

Kinetics and Isotherm Investigations on the Improved Adsorption of the Antibiotic Moxifloxacin from Aqueous Solution utilizing Agar Coated Magnetite Nanoparticles

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Abstract: In the current study, agar-coated magnetite nanoparticles (AG-MNPs) were made using the chemical co-precipitation process. They were then employed to adsorb the antibiotic moxifloxacin from an aqueous solution. The Debye Scherrer equation and XRD peaks were used to determine the mean size of the agar functionalized nanoparticles, which was determined to be 13.9 nm. FTIR, TGA, FESEM, and VSM techniques were used to characterize these surface-coated magnetite nanoparticles. Thus, utilizing the batch adsorption technique and considering several factors such as the quantity of AG-MNPs, drug concentration, and solution pH, surface functionalized MNPs were employed to adsorb the moxifloxacin from the aqueous solution. When the drug concentration reached 50 ppm, it was revealed that AG-MNPs had the highest dye removal efficacy (more than 97%). According to the isotherm analysis, the Freundlich model provided a superior fit to the experimental equilibrium data, indicating heterogeneous multilayer adsorption on the surface of the nanoparticles. Additionally, the analysis of the kinetics data pointed to a pseudo-second-order rate for the moxifloxacin adsorption process.

Keywords: magnetite nanoparticles; agar; moxifloxacin; adsorption; kinetics.

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1. Introduction

In recent years, antibiotic contamination of surface and groundwater has become ubiquitous. These "emerging contaminants" categories have received great attention in aquatic environments [1,2]. Antibiotics are a group of medicinal substances used worldwide to treat and prevent illnesses, increase human health generally, and promote animal growth. Due to their poor metabolism, 30–90% of antibiotics are expelled from the body as the original molecule and enter into water bodies, which have detrimental ecological consequences [3]. Modern synthetic antibiotics used to treat human and veterinary illnesses include fluoroquinolones. These broad-spectrum antibiotics were first made available in the 1980s. There have been reports of extremely high fluoroquinolone concentrations in hospitals and antibiotic production effluent [4]. A member of the fluoroquinolone family of antibiotics, i.e.,

moxifloxacin, is a broad-spectrum antibacterial. Typically, ocular infections are treated with moxifloxacin. Compared to other antibiotics, moxifloxacin has strong antibacterial action and is extremely toxic to respiratory tract infections [5,6]. Numerous physical and chemical methods are used to remove antibiotics from an aqueous medium. These include the advanced oxidation process, adsorption [7], ultrasonic-activation effect method [8], membrane process [9], electrochemical process [10], chlorination [11], and biological treatment [12]. Adsorption is the most efficient process for removing antibiotics from the water out of all of them because it is inexpensive, doesn't produce any toxic by-products, and is simple to design and use [13,14]. Nanostructured substances have a huge surface-area-to-volume ratio; hence, they have extra advantages for an effective adsorption process with various good adsorbents. Moreover, Fe₃O₄ nanoparticles are also a good adsorbent for drug adsorption due to their characteristic structural, optical, and magnetic properties. Due to high magnetic saturation, minimal toxicity, and biocompatibility, superparamagnetic iron oxide (Fe₃O₄) nanoparticles have emerged as promising candidates for various modern technology applications [15–18]. The capacity of AG-MNPs to remove moxifloxacin from aqueous solution by adsorption behavior is therefore thoroughly examined in this paper. The effectiveness of the utilized adsorbent's adsorption was then tested under various experimental conditions. Finally, extensive kinetics and isotherm studies were also carried out.

2. Materials and Methods

2.1. Chemicals used.

All of the chemicals, including ferrous sulfate heptahydrate (FeSO₄·7H₂O, 98 percent), ferric chloride hexahydrate (FeCl₃·6H₂O, 98 percent), NH₄OH solution (25 percent), moxifloxacin and agar, were bought by SRL (India). Throughout the experiment, analytically graded compounds were utilized with no additional purification.

2.2. Instruments.

The infrared spectra of magnetite nanoparticles that were uncoated and coated with agar were captured using an ABB MB-3000 FTIR spectrometer. Perkin Elmer STA-6000 thermogravimetric analyzer was utilized to conduct thermal examination on both uncoated and coated nanoparticles. The UV-Vis spectrophotometer T90 PG Instrument Limited was used to measure the absorbance investigations. The mean size of uncoated and coated Fe₃O₄ nanoparticles was measured with the help of Hitachi SU-8000 FESEM. X-ray diffraction patterns were captured utilizing source radiation with a wavelength of 1.5406 Å at ambient temperature. Using a digital overhead stirrer, magnetic nanoparticles that were both uncoated and coated were synthesized (2000 rpm).

2.3. Synthesis of Fe₃O₄ and AG-MNPs.

The co-precipitation method was utilized to synthesize magnetite nanoparticles that were both bare and coated. By using a 50 ml solution of 0.2 M FeCl₃·6H₂O and a 50 ml solution of 0.1 M FeSO₄·7H₂O, 100 ml of a 2:1 molar ratio Fe³⁺/Fe²⁺ solution was prepared. In an atmosphere of inert gas, the resultant solution was heated to 85°C by vigorously spinning it for over 30 minutes. The resulting mixture added 20 mL of ammonia solution until the pH level reached 9-10. The iron solution's brown-black color changed to a deep black, indicating the

synthesis of magnetite nanoparticles [19]. In 50 mL of distilled water, 1 g of pure agar was dissolved. The agar solution was promptly added to the above Fe₃O₄ solution with one hour of additional agitation [20]. An external magnetic field was used to separate the agar-coated Fe₃O₄ nanoparticles from the solution, and they were then repeatedly cleaned with deionized water. The resulting AG-MNPs were dried in an oven. The surface functionalized magnetite nanoparticles were then examined using XRD, FTIR, FESEM, VSM, and TGA.

2.4. Batch adsorption analysis.

Moxifloxacin was individually dissolved in distilled water to prepare a 50 ppm stock solution. The standards used to obtain the calibration curve had a coefficient of determination of 0.992 (Figure 1). The effect of various parameters, i.e., amount of AG-MNPs (5-30 mg), contact time (10-100 min), pH (3-11), and moxifloxacin concentrations of 10 to 50 ppm on moxifloxacin adsorption from aqueous solution was investigated. In order to change the pH of the water sample, 0.1 N HCl or 0.1 N NaOH solutions were added. A UV-visible recording spectrophotometer was used to measure the solutions' starting and final moxifloxacin concentrations. The absorbance was measured at a maximum wavelength value of 288 nm. Based on the following formulas, the percentage removal and adsorption capacity of the investigated parameters from moxifloxacin was determined [21–23]:

$$\%R = \frac{(C_o - C_e)100}{C_o}$$

$$q_e = \frac{(C_o - C_e)V}{M}$$

where M is the weight of the adsorbent (g), C_o and C_e are the initial and equilibrium concentrations (mg/L) of moxifloxacin, and V is the volume of moxifloxacin solution in liter.

Table 1. The isotherms and kinetics equations.

Model	isotherms	
Langmuir	Freundlich	Temkin
$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$q_e = k_1 \ln k_2 + k_1 \ln C_e$
Model	kinetics	
Pseudo-first-order	Pseudo-second-order	
$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	

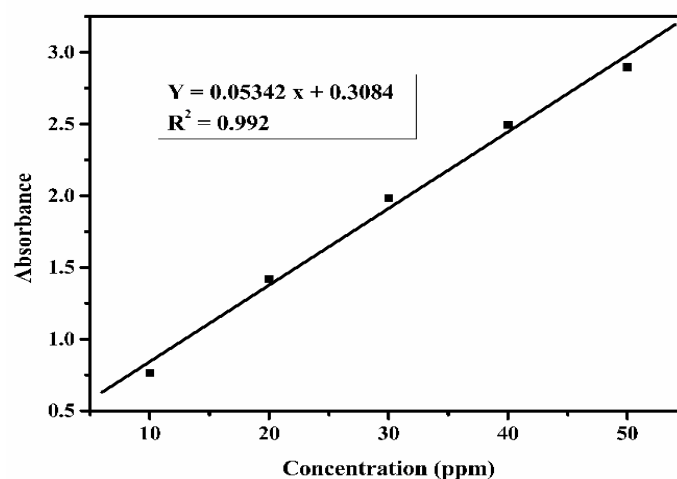


Figure 1. Standard curve for determination of moxifloxacin drug concentration.

For the study of experimental data and the description of adsorption equilibrium, numerous isotherm models, including the Langmuir, Freundlich, and Temkin models, are available. In this study, the moxifloxacin adsorption process on the nanoparticle's surface was assessed utilizing the models for pseudo-first-order and pseudo-second-order kinetics. Table 1 displays the adsorption kinetics and isotherms equation [24–28].

3. Results and Discussion

3.1. Characterization of Fe_3O_4 and AG-MNPs.

3.1.1. IR spectral study.

The FTIR spectra of Fe_3O_4 and agar-coated Fe_3O_4 nanoparticles are displayed in Figure 2. The functional group peaks in the IR spectra of agar-coated Fe_3O_4 nanoparticles provide evidence of agar's coating on the surface of Fe_3O_4 nanoparticles. In IR spectra of Fe_3O_4 nanoparticles, the absorption band at 580 cm^{-1} is due to Fe-O stretching vibrations. Whereas, in the IR spectra of AG-MNPs, the broad and intense band at around 3400 cm^{-1} is due to stretching vibrations of hydroxyl groups. A band at 2956 cm^{-1} corresponds to $-\text{CH}_2$ stretch. The peak at 1634 cm^{-1} , attributed to agar, is the typical polysaccharide absorption band [29]. The strong band shows C-O stretching vibration at 1150 cm^{-1} . The value reflects the C-O-C stretch at 1049 cm^{-1} , which is attributed to the glycosidic bonding vibrational mode. Additionally, a band at 554.86 cm^{-1} results from the stretching vibrations of Fe-O. The magnetic nanoparticle peak and the presence of agar peaks in the FT-IR spectrum of agar-coated Fe_3O_4 indicated the presence of an agar coating on the surface of the magnetic nanoparticles.

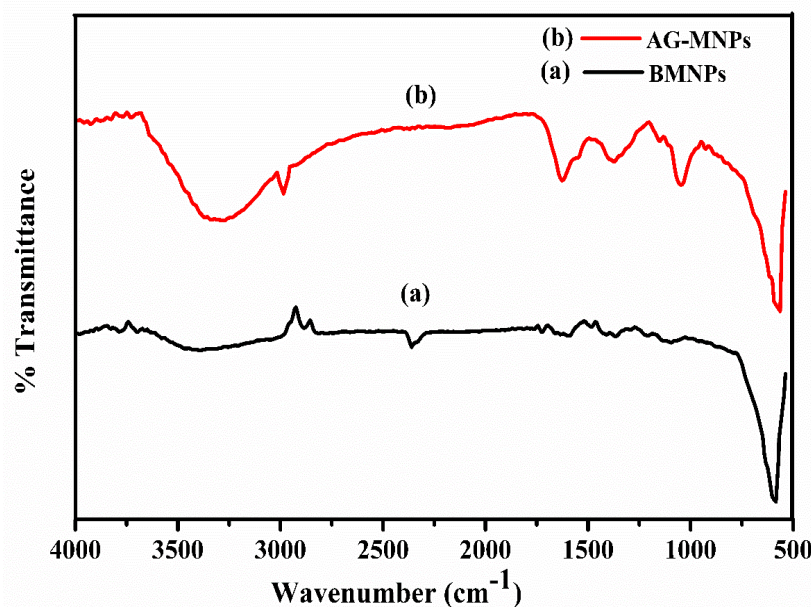


Figure 2. FTIR spectra of bare magnetic nanoparticles (BMNPs) and agar-coated magnetic nanoparticles (AG-MNPs).

3.1.2. X-Ray diffraction (XRD).

Using an X-ray diffractometer, the synthesized nanoparticles' crystallite sizes were studied. Figure 3 represents the diffraction pattern of the uncoated and coated nanoparticles. The average crystallite diameters for uncoated Fe_3O_4 and agar-coated Fe_3O_4 nanoparticles were

determined to be 11.9 and 13.9 nm, respectively, using the Scherrer equation and FWHM of the most intense peak [30,31]. The Debye Scherrer equation's prediction of the crystallite size of uncoated Fe₃O₄ and agar-coated Fe₃O₄ nanoparticles was found to be very close to the result of the FESEM study. Thus, the size (in nm) of uncoated and coated MNPs was confirmed by both XRD and FESEM studies.

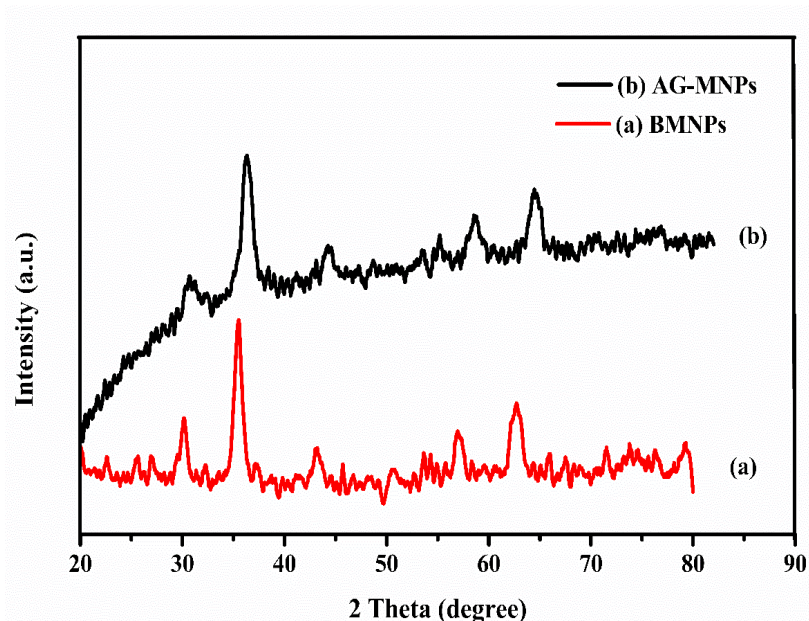


Figure 3. XRD patterns of bare magnetic nanoparticles (BMNPs) and agar-coated magnetic nanoparticles (AG-MNPs).

3.1.3. Field emission scanning electron microscopy (FESEM) study.

FESEM was used to determine the size of uncoated and agar-coated Fe₃O₄ nanoparticles (Figure 4). The FESEM image of the nanoparticles revealed that the average particle size of bare nanoparticles was 13.41 nm. However, the FESEM studies revealed that the average size of the coated nanoparticles was 23.75 nm. The increase in the size of the coated nanoparticles confirmed the surface coating of Fe₃O₄ nanoparticles with agar.

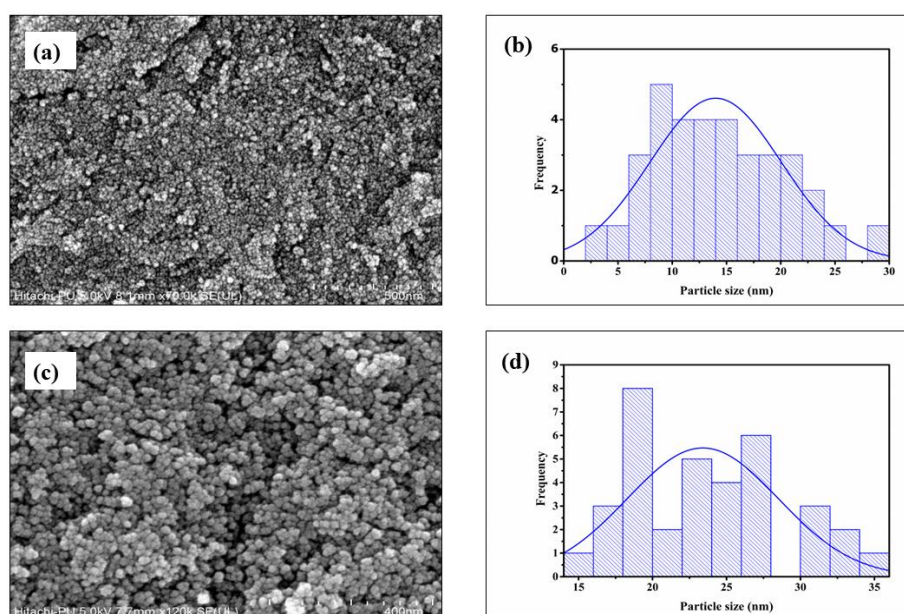


Figure 4. (a,b) FESEM micrograph of bare Fe₃O₄ nanoparticles with size distribution histogram and (c,d) FESEM micrograph of AG coated Fe₃O₄ nanoparticles with size distribution histogram.

3.1.4. Thermogravimetric analysis (TGA).

Thermogravimetric analysis was used to analyze the thermal studies of the prepared nanoparticles (Figure 5). The TGA curves of uncoated and coated MNPs showed various stages of the same deterioration at various temperatures. At the initial stage, both coated and uncoated samples displayed weight loss at about 100°C, which may have been caused by the removal of the samples' adsorbed moisture. Agar-coated magnetite nanoparticles showed weight loss of around 30% above 100°C, which the coating degradation can explain, i.e., agar from the surface of Fe₃O₄ nanoparticles (NPs). These thermal study findings also concluded that agar was successfully coated on the surface of magnetite nanoparticles (MNPs).

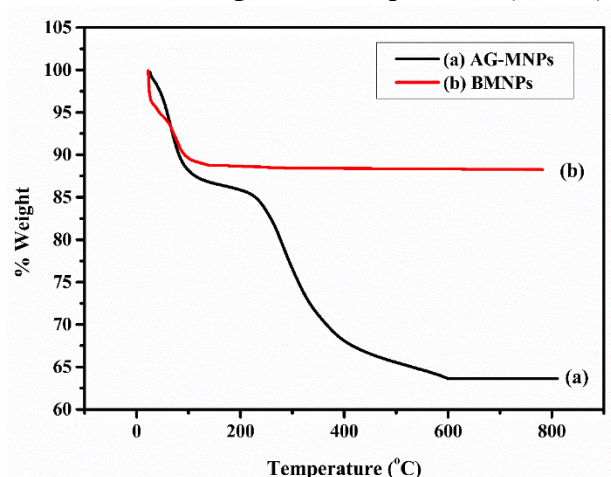


Figure 5. TGA curve of bare magnetic nanoparticles (BMNPs) and agar-coated magnetic nanoparticles (AG-MNPs).

3.1.5 Vibrating sample magnetometer (VSM) study.

Utilizing VSM analysis, the magnetic characteristics of produced magnetite nanoparticles were investigated. At 300 K, the magnetic hysteresis curves of agar-coated Fe₃O₄ NPs and Fe₃O₄ NPs were measured (Figure 6). Hysteresis loops verified the superparamagnetic behavior of both Fe₃O₄ NPs and agar-coated Fe₃O₄ NPs. The M_s value of agar-coated Fe₃O₄ NPs (45.83 emu/g) was found to be lower than the M_s value of bare Fe₃O₄ NPs (59.76 emu/g). Hence, these data evidenced the successful coating of non-magnetic material on the surface of MNPs. The findings, however, demonstrated that there was no appreciable decrease in M_s value for the nanoparticles after agar coating, demonstrating that the coating had no impact on the superparamagnetic behavior of the Fe₃O₄ NPs.

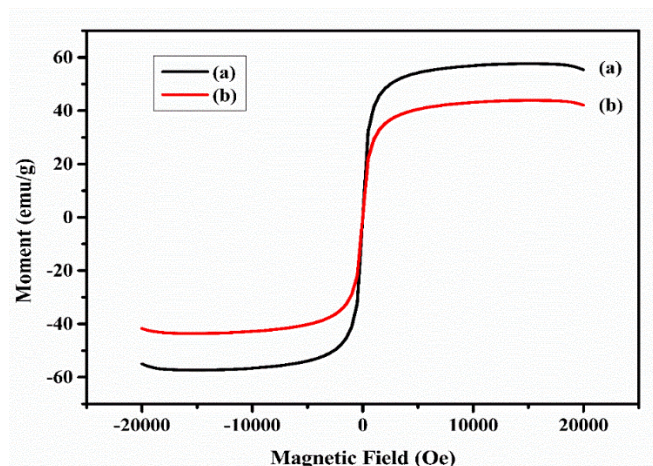


Figure 6. Magnetic hysteresis loops of (a) Fe₃O₄ NPs and (b) AG-MNPs at 300 K.

3.2. Adsorption studies.

The synthesized coated MNPs were used for moxifloxacin drug adsorption from the aqueous solution. The adsorption of moxifloxacin was investigated by using agar-coated MNPs as an adsorbent by changing the parameters affecting adsorption capacities like the quantity of adsorbent, pH, initial concentration of moxifloxacin drug and contact time.

3.2.1. pH.

The ability of nanoparticles to bind drugs can be hampered by changes in their surface charge density. With varying initial concentrations of moxifloxacin drug solution and a fixed quantity of AG-MNPs (30mg), the impact of pH fluctuation on the moxifloxacin drug adsorption was observed in the pH range of 3 to 11. The adsorption capacity steadily increases as the pH of the solution increases from 3 to 7, then it starts to decline from 7 to 11 (Figure 7). This increasing impact might be acknowledged due to the electrostatic interactions between the moxifloxacin drug that is adsorbate (having cationic character) and AA-MNPs (adsorbent). The pH of the solution has no significant effect on the adsorption capacity once the adsorption system has reached equilibrium [32]. The moxifloxacin solution and agar-coated Fe_3O_4 nanoparticles are negatively charged at pH values greater than 7. Repulsion forces consequently develop, and the adsorption capabilities reduce [33].

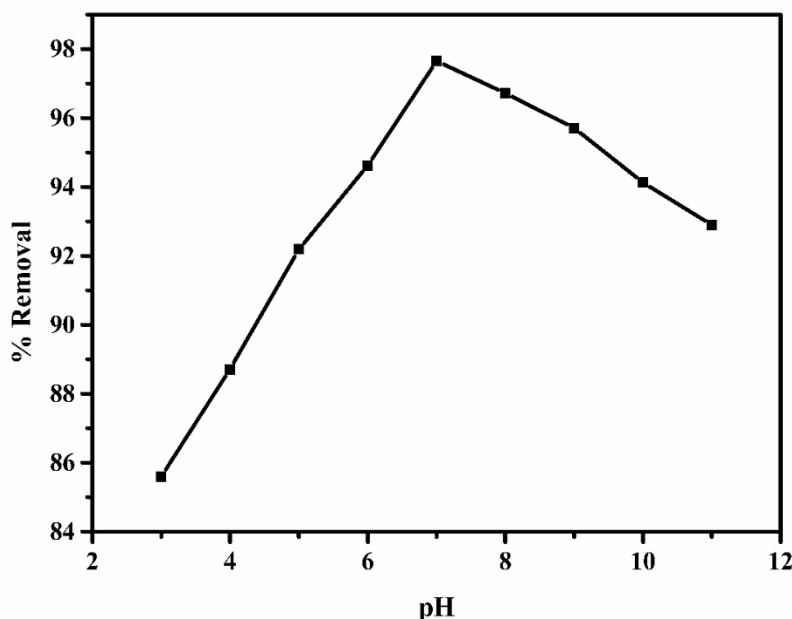


Figure 7. Effect of pH on moxifloxacin removal by AG-MNPs

3.2.2. Effect of contact time.

By holding other variables constant, such as pH 7, the concentration of moxifloxacin drug solution (50 ppm), and the amount of AG-MNPs (30mg), Figure 8 illustrates the effect of contact time on moxifloxacin adsorption at various time intervals (10-100 min). Moxifloxacin adsorption rises gradually with contact time because there were initially more vacant sites, which boosted the adsorption. However, after 80 minutes, there is no longer any rise in moxifloxacin adsorption, showing that after 80 minutes system reaches a stable stage.

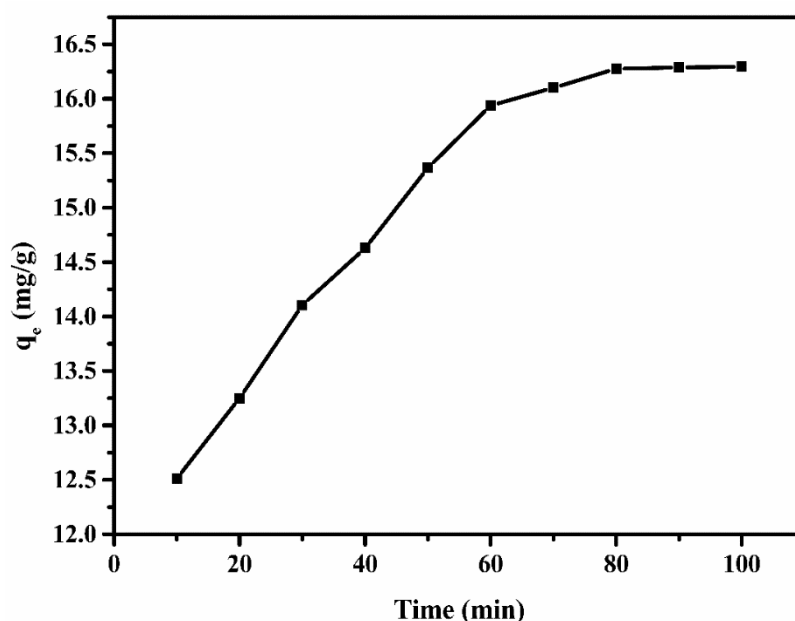


Figure 8. Adsorption efficiency of AG- MNPs for moxifloxacin removal at different contact times

3.2.3. Effect of adsorbent amount.

Keeping a fixed volume of moxifloxacin solution (10 mL) under specific conditions, the effect of varying the amount of adsorbent, i.e., agar-coated Fe_3O_4 (5-30 mg) on the adsorption of moxifloxacin (10-50 ppm), showed that the efficiency of removal of moxifloxacin drug increases with an increase in the quantity of agar-coated magnetite nanoparticles (Figure 9). Hence, it was concluded that the percentage removal of the moxifloxacin drug was raised with the rise in the agar-coated magnetite nanoparticle, possibly due to the presence of additional active sites.

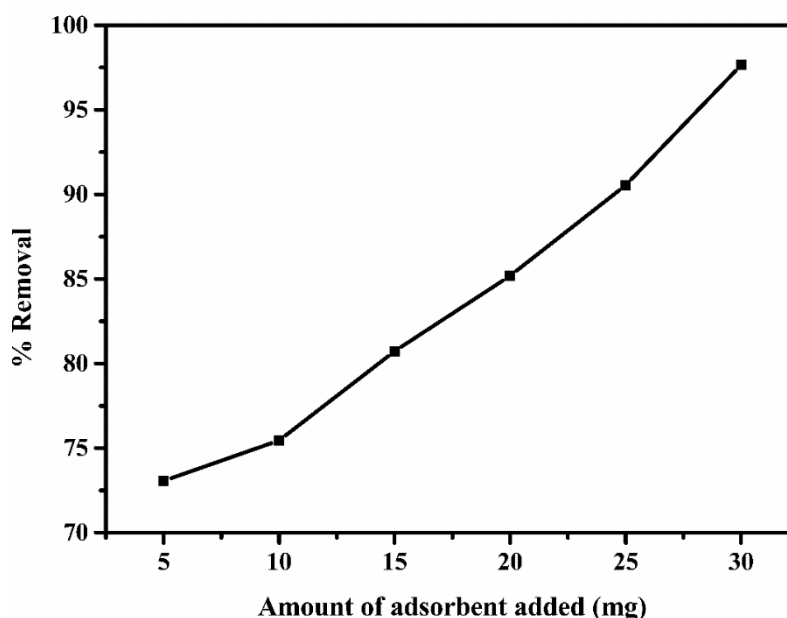


Figure 9. Effect of adsorbent dose on the removal efficiency of moxifloxacin drug.

3.2.4. Effect of initial drug concentration.

The effect of changing drug concentrations in the range of 10–50 ppm on the drug adsorption capability by AG-MNPs under equilibrium circumstances was examined while

maintaining a fixed amount of adsorbent, with the expected outcomes. The adsorption capacity decreased as the moxifloxacin drug concentration increased progressively from 10 to 50 ppm in a profile for moxifloxacin drug adsorption with varying beginning concentrations (Figure 10). This observation can be explained by the fact that, while maintaining a constant amount of adsorbent, the number of active functional sites of the adsorbent is blocked as the concentration increases. It is therefore supposed that the surface might become drug-saturated.

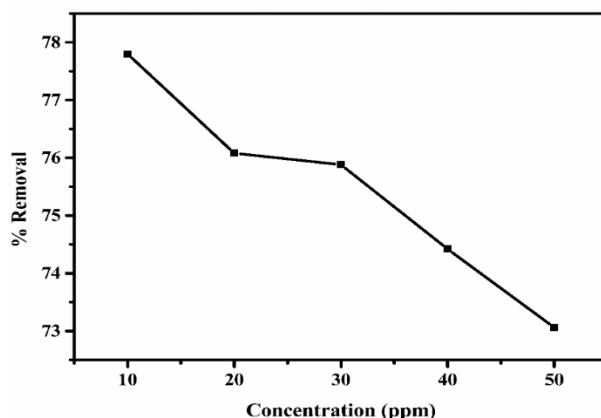


Figure 10. Effect of initial drug concentration on the moxifloxacin removal efficiency.

3.2.5 Adsorption isotherm and kinetics studies.

Kinetics is crucial for the adsorption study because it helped to establish the rate at which a certain drug may be removed from an aqueous solution and to learn more about the adsorption mechanism. Also, to optimize the design of an adsorption system for moxifloxacin drug adsorption, a number of isotherm models, including Langmuir, Freundlich, and Temkin, have been utilized to characterize the equilibrium features of the adsorption. To observe the interactions and reaction rate of the adsorption process, isotherm and kinetic studies were conducted (Table 2, Table 3). The results showed that the adsorption isotherm fit better with the Freundlich model with a high value of the coefficient of determination (0.998), while the kinetics study obeys a pseudo-second-order model (Figure 11, Figure 12). The kinetic study revealed the moxifloxacin drug's chemisorption onto the surface of agar-coated Fe₃O₄ nanoparticles, which also suggested that the adsorption capacity was correlated with the active sites of the adsorbent [34].

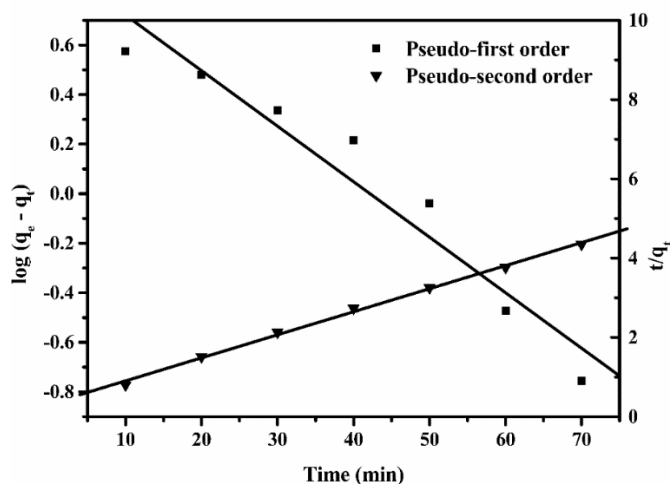


Figure 11. Pseudo 1st order kinetic plot and pseudo 2nd order kinetic plot for adsorption of moxifloxacin drug on AA-MNPs.

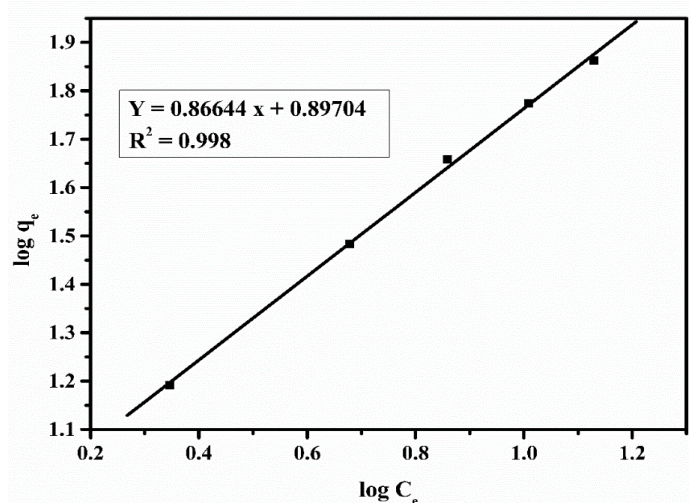


Figure 12. Freundlich isotherm model.

Table 2. Kinetics parameters for the moxifloxacin drug adsorption on AG-MNPs.

Pseudo 1 st order kinetic model			Pseudo 2 nd order kinetic model		
R ²	k ₁ (min ⁻¹)	q _e (mg/g)	R ²	k ₂ (g mg ⁻¹ min ⁻¹)	q _e (mg/g)
0.936	19.417	8.801	0.997	0.0105	17.196

Table 3. Isotherm parameters calculated from different isotherm models for the adsorption of moxifloxacin drug on AG-MNPs.

Langmuir Model			Freundlich Model			Temkin Model		
R ²	q _m	K _L	R ²	K _F	1/n	R ²	k ₁	k ₂
0.966	284.09	0.0259	0.998	7.889	0.866	0.962	31.669	0.645

4. Conclusion

In the current study, agar-coated magnetite nanoparticles (AG-MNPs) were made using the chemical co-precipitation method. FTIR, TGA, FESEM, and VSM techniques were used to characterize these surface-coated nanoparticles. The adsorption of contaminants from aqueous solutions played a significant role. For this purpose, the adsorbent, i.e., AG-MNPs, was utilized to adsorb the antibiotic moxifloxacin from an aqueous solution. Due to the inclusion of extra functional groups, the adsorption analysis revealed that agar-coated magnetite nanoparticles displayed a good adsorption capacity for the antibiotic moxifloxacin and removed around 97% of the moxifloxacin drug from aqueous solution at optimum conditions. Understanding the mechanism of moxifloxacin drug adsorption onto AG-MNPs was aided by kinetics and isotherm analysis. The results of the experimental work determined that the Freundlich isotherm model was the most appropriate for describing the heterogeneous multilayer adsorption on the surface of nanoparticles. The study of the kinetics data showed that the moxifloxacin drug adsorption on the surface of agar-coated magnetite nanoparticles obeys pseudo-2nd order, and the adsorption process is a chemisorption process. As a result, these findings showed that agar-coated nanoparticles might be employed as an efficient adsorbent for removing the antibiotic moxifloxacin from contaminated wastewater.

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Conflicts of Interest

The authors declare no conflict of interest.

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