

Adsorption Equilibrium and Thermodynamic Studies of Ciprofloxacin from Aqueous Solutions by Magnetic Bentonite Nanocomposites

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ABSTRACT

Objectives: Today, due to increasing usage of antibiotics and their destructive effects on health and environment, it is necessary to remove them from receiving waters. Although there are few studies on the use of magnetic nanocomposites for removal of different antibiotics, but the effect of this adsorbent on the removal of Ciprofloxacin (CIP) has not been evaluated yet. Therefore, this study was conducted to investigate the removal of CIP by magnetic Bentonite nanocomposites (Fe₃O₄-BNP) as an adsorbent. **Methods:** Batch studies were performed to evaluate and optimize the effects of various parameters such as contact time, temperature of the solution, CIP concentrations and Fe₃O₄-BNP dosage. The adsorbent characteristics were determined using SEM and FTIR spectroscopy. Also, the adsorbent surface area was measured by BET technique. **Results:** the optimal values for the factors affecting CIP removal were calculated. It was revealed that the maximum CIP removal was obtained at pH = 7, temperature = 55°C, CIP concentration = 10 mg/L, Fe₃O₄-BNP dosage = 1.25 g/L and contact time= 90 min. The

maximum removal percentage was 99.25%. It was also revealed that Langmuir isotherm is the best fitted isotherm model. The thermodynamic parameters like ΔG° , ΔH° and ΔS° changes for the adsorption of CIP have also been computed and discussed. The heat of adsorption implied that the adsorption was exothermic in nature. **Conclusion:** The Fe₃O₄-BNP was successfully applied for the uptake of CIP from industrial wastewater and separated easily by means of magnetic separation.

Key words: Fe₃O₄-BNP, Adsorption, Ciprofloxacin, Isotherm, Thermodynamics.

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INTRODUCTION

Now days, the confrontation of environmental effluence is a crucial and worthwhile task over the globe because of drastic ecological pollution.^{1,2} Pharmaceutical compounds can be evacuated in the environment through different sources such as hospital wastewater, pharmaceutical industries, domestic wastewater and veterinary clinics.^{3,4} Among them, antibiotics due to annual consumption of 100,000 to 200,000 tons worldwide are important and have high potential effect for environmental pollution, especially water and soil because of high stability and biological activity and acute effects on ecosystems.^{5,6}

The presence of antibiotics in aquatic environments has raised concerns, because of not only the high potential for biocompatibility of these compounds, but also the increased antibiotic resistance of bacteria.^{7,8} Ciprofloxacin (CIP) is one of the third-generation Fluoroquinolones, which has widely been used as an antibacterial agent in recent years.⁹ Fluoroquinolones may also cause physiologically teratogenic effects on plants and algae; they are also genotoxic and carcinogenic to organisms.¹⁰ Unfortunately, since these types of antibiotics are less biodegradable, conventional biological wastewater treatment processes are not able to successfully remove these compounds from wastewater.¹¹ Therefore, the development of effective treatment methods is of great importance.

In developed countries, removal of antibiotics from wastewater is normally achieved by advanced technologies such as ion exchange, chemical precipitation and electrochemical deposition.¹² But these

technologies do not seem to be economically feasible because of their relatively high costs and that developing countries may not afford such technologies.^{13,14} Therefore, there is a need to look into alternatives to investigate a low-cost method, which is effective and economical.¹⁵ To overcome this difficulty there is a strong need to develop cheap adsorbents, which can be used in developing countries.¹⁶ At present, there is growing interest in using low-cost, commercially available materials for the adsorption of antibiotics.¹⁷ The use of mineral materials for the treatment of polluted water is also an attractive and promising option for the environment.¹⁸ A wide variety of mineral materials such as bentonite, zeolite, sepiolite, montmorillonite are being used as low-cost alternatives to expensive adsorbents.^{19,20}

The main objective of this study is to optimize the adsorption performance of Fe₃O₄-BNP for the removal of CIP from aqueous solution. The isotherm models of Freundlich, Langmuir, Temkin and Dubinin-Radushkevich were used for the equilibrium studies. Moreover, thermodynamic study was also performed.

MATERIALS AND METHODS

Ciprofloxacin (CIP) (Formula: C₁₇H₁₈FN₃O₃, formula mass 367.8 g/mol and Drug class:m Fluoroquinolone) with purity higher than 99.6% was supplied by Sigma-Aldrich. The structure of the CIP is given in Figure 1.

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Stock solution of Ciprofloxacin were prepared by dissolving 1 g Ciprofloxacin into distilled water to a concentration of 1000 mg/L. Stock solution was further diluted to different desired concentrations. All the chemicals used were of analytical reagent grade and were obtained from Sigma-Aldrich.

Batch adsorption studies were carried out by shaking 0.5 g of the Fe₃O₄-BNP with 50 ml of the aqueous solutions of CIP in different conical flasks using a temperature-controlled shaker. The solution-adsorbents mixtures were stirred at 150 rpm and at the end of pre-determined time interval the reaction mixtures were filtered out and analyzed for its CIP ion concentrations using UV-vis spectrophotometer at λ_{max} = 277 nm. The adsorption experiments were also conducted to determine the equilibrium time (10, 20, 30, 45, 60, 90, 120, 150 min.), initial concentrations (10, 25, 50, 75 and 100 mg/L), dosage of the adsorbent (0.1, 0.2, 0.4, 0.6, 0.8, 1, 1.25, 1.5, 1.75 and 2 g/L) and temperatures (10, 25, 40 and 55°C) at fixed PH=7 for maximum adsorption. All the investigations were carried out in triplicate to avoid any discrepancy in experimental results. CIP solution controls were kept throughout the experiment to maintain quality control. The percentage of CIP adsorption by the adsorbents was computed using the equation:^{21,22}

$$R = \frac{(C_0 - C_e)}{C_0} \times 100$$

Where C₀ and C_e are the initial and equilibrium concentration of CIP ion (mg/L) in the solution.

Adsorption isotherm is a curve that expresses the variation in the amount of material adsorbed by the adsorbent. In order to express the relationship between adsorption and the concentration of the CIP remaining in the solution, various different models are usually used, among which the models of Langmuir, Freundlich, Temkin, D-R were used in the present study.

The Langmuir equation is expressed in Eq. (2):²³

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max} K_L}$$

Where C_e denotes the concentration of the adsorbate in a balance mode, parameter K_L are the Langmuir adsorption constants and q_e is the amount of adsorbed CIP per weight of the Fe₃O₄-BNP.

The Freundlich equation is expressed in Eq. (3):²⁴

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Where K_F and n are Freundlich constants, log K_F denotes y-intercept, 1/n is the slope of Freundlich curve and q_e denotes the adsorption capacity in a balance mode.

The Temkin isotherm equation is expressed as Eq. (4):²⁵

$$q_e = B_1 \ln(K_T) + B_1 \ln(C_e)$$

Where K_T is the equation constant (L/mg). The constants of K_T and B₁ can be calculated through drawing the q_e curve according to ln C_e.

The D-R isotherm is presented in Eq. (5):²⁶

$$\ln(q_e) = \ln(q_{max}) - B\varepsilon^2$$

Where q_{max} denotes maximum adsorption capacity (mg/g) and ε is the D-R constant and is obtained through Eq. (6):²⁷

$$\varepsilon = [RT \ln(1 + 1/C_e)]^2$$

Where R is the ideal gas constant (8.314 J/mol.K) and T denotes temperature (K).

The most important parameters that would be studied in this section would be enthalpy changes (ΔH°), changes in Gibbs free energy (ΔG°) and entropy changes (ΔS°). In order to perform thermodynamic

calculations, first, the constant of apparent valance of adsorption (K_d) will be expressed through Eq 7:²⁸

$$K_d = q_e / C_e$$

Where q_e denotes the amount of CIP removed by the adsorbent in the moment of balance and C_e denotes the balanced concentration of CIP in the solution (mg/L). Changes in Gibbs free energy (ΔG°) show the level of spontaneity and it is calculated through Eq 8:²⁹

$$\Delta G^0 = -RT \ln K$$

Where R denotes the ideal gas constant, which is equal to 8.314 J/mol.K and T denotes absolute temperature (K) yet the most important thermodynamic values such as ΔG°, ΔH° and ΔS° are related to each other through Eqs 9 and 10:³⁰

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\ln(k_1) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$

RESULTS

SEM micrograph for the synthesized Fe₃O₄-BNP is represented in Figure 2. It is clearly evident that the all these nanoparticles were well separated from each other suggesting the Fe₃O₄-BNP were free from aggregation and spherical. The SEM image of Fe₃O₄-BNP shows that the particles size ranged between 20 and 40 nm. The EDX spectrum (Figure 3) contains intense peaks of O, Na, Mg, Al, Si, Ca and Fe. Presence of these elements on the surface of the Fe₃O₄-BNP indicate a large possibility of removal of pollutant.

The effect of time and amount of CIP ions adsorbed for different initial concentration by Fe₃O₄-BNP is shown in Figure 4. It can be seen from the figure that the adsorption at different concentrations is rapid in the initial stages and gradually decreases with the progress of adsorption until the equilibrium is reached.

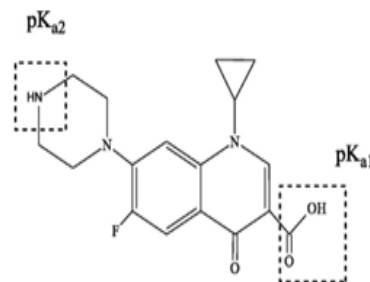


Figure 1: The chemical structure of CIP.

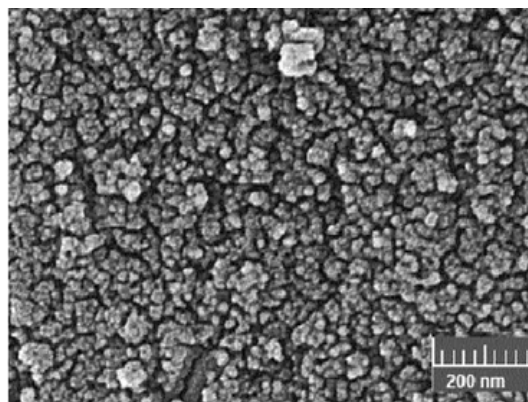


Figure 2: SEM image of Fe₃O₄-BNP.

The effect of the initial CIP concentration on the CIP removal efficiency is shown in Figure 4. The initial concentration varied from 10 to 100 mg/L, when other parameters; adsorption dose, contact time, pH were constant. According to results by increasing the initial concentration of CIP the removal efficiency of antibiotic decreased. Based on Figure 3, when concentration increased from 10 to 100 mg/L, the removal efficiency of CIP reduced from 98.91% to 76.34 %, which confirmed unsuitable effect of high initial concentration on the adsorption process. Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given concentration of the adsorbate.

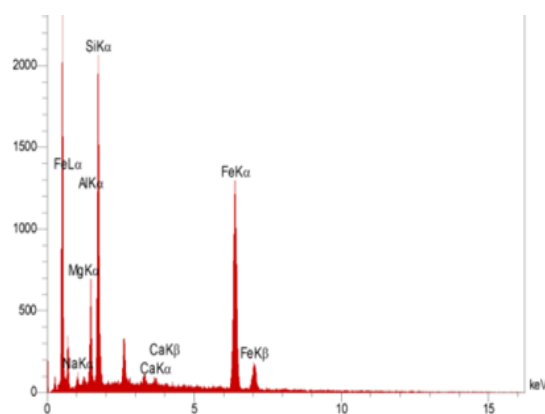


Figure 3: EDX spectrum obtained for Fe₃O₄-BNP.

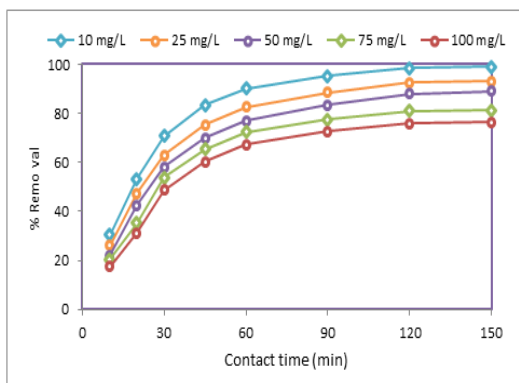


Figure 4: Effect of contact time and concentration on CIP removal efficiency (pH= 7, dose= 1.25 g/L, Tem= 25°C).

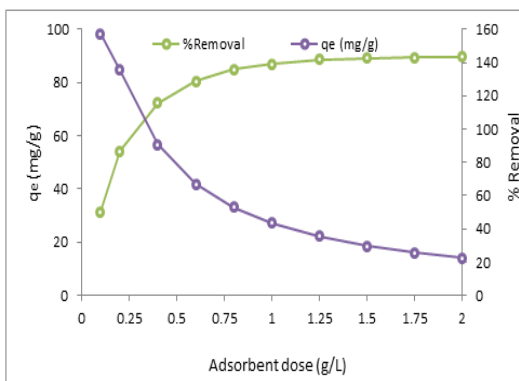


Figure 5: Effect of Fe₃O₄-BNP mass on CIP removal efficiency (C₀ = 100 mg/L, pH= 7, time= 90 min, Tem= 25°C).

The adsorption studies of CIP ions on Fe₃O₄-BNP was done at 30°C temperature by varying the quantity of adsorbent from 0.1 g to 2 g while keeping the volume of the CIP solutions constant at pH 6. When the adsorbent dosage was increased from 0.1 to 2 g the amount adsorbed per unit mass of adsorbent decreases considerably as shown in Figure 5. In the present study, the above-mentioned isotherm models were used to evaluate and analyze the data obtained from the experiments. The equilibrium adsorption data of CIP onto Fe₃O₄-BNP were analyzed using four isotherm models including Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and the results of isotherms are shown in Table 1. Also, in order to determine the best model for adsorption isotherm, correlation coefficient was used in the present study. The correlation coefficients of five isotherm models under study (Table 2) shows that the Langmuir isotherm is the most suitable model for the adsorption of CIP using Fe₃O₄-BNP adsorbent. Thermodynamic parameters for CIP removal by Fe₃O₄-BNP are summarized in Table 2.

DISCUSSION

The adsorption of CIP ions increases with time and attain saturation in about 75-90 min. The adsorption capacity of CIP ions is rapid initially but it is constant with the lapse of time. The figure reveals that maximum adsorption of CIP ions was attained after about 90 min. The rate of adsorption capacity is higher in the beginning due to larger surface area of the Fe₃O₄-BNP being available for the adsorption of the CIP ions and

Table 1: Isotherm parameters for adsorption of CIP onto Fe₃O₄-BNP at various temperatures.

Isotherm models	283 K	298 K	313 K	328 K
Langmuir				
q _m (mg/g)	64.04	68.11	71.02	75.73
K _L (L/mg)	0.0044	0.0057	0.0066	0.0084
R _L	0.456	0.591	0.711	0.925
R ²	0.986	0.991	0.998	0.995
Freundlich				
K _F	2.841	3.525	4.729	4.986
1/n	0.521	0.719	0.824	0.891
R ²	0.945	0.954	0.931	0.926
Temkin				
K _T	0.825	0.796	0.928	0.911
B _T	41.25	38.94	46.58	46.73
R ²	0.941	0.895	0.902	0.908
D-R				
q _m (mg/g)	31.24	34.46	29.71	39.48
E	5.189	6.841	7.146	7.891
R ²	0.811	0.825	0.804	0.832

Table 2: Values of thermodynamic parameters for the adsorption of CIP onto Fe₃O₄-BNP.

Temperature (K)	G ⁰ (KJ/mol)	H ⁰ (KJ/mol)	S ⁰ (KJ/mol K)
283	-3.25		
298	-4.17	31.96	0.246
313	-4.94		
328	-6.71		

after a lapse of time the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases.³¹ For subsequent experiment, the contact time was thus maintained for 90 min to ensure that equilibrium could be achieved. On changing the initial concentration from 10 to 100 mg/L, the amount adsorbed increased from 8.25 to 65.96 mg/g. The plots are smooth and continuous, suggesting the possible monolayer adsorption of CIP ions on the surface of Fe₃O₄-BNP.³² Consequently, the concentration of CIP ions will greatly affect the extent and rate of CIP ions uptake onto surface of Fe₃O₄-BNP.

The decrease in unit adsorption with increase in the dose of adsorbent is due to the increase in active sites on the adsorbent and thus making easier penetration of the CIP ions to the adsorption sites.³³

According to Figure 4, the CIP concentration of 10 mg/L is selected as the best concentration under the mentioned conditions. But as the concentration of CIP increases, the percentage of removal decreases, because every adsorbent has limited number of active sites which will be saturated at high CIP concentrations.³⁴ In this case, the surface of the adsorbent will no longer be able to adsorb and as a result, the CIP removal percentage decreases.³⁵

The Langmuir adsorption isotherm model includes single-layer adsorption, assuming that adsorption takes place monotonously.³² Based on this adsorption energy model, when the adsorbent surface is all unified, the molecules of the adsorbate will not be able to move on the surface of the adsorbent.³⁰ Also Freundlich model expresses adsorption in a heterogeneous surface in terms of adsorption energy.²⁹ Temkin model is used to estimate the effects of indirect interactions between the adsorbent and adsorbate in the process of adsorption.²⁸ It is worth mentioning that this isotherm is only applicable to a medium range of ion concentration.²⁴ D-R Isotherm model, the mechanism of adsorption is described through distribution of Gaussian energy for heterogeneous surfaces.³⁰

As shown in Table 1, R_L is in the range of $0 < R_L < 1$ for Langmuir isotherm and it can be concluded that CIP removal by Fe₃O₄-BNP is done well. In addition, the numerical value of n is less than one for Freundlich isotherm. Since, n represents the distribution of adsorbed particles attached to the surface of the adsorbent, so it can be concluded that the adsorbent surface has a heterogeneous state.³⁶ The Langmuir isotherm is only valid for the adsorption of adsorbate in aqueous solutions by adsorbents with limited number of unified sites in a single layer, it can be concluded that CIP is adsorbed by Fe₃O₄-BNP in a single layer and relatively monotonous state.

By performing thermodynamics studies, one can find out whether a process is endothermic, exothermic, spontaneous, or non-spontaneous. According to Table 2, the positive enthalpy changes show that the process of adsorption of CIP by Fe₃O₄-BNP is an endothermic process in nature.³⁰ In addition; the magnitude of the enthalpy gives information on the characteristics of adsorption process including physical, chemical and physiochemical absorption.²⁴ Nevertheless, the negative values of Gibbs free energy showed that the adsorption process is spontaneous.²⁸ Positive ΔS° value reflects the affinity of the Fe₃O₄-BNP for CIP as well as the increase in randomness at solid-solution interface during CIP adsorption.³⁷

CONCLUSION

The effects of Fe₃O₄-BNP dose, contact time, temperature and initial CIP concentration on the CIP removal from aqueous solution using Fe₃O₄-BNP have been investigated. The results confirmed that suggested Fe₃O₄-BNP has ability to remove CIP because of porous surface and functional groups. Furthermore, aforementioned variables have important effects

on the process; high concentration of CIP negatively affected the removal efficiency, the adsorbent at the higher dose increased the CIP removal. The results of isotherm and Thermodynamic studies showed that Langmuir isotherm are suitable models to describe the experimental data and is the process of adsorption Endothermic.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

ABBREVIATIONS

Fe₃O₄-BNP: magnetic Bentonite nanocomposites; CIP: Ciprofloxacin.

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