Optimization of nickel oxide nanoparticle synthesis through the sol–gel method for adsorption of Penicillin G

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Abstract

In this study, nickel oxide nanoparticle (NiO) was synthesized by sol–gel method. The experiments were carried out to explore penicillin G uptake by NiO. The influence of various experimental factors such as contact time and initial penicillin G concentration at constant temperature 25 ^{0}C and pH 7 were performed. The results demonstrated that the maximum removal efficiency of penicillin G was found to be contact time 90 min and initial concentration 10 mg/L and was 98.5%. Experimental data were fitted into linearized pseudo-first order and pseudo-second order kinetic models.

Pseudo-second order better fitted the experimental data based on R^2 results and adapting the adsorption capacity q_e cal and q_e exp. Computations from intra-particle diffusion kinetic model reveal that intra-particle diffusion is not the only rate-limiting step governing the adsorptive process. According to results, it was clear that nickel oxide nanoparticle can be used as an effective and economic adsorbent in antibiotics wastewater treatment processes.

Keywords: Nickel oxide nanoparticle, Penicillin G, Adsorption kinetics, Sol–Gel.

Introduction

Drug compounds cannot be distinguished from other chemicals such as pesticides and herbicides in terms of environmental hazards[1,2]. This compound enters the aquatic environment through pharmaceutical industry wastes as well as end users in forms that are metabolized or not metabolized[3]. Among active pharmaceutical ingredients, antibiotics contribute significantly to environmental pollution due to high consumption of drugs and veterinary medicine[4,5].

Penicillin G ($C_{16}H_{17}KN_2O_4S$ with the molecular weight 356.37 and pKa =2.75) is a conventional antibiotic which is used for treatment of different kinds of infectious diseases such as soft tissues, bacterial and respiratory infections[6]. It is soluble in water and the mechanism of destruction of bacteria's cell wall is by preventing production of peptidoglycan layer. The biological halflife is 30-60 min and excreted mainly by kidney[7]. Recent studies applied various methods for removing pharmaceutical compounds such as reverse osmosis, adsorption on activated carbon and ozonation as well as advanced oxidation systems (AOP) such as Fenton or Photo-Fenton, ultrasound, preoxidation using UV lamps and photocatalysis[8,9]. Due to some troubles in using the aforementioned processes, adsorption system has gained interest in recent years[10,11].

The application of this classic processing method requires the introduction of sustainable chemicals, high costs and great environmental damage[12]. Given the ease of operation, high efficiency, economy and availability of various types of adsorbents, adsorption seems to be the most attractive method compared to other methods[13,14]. Activated carbon is one of the best adsorbents for the adsorption process because it has a high absorption capacity and an attractive surface, but has relatively low selectivity, high cost and low regeneration[15,16].

Nanoparticles of metal oxides have a high rate of surface to volume ratio and can adsorb a large amount of materials[17,18]. Because of non-toxicity, low price, availability, chemical stability and high light activity, nanoparticles are used as adsorbent for the removal of contaminants from water and air[19,20]. Thus the present study aimed to assess the adsorption capacity of nickel oxide nanoparticle at different concentration of penicillin G. Optimization of adsorption at various initial concentrations and contact time was performed to achieve maximum adsorption. Further the data obtained was subjected to kinetic studies to find out the adsorption kinetics by NiO.

Material and Methods

Penicillin G sodium salt with 99% purity was purchased from Sigma-Aldrich Company (USA). The rest of chemicals were purchased from Merck (Germany). The chemical structure of Penicillin G antibiotics is shown in fig. 1.

Adsorption Experiments: Nickel oxide nanoparticles were prepared using the sol-gel process [21]. The ability of NiO nanoparticles to remove penicillin G was evaluated by contacting the NiO nanoparticles with aqueous solutions of penicillin G. Batch adsorption experiments were performed in 200-mL conical flasks by mixing a known amount of prepared NiO nanoparticles with 100 mL penicillin G aqueous solution at varying concentrations at 25 ◦C under stirring at 150 rpm. After an appropriate time, the suspension was centrifuged at 3600 rpm for 10 min and the residual

concentration of penicillin G in supernatant was determined by a flame atomic absorption spectrophotometer. The adsorption capacity (q_e) of the NiO for penicillin G removal was calculated from the following formula [19, 20]:

$$q_e = (C_0 - C_e)\frac{V}{M} \quad (1)$$

where q_e is the amount of penicillin G adsorbed per unit mass of NiO nanoparticles (mg/g); C_0 is the initial concentration (mg/L) of penicillin G; Ce is the concentration of penicillin G after a certain period of time (mg/L); V is the initial solution volume (L) and m is the NiO mass adsorbent (g). The effects of the NiO mass, contact time and initial concentration of solution (C_0) on the penicillin G adsorption were investigated at 25◦C and pH 6.5-7.

Adsorption isotherm studies were conducted by mixing 0.1 g of NiO nanoparticles with 100 mL of aqueous penicillin G aqueous solutions of different concentrations varying from 10 to 100 mg/L at 25 ◦C and pH 7 for 90 min. The pH of test solutions was adjusted to the desired value using 0.1 M HCL or 0.1 M NaOH. A control penicillin G solution in the absence of NiO nanoparticles was run in parallel with each experiment under the same experimental conditions. All experiments were performed in triplicate and the average values are reported here.

For penicillin G, detection a HPLC with C18 column columns was calibrated and tested prior to injection of the samples. The mobile phase included methanol and water (20/80 V/V) with the flow rate of 0.5 ml/min. A UV absorbance detector at 209 nanometer wavelength was used to detect Penicillin G in the samples. The retention time for the antibiotic is 7.2 minutes.

Results and Discussion

Kinetic studies: Kinetic studies were performed at different concentrations and contact times. As shown in fig. 2, as the contact time increases, the percentage of removal also increases. Adsorption process of penicillin G consists of two stages. In the first stage, rapid initial adsorption was observed at 30 min and in second stage, adsorption process was slow and was performed during time of 30-90 min. In this stage, the absorption capacity was slower than first stage. It was clear that increasing time over 90 min had no significant effect on adsorption capacity[22].

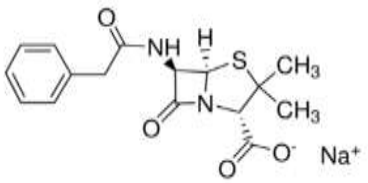

Fig. 1: Molecular structure of Penicillin G

It can be stated that in this time with regard to dynamic equilibrium, adsorption and desorption for penicillin G are the same. This may be due to the fact that during the adsorption process, the penicillin G molecules by the process of mass transfer are rapidly received to boundary layer[23,24]. Then they were slowly released from the boundary layer into the absorber surface. Because the most active adsorption sites were occupied, the penicillin G particles were dispersed into the adsorbent pores[25,26].

Effect of initial penicillin G concentration showed that the removal efficiency decreases with increasing the concentration of 10 to 50 mg/L (Fig. 2). Thus it can be said that for a specified amount of NiO, adsorption site is constant and the available active sites on the NiO surface further reduced over time. On increasing the amount of concentration, adsorption is decreased and increasing the penicillin G concentration can increase the repulsive forces between the penicillin G molecules and the repulsion caused by adsorption onto the adsorbent is prevented[27,28].

In a study conducted by Balarak et al,[27] fast and efficient removal of tetracycline from aqueous solution by azolla has shown that by increasing concentration, the removal efficiency decreases due to the number of fixed positions over a specified amount of adsorbent.

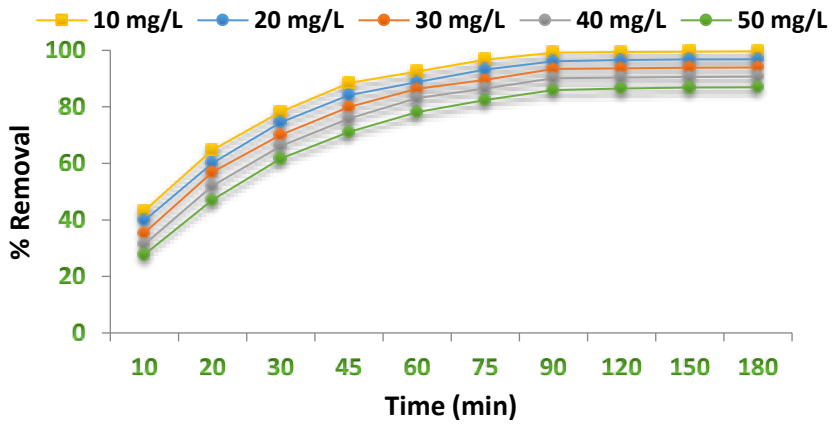

Fig. 2: Effect of Contact time and initial penicillin G concentration on removal efficiency (pH=7, adsorbent dose=0.8 g/L)

Three models were investigated to find the suitable model for the interaction between the NiO and the penicillin G[31]. These models are the pseudo-first-order model, pseudo-second-order model, mass transfer and intra-particle diffusion models[32,33]. Table 1 shows the results of experiments and calculated values of models for the adsorption process.

$$\text{Log}\,(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \quad (2)$$

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

$$t^{1/2} = \frac{1}{K_2 q_e} \quad (4)$$

$$h = K_2 q_e \quad (5)$$

$$q_t = K\, t^{1/2} + C \quad (6)$$

Eq. (2) is used to find values of the pseudo-first-order model. Eq. (3) shows the pseudo-second-order model. The half-life time of the adsorbing kinetic is shown in eq. (4). The first rate of adsorption is shown by eq. (5). In these equations, q_e and q_t represent respectively, equilibrium time and at any time amount of adsorption. Penicillin G. K_1 and K_2 are rate constants and t is time (min). These two values were found from the plots of Log (q_e-q_t) and t/q_t with time (Figs 3 and 4). $T^{1/2}$ expresses the half-time of the process. Eq. (6) was used for calculation of intra-particle diffusion model.

In this equation, K_d (mg ($gmin^{-1/2)-1}$) is a rate constant of diffused intra-particle which was calculated from the slope of the graphic in fig. 5 and calculated values K_d are given in table 1. The q_t is the amount of adsorbed penicillin G.

Previous studies showed that the graph of q_t versus $t^{1/2}$ is multi-linear. Thus, similar adsorption events can be characterized by two or more steps[34,35]. As can be seen in fig. 5, the adsorption phenomenon takes place in two or three phases. It occurs in high concentrations in three steps and in low concentrations in two steps.

The adsorption event occurred according to the initial linear portion in 30 min; after this period, the process will occur according to the second and third linear portion. The first curve in the graph shows rapid adsorption, while the second and third curve show that adsorption was slowed by pore filling. The various studies support this theory [36-38].

It can be said that the adsorption was compatible with pseudo-second-order according to values of R^2 in table 1. The calculated values K_{d1} and K_{d2} at different conditions are given in table 1. In table 1, it is found that K_{d1} values are higher than K_{d2}.

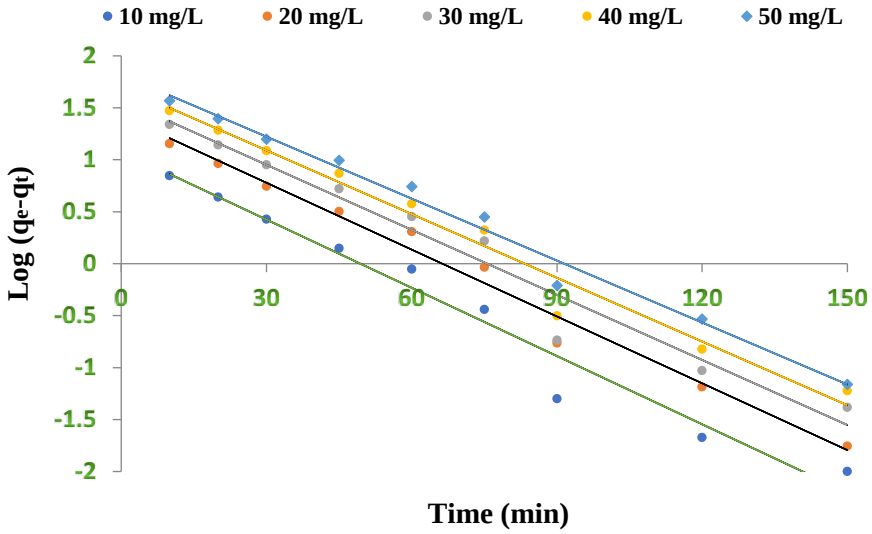

Fig. 3: Pseudo-first-order model plot of penicillin G adsorption on NiO

Table 1
Kinetic parameters for the adsorption of penicillin G onto NiO at various concentration

C_0 (mg/L)	q_e exp	Pseudo-first order			Pseudo-second order			Intraparticle diffusion					
								Stage 1			Stage 2		
		K_1	q_e	R^2	K_2	q_e	R^2	K_{d1}	C	R^2	K_{d2}	C	R^2
10	13.12	0.048	12.11	0.945	0.0066	13.51	0.998	1.34	1.74	0.941	0.059	11.71	0.651
20	26.94	0.043	26.52	0.951	0.0028	27.02	0.997	2.68	2.57	0.932	0.155	22.27	0.672
30	39.02	0.032	37.74	0.934	0.0017	39.84	0.997	4.12	2.94	0.908	0.265	31.92	0.694
40	51.74	0.019	50.65	0.938	0.0011	52.63	0.998	5.60	3.71	0.914	0.344	41.05	0.713
50	61.83	0.012	65.83	0.947	0.0008	62.5	0.996	6.86	4.32	0.933	0.479	48.31	0.704

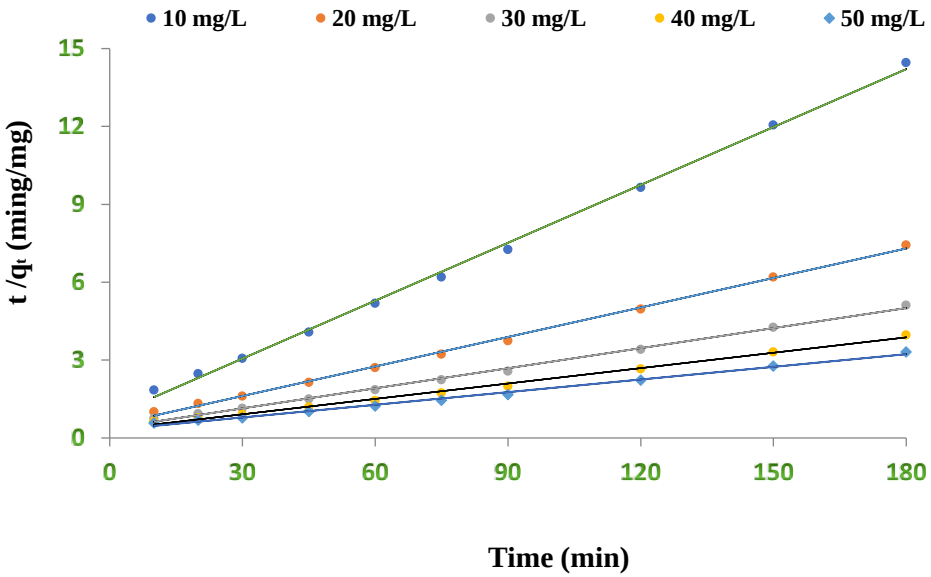

Fig. 4: Pseudo-second-order model plot of penicillin G adsorption on NiO

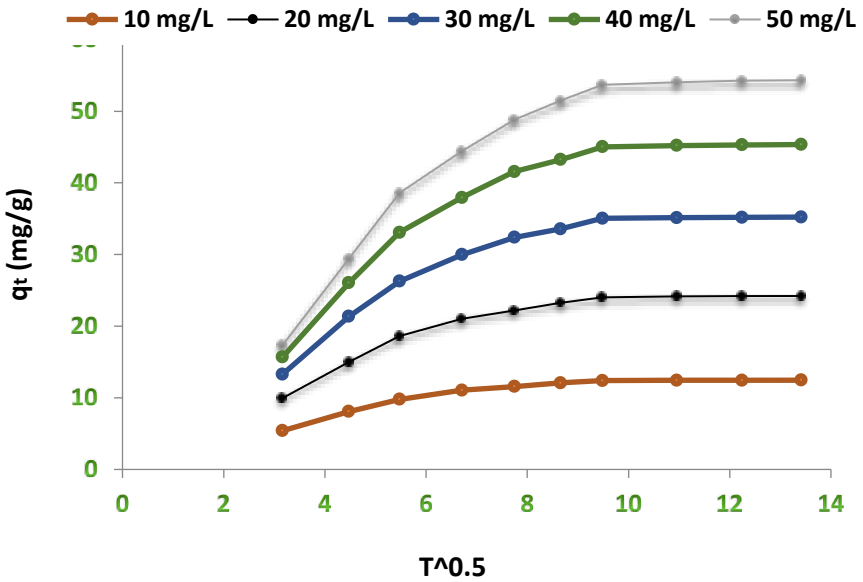

Fig. 5: Intraparticle diffusion model plot of penicillin G adsorption on NiO

Conclusion

The present study shows that the NiO can be used as an effective adsorbent for removing penicillin G from contaminated water sources. The adsorption of penicillin G on NiO was strongly dependent on the contact time and the maximum removal was attained at time 90 min. The adsorption process decreases with increasing initial concentration of penicillin G. Kinetic studies demonstrated that the adsorption mechanism of penicillin G followed the pseudo-second-order model.

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