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Magnetic mesoporous silica material ($\text{Fe}_3\text{O}_4@\text{mSiO}_2$) as adsorbent and delivery system for ciprofloxacin drug

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Abstract: Magnetic mesoporous materials covered with mesoporous silica shells ($\text{Fe}_3\text{O}_4@\text{mSiO}_2$) are the most promising material, which is fulfilling many applications especially for adsorption and delivering drugs system. The present research involves the preparation of magnetic nanoparticles Fe_3O_4 and mesoporous silica mSiO_2 as core-shell materials using sol-gel method in the presence of amid propyl betaine surfactant as template. The surface texture, morphology and particle and crystalline size of the prepared adsorbent were characterized using SEM, TEM, XRD, and nitrogen adsorption-desorption techniques. The results show that the prepared adsorbent has surface area equal to $1670 \text{ m}^2/\text{g}$, mesopores in range 2-10 nm with a high degree of ordering of the porous structure and has a crystalline size equal to 30.16 nm. The adsorption behavior of Ciprofloxacin drug from aqueous systems onto the adsorbent has been studied using a batch experiments method. The equilibrium of the process at temperature 293K was achieved within 120 min and 0.06 g of adsorbent dose. Adsorption isotherms were fitted with the Langmuir, Freundlich, Temkin, and Dubinin –Radushkevich models and the results show the Langmuir and Temkin model was best fitted, and the adsorption process is physical adsorption type. The kinetic data were analyzed and found to match well with pseudo-second order kinetic model. Ciprofloxacin drug loading and capacity of release of the $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ carrier was also studied.

Keywords: Adsorption Isotherm, Ciprofloxacin, $\text{Fe}_3\text{O}_4@\text{mSiO}_2$, Drug Delivery, Mesoporous Silica

1. Introduction

Mesoporous materials with large surface area and porosity have been extensively studied because of their broad applications in many areas, such as catalysis, sensors, controlled-release delivery system, and separation¹⁻⁶. Magnetite Mesoporous materials enveloped with meso-silica shells ($\text{Fe}_3\text{O}_4@\text{mSiO}_2$) are seen to be the most attractive material, fulfilling most of the above applications especially in adsorption and delivering drugs system. Zhu Y and coworkers⁷ prepared hollow $\text{Fe}_3\text{O}_4@\text{SiO}_2$ which has spheres particles of size about 900 nm and has high loading and drug-releasing capacity for aspirin medicine. Xu et al.⁸ progressed $\text{Fe}_3\text{O}_4@ \text{mSiO}_2 @ \text{mSiO}_2$ composite nanoparticles which have average particle size of about 400 nm and excellent release percentage for ibuprofen drug. Sol-gel and hydrothermal techniques are performed to prepare magnetite core – mSiO_2 shell nanoparticles of different shell thicknesses⁹. After characterization of the nanostructures using different techniques, the loading and then releasing capacity of the prepared materials were estimated by ibuprofen drug as a model.

Functionalized magnetic mesoporous silica material was synthesized and determining its efficiency in copper removal from aqueous solutions was investigated¹⁰. These materials were characterized by X-ray diffraction, TEM, SEM, N_2 adsorption-desorption (BET and BJH), and FT-IR. The experimental data were fitted by the Langmuir and Freundlich models of adsorption. Mesoporous Core-shell



$\text{Fe}_3\text{O}_4@\text{mSiO}_2$ nanoparticles have been prepared by sol-gel method with surface active agent as template and applied as additive in a carbonyl iron -based magnetorheological to improve the stability¹¹

The current study aims to prepare magnetic Fe_3O_4 as core and mesoporous silica mSiO_2 as shell materials ($\text{Fe}_3\text{O}_4@\text{mSiO}_2$) using sol-gel method in the presence of Cocamidopropyl betaine surfactant as template. The properties of the synthesized adsorbent were characterized through TEM, SEM, XRD, and N_2 adsorption-desorption (BET and BJH) methods. After characterization, the adsorption behavior of Ciprofloxacin drug from aqueous systems onto the adsorbent has been studied using batch experiments method. The loading and then releasing capacity of the $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ adsorbent have been estimated by ibuprofen drug as a model.

2. Experimental

2.1. Chemicals

Sodium silicate (14% NaOH, 27% SiO_2) as silica precursor and Cocamidopropyl betaine (CABP) as template were obtained from the state company of vegetable oils – Iraq. Ciprofloxacin (CIP), as an antibiotic, molar mass 331.346 g/mol, $\lambda_{\text{max}} = 277\text{nm}$ in aqueous solution, is purchased from DSM with purity 98%. Its structure is as in Figure 1.

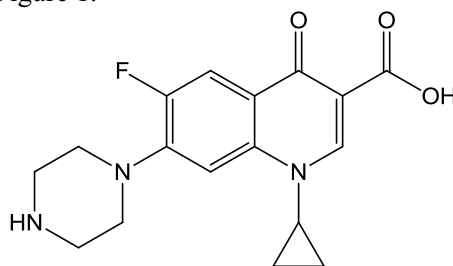


Figure 1. Chemical structure of Ciprofloxacin drug.

2.2. Characterization

Scanning electron microscopy (SEM; Oxford instruments model SEM: S-3200N) and transmission electron microscopy (TEM, Philips model: CM120) have been used to analyze the size and morphology of the prepared materials. BET surface area and BJH porosity of the samples and their N_2 adsorption-desorption isotherms at 77 K were determined using Autosorb-1 Quantachrome Instrument (Quantachrome Instruments, Boynton Beach, FL, USA). The X-ray diffraction (XRD) patterns were obtained with a Rigaku diffractometer using $\text{Cu K}\alpha$ ($\lambda = 0.154\text{ nm}$) radiation.

2.3. Preparation of Adsorbent

2.3.1 Preparation of magnetite Fe_3O_4

Magnetic Fe₃O₄ was prepared according to previously reported procedure¹². 0.9g of urea (BDH : England : 99%) was dissolved in 60 mL of mixed solvent(2:58 mL of water and ethylene glycol) (HIMEDIA; 99%) and 0.54g of FeCl₃.6H₂O (HIMEDIA: 98%) was added with stirring at 40 °C until totally dissolved. The mixture was poured into 100 mL Teflon –line autoclave, heated to 200 °C and preserves for 24h. After cooling the mixture was centrifuged, separated, washed, and dried at 80 °C for 6 h in an oven.

2.3.2. Preparation of Fe₃O₄@mSiO₂

10 mg of Fe₃O₄ were dispersed in 50mL of ethanol under ultrasonic agitation. The Fe₃O₄ was separated and mixed with 12 g of CABP surfactant, 17mL H₂SO₄ (1M), and 150 mL water. 3.5g of sodium silicate solution dissolved in 150 mL distilled water was added to the mixture drop by drop from burette for 3h. The solution was aged in room temperature for one day, then the precipitate formed was recovered by filtration and washed with distilled water. The precipitate was dried at 80°C for 2h and calcined at 600°C for 5h.

2.4. Adsorption Procedure

The adsorption isotherm was performed using 100 mL of aqueous solution, which have different CIP concentration (2, 8, 14, 20, 26, 32, 38, 44, 50 mg/L), with 0.06 g of Fe₃O₄@mSiO₂ adsorbent. The CIP-Fe₃O₄@mSiO₂ mixture system was shaken well for 120 min to reach equilibrium. Then, 2ml has been pipetted and placed in the centrifuge for 15 minutes; the concentrations of the CIP solution before and after the adsorption are determined by measuring UV-Vis absorption value at λ_{max} 277 nm. The amount of CIP adsorbed was determined by the equation:

$$q_e = \frac{(C_0 - C_e) v}{w} \quad (1)$$

Where q_e is the equilibrium adsorption capacity of CIP adsorbed on unit mass of the adsorbent (mg /g), C_0 is the primary CIP concentration (mg L⁻¹) and C_e is concentration at equilibrium, v is the CIP solution volume (L) and W (g) is adsorbent weight. R % (removal percentage) was determined according to the equation:

$$R\% = \frac{(C_0 - C_e) \times 100}{C_0} \quad (2)$$

2.5. Drug Loading

The CIP loading capacity of the prepared Fe₃O₄@mSiO₂ was performed using a modified procedure reported in reference¹³; about 30 mg of the Fe₃O₄@m-SiO₂ sample was poured into vessel contains 5 mL of 100 mg/mL CIP drug solution with stirring for 24 h. Then, the precipitate was isolated by centrifuge for 15 min and dried at 60 °C for 24 h in an oven.

2.6. In Vitro Drug-Release

The prepared CIP – $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ samples were immersed in 100 mL of water or phosphate Buffered Saline (PBS, pH = 7.4) with stirring at 37.5 °C. 1 mL of aliquot at intervals time were removed from the solution, the amount of CIP released was estimated by the UV–Vis absorption spectra of the aliquots.

3. Results and Discussion

3.1. Adsorbent Characterization

The XRD patterns of the prepared magnetic mesoporous Fe_3O_4 core and mSiO_2 shell are shown in Figure 2. The Fe_3O_4 nanoparticles indicated peaks with 2θ at 18.19, 30.25, 34.12, 35.61, 43.25, 53.42, 57.15 and 62.76 are quite identical to those of pure magnetite (JCPDS No. 19-692)¹⁴. The presence of a broad peak at $2\theta = 20\text{--}28$ in the $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ spectrum confirms formation of silica layer without changing in the crystalline structure of the Fe_3O_4 ¹⁵. Using the data obtained (Table 1) and Scherer equation ($D = 0.9 \lambda / B \cos \theta$), where λ is wavelength of x-ray (Å), B is (Full width half-maximum) FWHM (radian) and θ is the corresponding Bragg diffraction, the calculated crystalline size are 30.66 nm and 29.61 nm for Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ respectively.

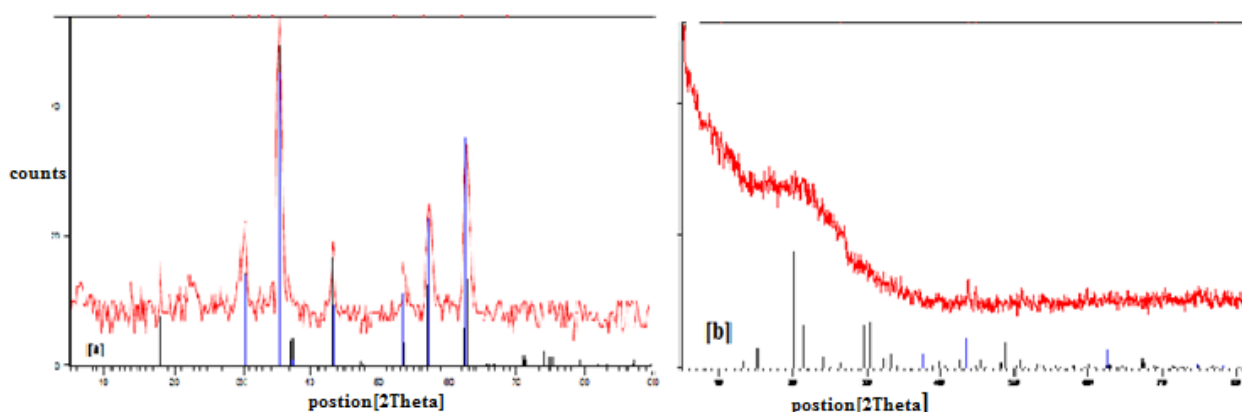


Figure 2. The x-ray diffraction patterns of a) Fe_3O_4 and b) $\text{Fe}_3\text{O}_4@\text{mSiO}_2$.

Table 1. The analysis of XRD spectrum of the Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{mSiO}_2$.

Sample Peak	No.1	2θ	$d(\text{\AA})$	FWHM (deg)	Intensity (counts)	$D = 0.9 \lambda / B \cos \theta$
Fe_3O_4	1	35.6	2.521	0.275	100	30.66
$\text{Fe}_3\text{O}_4@\text{mSiO}_2$	1	43.654	2.07	0.295	100	29.61

The TEM and SEM images of the Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ nanoparticles are shown in Figure 3. The average particle sizes of Fe_3O_4 are observed to be in the range of nanometer (10-20 nm) and $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ has porous morphology. On the other hand, TEM showed agglomeration of many ultrafine spherical-like particles which display dark magnetite cores surrounded by a mesoporous shell with a narrow distribution of particle size about 20 nm.

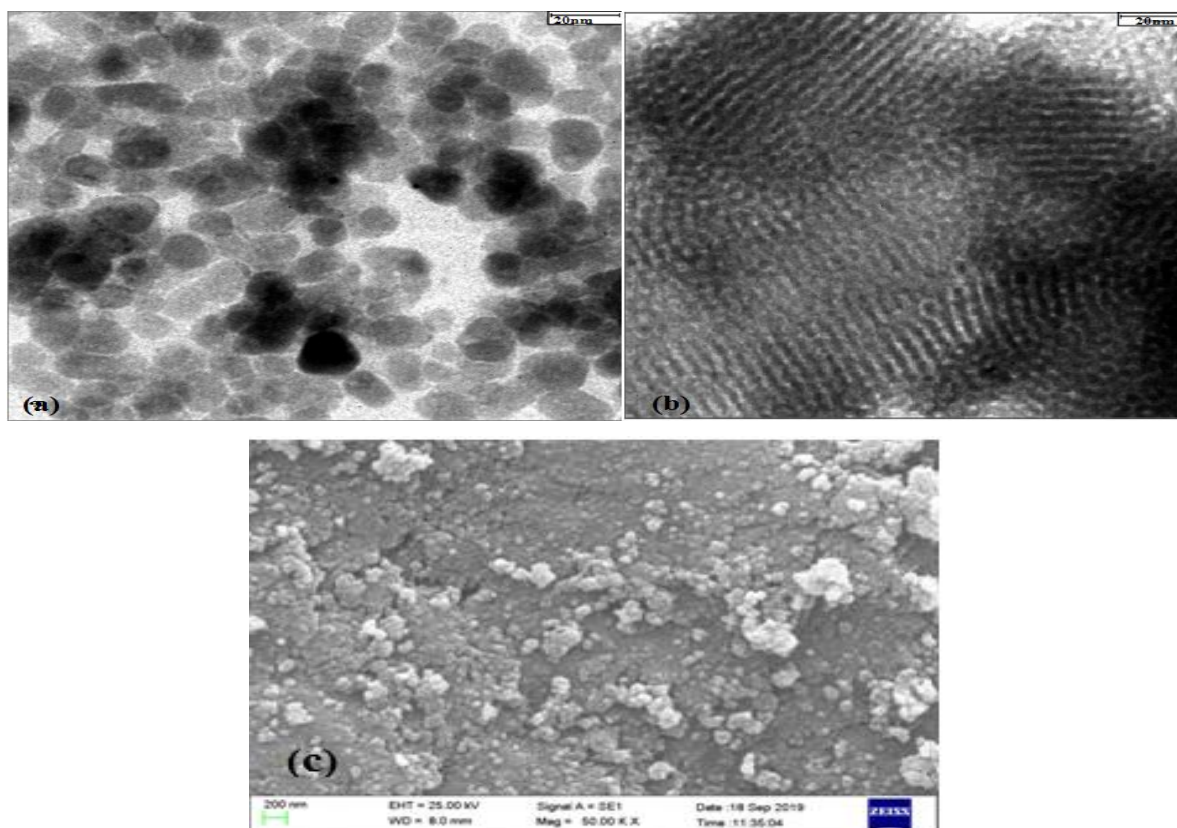


Figure 3. TEM images of (a) Fe_3O_4 nanoparticles and (b) $\text{Fe}_3\text{O}_4@\text{mSiO}_2$. (c) SEM image of $\text{Fe}_3\text{O}_4@\text{mSiO}_2$

Nitrogen adsorption-desorption isotherms, pore volume distribution, BET surface area, the average pore sizes (d_{BJH}) and pore volume of the synthesized Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ assessed from N_2 adsorption isotherm at -196°C are presented in Figures 4 and 5 and Table 2.

Table 2. The texture properties of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{mSiO}_2$.

Sample	SBET (m^2/g)	Pore Volume (cc/g)	BJH (nm)
Fe_3O_4	54.14	0.226	15.325
$\text{Fe}_3\text{O}_4@\text{mSiO}_2$	1670	0.886	2.886

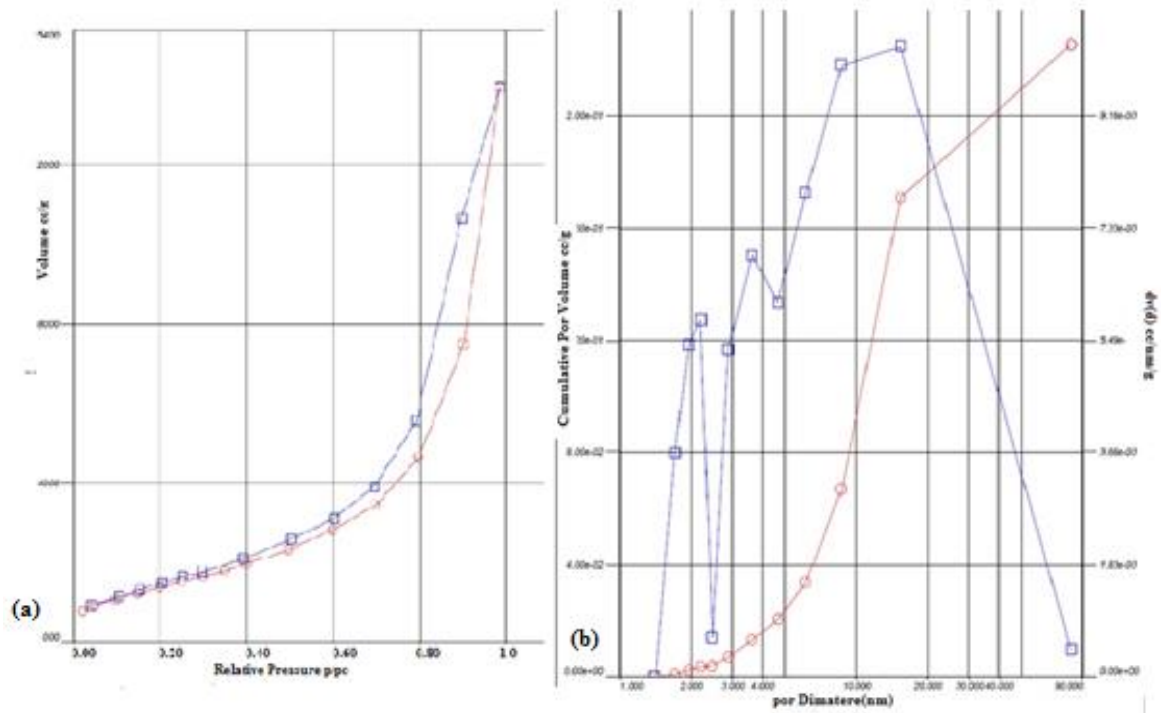


Figure 4. a) N₂ adsorption-desorption isotherm and b) pore size distribution of Fe₃O₄.

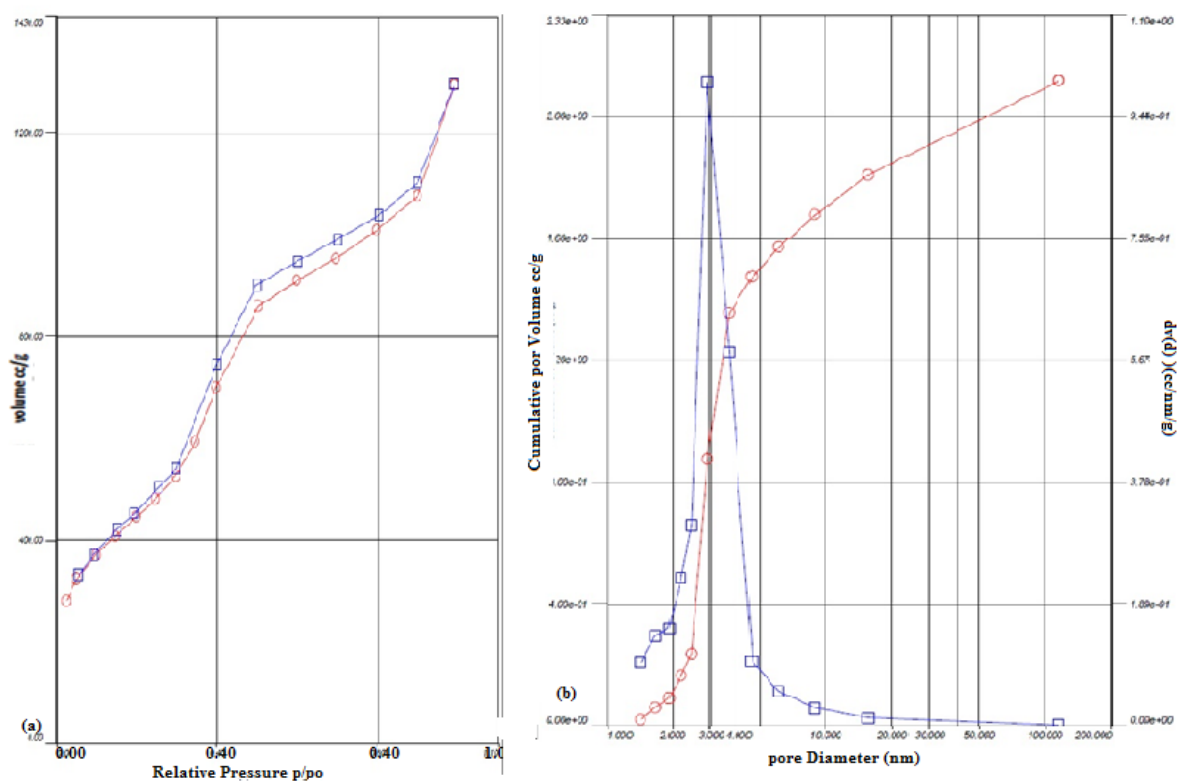


Figure 5. a) N₂ adsorption-desorption isotherm and b) pore size distribution of Fe₃O₄@mSiO₂.

The illustrated isotherms for the two samples were Type IV which indicates the formation of mesopores with ordered pore structure for Fe₃O₄@mSiO₂ sample. The hysteresis loops were type H1 and H4 for Fe₃O₄ and Fe₃O₄@mSiO₂ respectively which indicate that the cylindrical and slit-like type mesopores were present respectively. According to the BJH method calculation of the desorption branch of N₂ isotherm, the average mesopore sizes (d_{BJH}) of Fe₃O₄ and Fe₃O₄@mSiO₂ were 15.325 and 2.886 nm respectively.

3.2. Adsorption study

3.2.1. Contact time and adsorbent quantity effect

The effects of contact time and adsorbent quantity on the CIP adsorption on Fe₃O₄@mSiO₂ adsorbent are studied for CIP solutions in which the concentration was 20 mg L⁻¹. We observed the adsorption of a satisfactory amount of CIP adsorbate after 120 min (Fig. 6). From figure 6, one can see that R % of the CIP drug increase when the adsorbent dose increased. This may be due to the conglomeration of the adsorbent and the availability of surface active sites resulting from the increased dose¹⁶. This increase is found to be meager after 0.06 g dose. Therefore, this value (0.06 g adsorbent) is fixed as optimum dose of adsorbent for further studies.

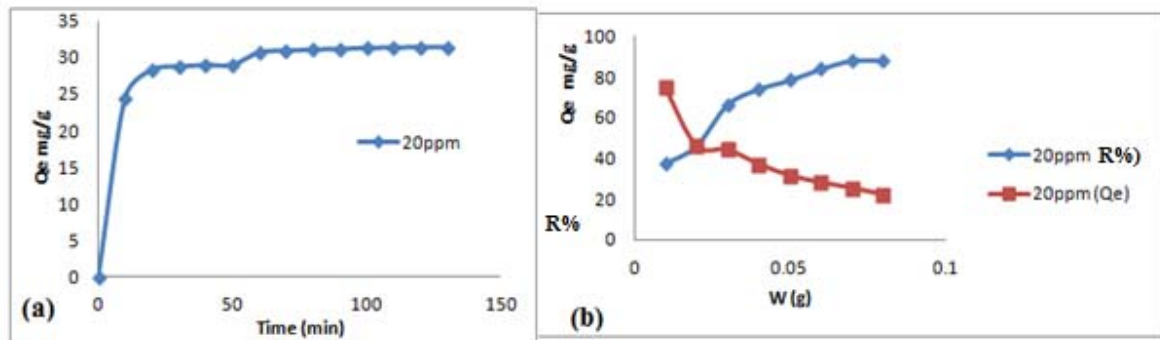


Figure 6. Relationships of (a) Q_e with contact time (b) Q_e and $R\%$ with quantity of adsorbent (W), for the adsorption CIP drug at 298 K.

3.2.2. Adsorption Isotherm

Four adsorption models Langmuir (Equation 3), Freundlich (Equation 4), Temkin (Equation 5) and Dubinin- Radushkevich (Equation 6) isotherms were plotted (Figure 7) by using standard straight line equation and corresponding parameters for adsorption were calculated from their respective graphs.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

$$q_e = K_f (C_e)^{1/n} \quad (4)$$

$$q_e = (B \ln K_t + B \ln C_e) \quad (5)$$

$$\ln q_e = (\ln q_m - \beta \epsilon^2) \quad (6)$$

K_L , q_m , K_f , $1/n$, B , K_t , β , and ϵ are the constants related to Langmuir adsorption equilibrium constant, the maximum adsorption, adsorption capacity and adsorption intensity, constant of Temkin where $B = RT / b$ and b is an equilibrium constant, β is related to mean sorption energy E (J/mol) through the equation: $E = (-2 \beta)^{-0.5}$, and ϵ is the Polanyi potential described as: $\epsilon = RT \ln (1 + 1/C_e)$. The parameters values obtained are listed in Table (3).

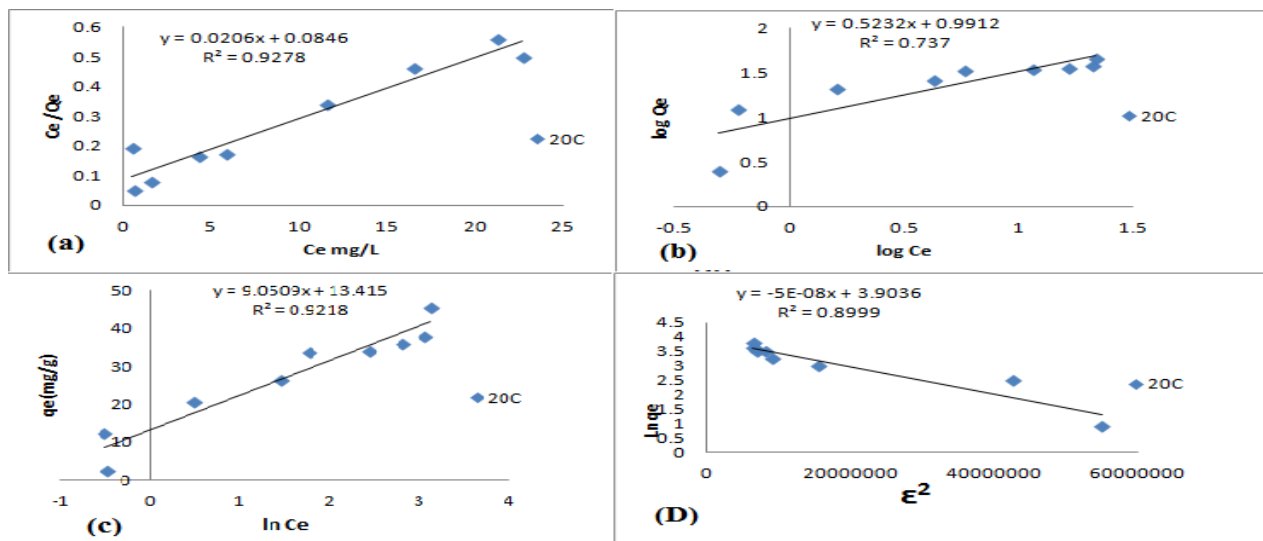


Figure 7. The linear plots of: a) Langmuir, b) Freundlich, c) Temkin, d) Dubinin- Radushkevich models.

Table 3. The parameters obtained of the four isotherms for CIP adsorption $\text{Fe}_3\text{O}_4@\text{mSiO}_2$.

Langmuir	q_m (mg/g)	K_L (mg/l) ⁻¹	R_L	R^2
	48.5	0.243	0.191	0.927
Freundlich	n	K_f (L. g ⁻¹)		R^2
	1.912	0.991		0.794
Temkin,	B (L/mg)	K_T (J/mol)		R^2
	9.05	4.40		0.921
Dubinin – Radushkevich	B (mol ² J ⁻²)	q_m (mg/g)	E (kJ/mol)	R^2
	-5×10^{-8}	49.55	3.166	0.899

It is evident from comparing R^2 values obtained from Langmuir, Freundlich and Temkin plots that the experimental data are the best fit with Langmuir and Temkin isotherms. (R_L) was additionally determined using equation: $R_L = 1 / (1 + K_L C_0)$, R_L value obtained is 0.191 which shows that $0 < R_L < 1$, so adsorption occurs normally and it is a favorable adsorption at 298 K. Furthermore, large K_F value (0.991) indicated that the magnetic nano-adsorbent had high adsorption capacity for CIP [10]. The value of the Freundlich constant $n = 1.912$, n ($1 < n < 10$) is an indication that $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ has a high affinity for CIP molecules. The obtained E value for the adsorption reveals that the adsorption process was physical adsorption since the value is less than 8 kJmol^{-1} [17].

Table 4. Kinetic parameters for adsorption of CIP drug on $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ at 298K

q_e (exp.)	pseudo-first -order			pseudo-second -order			intrapartical diffusion		
	q_e calc (mg/g)	K_1 (min ⁻¹)	R^2	q_e (calc.)	K_2 (mg min ⁻¹)	H (mg g ⁻¹ min ⁻¹)	R^2	K_D (mg g ⁻¹ min ⁻²)	R^2
32.702	11.212	0.0433	0.962	32.46	0.0139	76.54	0.9992	0.553	0.851

3.2.3. Adsorption Kinetic

The adsorption kinetic behavior of 20 mg/L drug onto $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ at 298K is studied by applying three of the most widely used kinetic models: Lagergren pseudo- first order equation (equation 7), pseudo-second order equation (equation 8), and intraparticle diffusion equation (equation 9) and the results obtained are given in Table 4 and illustrated in figure 8.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

$$q_t = K_D t^{1/2} + c \quad (9)$$

Where q_e is the adsorption capacity (mg g⁻¹) at equilibrium and q_t at time t , k_1 is the rate constant for pseudo-first order model (min⁻¹), k_2 is the rate constant for the pseudo- second order model (mg min⁻¹). Herein, the initial adsorption rate $h = k_2 q_e^2$, K_D is rate constant of intrapartical diffusion (mg g⁻¹ min^{-1/2}), and C is the intercept. The constants q_e , k_1 , k_2 and K_D are calculated using the values of slopes and intercepts of linear plots of the three equations (Figure. 8) in addition to h value are listed in Table 4.

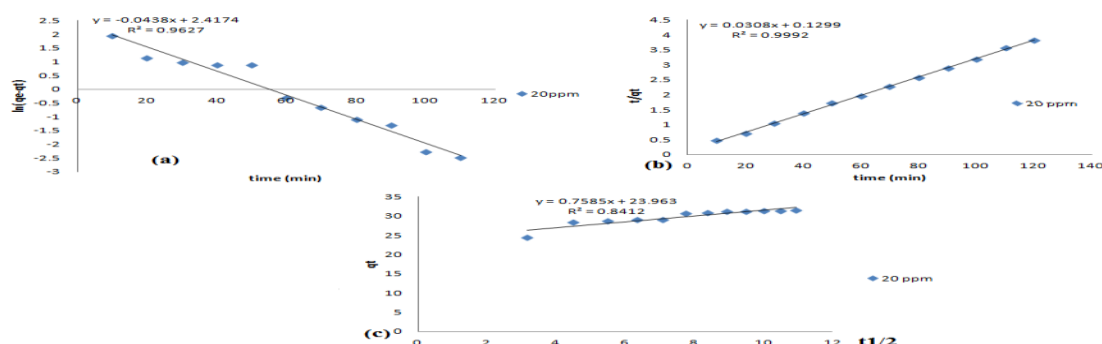


Figure 8. The linear plots of three kinetics models: a) the pseudo-first order b) the pseudo-second order c) the intraparticle diffusion.

From the correlation coefficient (R^2) values presented in Table 4, it can be seen that the adsorption obeys pseudo-second order model. It can also be seen from the plot of intra-particle diffusion model that the straight line at extrapolation did not reach to the origin which indicates that the intraparticle diffusion step is not the sole rate-controlling step but some other steps play an important role^{18, 19}.

3.2.4. Loading and release study

The amount of drug loaded in magnetite samples has been determined using the following equation¹³.

$$\text{Loading (mg drug/mg sample)} = \frac{m(\text{cip. orig}) - m(\text{cip. solution})}{m(\text{sample})} \quad (10)$$

Where $m_{\text{cip orig}}$ is weight of CIP in the 5ml of solution and $m_{\text{cip solution}}$ is weight of CIP in the solution after impregnation and m_{sample} is the weight of the $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ sample. The calculated amount of CIP loaded in the samples was 15.66 mg drug/mg sample. This capacity of loading for our adsorbent is comparable to the capacity of other adsorbents- drug reported by references¹³ and ²⁰. Figure 9 shows the release profiles of the Ciprofloxacin loaded $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ sample up to 90 minutes in water and PBS solution. Ciprofloxacin amount released in the water and PBS solution was determined using absorption spectra. As can be seen, after 80 min, about 79 and 99.8% of Ciprofloxacin drug were released from the $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ sample in water and PBS solution respectively. Also one can see that the release rate is fast for the first 60 min which indicates that the drug adsorbed at the porous external surface of the adsorbent is released initially. The drug adsorbed inside the mesopores is released slowly which may be due to the strong capillary force⁹.

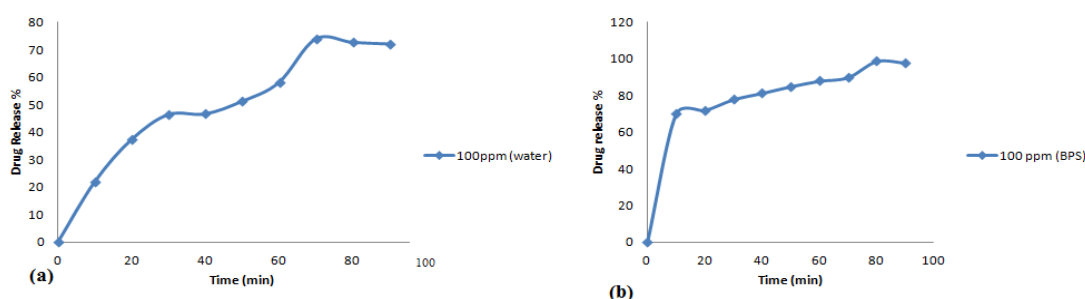


Figure 9. The release profile of CIP loaded $\text{Fe}_3\text{O}_4@\text{mSiO}_2$ in (a) water, (b) BPS at 37 °C.

4. Conclusions

The foregoing results of this study confirm the synthesis of mesoporous Fe₃O₄@m-SiO₂ core-shell type which has surface area of 1670 m²/g and 2.886 nm of pore size. The one gram prepared sample can load 15.66 mg from Ciprofloxacin drug. Fe₃O₄/mSiO₂ nanoparticle was used for the adsorptive removal of Ciprofloxacin drug from aqueous solutions and shows 99.8 % release of the loaded drug in BPS solution. The equilibrium data of CIP-Fe₃O₄@m-SiO₂ adsorption system demonstrated good compatibility with Langmuir and Temkin models. The kinetic pseudo-second order model is the best model.

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