Adsorption performance of magnesium/aluminum layered double hydroxide nanoparticles for metronidazole from aqueous solution

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Abstract Magnesium/aluminum layered double hydroxide (LDH) nanoparticles were synthesized by hydrolyzing urea and used to remove metronidazole (MN) from aqueous solution. The surface morphology images of the LDH nanoparticles showed that the adsorbent surface consisted of hexagonal nanosheets with a diameter of 200–1000 nm. The MN removal efficiency was strongly dependent on the solution pH ranging from 3 to 9. The addition of nitrate, sulfate, and carbonate did not remarkably affect MN adsorption, while hardness slightly improved MN removal efficiency. The adsorption isotherm data could be well described using the Sips equation. The analysis of kinetic data showed that the adsorption of MN onto LDH closely followed the Avrami model and that several kinetic processes may control the rate of sorption. The adsorption process was non-spontaneous and exothermic in nature. The maximum Langmuir adsorption capacity was 62.804 mg/g, demonstrating that LDH is an efficient adsorbent that can be used for the removal of MN compounds.

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1. Introduction
Nowadays, antibiotics are among the most important pharmaceuticals, mainly used in human and veterinary medicine to prevent and cure bacterial infections. Antibiotics can enter into different environmental sections as parent compounds or metabolites, mainly due to excretion, improper disposal of expired drugs, or surplus medications. In general, these materials reach waterways through the discharge of wastewaters and effluents, which are often not properly treated. As a result, various
antibiotics and their metabolites have been detected in the surface and groundwater (Lindberg et al., 2004; Hirsch et al., 1999; Giger et al., 2003). Among the antibiotics, metronidazole (MN) is widely used to treat intestinal and intra-abdominal infections caused by anaerobic and protozoan bacteria (Çahyan and Göktürk, 2010; Tally and Sullivan, 1981; Lau et al., 1992). Besides its use as an antibiotic in humans, MN is also employed in veterinary medicine as an additive in poultry and fish feed, leading to their accumulation in animals and wastewater from fish farms and, especially, meat industries (Kümmener, 2001).

Many antibiotics are not completely removed by conventional wastewater treatments and can be released into the aquatic environment. There is considerable evidence of the risks related to their presence in surface water resources and their potential to cause antibiotic resistance among bacteria, thus leading to untreatable human diseases (Cunningham et al., 2006; Gobel et al., 2005). Moreover, the presence of antibiotics in raw wastewater treatment plants may produce unwanted by-products during chlorination or ozonation of wastewater, which may be toxic and carcinogenic to humans (Zhou et al., 2013; Le-Minh et al., 2010). Hence, various treatment technologies that are being developed should be properly tested to avoid such hazardous contamination (Dantas, 2008).

Among the many treatment technologies, adsorption has attracted significant attention for antibiotic removal from aqueous solutions, owing to its advantages of being technically simple, excellent regeneration potential, and sludge-free operation properties (Ranjan et al., 2009; Sulaymon et al., 2013). Recently, layered double hydroxides (LDH) have been reported to have potential application in medicine as matrices when intercalated with organic anions of pharmaceutical interest (Tronto et al., 2004; Guo et al., 2011, 2008).

LDH, also known as anionic clays, are nano-sized particles that can be synthesized in the laboratory via simple and economic methods. They possess unique properties such as large surface areas, high porosity, high anion exchange capacities (2–3 meq/g), and substantial thermal stability, which favor their use in water and wastewater treatments (Kameda et al., 2015). Furthermore, LDH have brucite-like structure and a general formula of \([\text{M}_2^{2+}\text{M}_3^{3+}] (\text{OH})_2\text{O}\), where \(\text{M}^{2+}\) and \(\text{M}^{3+}\) are divalent and trivalent cations, respectively, which occupy octahedral positions in the hydroxide layer with excessive positive charges; \(\text{A}^{x-}\) is the charge compensating anion; and \(m\) and \(n\) are the numbers of moles of co-intercalated water and \(\text{M}^{2+}\) per formula weight of the compound, respectively (Wimonsong et al., 2014). The excessive positive charge in the LDH is formed by the replacement of divalent cations (\(\text{M}^{2+}\)) with trivalent cations (\(\text{M}^{3+}\)), and is balanced by the anions (\(\text{A}^{x-}\)) in the interlayer. These cations can be exchanged with other anions, leading to higher anion exchange capacity, which is a unique property of LDH (Lin et al., 2014; Kameda et al., 2014). Although LDH is well known as an active adsorbent, the effects of different environmental parameters on the MN removal efficiency have not been adequately explored. With this background, the present study focused on the synthesis of LDH nanoparticles for the adsorption of MN. The objectives of this study were to investigate the adsorption equilibrium, kinetics, and thermodynamics of MN on LDH nanoparticles and to study the removal of MN from aqueous solution using LDH under different experimental conditions, including pH, shaking time, initial MN concentration, and competing ions.

2. Materials and methods

2.1. Chemicals

The stock MN solution (100 mg/L) was prepared by dissolving appropriate amount of powdered MN (chemical formula, \(\text{C}_6\text{H}_9\text{N}_3\text{O}_3\); molecular weight, 171.15 g/mole; and purity, 97%; purchased from Sigma Aldrich, USA) in ultrapure water/methanol solution (3:1 ratio) and stored in a glass container at room temperature. The pH of the solution was adjusted using NaOH or \(\text{H}_2\text{SO}_4\) (1 M). The stock solution was diluted in accurate proportions to achieve different initial concentrations of the antibiotic. A standard curve was developed for each MN concentration by measuring the absorbance of MN solution at a wavelength of 320 nm using UV/Vis spectrophotometer (Model 1700, Shimadzu, Japan). Furthermore, \(\text{Mg(NO}_3)_2\cdot\text{6H}_2\text{O}, \text{Al(NO}_3)_3\cdot\text{9H}_2\text{O}, 30\% \text{H}_2\text{O}_2\), and urea used in the synthesis of LDH nanoparticles were purchased from Merck (Germany).

2.2. Synthesis and characterization of LDH nanoparticles

The LDH nanoparticles were synthesized following procedures published elsewhere (Sepehr et al., 2014a, b). Briefly, 1.9 g of Al (\(\text{NO}_3\))\(_2\)·9\(\text{H}_2\text{O}, 2.6\) g of Mg (\(\text{NO}_3\))\(_2\)·6\(\text{H}_2\text{O}\), and 3.0 g of urea were dissolved in 100-mL solution (containing 90 mL of deionized water and 10 mL of 30\% \(\text{H}_2\text{O}_2\)) and stirred at room temperature for 10 min. This solution contained approximately \(0.01\) M \(\text{Mg}^{2+}\), \(0.005\) M \(\text{Al}^{3+}\), and \(0.05\) M urea. The solution pH was recorded, but not controlled, and was approximately 9 due to the release of ammonia. Subsequently, the solution was transferred to a Teflon tube, sealed, and heated at 150°C for 24 h. The pressure in the tube increased gradually with the reaction time and reached a stable value of 12 MPa after 2.5 h (Soori et al., 2016). Then, the suspension was extracted and washed several times with ultrapure deionized water. The product was washed continuously until no leakage of the material structure was observed. The final product was dried at 120°C for 24 h for subsequent experiments.

The surface morphology of the prepared LDH nanoparticles was observed under a scanning electron microscope (SEM; using Philips-XL30 device, Netherlands) equipped with energy dispersive X-ray microanalysis hardware, transmission electron microscope (TEM; using TEM EM 900 device, ZEISS), and field emission scanning electron microscope (FESEM; JSM 6400 device, JEOL). The specific surface area was measured using a nitrogen adsorption technique based on the Brunauer–Emmett–Teller (BET) isotherm model (Micromeretics/Gemini-2372). The functional groups on the surface of the prepared adsorbent were detected by fourier-transformed infrared (FTIR) spectroscopy at 400–4000 cm\(^{-1}\) (Bruker-VERTEX 70, Germany). The X-ray diffraction (XRD) patterns of the prepared adsorbent were obtained using Philips-Magix Pro MD (Philips Electronics Co., Netherlands) with a high-power CuK\(_\alpha\) radioactive source (wavelength: 0.154 nm) generated at 40 kV/40 mA. All the samples were scanned with a step width of 0.028° in 2\(\theta\) at a scanning rate of 88° 2\(\theta\)/min.

2.3. Experiments

Batch experiments were conducted in 500-mL stoppered flasks to observe MN removal by LDH nanoparticles. Different factors that influence MN adsorption, including solution pH (3, 5, 7, 9, and 11), shaking time (1–200 min), initial antibiotic concentration (10, 20, 40, and 60 mg/L), temperature (10, 15, 20, 25, and 30°C), and adsorbent mass (2, 4, 6, 8, and 10 g/L) were investigated. In addition, the effects of co-existing agents, such as nitrate (50, 100, and 150 mg/L), sulfate (100, 300, and 500 mg/L), carbonate (50, 75, and 100 mg/L), and hardness
(150, 300, and 450 mg/L) were also examined. For the experiments, 300 mL of the MN solution was mixed with the corresponding amount of the prepared LDH nanoparticles. The flasks were placed inside a shaker incubator with a constant shaking speed of 350 rpm until equilibrium time was reached, which was found to be 2 h in preliminary experiments. Subsequently, 2–3 mL of the samples was withdrawn from each flask, filtered immediately, and centrifuged, and its final antibiotic concentration was determined using UV/Vis spectrophotometer. The results of the experiments investigating the effects of initial MN concentration, shaking time, and temperature on the MN removal efficiency were used for isotherm, kinetic, and thermodynamics studies, respectively.

The point of zero charge (pH pzc) of the prepared adsorbent was determined by the conventional method. Briefly, the initial pH values of 50 mL of 0.1 M NaCl were adjusted to a pH range of 2–12 with 1 M NaOH or H₂SO₄ solution. Subsequently, 0.5 g of the adsorbent was added to each solution and the obtained suspension was shaken for 48 h. The adsorbent was filtered and the final solution pH was measured. The pH pzc of the prepared medium was determined from the intersection of the curve of final vs. initial pH.

For all the experiments and after reaching equilibrium, the MN removal efficiency (%) and equilibrium adsorption capacity (qₑ, mg/g) were calculated using the following equations:

\[
\text{Removal Efficiency} (%) = \left( \frac{C_o - C_e}{C_o} \right) \times 100
\]

\[
q_e = \frac{V}{m} \left( \frac{C_o - C_e}{C_o} \right)
\]

where \(C_o\) and \(C_e\) are the initial and equilibrium concentrations of MN (mg/L), respectively, \(V\) is the volume of the used solution (L), and \(m\) is the mass of the used adsorbent (g).

3. Results and discussions

3.1. Characterization of the adsorbent

3.1.1. Surface morphology analysis

The surface area of the LDH nanoparticles was found to be 109 m²/g. This large surface area attests the high binding capacity of LDH. The surface morphology of the prepared adsorbent was observed under the SEM at two different magnifications (Fig. 1 A). It can be observed from the figure that the LDH particles were uniformly shaped sheets, with most of them being hexagonal (gray parts), and the particle size ranged from 200 to 1000 nm in diameter. In addition, several heterogeneous small pores (dark parts) could be noted, which are known to provide larger surface area for contaminant adsorption, thus making the LDH nanoparticles as a well-supported material (Samarghandi et al., 2015). This finding was also confirmed by the high-resolution micrographs of the internal structure obtained using TEM (Fig. 1 B), and the thickness of the hexagonal plates was 40–120 nm. In addition, the LDH nanoparticles were also observed under FESEM before and after MN adsorption (Fig. 1 C and D). The FESEM images indicated that the sorption of MN did not affect the surface morphological features of the LDH material and that the circular spots noted may be the adsorbed MN molecules.

![Figure 1](https://example.com/figure1.jpg)

**Figure 1** SEM (A) images, TEM image (B) of the prepared LDH before MN adsorption, and FESEM image of LDH before and after MN adsorption (C and D).
3.1.2. FTIR spectroscopy and XRD analysis

The structural properties of the LDH nanoparticles were confirmed by both FTIR analysis and XRD patterns. Fig. 2 shows the FTIR spectra of the synthesized adsorbent before (black solid line) and after (blue dashed line) MN adsorption. The intense and broad peak at approximately 3449 cm\(^{-1}\) could be attributed to the stretching vibration of the O–H group from both the hydroxide layers and interlayer water (Parry et al., 2007). The corresponding band close to 1665 cm\(^{-1}\) could be attributed to bending vibration of the H–OH molecules. A strong absorption band near 1377 cm\(^{-1}\) corresponded to nitrate anions (Soori et al., 2016). However, carbonate anions did not show any peak near 1356 cm\(^{-1}\), indicating minimal amount of carbonate anions intercalated to the prepared LDH owing to the low CO\(_2\) level during LDH synthesis as a result of using sealed Teflon tube (closed system). The bands below 1000 cm\(^{-1}\) were assigned to M–O stretching and M–OH bending vibrations in the brucite layer. When compared with the FTIR spectra of the raw adsorbent, several peaks exhibited changes in the percent transmittance values after the reaction of the adsorbent with MN. In addition, some peaks shifted to new values, while some disappeared, confirming the binding of the MN molecules to the LDH surface (Soori et al., 2016).

Fig. 3 shows the XRD pattern of the LDH before (black line) and after (gray line) MN adsorption. Indexing of the diffraction peaks was achieved by using a standard JCPDS file. As indicated in the figure, the XRD pattern of the prepared adsorbent before adsorption presented sharp and symmetrical peaks and some high-angle asymmetrical peaks, demonstrating the formation of highly crystalline Mg/Al LDH structure. A distinct reflection peak at \(2\theta = 10.00^\circ\) corresponding to (003) showed the initial LDH-NO\(_3\) phase, while the other peaks at \(2\theta = 19.90^\circ, 34.64^\circ, 38.32^\circ,\) and \(44.42^\circ\) were associated with (006), (009), (012), and (018), resembling the typical LDH nanostructure. Furthermore, the sharp peak at \(2\theta = 28.16^\circ\) resulted from the formation of MgO. The peak at \(2\theta = 10.49^\circ\) represents the thickness of the brucite-like layer and the interlayer distance. The peak at \(2\theta = 60.46^\circ\) is related to arrangement of ions along the plane of host layer.

Figure 2 FTIR spectra of the raw LDH (black solid line) and LDH after antibiotic adsorption (blue dashed line).

Figure 3 XRD pattern of the LDH before (black line) and after (gray line) MN adsorption.
The peaks observed at 2\(\theta\) = 10.00\(^\text{\circ}\), 19.90\(^\text{\circ}\), 34.64\(^\text{\circ}\), 38.32\(^\text{\circ}\), 44.42\(^\text{\circ}\) and 60.46\(^\text{\circ}\) remained the same after MN adsorption, indicating that the structure of the prepared adsorbent did not change during intercalation of MN. The peak at 2\(\theta\) = 10.49\(^\text{\circ}\) was shifted to stronger angle after MN adsorption suggesting that the interlayer distance of Mg/Al LDH decreased.

3.2. Effect of pH

Solution pH is an important parameter that can influence the surface charge of the medium and equilibrium ionization of the solute (Mohammed et al., 2016). The influence of solution pH on the surface charge of the medium could be explained by pH\(_{ZPC}\). Accordingly, below or above pH\(_{ZPC}\), the adsorbent will have a positive or negative charge on its surface, respectively. The results of the present study showed that the pH\(_{ZPC}\) value of the used adsorbent was 5.5 as shown in Fig. 4a, indicating that the surface of the LDH nanoparticles will be occupied by positive metal oxide at pH less than 5.5 (Xu et al., 2008). However, MN is a weak base with two p\(K_a\) values (p\(K_{a1}\) = 2.58 and p\(K_{a2}\) = 14.48), as shown in Fig. 4b. Hence, MN will have a positive charge at pH less than 2.58 and remain neutral at pH more than 2.58. Fig. 4c presents the UV/Vis spectra of MN adsorption at different pH values. The black dotted line is the UV/Vis spectrum of pure MN solution at pH 5 before MN adsorption. The remaining lines are the UV/Vis spectra recorded after the addition of 6 g/L LDH to the MN solution.

![Figure 4](image)

**Figure 4** Influence of solution pH on MN adsorption: zero point charge of LDH (a), p\(K_a\) values (b), UV/Vis spectra (c), variation of removal efficiency (d), and zeta potential (e), at LDH concentration of 6 g/L, MN concentration of 40 mg/L, contact time 2 h at room temperature.
at different pH values. When compared with the pure MN solution spectra, the maximum absorbency remained unchanged after the addition of LDH and no new bands appeared. However, it can be noted that the spectrum at pH 3 is unusual and differs from other spectra (Fig. 4c, red dashed line). At pH 3, the spectrum appeared above the original MN spectrum, which may be attributed to the decomposition of the prepared adsorbent structure in acidic medium resulting in highly turbid solution that can absorb high amount of UV light, leading to higher absorbance values (Khan and O’Hare, 2002; Leroux and Taviot-Gueho, 2005). Fig. 4d shows the variation in the MN removal efficiency at different pH values. It can be seen that the solution pH significantly affected MN adsorption onto the LDH nanoparticles, especially between pH 3 and 9. At pH 5, about 7.3% of MN was removed, and this percentage reached the maximum value at pH 9 (35%); however, above pH 9, the removal efficiency remained remarkably unchanged. This trend can be reasoned based on the degree of ionization of MN and surface charge of the adsorbent. The effect of solution pH on MN removal in the pH 5–11 can be categorized to different groups. First, from pH 5 to near neutral pH (pH 7.5), the net negative charge on adsorbent surface is lesser if compared to alkaline environment (from neutral pH to pH 11). Then, the main phenomena for MN adsorption may be due to the π–π interaction. Second, from near neutral pH to pH 11, the main mechanism in MN adsorption may be due to the complex formation between metal hydroxide and MN molecules and also π–π interaction. Therefore, at higher pH values both π–π interaction and adsorption on metal hydroxide involved; resulting an increase in sorption rate. From the initial pH 5 to approximately pH 8, the final solution pH increased (Fig. 4d), demonstrating the involvement of adsorption phenomenon in the removal of MN by positive metal oxide on the surface of the adsorbent. In addition, the UV/Vis spectra of MN with LDH at pH 5–11 were similar to that of the original MN solution spectra, which further confirmed that the π–π interaction/adsorption phenomenon is the dominant mechanism in the adsorption process. Fig. 4e shows the results of the positive zeta potential values of the prepared adsorbent. It can be observed from the figure that the positive metal oxide on the surface of LDH may participate in the complex formation of MN with Mg²⁺ and Al³⁺. The final solution pH exhibited a natural pH range (5–7) owing to the amphoteric character of LDH, especially at higher initial pH of the solution. At higher alkaline pH (above pH 10) the net negative charge of adsorbent surface is plenty resulting in repulsive interaction with negatively charged MN molecules. These results are in agreement with those presented in previous studies (Mohammed-Ali, 2012; Diirckheimer, 1975).

3.3. Influence of competing ions

Khand and O’Hare (2002) showed that band formation between foreign ions and LDH host is affected by various chemical parameters such as the dimensions and functional groups of the guest molecules, number (monolayer, multilayer), size, and orientation of the foreign ions, as well as the interactions between the negatively charged foreign ions and positively charged host. To investigate the influence of foreign ions such as nitrate, sulfate, carbonate, and hardness agent on the MN removal efficiency with and without LDH addition, 40 mg/L MN solution was prepared and subjected to different concentrations of nitrate, sulfate, carbonate, and hardness agent. Figs. 5a, 6a, 7a, and 8a show the UV/Vis spectra of MN solution after the addition of different concentrations of nitrate, sulfate, carbonate, and hardness agent, respectively. It can be observed that the peak wavelength occurred at 320 nm. The black dotted line indicates the spectrum of pure 40 mg/L MN solution at pH 9 before the addition of foreign ions and the removal efficiency was calculated to be 35% as shown previously in Fig. 4c. These figures revealed that the position of peak absorbency (320 nm) did not change after the addition of ions, and no new bands appeared, revealing that no interaction and complex formation occurred between MN molecules and these ions. The unusual spectrum indicated in Fig. 5a at lower band may be owing to the adsorption of UV light by nitrate anions because nitrate presents peak absorbency at 220 nm. The results obtained following the addition of 6 g/L LDH nanoparticles to the MN solution are depicted in Figs. 5b, 6b, 7b, and 8b. Furthermore, Fig. 9 depicts the effect of increasing concentration of nitrate, sulfate, hardness, and carbonate on MN removal efficiency. In the case of nitrate and sulfate and hardness, the MN removal efficiency was...
decreased with the increase of these two ions’ concentrations. This is may be due to the competing effect of nitrate, sulfate and hardness ions with MN molecules for adsorption on LDH surface. In addition, at studied pH range, MN is in neutral form and cannot compete with foreign ions. The adsorbed MN in the presence of competing ions may be due to the π–π interaction as discussed earlier in the effect of solution pH section. The fall down of removal efficiency from 35% to zero point in addition to 75 mg/L nitrate, may be due to the saturation of interlayer of LDH with nitrate ions and surface binding of nitrate with metal hydroxide of adsorbent surface (Bui and Choi, 2010; Cheng et al., 2016; Xuan and Heechul, 2010). These findings are in agreement with those found in previous literatures (Soori et al., 2016). In the case of carbonate anions, antagonistic attitude was observed. The MN removal efficiency was decreased at lower concentration of carbonate, and afterward the removal efficiency was increased with the increase of carbonate concentration. This may be due to the buttering effect of carbonate anions in solution. At lower concentration, carbonate anions may exchange with nitrate anions in the interlayer of LDH and then compete with MN molecules. At higher concentration, it may increase solution pH resulting in formation of more metal hydroxide and negatively charged MN molecules leading to an increase in removal efficiency (Yang et al., 2015).

3.4. Isotherm study

The mechanisms involved in the process of MN desorption and the adsorption capacity of LDH nanoparticles were determined by obtaining the corresponding adsorption isotherms. The equilibrium absorbency values, obtained at different initial concentrations, were used to construct the adsorption isotherms (Fig. 10), in which the equilibrium amount of MN adsorbed onto the LDH nanoparticles (qe, mg/g) was plotted as a function of the equilibrium MN concentration in the solution (Ce, mg/L). It can be observed that the amount of MN adsorbed increased with the increasing equilibrium concentration. Fig. 10 demonstrates that the adsorption capacity of MN did not reach the static saturation adsorption capability even when the equilibrium MN concentration reached 24.5 mg/L and further increased with the increasing equilibrium MN concentration.

To describe the experimental equilibrium adsorption data, the two-parameter Freundlich (Eq. (3)) and Langmuir (Eq. (4)) isotherms and the three-parameter Redlich–Peterson (Eq. (5)), and Sips (Eq. (6)) isotherms were adopted. The Freundlich equilibrium isotherm equation is an empirical equation used for the description of multilayer adsorption with interaction between the adsorbed molecules. The model is based on
adsorption onto heterogeneous surfaces by a uniform energy distribution and reversible adsorption. The Freundlich isotherm assumes that the adsorption energy exponentially decreases at the finishing point of the adsorption centers of an adsorbent. The Freundlich constants are empirical constants that depend on many environmental factors. The value of $1/n$ (Eq. (3)) indicates the intensity of adsorption or surface heterogeneity, revealing higher heterogeneity as it gets closer to zero. If $1/n < 1$, it indicates favorable adsorption (Freundlich, 1906; Rangabhashiyam et al., 2014).

The Langmuir model quantitatively describes the formation of a monolayer adsorbate on the outer surface of the adsorbent, after which no further adsorption occurs (Rangabhashiyam et al., 2014). The model represents the equilibrium distribution of the adsorbate between the solid and liquid phases. The Langmuir adsorption isotherm, the most widely used isotherm for the adsorption of pollutants from a liquid solution, is based on the following hypotheses: (1) monolayer adsorption; (2) adsorption takes place at specific homogeneous sites on the adsorbent; (3) once a pollutant occupies a site, no further adsorption can occur in that site; (4) the adsorption energy is constant and does not depend on the degree of occupation of an adsorbent’s active centers; (5) the strength of the intermolecular attractive forces is believed to decrease rapidly with distance; (6) the adsorbent has a finite capacity for the pollutant; (7) all sites are identical and

Figure 8 Influence of hardness ions on MN sorption rate before (a) and after (b) addition of 6 g/L LDH at pH 9 and 2 h contact time.

Figure 9 Effect of increasing concentration of nitrate, sulfate, carbonate and hardness on MN removal efficiency (pH = 9; LDH dose = 6 g/L; MN conc. = 40 mg/L; contact time = 2 h).
Adsorption performance of double hydroxide nanoparticles

Figure 10 Isotherm data of MN adsorption onto LDH (pH = 9; adsorbent dose = 2 g/L; MN conc. = 0–70 mg/L; 350 rpm for 2 h).

energetically equivalent; (8) the adsorbent is structurally homogeneous; and (9) there is no interaction between the molecules adsorbed onto the neighboring sites (Langmuir, 1918). The Redlich-Peterson isotherm model can be applied to express the sorption process when dealing with certain pollutants at high concentration. This model incorporates the features of both the Langmuir and Freundlich models into a single equation and presents a general isotherm (Quintelas et al., 2008; Brouers and Al-Musawi, 2015). The Sips model combines both the Langmuir and Freundlich isotherm equations. At low sorbate concentrations, the Sips isotherm assumes the form of the Freundlich model, while it predicts a constant, monolayer sorption behavior similar to that of the Langmuir model at high concentrations (Ho et al., 2002; Sips, 1948). By identifying the problem of continuous increase in the adsorbed amount with the increasing concentration in the Freundlich equation, Sips proposed an equation similar in form to the Freundlich equation, but which could predict a constant, monolayer sorption behavior similar to that of the Langmuir model at high concentrations (Ho et al., 2002).

\[ q_e = q_m K_L C_e \]
\[ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \]
\[ q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{n_{RP}}} \]
\[ q_e = \frac{k_h C_{m_h}}{1 + a_h C_e^{m_h}} \]

where \( K_F \) is the Freundlich constant related to the relative adsorption capacity (mg/g), \( n \) is the heterogeneity factor (g/L), \( q_m \) is the maximum adsorption capacity (mg/g), \( K_L \) is the Langmuir constant related to the free energy of adsorption (L/mg), \( K_{RP} \) (L/mg) and \( a_{RP} (L/mg)^{n_{RP}} \) are the Redlich-Peterson isotherm constants, \( b_{RP} \) is the exponent that lies between 0 and 1, \( k_h \) and \( a_h \) are Sips model isotherm constants (L/mg)\(^m_h\); and \( m_h \) is the exponent that lies between 0 and 1.

Nonlinear regression analysis using the software package STATISTICA was used for fitting and direct determination of the isotherm model parameters with the quality of fit assessed using the correlation coefficient \((R^2)\). However, several studies had concluded that the use of \( R^2 \) alone, even if it is estimated via nonlinear analysis, is not always an appropriate tool to evaluate the goodness of fit of the models (Ncibi et al., 2008; Ho, 2004). Therefore, the calculation of error deviation using another parameter is essential to evaluate the goodness of fit of an isotherm model and describe the sorption phenomena. Accordingly, the correlations of the above-mentioned models with the experimental data were further validated by Chi-square \((X^2)\) test, which can be defined as follows:

\[ X^2 = \sum \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \]

where \( q_{e,exp} \) and \( q_{e,cal} \) are the experimental and model equilibrium capacity data, respectively. If the data from the model are similar to the experimental data, the value of \( X^2 \) will be small; otherwise, the value of \( X^2 \) will be large.

The modeling results and error calculations are listed in Table 1. As shown in the table, all the used models correlated well with the experimental data \((R^2 > 0.9)\) in the following order: Sips > Redlich-Peterson > Langmuir > Freundlich. The higher values of \( R^2 \) and lower values of \( X^2 \) indicated that the Sips model was more suitable for describing the sorption equilibrium of MN onto the LDH adsorbent. However, the Freundlich model presented the lowest fit with lowest \( R^2 \) and highest \( X^2 \) values. The Sips model combines both the Langmuir and Freundlich isotherm equations. At low sorbate concentrations, the Sips isotherm assumes the form of the Freundlich model, while it predicts a constant, monolayer sorption behavior similar to that of the Langmuir model at high concentrations. In addition, this model predicts heterogeneous adsorption systems and circumvents the limitation of

Table 1 Isotherm modeling results related to the MN adsorption onto LDH.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
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</thead>
<tbody>
<tr>
<td><strong>Langmuir</strong></td>
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</tr>
<tr>
<td>( q_m ) (mg/g)</td>
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<td>( K_L ) (L/mg)</td>
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<td>( X^2 )</td>
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<td>( n ) (g/L)</td>
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</tr>
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<tr>
<td><strong>Sips</strong></td>
<td></td>
</tr>
<tr>
<td>( m_h )</td>
<td>0.626</td>
</tr>
<tr>
<td>( k_h (L/mg)^{m_h} )</td>
<td>0.221</td>
</tr>
<tr>
<td>( a_h (L/mg)^{m_h} )</td>
<td>0.008</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.994</td>
</tr>
<tr>
<td>( X^2 )</td>
<td>0.608</td>
</tr>
</tbody>
</table>

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increasing adsorbate concentration associated with Freundlich isotherm model (Sips, 1948). The exponent mS value of the Sips model was higher than 0.5, implying that the MN adsorption data obtained in the present study were better represented by the Langmuir form than by the Freundlich form, as confirmed by the R² and X² values in Table 1 (Mao et al., 2015). Such trend probably enlightens the monolayer MN adsorption onto homogenous adsorbent surfaces. Furthermore, according to the Langmuir model results, the maximum MN adsorption capacity of 62.804 mg/g was obtained, indicating that LDH is a promising adsorbent that can be used in the decontamination of water potentially polluted by MN compounds.

As pointed out earlier, the use of R² alone to determine the best fitting model is not sufficient and could lead to some ambiguities. Accordingly, the results of MN adsorption onto LDH (Table 1), obtained based on R², implied that both Freundlich and Redlich-Peterson models were adequate (R² = 0.960). However, Redlich-Peterson model presented lower X² value than Freundlich model, indicating that it was more suitable to describe the sorption of MN onto LDH. Thus, the present study confirmed that the use of coefficient of determination alone is not always sufficient to establish the most suitable model that can describe the experimental data. Owing to the limited data available in the literature on adsorption of MN using LDH, comparison of the results of the present study was not possible.

3.5. Kinetic study

Fig. 11 shows the typical concentration decay curves of MN adsorption at different initial concentrations of MN (10, 20, 30, and 40 mg/L). With the increasing shaking time/initial concentration, the removal efficiency of MN increased. The rate curves exhibited a rapid initial removal, followed by a relatively slow approach, and finally attaining equilibrium. Furthermore, it can be noted that the sorption rates were fast and more than 50% of total sorption occurred within the first 60 min of shaking time, while a relatively slow phase appeared after 100 min. The rapid adsorption is considered as an interesting property of an adsorbent for practical uses (Sepehr et al., 2015). This trend can be attributed to the existence of more binding sites on the adsorbent surface during the initial stage; however, the active sites get occupied as the adsorption proceeds thus decreasing the sorption rate. In addition, it was observed that the equilibrium time of LDH was up to 120 min. An increase in the shaking time to more than 150 min did not promote the adsorption capacity and the variation in the removal efficiency remained negligible. Therefore, 120 min was chosen as the equilibrium time in the subsequent experiments. A higher sorption rate was observed at the initial reaction time when 40 mg/L of MN was employed. At 60 min of shaking time, 7%, 17%, 21%, and 23% of MN were removed for the initial concentration of 10, 20, 30, and 40 mg/L, respectively. The higher removal efficiency at higher tetracycline concentration may be owing to an increase in the driving force with the increasing initial solute concentration, indicating that the internal part of the adsorbent was also utilized for antibiotic sorption (Sepehr et al., 2013; Chen et al., 2012).

As mentioned previously, time–concentration data were used as the kinetic data for MN adsorption. These data were examined by nonlinear analyses using three different kinetic models: pseudo-first-order (Eq. (8)), pseudo-second-order (Eq. (9)), and Avrami (Eq. (10)) equations. The pseudo-first-order kinetic model describes sorption in solid–liquid systems based on the sorption capacity of solids (Lagergren, 1898) by assuming that one of pollutant molecules is sorbed onto one sorption site on the adsorbent surface (Boparai et al., 2011). The pseudo-second-order kinetic model is based on the assumption that the rate of sorption follows second-order reaction (Ho and McKay, 1999). This model presumes that one of the pollutant molecules is sorbed onto two sorption sites on the adsorbent surface. The Avrami kinetic model was initially used for kinetic modeling of crystallization, but can be used for other phase changes such as chemical reactions and the estimated parameters for each model are shown in Table 2. The conformity between the experimental data and model-predicted values was determined from R² and X² values. It can be noted from Table 2 that the kinetic data accurately fitted onto all the tested kinetic models. However, the results indicated that the Avrami model could appropriately describe the time-dependent MN adsorption by LDH because the R² values were near unity for all the initial MN concentration and the X² values were low. The R² values for the pseudo-first and pseudo-second-order models, obtained at all the initial MN concentrations, were nearly equal. However, the pseudo-first-order equation showed more accurate prediction of equilibrium adsorption capacities (X² values low and qe - close to experimental values) than the pseudo-second-order model. The fractional number (nAV) of the Avrami model predicted from the adsorption process was higher than unity for all MN concentrations, and the predictions of equilibrium adsorption and capacities (qe) were close to the experimental values, similar to pseudo-first-order prediction. Hence, the adsorption mechanism of MN onto LDH could follow multiple kinetic orders (Lopes et al., 2003). In addition, higher values of pseudo-first-order constant at higher antibiotic concentration demonstrated that the LDH required shorter time to reach a specific fractional uptake at higher solute concentration (Karimaian et al., 2013).

It is widely accepted that most of the sorption reactions can be represented by three mechanisms (Chingome et al., 2006), namely: (1) film or surface diffusion, where the sorbate is transported from the bulk solution to the external surface of the sorbent; (2) intraparticle or pore diffusion, where the sorbate molecules move into the interior of the sorbent particles; and (3) sorption on the interior sites of the sorbent. To gain

Figure 11 Profile of the time-concentration of MN adsorption onto LDH (pH 9, adsorbent 6 g/L, 10–40 mg/L MN concentration).
insight into the mechanisms and rate-controlling steps affecting the kinetics, the kinetic data were further examined to check whether pore diffusion is the only rate-controlling step by using the pore diffusion Bangham equation (Eq. (11)) (Kalhori et al., 2013). The fitting of the kinetic data onto the Bangham model was high ($R^2 > 0.9$), indicating that the pore diffusion of MN onto LDH was not the only rate-controlling mechanism and that other kinetic processes may also control the rate of sorption (Itodo et al., 2010).

### 3.6. Thermodynamics study

The effect of temperature on the MN removal efficiency of LDH was examined at 10°C, 15°C, 20°C, 25°C, and 30°C, and the findings are shown in Fig. 12. These results were used to calculate the related thermodynamic parameters. The values of $K_d (q_e/C_e)$ at different temperatures were processed according to the following Van’t Hoff equation to obtain the thermodynamic parameters of the adsorption process (Sarin et al., 2006; Liu, 2009):

\[
\ln K_d = \frac{\Delta H^0}{R} \times \frac{1}{T} + \frac{\Delta S^0}{R}.
\]

where: $K_d$ is the equilibrium constant (L/mg), $\Delta H^0$ is the enthalpy of sorption (kJ/mol), $\Delta S^0$ is the entropy of sorption (J/K mol), $R$ is the gas law constant (8.314 J/mol K), and $T$ is the absolute temperature (K).

A plot of $\ln K_d$ vs. $1/T$ yielded a straight line from which $\Delta H^0$ and $\Delta S^0$ could be obtained from the slope and intercept, respectively. Table 3 summarizes the values of these two thermodynamic parameters together with Gibbs free energy ($\Delta G^0$) of adsorption (kJ/mol). The Gibbs free energy change is the

### Table 2 Parameters of kinetic models.

<table>
<thead>
<tr>
<th>Kinetic models</th>
<th>Parameters</th>
<th>Initial MN concentration</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Experimental</td>
<td>$q_e$ (mg/g)</td>
<td>3.000</td>
</tr>
<tr>
<td>Pseudo-1st-order</td>
<td>$q_e$ (mg/g)</td>
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<td>$k_1$ (1/min)</td>
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<tr>
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<td>$R^2$</td>
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</tr>
<tr>
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<td>$X^2$</td>
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<tr>
<td>Pseudo-2nd-order</td>
<td>$q_e$ (mg/g)</td>
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<td>$k_2$ (g/mg h)</td>
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<td>$X^2$</td>
<td>0.714</td>
</tr>
<tr>
<td>Avarmi</td>
<td>$q_e$ (mg/g)</td>
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<tr>
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<td>$k_{AV}$ (1/min)</td>
<td>0.023</td>
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<tr>
<td></td>
<td>$n_{AV}$ (1/min)</td>
<td>2.676</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.981</td>
</tr>
<tr>
<td></td>
<td>$X^2$</td>
<td>0.328</td>
</tr>
<tr>
<td>Bangham</td>
<td>$q_e$ (mg/g)</td>
<td>3.198</td>
</tr>
<tr>
<td></td>
<td>$k_{AV}$ (1/min)</td>
<td>0.016</td>
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<td>$n_{AV}$ (1/min)</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.981</td>
</tr>
<tr>
<td></td>
<td>$X^2$</td>
<td>0.328</td>
</tr>
</tbody>
</table>

where: $q_t$ is the metal uptake capacity (mg/g) at any time $t$, $q_e$ is the metal uptake capacity (mg/g) at equilibrium, $k_1$ is the observed rate constant of pseudo-first-order kinetic model (1/min), $k_2$ is the observed rate constant of pseudo-second-order kinetic model (g/mg min), $n_{AV}$ is the fractional number (1/min), $k_{AV}$ is the Avarmi model constant (1/min), and $k_o$ and $a$ are Bangham model constants.

### Table 3 Thermodynamic parameters for the adsorption of MN by LDH.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$C_e$ (mg/L)</th>
<th>$K_d$ (L/mg)</th>
<th>$\Delta G^0$ (kJ/mol)</th>
<th>$\Delta H^0$ (kJ/mol)</th>
<th>$\Delta S^0$ (J/K mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>283</td>
<td>24.8</td>
<td>0.102</td>
<td>5367.602</td>
<td>−4.36701</td>
<td>−34.6694</td>
</tr>
<tr>
<td>288</td>
<td>25.6</td>
<td>0.094</td>
<td>5667.917</td>
<td>−4.36701</td>
<td>−34.6694</td>
</tr>
<tr>
<td>293</td>
<td>26</td>
<td>0.090</td>
<td>5872.71</td>
<td>−4.36701</td>
<td>−34.6694</td>
</tr>
<tr>
<td>298</td>
<td>26</td>
<td>0.090</td>
<td>5972.927</td>
<td>−4.36701</td>
<td>−34.6694</td>
</tr>
<tr>
<td>303</td>
<td>26</td>
<td>0.090</td>
<td>6073.144</td>
<td>−4.36701</td>
<td>−34.6694</td>
</tr>
</tbody>
</table>

Figure 12 Effects of temperature on MN removal efficiency using LDH nanoparticles.
fundamental criterion of spontaneity, which can be calculated from the following equation:

$$\Delta G^0 = -RT \ln K_d \quad (13)$$

The negative values of $\Delta H^0$ indicate that the adsorption process is exothermic in nature, because an increase in temperature does not usually favor the process. Furthermore, the negative values of $\Delta S^0$ reveal a decrease in the randomness at the solid/liquid interface during the sorption process (Sengil and Ozacar, 2008). The positive values of free energy ($\Delta G^0$) indicate that the adsorption process is nonspontaneous in nature. In addition, the increase in the values of $\Delta G^0$ with increasing temperature may be attributed to the exothermic nature of the reaction between the adsorbent’s active sites and MN ions (Elwakeel et al., 2014).

4. Conclusions

In the present study, MN removal using Mg/Al LDH nanoparticles was investigated. The adsorption of MN onto LDH was strongly dependent on pH and weakly dependent on foreign ionic strength. The SEM and TEM images of LDH indicated the presence of nanosheets, and the FESEM image showed that MN adsorption did not affect the surface morphological features. The Sips isotherm model was found to be the best to describe the equilibrium data with high coefficient of determination and low Chi-square values. These findings enlighten the monolayer MN adsorption onto homogenous adsorbent surfaces. The adsorption kinetic data were well described by the Avrami model. Furthermore, the present study confirmed that the use of coefficient of determination alone is not always sufficient to determine the most suitable theoretical model, and that pore diffusion is not the dominant mechanism during MN adsorption onto LDH. Finally, the thermodynamic study results showed that the adsorption of MN is nonspontaneous and exothermic in nature.

Acknowledgment

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References


Adsorption performance of double hydroxide nanoparticles


