Efficiency of Chitosan Extracted from Persian Gulf Shrimp Shell in Removal of Penicillin G Antibiotic from Aqueous Environment

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ABSTRACT: *Antibiotics are discharged into the aqueous environment in various ways. The disposal of wastewater containing antibiotics creates serious environmental problems. Today, given the necessity of using natural materials, natural-based adsorbents have been taken into consideration. Chitosan is a natural polysaccharide derived from the crust of crustaceans of the sea with many useful aspects such as hydrophilicity, biodegradability, and biocompatibility. In this study, after the preparation of chitosan, the effect of various parameters such as pH (3-11), adsorbent dosage (0.25-1g/L), penicillin G concentration (10-70 mg/L), and contact time (5-90 min) in the removal of antibiotic was investigated. Structural characteristics of synthesized chitosan were determined by Scanning Electron Microscopy (SEM), and X-Ray Diffraction (XRD). Also, the isotherm, thermodynamics, and kinetics of the adsorption process were studied. The results of this study showed that the maximum adsorption capacity of chitosan in optimum condition (pH=7, adsorbent dose: 0.25 g/L, the concentration of antibiotics: 70 mg/L, and contact time: 10 min) was 101.44 mg/g. SEM image showed that the size of chitosan was ranging from 700 nm to 5 microns. The results of XRD analysis showed the successful synthesis of chitosan. Experimental data indicate that the results are consistent with the Langmuir isotherm model and that the adsorption process was followed by a pseudo-second-order model. According to the results of thermodynamic studies, the standard entropy variations (ΔS) were 20.68 (J/mol k) and standard enthalpy changes (ΔH) were 5.69 kJ/mol and standard Gibbs free energy (ΔG) values were negative and respectively indicates that adsorption process of penicillin G by chitosan is spontaneous and endothermic.*

KEYWORDS: *Chitosan; Antibiotics; Penicillin G; Adsorption.*

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1021-9986/2020/4/235-244 10/$/6.00

INTRODUCTION

In recent years, concerns have been raised about the use of compounds and pharmaceutical substances and the entry of these materials into the environment, especially water resources and are regarded as a serious environmental issue [1, 2]. Among the drug compounds, antibiotics are of particular importance due to their high consumption in the treatment of diseases and the widespread use in medicine and veterinary medicine and creating resistance in bacteria [3, 4].

The production of these antibiotics in the world is very widespread so that as many as 11100 tons of antibiotics are produced annually in 20 countries [5]. Antibiotics are classified into beta-lactam and non-beta-lactam groups based on the presence of beta-lactam rings in their structures. Penicillin G or benzyl penicillin G with chemical formula $C_{16}H_{18}N_2O_4S$ is in the category of β-lactam antibiotic. This antibiotic is sensitive to heat and acid and is considered as a weak acid (pKa=2.75) [6-8].

Antibiotics are discharged into the aqueous environment in a variety of ways, including household wastewater, pharmaceutical wastewater, agricultural products, and wastewater from hospitals, veterinary clinics and fish farming ponds [9]. The concentration of antibiotics in the wastewater can be up to 400 mg/L [10]. Some studies have shown that many antibiotics are present in the environment, including surface water and underground waters, as well as in sewage and drinking water [11]. The point about antibiotics is that only 10% of these drugs are deformed and absorbed into the body, and the rest of them is excreted unchanged from the body [12]. These compounds also have enduring effects on the environment and because of their low degradability; cumulative property and high toxicity in aqueous environments causes complications and problems in humans and animals [13-15]. In addition, wastewater containing antibiotics may promote bacterial resistance and disrupt with various vital processes for aquatic ecology (nitrification/ditiarification) or crop (fertility) and animal production (primary processes) [16]. Therefore, it is very important that antibiotic residues be removed before the sewage is disposed of.

Several methods have been proposed to removal of antibiotics from aqueous environments such as fenton and electrofenton [4], electrochemical [17], adsorption process [18], nanofiltration [19], ion exchange [20], etc. These methods have various problems, such as production of by products, low efficiency, and the high costs [21]. Among these, the adsorption process is a simple, low-cost and useful method for separating contaminants from aqueous media. Therefore; due to the advantages of high flexibility and availability of many adsorbents it has been considered [22].

Today, given the necessity of using natural materials, low cost, economical and natural-base adsorbents also have been taken into consideration [23]. Several studies have been conducted on the use of natural adsorbents such as peanut husk [24], clay minerals [25], natural zeolite [26], kaolinite [27], bentonite [28], montmorillonite [29], bamboo charcoal [30], activated carbon prepared from vine wood [31], Rhizopus arrhizus [12] for the removal of antibiotics.

Chitosan is a natural polysaccharide derived from the crust of crustaceans of the sea with many useful aspects such as hydrophilicity, biodegradability, biocompatibility and antibacterial properties [32, 33]. The chitosan polymer structure is shown in Fig. 1. The chitosan is a fiber that has many characteristics such as ability to form film and optical structural characteristics, and also because of the presence of a positive ionic charge, the ability to bond with different materials such as lipids and fats. Chitosan is unstable under acidic conditions, so that it is at pH below 6 become water soluble and makes biocompatible and biodegradable polymers in homogeneous solutions [34, 35].

Considering that there is not study about the removal of penicillin from aqueous solutions by chitosan adsorbent. So in this study, the removal of penicillin G antibiotic using chitosan as an adsorbent with unique properties and its numerous benefits in water treatment were used. In our study, the effect of different factors on the removal of penicillin G with chitosan such as pH, initial penicillin G concentration, adsorbent dosage and isotherm, kinetic and thermodynamic process were investigated.

EXPERIMENTAL SECTION

Materials and Equipment

In this study, the chitosan extracted from Persian Gulf shrimp shell. Penicillin G with a purity of 98% was prepared from sigma aldrich. Other chemical such as HCl and NaOH was obtained from Merck Company. Also,

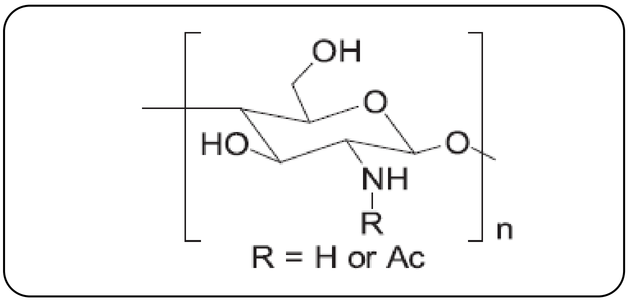

Fig. 1: Chitosan structure [36].

shaker (Multi shaker, NB-101MT, Korea) and pH meter (HACH, HQ411d, USA) was used to mixing and to adjust the pH of solutions, respectively. The concentration of penicillin G was measured using a spectrophotometer (UV/Vis spectrophotometer T80$^+$, PG Instrument Ltd) at 290 nm wavelength [31].

Adsorbent preparation

Initially shrimp was prepared and then was synthesis in two stages of Demineralization and deproteinization of chitosan. In the first step, 0.25 mol/L of HCl was mixed with shells and the minerals were separated from chitin for 15 minutes at ambient temperature. Then filtration was performed and allowed to dry, and at the next step, using 1 mol/L NaOH at 70° C for 24 hours, the flesh and organic materials were separated from chitin and it was dried at ambient temperature and at the last stage chitosan was extracted from chitin [37, 38]. The structural properties of adsorbent by XRD, SEM analysis were investigated.

Adsorption experiment

Effect of pH

At this stage, an antibiotic solution with a concentration of 30 mg/L. Initial pH of solutions was adjusted to 3, 5, 7, 9 and 11 by pH meter and to adjust the pH NaOH and HCI 0.1 and 1 N was used. Then 0.5 g/L of adsorbent was added to the solutions and mixed for 60 minutes. After passing time, the solutions were passed through Whatman filter and the concentration of the penicillin G was measured by spectrophotometer. At each pH that has the highest adsorption of penicillin G; it is selected as the optimum pH.

Effect of adsorbent dosage

After determining optimum pH , to determine the effect of adsorbent dose on the adsorption of penicillin G by chitosan, the adsorption process using four adsorbent dosage (0.25, 0.5, 0.75 and 1 g/L), penicillin G at a concentration of 30 mg/L and contact time of 60 was investigated.

Effect of penicillin G concentration and contact time

After determining optimum pH and adsorbent dosage, the adsorption of penicillin G by chitoan was determined for each concentrations of antibiotic solution (10, 30, 50, and 70 mg/L) at contact times of 5, 10, 20, 40, 60, and 90 minutes.

Effect of temperature

At this stage, the adsorption process of penicillin G by chitosan was performed at 288, 298, 308 and 318 K temperatures under optimum conditions obtained from the previous steps.

Isotherms, kinetics, and thermodynamic adsorption

By using the formulas in Table 1, adsorption capacity, isotherms, kinetics, and thermodynamic process of the penicillin G removal by chitosan were investigated [39-42].

RESULTS AND DISCUSSION

Adsorbent characterization

SEM analysis

Scanning electron microscope (SEM) is tool by which high-magnification image are obtained from the materials such as adsorbent so that details can be study carefully [43]. To analyze the morphology of adsorbent level, SEM analysis was used. Fig. 2 shows the SEM image of chitosan. According to the image, the size of chitosan particles ranges from 700 nm to 5.15 µm. It also shows irregular and non- smooth surface of nanoparticles [34, 44].

XRD analysis

X-Ray Diffraction (XRD) is an old and widely used technique for investigating the properties of crystals. In this method, X-ray diffraction is used to examine the particle's morphology [45]. XRD analysis of chitosan particles synthesized in the present study has been shown in Fig. 3. The position and pattern of the two peaks around 2θ= 9.29 and 2θ=19.33 are related crystal I and II respectively and indicates the formation of chitosan crystalline particles [34, 46]. Image of XRD analysis confirms this issue.

Table 1: The adsorption capacity, isotherms, kinetics, and thermodynamic equations used for the removal of penicillin G by chitosan.

Adsorption capacity	Isotherms	Kinetics	Thermodynamic
Adsorption capacity	Langmuir	Pseudo-first-order	Van' t Hoff
$qe = \frac{C_0 - Ce}{m} V$	$\frac{C_e}{qe} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	$ln\,(q_e - q_t) = lnqe - K_1 t$	$\Delta G^\circ = -RT \ln kd$
	Separation factor (R_L)	Pseudo-second-order	Free energy of adsorption
	$R_L = \frac{1}{(1 + bC_0)}$	$\frac{t}{q_t} = \frac{1}{K_2 qe^2} + \frac{t}{qe}$	$\mathrm{Lnk_d} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$
	Freundlich		
	$lnqe = lnK_f + \frac{1}{n} \ln Ce$		
	BET		
	$\frac{C_e}{qe\,(C_s - C_e)} = \frac{1}{q_s C_{BET}} + \frac{(C_{BET} - 1)}{q_s} \frac{C_e}{C_s}$		
	Temkin		
	$qe = \frac{RT}{b_t} \ln A_T + \left(\frac{RT}{b_t}\right) \ln C_e$		
	Dubinin-Rudeshkuvich		
	$\ln q_e = \ln q_m - K_{ad} \varepsilon^2$		
	Polanyi potential		
	$\varepsilon = RT \ln(1 + \left(\frac{1}{C_e}\right))$		

qe (mg/g), Co (mg/L), Ce (mg/L), m (g), V (L), Q_m (mg/g), K_L (L/mg) C_{BET} (L/mg), Cs is (mg/L) b_T (J/mol), Kad (mol^2/kJ^2), A_T (L/g), β (mol^2/kj^2), ε (J/mol), K_1 (1/min), K_2 (g/mg.min), q_t (mg/g), R (8.314 J/mol.K), ΔH° (kj/mol), ΔS° (J/mol.K), T (K)

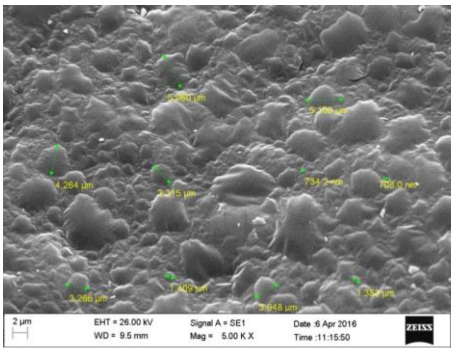

Fig. 2: SEM image of chitosan

Effect of pH

The results of the effect of pH on penicillin G adsorption are shown in Fig. 4. In this research the effect of solution pH in range of 3 to 11 on the removal of penicillin G antibiotic by chitosan was studied. Penicillin G solution with concentration of 30 mg/L and adsorbent dose of 0.5 g/L and contact time 60 minutes is used for all the solutions. According to the diagram, the highest amount of penicillin G adsorption occurred at pH=7 which its adsorption capacity was 23.59 mg/g. In the next experiments, this pH was chosen as the optimum solution pH.

The results of the study on the removal of penicillin G antibiotics in different pH range showed that the amount of antibiotic removal in the neutral range was significantly higher than other pH values. With increasing and decreasing pH, the penicillin absorption capacity decreased. According to pka, Penicillin becomes an anion at higher pH of pKa. As a result of the negative effect of chitosan superficial load and anionic contaminant at pH above 7, there is an electrostatic force between penicillin and chitosan and the absorption rate in this range is reduced [47]. In study of *Aksu et al.* (2011) on the removal of penicillin G, the appropriate adsorption pH was reported to be 6. They expressed the adsorption of penicillin anions on the adsorbent is due to the effect of physical and chemical forces as well as adsorbent at pH 2.5-3.5 with negative load [12].

Effect of adsorbent dosage

At this stage, the effect of adsorbent dose on penicillin G absorption at different dose levels (0.25, 0.5,

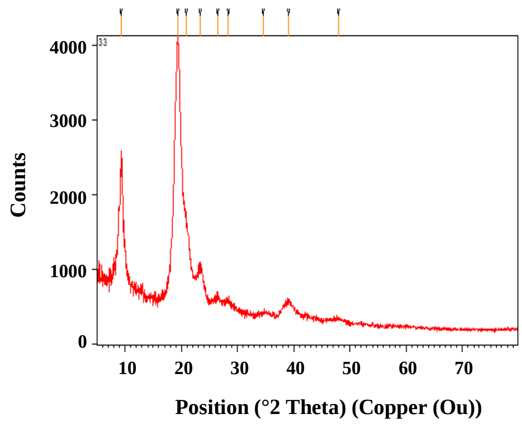

Fig. 3: XRD analysis of chitosan.

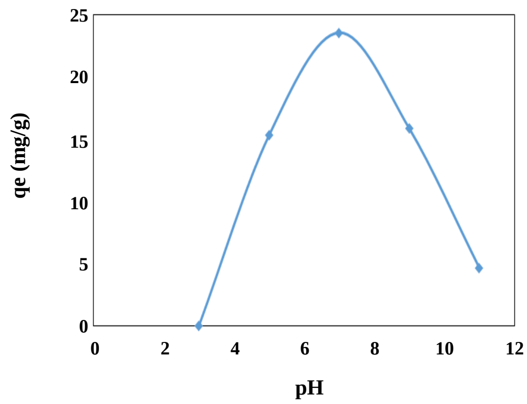

Fig. 4: Effect of pH on the removal of penicillin G by chitosan (Penicillin G concentration: 30 mg/L, adsorbent dosage: 0.5 g/L, contact time: 60 min).

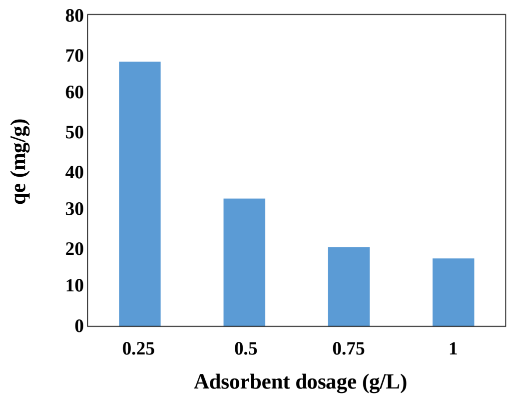

Fig. 5: Effect of adsorbent dosage on the removal of penicillin G by chitosan (pH: 7, Penicillin G concentration: 30 mg/L, contact time: 60 min).

0.75, 1 g/L) at pH=7 and contact time = 60 min and antibiotic concentration= 30 mg/L was investigated. Fig. 5 shows the effect of adsorbent dose on the removal of penicillin G. As the adsorbent dose increased from 0.25 to 1 g/L, the adsorption capacity decreased from 68 mg/g to 17 mg/g. As a result, 0.25 g/L were used as the optimum adsorbent dose to continue the tests.

According to the findings of this study, with the constant concentration of antibiotics, the adsorption capacity decreases with an increase in the adsorbent dose. The reason for this can be stated that at the constant concentrations of antibiotics with an increase in adsorbent amount under the same conditions, the number of active and available sites for interactions between adsorbent and contaminant increases and adsorption capacity is decreased by chitosan adsorbent. This is due to the inadequate utilization of the total adsorbent capacity, which, with increase in adsorption, some active adsorbent sites remain unsaturated, thus the amount of adsorption capacity of the contaminant is decreased [48]. The results of this study are consistent with the results of a study by *Balark, et al.* (2016) on the removal of amoxicillin by single-wall carbon nanotubes [49].

Effect of contact time and initial penicillin G concentration

The effect of concentrations of penicillin G solution (10, 30, 50 and 70 mg/L) and contact times (5, 10, 20, 40, 60 and 90 min) on the adsorption of Penicillin G by chitosan under optimum pH conditions and adsorbent dose has been shown in Fig. 6. The maximum penicillin G antibiotic adsorption capacity at various concentrations at 10 minutes was 11.65, 29.93, 56.83 and 101.44 mg/g, respectively.

According to the Fig. 6, antibiotic adsorption in the first 10 minutes was higher than other times, after which it was almost constant and did not increase significantly. The reason for this is the presence of active empty adsorbent sites in the early moments, which after time these empty sites are saturated and due to the repulsive force between the antibiotic molecules, adsorption decreases and reaches a nearly balanced state [50]. Other important parameters affecting the adsorption process are the initial concentrations of the contaminant. As antibiotic concentration increased, the amount of adsorption capacity enhanced which is due to the increase of antibiotic molecules in the solution and also

Table 2: Isotherms models for penicillin G antibiotic adsorption on the chitosan.

Isotherms	Constants	Values
Langmuir	q_{max} (mg/g)	113.62
	K_L (L/mg)	0.01
	R_L	0.50
	R^2	1.00
Freundlich	k_f (mg/g)	0.50
	1/n	1.34
	n	0.75
	R^2	0.98
BET	1/A.Xm	1.42
	(A-1)/(A.Xm)	2.13
	A	4.03
	Xm	1.89
	R^2	0.64
Temkin	A_T, L/mg	0.11
	b_T	50.96
	B	48.61
	R^2	0.82
Dubinin-Rudeshkuvich	β, $mole^2/kJ^2$	0.00
	E, kJ/mole	0.13
	q_m, mg/g	69.50
	R^2	0.83

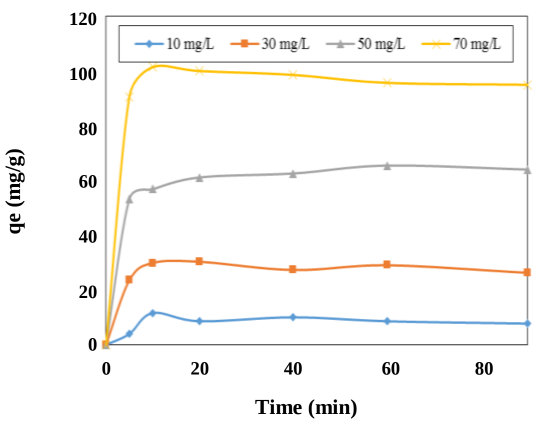

Fig. 6: Effect of contact time and initial concentration on the removal of penicillin G by chitosan (pH: 7, adsorbent dosage: 0.25 g/L).

the increase in the collision of adsorbent and contaminant molecules [51]. *Bajpai et al.* in their study, on the removal of ciprofloxacin antibiotic by sawdust, found that increasing the antibiotic concentration increases adsorption capacity [52].

Isotherms adsorption

Table 2 shows the isotherms associated with the penicillin G antibiotic absorption on chitosan. Langmuir isotherms based on homogeneous monolayer adsorption of adsorbate have finite and uniform locations. The tendency of penicillin G adsorption on adsorbent was evaluated using a dimensionless parameter (R_L) derived from the Langmuir model. Absorption is reversible (R_L=0), favorable (0<R_L<1) and linear (R_L=1) and unfavorable (1<R_L). The Freundlich isotherm is also based on the multilayer adsorption on heterogeneous surfaces in terms of energy absorption [53]. Given the isotherm values and the values of linear regression coefficients, the Langmuir model is R_2=1 for adsorption data, which is more suitable than Freundlich type model with R_2=0.98. The results of this study are consistent with the study of the adsorption of penicillin G by Lemma adsorbent [54].

Kinetics adsorption

Table 3 shows the kinetics of adsorption of antibiotics on chitosan. R_2 coefficients in the two kinetic models indicate that the adsorption process is better described by the pseudo-second-order kinetic model, hence the penicillin absorption on chitosan is highly correlated with second order kinetics. Regression coefficients in different concentrations are 0.98, 1, 1 and 1, respectively. When surface absorption by penetration occurs from within a layer, in most cases the process follows the first-order kinetics, and the follow-up of the second-order kinetics indicates that the chemical absorption slows down the speed and controls adsorption processes. Therefore, in the present study, chemical absorption and physical absorption are likely to occur together [12, 54]. In the study by *Ferdowsi et al.* on the removal of amoxicillin antibiotic, they stated that removal of amoxicillin follows a second-order kinetics [55].

Thermodynamics adsorption

The effect of temperature on the adsorption of penicillin G antibiotic by chitosan was investigated.

Table 3: Kinetic coefficients for the adsorption of penicillin G antibiotic on the chitosan.

C_0 (mg/L)	Pseudo-first-order			Pseudo-second-order			q_e,exp(mg/g)
	K_1 (min^{-1})	q_e, cal (mg/g)	R^2	K_2 (g/mg min)	q_e,cal(mg/g)	R^2	
11.42	0.01	1.09	0.12	0.12	8.10	0.98	11.75
33.08	0.01	1.79	0.16	0.04	26.84	1.00	31.36
53.35	0.01	5.12	0.15	0.02	64.98	1.00	66.47
75.11	0.02	2.08	0.28	0.02	95.02	1.00	102.44

For this purpose, the solution with concentration=70 mg/L, pH=7, contact time=10min, adsorbent dosage=0.25 g/L was placed at different temperatures (288, 298, 308 and 313 ˚K) and results were determined in Table 3. For penicillin G antibiotic, Negative value of ΔG and positive value of ΔH (5.69 kJ/mol) for all temperatures show adsorption process of penicillin G by chitosan is spontaneous and endothermic, it means that as temperature increases adsorption amount decreases. Also, the amount of ΔG indicates the type of absorption, In the case of physical absorption, this value is between 0 to -20 (kJ/mol) and in the case of chemical adsorption this value is between -81 to -400 (kJ/mol). In the study on penicillin G antibiotic, ΔG values vary from -0/24 to -1/71 (kJ/mol) which this shows the physical adsorption of this antibiotic on chitosan. Also, positive value of ΔS =20.68 (J/mol K) for penicillin G antibiotic showed that during the adsorption process, the irregular surface has increased in the adsorbent and solution surface. This amount indicates an increased irregularities during the adsorption process [12, 56].

CONCLUSIONS

This research showed that chitosan is an effective adsorbent in the removal of penicillin G antibiotic. Under optimal conditions (pH=7, contact time=10min, drug concentration=70 mg/L and adsorbent dose=0.25 g/L), adsorption capacity is 101.44 mg/g. Finally, given the fact that chitosan is cheap and natural, it can be used as an effective absorbent to remove penicillin G antibiotic from aqueous solutions.

Received : Dec. 3, 2018 ; Accepted : Mar. 11, 2019

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