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Investigation of the efficiency of powdered and granular magnetic activated carbon nano composites for the adsorption of metronidazole from aqueous solutions (isotherms and kinetics study)

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ABSTRACT

Pharmaceutical pollutants, especially antibiotics, are a serious concern and one of the most polluting sources of the environment, and are harmful to the environment and human health. The purpose of this study was to evaluate the removal of metronidazole (MNZ) using powdered and granular magnetic activated carbon nanocomposites (magnetic powdered activated carbon (PAC) and magnetic granular activated carbon (GAC)) with adsorption from aqueous solutions. In this experimental-laboratory study, the adsorbent characteristics were determined by scanning electron microscopy (SEM), X-ray diffraction, vibrating sample magnetometer, Brunauer–Emmet–Teller (BET), Fourier transform infrared spectroscopy, and energy-dispersive X-ray spectroscopy analyses. The effects of different parameters including pH (3–11), MNZ concentration (10–30 mg/L), adsorbent dosage (0.2–3 g/L) were investigated on the adsorption process. Then, the adsorption isotherm and kinetics equations were investigated. The obtained results of SEM images showed the porosity on the magnetic activated carbon surface with varied sizes, almost uniform dispersion, and a diameter between 20 and 50 nm. Furthermore, the BET results showed that the specific surface area and the pore volume were 109.91 m^2/g, and 0.2552 cm^2/g for the Magnetic PAC, and 561.16 m^2/g and 0.2898 cm^2/g for the magnetic GAC. Also, the magnetization curve showed that the nanoparticles have super paramagnetic nature, whose magnetic saturation value was 30.717 emu/g for the powdered magnetic activated carbon nanoparticles, and 32.992 emu/g for the granular magnetic activated carbon nanoparticles. The results showed that the highest efficiency of magnetic GAC in the removal of MNZ (92/4%) was in conditions with an initial antibiotic concentration of 20 mg/L, pH = 7, adsorbent dosage 1 g/L, and for 90 min. The highest efficiency of magnetic PAC in the removal of MNZ (29.94%) was in conditions with pH = 3, adsorbent dosage of 0.2 g/L and for 30 min. The data obtained from equilibrium isotherms revealed that the MNZ absorption process through the magnetic GAC adsorbent (Langmuir (R^2 = 0.83), Freundlich (R^2 = 0.98)), magnetic PAC adsorbent (Langmuir (R^2 = 0.89), and Freundlich (R^2 = 0.94)) were in consistent with the Freundlich model. Also, the data obtained from the reaction kinetic calculations showed that the absorption of MNZ by the adsorbents was in accordance with a pseudo-second-order model (R^2 = 0.98 for magnetic GAC adsorbent and R^2 = 1 for magnetic PAC adsorbent). The results obtained in this study showed that magnetic GAC as an effective adsorbent and magnetic PAC along with other methods could be used to remove MNZ from the aqueous solutions.

Keywords: Adsorption; Metronidazole; Aqueous solutions; Magnetic activated carbon nanocomposite; Isotherms; Kinetics

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1. Introduction

The presence of organic pollutants in water resources is a serious threat to the environment and human health in recent decades. Pharmaceutical compounds are of the types of these pollutants that enter the surface and underground water resources, mainly due to urban and industrial sewage and wastewater. The presence of drug substances in the environment, due to their high stability, not only disrupts the conventional processes of wastewater treatment, but also imposes toxic effects on humans and other living organisms; for this reason, the removal of this pollutant has attracted further attention of researchers [1,2]. One of the drug pollutants is antibiotics that are metabolized incompletely in the human body after ingestion. The metabolized portion runs into wastewater treatment plants through waste materials, and the non-metabolized portion is discharged into the environment as activated compounds. Research in this area in Germany found that 70% of the used antibiotics are excreted unchanged [3]. It should also be noted that the wastewater treatment plants are often unable to treat the antibiotics discharged and eventually penetrate with wastewater into the recipient water [4]. Antibiotics have a negative effect on the environment in two ways: the effect on non-target animals and the development of bacterial resistance [5].

Metronidazole (MNZ), as one of the most commonly used antibiotics in the world, belongs to the Nitro imidazole group [6]. This antibiotic has a ring structure [7], whose applications include the treatment of infectious diseases caused by anaerobic bacteria and protozoans, and antiparasitic drugs in chicken and fish food [1]. The International Agency for Research on Cancer (IARC) has reported the mutagenicity and Geno toxicity of MNZ on human cells and carcinogenicity on animals. The carcinogenesis of this antibiotic on humans has not yet been proven [6]. The MNZ is highly soluble in water, has a low degradability, and is not well-removed by conventional treatment methods [8].

Various methods, such as adsorption [9], photochemical oxidation [7], electro-Fenton process [10], and biological methods [11] have been used to remove the MNZ. Many researchers have used activated carbon to adsorb antibiotics from aqueous solutions [12]. The activated carbon as an adsorbent is proposed due to porosity and high surface area, an appropriate option for effective removal of aqueous solutions, but its use on a large scale is limited due to problems such as filtration, dispersion, and opacity and high cost of reduction [13]. Hence, magnetization, adsorbing contaminants with the help of an external magnet, can provide conditions for the optimal use of activated carbon and the production of effluent with very low opacity. Recently, the magnetic field has been widely considered due to low cost, simplicity, and proper separation rate as well as high efficiency. In this regard, there are various adsorbents, such as ion-exchange resins, zeolites, activated carbon fibers, polymeric and waste adsorbents, and even magnetic nanoparticles [14]. However, the requirement for magnetic separation of adsorbents is their synthesis or combination with nanoparticles mainly in the form of Fe_3O_4 MNPs, which are adsorbed by a magnet to combine or pollute the target and eventually separate or remove from aqueous solutions. In addition, the presence of magnetic iron oxide (Fe_3O_4) leads to chemical stability, toxicity reduction, and excellent adsorption capability [15]. The advantage of using this separation technology is that harmful substances are separated from the environment with magnetic particles, using a magnetic field. After magnetic separation, harmful compounds are easily removed from magnetic particles, and retrieved magnetic particles can be reused [16].

Ahmed and Theydan [17] investigated the adsorption of MNZ on activated carbon from an agricultural waste and showed that the adsorption rate followed a pseudo-second-order kinetic model. Also the removal process of MNZ from aqueous solutions over nanozerovalent iron (NZVI) encapsulated within poly (acrylic acid) (PAA)/poly (vinylidene fluoride) (PVDF) membranes was reported [18].

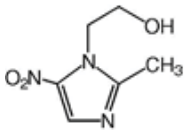
In this study, a new substrate was provided for the removal of MNZ and the in vitro conditions were optimized to increase its adsorption capacity and then to describe the adsorption mechanism and the mechanism of adsorption isotherm equations, as well as to describe the adsorption process behavior. The kinetic equations of adsorption were used in time unit and prediction of adsorption rate.

Due to the absence of any study on the adsorption of MNZ antibiotic using magnetic activated carbon nanocomposite (magnetic powdered activated carbon (PAC) and magnetic granular activated carbon (GAC)), this study was conducted to compare the efficiency of magnetic activated carbon nanoparticles (powdered and granular) in adsorbing the MNZ from the aqueous solutions.

2. Materials and methods

The materials used in this study included the pure powder of MNZ (Sigma-Aldrich, Germany), which is described in the table, powdered and granular activated carbon (Merck, Germany), 0.1 N HCL and NaOH, iron salts of $FeCl_3$ and $FeSO_4$ (Merck, German), and DMSO solution (Sigma-Aldrich, Germany). A scanning electron microscopy (SEM, SIGMA VP-500 model, ZEISS, Germany) equipped with an X-ray diffraction spectrometer (XRD) was used to study the shape, mean diameter, surface detail, and structural analysis of powdered and granular activated carbon nanoparticles. The XRD device (model Pert x, Pro, Panalytical) was used to determine the crystalline structure of nanoparticles, the Fourier transform infrared spectroscopy (FT-IR) analysis (FT-IR device, model AVATAR 370) to detect the functional groups on the adsorbent surface, the vibrating sample magnetometer (VSM) test using the vibration sampling magnetometer device (VSM 7400) was employed to measure the magnitude of the magnetic property, and the Brunauer–Emmet–Teller (BET) test was used to determine the specific surface area of the adsorbent. The BET test, using adsorption and desorption of nitrogen gas on the adsorbent, can determine the specific surface area, pore-volume, and pore size. The test was carried out by the American–Japanese device Belsorp, D-Petronik, and the energy-dispersive X-ray spectroscopy (EDS) analysis to measure the percentage of adsorbent-forming elements with the help of DayPetronik, Ranian. Table 1 describes the physicochemical properties of MNZ [1,6].

Table 1
Structure and physicochemical properties of metronidazole (MNZ)

Trade name	1-(β-Hydroxyethyl)-2-methyl-5-nitroimidazole
Chemical formula	$C_6H_9N_3O_3$
Molecular weight	171.5 (g/mol)
Water solubility	9.5 (g/L)
Pka	2.55
V_p (Pa)	4.07×10^{-7}
Molecular structure	

2.1. Preparation and modification of magnetic activated carbon nanocomposite (magnetic GAC and magnetic PAC)

The adsorbents used in this study, powdered, and granular activated carbon nanoparticles, find a magnetic property stoichiometrically by co-precipitation of iron sulfate ($FeSO_4 \cdot 7H_2O$) and iron chloride ($FeCL_3 \cdot 6H_2O$).

In the first step, 1 g of activated carbon and 100 mL of sodium hydroxide (with a purity of 49% by mass) are stirred for 2 h, and then the mixture is filtered with filter paper to remove excess sodium hydroxide. In the second step, 2.7 g of iron chloride and 1.2 g of iron sulfate are dissolved in 300 mL of DM water (which is deoxygenated by nitrogen gas and heated at 60°C–70°C). In the third step, the activated carbon impregnated with sodium hydroxide is gradually added to the iron salts solution to precipitate the iron ions present in the solution as iron oxide (Fe_3O_4) inside the activated carbon pores. At this stage, stirring is very effective in reducing the size of the deposited Fe_3O_4 nanoparticles on the activated carbon. The composite is collected by a strong magnet at the bottom of the container and washed several times with DM water to remove excess sodium hydroxide and then dried in an oven at 80°C for 1 h. PAC and GAC were mixed in alkaline solution over a specified period and added to bivalent and trivalent iron salts, and blended with nitrogen gas for deoxygenation, and thus the adsorbents were synthesized [19], and used for the adsorption experiments.

2.2. MNZ adsorption stage

The adsorption experiments were carried out in a discontinuous adsorption system using MNZ as an adsorbent by powdered and granular magnetic activated carbon adsorbents. We prepared MNZ stock solution by dissolving the pure antibiotic powder in double distilled water. The amount of drugs was calculated based on molecular mass and its purity, and the stock solution was prepared at a concentration of 100 mg/L.

The experiment was performed discontinuously in 100 cc flasks on a shaker. The stock solution was used to prepare various concentrations of MNZ. To perform experiments, at first, 50 cc of the sample was taken at a specific concentration, and after adjusting the pH, a certain adsorbent dosage was weighed and added to the solution, and the mixing was carried out on a shaker at different contact times and concentrations. In this regard, the contact time in the reactor (5, 10, 15, 30, 60, 90, 120, and 200 min) and the initial pH values (3, 5, 7, 9, and 11), the initial MNZ concentration (10, 15, 20, 25, and 30 mg/L), and the adsorbent dosage (0.2, 0.5, 1, 2, and 3 g/L) were adjusted with a stirring rate of 300 rpm and the ambient temperature. To measure residual MNZ concentration, a calibration curve was drawn at different concentrations of MNZ (0.1, 0.15, 0.25, 0.5, 1, 2, 3, 5, 7, and 10 mg/L), whose R^2 was equal to 0.99. Then, the residual MNZ concentration was measured using a spectrophotometer device at a wavelength of 320 nm [20]. The isotherms of adsorption were investigated using Langmuir and Freundlich models. The kinetics of adsorption was investigated using pseudo-first-order and pseudo-second-order equations.

The Freundlich equation states the adsorption on heterogeneous surfaces in terms of adsorption energy. Indeed, the Freundlich model assumes a monolayer adsorption but in a no uniform manner. The following equation represents the mathematical model of Freundlich adsorption isotherm.

$$q_e = KC_e^{1/n} \tag{1}$$

where q_e is the mass ratio of the solid phase, which is the adsorbed mass/adsorbent mass ratio (mg/g), C_e is the equilibrium concentration (mg/L), K is the experimental constant (Freundlich equation coefficient).

In the Langmuir adsorption isotherm, the adsorption is monolayered and the adsorption areas on the adsorbent surface are uniform with the equal adsorption capacity. Moreover, the connections and bonds of adsorption are reversible. The mathematical model of Langmuir adsorption isotherm is shown by the following equation.

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{2}$$

where $q_{\max}$ is the maximum adsorption capacity (mg/g), K_L is the experimental constant (Langmuir equation coefficient). C_e and q_e parameters are similar to Freundlich adsorption isotherm.

3. Results and discussion

3.1. Charactristics of magnetic PAC and magnetic GAC

Investigating spectra related to the profile of magnetic adsorbents (magnetic PAC and magnetic GAC). The adsorbents were characterized by specific diagnostic techniques, whose findings are illustrated as follows.

The FT-IR spectrum shows that the presence of the peak adsorption band of iron ferrite nanoparticles below 600 cm^{-1} is related to $Fe^{2+} \leftrightarrow O$ and $Fe^{3+} \leftrightarrow O$, indicating the formation of Fe_2O_4 or Fe_3O_4 nanostructures. In fact, it is a proof of the Fe–O vibration. The presence of peaks at the range of 1,000–1,300 and 2,000–3,000 cm^{-1} is related to C=H and C–O stretching modes and the peaks above 3,000 cm^{-1}

is related to O–H vibration groups in the composition, all confirming the presence of existing functional groups in the nanostructure. These changes in the IR spectrum show that the desired nanoparticles have been successfully synthesized (Fig. 1).

The nanoparticles were studied by a magnetometer, sample vibration (VSM) at room temperature, to evaluate the magnetic properties. The plot of the magnetic moment vs. magnetic field (M–H ring) in the 300 K for magnetic activated carbon nanoparticles is given in Fig. 2 The magnetization curve shows that the nanoparticles have super paramagnetic nature, whose magnetic saturation value is 30.717 emu/g for the powdered magnetic activated carbon nanoparticles, and 32.992 emu/g for the granular magnetic activated carbon nanoparticles. The synthesized adsorbent is dispersed in water, can be easily collected by the external magnetic field in a few minutes, and can then be re-dispersed with a slight flicker. The results show that the particles have a good magnetic property, and can be re-dispersed, which indicates a simple application of magnetic adsorption.

The crystalline structure of the nanoparticles by the XRD is represented in Fig. 3. The XRD patterns provide specific peaks for the magnetic PAC at 272.30 (2 2 0), 659.35 (3 1 1), 301.37 (2 2 2), 341.43 (4 0 0), 778.53 (4 2 2), 331.57 (3 3 3), 949.62 (4 4 0), 603.26 (6 0 0), and 402.18 (1 1 1), indicating the consistency with the JCPDS database.

The XRD patterns indicate specific peaks for magnetic GAC at 272.30 (2 2 0), 659.35 (3 1 1), 301.37 (2 2 2), 341.43 (4 0 0), 778.53 (4 2 2), 331.57 (3 3 3), 949.62 (4 4 0), 603.26 (3 0 0), and 402.18 (1 1 1), which are consistent with the JCPDS database.

The shape and size of the nanoparticles were determined by SEM.

The SEM is widely used to determine the morphology, shape, and particle size estimation in the micro and nano dimensions. These images represent the formation of nano-scale structures. The surface properties of magnetic activated carbon obtained from the SEM in 15 kev are shown in Fig. 4. The figure shows porosity on the magnetic activated carbon surface with varied sizes, almost uniform dispersion, and a diameter between 20 and 50 nm.

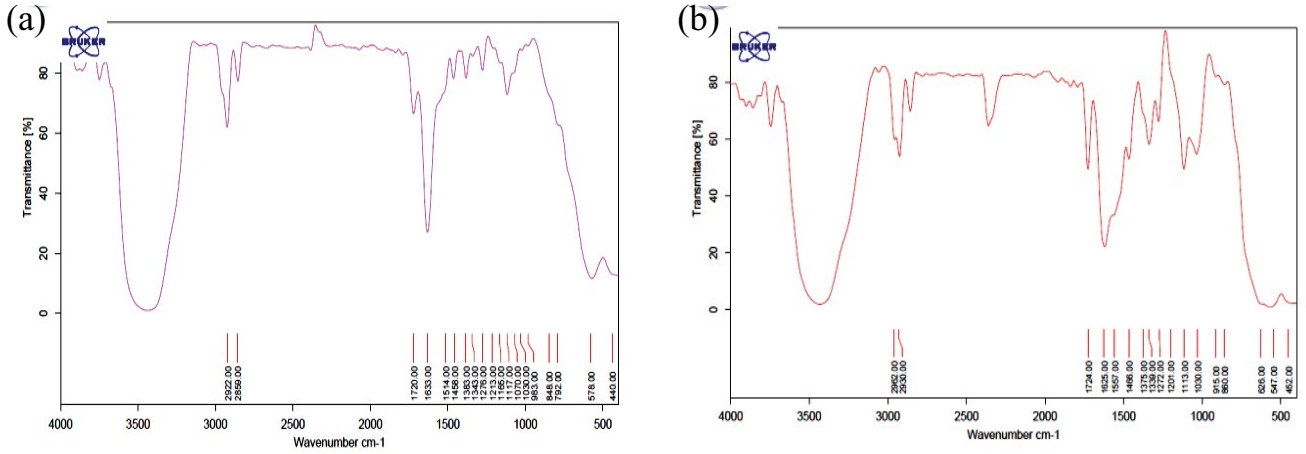


Fig. 1. FT-IR spectrum of magnetic PAC (a) and magnetic GAC (b).

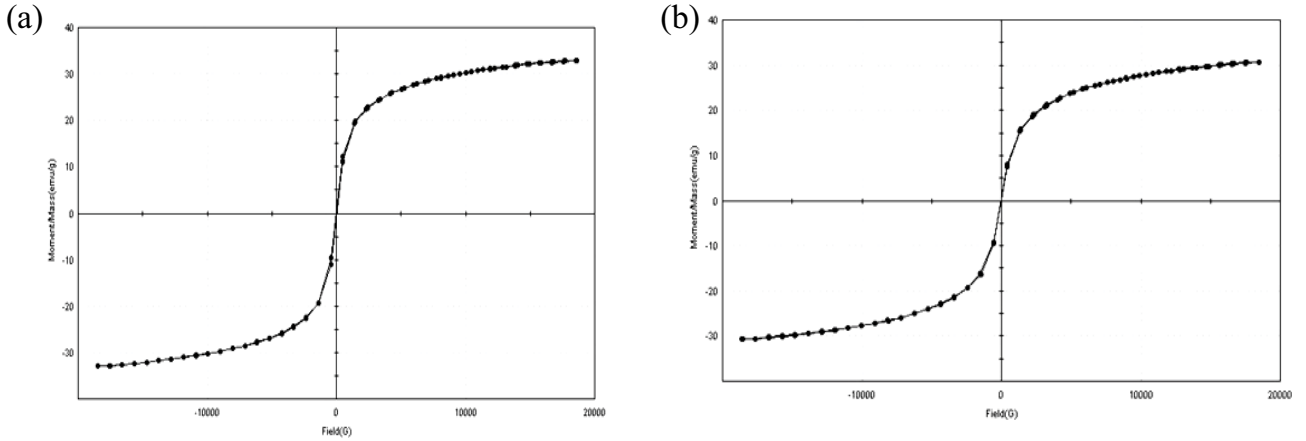


Fig. 2. VSM curve of magnetic PAC (a) and magnetic GAC (b).

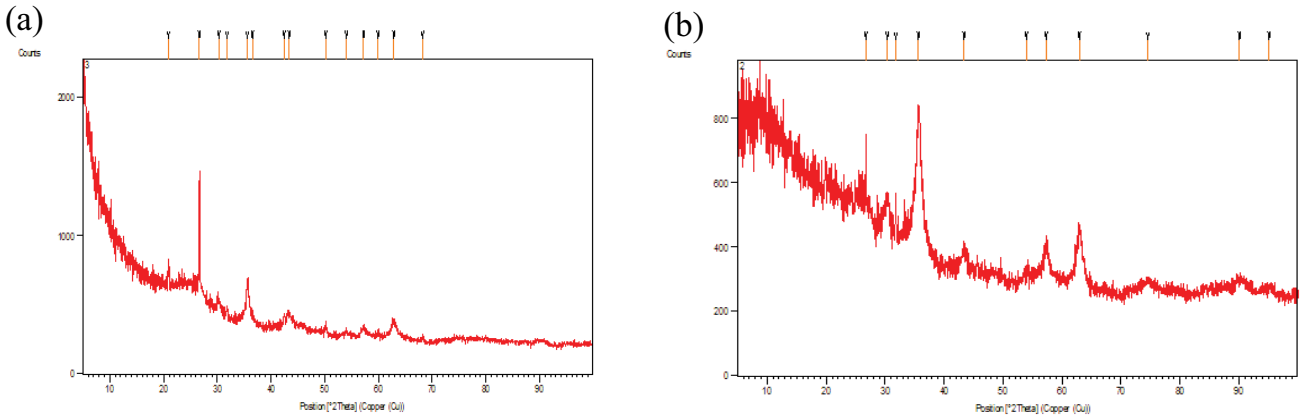


Fig. 3. XRD spectrum of magnetic PAC (a) and magnetic GAC (b).

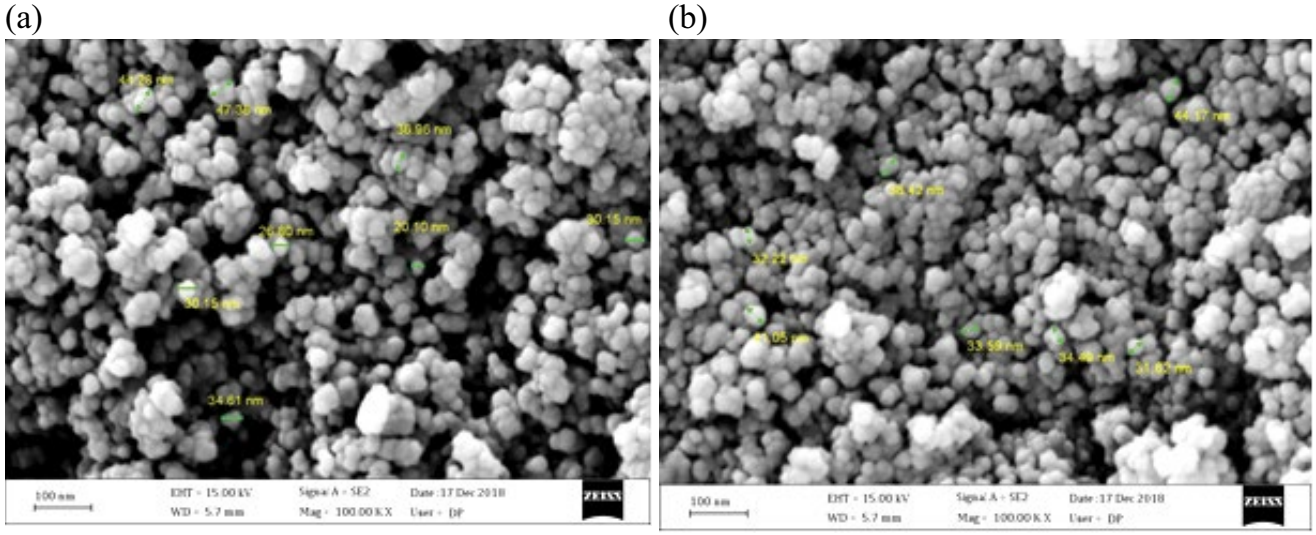


Fig. 4. SEM image of magnetic PAC (a) and magnetic GAC (b).

The SEM images of these nanoparticles indicate that the size of the magnetic PAC was in the range of 20.10–41.05 nm, which changed to 31.44–43.67 nm after the MNZ adsorption; and the size of the magnetic GAC was in the range of 27.98–46.12 nm, which increased to 24.38–51.95 nm after the MNZ adsorption.

The specific surface area test (BET) showed that the specific surface area and the pore volume were 109.91 m^2/g, and 0.2552 cm^2/g for the magnetic PAC, and 561.16 m^2/g and 0.2898 cm^2/g for the magnetic GAC (Fig. 5). This type of isotherm is used for porous materials. It indicates that the material has very thin pores and capillaries, in which case the adsorption rate is significantly increased and the adsorbed material is concentrated on the surface. This type of isotherm is often observed for industrial catalysts and the corresponding curve is used to determine the pore size distribution. The reversibility of the adsorption reaction is also illustrated in the diagram (Fig. 5).

The EDS analysis in Fig. 6 shows that iron, carbon, and oxygen elements had a percent weight of 44.2, 37.9, and 17.9 for the powdered magnetic activated carbon nanoparticles, and 77.9, 16.8, and 5.3 for the granular magnetic activated carbon adsorbents, respectively.

3.2. Effect of pH

According to the results of the experiments on powdered and granular magnetic activated carbon adsorbents coated with iron oxide magnetic nanoparticles, it was found that the reduction of pH resulted in an increase in the efficiency of magnetic PAC nanoparticles and this nanocomposite had the highest removal efficiency at pH = 3. At high pH values, negatively charged hydroxyl functional groups on the surface of adsorbate can cause the repulsive of MNZ anions. Increasing pH reduces MNZ adsorption efficiency by magnetic PAC, while low pH values, due to the negative charge of MNZ, increase electrostatic forces between adsorbent and pollutant, thus enhancing the adsorption efficiency.

According to the adsorption curve of MNZ by magnetic GAC (Fig. 7a) it is shown that the antibiotic adsorption level is higher at lower pH values in the initial contact

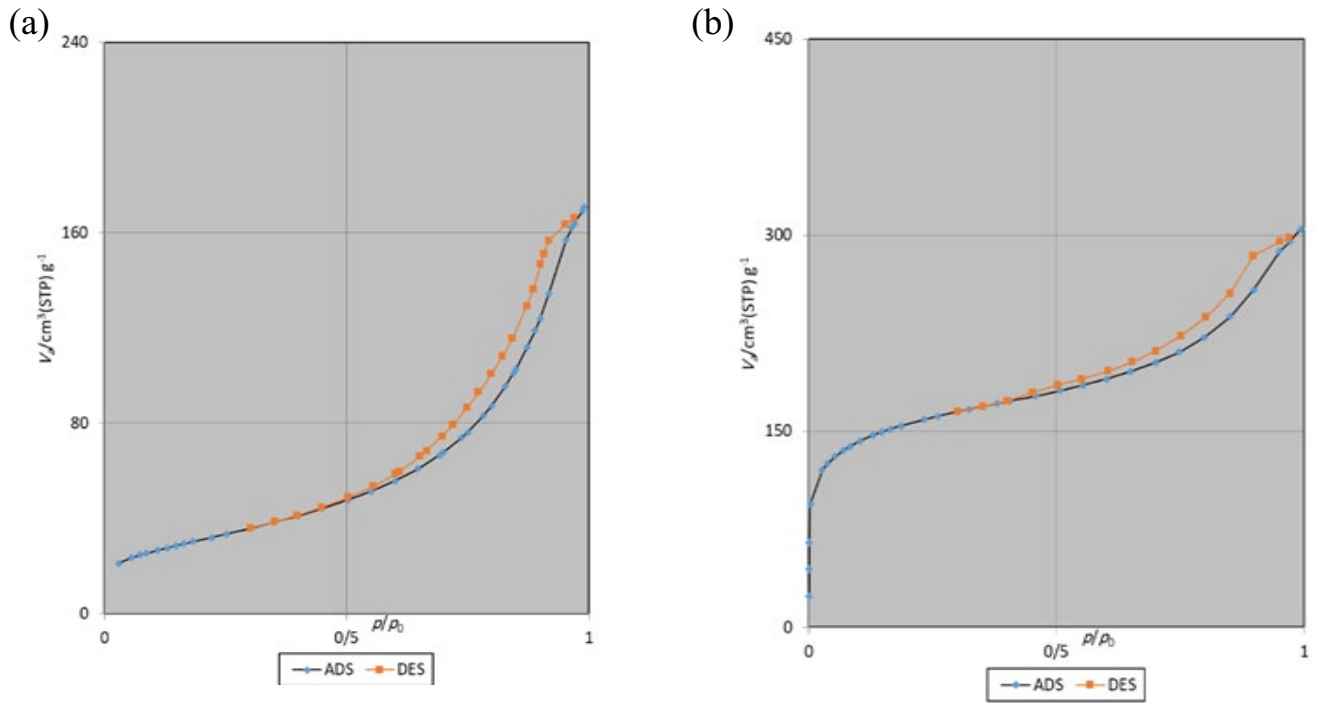


Fig. 5. Adsorption and desorption hysteresis of magnetic PAC (a) and magnetic GAC (b).

time, but this adsorbent has high removal efficiency at all pH values with prolongation of the contact time; for this reason, pH = 7 was selected as the optimal pH value that could reduce the consumption of laboratory materials and to advance the test in the natural conditions.

pH of solution is an important parameter that determines the adsorption amount of contaminant over the sorbent. According to result, pH_{zpc} for powder activated and magnetic granule carbon nanoparticles is 9 and 7, respectively. These results show that the level of magnetic powder activated carbon nanoparticles is negative per pH > 9; therefore, the adsorption amount of materials such as MNZ bearing negative charge reduces in alkaline pHs. In addition, it is more probable that higher pHs due to abundance of hydroxyl ion create repulsion between the sorbent level of magnetic powder activated carbon and MNZ, both possessing negative charges which might be the reason for little adsorption of MNZ in higher pHs. The reduction of removal efficiency in alkaline pHs can be the result of electrostatic repulsion between the negative activated carbon level and anions for adsorption over the activated sites on the sorbent level. In acid pHs, due to the released positive ions from sorbent level, attraction force is created between ions and negative MNZ that adsorb antibiotic and increase removal efficiency by magnetic powder activated carbon. According to the experiments, pH-optimum is 3 for powder activated carbon which is in line with Kakavandi being equal with optimal 5 [21].

Fang et al. [1] and Chen et al. [22] reported pH = 3 as pH-optimum in studying MNZ adsorption by nanoscale zero-valent iron.

According to the diagram of MNZ adsorption by magnetic GAC, the amount of antibiotic adsorption in lower pHs at initial times is higher, but the contact of this sorbent in all pHs possesses high removal efficiency and solution pH does not have any effect on removal efficiency. If adsorption occurs for all pHs during the adsorption process of contaminants by sorbents, reduction, or increase in adsorption on the sorbent will not be due to the electrostatic attraction but it is related to the chemical attraction force with enough energy to overcome ionic repulsion force. To do so, pH = 7 is selected as pH-optimum to reduce the consumption of laboratory materials to regulate pH and develop test in natural conditions. Rivera-Utrilla et al. [23] showed that pH of solution does not have a certain effect on the removal efficiency of MNZ by means of activated carbon. In the study performed by Nasseh et al. [20]. Considering the efficiency of the newly synthesized nanocomposites in MNZ adsorption, the highest percentage of the pollutant adsorption was observed at pH = 7 [20].

3.3. Effect of adsorbent dosage

As shown in Fig. 8a, increasing the adsorbent dosage of magnetic GAC increases the efficiency of MNZ removal. The adsorbent dosage was in the range of 0.2–3 g/L. In the doses of 1, 2, and 3 g/L, the increase in adsorbent dosage had no significant effect on the removal efficiency, because the number of active sites on the adsorbent is increased and further active site can be presented to the metal ions by increasing the adsorbent dosage. Therefore, the number of trapped metal ions in the adsorbent phase rises. According to this, 1 g/L of adsorbent was selected. This may be due to an increase in adsorbent surface or an increase in the availability of MNZ molecules to activated carbon pores. In a study of Rivera-Utrilla et al. [23] on the removal of MNZ

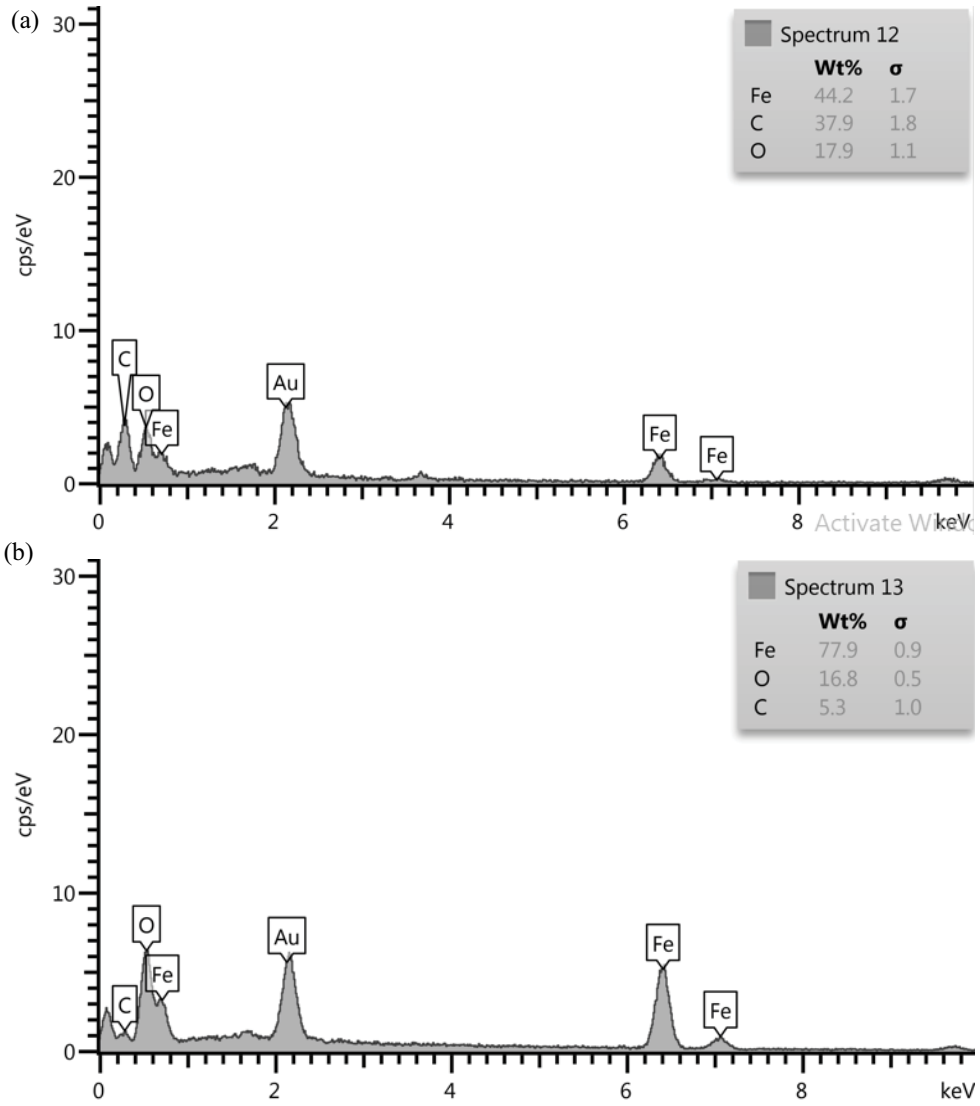


Fig. 6. EDS analysis of magnetic PAC (a) and magnetic GAC (b).

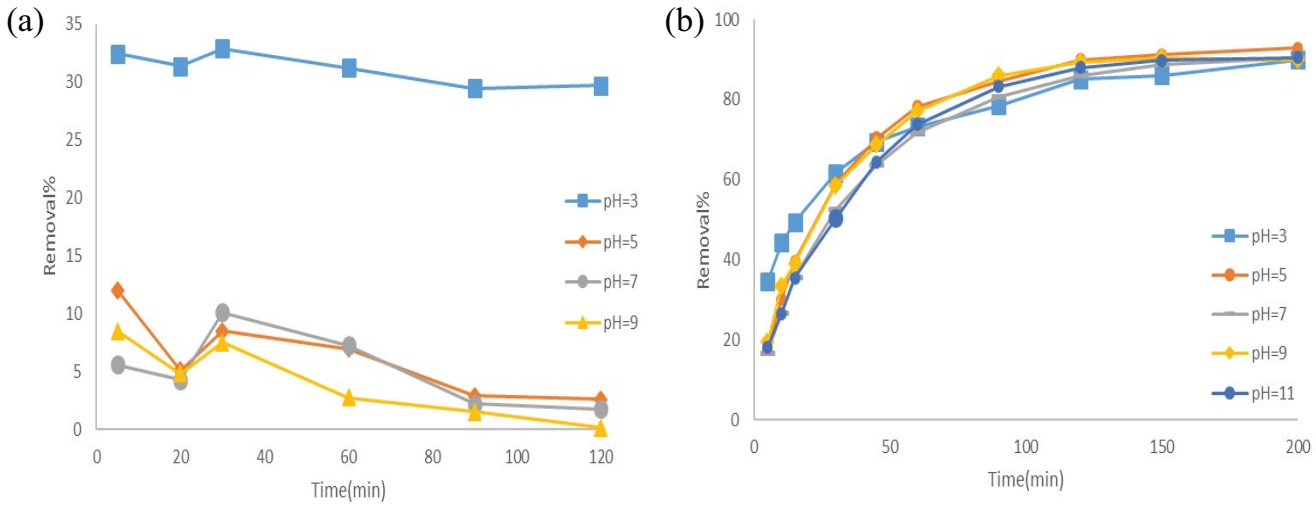


Fig. 7. Effect of changes in pH values in the efficiency of metronidazole removal by magnetic PAC (a) and magnetic GAC (b) [metronidazole concentration = 20 mg/L, adsorbent dosage = 1 g/L, and v = 300 rpm].

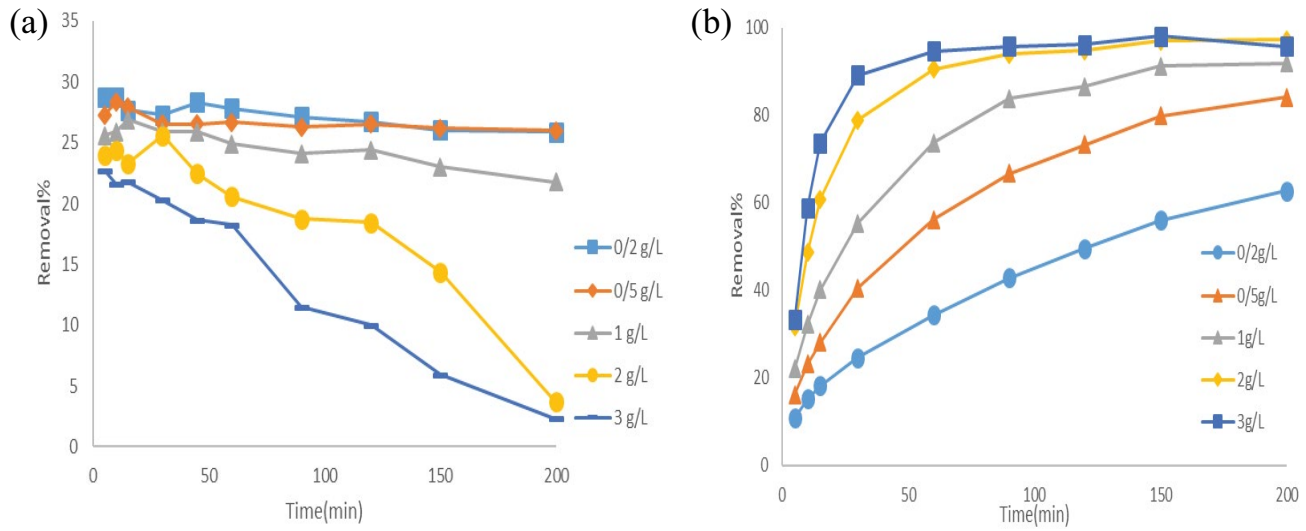


Fig. 8. Effect of adsorbent dosage in the efficiency of metronidazole removal by magnetic PAC (a) and magnetic GAC (b) [metronidazole concentration = 20 mg/L, pH (magnetic PAC) = 3, pH (magnetic GAC) = 7, and v = 300 rpm].

by activated carbon, and also in a study of Abdoli et al. [24] on the removal of MNZ by activated carbon coated with magnesium oxide, increased adsorbent dosage enhanced the removal efficiency of nitroimidazole.

Depending on Fig. 8b of MNZ removal by magnetic PAC, according to the chromogenic nature of the powdered activated carbon and its solubility in water, the removal efficiency decreases by increasing the adsorbent dosage. For this reason, the lowest adsorbent dosage was selected at 0.2 g/L as the optimal dosage. In a study of Salehnia et al. [25] the increase in adsorbent dosage had no effect on the removal efficiency.

Magnetic GAC had the highest efficiency of adsorption of MNZ at 3 g/L dose (97/24%) and magnetic PAC also had the highest MNZ adsorption at 0.2 g/L (29/94%).

3.4. Effect of contact time and concentration

Prolonging the contact time increases the removal efficiency of granular activated carbon coated with iron oxide nanoparticles, and the removal efficiency has a steady gradient from 90 min later. It should be noted that the contact time had no much effect on the removal efficiency of powdered magnetic activated carbon. The optimal contact time for magnetic PAC and magnetic GAC was obtained at 90 and 30 min, respectively, as shown in Fig. 9. Increasing the initial MNZ concentration reduces the removal efficiency and increases the adsorption capacity, due to the occupation of active adsorption sites on the nanoparticle surfaces. Increasing the MNZ concentration gradually leads to the desorption process from the surface of nanoparticles.

Given the results presented in the contact time and removal efficiency curves, it is clear that the adsorption of MNZ by the magnetic GAC is fast in the first minutes and then there is a steep slope in the curve that is related to physical adsorption. Then, the slope becomes a bit milder due to resistance to penetration, so that after occupation of free sites by antibiotics, creation of repulsive forces between the fluid bulk, and the adsorbed molecules and reduction of removal efficiency, the adsorption reaches saturated state finally. From this time onwards, the removal efficiency does not increase with time, which is the time of equilibrium, and the removal efficiency after that is kept constant or slightly reduced. This decrease in adsorption may be due to desorption [26]. Akbar et al. [27], and Altun and Pehlivan [28] also achieved similar results. Therefore, contact time had no significant effect on the MNZ removal by magnetic PAC, and the contact time of 30 min was considered as optimum. These results are in line with a study by Salehnia et al. [25].

Fig. 9 shows that an increase in the initial antibiotic concentration reduces the efficiency of MNZ removal, because the adsorbents had a limited number of active sites that are saturated at high concentrations. Reducing the initial antibiotic concentration reduces the amount of adsorbate and causes the adsorption of a high percentage of MNZ [21,29]. Because the concentration of the solution is a limiting factor for adsorption at low concentrations, the adsorption capacity has little effect on the antibiotic removal efficiency, and vice versa, the adsorbent mass unit plays a more important role in adsorbing MNZ at higher concentrations, due to the increased concentration of MNZ for binding sites available on the adsorbent surface. Investigations on the adsorption of various antibiotics by different adsorbents frequently examined the effect of the initial antibiotic concentration on the removal efficiency of these pollutants. In most cases, the results of studies have shown that increasing antibiotic concentration in the solution reduces the removal efficiency.

The pharmaceutical industry wastewaters often have different concentrations of antibiotics. Therefore, the study of the efficacy of MNZ removal as a function of initial antibiotic concentration is very important. The effects of the initial MNZ concentrations were observed in the range of 10–30 mg/L. At the concentrations of 10, 15, 20, 25, and 30 mg/L, the removal efficiency was 93%, 93.001%,

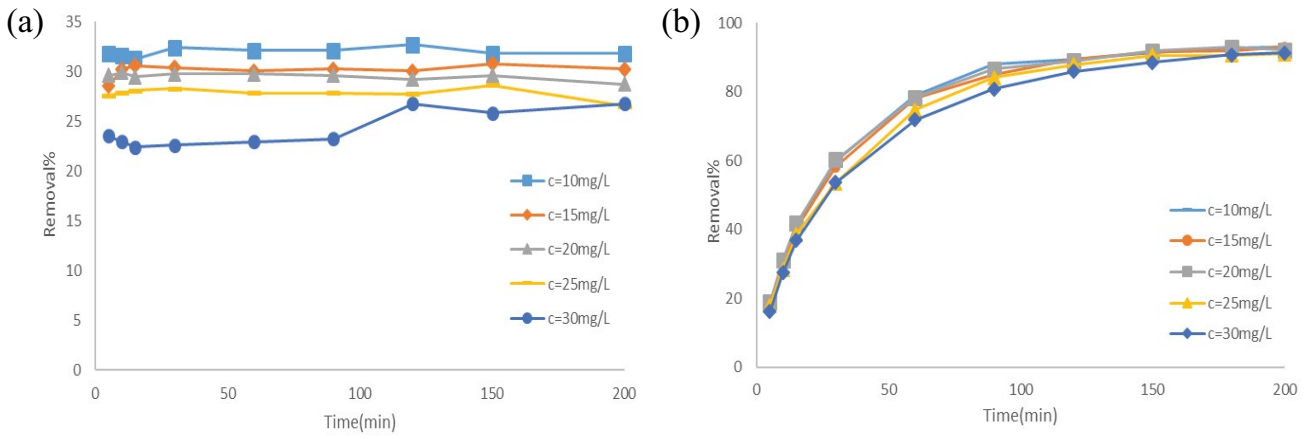


Fig. 9. Effect of the contact time and initial metronidazole concentration in the efficiency of metronidazole adsorption by magnetic PAC (a) and magnetic GAC (b) [pH (magnetic PAC) = 3, dose (magnetic PAC) = 0/2 g/L, pH (magnetic GAC) = 7, dose (magnetic GAC) = 1 g/L, and v = 300 rpm].

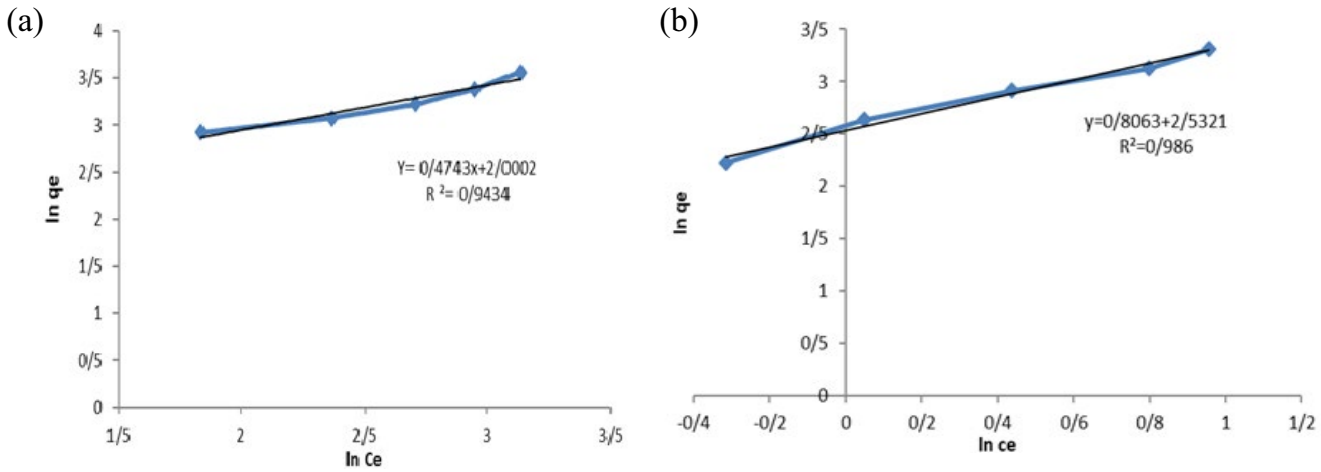


Fig. 10. Results of equilibrium data fit to determine the isotherms of magnetic PAC (a) and magnetic GAC (b).

92.24%, 91.11%, and 91.33% using the magnetic GAC as well as 31.8%, 30.24%, 28.71%, 26.53%, and 26.77% using the magnetic PAC adsorbent, respectively. Increasing initial pollutant concentration in optimal conditions reduces the removal efficiency, which is similar with studies performed by Bahrami Asl et al. [30] and Seidmohammadi et al. [31] in removing MNZ, which showed that the rate and efficiency of the reaction are affected by increasing the initial pollutant concentration.

3.5. Study of adsorption isotherms

In studies on adsorption of pollutants on various adsorbents, determination of adsorption isotherm is one of the most important characteristics to be considered. In fact, isotherm parameters provide important information for designing and modeling the adsorption process. The adsorption isotherms are often used to explain the adsorption of materials on the adsorbent. This study examined the Langmuir and Freundlich isotherms for magnetic PAC and magnetic GAC adsorption.

As shown in Fig. 10, the correlation coefficient also shows that the MNZ adsorption behavior on both adsorbents is more consistent with the Freundlich isotherm. Therefore, the surface of the nanoparticles studied is heterogeneous and the MNZ is adsorbed as multilayered manner. In other studies, various results have been obtained due to the removal of various pollutants with magnetic activated carbon nanoparticles. According to the nature of various pollutants, other authors reported different isotherm models. In a study by Liu et al. [12] on the adsorption of cefalexin antibiotic by the activated carbon, the Freundlich model was found to be suitable for the adsorption process. Hu et al. [32] analyzed the MNZ adsorption on the modified magnetite with polymer and reported that MNZ adsorption on the magnetite with Freundlich and Langmuir models.

3.6. Study of adsorption kinetics

The chemical kinetics indicates the rate of chemical reactions. In this study, the rate constant of MNZ adsorption by powdered and granular magnetic activated carbon

adsorbents was matched with pseudo-first-order and pseudo-second-order kinetics models and the most appropriate model was determined.

One of the important factors for explaining the adsorption system and determining the optimal contact time is to determine the adsorption process rate.

Adsorption kinetics provides important information about the mechanism of adsorption, the rate of adsorption of the adsorbed material, and the time control of the adsorption process [33]. In the pseudo-first-order kinetic model, it is assumed that the rate of change in the uptake by time is directly proportional to the changes in saturation concentration and the amount of uptake by time [34]. In the pseudo-quadratic model, it is assumed that the chemical adsorption controls the adsorption phenomenon and the rate of occupation of the adsorption sites is proportional to the square of the number of unoccupied sites [35].

In this study, the laboratory data showed that the MNZ adsorption follows the second-order equation. The second-order reactions proceed at a speed proportional to the second exponent of the primary material [35].

The kinetics of MNZ adsorption by the powdered and granular magnetic activated carbon adsorbents was the concentration of 20 mg/L and the adsorbent dosage of 0.2 g/L for the powdered magnetic activated carbon, and 1 g/L for the granular magnetic activated carbon in the contact time of 5–90 min, and pH = 3 for magnetic PAC and pH = 7 for magnetic GAC. The adsorption data from pseudo-first-order and pseudo-second-order models were used to determine the kinetics of the reaction.

$$\ln\left(q_e - q_t\right) = \mathrm{Ln}\, q_e - K_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where q_e is the equilibrium concentration of adsorbent phase (mg/g), q_t is the antibiotic concentration at the time t (mg/g), and k_1 and k_2 are the rates constant of pseudo-first-order and pseudo-second-order equations. Based on the results of the adsorption kinetics (Fig. 11), the correlation coefficients in the pseudo-first-order and pseudo-second-order kinetics were 0.9889 and 0.9893 for the powdered magnetic activated carbon, and 0.9698 and 1 for the granular magnetic activated carbon.

The values obtained from the correlation coefficient of the kinetic models of the MNZ adsorption process on powdered and granular activated carbon nanoparticles indicate that the adsorption process follows the pseudo-second-order kinetic model.

The pseudo-quadratic model shows position fit using revised experiences and can follow MNZ pseudo-quadratic model. These explanations show that you can succeed and work with honor. In fact, Greece is in the solution through a chemical bond that binds you covalently to the adsorbent surface.

The pseudo-quadratic model fits better with the experimental data and the MNZ uptake follows the pseudo-quadratic model. This suggests that the uptake of antibiotics by activated carbon occurs through chemical processes that are related to electron sharing or exchange. In fact, the ions in the solution are bonded to the adsorbent by chemical bonding, which is usually covalent.

In research by Putra et al. [36] on the adsorption of amoxicillin on the granular activated carbon, the adsorption behavior followed the pseudo-second-order kinetics.

According to Table 2, the comparison different adsorbent for MNZ adsorption, magnetic PAC, and magnetic GAC had a high adsorption capacity.

4. Conclusion

The efficiency of MNZ adsorption by magnetic GAC is not affected by the acidity of the media and is increased by prolonging contact time and increasing adsorbent dosage as well as decreased by increasing the initial MNZ concentration. The removal of this pollutant by magnetic PAC is higher at lower pH values and the removal of the pollutant is not dependent on the contact time. Increasing the adsorbent dosage and the MNZ concentration reduces the removal efficiency. Both adsorbents follow the adsorption isotherms of the Freundlich model and pseudo-second-order kinetics.

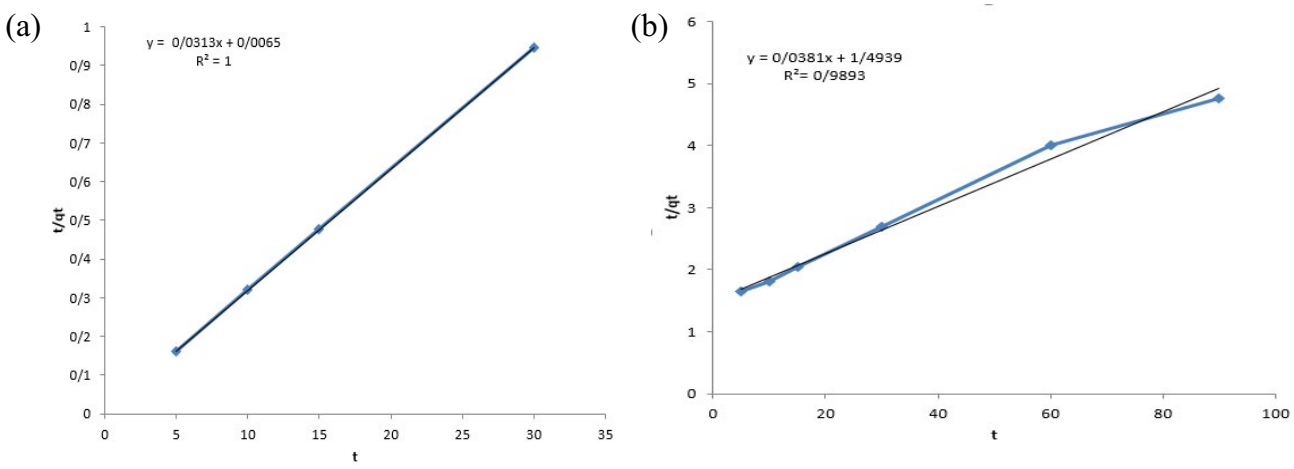


Fig. 11. Results of the kinetics of magnetic PAC (a) and magnetic GAC (b).

Table 2
Comparison of MNZ maximum capacity onto different adsorbents

Sorbent	T (K)	t (h)	Dose (g/L)	q_{max} (mg/g)	Reference
GAC (Fe_3O_4)	298	1.5	1	83/52	This study
PAC (Fe_3O_4)	298	0.5	0.2	13/95	This study
MWCNT	298		1	49/85	[37]
MWCNT–HNO_3	298		1	54/40	[37]
Petroleum coke-carbon	298	192	1.0	287.53	[23]
Natural clinoptilolite	298	24	50	1.19	[38]
Commercial-carbon	298	192	1.0	328.61	[23]
Attapulgite clay	310	2	50	7	[39]
Siris seed pods-carbon	323	1.5	0.5	196.31	[17]
$FeNi_3/SiO_2/CuS$	293	3	0.1	147	[20]

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