β-CD/Ag were studied by FESEM images, as shown in Figure 3. GO presents a layered-like structure with a smooth surface, high number of wrinkles and without any order or crystalline particles. In addition, the morphological structure of GO/β-CD/Ag shows that Ag nanoparticles were distributed at the surfaces of GO nanoparticles. The average size of GO/β-CD/Ag was about 25 nm (Liu et al. 2013).

Adsorption properties

Taguchi approach for optimization of MNZ adsorption on GO/β-CD/Ag

In this study, the amount of MNZ was measured before and after each test. The pollutant removal efficiency in Tests 1–16, with one replicate measured for MNZ according to the method and Equation (2) (Table 2), and the S/N ratio of each test condition were determined (Table 2). In this

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### Table 2: Experimental results obtained by Taguchi method

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<th>Experimental number</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
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<th>Second results</th>
<th>S/N</th>
<th>The efficiency of each step (%)</th>
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</table>
table, increasing S/N ratio shows an improvement in the situation. Subsequently, the S/N ratio values were substituted into Equation (1). As shown in this table, the maximum removal efficiency of MNZ for initial MNZ concentrations 0.25, 0.5, 1, and 10 mg/L were obtained as 82, 89, 72.5, and 43.5%, respectively. By analyzing the results in Table 2, according to the Taguchi method, the influence of each parameter on the removal percentage of MNZ and optimum condition was obtained.

The effect of initial concentrations

Figure 4(a) shows the effect of initial concentrations on the S/N ratio in the removal of MNZ. The highest removal rate of MNZ was observed (16.247) in the first level of concentration of 0.25 ppm, which was followed by a decrease in the average with increasing initial concentration of MNZ. Decreased removal efficiency can be derived from increasing the initial concentration of contaminant, which is due to the presence of competing ions for adsorption places. At low contaminant concentrations, the removal efficiency of contaminant is higher, due to the abundance of more surface reactive sites (Ahmadi et al. 2011).

The effect of contact time

The effect of contact time (Figure 4(b)) in the first 10 min of reaction is high and then by increasing the contact time to 20 min the highest MNZ removal rate occurred (4.86). But, further increase in the contact time led to decreasing removal efficiency of MNZ. That observation is probably due to reversibility of the silver and MNZ complex according to Çalışkan & Göktürk (2010). As a result, the contact time of 20 min was selected as an optimum time.

The effect of solution pH

Figure 4(c) shows the results of effect of solution pH on the adsorptive removal of MNZ from aqueous solution. The maximum removal of MNZ was observed in lowest pH values which was followed by a sharp decrease with an enhancement in solution pH. With increasing pH, adsorbent surface charge goes to the negative side. On the other hand, reducing the removal rate of MNZ at pH values above 2 can be due to the formation of anionic compounds that reduce the adsorption of MNZ. MNZ, due to the presence of nitrogen and oxygen in the its structure, may have formed a complex with silver in the composite, which increases the adsorption of drug. Silver also reacts with hydroxide ions at high pH and reduces the adsorption of MNZ. Therefore, pH = 2 was selected as an optimum pH value for adsorption of MNZ in further experiments. Electrostatic forces do not play an important role in the adsorption of MNZ in pH between 4 and 11. Since the MNZ molecules are neutral in this situation, the oxygen groups of graphene gradually will be ionized by increasing solution pH. When the pH of solution increases, the number of positive available sites reduces and the number of negative charged sites increases. The pKa of MNZ is 2.55 and when the pH is more than 2.55 MNZ surfaces will be negative, which is why the electrostatic repulsion is created. At pH values less than 2.55, positive charges will be created on the surfaces of MNZ. The average effect has decreased by increasing the pH, which corresponds with other studies (Çalışkan & Göktürk 2010).
The effect of ionic strength

Figure 4(d) represents the effect of ionic strength on S/N ratio in the removal of MNZ from aqueous solution. In the beginning at the first level (0.001 mol/L), average effect is high, followed by NaCl further increasing the average effect of ionic strength to the highest value (5.19), followed by a reduction. Increase in the amount of effect
can be due to decreasing the solubility caused by increasing ionic strength in solution. As a result, the presence of ionic strength in the solution has not changed significantly the adsorption capacity. In addition, these results confirmed that there are not electrostatic interactions.

The effect of adsorbent dosage

Figure 4(e) illustrates the influence of adsorbent dosages on S/N ratio for adsorptive removal of MNZ. The removal efficiency is negligible at the first level of adsorbent dosage of 0.2 g/L and has been raised to the maximum value (4.714) by increasing the amount of adsorbent dosage to 0.4 g/L. This finding can be explained by the fact that an increase in the adsorbent dosage provides more active sites or greater surface area for adsorption of MNZ (Çalıskan & Göktürk 2010).

According to Figure 4(e), by increasing the amount of adsorbent (>0.4 g/L), the removal efficiency was decreased. This phenomenon could be ascribed to the fact that the increase of adsorbent concentration leads to less dispersion of particles in the solution; as a result adsorption of MNZ decreases. This problem can be solved by increasing the volume of the solution.

Analysis of variance

Analysis of variance (ANOVA) was carried out after the analysis of the S/N ratio in order to estimate the error variance and relative importance of each factor. The data obtained for the removal of MNZ were analyzed by ANOVA, as shown in Table 3. The purpose of ANOVA analysis was to obtain the variance of each factor to total variance. The degrees of freedom (DOF), in this study, was calculated for each factor equal to 3 and total DOF was 15. Therefore, DOF for error was zero and error variance was determined by sum of squares divided by DOF. The F-ratio was calculated by dividing the variance of each factor by an error period. In this study, error period was considered zero, so calculating F-ratio is important. Table 3 shows ANOVA results according to the removal percentage of MNZ. Since in this study five variables were considered at four levels, the DOF is 3 for comparing the answer values for four levels of each factor. The last column represents the percentage of impact of each factor on the response. Therefore, the most effective factor is antibiotic concentration (84.862%), which is followed by solution pH (12.522%), ionic strength (1.107%), contact time (0.815%), and adsorbent dosage (0.691%), respectively (Figure S1, in Supplementary data, available with the online version of this paper).

Determination of the optimum conditions

According to the figures representing the effect of each parameter and ANOVA table, the optimum experimental conditions of the adsorption process can be obtained.

Table 4 shows optimum conditions for the removal of MNZ determined by Taguchi method, which are the contact time of 20 min, the initial MNZ concentration of 0.25 ppm, the ionic strength of 0.01 mol/L, the adsorbent dosage of
0.4 g/L, and the solution pH of 2. According to the results, by applying optimum conditions obtained from the Taguchi method, the improvement of response function is significant where the response value will be improved more than 26 units and enhanced to 29.809. The advantage of this new response in statistical analysis is the comparison of the magnitude of effects of each main factor to effects of error and disturbance factors in measurements, which consequently leads to a more precise perception of the actual effect of factors in the system. The maximum removal efficiency of

\[ \text{Figure 4} \] Effect of (a) initial MNZ concentration (con), (b) contact time, (c) solution pH, (d) ionic strength (is) and (e) adsorbent dosage (dos) on the S/N ratio in the adsorptive removal of MNZ from aqueous solution.
93.5% was observed for optimum conditions. Thus, based on the optimum conditions, the removal efficiency of MNZ was increased.

### Adsorption isotherms

An adsorption isotherm shows the distribution of the amount of the adsorbed substances per adsorbent mass unit in a constant temperature in equilibrium conditions (Zolfaghari et al. 2011). These equations are used to describe the adsorption capacity and determine the mechanism of adsorption onto the GO/β-CD/Ag. In this study, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D-R) isotherms were examined. Modeling isotherms under optimum conditions was performed using various MNZ concentrations (0.1, 2, 4, 6, 8, 10 mg/L). The sorption data were fitted to Freundlich (R² = 0.9827) and D-R (R² = 0.9861) isotherm models, as described in Table 5. The Freundlich model is used for the adsorption by heterogeneous adsorbent surfaces with exponential distribution of energy. The value of ‘n’ (constant sorption intensity) is over 1 (1.04), which shows the chemisorption nature of the process of MNZ adsorption. The D-R isotherm model is used to determine whether the adsorption process is chemical or physical and obtain heterogeneity of the surface energies. For Es values (sorption energy) between 8 and 16 kJ/mol, the adsorption process is chemical, while Es < 8 kJ/mol represents a physical adsorption (Atia et al. 2009). For the adsorption of MNZ onto GO/β-CD/Ag, the value of E was calculated as 7.07 kJ/mol, indicating the adsorption process occurs physically. The plots of adsorption isotherms are presented in Figure S2, in Supplementary data, available with the online version of this paper). The maximum adsorption capacity in terms of the Kf constant for the Freundlich isotherm was 0.67 mg/g, compared to 0.43 mg/g for D-R isotherm, 6.5 mg/g for...
Langmuir and 6.92 for Temkin isotherm (Table 5). Also the Freundlich model represents a multilayer adsorption. The other studies also corresponded to this model (Rivera-Utrilla et al. 2009; Çalışkan & Göktürk 2010; Ahmed & Theydan 2013).

### Adsorption kinetics

Kinetic models to evaluate the procedures of adsorption and steps of potential speed control, including mass transfer and chemical reaction processes, were used to fit the experimental data. Adsorption kinetics remove speed of dissolved substance that controlled retention time in reactions. Kinetic models have been created for understanding the kinetics of adsorption and limiting speed steps (Febrianto et al. 2009). In this study, pseudo-first and pseudo-second order kinetic models were studied to determine the adsorption mechanism. Modeling kinetics under optimum conditions was performed five times (4, 8, 12, 16 and 20 min). The kinetic parameters and correlation coefficients of pseudo-first order and pseudo-second order kinetic models are shown in Table 6. The rate of the adsorption process generally depends on the number of ions in the solution, and hence most of the adsorption processes follow a pseudo-first order kinetic behavior. For this reason, the experimental data in this study were fitted to the pseudo-first order model ($R^2 = 0.9928$). But the kinetic of MNZ adsorption was better explained by the pseudo-second order type 1 kinetic model ($R^2 > 0.9995$). This result showed that the MNZ adsorption onto adsorbent is affected by two parallel reactions; the first reaction is faster and the second reaction is slower in longer reaction time (Nadeem et al. 2008), and type 1 pseudo-second order model ($R^2 = 0.9995$). Similar studies also corresponded to pseudo-first order and pseudo-second order models (Ocampo-Pérez et al. 2013; Flores-Cano et al. 2016). The plots of adsorption kinetics are presented in Figure S3 in Supplementary data (available with the online version of this paper).

### Desorption and reusability

Reusing the adsorbent materials that have been used previously is an important factor in the adsorption process and can help to reduce costs. According to the optimum conditions, the adsorption and desorption tests were performed using acetone and deionized water. Results of adsorption and desorption by acetone showed that this solution is good for MNZ. Hence, the desorption of MNZ from the adsorbent surface in three consecutive cycles were 85.2, 79.6 and 65.62%, respectively (Figure S4, in Supplementary data, available with the online version of this paper). Results showed that the removal efficiency of MNZ in three cycles of adsorption and desorption was 89.3 84.5 and 75.28%, respectively. According to a study of Carrales-Alvarado et al. (2014), on desorption of MNZ using different types of carbonaceous adsorbents, the used adsorbents can be revived by contact with an aqueous solution without MNZ.

### Real samples

To evaluate the effect of adsorbent on adsorption of MNZ from real samples, several raw hospital-sewage samples were collected. The experiments were conducted on the basis of optimum conditions. Removal efficiency of MNZ in the raw sewage was 72%. The low adsorption efficiency in hospital wastewater can be due to the presence of other substances that can occupy the adsorption sites. Findings of the adsorption of MNZ in hospital wastewater showed that GO functionalized nanocomposite is applicable in real environments. According to a study by Ocampo-Perez et al. (2013) on the adsorption of MNZ on activated

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**Table 6 | Kinetic parameters of MNZ adsorption with initial MNZ concentration 0.25 mg/L, adsorbent dosage 0.4 g/L and solution pH 2**

<table>
<thead>
<tr>
<th>Kinetics models</th>
<th>Variable coefficients</th>
<th>Values of the coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order</td>
<td>$K_1$ (1/min)</td>
<td>0.2761</td>
</tr>
<tr>
<td></td>
<td>$q_{e \text{ cal.}}$ (mg/g)</td>
<td>0.009882399</td>
</tr>
<tr>
<td></td>
<td>$q_{e \text{ exp.}}$ (mg/g)</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9928</td>
</tr>
<tr>
<td>Type 1 pseudo-second order</td>
<td>$K_2$ (g/mg.min)</td>
<td>48.35018536</td>
</tr>
<tr>
<td></td>
<td>($mg/g$ $q_{e \text{ cal.}}$)</td>
<td>0.016013087</td>
</tr>
<tr>
<td></td>
<td>($mg/g$ $q_{e \text{ exp.}}$)</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9995</td>
</tr>
<tr>
<td>Type 2 pseudo-second order</td>
<td>$K_2$ (g/mg.min)</td>
<td>42.33655751</td>
</tr>
<tr>
<td></td>
<td>($mg/g$ $q_{e \text{ cal.}}$)</td>
<td>0.016232449</td>
</tr>
<tr>
<td></td>
<td>($mg/g$ $q_{e \text{ exp.}}$)</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9917</td>
</tr>
<tr>
<td>Type 3 pseudo-second order</td>
<td>$K_2$ (g/mg.min)</td>
<td>42.82233442</td>
</tr>
<tr>
<td></td>
<td>($mg/g$ $q_{e \text{ cal.}}$)</td>
<td>0.0162</td>
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<tr>
<td></td>
<td>($mg/g$ $q_{e \text{ exp.}}$)</td>
<td>0.015</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.985</td>
</tr>
<tr>
<td>Type 4 pseudo-second order</td>
<td>$K_2$ (g/mg.min)</td>
<td>42.06296306</td>
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<tr>
<td></td>
<td>($mg/g$ $q_{e \text{ cal.}}$)</td>
<td>0.016244695</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.985</td>
</tr>
</tbody>
</table>

$K_1$: pseudo-first order rate constant; $K_2$: pseudo-second order kinetic model constant; $q_{e \text{ cal.}}$: Calculated sorption capacity; $q_{e \text{ exp.}}$: experimental sorption capacity.
carbon in different aquatic environments, the adsorption process in wastewater was less effective than in surface water. That observation was due to the fact that some parts of dissolved organic matters in wastewater were adsorbed on the carbon surfaces and thus the available surface area for adsorption of MNZ molecules was reduced.

CONCLUSIONS

In the present research, GO/β-CD/Ag nanocomposite and Taguchi method were used to obtain the optimum conditions of MNZ adsorption in aqueous solution. The optimum conditions of removal of MNZ are the contact time of 20 min, the initial concentration 0.25 ppm, the ionic strength 0.01 mol/L, the adsorbent dosage 0.4 g/L, and the solution pH 2. The highest removal efficiency of 93.5% was observed for optimum conditions. Based on the experimental results of GO/β-CD/Ag, it can be deduced that this nano-porous carbon is highly effective in removing MNZ with a high PRE (93.5% under optimum conditions). The pollutant removal efficiency increased by GO/β-CD/Ag composite due to the cavity-like molecular structure of β-cyclodextrin which allows the formation of complexes with the MNZ molecules. On the other hand the silver nanoparticles with catalytic activity in a redox reaction enhance the performance of the nanocomposite in the removal of MNZ. Pseudo-first order and pseudo-second order type 1 kinetic models, compared to other models used in this study, were best-fitted with the experimental data. The adsorption isotherm of MNZ followed the Freundlich and D-R models. According to obtained results, it can be concluded that the application of carbon adsorbents such as GO/β-CD/Ag can be considered as an efficient method for final treatment of effluents containing antibiotics.

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