One step synthesis of Mn doped Fe$_2$O$_3$/GO core shell nanocomposite and its application for adsorption of levofloxacin in aqueous solution

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Supplementary information

1.1 Instrumentation

Brunauer Emmett Teller (BET) measurements were carried out with a Micromeritics ASAP 2460 surface area and porosity analyser. Prior to the analysis, the synthesized materials were degassed with nitrogen gas at 90 °C for 12 hours. All the measurements were taken at -195.8 °C and the pore volume and the pore sizes were calculated from the adsorption curves using the BJH model. The UV-vis spectra of the synthesized adsorbents were recorded using a Shimadzu UV1800 spectrophotometer (RF-5301PC, Shimadzu, Kyto, Japan), connected with a light source of 150W Xenon lamp.

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The powder X-ray diffraction (P-XRD) measurements of the GO, MnFe$_2$O$_3$ core shell and MnFe$_2$O$_3$/GO core shell nanocomposites were acquired by using PANalytical X’Pert Pro powder diffractometer instrument (PANalytical, Almelo, Netherlands). The instrument was equipped with 1D X’Celerator detector (PHD lower level and upper level of 6.67 and 12.78 keV, respectively) and programmable divergence slit (10 mm radiation length). The P-XRD synthesized samples were grinded using pestle and mortar and transferred onto the low background silicon sample holder. The measurements were conducted in the $2\theta$ range from 5 to 90° with Cu Kα radiation ($\lambda=0.15405$ nm) at 40 kV and 40 mA working conditions. The diffractometer configuration was sample spinner (Spinner PW3064) with a rotation time of 1s (to get the preferred orientation of crystallites). Scan axis was Gonio with continuous scan type, 0.0170° 20 step size and 87 s scan step time. The P-XRD patterns were predicted by using High Score (Plus) software and ICDD PDF-4+ 2015.

Transmission electron microscopic (TEM) analyses were carried out at an acceleration voltage of 200 kV by using a Jeol JEM-2100F TEM machine (JOEL Ltd., Tokyo, Japan) equipped with a LaB6 source. The TEM samples were prepared by individually dropping small amount of synthesized material onto a TEM grid (200 mesh size Cu-grid) coated with a lacy carbon film. The images of the composites were acquired using a digital charge coupled device (CCD) camera connected to the transmission electron microscope.

The Scanning electron microscope (SEM) measurements were performed using a Tescan Vega 3 LMH (Tescan, Brno, Czech Republic), operated at 20 kV accelerating voltage, using secondary electron detector (SE) and equipped with energy dispersive spectroscopy (EDS). The materials were initially carbon-coated with the Agar Turbo Carbon coater to improve their conductivity.

X-ray photoelectron spectroscopy (XPS) measurements were investigated with a Thermo Fisher Scientific Spectroscope, model ESCAlab 250 Xi (Thermo Fisher Scientific, Waltham, USA) using a monochromator Al Kα (1486.7 eV) as an excitation source at a working pressure of < 10$^{-8}$ mBar. Fourier transformed infrared (FTIR) spectra were measured by using a Bruker Tensor 27 FTIR spectrophotometer (Bruker Optics, GmbH, Germany) with the KBr wafer system. The synthesized materials were mixed with KBr and compressed to pellet. Throughout the analysis the data was recorded from 400 to 4000 cm$^{-1}$ range.
1.2 Data analysis (equations)

The percentage removal (%RE) and adsorption capacity were calculated by using equations (S1) and (S2), respectively:

\[
\%RE = \left( \frac{C_0 - C_e}{C_0} \right) \times 100\% 
\]

(S1)

Where \( C_0 \) and \( C_e \) (mg L\(^{-1}\)) are the initial and equilibrium lev concentrations

\[
q_t = \frac{(C_0 - C_e)V}{m} 
\]

(S2)

Where \( C_0 \) and \( C_t \) (mg L\(^{-1}\)) are the initial lev concentration and lev concentration at time, \( t \), respectively, \( V \) (L) is the solvent volume, and \( m \) (g) is the mass of the adsorbent.

\[
q_e = \frac{(C_0 - C_e)V}{m} 
\]

(S3)

Where \( C_0 \) and \( C_e \) (mg L\(^{-1}\)) are the initial lev concentrations and equilibrium lev concentration, respectively, \( V \) (L) is the solvent volume, and \( m \) (g) is the mass of the adsorbent.

The achieved adsorption kinetics data were fitted to the pseudo first order and second order models by the following equations:

**Pseudo first order model:**

\[
\ln(q_e - q_t) = \ln q_e - k_1 t 
\]

(S4)

**Pseudo second order model:**

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} 
\]

(S5)

Where \( q_e \) and \( q_t \) (mg g\(^{-1}\)) are the amounts of Lev adsorbed per mass of adsorbent (g) at time \( t \) (min) and at equilibrium, respectively, \( k_1 \) (1/min) and \( k_2 \) (mg/ (g.min)) are the equilibrium rate constants of the pseudo first order and second order models, respectively.

The initial adsorption rate (\( h \)) can be attained from the \( 2^{nd} \) order rate constant as follows:

\[
h = k_2 q_e^2 
\]

(S6)

The intraparticle diffusion model was defined by the following equation:

\[
q_t = k_{i/2}^{1/2} + C 
\]

(S7)
Where \( C (\text{mg g}^{-1}) \) is a constant representing the boundary layer effects and \( k_{i} (\text{mg g}^{-1} \text{min}^{1/2}) \) is the intraparticle diffusion rate constant, which can be calculated from the slope of the linear plots of \( q_{t} \ vs \ t^{1/2} \).

The adsorption isotherms were studied to fit the experimental data at different temperatures using Langmuir, Redlich-Peterson, Freundlich, Sips, Dubinin-Radushkevich and Temkin models.

Langmuir adsorption isotherm equation:

\[
\frac{C_{e}}{q_{e}} = \frac{C_{e}}{q_{\text{max}}} + \frac{1}{K_{L}q_{\text{max}}} \tag{S8}
\]

Freundlich adsorption isotherm model:

\[
\ln q_{e} = \ln K_{F} + \frac{1}{n} \ln C_{e} \tag{S9}
\]

Redlich-Peterson isotherm model:

\[
\ln \left( \frac{K_{R}C_{e}}{q_{e} - 1} \right) = \beta \ln(C_{e}) + \ln(\alpha R) \tag{S10}
\]

Sips model:

\[
\frac{1}{q_{e}} = \frac{1}{Q_{\text{max}}K_{s}} \left( \frac{1}{C_{e}} \right)^{1/n} + \frac{1}{Q_{\text{max}}} \tag{S11}
\]

Dubinin-Radushkevich model:

\[
\ln q_{e} = \ln q_{DR} - \beta e^{2} \tag{S12}
\]

Temkin model:

\[
q_{e} = B_{1} \ln K_{T} + B_{1} \ln C_{e} \tag{S13}
\]

Where \( C_{e} \) and \( q_{e} \) have the common meaning as previously stated\(^{34} \), \( q_{\text{m}} (\text{mg g}^{-1}) \) is the maximum adsorption capacity, \( K_{L} \) (L mg\(^{-1}\)) is the Langmuir constant defined adsorption attraction for the adsorbent, \( K_{F} (\text{mg g}^{-1}) \) (L mg\(^{-1}\)) \( 1/n \) is the Freundlich constant correlated to the multilayer adsorption capacity, \( n \) is the heterogeneity factor, which characterizes the extent to which the adsorption depends on the equilibrium concentration and \( K_{R} \), \( \alpha R \) and \( \beta \) \( (0 < \beta < 1) \) are three Redlich-Peterson constants. Where \( K_{s} \) is the sips equilibrium constant \((1/\text{mg})\), \( Q_{\text{max}} \) represents the
maximum adsorption capacity (mg g\(^{-1}\)) and \(n\) defines the surface heterogeneity. The \(q_e\) is the amount of Lev adsorbed onto per unit amount of MnFe\(_2\)O\(_3\)/GO core shell nanocomposite (mol g\(^{-1}\)), \(q_{\text{dor}}\) is the theoretical monolayer sorption capacity (mol g\(^{-1}\)), \(\beta\) is the constant of the sorption energy (mol\(^2\) J\(^{-2}\)) and \(\varepsilon\) is the Polanyi potential, \(\varepsilon = RT\ln\left(1 + \frac{1}{Ce}\right)\), where \(R\) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \(T\) is the reaction temperature (K). Where \(B = RT/\beta\), \(\beta\) is the Temkin constant related to heat of sorption (J mol\(^{-1}\)), \(A\) is the Temkin isotherm constant (L g\(^{-1}\)).

The thermodynamics parameters are described by the following equations:

\[
\ln K_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (S14)
\]

\[
\Delta G = \Delta H - T\Delta S \quad (S15)
\]

Where \(K_d\) is a distribution constant, which is calculated from \(\frac{q_e}{Ce}\), \(R\) is a universal constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \(T\) (K) is the adsorption temperature.
Figure S1: Pareto chart of standardized effects on variables for the adsorptive removal of Lev.
Figure S2: Zeta potential measurements vs. pH of Mn doped Fe$_2$O$_3$/GO core shell nanocomposite.

Figure S3: Desirability functions for optimization of independent variables.
Figure S4: Effect of contact time on adsorption of Lev. Experimental conditions: sample pH (7), contact time (10 to 40 min) and MnFe$_2$O$_3$/GO core shell nanocomposite dosage (0.007g).
Figure S5: Pseudo-1\textsuperscript{st}-order: Experimental conditions: sample pH (7), contact time (10 to 40 min) and MnFe$_2$O$_3$/GO core shell nanocomposite dosage (0.007g).
Figure S6: Pseudo-2\textsuperscript{nd}-order. Experimental conditions: sample pH (7), contact time (10 to 40 min) and MnFe\textsubscript{2}O\textsubscript{3}/GO core shell nanocomposite dosage (0.007g).
Figure S7: Intraparticle diffusion at (A) 10 ppm, (B) 20 ppm and (C) 30 ppm. Experimental conditions: sample pH (7), contact time (10 to 40 min) and MnFe$_2$O$_3$/GO core shell nanocomposite dosage (0.007g).
Figure S8: Thermodynamics for Lev adsorption onto MnFe$_2$O$_3$/GO core shell nanocomposite