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Kinetics adsorption of Amoxicillin from aqueous solution by Graphen Oxide- Gold nanoparticles (GO-AuNPs) nanocomposite as novel adsorbent

*Soheila Tahmasebi [1]; Omid Moradi [1, *]; Mohammad Yari [2]*

[1]*Department of Chemistry, Shahr-e-Qods Branch, Islamic Azad University, Tehran, Iran*
[2]*Department of Chemistry, Eslamshahr Branch, Islamic Azad University, Eslamshahr, Iran*

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ABSTRACT: In this study, Graphene Oxide- Gold nanoparticles (GO-AuNPs) nanocomposite as novel adsorbent was synthesized by direct reaction between GO and chloroauric acid for removal of amoxicillin from aqueous solution. Nanocomposite (GO-AuNPs) was characteristic by FT-IR spectroscopy. The changes of parameters such as contact time, pH of solution, initial amoxicillin concentration and temperature were measured and investigated by several adsorption experiments various factors affecting the uptake behavior. The adsorption kinetics well described by a pseudo-second-order rate model.

Keywords: *Adsorption; Amoxicillin; Chloroauric acid; Gold nanoparticles; Graphene Oxide; Kinetics parameters.*

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INTRODUCTION

Antibiotics are specially designed to control bacteria in for organisms are routinely used as veterinary medicine and human [1]. Pharmaceuticals are not environmentally different from other chemicals, such as pesticides and herbicides, but they have not aroused attention as potential pollutants until fairly recently. It is usually considered that pharmaceutical chemicals are in very low concentrations and therefore would not perilous the environment, so up to now there is not enough data available on the incidence, fate and effects of pharmaceutical chemicals in the environment and the related risks for humans and the environment [2]. Amoxicillin wastes because disagreeable odor, skin disorder, and may cause microbial persistence among pathogen organisms or the death of microorganism which are efficient in wastewater treatment. The persistent bacteria may cause disease that cannot be treated by conventional antibiotics [1]. For those reasons, amoxicillin waste need to be treated before bowed to the environment. There are many methods for the removal of amoxicillin from sewage water, such as cover process, ion exchange, biological degradation, and adsorption using various kinds of adsorbents [1, 4, 5].

Adsorption is unit operation by which remaining molecular forces at the surface of solids attract molecules of gases, vapors and liquids. In air pollution control the gases and vapors are the pollutants which have to be separated from an inert gas stream before emitted into the atmosphere. Adsorption therefore is a useful means of their disposal or recovers [4]. Graphene is a monolayer of carbon atoms ordered in hexagonal lattice [4,5]. It has attracted considerable attention due to its unique two-dimensional structure and its excellent mechanical, electronic and optical properties [5]. Also, Graphene oxide (GO) is a single-atomic-layered

*Corresponding Author: *Omid Moradi*
Email: *o.moradi@qodsiau.ac.ir*
Tel.: (+98) 21 468965000; Fax: (+98) 21 468965000

material derived from graphite oxide crystal and its prepared by oxidation of Graphene. It has the ability to dissolve and disperse in a variety of solutions including water. GO can be used in solar cells, medicine, biology and inorganic optoelectronic devices [6]. Graphene oxide (GO), a derivative of graphene, is obtained through the intense oxidation of natural graphite [7]. Au nanoparticles (Au-NPs) are often employed in biomedicine, electronic materials, the detection of heavy metal ions, and catalysis, due to their unique optical properties, surface plasmon resonance, stability and biocompatibility [6,7]. Recently, the catalytic behavior of Au-NPs has been a popular and active topic [8]. Nanoparticles (NPs) tend to aggregate when fabricated alone and therefore a supporting material is needed to grow and anchor the metal NPs GO has been used as a support material for many types of NPs including Au, Ag, Pd, Pt, and Ni [9].

EXPERIMENTAL

Materials

Amoxicillin sodium salt was purchased from The General Pharmaceutical Factory of Harbin Pharmaceutical Group. Other inorganic reagents were purchased from Tianjin Kermel Chemical Reagents Development Centre. All chemicals were of analytical grade and used without major filtration.

Preparation of Au nanoparticle/graphene oxide hybrids

A $HAuCl_4$ aqueous solution (10 mL, 0.047 mg/mL) was mixed with various amounts of aqueous GO suspension (0.275mg/mL). The mixture was stirred for 24 hours at 84 ^{0}C, during which time the Au nanoparticles were deposited on the surface of the GO sheets to form Au-NP/GO.

Batch mode adsorption studies

The effects of experimental parameters, such as Amoxicillin initial concentration (10-50 mg/L), pH (6, 7 and 8) and temperature (323, 313, 303 K) on the adsorption amount of various Amoxicillin were studied in a batch mode of function for the special period of contact times (1-14 h). In order to determine the effect of each parameter, the other parameters were kept constant during the experiment. For contact time studies, 30 mL of Amoxicillin solution of known initial concentration, some pH was taken with a stable amount of adsorbent (20 mL GNPs) and stormy in a thermo stated rotary shaker, with the speed of 250 rpm at 303 K. Also, the quality assurance of the analytical measurements was performed by the researchers. Amoxicillin standard solutions of 10, 20, 30, and 40 and 50 mg/L ±0.1% were used for the measurement. Calibration curves between 10 and 40 mg/L were gathered and the discovery limit was found to be 1 mg/L. The adsorption percentage of each adsorbed Amoxicillin was calculated as follows [8]:

$$\text{Adsorptivity}\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

Where C_i and C_f are the initial and final Amoxicillin concentrations (after contact to the adsorbent) respectively.

RESULTS AND DISCUSSION

Characterize of Nano composite Au-NPs/GO

The FT-IR spectrum was recorded to investigate the chemical structure and the possible boundary of products, as depicted in Fig. 1(a) and 1(b) for the GO and (GO-AuNPs) nanocomposite, respectively, at a frequency range of 4000 to 300 cm^{-1}. The FT-IR peaks were sorted in Table 1. The FT-IR spectrum of the GO was revealed at the C-H stretching vibration at 2923 cm^{-1} and 2924 cm^{-1}, the C-OH stretching peak at 1422 cm^{-1}, the C-O-C stretching peak at 1220 cm^{-1}, and the aromatic C-H peak at 864 cm^{-1}. The FT-IR spectrum of the Au-NPs/GO composites indicated similar peaks. In addition, new peaks at 1458 cm^{-1}, 1163 cm^{-1}, and 455 cm^{-1} corresponded to the OH deformation vibration [9] for C-O stretching and the vibration bands of COOH and the Au-NPs, respectively. Indeed, the appearance of two peaks at 1163 cm^{-1} and 1400 cm^{-1} was due to the strong link of COO^- and OH to the Au-NPs [10,11]. Hence, the Au-NPs are strongly capped with the COO^- and OH groups for the GO sheets. Fig. 1(a) shows the GO sheet before the ablation of gold plate; as mentioned above, the Au-NPs are decorated on the surface and between the GO sheets as shown in Fig. 1(b). It is worth mentioning that no impurity was observed in the final products, which was the consequence of the considerable advantages of the laser ablation method.

Kinetics Adsorption

In the present research, three kinetic videlicet models, pseudo-first-order, pseudo-second-order and

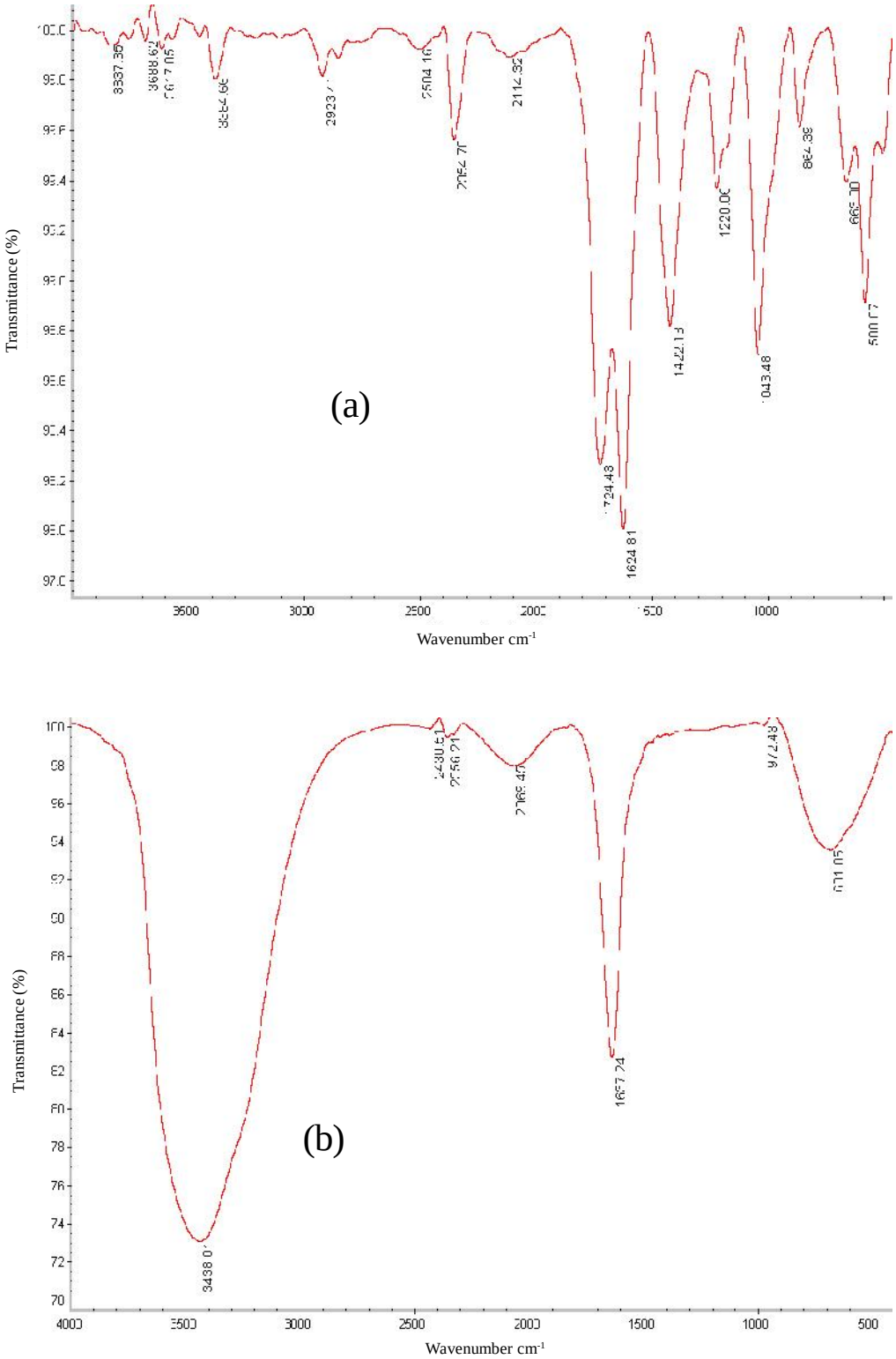

Fig. 1: a) FT-IR spectra of GO, b) FT-IR spectra of GO-AuNPs nanocomposite

Table 1: The FT-IR peaks for GO and GO-AuNPs nanocomposite

GO	GO-AuNPs	Definition of peaks
–	455	Au-NPs
864	972	Aromatic C-H
–	1163	Vibration band of COOH
1220	1637	C-O-C Stretching
1422	1400	C-OH Strectching
–	1458	OH deformation vibration of C-O stretching
2924	2924	C-H stretching vibration
2923	2923	C-H stretching vibration

in trap article model were tested to obtain price stable. Equilibrium adsorption valency and adsorption mechanism at several temperatures were investigated. The pseudo-first-order price stable (k_1) and the equilibrium adsorption valency, qe at several temperatures were determined from the slope and intercept of the plots of log (qe-qt) versus t (Figure not shown) and are listed in Table 2 along with the solidarity coefficient, R^2. From the kinetic data in Table 2, it can be seen that at all studied temperatures, the solidarity coefficients for the pseudo-first-order kinetic model were very low.

Moreover, a large difference between theoretical and experimental equilibrium adsorption valency, qe is observed at all temperatures, indicating a poor fit of the pseudo-first-order equation to the experimental data.

The kinetics followed the same path as the pseudo-first-order and pseudo second-order models, which are extensively used in kinetic studies. The pseudo-first-order model can be expressed as [8]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

Where k_1 is the first-order rate stable. The values of ln(qe -qt) are calculated from the experimental data and plotted against t, k_1 is calculated from the slope of the plot. The pseudo-second-order model can be expressed as [8]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Where k_2 is the second-order rate constant. The values of t/q_t are plotted against t, q_e and k_2 are calculated from the slope and intercept of the plot.

The kinetic data of GO-AuNPs nanocomposite adsorption onto amoxicillin from aqueous solution was further analyzed using the pseudo-second-order equation (Eq. (2)).

The pseudo-second-order model constants were determined from the slope and intercept of the plot of t/q_t against t. The plot of t/qt against t at different temperatures is shown in Table 2. Contrary to the pseudo-first-order equation, the suitable of the kinetic data in the pseudo-second-order equation showed excellent linearity with high correlation coefficient ($R^2 > 0.999$) over the temperature range of 303-333 K. The data obtained for the pseudo-second-order kinetic model at the four different temperatures is tabulated in Table 2. An analysis of the data in Table 2 suggests that the kinetics of adsorption of GO-AuNPs on amoxicillin from aqueous solution can be sided more accurately by the pseudo-second-order kinetic model. It is also displayed from Table 2 that rate constant, k_2 decreased as the temperature increased indicating exothermic nature of adsorption of GO-AuNPs onto amoxicillin from aqueous solution. Furthermore, the calculated qe values were found to be fully close to the experimental q_e values at all the temperatures studied (303-333 K). So, it was inferred that the adsorption of GO-AuNPs nanocomposite by amoxicillin from aqueous solution followed pseudo-second-order kinetics.

From, the pseudo-second-order kinetic parameters, the initial adsorption rate, h (mg g^{-1} min^{-1}) at different temperatures was calculated using Eq. (3) [14] and are presented in Table 2.

From, the pseudo-second-order kinetic parameters, the initial adsorption rate, h (mg g^{-1} min^{-1}) at different temperatures was calculated using Eq. (4) [14] and are presented in Table 2.

$$h = k_2 q_2 e \quad (4)$$

Table 2: Kinetic parameters for adsorption of GO, GO-AuNPs nanocomposite by amoxicillin from aqueous solution at 25 °C

Temperature (K)	$q_{e,exp}$ (mg/g)	k_1 (1/min)	R^2	Materials
Pseudo first-order model				
323	25.7	-0.3313	0.9855	GO
323	29.2	-6.360	0.9871	GO-AuNPs
Temperature (K)	$q_{e,exp}$ (mg/g)	k_2 (1/min)	R^2	
Pseudo second-order model				
323	25.7	2.73×10^{-2}	0.9989	GO
323	29.2	2.85×10^{-2}	0.9992	GO-AuNPs
Temperature (K)	$q_{e,exp}$ (mg/g)	k_i (1/min)	R^2	
Intra-particle diffusion model				
323	9.5603	5.2846	0.8744	GO
323	10.272	7.6371	0.8942	GO-AuNPs
Temperature (K)	α	β	R^2	
Elovich				
323	2.1794	5.3904	0.9576	GO
323	2.1831	6.4279	0.9560	GO-AuNPs

As evident from Table 2, the initial adsorption rate, h, decreased with increase in temperature suggesting that adsorption of GO-AuNPs by amoxicillin from aqueous solution was not favorable at higher temperatures [14]. The in trap article diffusion was investigated using the empirical relationship based on the model of Weber-Morris [15].

Adsorption of (GO-AuNPs) nanocomposite on amoxicillin from aqueous solution at different temperatures was multimodal with three distinct regions (Fig. not shown). The initial curved region corresponds to the external surface uptake, the second stage relates the gradual uptake reflecting in trap article diffusion as the rate limiting step and final plateau region indicates equilibrium uptake. Based on these results it might be concluded that in trap article diffusion was involved in amoxicillin from aqueous solution by (GO-AuNPs) nanocomposite removed, but it was not the sole rate determining step and that some other mechanisms also play an important role. Similar trend has heretofore been reported for some toxic material from aqueous solution adsorbed by surface adsorbents [15,16].

Effect of contact time

The effect of contact time, initial concentration pH and temperature on adsorption of amoxicillin by Nano composite adsorbent (GO-AuNPs) was investigated. The amoxicillin surfaces were absorbed by the (GO-AuNPs) in the solutions with different concentrations (20, 30,40 and 50 mg/L), pHs (6.6, 7.6 and 8.6) and temperatures (303, 313,323 and 333± 0.1 K). The amounts of amoxicillin adsorbed by the (GO-AuNPs) as adsorbent surfaces show the percentage of adsorbed amoxicillin by (GO-AuNPs) surfaces as a function of contact time, temperature and initial concentration at pH (pH =7). Also was indicated the percentage of adsorbed Amoxicillin by GNPs surfaces as a function of contact time, temperature and initial concentration at pH=7, respectively.

It can be seen that the amount of the Amoxicillin molecules adsorbed by (GO-AuNPs) nanocomposite with the increase of time was increased. Also, we can see the amount of Amoxicillin adsorbed is at the highest by (GO-AuNPs) at an 8 h period for all conditions (initial concentration, temperature and pH) and with the increase of time the amount of amoxicillin from aqueous solution adsorbed remained unchanged with time or better to say reached the equilibrium state. Therefore, the 8 h period was chosen as the optimum contact time for all conditions.

CONCLUSION

GO is identified to be an effective adsorbent for the adsorption of Amoxicillin molecules from the aqueous medium. The adsorption is highly dependent on various operating parameters like; contact time, pH, initial Amoxicillin concentration and temperature. It has been observed that the adsorption percentage increased with an increase in the contact time and becomes gradual after 8 h. The adsorption percentage of Amoxicillin adsorbed by GO is

maximized at a pH value of 7 and decreases with decreasing of the solution pH. The adsorption percentage increased with increasing initial concentration of Amoxicillin and pH of solution, also adsorption percentage decreased with increasing of the temperature of the solution. The pseudo-second-order model gives satisfactory fitting, and the in trap article diffusion model describes the adsorption process well. Steric effects on adsorption kinetics were found for GO-Au-NPs and Amoxicillin, due to the limitation of the pore structure and the retardation of the adsorbed molecules.

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