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Adsorption Characteristics of Sulfamethoxazole and Metronidazole on Activated Carbon

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In this work, the removal of two pharmaceuticals i.e., an antibiotic drug, sulfamethoxazole and an antiparasitary drug, metronidazole onto activated carbon from aqueous solutions were studied. Batch adsorption studies were carried out at different pH, adsorbent concentrations, and temperatures. Adsorption isotherms have been modeled by Freundlich, Langmuir, and Dubinin-Raduskevitch (D-R) equations. The adsorption of these drugs was better represented by the Langmuir equation. The effect of the solution pH on the adsorbed amount of SM and MN was studied by varying the initial pH under constant process parameters at equilibrium conditions. The increase in pH of the solutions caused to decrease adsorption of SM and MN on AC. The kinetics of adsorption in view of three kinetic models, i.e., the first-order Lagergren model, the pseudo-second-order model, and the intraparticle diffusion model was discussed. The pseudo-second-order kinetic model describes the adsorption of both sulfamethoxazole and metronidazole on activated carbon. Rate constants for adsorption and desorption, and surface coverage have been evaluated with the help of another approach of the kinetic scheme. The effect of temperature was also studied at the range between 293 and 313 K. Thermodynamic parameters were calculated. The negative value of enthalpy change (ΔH°) indicated the exothermic nature of the adsorption process, and the negative values of free energy change (ΔG°) were indicative of spontaneity of the adsorption process. In this work adsorption behaviour of SM and MN on activated carbon was also evaluated by the data obtained from column experiments.

Keywords activated carbon; metronidazole; pH effect; sulfamethoxazole; surface coverage

INTRODUCTION

Recently, pharmaceuticals have been detected in the effluent of sewage treatment plants, in surface waters, and in groundwaters worldwide. In industrial countries most human use antimicrobials and other pharmaceuticals reach the aquatic environment, unchanged or transformed, mainly via discharge of effluents from municipal wastewater treatments plants. The residual concentrations of

these bioactive compounds in the treated effluents depend on their removal during wastewater treatment. They can potentially pose a hazard for aquatic and soil organisms if the removal is incomplete (1–15).

The occurrence of antibiotics in the environment has therefore received considerable attention. Antibiotics are an important group of pharmaceuticals in today's medicine and particularly important due to the possible spread and maintenance of bacterial resistance. Antibiotics are regarded as "pseudopersistent" contaminants due to their continual introduction into the ecosystem. Another concern about antibiotic residues in the environment is their potential adverse effects to various organisms (16–20).

Sulfamethoxazole (SM) is a sulfonamide bacteriostatic antibiotic and commonly used to treat urinary tract infections. Metronidazole (MN) is a nitroimidazole anti-infective medication very effective for the treatment of intestinal and intraabdominal infections. Toxic effects of MN, which is the most important nitroimidazoles in low mg/L concentrations against algae and daphnids have been reported recently (21–24). Some physical characteristics and molecule structures of SM and MN are shown in Table 1.

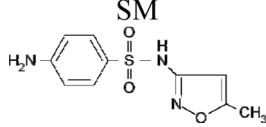
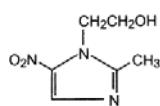
Activated carbons (AC) are widely used as adsorbents in technologies related to pollution abatement, pharmaceutical, and food industries due to their highly porous structure and large adsorption capacity (25–32). Furthermore, drug poisoning is a very common clinical problem and many drugs used in the treatment of a variety of diseases do not have a specific antidote for the management of accidental poisoning caused by the drugs. In cases where no specific antidote exists, prevention of further absorption by oral administration of adsorbents may be of immense benefit in the management of drug over dose and/or poisoning. It is well known that oral administration of the AC has been successfully applied in the cases of overdosing different pharmaceuticals (33–36).

Within the above scope, the present work intends to carry out the adsorption of two drugs having a different molecular structure, i.e., SM and MN on AC. The effects of the adsorbent dose, pH, temperature, initial drug

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TABLE 1
Chemical structures and characteristics of SM and MN

Molecular structure	Molecular formula	Molecular weight (g/mol)	Water solubility (mg/L) at 298 K	pKa at 298 K
	C ₁₀ H ₁₁ N ₃ O ₃ S	253.28	600 ^a	1.7 (pK ₁) ^b 5.6 (pK ₂) ^b
	C ₆ H ₉ N ₃ O ₃	171.15	10500 ^c	2.62 ^d

^{a,b,c,d} Were taken from the literatures (37), (38), (39), and (40) respectively.

concentration, equilibrium time, and adsorption kinetics have been studied. For evaluating various kinetic and adsorption parameters of the adsorption process, we attempted to apply the adsorption rate expression model to the current study and the results are discussed. Adsorption in column is the most common and efficient way for purification of wastewater. With this purpose column experiments were also carried out in this study.

MATERIALS AND METHOD

Coal based AC was purchased from Norit Nederland B.V. and used in powder form. AC was heated at 378 K for 24 hours to remove moisture and stored in airtight containers. Chemical and physical characteristics of activated carbon used in this study such as BET surface area, volume of micropores, and point of zero charge of the adsorbent are 851 m²/g, 0.239 cm³/g and 2.8 respectively with the elemental analysis of the adsorbent quoted at C: 65.30%, N: 1.84%, H < 1.0% (w/w). Chemical and physical characteristics of AC were done by Turkish Scientific and Technical Research Center. SM and MN were obtained from Sigma and Fluka respectively. All reagents used were of the highest purity available (>98%) and used without further purification. All stock solutions were prepared by dissolving weighed amount of substances with double distilled water and used to prepare the test solutions of different concentrations by diluting. Reagent grade HCl and NaOH solutions were used to adjust the pH of the test solutions for pH effect studies.

Procedure

Laboratory batch studies were conducted at different adsorbent concentrations, initial adsorbate concentrations, pH, and temperatures. The method to do adsorption consist of shaking a known volume of SM and MN solutions of definite concentration containing 0.01 g of AC for about 5 hours of SM and 3 hours of MN which were found to be

a sufficient time for an equilibrium to be attained. In each experiment excluding the effect of the adsorbent dose study, 0.01 g of adsorbent contacted with 125 mL of adsorbate solution in a 250 mL flask at a desired temperature was shaken in a thermostat rotary shaker at constant agitation speed (250 rpm) for predetermined time intervals. After the flasks were successfully removed, centrifugation was used to separate the liquid from the solid. Centrifugation was conducted at 4000 rpm for 5 minutes.

Analysis

Residual concentration of substances in supernatant liquid were recorded with an UV-Visible Spectrophotometer Shimadzu 2100S at the wavelength of 268 and 320 nm for SM and MN, respectively. The equilibrium experiments were conducted at 298 K and thermodynamic studies were evaluated at four different temperatures. The experiments were conducted in triplicate under identical conditions and were found reproducible (experimental error within 3%). In order to calculate the concentration retained in the adsorbent phase (q, mg/g), the following equation was used:

$$q = (C_0 - C)V/W_s \quad (1)$$

where, C₀ is the initial concentration of the adsorbate (mg/L) and C is concentration of the adsorbate (mg/L) at any time (t). V is the volume of the solution (L) and W_s is the mass of activated carbon (g) used in the experiments.

Column Experiments

2.5 g of adsorbent was fixed in the column and the column was fully filled with distilled water for 24 hours in order to expelling air exist among adsorbent particles. Then the column was flushed with distilled water. The adsorbate solution was pumped vertically downward inside the column at constant flow rate. The experiments were carried out using three different flow rates (0.8 L/h, 1.2 L/h, and

1.8 L/h) at constant concentration (200 mg/L for SM and MN) to show the effect of the flow rate on the column capacity. When C/C_0 ratio reached a constant value ($\frac{C}{C_0} = 1$), the experiments were considered to be finished. Concentrations were measured with the method given above.

RESULTS AND DISCUSSION

Effect of Adsorbent Dose

The effect of the adsorbent dose on the removal of SM and MN was studied with the adsorbent dose varying from 0.0025 to 0.1 g/125 mL at 298 K and fixed adsorbate concentration (20 mg/L). The study shows an enhancement in adsorption with the increase in dose of the adsorbent. As seen in Fig. 1, when the amount of AC is increased from 0.005 to 0.01 g, the adsorbed amount of drug increased from 71.25 to 138.5 mg/g for SM and from 62.29 to 102.91 mg/g for MN, respectively. It can be attributed to the greater availability of the active sites or surface area at higher adsorbent doses.

Effect of Contact Time

Figure 2 shows the variation of concentration of SM and MN with different contact times at different initial concentrations at 298 K. The concentrations of SM and MN decreased with time. As seen in Fig. 2 while the concentration of SM decreased with time up to 290 minutes the concentration of MN decreased with time up to 150 minutes and then the curves become flattened i.e., the equilibrium time of MN is much quicker than that of SM. It has also been observed that the equilibrium time

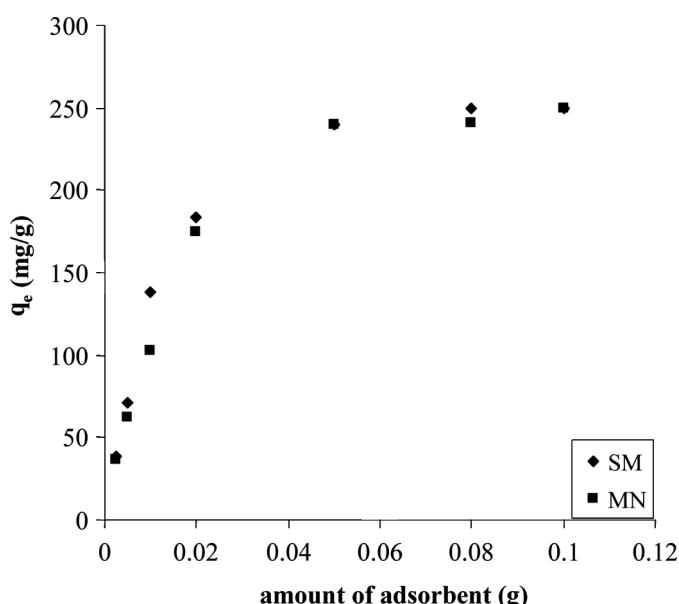


FIG. 1. Effect of adsorbent dose on the adsorption of SM and MN (20 mg/L).

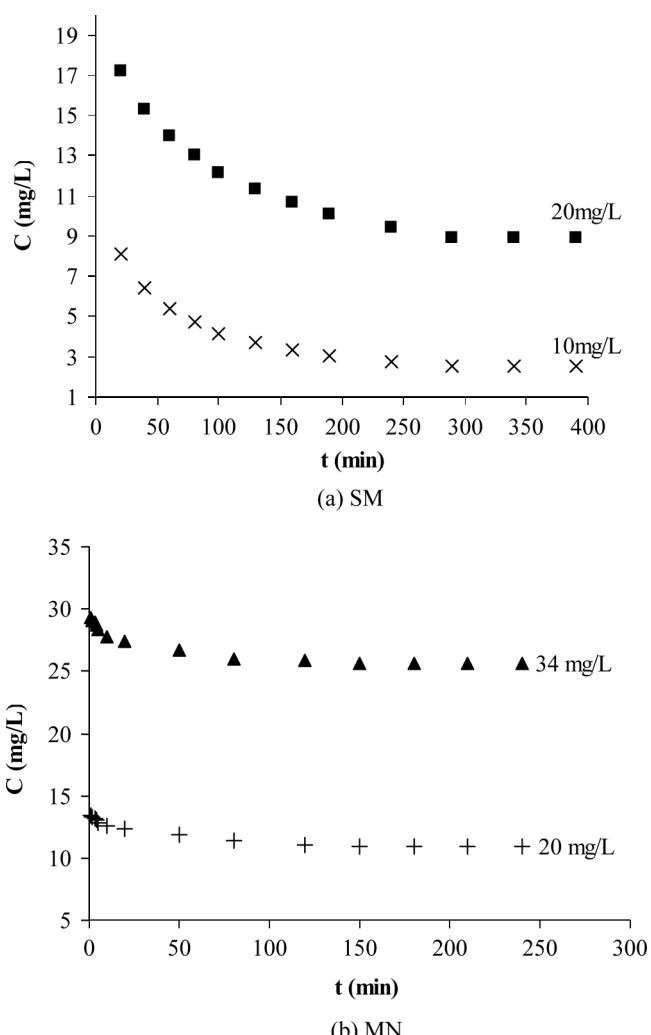


FIG. 2. Variations of the initial concentrations of SM (a) and MN (b) with time.

is independent of solution concentration for the different initial concentrations of SM (10 and 20 mg/L) and MN (20 and 34 mg/L).

Equilibrium Isotherms for SM and MN Adsorption on AC

Adsorption isotherm data of SM and MN at 298 K are illustrated in Fig. 3. The MN adsorption by AC shows a different behavior from the one observed for the SM, being evidenced a greater affinity for the latter. The shape of the isotherms indicates H behavior according to Giles and Smith classification and associated with high affinity (41).

Equilibrium Isotherm Models

Langmuir, Freundlich, and D-R isotherm equations were used to analyze the equilibrium data in order to disclose the adsorption behavior of molecules to AC. Linear forms of Langmuir, Freundlich, and D-R isotherm equations are

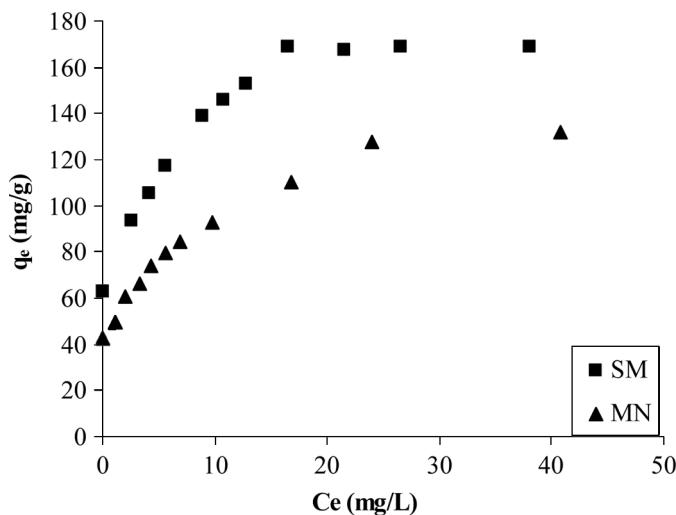


FIG. 3. Adsorption isotherms of SM and MN on AC at 298 K.

given below as Eqs. (2), (3), and (4) respectively. Related constants were calculated and given in Table 1.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \quad (2)$$

$$\ln q_e = \ln K_F + n \ln C_e \quad (3)$$

$$\ln q = \ln q_m - K \epsilon_p^2 \quad (4)$$

where, C_e is the final concentration at equilibrium in mg/L; q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium in mg/g; q_m is the maximum adsorption at monolayer coverage in mg/L; b is the adsorption equilibrium constant related to the energy of adsorption in L/mg; K_F and n , Freundlich constants representing the adsorption capacity and intensity respectively; K is the equilibrium constant related to the adsorption energy; ϵ_p is the Polanyi potential and it was calculated using the following equation:

$$\epsilon_p = RT \ln(1 + 1/C_e) \quad (5)$$

where, R is the gas constant and T is temperature. E is the mean free energy of adsorption and can be calculated using the following equation:

$$E = (-2K)^{-0.5} \quad (6)$$

As seen in Table 2, the Langmuir model gave a better fit than the Freundlich model for this process on the basis of the correlation coefficients values (R^2). Langmuir and Freundlich isotherms of these drugs are shown in Figs. 4a and 4b, respectively. The high adsorption capacity of SM compared to MN can also be illustrated from the values of q_m using the Langmuir model. The n values for all adsorption systems studied were less than unity, which reflects the favorable adsorption of these drugs over the entire concentration range used in this study. Furthermore, the surface of AC is known to be highly variable, which would also tend to make the values n less than unity (42,43). It can be said that the applicability of the Langmuir isotherm suggests the monolayer coverage of these drugs on the surface of AC. The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter, R_L (44) defined by

$$R_L = \frac{1}{(1 + bC_0)} \quad (7)$$

where b is the Langmuir constant and C_0 is the initial drug concentration, R_L values indicate the type of isotherm. An R_L value between 0 and 1 indicates favorable adsorption. The R_L values were obtained less than unity at all studied conditions i.e., the adsorption process in all cases are favorable. The R_L values calculated as the above equation were found to be as 0.22 and 0.12 for the initial concentrations of 10 and 20 mg/L for SM and 0.16 and 0.10 for the initial concentrations of 20 and 34 mg/L for MN respectively. This again confirmed that the Langmuir isotherm was favorable for adsorption of SM and MN on AC under the conditions used in this study. In order to understand the adsorption type, equilibrium data was tested with D-R. isotherm. Straight lines are obtained upon plotting $\ln q$ versus ϵ_p^2 indicating that the adsorption of both MN and SM on AC also obey the D-R isothermal equation in the entire concentration range studied (Fig. 4c). Values of q_m and K calculated from the intercepts and slopes of the plots were given in Table 2. From the value of K it is possible to calculate the mean free energy of adsorption (E), defined as the free energy change when 1 mol of ion is transferred to the surface of the solid from infinity in

TABLE 2
Adsorption isotherm parameters of SM and MN on AC

	Langmuir isotherm			Freundlich isotherm			D-R Isotherm		
	q_m (mg/g)	b (L/mg)	R^2	K_F	n	R^2	q_m (mg/g)	E (kJ/mol)	R^2
SM	185.19	0.351	0.9951	68.89	0.31	0.9945	156.24	0.712	0.9527
MN	144.93	0.263	0.9937	47.62	0.30	0.9908	93.20	0.791	0.9485

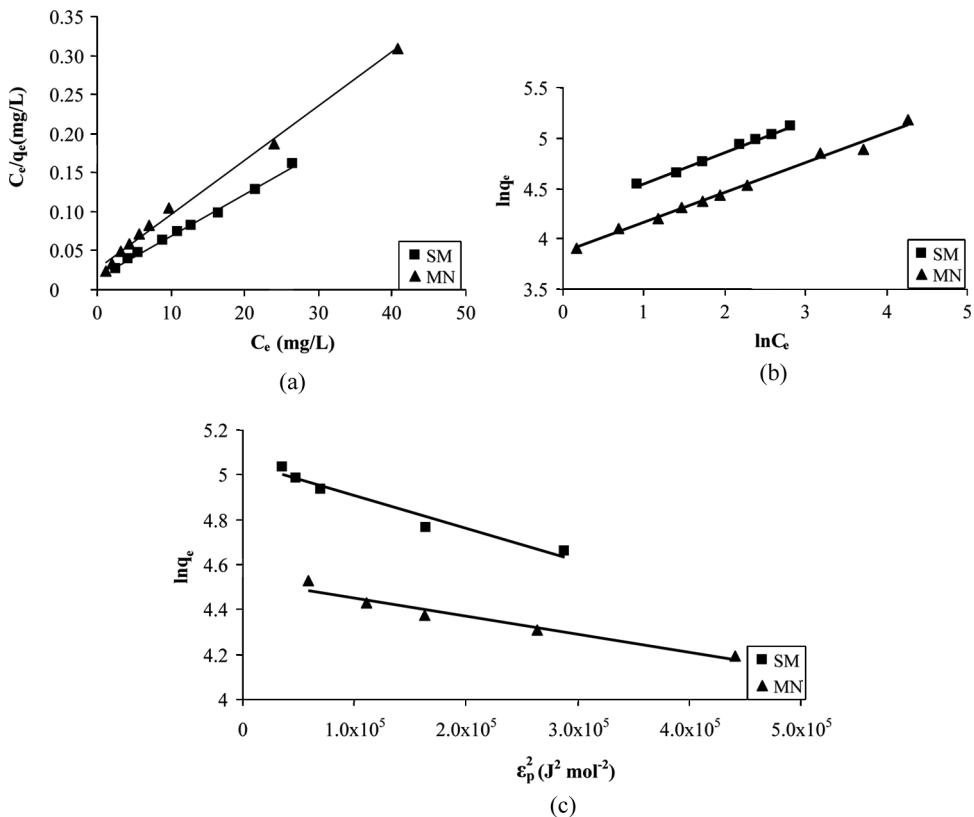


FIG. 4. (a) Langmuir plot for the adsorption of MN and SM on AC at 298 K; (b) Freundlich plot for the adsorption of MN and SM on AC at 298 K; (c) D-R plots for the adsorption of MN and SM on AC at 298 K.

solution using Eq. (6). It is known that the magnitude of E is useful for estimating the type of adsorption and if this value is between 8 and 16 kJ/mol the adsorption type can be explained by ion exchange. But the value of E found in this study is within the energy range of physical adsorption ($E < 8$). As seen in Table 2 the calculated values of E are smaller than 8 kJ/mol for SM and MN. This indicates that adsorption of both SM and MN on activated carbon is physical in nature.

Effect of Solution pH

The effect of solution pH on the adsorption was studied at different pH values at fixed initial concentrations of 20 mg/L and constant temperature (298 K). The UV absorbance spectra of 20 mg/L MN and SM at different pH values before and after contacting with AC were recorded. The results are presented in Fig. 5 which indicates that the adsorption behavior of each drug was different. It was also observed that no significant changes for UV absorbance spectra of MN aqueous solutions at different pH values before contacting with AC. This shows a negligible dependence on pH. After contacting with AC UV absorbance spectra of MN, the position of maximum absorbance remained unchanged and no new bands appeared. The

differences between UV spectra of MN solutions before and after the contact with AC at different pH values are very small, indicating a negligible variation of MN levels after the interaction. This fact is related to the MN

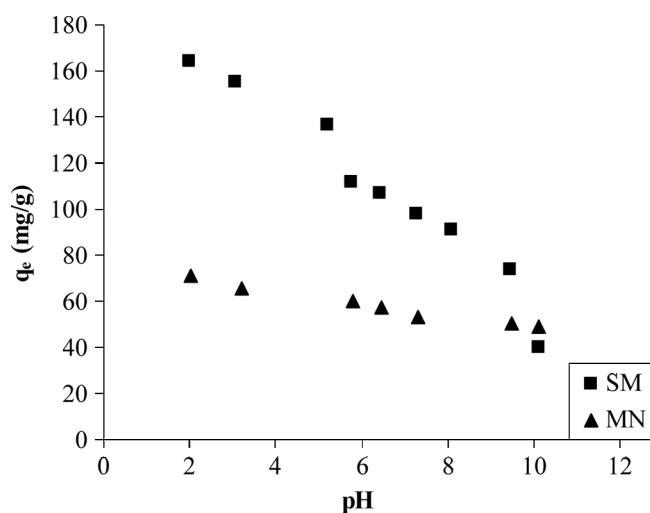


FIG. 5. Effect of varying pH of adsorption system on adsorbed amounts of SM and MN at fixed initial concentration (20 mg/L) (298 K).

equilibrium as a function of the solution pH. At pHs below the pKa value of MN reported as 2.62 (40) the molecule is protonated while at higher pH values it is neutral. It can be concluded that the adsorption of MN on AC is only physical in nature and so weak with the considered pH range. The effect of pH on the adsorption of SM is different from the adsorption of MN on AC. The absorbance values of SM varied with changing pH values. The absorbance maximum that identifies SM shows pronounced dependence on the pH. In acidic medium the maximum appears at 268 nm, while in a basic medium the band appears at 260 nm. At the pH below the pKa value for SM reported as 5.6 (45) the molecule is stable in its protonated form, particularly at the free $-\text{NH}_2$ group. On the other hand the $-\text{NH}_-$ group shows acidic properties and is able to donate the proton at high pH values. Both facts are likely to strongly affect the UV spectrum.

Activated carbons are materials with amphoteric character; thus depending on the pH their surfaces might be positively or negatively charged, which has a direct influence regarding the interactions of electrostatic nature already known. At $\text{pH} > \text{pH}_{\text{PZC}}$ the carbon surface becomes negatively charged, favoring the adsorption of cationic species. On the other hand adsorption of anionic species, which is the case under discussion will be favored at values of $\text{pH} < \text{pH}_{\text{PZC}}$. In our study pH_{PZC} value of AC has been determined as 2.8 (Fig. 6). At pH values above 5.6, SM exists predominantly as an anionic species; at pH values between 1.7 and 5.7, SM is uncharged, while at pH values below 1.7 it is positively charged (45). At pH values lower than the pH_{PZC} , the net surface charge of AC is positive and anion adsorption is dominant; at pH values higher than the pH_{PZC} the net charge is negative and cation adsorption occurs. All these facts clearly explains the inhibitory effect of solution pH on the adsorption of these drugs. As seen in Fig. 5, it can be said that the adsorption

of both drugs on AC decreased with increasing pH of the solution. When the pH of the solution increases the number of positively charged available sites decreases and the number of the negatively charged sites increases. The surface of AC gets negatively charged which inhibits anions through electrostatic repulsion and therefore the adsorption of drug anions by AC decreases at higher pH values.

Adsorption Kinetics

The study of adsorption kinetics of SM and MN describe the solute uptake rate and evidently this rate controls the residence time of the adsorbate uptake at the solid-solution interface. Adsorption rate constants for the SM and MN were calculated by using pseudo-first-order, second-order and intraparticle diffusion kinetic models which were used to describe the mechanism of the adsorption. The conformity between the experimental data and the model-predicted values was expressed by the correlation coefficients (R^2). A relatively high R^2 values indicate that the model successfully described the kinetics of the SM and MN adsorption. Figure 7 presents the pseudo-second-order graphics for the adsorption kinetics of these drugs studied. The data showed good compliance with the second-order kinetic model in terms of higher correlation coefficients (>0.995) and very close values of predicted and experimental q_e for the drug-adsorption system (Table 3). This indicates that the adsorption follows the second-order kinetic model in this study.

$$\ln(q_e - q) = \ln(q_e) - k_1 t \quad (8)$$

$$\left(\frac{t}{q}\right) = \frac{1}{k_2 q^2} + \frac{1}{q_e} (t) \quad (9)$$

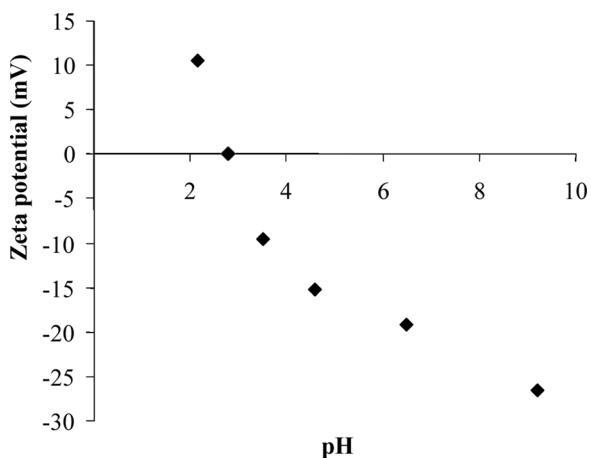


FIG. 6. Zeta potential of AC as a function of pH.

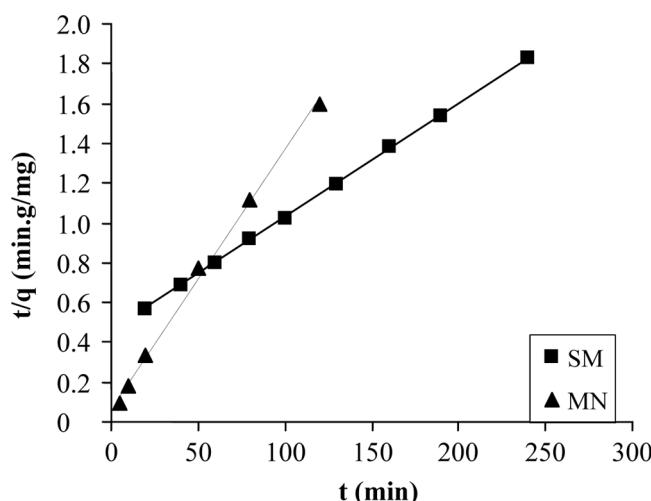


FIG. 7. Kinetic plots for the adsorption of SM and MN on AC at 298 K. $[\text{SM}] = [\text{MN}] = 20 \text{ mg/L}$.

TABLE 3

Comparison of the first- and second-order adsorption rate constants with calculated and experimental q_e values for different initial drug concentrations

Initial drug concentration (mg/L)	First-order kinetic model		Second-order kinetic model			R^2
	k_1 (1/min)	R^2	k_2 (g/mg · min)	q_e (mg/g)	$q_{e(\text{exp})}$ (mg/g)	
SM						
10	1.30×10^{-2}	0.9814	1.27×10^{-4}	119.05	95.96	0.9970
20	1.19×10^{-2}	0.9956	7.11×10^{-5}	175.44	159.38	0.9990
MN						
20	1.94×10^{-2}	0.9901	2.66×10^{-3}	76.92	77.66	0.9979
34	2.51×10^{-2}	0.9883	2.23×10^{-3}	107.53	106.97	0.9989

The pseudo-first-order and second-order kinetic models can not identify the diffusion mechanism and the kinetic results were then analyzed by using the intraparticle diffusion model. The intraparticle diffusion graphic was plotted by using the following equation and shown in Figs. 8a and 8b.

$$q = k_{id} t^{1/2} \quad (10)$$

The initial curved part of the plot can be explained by the boundary layer effect while linear sections indicate the intraparticle diffusion. The k_{id} values were obtained from the slope of the linear portions of the curves and were found to be as 10.517 and 11.71 mg/g min $^{0.5}$ for the initial concentrations of 10 and 20 mg/L for SM and 5.01 and 9.23 mg/g min $^{0.5}$ for the initial concentrations of 20 and 34 mg/L for MN respectively. These linear sections do not pass through the origin indicating that intraparticle diffusion is not the only rate controlling step for the process. The rate controlling mechanism may change during the course of adsorption process. As seen in Figs. 8a and 8b the adsorption process tends to be followed by two phases. It was found that an initial linear portion ended with a smooth curve followed by a second linear portion. The two phases in the intraparticle diffusion plot suggests that the adsorption process proceeds first by surface adsorption and then the intraparticle diffusion. The initial curved portion of the plots indicates boundary layer effect while the second linear portion is due to intraparticle or pore diffusion.

Surface Coverage (θ)

The fraction of the surface occupied by the adsorbate molecules is commonly termed the surface coverage (θ). The surface coverage by the SM and MN molecules at various times has been calculated by the following equation (46,47).

$$\theta = \frac{C_0 - C}{C_0 + K'} \quad (11)$$

where C_0 is the initial concentration of the adsorbate solution and C is the concentration of the adsorbate solution at any time t . K' is a constant and equals to k_2/k_1 . θ values at different times have been calculated and are shown in Fig. 9 according to Eq. (10). It can be seen in Fig. 9 that the surface coverage (θ) increases with increasing

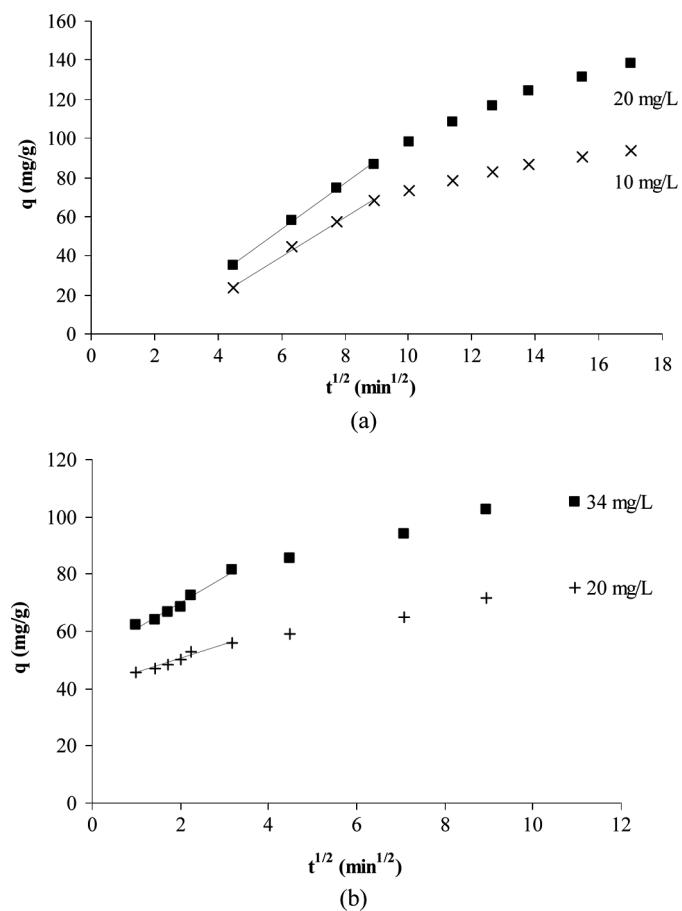


FIG. 8. (a) Plots of amount of SM adsorbed vs. $t^{1/2}$ for intraparticle diffusion of SM. (b) Plots of amount of MN adsorbed vs. $t^{1/2}$ for intraparticle diffusion of MN.

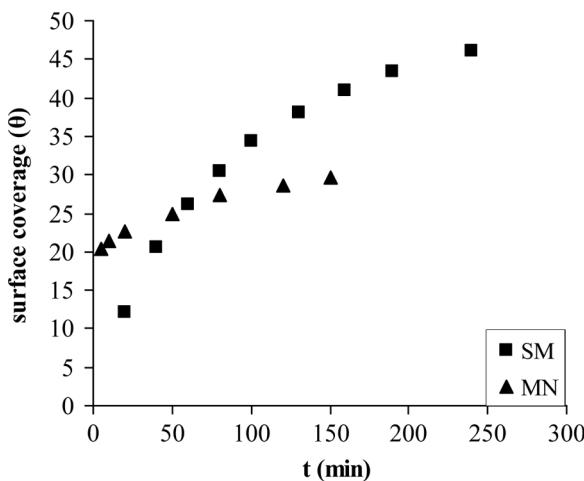


FIG. 9. Variation of surface coverage (θ) with time at fixed concentration of drugs. $[SM]=[MN]=20\text{ mg/L}$.

time of the adsorption. The fraction of the AC surface gets progressively occupied by the SM and MN molecules. Comparing with the variation of θ values of MN and SM it is clearly seen that MN molecules occupied the surface of AC faster than SM molecules. This was also confirmed by kinetic studies i.e., the rate constants of MN are higher than the rate constants of SM.

Determination of k_a and k_d

It can be calculated that the rate constants for adsorption (k_a) and (k_d) desorption using by the following equation;

$$\frac{1}{C} = \frac{k_a}{C_0} t + \frac{1}{C_0} \quad (12)$$

It is clear that a plot between $1/C$ and t should yield a straight line; from the slope and intercept k_a can be calculated. The plots are shown in Fig. 10 for both SM and MN. It is also

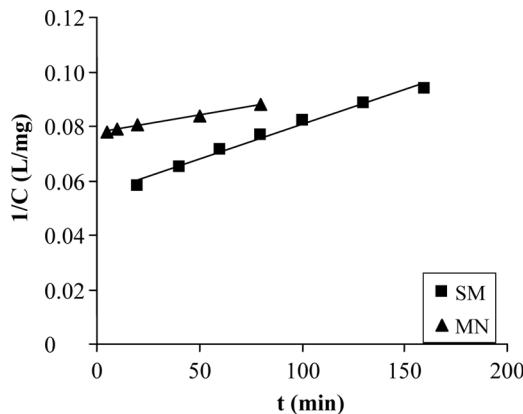


FIG. 10. Plot of $1/C$ versus time for the evaluation of k_a .

known that b value of Langmuir equation equals to k_a/k_d , and then it can be easily calculated k_d values. In the present case the values of k_a and k_d were found as $5.0 \times 10^{-3} \text{ 1/min}$ and $14.3 \times 10^{-3} \text{ mol/Lmin}$ for SM and $2.2 \times 10^{-3} \text{ 1/min}$ and $8.6 \times 10^{-3} \text{ mol/Lmin}$ for MN, respectively.

Effect of Temperature on the Adsorption and Thermodynamics

The adsorption of SM and MN on AC were carried out at the temperatures of 293, 298, 303, 313 K for the initial concentration of 20 mg/L. The free energy of adsorption (ΔG) was calculated from the following equation;

$$\Delta G = -RT \ln K \quad (13)$$

where K is the equilibrium constant and T is the solution temperature (K); R is the gas constant (8.314 J/mol K). The apparent enthalpy of adsorption, (ΔH), and entropy of adsorption, (ΔS), were calculated from adsorption data at different temperatures using the Van't Hoff equation (48):

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (14)$$

Values of ΔH and ΔS were computed from the slopes and intercepts of linear variations of $\ln K$ with the reciprocal of temperature (Fig. 11) and these thermodynamic parameters are being given in Table 4. As seen in Table 4 ΔG° values were negative in the studied temperature range of 293–313 K for both SM and MN indicating that the adsorption process led to a decrease in Gibbs free energy. Negative ΔG° indicates the feasibility and spontaneity of the adsorption process. However, this spontaneity decreases with an increase in temperature. The negative values of ΔH° indicate that the process is exothermic. Physical

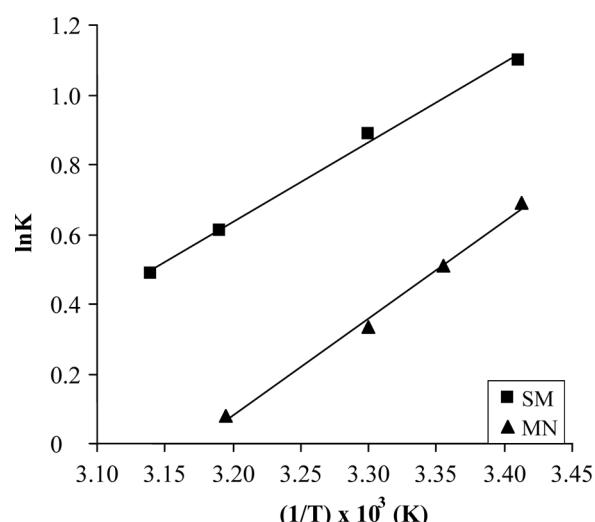


FIG. 11. Van't Hoff Plots of SM and MN adsorption on AC for 20 mg/L initial drug concentrations.

TABLE 4
Thermodynamic parameters for SM and MN adsorption on activated carbon under different temperatures

T(K)	SM			MN		
	ΔH° (J/mol)	ΔS° (J/mol · K)	ΔG° (J/mol)	ΔH° (J/mol)	ΔS° (J/mol · K)	ΔG° (J/mol)
293	-18984	-55.47	-2680	-23194	-73.55	-1684
298			-2242			-1261
303			-1587			-842
313			-1295			-211

adsorption and chemisorption can be classified, to a certain extent, by the magnitude of the enthalpy change. It is accepted that bonding strengths of <84 kJ/mol are those of physical adsorption type bonds. Chemisorption bond strengths can range from 84 to 420 kJ/mol. Based on this the adsorption of SM and MN on AC appears to be a physical adsorption process. The negative values of ΔS° suggest that the decreased randomness at the solid–solution interface during the adsorption of the SM and MN in aqueous solution on AC. The less negative value of ΔS° found for SM reveals that a more ordered arrangement of SM molecules is shaped on the adsorbent surface.

Adsorption of SM and MN in Columns

Adsorption isotherms are used for preliminary investigations to obtain operational parameters before running more costly column tests, but in practice treatment plants use columns. Results obtained fail to give accurate scale-up data as adsorption in a batch test will be at equilibrium whereas adsorption in a flow column is not. Therefore it is necessary to carry out flow tests using columns (49–51). Figures 12a and 12b show the breakthrough curves obtained from the fixed bed experiments for SM and MN respectively, at constant concentration and three different flow rates. The results obtained from column studies are given in Table 5. The experiments were performed at three different flow rates and constant initial concentration to examine the effect of flow rate on the column capacity. It can be seen from the figures (Figs. 12a and 12b) that breakthrough curves being produced for different flow rates are identical. The parameters and their meanings are as follows: V_i is the volume of effluent at the breakthrough point of the column; X_i is the amount of adsorbate (mg) adsorbed per g of adsorbent at the breakthrough point; V_s is the volume of effluent at the close point of the column (when C/C_0 reaches a plateau); X_s is the amount of adsorbate (mg) adsorbed per g of adsorbent at the close point (52).

Comparison of the breakthrough curves obtained at three flow rates showed a consistent trend where in the breakthrough curves for the faster flow rates were shifted leftward of the slow flow rate. When the flow rate increases,

the residence time in the column decreases which results in lower bed utilization. Therefore as can be seen in Table 5, the breakthrough time and the bed capacity decrease with increasing flow rate (52,53). It is also seen that the amount of adsorbate adsorbed per g of adsorbent for each flow rate is greater for the fixed bed than for the batch experiments. Same dissimilarities between the adsorption capacity found by batch and column studies were reported by several

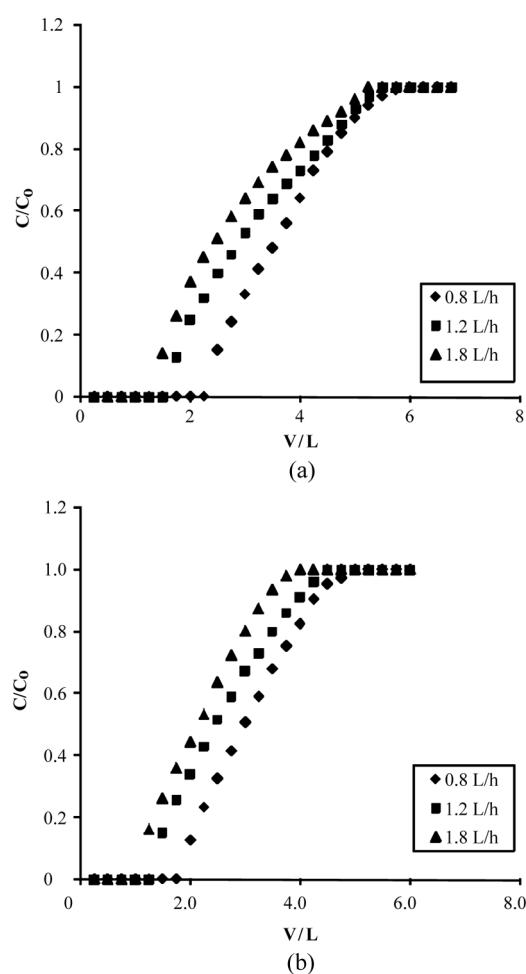


FIG. 12. (a) Breakthrough curves for different flow rates of SM. (b) Breakthrough curves for different flow rates of MN.

TABLE 5

Parameters calculated for initial concentration of 200 mg/L (for SM and MN) at different flow rates

		Flow rate (L/h)		
		0.8	1.2	1.8
V_i/L	SM	2.25	1.50	1.25
	MN	1.75	1.25	1.00
$X_i/mg\ g^{-1}$	SM	180	120	100
	MN	140	100	80
V_s/L	SM	6.00	5.50	5.25
	MN	5.00	4.50	4.00
$X_s/mg\ g^{-1}$	SM	280	232	209
	MN	233	196	166

researchers (50–55). In batch studies, the adsorbate concentration decreases and desorbed solutes increases with equilibration time until the equilibrium is attained. In column studies, the adsorbates removed from solution by adsorption are constantly being replaced and the desorbed solutes are flushed out. If the column is considered as a stack of sorption cells, removal of adsorbate from solution can be considered as a step function. As the sites in any one cell approach saturation, fewer solutes are removed from the solution and move into the next cell. This implies that there are more adsorbates available for sorption in the flow-through or column studies and that greater exposure of adsorbates increases the adsorption. This is consistent with the Le Chatelier's principle of equilibrium (56–58).

CONCLUSION

On the basis of the data obtained from both batch and column studies, it is concluded that AC can be used to remove SM and MN from aqueous solutions. The adsorption of SM and MN on AC is physical in nature. The experimental adsorption data showed good correlation with the Langmuir isotherm model. MN, having the smaller molecular size, is quickly adsorbed onto activated carbon surface when comparing with the equilibrium time data of SM. This is confirmed by kinetic studies i.e., the rate constants of MN are higher than the rate constants of SM. On the other hand the lowest adsorption affinity of MN on AC comparing with SM can be explained by the solubility which are the main physicochemical features that play an important role in adsorption mechanisms. The solubility of MN was higher than SM, thus, MN could be dissociated easily in the water. Surface coverage values were also in agreement that the adsorption affinity of SM is higher than the adsorption affinity of MN on AC. The pH of the solutions has also an important role on the adsorption performance, since it influences the surface charge of AC and consequently the intensity of the

interactions between drugs and the adsorbent surface. Thermodynamical parameters were also evaluated for these drugs that the adsorption is exothermic in nature. The increase in temperature resulted in decreasing the adsorption of both these drugs on AC.

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