Preparation of CoFe$_2$O$_4$/activated carbon@chitosan as a new magnetic nanobiocomposite for adsorption of ciprofloxacin in aqueous solutions

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ABSTRACT

Ciprofloxacin (CIP) is considered as a biological resistant pollutant. The CoFe$_2$O$_4$/activated carbon@chitosan (CoFe$_2$O$_4$/AC@Ch) prepared as a new magnetic nanobiocomposite and used for adsorption of CIP. CoFe$_2$O$_4$/AC@Ch was characterized by Fourier transform-infrared (FT-IR), field emission scanning electron microscope (FESEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), vibrating-sample magnetometer (VSM), and Brunauer-Emmett-Teller (BET) surface area measurements. The pH$_{ZPC}$ value of the nanobiocomposite was estimated to be 6.4 by solid addition method. The prepared magnetic nanobiocomposites can be separated easily from water by an external magnet and reused. The effect of CIP concentration (10–30 mg/L), adsorbent dosage (12–100 mg/L), contact time (5–30 min) and pH (3–11) as independent variables on ciprofloxacin removal efficiency was evaluated. Optimum conditions were obtained in CIP concentration: 10 mg/L, adsorbent dosage: 100 mg/L, contact time: 15 min and pH: 5. In this condition, maximum CIP removal was obtained as 93.5%. The kinetic and isotherm equations showed that the process of adsorption followed the pseudo-second order kinetic and Langmuir isotherm. The results indicate that the prepared magnetic nanobiocomposite can be used as good adsorbent for the removal of CIP from aqueous solution and can be also recycled.

Key words | adsorption, chitosan, ciprofloxacin, magnetic nanobiocomposite

INTRODUCTION

The widespread use of drugs and antibiotics has led to their frequent detection in the wastewater treatment systems (Jiang et al. 2013). The presence of antibiotics in the environment causes many problems, such as drug resistance in humans and animals, effect on the non-target pathogens, alteration of the structure of algae in aquatic resources, and interference with the photosynthesis of plants. In addition, many antibiotics have low biodegradability and are resistant in the environment. Mainly, antibiotics enter the environment through four routes: the process of antibiotics production, sewage, land application of municipal biosolids and incorrect disposal of expired drugs (Yu et al. 2016). Among the common antibiotics used, quinolone antibiotics are a group with low biodegradability. Ciprofloxacin (CIP) is a broad-spectrum antibiotic from the fluoroquinolones group that is widely used in hospitals to treat bacterial infections caused by Gram-positive and -negative bacteria. CIP has high solubility under different pH conditions in aquatic environments and high stability in the soil and wastewater systems. CIP is detected in the aqueous environments at concentrations of ng/L to mg/L (Jiang et al. 2013).

Although their concentrations may be low in these environments, their continued access due to cumulative effects can increase the potential risks for aquatic ecosystems and microorganisms, and increase concerns about the harmful biological and genetic effects associated with them. Therefore, the removal of antibiotics is very important. Several methods have been used to remove antibiotics; these include adsorption (Fukahori et al. 2013; Yu et al. 2016; Malakootian et al. 2018a), advanced oxidation processes (Malakootian et al. 2018c; Mondal et al. 2018), oxidative enzymes system (Gao et al. 2018), electrocoagulation technique (Ouissa et al. 2014) and reverse osmosis (Alonso et al. 2018). Among these methods, adsorption...
process has the advantages of easy operation, low cost, high efficiency and no risk of exposure to toxic substances (Yu et al. 2016).

This process is one of the promising technologies. Although activated carbon is often used in adsorption processes, it could not be separated from aqueous solutions due to the small size of carbon particles. Thus far, much research has been done to remove nanoparticles from aquatic environments. Recently, magnetic separation was developed for the collection of nanoparticles. Magnetic hybrid material also has advantages such as high adsorption, rapid separation, ease of use and environmental compatibility with other techniques (Zhou et al. 2014). Cobalt ferrite and the composites due to its excellent ferromagnetic performance, high chemical stability and mechanical hardness, has been studied for adsorption of pollutants (Zheng & Lian 2015).

To further maximize the performance of magnetic adsorbents, further modification is required. Modifying organic ligands (e.g. thiol), polymer bonding (such as chitosan) and inorganic species (e.g. silica) can increase adsorption. The goal of such modifications is to develop low cost bio-adsorbs that are suitable for the removal of pollutants (Zhu et al. 2014).

Chitosan is a non-toxic and low-cost polysaccharide that is obtained from chitin deacetylation, with biological properties (e.g. biological compatibility and bio-degradability) and significant physical properties. Chitosan has two reactive groups: amino and hydroxyl groups, which have high reactivity, high chelation and high selectivity for various pollutants, making them useful as a bio-adsorbent and potentially used to adsorb pollutants (Chi & Cheng 2006; Zhang et al. 2018).

The aim of this study was to evaluate the removal of ciprofloxacin from aqueous solutions by CoFe$_2$O$_4$/AC@Ch as a new magnetic nanobiocomposite. The effects of different parameters such as initial concentration of ciprofloxacin, pH, adsorbent concentration and contact time were investigated, and the removal efficiency of CIP and the equilibrium capacity of the recovered absorbent under optimal conditions were determined.

**MATERIALS AND METHODS**

**Materials**

FeCl$_3$.6H$_2$O, CoCl$_2$.6H$_2$O, NaOH, activated carbon (AC) and chitosan (Ch) were purchased from Merck Company. CIP used in this study was purchased from Temad Pharmaceutical Company in Iran. All the chemicals were of analytical grade and used as received without further purification. All synthetic solutions of this study were prepared by twice distilled water.

**Preparation of magnetic CoFe$_2$O$_4$/AC@Ch nanobiocomposite**

FeCl$_3$.6H$_2$O and CoCl$_2$.6H$_2$O in ratio of 2:1 were dissolved in 50 mL deionized water. Then, AC was added to the solution and the mixture was vigorously stirred at room temperature. After that, NaOH was added to the suspension within 1 h to adjust the pH to 13. Dark brown solution was subjected to microwave irradiation, then lightweight massive powder of magnetic nano-adsorbent formed quickly and the black powder that was isolated by a magnet, was washed with deionized water many times, and dried at 100°C for 24 h. Magnetic nano-adsorbent was functionalized with chitosan. Chitosan (1 g) was added to the magnetic nano-adsorbent under ultrasonic conditions.

**Characterization of magnetic nano-adsorbent**

The Fourier transform-infrared spectroscopy (FT-IR) of samples were obtained using an FT-IR 6300, Japan. X-ray diffraction (XRD) of magnetic nano-adsorbent was recorded in the diffraction angle range $2\theta = 10–80^\circ$ by an Rigaku Ultima IV (made in Japan) using Ni-FILTERED Cu Ka radiation. The magnetic properties of CoFe$_2$O$_4$/AC@Ch were determined by vibrating-sample magnetometer (VSM) (LakeShore Cryotronics-7404) at room temperature. The microstructure, morphology and chemical composition of magnetic nanobiocomposite were investigated by field emission scanning electron microscopy (FESEM-EDS) (TESCAN mira3, Czech Republic). The Brunauer–Emmett–Teller ($S_{BET}$) specific surface area and adsorption/desorption isotherm were determined using a specific surface analyzer (Belsorp Mini II, Japan). The pH point of zero charges ($\text{pH}_{\text{pzc}}$) of the CoFe$_2$O$_4$/AC@Ch was determined by solid addition method. 100 mL of KCl solution (0.1 mol/L) was prepared at 10 different pH (2–11) values. 0.01 g of magnetic nanobiocomposite was added to each solution. The prepared mixtures were kept at room temperature for 24 h. The pH$_{\text{initial}}$ and final pH (pH$_f$) values of the solutions were measured using pH meter (Hanna). $\Delta$pH = pH$_f$ – pH$_i$ and pH$_i$ plot was drawn for determination of the pH$_{\text{pzc}}$. The intersection point of $\Delta$pH = 0 was taken as...
pH_{zpc} (Datta et al. 2017). The pH of solutions was adjusted by NaOH and HCL 0.1 N.

**Adsorption test**

Experiments were performed for optimum values with different values of each factor in order to evaluate the effectiveness and efficiency of each of these factors (pH: 3, 5, 7, 9 and 11; contact time: 5, 10, 15, 20, 25 and 30 min; amount of magnetic nanobiocomposite: 12, 25, 50 and 100 mg/L (0.0012, 0.0025, 0.005, 0.01 g/100 mL); the initial concentration of CIP: 10, 15, 20, 30 mg/L). The experiments were repeated three times to increase the reliability and accuracy.

After the adsorption process, a certain volume of the solution was taken and the magnetic bio-adsorbent by a magnet was separated from the solution. The residue concentration of CIP solution was measured at maximum wavelength of 276 nm by UV-Vis spectrophotometer (Shimadzu 1800, Japan). For adsorbent recovery, the separated magnetic nanobiocomposite was washed several times with ethanol and distilled water, then dried at 100 °C to distribute the nanobiocomposite. The adsorption process was carried out in the room temperature at 25 °C and the temperature was constant during the process.

The adsorption capacity (q) which is the amount of adsorbed CIP on magnetic nanobiocomposite was calculated by Equation (1) (Zhu et al. 2015; Zhang et al. 2014).

\[
q_e = \frac{(c_0 - c_t)v}{m}
\]

(1)

C₀ and Cᵣ are the CIP concentration (mg/L) at time 0 and t; v is the volume of solution (L) and m is the mass of dry magnetic nanobiocomposite used (g).

The removal efficiency of CIP was calculated using Equation (2) (Zhu et al. 2015; Zhang et al. 2014).

\[
R = \frac{(c_0 - c_t)}{c_0} \times 100
\]

(2)

A shaker with constant speed (200 rpm/min) was used to distribute the nanobiocomposite. The adsorption process was carried out in the room temperature at 25 °C and the temperature was constant during the process.

All experiments in this paper were performed according to the instructions mentioned in Standard Methods for the Examination of Water and Wastewater, 20th edition (APHA et al. 1999). Then, adsorption isotherms were calculated and the kinetics of reaction determined. SPSS-16 software was used to analyze the results.

**RESULTS AND DISCUSSION**

**Characterization of magnetic nanobiocomposite**

**FT-IR of magnetic CoFe₂O₄/AC@Ch nanobiocomposite**

FT-IR spectra of Ch and magnetic nanobiocomposite was studied in the range of 500–4,000 cm⁻¹ and compared as shown in Figure 1(a) and 1(b).

According to the FT-IR spectrum of Ch (Figure 1(a)), the wide absorption peak observed at 3,415 cm⁻¹ is due to the stretching vibrations of OH and NH, CH stretching vibration at 2,873 cm⁻¹, OH bending vibration at 1,638 cm⁻¹, and CH symmetric bending vibration in CHOH group 1,384 cm⁻¹ (Li & Bai 2006). Further, it also shows an absorption band corresponding to its COH at 1,079 cm⁻¹, due to asymmetric stretching of the C-O-C bridge of β-(1,4)-glycosidic bond and another absorption peak at 1,632 cm⁻¹ attributing to the bending vibrations of NH appear in FT-IR spectra of Ch (Zhang et al. 2017).

According to the FT-IR spectrum of CoFe₂O₄/AC@Ch (Figure 1(b)), the absorption peaks at 5,411 cm⁻¹ attributing to the stretching vibrations of O-H and NH appear in FT-IR spectra of CoFe₂O₄/AC/Ch composite (Deligeer et al. 2011). In addition, the strong absorption peak at 583 cm⁻¹ was related to the Fe-O bond stretching vibration of tetrahedral, which ascribed to the characteristic peak of CoFe₂O₄ (Do et al. 2011; Zhang et al. 2015). The absorption peak at 583 cm⁻¹ of CoFe₂O₄/AC@Ch, which demonstrates that the presence of AC and Ch have no effect on the crystallite structure of CoFe₂O₄ (Griffiths & De Haseth 2007).

**Magnetic properties of nanobiocomposite**

The magnetic properties of the nanobiocomposite was evaluated by VSM at room temperature and due to high value of Ms, the magnetization curve of nanobiocomposite proved a ferromagnetic character (Figure 2).

In addition to ferromagnetic properties, the room temperature specific magnetization (M) versus applied magnetic field (H) curve measurement of the nanobiocomposite indicates that the values of coercive force (Hc), saturation magnetization (Ms) and remanent magnetization (Mr) are 433.02 Oe, 22.03 emu/g and 7.16 emu/g, respectively. All these confirm adequate magnetization for simple separation by external magnetic field. CoFe₂O₄/AC@Ch was uniformly dispersed in CIP solution as shown in the inset of Figure 2. After finishing adsorption process, magnetic
nanobiocomposite were easily separated from the CIP solution by the external magnetic field. The gathering of nanobiocomposite from effluent do not require time-consuming and costly methods such as filtering and centrifuging and does not cause secondary pollution and can be recycled and reused for future runs.

The saturation magnetization of CoFe$_2$O$_4$/AC@Ch ($M_s = 22.03$ emu/g) was higher than the other reported by Zhu et al. for m-CS/c-Fe$_2$O$_3$/MWCNTs ($M_s = 4.81$ emu/g) (Zhu et al. 2013), Nguyen and Huynh for CoFe$_2$O$_4$ nanoparticles ($M_s = 4.81$ emu/g) and CoFe$_2$O$_4$/CS-graft-PAA nanocomposite ($M_s = 2.65$ emu/g) (Nguyen & Huynh 2014), Yadaei et al. for magnetic CMK ($M_s = 18.16$ emu/g) and magnetic CMK-CS ($M_s = 5.55$ emu/g) (Yadaei et al. 2018). Increasing the value of saturation magnetization ($M_s$) can improve magnetic separation. Therefore, the separation of adsorbent from aqueous phase becomes simpler.

**FESEM and EDS element mapping of magnetic nanobiocomposite**

Figure 3 shows the FESEM and energy dispersive spectroscopy (EDS) element mapping images of the magnetic nanobiocomposite. The FESEM images (Figure 3(a)) show the formation of nanoparticles with an average particle size of about 30 nm. The surface morphology of

![Figure 1 | FT-IR of chitosan (a) and CoFe$_2$O$_4$/AC@Ch (b).](image-url)
The nanobiocomposite clearly shows the formation of cobalt ferrite particles on the surface of activated carbon and small aggregates were observed.

To investigate the chemical composition of the as-synthesized nanobiocomposite CoFe$_2$O$_4$/AC@Ch adsorbent, the EDS element mapping was employed. EDS element mapping reveals the presence of Co, Fe, N, O and C that confirms the chemical structure of nanobiocomposite adsorbent (Figure 3(b)).

The XRD analysis of magnetic nanobiocomposite

Figure 4 shows the XRD diffraction pattern of CoFe$_2$O$_4$/AC@Ch nanocomposite that indicates the crystalline nature of nanobiocomposite.

The XRD pattern of adsorbent with the crystal phase structure of magnetic nanobiocomposite had diffraction peaks at $2\theta$ of about 18.42$^\circ$ (111), 30.25$^\circ$ (220), 35.58$^\circ$ (311), 43.2$^\circ$ (400), 53.59$^\circ$ (422), 57.15$^\circ$ (511), 62.71$^\circ$ (440) and 74.14$^\circ$ (533). These peaks that are well indexed to the cubic spinel phase of CoFe$_2$O$_4$ are also in agreement with the literature data (JCPDS 96-591-0064). Additionally, carbon characteristic peaks appear at $2\theta$ of about 27$^\circ$ (002) has confirmed the presence of amorphous carbon (Jiang et al. 2015; Yadaei et al. 2018) and reveals that, even in the reaction with AC and Ch, the crystal structure of the CoFe$_2$O$_4$ is well preserved (Figure 4).

The intensity of the peaks and their relatively low widths represent the high degree of crystallinity in nanoparticles. Mehran et al. (2016) found crystalline peaks at (220), (311),
(400), (422), (511), (440), (533) for CoFe$_2$O$_4$ nanocomposite powder (Mehran et al. 2016). Similarly, Wang et al. (2009) reported that XRD patterns of magnetite nanoparticles in Chitosan Hydrogel exhibited their major characteristic peak at [(111), (220), (311), (400), (422), (511), (440), (533)] (Wang et al. 2009).

The BET analysis of magnetic nanobiocomposite

The BET surface area of CoFe$_2$O$_4$/AC@Ch nanocomposite was investigated using N$_2$ adsorption/desorption measurements (Figure 5).

The BET equation was utilized to determine the monolayer volume of adsorbed gas, from which, the surface area of adsorbent can be calculated (Kacan 2016). The BET surface area of CoFe$_2$O$_4$/AC@Ch nanocomposite was 474.36 m$^2$/g, which was relatively high and the total pore volume ($p/p_0 = 0.987$) was obtained as 0.3745 cm$^3$/g. Adsorption isotherms are classified based on the strength of the interaction between the sample surface and adsorptive surface, and the existence or absence of pores. In this study, the isotherm is of type IV which is characteristic of mesoporous material. Comparison between the surface area ($S_{BET}$) of adsorbents in previous literature and the present study is shown in Table 1.

As shown in Table 1, the value of BET specific surface area of CoFe$_2$O$_4$/AC@Ch nanocomposite in this research was much greater than most of those obtained on other adsorbent composites that have been reported in the literature (Table 1). In fact, the adsorbents with relatively larger specific surface areas are more appropriate for removal of pollutants from water and wastewater.
Effect of CIP initial concentration

Changes in the removal efficiency and equilibrium adsorption capacity (\(q_e\)) of CIP by the magnetic nanobiocomposite at different concentrations of CIP (10–30 mg/L), pH: 5 and adsorbent dose of 100 mg/L are demonstrated in Figure 6.

At the constant level of magnetic nanobiocomposite, with increase in the initial concentration of CIP from 10 to 30 mg/L, \(q_e\) value increased from 93.5 to 177 mg/g. The initial concentration of CIP provides an important driving force of concentration gradient to overcome the resistance force of mass transfer of CIP between the solution and solid phase (Aksu & Yener 2001). On the other hand, increase in the concentration reduces the removal efficiency from 93.5 to 59%. With increase in the initial concentration, the number of available sites for adsorption of CIP decreases (Senthilkumar et al. 2011). In addition, due to increased repulsion force between the CIP molecules, the removal efficiency reduced (Senthilkumar et al. 2011). Therefore, the optimal concentration of CIP was considered to be 10 mg/L. Before nanobiocomposite surface saturation, with increase in contact time to 15 min, the removal efficiency also increased. With the continuation of the process and saturation of the adsorbent surface, desorption occurred and removal efficiency reduced.

In a study conducted by Jiang et al. (2015) in China for the adsorption of methyl orange by a magnetic composite (activated carbon/NiFe\(_2\)O\(_4\)), with the increase of MO initial concentration from 100 to 700 mg/L, due to increase of the ratio of initial mole numbers of MO to the available surface area of adsorbent, the equilibrium adsorption capacity (\(q_e\)) increased and due to the increased repulsion force between the dye molecules, the removal efficiency (R) dropped rapidly (Jiang et al. 2015). The results of this research are congruent with those obtained by Jiang et al. (2015).

Effect of magnetic nanobiocomposite dosage

The variations in the removal efficiency and equilibrium adsorption capacity (\(q_e\)) of CIP versus different concentrations of the magnetic nanobiocomposite (12–100 mg/L) with prolongation of contact time at pH: 5 and CIP concentration of 10 mg/L, are indicated in Figure 7.

By increasing the nanobiocomposite dose from 12 to 100 mg/L, the CIP removal efficiency increased from 64.7 to 93.5%. At low concentrations, the nanobiocomposite surface was saturated more quickly due to the lower amount

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>(S_{\text{BET}}) (m(^2)/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe(_2)O(_4)/AC@Ch</td>
<td>474.36</td>
<td>This research</td>
</tr>
<tr>
<td>CoFe(_2)O(_4)-reduced graphene oxide</td>
<td>169.9</td>
<td>Zhang et al. (2014)</td>
</tr>
<tr>
<td>Chitosan-modified magnetic graphite multi-walled carbon nanotubes (CS-m-GMCNTs)</td>
<td>39.20</td>
<td>Zhu et al. (2013)</td>
</tr>
<tr>
<td>Activated carbon produced from textile sewage sludge’s</td>
<td>310.62</td>
<td>Kacan (2016)</td>
</tr>
<tr>
<td>MMWCNT nanocomposite</td>
<td>61.74</td>
<td>Gong et al. (2009)</td>
</tr>
<tr>
<td>Graphenes magnetic material (Fe(_2)O(_3)-GS)</td>
<td>62.43</td>
<td>Guo et al. (2014)</td>
</tr>
<tr>
<td>CoFe(_2)O(_4)-SiO(_2) core-shell-structured nanoparticles</td>
<td>150</td>
<td>Wang et al. (2018)</td>
</tr>
</tbody>
</table>
of the adsorbent and less active adsorption sites. Therefore, the removal efficiency also increased with increase in the amount of adsorbent and subsequently increasing the active sites available for antibiotic adsorption (Zhang et al. 2014). On the other hand, with increase in the nanobiocomposite dose, the amount of adsorbed CIP per gram of adsorbent decreased. In the constant concentration of CIP, the active sites on the adsorbent surface remain unsaturated during adsorption process. An increase in concentration of magnetic nanocomposite caused the accumulation of the particle and the amount of adsorbed CIP per gram of adsorbent decreased (Senthilkumar et al. 2011).

Almost all the literature has reported that with the increase in the amount of adsorbent, the removal efficiency increased, due to elevated surface of the adsorbent and more availability of adsorption sites (Gong et al. 2009; Nguyen & Huynh 2014; Zhang et al. 2014).

**Effect of pH**

Changes in CIP removal efficiency and equilibrium adsorption capacity (qₑ) with increase in contact time in pH: 3, 5, 7, 9, 11; adsorbent dosage of 100 mg/L and concentration of CIP 10 mg/L is shown in Figure 8.

The pH of the solution is one of the most important parameters that affect the adsorption process. Indeed, the solution pH alters both the chemistry of the solution and the superficial coupling sites of the adsorption (Li et al. 2009). Changes in pH result in an altered profile of the charge of adsorbate agents, which in turn influences the interaction between the adsorbate and adsorbent agents (Li et al. 2009).

The effect of pH may be explained in terms of pHₚₑｃ of the adsorbent. The pHₚₑｃ of CoFe₂O₄/AC@Ch was determined by solid addition method and obtained 6.4 (Figure 8(c)). At pH below pHₚₑｃ, the surface charge of the
CoFe$_2$O$_4$/AC@Ch is positive, thereby increasing the chance of absorption of CIP ions. At pH above $pH_{zpc}$, the surface of the CoFe$_2$O$_4$/AC@Ch is negative. As a result, the repulsion between the interfaces increased in the solution (Datta et al. 2011; Zhao et al. 2013). On the other hand, high pH results in higher concentrations of OH$^-$/C$_0$ in the solution, inhibiting scattering of CIP ions, thereby decreasing the chance of their absorption (Datta et al. 2011). Therefore, pH 5 was selected as the optimum.

In a study conducted by Nguyen & Huynh (2014) for Ni(II) removal by nanocomposite of CoFe$_2$O$_4$/chitosan-graft-poly (acrylic acid), the maximum adsorption capacity of Ni(II) ions occurred at pH 5.3. They reported that in pH above of 7.6, OH$^-$ ions reacts with Ni$^{2+}$ to form the corresponding precipitations, which causes the decline of adsorption capacity (Nguyen & Huynh 2014).

**Recovery and reuse of CoFe$_2$O$_4$/AC@Ch**

The average removal efficiency ($R$) and the equilibrium adsorption capacity ($q_e$) of CIP by CoFe$_2$O$_4$/AC@Ch under optimal conditions in three cycles are shown in Table 2.

After recovering the adsorbent during three consecutive stages, it was determined that this magnetic nanocomposite

| Recovery and reuse of CoFe$_2$O$_4$/AC@Ch in three cycles for CIP adsorption (adsorbent: 0.01 g/100 mL, contact time: 30 min, CIP: 10 mg/L, pH: 5) |
|---|---|---|
| Runs | CIP removal efficiency ($R$) | Equilibrium adsorption capacity ($q_e$) |
| 1 | 93.5% | 93.5 mg/g |
| 2 | 89% | 89 mg/g |
| 3 | 85% | 85 mg/g |
can be used and recovered in several stages to remove pollutants of the water and wastewater industry.

Adsorption isotherm studies

Isotherm models describe the interaction between adsorbate and adsorbent. Here, Langmuir and Freundlich models have been applied for the interpretation of adsorption data (Chen et al. 2016).

Langmuir theory based on this assumption that the adsorption occurs at a series of specific and homogeneous sites within the adsorbent. Freundlich isotherm is obtained by assuming a homogeneous surface with distribution of non-uniformity of adsorbed heat on the surface. The linear form of Langmuir equation is represented by Equation (3) (Chen et al. 2016; Kalagatur et al. 2017).

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{3}
\]

where \(q_m\) is the maximum adsorption capacity (mg/g), \(C_e\) is the equilibrium concentration of CIP (mg/L), \(q_e\) is the amount adsorbed at equilibrium (mg/g), and \(K_L\) is the Langmuir coefficient related to the affinity of the binding sites (L/mg) (Kalagatur et al. 2017).

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor or equilibrium parameter \(R_L\) which is used to predict whether the studied adsorption system is favorable or unfavorable. It was defined by Equation (4) (Chen et al. 2016):

\[
R_L = \frac{1}{1 + K_L C_0} \tag{4}
\]

where \(C_0\) is the CIP initial concentration (mg/L) and \(K_L\) is the Langmuir adsorption equilibrium constant (L/mg). The value of \(R_L\) indicates the adsorption to be unfavorable \((R_L > 1)\), linear \((R_L = 1)\), favorable \((0 < R_L < 1)\) or irreversible \((R_L = 0)\) (Chen et al. 2016; Kalagatur et al. 2017).

The Freundlich isotherm based on sorption onto a heterogeneous surface and assumes that different sites with several adsorption energies are involved (Chen et al. 2016). This isotherm was also adapted to the adsorption equilibrium data. The Freundlich model is expressed as Equation (5) (Chen et al. 2016; Malakootian et al. 2018b; Yadaei et al. 2018):

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{5}
\]

where \(K_f\) and \(1/n\) are the Freundlich constants related to the adsorption capacity and adsorption intensity (or heterogeneity factor), respectively (Zhu et al. 2013; Guo et al. 2014). Therefore, a plot of \(\log q_e\) versus \(\log C_e\) enables the constant and exponent \(n\) to be determined. In Freundlich isotherm model, a value for \(1/n < 1\) indicates a normal adsorption. On the other hand, \(1/n > 1\) is indicative of cooperative adsorption (Chen et al. 2016).

The constant and correlation coefficients of Freundlich and Langmuir adsorption isotherms are presented in Table 3.

The results presented in Table 3 indicate that the Langmuir isotherm model is more suitable for the adsorption process. The \(R^2\) value of Langmuir model \((R^2 = 0.9936)\) was found to be larger than the value of Freundlich model \((R^2 = 0.9876)\). Also, the values of \(1/n < 1\) attained from Freundlich model indicate a normal Langmuir isotherm adsorption (Chen et al. 2016).

Kinetic models

Kinetic models are used to investigate the adsorption mechanisms. Absorption is a physiochemical process involving mass transfer of the adsorbate from the solution phase to the surface of the adsorbent. This reaction together with the transfer behavior of the adsorbate molecules is analyzed by different kinetic models. The pseudo-first and -second order kinetic models are among the adsorption reaction models (Zhu et al. 2013; Guo et al. 2014).
Pseudo-first-order kinetic model, which is based on absorption capacity, is used when the adsorption occurs by diffusion through a boundary.

The linear forms of pseudo-first order rate equation is as follows (Chen et al. 2016):

\[
\ln \left( \frac{q_e}{C_0} - \frac{q_t}{C_0} \right) = \ln \frac{q_e}{C_0} - K_1 t \quad (6)
\]

where \( K_1 \) (min\(^{-1}\)) is the constant of pseudo-first-order model, \( q_e \) and \( q_t \) (mg/g) represent the amount of CIP adsorbed at equilibrium and any time (min), respectively. The adsorption rate constant \( K_1 \) and adsorption capacity \( q_e \) can be obtained from the intercept and slope of the plot of \( \ln \left( \frac{q_e}{C_0} - \frac{q_t}{C_0} \right) \) against \( t \) (Chen et al. 2016; Yadaei et al. 2018).

Pseudo-second-order kinetic equation, which is based on absorption of the solid phase, indicates that chemical absorption is the rate slowing stage, controlling the adsorption processes. Second order reaction progress at a rate in proportion to the second power of a precursor. In pseudo-second-order kinetics, it is assumed that two reactions occur: one taking place quickly reaching equilibrium, while the other occurring slowly, which can continue for long periods of time (Zhu et al. 2013; Guo et al. 2014).

The linear forms of pseudo-second-order rate equation is expressed by Equation (7) (Chen et al. 2016).

\[
\frac{t}{q_i} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \times t \quad (7)
\]

where \( k_2 \) (g/mg min) is the constant of pseudo-second order model, \( q_e \) and \( q_t \) (mg/g) represent the amount of CIP adsorbed at equilibrium and any time (min), respectively. The value of \( k_2 \) can be obtained from the intercept and slope of the linearized plot by Equations (7) (Chen et al. 2016; Yadaei et al. 2018).

The pseudo-first and second-order kinetic models were studied for the experimental data and the results are presented in Table 4.

In this study, the initial rate of the adsorption was also high and adsorption process occurred very rapidly, then continued at a slower rate.

The correlation coefficients (R\(^2\)) presented in the Table 4 indicate that the R\(^2\) value of the pseudo-second-order model (R\(^2\) = 0.9964) is much higher than the value of the pseudo-first-order model (R\(^2\) = 0.1117). Thereby, the pseudo-second-order kinetic is more appropriate to describe the adsorption behavior of CIP onto CoFe\(_2\)O\(_4\)/AC@Ch.

**CONCLUSION**

In this study, CoFe\(_2\)O\(_4\)/AC@Ch was prepared by microwave irradiation co-assisted by ultrasonic waves in water without the use of toxic solvents and used as a magnetic nanobiocomposite and was characterized. The maximum adsorption capacity (\( q_m \)) of CIP onto CoFe\(_2\)O\(_4\)/AC@Ch could reach 188.68 mg/g. The S\(_{BET}\) surface area of adsorbent was 474.36 m\(^2\)/g. The adsorption of CIP followed Langmuir isotherm. Kinetic studies showed that the adsorption process followed the pseudo-second-order kinetic model. CoFe\(_2\)O\(_4\)/AC@Ch as a new nanobiocomposite can be utilized as environment-friendly biosorbent for the removal of antibiotics from aqueous solution due to high adsorption capacity, as well as simple and convenient magnetic separation.

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**REFERENCES**


Guo, X., Du, B., Wei, Q., Yang, J., Hu, L., Yan, L. & Xu, W. 2014 Synthesis of amino functionalized magnetic graphenes composite material and its application to remove Cr (VI), Pb (II), Hg (II), Cd (II) and Ni (II) from contaminated water. *Journal of Hazardous Materials* 278, 211–220.


Zhang, Y., Yan, L., Xu, W., Guo, X., Cui, L., Gao, L., Wei, Q. & Du, B. 2014 Adsorption of Pb (II) and Hg (II) from aqueous solution using magnetic CoFe2O4-reduced graphene oxide. *Journal of Molecular Liquids* 191, 177–182.


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