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ADSORPTION CHARACTERISTICS OF METRONIDAZOLE FROM INDUSTRIAL WASTEWATER ONTO POLYANILINE NANOCOMPOSITE

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ABSTRACT

Over the past few decades, occurrence of organic micro-pollutants such as pharmaceuticals in the aquatic ecosystems has been considered as a major environmental and health issue globally. Pharmaceuticals have become chemicals of emerging concern to the public because of their potential to reach drinking water. A novel Polyaniline/humic acid (PA/AH) composite was synthesized and investigated for adsorption of Metronidazole antibiotics (MTZ) from aqueous solutions. The nature and morphology of synthesized adsorbent were characterized by scanning electron microscope, Surface adsorption (BET). Batch experiments were performed to study the influence of various experimental parameters such as contact time, initial concentration of the MTZ and temperatures at fixed solution pH and adsorbent dosage. A comparison of kinetic models was evaluated for the pseudo-first-order, pseudo-second-order, Elovich, intraparticle diffusion and Bangham's kinetics models. The experimental data fitted very well the pseudo second-order kinetic model and also followed by intra-particle diffusion model; whereas diffusion is not only the rate-controlling step, and likely that both adsorption steps, bulk and intra-particle diffusion, control the rate of adsorption process. The results show that the sorption capacity increases with increase in solution temperature from 10 to 55 ^{o}C. As adsorption capacity of 42.2 to 49.95 mg/g increases when the temperature increases from 10 to 55 ^{o}C. The developed polyaniline nanocomposites in this study have considerable potential for the removal of MTZ and could be considered as a promising adsorbent for the removal of other antibiotics also from aqueous solutions.

KEYWORDS: ***Polyaniline, Nanocomposite, Adsorption, Metronidazole, Kinetics, Thermodynamics.***

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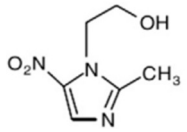
INTRODUCTION

In the last few decades, the presence of emerging contaminants in different types of water appeared as a new environmental threat which needs to be faced by several governments around the world [1-3]. Among the emerging contaminants found in waters, the class of pharmaceuticals has been detected in surface water and sewage wastewater treatment plants (SWTP) effluents [4-5]. Generally, pharmaceuticals reach waterways through the discharge of wastewaters and effluents on environment, which often are not properly treated.[6-7] On the other hand, it was proved that when pharmaceuticals reach SWTP, they are not completely removed [8].This circumstance leads to the development of new water treatment technologies, which should be properly tested in order to face this new type of contamination. [9-10] Removing antibiotics is difficult and requires an expensive process. In recent years, there has been an increasing interest in the treatment of pollution generated by drug residues, including antibiotics.[11-12] Biological processes, the most cost-effective for wastewater treatment, which are destructive and have been extensively studied, do not always appear relevant for the removal of recalcitrant compounds, owing to their low biodegradability.[13] Physical and Physico-chemical techniques have proved their efficiency in this matter.[14] Amongst the Physical techniques adsorption, flocculation, electro-flocculation, reverse osmosis, ultrafiltration and coagulation have been applied to remove recalcitrant pollutants. [15-17] Adsorption, due to its easy operation, presents a practically-feasible alternative for antibiotics removal. Various adsorbents, including activated carbon, aluminum oxide, Azolla Filiculoides, Lemna minor, Canola, Rice husk, Activated carbon, single and multi-walled carbon nano tubes and chitosan have been reported to remove antibiotics by means of surface adsorption, Van der Waals forces, and p–p interactions between antibiotics and different adsorbents. [18-20] However, such adsorbents are quite unaffordable for the treatment of a mass of sewage. Therefore, how to remove antibiotics from wastewater with low-cost adsorbents is an imperative subject faced by environmental researchers.[21-23] Recently, nano structured materials have been used for antibiotics removal from water/wastewater and have proven advantageous over traditional adsorbents due to very large surface area, accessible active sites and a short diffusion length, which results in high adsorption capacity, rapid extraction dynamics and high adsorption efficiencies. However, most nanomaterial has some limitations in adsorption and separation of pollutants from large volume of environmental samples. [24-25] When column dynamic separation mode is used, the nano sized particle packed on column exhibit high back pressure and it is very difficult to achieve high flow rates and in case of static batch mode, nano sized adsorbents lead to a very low subsequent filtration rate. [26] Therefore, it is advantageous to develop a well dispersed nano adsorbent with large surface area and suitable surface functionality that can remove antibiotics from large volume of environmental water. The application of nanoparticles has attracted attention to solve environmental problems. This is because nanoparticles besides having large surface area are highly dispersible in water and exhibit super paramagnetic properties. [27] The primary aim of this work is to present the results of a laboratory study focused on efforts to remove Metronidazole antibiotic in aqueous solutions by humic acid modified Polyaniline-nanocomposite. The physical and chemical characterization of the synthesized Polyaniline/humic acid nanocomposite was conducted. The applicability of synthesized Polyaniline/humic acid in Metronidazole adsorption was evaluated in view of the sorption kinetic and thermodynamics, and a possible adsorption mechanism was proposed.

MATERIALS AND METHODS

All chemicals, such as HCl and $(NH_4)_2\ S_2O_8$, were of analytical reagent grade and used as received (Sigma Aldrich). Aniline was distilled under reduced pressure before use. All solutions were prepared with deionized water. HCl and NaOH were used to adjust the solution pH. Also the chemical and physical characteristics of MTZ are summarized in Table 1.

Table 1
Physical and chemical characteristics of MNZ

Molecular formula	**$C_6H_9N_3O_3$**
Molecular weight (g mol^{-1})	171.2
Water solubility (g L^{-1})	9.5
pKa	2.55
Melting point (°C)	159–163
Molecular structure	

Preparation of PA/HA nanocomposite

The typical preparation procedure of the PA/HA nanocomposite is as follows: 2.35 mL aniline monomer and 7.75 mL HCl were dissolved in 250 mL deionized water. Then 7.75 mL HCl, 0.6 g HA and 5.71 g (NH_4) $2S_2O_8$ dissolved in 250 mL of deionized water were dropped into the above solution with stirring at room temperature. After having been stirred for about 10 h, the resulting product was separated by filtration and finally washed with deionized water until the filtrate was colorless. The resulting product was dried under dynamic vacuum at 65 °C for 24 h. [26].

Adsorption experiment

Adsorption experiments were performed to determine the effect of time and temperature on the adsorption of MTZ by PA/HA nanocomposite under different environmental conditions. The experimental procedures were performed as follows:(1) a series of solutions of various MTZ concentrations were prepared; (2) the initial pH was measured, and a defined amount of the PA/HA nanocomposite was then added to the solutions; (3) these solutions were agitated on a magnetic stirrer for a certain period of time, at room temperature; (4) at defined points in time, a certain volume of the solution was removed and immediately filtered to collect the supernatant; and (5) the residual MTZ were determined by high performance liquid chromatography (HPLC, Shimadzu, LC10A HPLC) equipped with a UV detector (SPD-10AV) at 318 nm. A C18 column (5 μm, 250 mm ×4.6 mm) was used, and the mobile phase was composed of a mixture of acetonitrile and water (20/80, v/v). The flow speed was set at 1.0 mL/min, and 20 μL injections were used. The amount of MTZ adsorbed was determined by measuring the difference in the concentrations of the samples that were obtained at two consecutive time intervals over the course of the adsorption experiment. The adsorption capacity of the PA/HA nanocomposite (q_t, mg/g), which represents the amount of MTZ adsorbed per amount of PA/HA nanocomposite was calculated using a mass–balance relationship[25].

$$q = (C_0 - C_t)\frac{V}{M}$$

Where C_0 and C_t are the concentrations of MTZ in solution (mg/L) at time t=0 and t, respectively. V is the volume of the solution (L), and m is the mass of the dry adsorbent used (g).

The kinetic curves obtained were analyzed using various-order kinetic equations to obtain the parameters for understanding the adsorption process. Comparison between data was performed using regression coefficient of graphs created in Excel software.

RESULTS AND DISCUSSION

Fig. 1 shows the SEM images of the as-prepared PA/HA and -3 Fig b composites. As shown in Fig 2a, the two PA/HA particles display morphologies of short club shaped particles with average diameter of 35–60 nm. Small spherical particles are embedded in the short club-shaped particles, which may be attributed to the presence of HA in PA. Compared with PA/HA, the average diameter of PA/HA Nano composite is larger, which suggests that excessive HA may result in a twist aggregation.

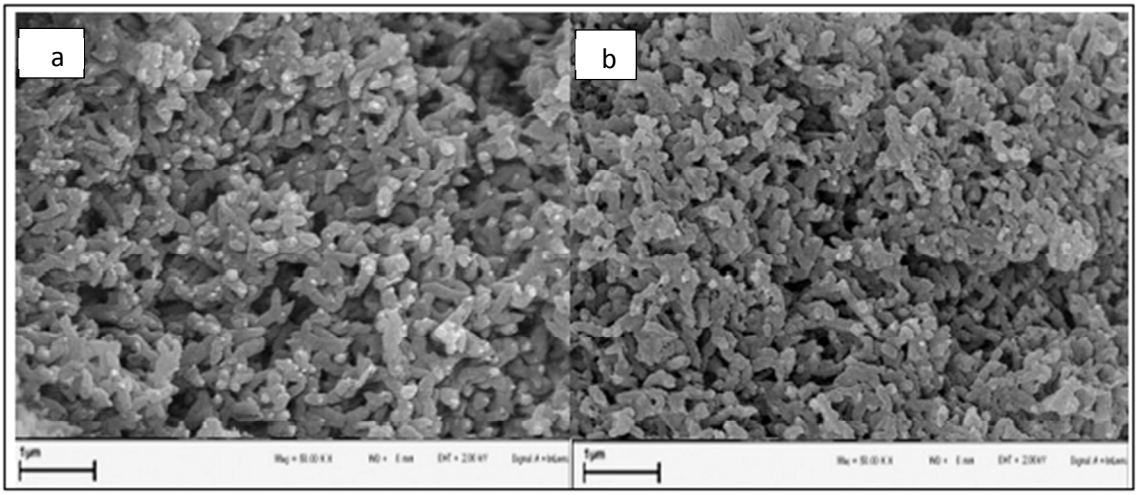


Figure 1
SEM image of PA/HA nanocomposite a: before used b: after used

Adsorption Mechanism

Adsorption equilibrium studies are important for determining the effectiveness of adsorption; however, it is also necessary to identify the type of adsorption mechanism in a system. In this study, we used five different models to predict MTZ adsorption kinetics in PA/HA nanocomposites (First and pseudo-second order, Elovich, internal particle diffusion, and Bangam).

Pseudo first-order model

The Lagergren's rate equation is one of the most widely used rate equation to describe the adsorption of adsorbate from the liquid phase. The linear form of pseudo first-order rate expression of Lagergren is given as[28-29].

$$\text{Log}\,(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t$$

Where, q_e and q_t are the amounts of MTZ adsorbed on adsorbent (mg/g) at equilibrium and at time t (min), respectively, and K_1 is the rate constant of pseudo first-order kinetics.

Figure 2(a) shows the plots of linearized form of pseudo first-order kinetic model for PA/HA nanocomposite. The plots were found linear with good correlation coefficients (>0.9) indicating the applicability of pseudo first- order model in the present study. The pseudo first-order rate constant (K_1) and q_e (cal.) values were determined for each adsorbent from the slope and the intercept of corresponding plot (Fig 2a) and are listed in Table 2.

Pseudo-second-order model

Based on equilibrium adsorption, the pseudo-second-order kinetic equation is expressed as[30]:

$$\frac{t}{q_t} = \frac{1}{k_2 q e^2} + \frac{t}{qe}$$

Where K_2 is the rate constant of pseudo-second-order adsorption (g/mg min) and q_t (mg/g) the amount of adsorbate retained at time (t). The initial adsorption rate, h, (mg/g min) is expressed as[31]:

$$h = K_2\, q_e^2$$

Both constants K_2 and h can be calculated from the intercept and slope of the line obtained by plotting t/q_t versus t. The values of model parameters (K_2, h and q_e) for different temperatures, are given in Table (2), It can be seen that the kinetics of MTZ adsorption onto PA/HA nanocomposite follow this model with correlation coefficients higher than 0.99 and the equilibrium adsorption capacity, q_e, increases as adsorption temperature increased from 10 ^oC to 55 ^oC. For

example, the values of q_e increased from 42.2 mg/g at 10 °C to 49.95 mg/g at 55 °C. Also, from Table (2), it was noticed that the initial adsorption rate, h, increases with increasing temperature. These results imply that chemisorption mechanism may play an important role for the adsorption of MTZ on PA/HA nanocomposite.

Elovich model

Elovich equation is also used successfully to describe second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate–adsorbent. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation. The linear form of this equation is given by[32-33].

$$q_t = \frac{\ln a_e b_e}{b_e} + \frac{1}{b_e} + ln\ t$$

Where parameter be is related to the extent of surface coverage and activation energy for chemisorption (g/mg), and the a_e is the initial adsorption rate (mg/g min).

The Elovich coefficient can be calculated from the graph qt versus Ln t. The a_e and be were calculated from the intercept and slope of the straight-line plots of q_t against Ln t. Table 2 lists the parameters obtained from the Elovich equation. It will be seen that Elovich equation was able to describe properly the kinetics of MTZ adsorption on PA/HA nanocomposite. The parameters obtained from the Elovich equation varied as a function of the solution temperature. Thus, when the temperature of the solution is rises from 25 to 55 °C, the value reduced from 0.92 to 0.28 g/mg because the surface area is less available for MTZ ions. Also increasing the temperature caused an increase in ae from 2.84 to 6.16 mg/g.min. This means that adsorption increased while desorption decreased during increasing solution temperature. However, experimental data do not provide a good correlation for these results at high solution temperatures.

Bangham's model

Attending to kinetic considerations, the applicability of the Bangham's correlation was tested in order to propose a kinetic mechanism adsorption[34-35:]

$$\text{Log}\ [\log (\frac{C_0}{C_{0-q.m}})] = \log (\frac{K_0\, m}{2.303\, V}) + \alpha \log t$$

Where C_0 is the initial MTZ concentration (mg/L), V is the volume of solution (mL), m the adsorbent dose (g/L), q is the adsorption capacity (mg/g) and α and k_0 are constant parameters.

Bangham plot for MTZ adsorption by the PA/HA nanocomposite was shown in Fig. 2e. The non-linearity of the plot indicates that pore diffusion of MTZ is not the only rate-controlling step of the adsorption process, since there is a previous transport of the adsorbate from the aqueous phase through the boundary layer of the adsorbent. This is in concordance to the results shown by Weber and Morris plot, intra-particle diffusion model, which was employed to explore whether the adsorption process involves film diffusion, particle diffusion or both.

Intra-particle diffusion model

The pseudo-second-order and Elovich kinetic models could not identify the diffusion mechanism and the kinetic results were then analyzed by using the intra-particle diffusion model. The intra-particle diffusion (IPD) is calculated by linearization of equation[36]:

$$q_t = K\, t^{0.5} + C$$

Where C is the intercept and K is the intra-particle diffusion rate constant (mg/g $min^{1/2}$) According to this model, the plot of uptake, q_t, versus the square root of time ($t^{1/2}$) should be linear if intra-particle diffusion is involved in the adsorption process and if these lines pass through the origin then intra-particle diffusion is the rate-controlling step. If the plots do not pass of origin, this shows some degree of boundary layer control and this further show that diffusion in particles is not the only rate limiting step, but other kinetic models can control the adsorption rate and everyone can work at the same time. The C and K result from the slope of the straight part of the diagram q_t versus $t^{1/2}$. The correlation coefficient (R^2) for the IPD model lies between 0.894 and 0.935 and decreases with increasing temperature (Table 2). The increase in temperature stimulates the diffusion of pores in the sorbent particles and causes an increase in the rate of diffusion of the particles intra. It is probably that lots of ions before are adsorbed will diffuse into the pores. Fig 2e shows that the three different stages proceed by surface sorption, intra-particle diffusion and a likely chemical reaction. The regression of q_t versus $t^{0.5}$ for MTZ was linear and did not pass through the origin and this further indicates that the intra-particle diffusion is not the only rate-controlling step and likely that both adsorption steps, bulk and intra-particle diffusion, are controlling the adsorption rate process.

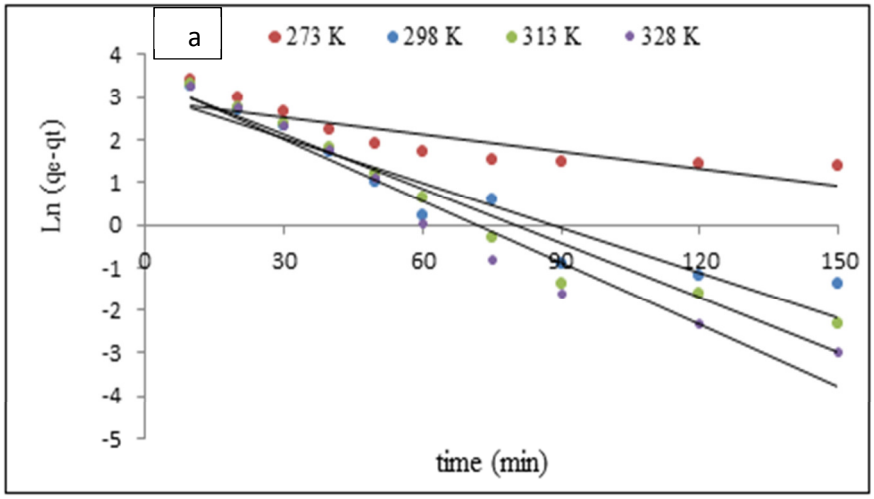


Figure 2a
Pseudo-first order kinetic model plots for MTZ adsorption onto PA/HA nanocomposite

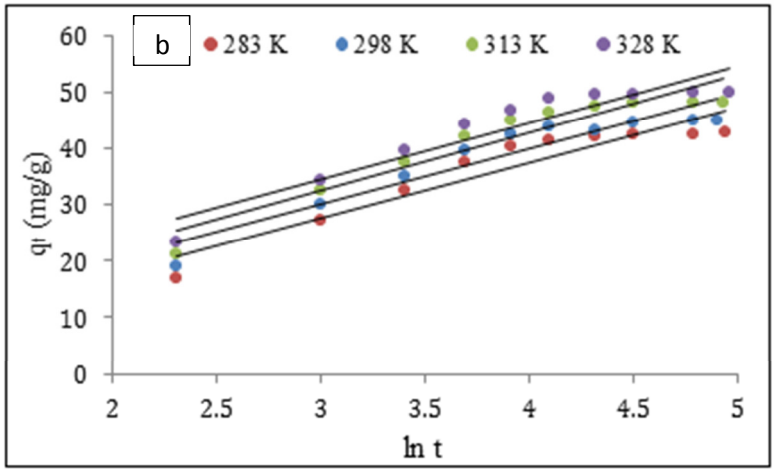


Figure 2b
Pseudo-second order kinetic model plots for MTZ adsorption onto PA/HA nanocomposite

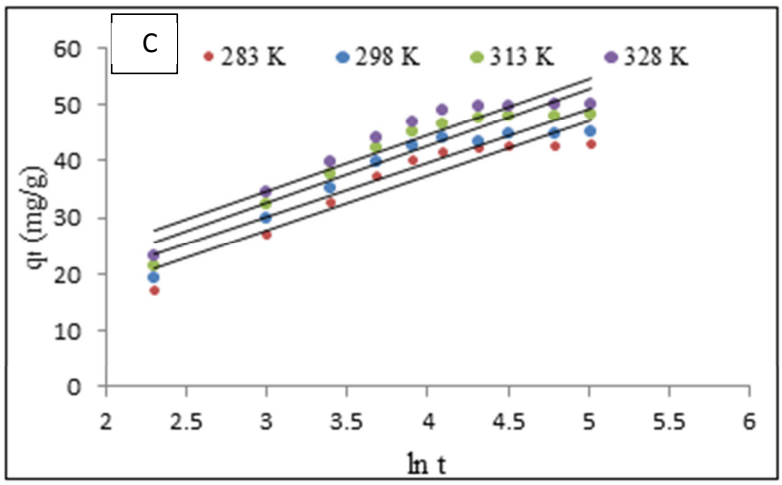


Figure 2C
Elovich kinetic model plots for MTZ adsorption onto PA/HA nanocomposite

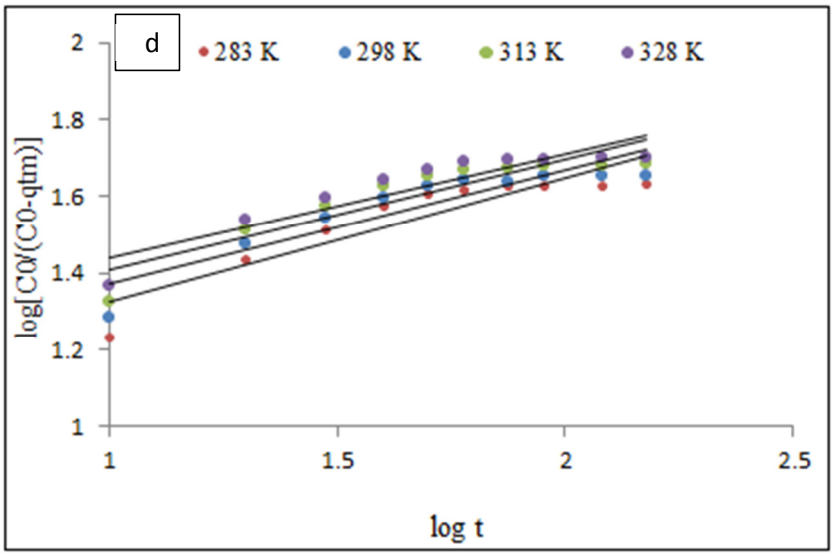


Figure 2d
Bangham's kinetic model plots for MTZ adsorption onto PA/HA nano composite

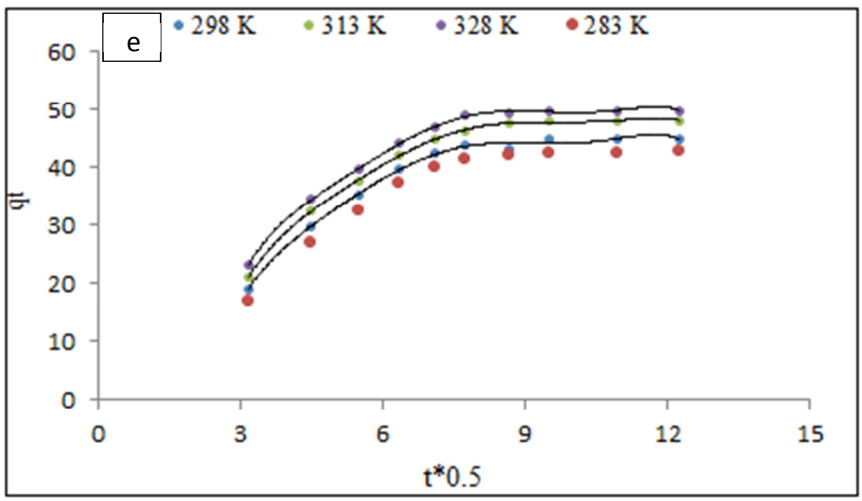


Figure 2e
Intra-particle diffusion kinetic model plots for MTZ adsorption onto PA/HA nanocomposite

Table 2
Kinetic parameters for the adsorption of MTZ onto PA/HA Nanocomposite at Various temperatures

Tem (°*K*)	283	298	313	328
Pseudo-first order				
qm(mg/g)	29.31	30.17	32.59	33.36
K1 (L/mg)	0.034	0.057	0.066	0.082
R^2	0.899	0.931	0.905	0.912
Second-order model				
qe (mg/g)	42.22	45.29	47.64	49.95
K2 (g/mg min)	0.084	0.142	0.195	0.236
h (mg/g min)	2.14	3.69	5.12	6.74
R^2	0.996	0.998	0.999	0.998
Elovich model				
a_e (mg/g min)	2.84	4.05	5.44	6.16
b_e (g/mg)	0.921	0.724	0.495	0.283
R^2	0.829	0.865	0.891	0.848
Intra-particle diffusion				
K (mg/g $min^{1/2}$)	0. 124	0. 371	0. 675	0. 942
C	2.17	1.85	3.14	2.78
R^2	0.935	0.926	0.909	0.894
Bangham's model				
Kb (mL*L/g)	0.712	1.29	1.83	2.47
α	0.792	0.571	0.369	0.284
R^2	0.971	0.965	0.961	0.987

CONCLUSION

The mechanism of MTZ adsorption on PA/HA nanocomposite from aqueous medium on the basis of kinetic studies was investigated. The fitting of the kinetic data demonstrate that the dynamics of sorption could be better described by pseudo second-order model indicating a chemisorptive rate-limiting for all the temperatures. Results obtained from the Intra-particle diffusion model suggests that the process is 'complex' with more than one mechanism limiting the rate of sorption. Finally the results showed that PA/HA nanocomposite are good adsorbents for removal of antibiotics from aqueous solutions.

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AUTHORS CONTRIBUTION STATEMENT

Eng. Amir Hossein Mansouri conceptualized and gathered the data with regard to this work. Dr. Davoud Balarak and Dr. Kethineni Chandrika analyzed these data and necessary inputs were given towards the designing of the manuscript. All authors discussed the methodology and results and contributed to the final manuscript.

CONFLICT OF INTEREST

Conflict of interest declared none

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