

COMPREHENSION TO DEXTROMETHORPHAN AND GUAIFENESIN ANTIBIOTICS ADSORPTION ON ACTIVATED CHARCOAL FROM WATER: KINETICS, THERMODYNAMICS, AND SOLUTION PARAMETERS

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Pharmaceuticals and personal care products (PPCPs) residues in water and wastewater have a thoughtful impact on man, animal and environment. In this paper, we studied the removal of dextromethorphan (Dex) and guaifenesin (Gua) as an example of hazardous PPCPs from an aqueous solution using activated charcoal (AC). The effect of adsorption time, sorbent mass, solution pH, and temperature were optimized. The adsorption kinetics was investigated at different temperatures, applying pseudo-first-order and the pseudo-second-order kinetic models. The results showed that the adsorption kinetic follows the pseudo-second-order model with the very good agreement. Also, the adsorption mechanism was studied for Dex and Gua via intra-particle diffusion and the liquid-film diffusion models; the results show partial agreement with both models particularly at 20°C, with acceptable linear regression coefficients. The adsorption isotherm of Dex and Gua fit well with a good agreement with Langmuir model. In addition, the thermodynamic parameters including free energy, enthalpy, and entropy have been calculated and discussed. AC showed relatively good removal efficiency especially at low concentration.

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Keywords: Adsorption, Activated charcoal, Dextromethorphan, Guaifenesin, Thermodynamics, Kinetics

1. Introduction

The wastewater treatment from Pharmaceuticals and personal care products (PPCPs) contaminants is a foremost challenge for many countries worldwide, in order to satisfy the expanded need of agricultural and industrial development for the water. It is recognized that the chronic exposure to the antibiotics residue in water, makes them ineffective or less effective, in addition to a serious of public health problems for both man and animal, one of the major problems is that the presence of biological antibiotics in water makes microorganisms immune to them. The presence of PPCPs in urban and farm wastewater found as consequences of their excretion in urine and feces. In addition to different operations in pharmaceutical manufacturing. Washing of machines and equipment, significantly contribute to this issue. Also, such pollutants may enter the water cycle through illegal discarding of expired materials in sewage systems [1-3].

Ali et al. (2018) reported that only 37% of the produced wastewater in KSA is treated in sewage treatment plants [4]. And it is planned that sewage treatment has to reach 100% by 2025. Recent studies have shown a positive incidence of pharmaceutical pollutants in the Red Sea. It is

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known that the Kingdom relies on desalinating the Red Sea waters for use in industries and drinking water [5, 6].

A literature review indicates that there are several approach to remove PPCPs from water, such as mesoporous activated charcoal (AC) [7], silicon-based materials [8], membrane bioreactor [9, 10], oxidation [11-13], bacterial consortium [14], electrocoagulation [15], multi-walled carbon nanotubes [16], ZnO-sepiolite heterostructured and solar photocatalytic degradation [17] and agricultural waste [18]. Among these sorbents, AC has been investigated as a pure material as well as composites with other chemicals. AC is known to be a powerful and cheap substance for the adsorption of PPCPs from water and wastewater.

Dextromethorphan (Dex) used as an antitussive drug with combination of guaifenesin (Gua) expectorant drug (Fig. 1). Dex and Gua pharmaceuticals have high solubility in water, and therefore their presence in water and wastewater is more probable. The aims of this paper are to investigate the simultaneous adsorption parameters of dextromethorphan (Dex) and guaifenesin (Gua) as an example of PPCPs using AC. This includes effects of adsorption time, sorbent mass, solution pH, ionic strength, and temperature.

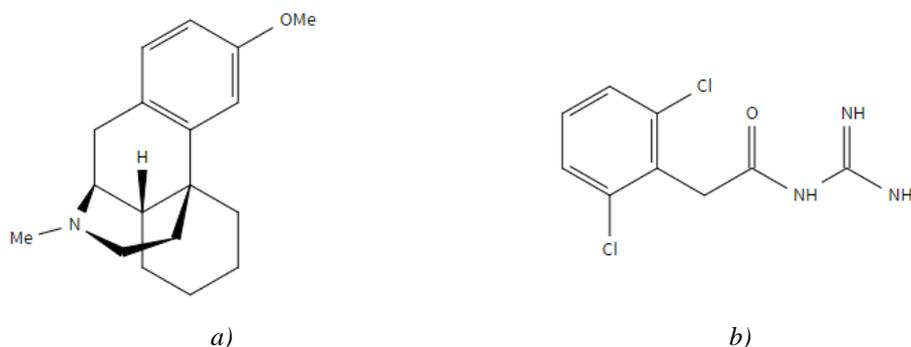


Fig. 1. Chemical structure of (A) dextromethorphan and (B) guanfacine.

2. Materials and methods

2.1. Materials

AC was obtained from Merk, Germany (particle size < 100 μm). The pharmaceutical drugs; Dex and Gua, were obtained from Riyadh Pharm laboratories. All other chemicals were analytical grade and all solutions were prepared from distilled water.

2.2. Analytical method

Gua and Dex concentrations were measured using high-performance liquid chromatography high-performance liquid chromatography (HPLC) apparatus (Perkin Elmer, USA) consisting of a Fluorescence detector, binary analytical pump, vacuum degasser, and auto-sampler equipped with a 100 μl loop. The chromatographic column used was a RP-Thermo C8 column (150 mm \times 4.6 mm with 3 μm particles). The excitation and emission wavelengths were set at 281 and 430 nm. The mobile phase was composed of methanol: water: formic acid (35:74:1, v,v,v). Isocratic elution with a flow rate of 0.8 ml min⁻¹ was used.

2.3. Adsorption experiments

Adsorption parameters, including adsorbent mass, adsorption time, solution pH, and initial Dex and Gua concentration, were studied. For adsorption time, A mixed solution containing 20.0 mg L⁻¹ of both Dex and Gua was prepared. The solution was adjusted to pH 6 using 0.1 M of hydrochloric acid and 0.1 M of sodium hydroxide; then, 25 mL of the solution and 25 mg of AC was placed into 50 mL falcon tubes. The mixture was shaken for 3, 6, 9, 15, 30, 45, and 60 minutes; after which, the solution was filtered using a nylon syringe filter (0.22 μm) and analyzed using HPLC.

The adsorption capacity q_t and percentage adsorption of Gua and Dex on AC in aqueous solution were calculated using equations (1) and (2), as follows:

$$\% \text{ Adsorption} = \frac{(C_0 - C_t)}{C_0} * 100\% \quad (1)$$

$$q_t = \frac{(C_0 - C_t) V}{M}, \quad (2)$$

where C_0 is the Dex and Gua initial concentrations (mg L^{-1}), C_t is the unabsorbed concentrations (mg/L) after a certain time, q_t is the adsorbed amount (mg/g) of Dex and Gua by AC, V is solution volume (L) and M is the AC mass (g). It noteworthy, each experiment was carried out in duplicate and the average was reported.

3. Results and discussion

3.1. Adsorption studies

The adsorption of PPCPs pollutants from aqueous solutions by AC, known to be controlled through Van der Waals interactions [18]. In this study, AC was used for the removal of Dex and Gua from an aqueous solutions. The factors that may affect adsorption such as the initial pollutant concentration, adsorbent mass, contact time, pH level and temperature were investigated. Figure 2 shows the effect of AC mass on the adsorption behavior of Dex and Gua. In general, it was found that the percentage of Dex and Gua adsorption increased as AC mass increased. This can be attributed to the availability of many adsorption sites, which interact with the Dex and Gua molecules.

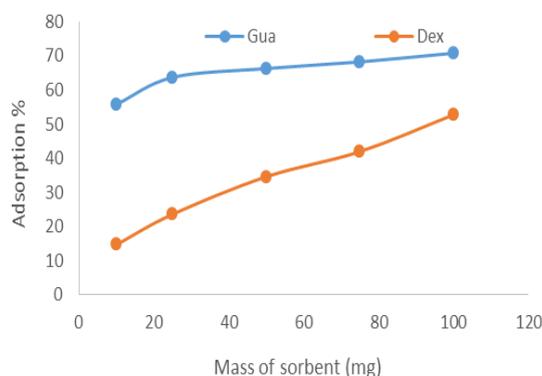


Fig. 2. Activated charcoal mass effect on the adsorption of Gua and Dex from aqueous solution at room temperature (25°C) and at a pH 6.0.

The contact time effect on the adsorption percentage of Gua and Dex on AC was demonstrated in Figure 3. The Figure exhibits that the percentage adsorption of Dex and Gua increased overtime for the first 15 minutes, after which no further significant adsorption was observed; hence, equilibrium was achieved. It was clear that the AC could rapidly and efficiently treat PPCPs pollutants in aqueous solutions.

The pH effect on the adsorption of Dex and Gua by AC was studied at pH values ranged from 3.0 to 10.0. The results were showed in Figure 4. The adsorption of both drugs by AC reached its maximum at pH 6. However, the adsorption percentage decreased by increasing pH above 6.0, particularly, for Dex solution. This decrease can be attributed to the deprotonation of acidic proton of Dex, and thus the electrostatic repulsion between the negatively charged Dex and AC sites.

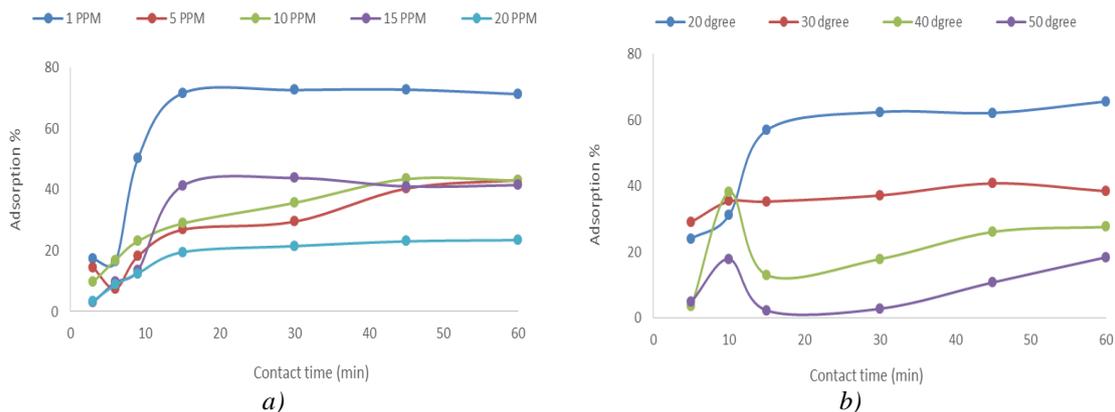


Fig. 3. The time effect on the adsorption different initial fed concentrations of a) Dex and b) Gua by activated charcoal from aqueous solutions at room temperature (25 °C) and at a pH level of 6.0.

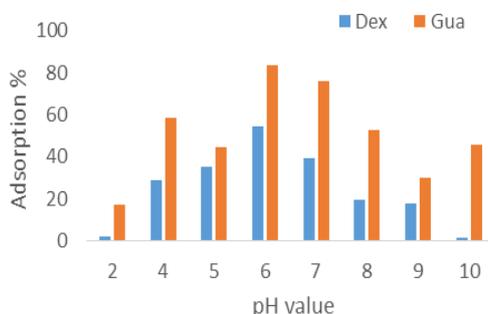


Fig. 4. The pH effect on the adsorption of Dex and Gua by activated charcoal from an aqueous solution (20 mg L⁻¹) at room temperature (25 °C).

Moreover, the initial concentrations effect of Dex and Gua on the adsorption percentage by AC were investigated. Figure 5 represents that, the adsorption efficiency decreased as the initial concentrations increased for both drugs. This trend illustrates that the AC is very efficient for the removal of Dex and Gua at low concentration (1 mg l⁻¹). Generally the concentration of PPCPs in the environment was expected to be at low levels.

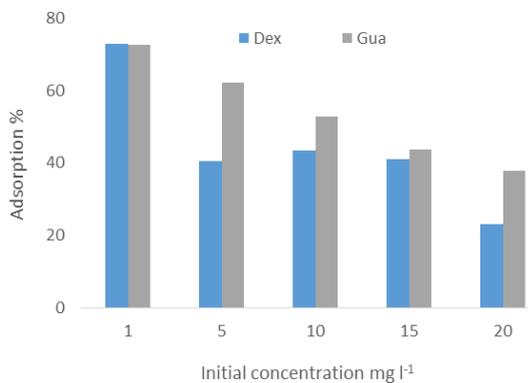


Fig. 5. The initial concentration effect of Dex and Gua on adsorption efficiency by activated charcoal at room temperature (25 °C) and at a pH level of 6.0.

3.2. Adsorption kinetics

The temperature effects on the adsorption of Dex and Gua on AC in aqueous solutions were studied. Figure 6 illustrates that the adsorption capacity of Dex and Gua decreases by raising the solution temperature. The reduction in adsorption capacity of Dex and Gua on AC sorbent by increasing the solution temperature indicates that the adsorption process is exothermic.

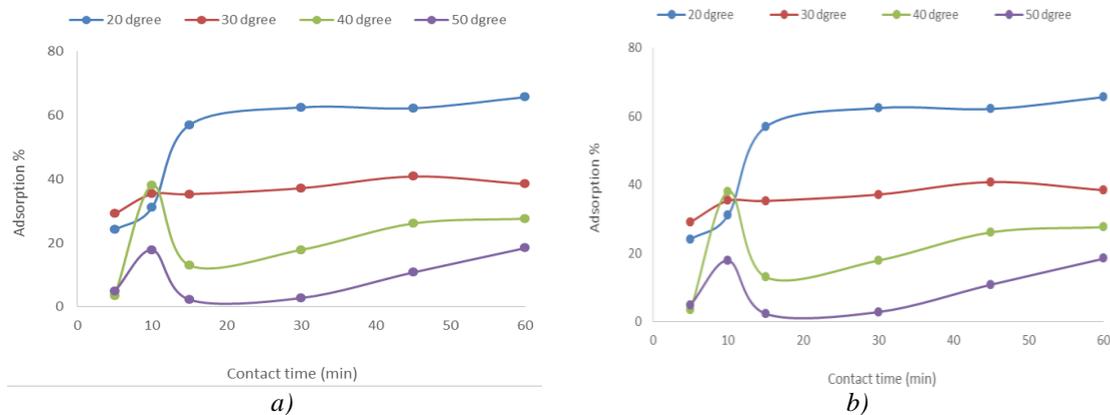


Fig. 6. The solution temperature effect on the adsorption percentage of a) Dex and b) Gua by activated charcoal in an aqueous solution.

The effect of temperature on the adsorption mechanisms and rate were also investigated by means of various kinetic models, including pseudo-first-order using Equation (3), and pseudo-second-order using Equation (4), as based on the Lagrange equation [19]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where k_1 (min^{-1}) is the adsorption rate coefficients of the pseudo-first-order, k_2 ($\text{g} (\text{mg min})^{-1}$) is the pseudo-second-order models, q_t is the adsorbed amount per unit mass at time t , and q_e is adsorbed amount at equilibrium.

The calculated and experimental parameters of the kinetic models for Dex and Gua were displayed in Table 1. The fitting of Dex and Gua to the kinetic models were determined on the bases of the correlation coefficient ($R^2 \geq 0.97$) and the agreement between experimental and calculated values of q_e . The Dex adsorption behavior was fitted the pseudo-second-order kinetic model at 20 °C and 30 °C, whereas, it obeys the pseudo-first-order kinetic model at 40 °C. On the other hand, Gua fitted the pseudo-second-order kinetic model at all tested temperatures.

3.3. Adsorption rate-controlling mechanism

The liquid film-diffusion and the intra-particle diffusion kinetic models were studied at different temperatures using equations (5) and (6), respectively:

$$\ln(1 - F) = -k_{fd} * t \quad (5)$$

where F is the equilibrium fractional attainment, and k_{fd} (min^{-1}) is the film diffusion rate coefficient.

$$q_t = k_{id} t + C \quad (6)$$

where q_t represents adsorption capacity at time (t), C is a constant related to the boundary layer thickness in (mg/g), and k_{id} represents the rate constant for intra-particle diffusion ($\text{mg/g min}^{1/2}$).

Table 1. The parameters of adsorption kinetic and adsorption rate-controlling mechanisms at different temperatures and pH 4.0 for Dex and Gua adsorption on activated charcoal sorbents.

Gua					Dex				
Pseudo-first-order kinetic model									
Temperature °C	q _e exp. (mg/g)	q _e cal. (mg/g)	k ₁	R ²	Temperature °C	q _e exp. (mg/g)	q _e cal. (mg/g)	k ₁	R ²
20	7.734	3.911	0.038	0.761	20	6.565	4.321	0.067	0.793
30	6.365	1.116	0.022	0.393	30	4.081	1.135	0.024	0.802
40	6.877	1.531	-0.004	0.041	40	3.803	3.699	0.022	0.970
50	6.628	3.826	0.004	0.056	50	1.841	2.208	0.020	0.052
Pseudo-second-order kinetic model									
Temperature °C	q _e exp. (mg/g)	q _e cal. (mg/g)	K ₂	R ²	Temperature °C	q _e exp. (mg/g)	q _e cal. (mg/g)	K ₂	R ²
20	7.734	8.285	0.017	0.970	20	6.565	7.794	0.012	0.976
30	6.365	6.079	0.114	0.983	30	4.081	4.036	0.141	0.997
40	6.877	5.179	0.194	0.996	40	3.803	4.401	0.007	0.565
50	6.628	2.872	0.057	0.980	50	1.842	2.589	0.004	0.048
Intra-particle diffusion model									
Temperature °C	K _{id} (mg/g min ^{1/2})	C (mg/g)	R ²	Temperature °C	K _{id} (mg/g min ^{1/2})	C (mg/g)	R ²		
20	0.491	3.651	0.830	20	0.737	1.451	0.765		
30	0.00001	5.788	0.000	30	0.160	2.826	0.739		
40	-0.284	6.661	0.276	40	0.226	1.001	0.157		
50	0.046	0.002	3.416	50	0.127	0.331	0.137		
Liquid film diffusion model									
Temperature °C	K _{fd} (min ⁻¹)	R ²	Temperature °C	K _{fd} (min ⁻¹)	R ²				
20	0.038	0.761	20	0.067	0.793				
30	0.022	0.393	30	0.024	0.802				
40	0.004	0.041	40	0.022	0.969				
50	0.004	0.056	50	0.020	0.052				

The rate-controlling mechanisms of Dex and Gua adsorption on AC is presented in Table 1. The results revealed that the adsorption of Gua on AC does not fit well both kinetic models except when a temperature of 20 °C was applied. On the other hand, the adsorption of Dex on AC partially fits the intra-particle diffusion model at temperature degrees of 20 °C and 30 °C, it also partially fits the liquid film diffusion model at temperature degrees of 20 °C, 30 °C, and 40 °C with acceptable linear regression coefficients.

These results indicate that the rate-determining step of the adsorption process for both drugs at the stated conditions is ruled by a liquid film-diffusion step for the adsorption of Gua on AC at 20 C and for the adsorption of Dex on AC at 20 °C, 30 °C, and 40 °C. In addition, the adsorption of Gua on AC follow the intra-particle diffusion model at 20 °C, while the adsorption of Dex on AC follow the intra-particle diffusion model at 20 °C and 30 °C. According to these results, the adsorption capacities of Dex and Gua by AC at 20 °C were 6.565 mg g⁻¹ and 7.734 mg g⁻¹, respectively. To our best knowledge, these results represent the first removal study for Dex and Gua from aqueous solutions using AC.

3.4. Adsorption isotherm studies

The Langmuir and Freundlich models were employed. Equations 7 and 8 represent the linearized equations for Langmuir and Freundlich, respectively:

$$q_e = \left(\frac{K_L b C_e}{1 + b C_e} \right) \quad (7)$$

$$\ln q_e = \ln k + \frac{1}{n} \ln c_e \quad (8)$$

The Dex and Gua adsorption isotherm on AC sorbent followed the linearized Langmuir model, with good agreement (Fig. 7). The parameters of adsorption isotherms of Gua on AC reported in Table 2.

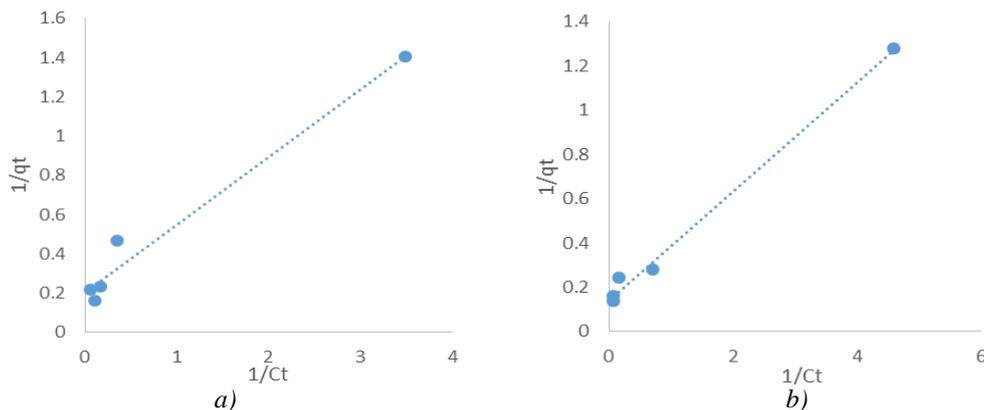


Fig. 7. The adsorption isotherm Langmuire for (A) Dex and (B) Gua on AC sorbent at 25°C and pH 6.0.

Table 2. The parameters of Dex and Gua adsorption isotherms at pH 6.0 and at a temperature of 25°C on AC sorbents.

Parameters	Gua	Dex
Freundlich		
K (l/g)	43.18	30.72
1/n	5.679	3.519
R ²	0.980	0.894
Langmuir		
b (l/g)	0.225	0.100
K _L (mg/g)	6.050	10.650
R ²	0.924	0.968

3.5. Thermodynamic studies

Thermodynamic parameters such as free energy (ΔG°), enthalpy, (ΔH°) and entropy (ΔS°) change of adsorption can be evaluated from the following equations (9) and (10):

$$K_e = \frac{(C_0 - C_t)}{C_t} \quad (9)$$

$$\Delta G^\circ = -RT \ln K_e \quad (10)$$

where K_e is the equilibrium constant and C_0 (in mg/l) are the initial fed concentration and C_t is the concentration of solute in the solution at equilibrium. The K_e values are used in Equations (10) and (11) to determine the ΔG° , ΔH° , and ΔS° . The K_e may be expressed in terms of the ΔS° (cal mol⁻¹ K⁻¹) and ΔH° (kJ mol⁻¹) as a function of temperature:

$$\ln K_e = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (11)$$

The values of these parameters are presented in Table 3 and 4. The negative values of ΔG° indicate the spontaneous nature of the process and less negative value with the increase of temperature indicates that an increase in temperature disfavors the sorption process. The positive values of ΔH° indicate that the sorption of Gua and Dex by AC was endothermic in nature.

Table 3. The thermodynamic parameters at different initial concentrations and pH 4.0 for Dex and Gua adsorption on the Activated charcoal sorbent.

Dex			Gua		
C_o (mg/l)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)	C_o (mg/l)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)
1	31.256	0.106	1	33.293	0.114
5	-24.585	0.073	5	19.638	0.067
10	22.478	0.068	10	6.981	0.021
15	33.927	0.104	15	34.549	0.106
20	21.526	0.058	20	41.302	0.125
Dex			Gua		
C_o (mg/l)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)	C_o (mg/l)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)
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10	22.478	0.068	10	6.981	0.021
15	33.927	0.104	15	34.549	0.106
20	21.526	0.058	20	41.302	0.125

4. Conclusions

The removal of Dex and Gua as an example of PPCPs from aqueous solutions by AC were thoroughly investigated. The present study shows that the AC is an effective adsorbent for Dex and Gua removal. From the kinetics studies, it was observed that the adsorption of Dex and Gua was rapid and efficient, as it approached equilibrium after a short period of time, using a wide range of initial concentrations and temperatures, and with relatively high efficiency. The adsorption process was found to be effective at neutral pH levels of 6-8. The percentage removal of Dex and Gua increased with the increases in adsorbent dosage.

Their experimental data related to adsorption isotherms were in good agreement with Langmuir model. The adsorption of Gua and Dex obeyed the pseudo-second-order processes with good linearity. The data were also partially fitted with the liquid film-diffusion and Intra-particle diffusion models, with acceptable linear regression coefficients. In addition, the thermodynamic parameters of adsorption of Gua and Dex by AC have been calculated and discussed. We recommended more studies on removal of PPCPs from contaminated water.

Conflict of Interest

The authors declare that they have no conflict of interest.

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