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Original Article

Investigation of Isotherm, Kinetics and Thermodynamics of Ciprofloxacin Adsorption by Molecularly Imprinted Polymer from Aqueous Solutions

Maryam Bazi[1], Davoud Balarak[2], Aram Dokht Khatibi[2], Shaziya Haseeb Siddiqui[3], Ferdos Kord Mostafapour[2,*]

[1]Student Research Committee, Zahedan University of Medical Sciences, Zahedan, IRAN.

[2]Department of Environmental Health Engineering, Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, IRAN.

[3]Department of Chemistry, Sam Higginbottom University of Agriculture Technology and Sciences (SHUATS), Allahabad, Uttar Pradesh, INDIA.

ABSTRACT

Background: Improper use of antibiotics and their discharge into the environment have serious and dangerous consequences. About 30-30% of antibiotics are not metabolized in the body and enter the environment through urine and feces, so the main source of antibiotics in the environment is wastewater treatment plant effluent. The aim of this study was to investigate the removal efficiency of ciprofloxacin (CIP) from aqueous media by molecularly imprinted polymer (MIP). **Methods:** This study is an experimental-laboratory study performed in a reactor with a discontinuous system. In this study, the effect of parameters such as solution pH, adsorbent dose, initial concentration of CIP, reaction contact time and reaction temperature on the reduction rate the antibiotics amoxicillin and CIP were administered. **Results:** Results showed that removal efficiency for both antibiotics was increased with increasing contact time and adsorbent mass and initial antibiotics concentration while decreased with increasing solution pH and the best pH to remove was neutral pH. Equilibrium data were analyzed by Freundlich and Langmuir isotherm models and the results showed that the data from Langmuir isotherm had a higher correlation coefficient. In addition, the reaction rate was performed with pseudo-first-order and pseudo-second-order models, and the data were consistent with pseudo second order kinetic kinetics. According to result of thermodynamic study, entropy changes (ΔS^O), enthalpy changes (ΔH^O) and Gibbs free energy (ΔG^O) were negative that represent the adsorption process is spontaneous and exothermic. **Conclusion:** The results of this study showed that the process of adsorption of MIP is a very effective process for removing the CIP from aqueous solutions.

Key words: Ciprofloxacin, Molecularly imprinted polymer, Thermodynamics, Kinetics, Aqueous solution.

Correspondence

Prof. Ferdos Kord Mostafapour,

Department of Environmental Health Engineering, Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, IRAN.

Email id: ferdoskord@gmail.com

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INTRODUCTION

Pharmaceutical products and effluents have been identified as potential contaminants in water resources, which is a concern as emerging contaminants.[1] In recent years, people's access to and consumption of drugs has increased due to the advancement of medical sciences and pharmacy. Iran is one of the largest drug users in the world, so that it is among the top 20 countries in the world in terms of drug consumption and in Asia, after China, it ranks second in drug consumption.[2] Drugs are known as environmental pollution and are classified as compounds with biological accumulation and are considered as hazardous chemicals.[3] Among all the drugs that cause environmental pollution, antibiotics have an important place due to their high consumption in medicine and veterinary medicine.[4] Antibiotics are widely used to treat many infectious diseases and fungi and are considered as contaminants of water and sewage.[5] Improper use of antibiotics and their discharge into the environment have serious and dangerous consequences. About 30-90% of antibiotics are not metabolized in the body[6] and enter the environment through urine and feces, so the main source of antibiotics in the environment is wastewater treatment effluent.[7] These compounds are not completely removed through wastewater treatment plant effluents and pollute water sources.[8] Characteristics of antibiotics include low biodegradability, high toxicity, carcinogenicity and mutagenicity.[9]

CIP is an antibiotic from the group of Fluoroquinolones used to treat bacterial infections. The presence of this antibiotic is dangerous even in low concentrations and leads to increased antibiotic resistance, effect on non-target pathogens, alteration of the structure of aquatic algae, interference with plant photosynthesis and apparent abnormalities in plants.[10] Therefore, the removal of antibiotics before entering the aquatic environment and also the reuse of water is necessary,[11] which due to their high polarity and resistant nature, which is a significant threat to human health.[12] Methods used for removal include: chemical oxidation, membrane processes, bioremediation, ozonation and adsorption techniques.[13] Elimination or reduction of antibiotics through bioremediation is difficult due to the presence of a stable naphthol ring (as the main structure) and its toxicity to microorganisms as well as its low biodegradability.[14] Membrane processes are also often hampered by the membrane's high vulnerability to organic solvents in wastewater containing antibiotics, thus reducing their efficiency.[15] Adsorption process compared to other treatment techniques in terms of initial cost, simplicity and flexibility in design, easy operation and insensitivity to pollutants and toxic compounds, production of high quality effluent, no free radicals and hazardous substances as one of it is the most valuable and effective method of removing various pollutants in water and wastewater.[16,17]

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MIP are synthetic polymeric materials with complementary mold sites for a particular molecule and the high dependence of the samples on a similar molecular structure[18] that have properties similar to natural receptors.[19] MIP have pre-defined holes for the identification of target samples and synthetic receptors capable of fabricating advanced analytical devices.[20] These materials are able to detect a specific molecule or a family of compounds in a simple and fast way[21] and in recent years have been widely used in many areas such as sensors, catalysts, solid phase extraction, etc.[22] and to The mass copolymerization device is prepared from the monomer and cross-linked in the presence of the mold molecule.[22,23] Therefore, the aim of this study was to investigate the isotherm, synthesis and thermodynamics of CIP adsorption by MIP form from aqueous solutions.

MATERIALS AND METHODS

This is an experimental-laboratory study that has been done in Zahedan University of Medical Sciences. In this study, iron chloride ($FeCl_3$), pyrrole and CIP were used as templates for a MIP purchased from Sigma Aldrich Co. To make stock solutions at a concentration of 500 mg/L for antibiotics, pour 0.5 g of CIP separately into a 1000 mg/L flask and add distilled water to the specified level and place on a magnetic stirrer. After complete dissolution of the antibiotic, the solution was made to volume. Stocks were stored in sealed containers and refrigerated and made weekly.

For MIP synthesis, 0.3 g of CIP powder was weighed and mixed with 100 ml of distilled water in a 250 ml beaker. (A watch glass was placed on the human mouth.) The mixture was placed under the hood and on a magnetic stirrer until CIP was completely dissolved in water. After about an hour, the solution was removed from the magnetic stirrer, and then the solution was placed in a dark place for 48 to 72 hr for polymerization.

After preparing the polymer, it was first rinsed with a vacuum filter and then placed in a Soxhlet machine for approximately 8 hr to completely separate the imprinted molecular (CIP) from the polymer. Finally, the polymer was dried in an oven at 100°C. It was left for 1.5-2 hr. Finally, the dried polymer was pulverized using a porcelain mortar. Simultaneously with the molecular mold polymer, as a reference, a non-molded polymer (NIP) was prepared simultaneously in the same molecular mold polymer method but without adding a pattern to be able to adsorb it into the molecule. Compare the target with the MIP. Finally, the polymer was placed in the oven for drying at a temperature of 100°C for 1.5-2 hr. Finally, the dried polymer was powdered using a Chinese mortar. Simultaneously with the MIP, as a reference, a non-imprinted polymer (NIP) was prepared simultaneously in the same MIP method but without adding a pattern to compare its adsorption capacity in the target molecular with MIP.

The experiments were performed optimally. In this study, by setting the desired parameter and setting other parameters, the process was performed and after determining the relevant efficiencies, the optimal value of the desired variable was determined, then the optimal value obtained was placed in the next step. Optimization by MIP and NIP was performed simultaneously at all stages. For example, to determine the effect of pH, experiments were performed at pH of 3-11. To adjust the pH, 0.1 N hydrochloric acid and sodium hydroxide were used. At this stage by keeping the polymer dose variables constant, initial antibiotic concentration, contact time and temperature; the effect of pH on the elimination of CIP antibiotics was investigated. A constant concentration of 25 mg/L was prepared from stock solution for CIP. After optimizing the pH, the other parameters were also optimized and the removal observation and the amount of adsorption were calculated through the following equations:[24,25]

$$\%R = \left(\frac{C_0 - Ce}{C_0}\right) \times 100 \quad (1)$$

$$q_e = \left(\frac{C_0 - C_e}{M}\right) V \quad (2)$$

In the above equations, C_0 and C_e are the initial and equilibrium concentrations of CIP after adsorption, q_e mg of CIP adsorbed on the adsorbent, M and V are the adsorbent mass (g) and solution volume (L), respectively.

Adsorption kinetics: The pseudo-first-order kinetics equation is based on the adsorbent capacity and is used when adsorption occurs by the diffusion mechanism inside a boundary layer. The pseudo-second-order kinetics equation indicates the chemical adsorption of the dominant and controlling mechanism in the adsorption process and according to the solid phase adsorption states that chemical adsorption is the slowing step of the adsorption process (6).

Equation 3: pseudo-first-order kinetic model.[26]

$$Log\ (q_e - q_t) = log\ q_e - t \quad (3)$$

q_e and q_t represent the adsorption capacity at equilibrium time and at time (mg/g) t and k_1, respectively, reaction rate coefficients are (min^{-1}). The values of q_e and k_1 are the width of the origin and the slope of the linear graph ln (q_e-q_t) versus t, respectively.

Equation 4: pseudo-second-order kinetic model.[27]

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

K_2 is a pseudo-second-order reaction constant in terms of (mg/g. min). The values of q_e and k_2 are determined by the slope and width from the linear origin t/q_t versus t, respectively (6).

Adsorption isotherms: In this study, Langmuir and Freundlich isotherm models were used to analyze the experimental data and describe the equilibrium state in the adsorption between solid and liquid phases. The Langmuir isotherm model shows the homogeneous adsorption of a layer of adsorbent with the same energy on all adsorbent surfaces, and also states that all adsorption sites have the same coherence with the adsorbent molecules and no transfer process from the adsorbent occurs at the adsorbent surface.[28] While Freundlich isotherm is based on multilayer and heterogeneous adsorption of adsorbent on adsorbent.[29]

Equation 5: Langmuir model:[30]

$$\frac{C_e}{q_e} = \frac{1}{q_m K_1} + \frac{C_e}{q_m} \quad (5)$$

In this equation (mg/L) C_e is the equilibrium concentration of CIP, (mg/g) q_e is the amount of CIP adsorbed at equilibrium, q_m (mg/g) is the maximum adsorption capacity and (L/mg) k_l is Langmuir constant.

The type of adsorption desirability of the adsorption process in the Langmuir model is determined by the R_L factor (Equation 6).

$$R_L = \frac{1}{1 + K_l C_0} \quad (6)$$

If R_L>1 indicates undesirable adsorption, if R_L=1 linear adsorption, and if R_L=0 irreversible adsorption and 1<R_L<0 indicates optimal adsorption.[30]

Equation 7: Freundlich model:[31]

$$Log\ q_e = log\ Ce + log\ K_F \quad (7)$$

In the Freundlich model equation, the K_F (mg/g(L/$mg^{1/n}$) and n parameters of the Freundlich constants depend on the adsorption capacity and

intensity, if the value n<1, it indicates poor adsorption, the value of n between 1-2 indicates the average adsorption and the value n =2-10 indicates the desired adsorption. The parameters n and K_L are determined by the slope and width from the origin of the linear graph Ln q_e versus Ln C_e, respectively.

Adsorption thermodynamics: In studying the adsorption process, three thermodynamic parameters should be examined and their values determined. These parameters are:[32]

1. Standard Free Energy (ΔG°)
2. Standard enthalpy (ΔH°)
3. Standard entropy (ΔS°)

The values of ΔH° and ΔS° are obtained from the following equations:

$$Ln\ K_0 = (\Delta S^0/R) - (\Delta H^0/RT) \quad (8)$$

$$K_0 = q_e/C_e \quad (9)$$

In the above equations, R represents the global constant of gases (8/31 J/mol. k), T is the temperature of the solution in terms of T (K) and K_0 (L/g), the ratio of the amount of CIP adsorbed on the adsorbent (mg/g) to the amount remaining in the solution (mg/L). ΔH° and ΔS° are also calculated from the origin of the linear graph Ln k_0 versus 1/T, respectively, through the slope and width. The value of ΔG° is also obtained from Equation 10.[33]

$$\Delta G^0 = -RT\ Ln\ K_0 \quad (10)$$

RESULTS

Examination of Figure 1, shows that by increasing the pH from 3 to 7, the removal efficiency decreases from 85.4% to 92.4%, and at pH equal to 9, the removal efficiency decreases to 88.7% and polymers destroyed at a pH equal to 11. When destroyed, the solution becomes colored and cloudy. As shown in Figure 2, with increasing initial concentration from 5 to 75 mg/L, the removal efficiency decreases from 73.6 to 96.25%, while with increasing initial concentration more than 75 mg/L, the removal efficiency decreases. The results of this study, which show in Figure 3, the maximum removal efficiency at 60 min of contact time is 99.3%. By increasing the MIP dose to 0.06 g, the removal efficiency increases due to the constant concentration of CIP in the solution. Increasing the amount of MIP helped to improve the removal process of CIP (Figure 4). The results obtained from the isotherm and kinetics and thermodynamics of the adjustment data are shown in Tables 1, 2 and 3, respectively.

DISCUSSION

The pKa levels of CIP are between 6.1 (for the carboxylic acid group) and 8.7 (for the amine group).[34] The effect of pH change on CIP molecule showed that at pH less than 6.1 times the surface antibiotic CIP appears cationic and positive due to protonation of amine groups. At pH above 8.7, the CIP molecule converts to the anionic form due to the loss of protons from the carboxylic group in the antibiotic structure. In the range of pH = 6.8-7.1, due to the deprotonation of the carboxyl group, it leads to the production of negatively charged carboxylates. However, the amine group remains protonated and positively charged.[35] Therefore, in this pH range, most of the CIP molecule in aqueous solution is uncharged, in other words, it has a positive and a negative part. The formation of the CIP molecule at a pH between 6.7-7.1 has also been confirmed in other studies,[15,36] since the pK_a of methacrylic acid in the polymer is reported to be about 4.65, the COOH functional groups of methacrylic acid in acidic media (pH 4.65 is converted to $COOH^{2+}$ which has a positive charge. [37] Therefore, in acidic and somewhat neutral solutions (pH = 6.1-6.8), the conditions for the interaction and adsorption mechanism between CIP and polymer particles are suitable.[38]

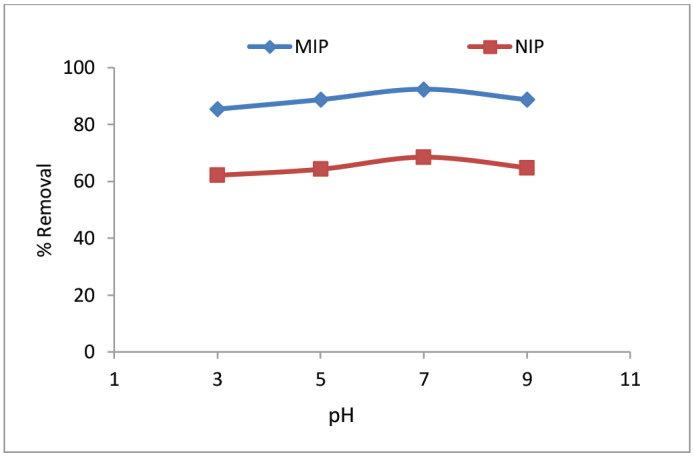

Figure 1: Effect of different pH on the removal of CIP antibiotic by MIP (CIP concentration: 25 mg/L, MIP dosage: 0.4 g/L, contact time: 60 min and tem; 25°C.

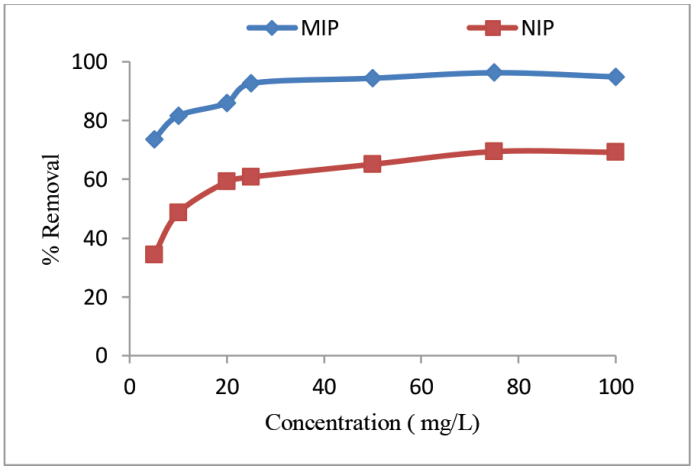

Figure 2: Effect of CIP concentration on the removal of CIP antibiotic by MIP (pH: 7, MIP dosage: 0.4 g/L, contact time: 60 min and tem; 25°C.

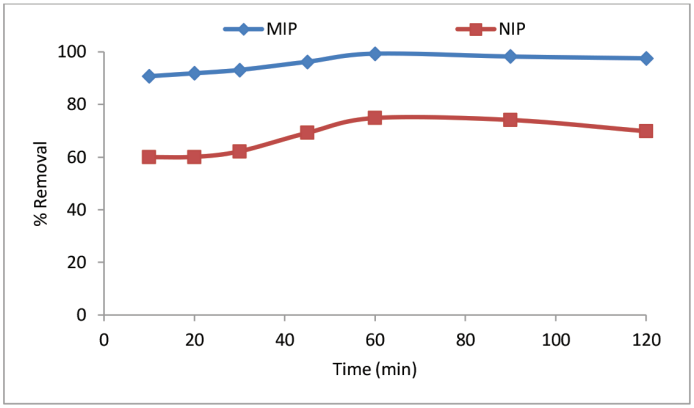

Figure 3: Effect of contact time on the removal of CIP antibiotic by MIP (CIP concentration: 25 mg/L, MIP dosage: 0.4 g/L, pH: 7 and tem; 25°C.

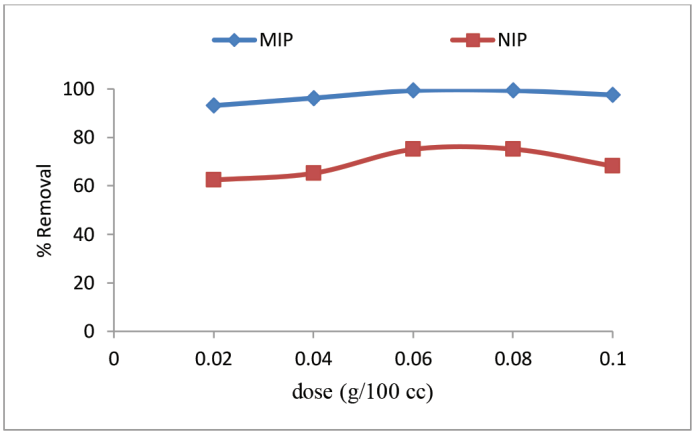

Figure 4: Effect of MIP dose on the removal of CIP antibiotic by MIP (CIP concentration: 25 mg/L, time: 60 min, pH: 7 and tem; 25°C.

Table 1: **Parameters of equilibrium isotherms of CIP adsorption on MIP.**

Freundlich	Langmuir
R^2= 0.941	R^2 =0.999
n=0.043	R_L = 0.0017
K_F=124/7	K_d=7/41
	Q_m=112.3

Table 2: **Kinetic parameters of CIP adsorption process on MIP.**

pseudo-second-order	pseudo-first-order
R^2= 0.999	R^2= 0.952
K_2=0.007	K_1=0.046
q_e. cal= 123.4	q_e. cal= 14.46

Table 3: **Values of thermodynamic parameters of CIP adsorption process on MIP.**

ΔS° (KJ/mol)	ΔH° (KJ/mol)	ΔG° (KJ/mol)
-0.00033	-9.27	20°C= -7.47
		30°C= -11.41
		40°C= -9.77
		50°C= -7.88

With increasing the initial concentration of CIP, the removal efficiency decreases, because in a constant dose of adsorbent, the active sites of adsorption are constant, but with increasing the concentration of the contaminant, the number of mole contaminants in the reaction medium increases and therefore the removal efficiency decreases.[39]

With increasing the duration of contact time of the contaminant with the adsorbent of the MIP in solution, the removal efficiency increases to some extent and with further increase of the contact time no significant effect on the removal efficiency is observed and CIP molecules appear to saturate the surface.[40]

The adsorbent dose is one of the important factors in the rate of removal of contaminants by adsorption method, which if it is less than the required amount, the adsorption step may not be performed completely and the whole sample of adsorbent adsorption may not be. In this study, the MIP was considered as an adsorbent for CIP removal.[41]

The results obtained from the adsorption parameters of ciprofloxacin in Table 1 show that the value of n in the Freundlich model is less than 1, which indicates poor adsorption. In the Langmuir model, the dimensionless coefficient of separation factor (R_L) is between one and zero, which indicates the optimal adsorption. Therefore, adsorption of CIP on MIP adsorbent follows the Langmuir model with high regression coefficient.

According to the values obtained from the adsorption synthetic models shown in Table 2, they show that the computational adsorption capacity (q_e, cal) obtained from the pseudo-second-order models compared to the pseudo-first-order kinetics, to the experimental adsorption capacity (q_e, exp) are closer, so the predominant mechanism of the ciprofloxacin adsorption process by MIP is chemical adsorption.

The negative values of the standard ΔH° parameter or enthalpy given in Table 3 indicate the exothermic process of ciprofloxacin CIP adsorption by MIP and the possibility of physical adsorption.[42] Negative values obtained for the ΔS° parameter indicate that the removal efficiency, or in other words the degree of irregularity, decreases with increasing temperature during the adsorption process in the solid-liquid interface.[43] This can be due to the reduction of the release of the contaminant on the adsorbent surface. Negative values of ΔG° indicate that the process of CIP adsorption by MIP is endothermic and occurs spontaneously. Decreasing the values of ΔG° with increasing temperature indicates that the adsorption process is not desirable at higher temperatures.[44]

CONCLUSION

In this study, the removal efficiency of CIP antibiotics by MIP was measured under optimal conditions with a value of 99.3%. The results of isothermal and kinetic studies showed that the equilibrium data follow the Langmuir isotherm and the pseudo-second-order reaction kinetics. Negative ΔG° and ΔH° results indicated that ciprofloxacin adsorption was exothermic and spontaneously. Decreasing the values of ΔG° with increasing temperature indicates that the adsorption process is not desirable at higher temperatures. Therefore, the results show that the MIP is an adsorbent with a very high and economically suitable ability to remove various contaminants from aqueous solutions.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

ABBREVIATIONS

MIP: Molecularly imprinted polymer; **CIP:** Ciprofloxacin.

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