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Removal of carbamate insecticides from drinking water through a fixed bed column of granular activated carbon: a thermodynamic, kinetic and equilibrium study of multicomponent adsorption

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ABSTRACT

Kinetics, equilibrium and thermodynamic parameters of adsorption were investigated for the removal of the carbaryl, methomyl and carbofuran pesticides by granular activated carbon (GAC) from the public water supply. The adsorption dynamics were evaluated by means of a fixed bed adsorption column of granular activated carbon (FBAC-GAC). The adsorption kinetics were described more precisely by the pseudo-second-order model, the monocomponent and multicomponent equilibrium data were better represented by the Langmuir–Freundlich isotherms for the three temperatures studied (15°C, 25°C and 35°C) and the parameters thermodynamics have demonstrated that the adsorption process is exothermic, of a physical and spontaneous nature. In FBAC-GAC, multicomponent saturation occurred after 196 h of adsorption column operation and carbaryl was the pesticide preferentially adsorbed by GAC when compared with methomyl and carbofuran. The real characteristics of the water treated by a conventional system (WTCS) influenced in the adsorption process were also verified, because the desorption of the pesticides occurred to the detriment of the adsorption of compounds with greater affinity with the GAC, which are inherent to WTCS. Finally, GAC has proven to be promising in the removal of carbamate insecticides.

Keywords: Adsorption; Breakthrough curve; Carbaryl; Methomyl; Carbofuran

1. Introduction

The pesticides carbaryl, methomyl and carbofuran belong to the chemical subgroup of carbamates and are mainly used as insecticides [1] in cotton, soybean, corn, rice, wheat, bean, potato and tomato crops [2], due to its broad spectrum of biological activities. However, agricultural crops, in general, do not fully assimilate these compounds, so carbamates are also found in aquatic environments in concentrations ranging from a few μg dm^{-3} to hundreds of mg dm^{-3} [3].

These pesticides cause different forms of intoxication through contact with the human population through the ingestion of contaminated water [4], such as deregulation of the immune system and predisposition to different types of

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cancers [5], the inhibition of the acetylcholinesterase enzyme, causing hypothyroidism, the reduction in sperm count and the excessive presence of abnormal spermatozoa [6]. In this way, the removal of these micropollutants, especially from the water used for human consumption, becomes essential.

However, the maximum permitted values (MPV) of these compounds should initially be considered for the appropriate choice of technology for the removal of these pesticides in the public water supply, according to each country. In Brazil, the MPV for carbofuran is 7 $\mu g\ L^{-1}$, as described by Ordinance N° 2914/2011 of the Ministry of Health [7], the other carbamates are not considered in the Brazilian Federal Law in terms of potable water. The MPV of carbaryl, methomyl and carbofuran were also determined by the legislation of countries such as Australia $\leq 30\ \mu g\ L^{-1}$ [8], Canada $\leq 10\ \mu g\ L^{-1}$ [9], China $\leq 10\ \mu g\ L^{-1}$ [10] and the European Economic Community $\leq 0.1\ \mu g\ L^{-1}$ [11].

Among the technologies for the removal of carbamate insecticides from the public water supply, fixed bed adsorption column of granular activated carbon (FBAC-GAC) have high efficiency in the removal of carbamate pesticides [12].

This technology is also notable due to the insensitivity to toxic substances, high adsorption capacity, the possibility of adsorbent material regeneration [13], as well as the low generation of transformation by-products [14].

Conversely, for the global understanding of the adsorption phenomena in FBAC-GAC, it is essential to obtain information on kinetics, thermodynamics and equilibrium relationships between the adsorbate and the adsorbent, defined by the adsorption isotherms.

The most common kinetic models applied to adsorption correspond to the pseudo-first-order and pseudo-second-order equations and acknowledge that the difference between the concentration of the solid phase (pesticides) at any reaction time and the concentration of pesticide in equilibrium is the force of adsorption. Consequently, the global adsorption rate is either proportional to the driving force in the case of the pseudo-first-order equation or is the square of the driving force as described by the pseudo-second-order model [15].

The thermodynamic adsorption parameters represented by the enthalpy, entropy and free energy of Gibbs determine whether the process is spontaneous, exothermic or endothermic and if the adsorbent has a high resemblance to the adsorbate. In addition, they can provide information on the physical or chemical nature of the adsorption and the heterogeneity of the adsorbent surface [16].

The isotherms responsible for describing the adsorption equilibrium of pure (monocomponent) or combined (multicomponent) compounds attest to the most adequate fit in relation to the theoretical or empirical models and provide an understanding of the adsorption process.

Faur et al. [13] verified through the analysis of multicomponent adsorption that the adsorption capacity of the pesticides was discrepant with each other, indicating the existence of competition for active sites of the adsorbent (activated carbon). Consequently, the pesticide with the highest saturation potential was responsible for occupying most of the active sites and hindering the additional adsorption of other pesticides that have lower affinity with the adsorbent.

Thus, the application of the FBAC-GAC for multicomponent adsorption must take into account the interactions between the mixture of the compounds. This knowledge is of great importance to obtain the operating conditions of an adsorption column operating with multicomponent removal in a continuous process [17].

Due to this, the objective of this research was to evaluate the multicomponent adsorption of carbaryl, methomyl and carbofuran pesticides in GAC from the *Orbignya phalerata* epicarp, as well as to predict the equilibrium, kinetics and thermodynamics of adsorption in the removal of these pesticides from water (FBAC-GAC) and batch reactor.

2. Materials and methods

2.1. Public water supply, adsorbent and adsorbates

The water used in this study came from the mixture between water from the Cubatão Sul and Rio Vargem do Braço rivers in Santa Catarina, Brazil. The water was treated by the local sanitation company (Casan-Florianópolis) by conventional system (water treated by a conventional system [WTCS]), that is, coagulation with aluminum polychloride, mechanical flocculation, decantation, rapid upward filtration (sand), pH correction with calcium oxide, chlorine gas disinfection and reservation (storage).

After the reservation, the water was collected in the Laboratory of Water Potabilization (LAPOÁ) and fortified with carbamates carbaryl, methomyl and carbofuran for the subsequent adsorption in GAC.

The commercial GAC adsorbent from the babassu epicarp was prepared according to the procedures presented in standard [18], which consisted of carefully washing the GAC with ultrapure water until all the GAC powder was removed and the pH of the wash water did not change. After washing the GAC, it was oven dried at 150°C ± 1°C for 4 h and stored in an amber bottle until the time of use.

The physicochemical parameters of this GAC and its respective applied methodologies were: surface area, pore size and pore volume [19]; apparent density [20]; granulometry [21]; pH and pH of the zero charge point (pH_{PCZ}) [22]; volatile material [23]; moisture content [24]; ash contents [25]; iodine value and methylene blue [26].

In the batch reactor adsorption, analytical grade carbaryl, methomyl and carbofuran adsorbates (Sigma-Aldrich®) were added individually and mixed. In the FBAC, the WTCS adsorbates were added to the mixture, under the initial concentration of 25 $\mu g\ L^{-1}$.

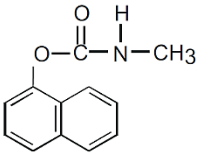
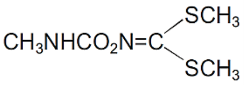
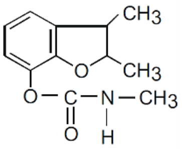
Some of the main characteristics [2] of the adsorbates are described in Table 1.

2.1.1. Determination of adsorbates

For the determination and quantification of analytical grade carbaryl, methomyl and carbofuran (Sigma-Aldrich®), the analytical technique applied was high performance liquid chromatography (HPLC).

Due to this, a liquid chromatograph (Thermo Scientific, Dionex UltiMate 3000) was utilized, equipped with reverse phase column (octadecyl C18 cartridges), with a fluorescence detector (emission at 340 nm/465 nm) and a post-column derivatizing agent (Pickering PCX 5200®). The ultrapure water (MilliQ®) and acetonitrile (J.T. Backer®) were used in

Table 1
Physicochemical properties of the carbamates carbaryl, methomyl and carbofuran

Parameters	Carbaryl	Methomyl	Carbofuran
Chemical structure		 $CH_3NHCO_2N{=}C(SCH_3)_2$	
Chemical name	1-Naphthyl methylcarbamate	*S*-Methyl *N*-(methylcarbamoyloxy) thioacetimidate	2,3-Dihydro-2,2-dimethylbenzofuran-7-yl
Molar mass (g mol^{-1})	201.2	162.2	221.3
Flash point	82°C and 759 mmHg	70.3°C and 714 mmHg	143.3°C and 760 mmHg
Fusion point (°C)	142	131	154
Solubility in water	120 mg L^{-1} and 23.5°C	57.9 g L^{-1} and 25°C	62 mg L^{-1}
Lethal dose LD$_{50rats}$ (mg kg^{-1})	1	21	8
Main product of degradation	1-Naftol	Methomyl metiol; sulfoxide oxime	3-Cetocarbofuran; 3-hidroxicarbofuran

the mobile phase in order to separate the chromatographic peaks. These solvent gradient systems were maintained between 30% and 100% for approximately 16 min of analysis.

The analytical procedures were performed according to standard 531.2 [27]. However, in order to guarantee the reliability of the values obtained in the analyzes and due to the changes in the methodology regarding the removal of a mobile phase (methanol) and the reduction of the detection time of the chromatographic peaks, the analytical method was validated according to the procedures described by Resolution N° 899/2003 [28]. In this way, the methodology demonstrated linear in the range of the concentration (0.5–100 µg L^{-1}), precise (relative standard deviation <5%), exact (98.6% at 103.6%) and selective (there was no overlap of chromatographic peaks). Detection limits and qualification limits were 0.0082 and 0.0273 µg L^{-1} (carbaryl), 0.0472 and 0.0157 µg L^{-1} (methomyl), 0.0042 and 0.0140 µg L^{-1} (carbofuran), respectively.

2.2. Batch adsorption (lab test)

The batch reactor adsorption assays were performed using a ratio of adsorbent mass/volume of 4 g L^{-1} solution containing carbaryl, methomyl and carbofuran under different concentrations (1, 5, 15, 25 and 50 µg L^{-1}) at different temperatures (15°C, 25°C and 35°C) and adsorption time (1, 2, 4, 8, 10, 15, 20 and 30 min).

2.2.1. Balance and adsorption kinetics

To determine the adsorption equilibrium, the GAC remained in contact with the adsorbate under temperature and constant stirring, 25°C and 200 rpm (3.33 s^{-1}), respectively, in a bench incubator. To determine the equilibration time of the aliquots, they were analyzed after 1, 2, 4, 8, 10, 15, 20 and 30 min of the adsorption test.

Subsequently, the sample was preserved with chloroacetic acid (pH between 3.5 and 4.0), the cellulose acetate membrane samples were filtered, the pore aperture was 0.22 µm and the sample remained under refrigeration at 4°C for further investigation of the carbamate concentration.

The adsorption capacity of the adsorbent was determined by Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{m_a} \tag{1}$$

where q_e is the amount of adsorbate adsorbed by adsorbent gram in balance (mg g^{-1}); C_0 is the initial adsorbate concentration (mg L^{-1}); C_e is the concentration of the remaining adsorbate in solution at equilibrium (mg L^{-1}); V is the volume of solution (L) and m_a is the GAC mass (g).

The results of the equilibrium study of the monocomponent adsorption were adjusted to the Langmuir (Eq. (2)), Freundlich (Eq. (3)) and Langmuir–Freundlich (Eq. (4)) models, called the three parameter models (q_{max}, K_{LF} and n). If $n \geq 1$ means the system is homogeneous, corresponding to the Langmuir model [29], then $n < 1$ represents the increase in heterogeneity. The three parameters of this equation were determined from non-linear regression analysis.

$$q_e = \frac{Q_{\text{máx}} K_L C_e}{1 + K_L C_e} \tag{2}$$

where Q_{max} is the maximum adsorption capacity (mg g^{-1}); K_L is the Langmuir constant (L mg^{-1}), the parameters K_L and Q_{max} were calculated using the angular and linear coefficients of a graph C_e/q_e vs. C_e.

$$q_e = K_F C_e^{1/n} \tag{3}$$

where K_F is the Freundlich constant (L mg^{-1}) and n is the constant related to surface heterogeneity.

$$q_e = \frac{Q_{\text{máx}}(K_{\text{LF}}C_e)^n}{1+(K_{\text{LF}}C_e)^n} \tag{4}$$

where K_{LF} is the Langmuir–Freundlich adsorption affinity constant (L mg^{-1}).

The results of the equilibrium study of the multicomponent adsorption were adjusted to the Langmuir–Freundlich models (Eq. (5))

$$q_{ei} = \frac{q_{\text{LF},i}^{\text{máx}} K_{\text{L},i} C_{e,i}^{\text{mLF},i}}{1+\sum_{i=1}^{n} K_{\text{LF},i} C_{e,i}^{\text{mLF},i}} \tag{5}$$

where $q_{\text{LF},i}^{\max}$ and $K_{\text{LF},i}$ were obtained from monocomponent system data.

The results of adsorption kinetics (Eqs. (6) and (7)) were evaluated by pseudo-first-order and pseudo-second-order models [30].

$$\ln\left(q_e - q\right) = \ln q_e - k_1 t \tag{6}$$

where q is the amount adsorbed at time t (mg g^{-1}); k_1 is the constant of the pseudo-first-order model, determined by the slope of the line of ln($q_e - q$) (mg g^{-1}) vs. t (h); t is the time (h).

$$\frac{1}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t_1 \tag{7}$$

where k_2 is the pseudo-second-order constant (h g mg^{-1}).

By means of the Arrhenius graphs that determine the energy of activation in the adsorption, starting from experimental kinetic data and Eyring graphs, the kinetic parameters of activation energy (E_a), Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were obtained.

2.2.2. Adsorption thermodynamics

In order to evaluate the influence of the temperature on the adsorption of the carbamates in GAC, the adsorption batch reactor was carried out under different temperatures (15°C, 25°C and 35°C), maintaining the initial concentrations of 1, 5, 15, 25 and 50 μg L^{-1} of carbaryl, methomyl and carbofuran, the adsorbent mass/volume ratio of the solution and the adsorption equilibrium time obtained in the monocomponent adsorption kinetics.

The values of the thermodynamic parameters of the adsorption process, such as adsorption enthalpy ($\Delta H°_{\text{ads}}$), adsorption free energy ($\Delta G°_{\text{ads}}$) and adsorption entropy ($\Delta S°_{\text{ads}}$) were obtained by means of Eqs. (8) and (9).

$$\ln K_e = \frac{\Delta H°_{\text{ads}}}{RT} + \frac{\Delta S°_{\text{ads}}}{\text{R}} \tag{8}$$

where K_e is the equilibrium constant at defined temperatures from the adsorption isotherm employed in the adjustment of the data; $\Delta H°_{\text{ads}}$ is the adsorption enthalpy (kJ mol^{-1}); R is the universal constant of gases (K^{-1} mol^{-1}); T is the temperature (K); $\Delta S°_{\text{ads}}$ is the adsorption entropy (J mol^{-1} K^{-1}).

$$\Delta G°_{\text{ads}} = \Delta H°_{\text{ads}} - T\Delta H°_{\text{ads}} \tag{9}$$

where $\Delta G°_{\text{ads}}$ is the Gibbs free energy in adsorption (kJ mol^{-1}).

2.3. Adsorption (pilot test)

Continuous adsorption (FBAC-GAC) occurred at room temperature (25°C ± 2°C) and without significant alteration of the WTCS pH (6.51 ± 0.15), even after the fortification of WTCS by carbaryl, methomyl and carbofuran (25 μg L^{-1}).

FBAC-GAC was made from polyvinyl chloride. The reservoir, homogenization and pumping system of the WTCS were fortified with carbamates and composed of two reservoirs with a maximum volume of 1,000 L, both made of medium density polyethylene (DMSO). The homogenization of WTCS and carbamates in the reservoirs was done by recirculating the WTCS with the aid of a centrifugal pump with a power of ½ hp.

By means of gravity, the water reached the continuous level reservoir with vertical float and a maximum volume of 25 L, from this reservoir, the water went to the FBAC-GAC by means of a peristaltic pump.

The flow of water was downstream and the treated water was collected above the granular medium (Fig. 1) in order to avoid trapping air between the GAC grains inside the FBAC.

To determine the efficiency of FBAC-GAC in relation to the removal of carbamates, aliquots of raw and treated water were collected at the entrance (in order to avoid losses of pesticides in the reservoir system) and at the exit of the FBAC-GAC. These samples were collected and analyzed every 4 h.

The main design parameters of the FBAC-GAC were: 0.297 mm of mean diameter of GAC (mesh 40 × 50); 17.0 mm of internal diameter of the adsorption column; flow rate of 2.27 L h^{-1}; 10 cm of fixed bed of GAC; 3 cm of support layer, composed of glass beads of 1, 3 and 5 mm in diameter; 0.60 min of empty bed contact time and surface application rate of 240 m^3 m^{-2} d^{-1}. The ratio of the GAC particle diameter to the adsorption column diameter was greater than 50 (1:53.89), thus avoiding preferential flow near the adsorption column wall.

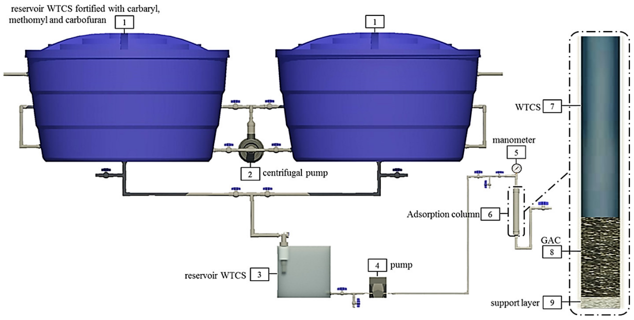


Fig. 1. Schematic representation of the adsorption column in a fixed bed of granular activated carbon.

3. Results and discussion

3.1. Physicochemical characteristics of GAC

The values of the GAC characterization parameters corresponded to: 754.00 m^2 g^{-1} surface area, pore size between 15.1722 and 450.7526 Å, 0.037 ± 0.001 g cm^{-3} pore volume, 11.32% ± 1% ash content, 0.47 ± 0.01 g cm^{-3} apparent density, 10.01 ± 0.02 pH, 7.49 ± 0.01 pH$_{PCZ}$, 7.36% ± 0.5% volatile materials, 2.22% ± 0.1% moisture content, 837.0 ± 4.92 mg g^{-1} of iodine number and 113.5 ± 1.57 mg g^{-1} of methylene blue index.

3.2. Adsorption of carbamates in batch reactor (lab test)

In adsorption kinetics, the amount of carbaryl, methomyl and carbofuran adsorbed by GAC reached the adsorption equilibrium after 15 min of contact between the adsorbate and the adsorbent (monocomponent) and 10 min (multicomponent), Figs. 2(a)–(c) and (d), respectively. In the multicomponent adsorption, the time for the adsorption to occur is lower than in the adsorption of the same individual compounds, due to the competition between the adsorbates [31].

It was also observed that the largest amount of adsorbate, isolated or in the mixture, was removed at the beginning of the adsorption process, as a result of the greater availability of adsorptive sites in the GAC. Consequently, the adsorption became slower at the end of the adsorption process in both cases, this being the result of the saturation of the active sites and the reduction of the concentration of the insecticide carbamates in the solution.

Table 2 shows the kinetic parameters of adsorption considering the pseudo-first-order (k_1) and pseudo-second-order (k_2) models.

According to the results presented in Table 2 and considering Fig. 2, the adsorption kinetics were described more precisely by the pseudo-second-order model, since the linear correlation coefficients (LCC) presented values of r_2 closer to 1.

This result corroborates the study by Salman and Hameed [32]. Among the kinetic models used by the authors in the adsorption of carbamate carbofuran in GAC, the pseudo-second-order obtained the best data adjustment, with LCC between 0.991 and 0.999.

The effect of temperature (15°C, 25°C and 35°C) on the amount of monocomponent and multicomponent carbamates adsorbed by GAC under initial concentration of 25 μg L^{-1} is presented in Figs. 3(a)–(c) and Figs. 3(d)–(f), respectively.

From Fig. 3, it can be seen that as the temperature increased from 25°C to 35°C, the amount of the carbamate adsorbed for the GAC decreased. This result is related to two important effects of temperature on the adsorption process. The increase in temperature elevates the diffusion rate of the adsorbate molecules in every inner and outer boundary layer in the pores of the adsorbent particle owing to the decrease in the viscosity of the solution and the temperature variation changes the equilibrium state of the adsorption for a given adsorbate [33,34].

The values of the kinetic parameters for the three temperatures to which the adsorbents and the adsorbate were submitted are shown in Table 3, considering the results obtained in the pseudo-second-order model, where the best data adjustment was performed.

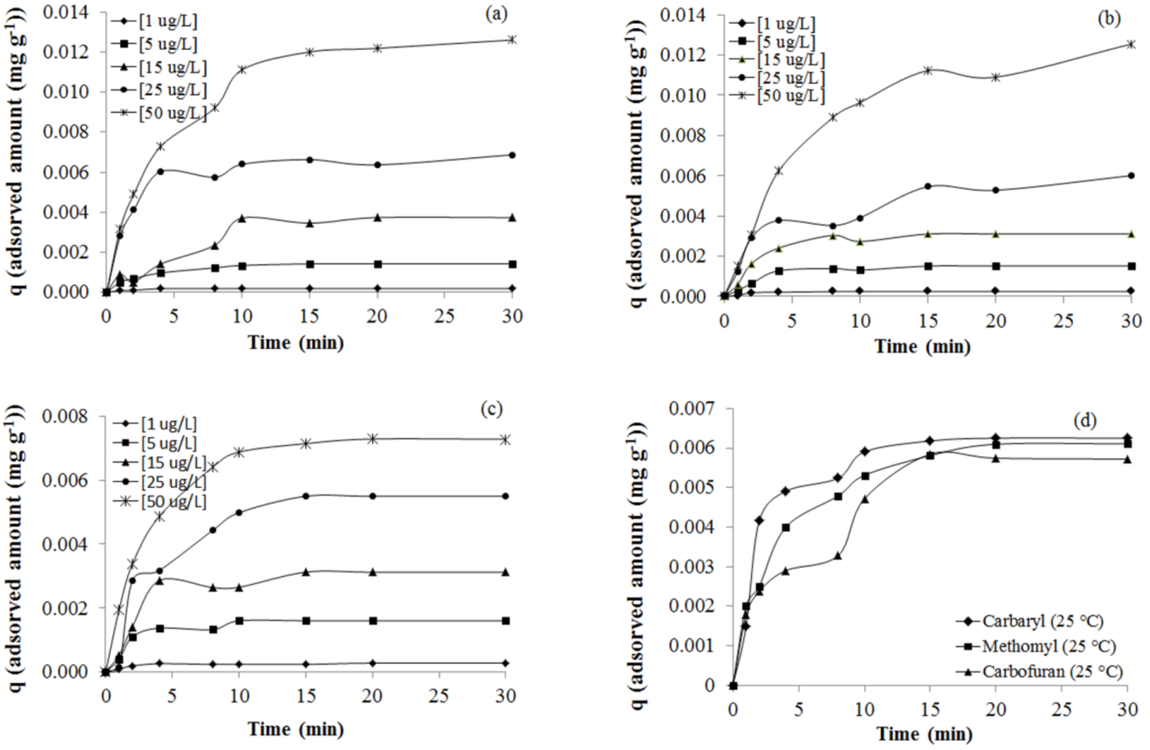


Fig. 2. Carbamates under initial concentration of 25 μg L^{-1} adsorbed on GAC at 25°C vs. time (min). (a) Carbaryl, (b) methomyl, (c) carbofuran and (d) carbaryl, methomyl and carbofuran, multicomponent.

Table 2
Kinetic parameters of adsorption calculated by the models (k_1) pseudo-first-order and (k_2) pseudo-second-order (T = 25°C)

Adsorbate	Concentration (mg L^{-1})	q_e (mg g^{-1})	k_1	$r_{2(1)}$	k_2	$r_{2(2)}$
Carbaryl	0.001	0.0002	19.1690	0.4414	212.9759	0.9991
	0.005	0.0012	18.1710	0.5796	418.7989	0.9938
	0.015	0.0027	7.5595	0.4365	44.7659	0.9512
	0.025	0.0056	7.7853	0.3951	122.8501	0.9978
	0.050	0.0111	2.4700	0.3501	28.43530	0.9986
Methomyl	0.001	0.0002	18.6040	0.4328	526.5495	0.9986
	0.005	0.0013	18.3970	0.5343	294.9039	0.9826
	0.015	0.0027	16.0650	0.5643	160.8123	0.9840
	0.025	0.0057	0.2460	0.5403	49.4960	0.9724
	0.050	0.0109	12.637	0.5816	11.0358	0.9463
Carbofuran	0.001	0.0002	15.275	0.3708	918.5905	0.9923
	0.005	0.0013	12.536	0.3649	855.5529	0.9967
	0.015	0.0026	14.188	0.3009	408.6693	0.9882
	0.025	0.0050	15.422	0.5895	155.8881	0.9845
	0.050	0.0112	6.3308	0.1721	113.2631	0.9980

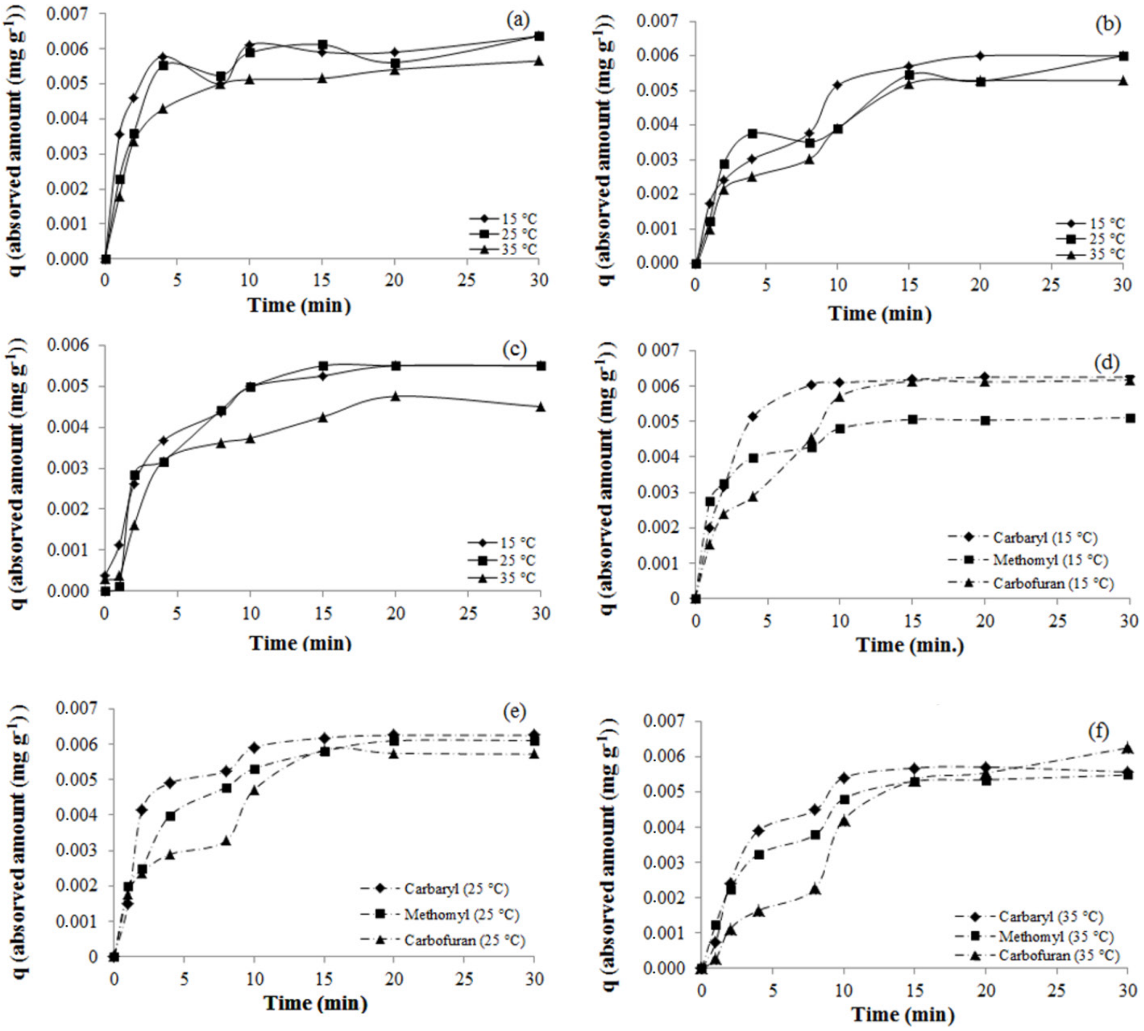


Fig. 3. Amount of carbaryl, methomyl and carbofuran adsorbed in GAC at three different temperatures (15°C, 25°C and 35°C). (a) Carbaryl, (b) methomyl, (c) carbofuran, (d) multicomponent at 15°C, (e) multicomponent at 25°C and (f) multicomponent at 35°C.

By means of the respective values of the velocity constants, k_2 of Table 3, the Arrhenius (Figs. 4(a.1), (b.1) and (c.1)) and Eyring plots were plotted (Figs. 4(a.2), (b.2) and (c.2)).

According to the data obtained through Figs. 4(a.2), (b.2) and (c.2) and applying Eq. (7), the energy of thermodynamic activation for each carbamate was calculated and presented in Table 4. By means of Eq. (8), Gibbs activation energy calculated at a temperature of 25°C was obtained.

The negative values of ΔS are interpreted as a reduction in the randomness at the adsorbent/adsorbate interface (GAC/carbamates), that is, the interface tended to a larger organization [35].

The value of $\Delta H < 0$ indicates adsorption of an exothermic nature. Therefore, adsorption decreases with increasing temperature [36]. The enthalpy change caused by the chemisorption had values between 84 and 420 kJ mol^{-1}, then enthalpy values below 84 indicated that the adsorption nature is physical, involving weak attraction forces [36].

Table 3
Kinetic parameters of GAC adsorption at three different temperatures and 25 μg L^{-1} concentration of carbamates

Adsorbate	Temperature (°C)	q_e (mg g^{-1})	k_2	r_2
Carbaryl	15	170.6210	0.0064	0.9997
	25	130.1516	0.0065	0.9990
	35	65.75209	0.0064	0.9956
Methomyl	15	49.4960	0.0066	0.9724
	25	45.2055	0.0065	0.9562
	35	40.25719	0.0060	0.9505
Carbofuran	15	165.4752	0.0056	0.9875
	25	155.8881	0.0057	0.9837
	35	143.9170	0.0045	0.9782

The spontaneity of an adsorption process can be predicted by the standard Gibbs free energy value, when this is negative, adsorption is spontaneous, similarly positive values indicate non-spontaneous adsorption [33].

In Figs. 5(a) and (b) the effect of the initial carbamate concentration and the adsorbed amount in equilibrium at 25°C can be observed.

By means of Figs. 5(a) and (b), it is observed that the amount of carbaryl, methomyl and carbofuran adsorbed at equilibrium increased by raising the initial carbamate concentration until reaching a concentration of 50 μg L^{-1}.

The sum of the adsorbed species represented in the denominator of Eq. (5) implies a reduction of the adsorbed amount of a certain species when in a mixture compared with its adsorption as a pure substance, evidencing competition for adsorption sites.

The adsorption isotherms related to the Langmuir (Eq. (2)), Freundlich (Eq. (3)) and Langmuir–Freundlich (Eq. (4)) models, as well as the Langmuir–Freundlich multicomponent isotherm (Eq. (5)), consistent with carbaryl, methomyl and carbofuran isolated and mixed are shown in Figs. 6(a)–(d), respectively.

In Table 5, the isotherms parameters for the removal of carbaryl, methomyl and carbofuran for three different temperatures are presented.

Table 4
Thermodynamic activation parameters for the adsorbent (GAC)

Adsorbate	ΔS (J Kmol^{-1})	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})
Carbaryl	–43.9542	–8.8636	13.0895
Methomyl	–55.5636	–10.0807	17.1181
Carbofuran	–27.6293	–5.1372	8.3755

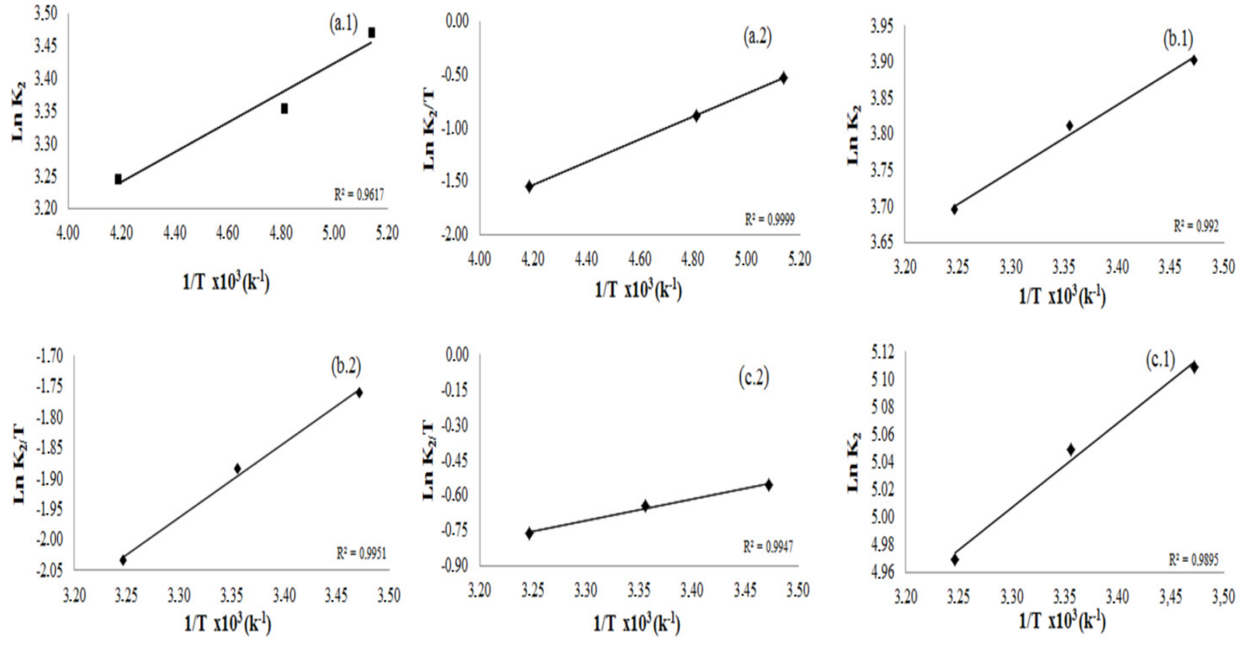


Fig. 4. Arrhenius plots and Eyring plots for carbamates adsorption in GAC (temperature in Kelvin). (a.1) Arrhenius carbaryl; (a.2) Eyring carbaryl; (b.1) Arrhenius methomyl; (b.2) Eyring methomyl; (c.1) Arrhenius carbofuran and (c.2) Eyring carbofuran.

Although the LCC of the Freundlich isotherms for the adsorption of the carbaryl, methomyl and carbofuran indicate their validity in the study (Table 5), it was observed that the Langmuir–Freundlich isotherm is better suited to the experimental data for the monocomponent and multicomponent (Fig. 6).

Table 5 shows that the experimental results obtained for the carbamates, both monocomponent and multicomponent, were in the ascendancy of the equilibrium isotherms (Fig. 6), demonstrating that the adsorbents can still retain larger amounts of adsorbate until reaching their maximum capacity.

The carbofuran adsorption equilibrium and kinetics study performed by Salman and Hameed [32] using GAC and the carbofuran pesticide in the concentration range of 50–225 mg L^{-1}, concluded that the equilibrium data fit well with the equilibrium model of Langmuir, with the single-layer adsorption capacity of GAC being 96.15 mg g^{-1} for carbofuran. Subsequently, another GAC presented the best fit for the Langmuir isotherm as well [37].

Equilibrium studies were performed for adsorption of methomyl insecticide on GAC. Parameters that affected the adsorption were the contact time and size of the adsorbent. The linear regression was used to determine the best fit and it was discovered that the equilibrium data are better represented by the Langmuir model, suggesting the monolayer adsorption of methomyl. Adsorption decreases with increasing temperature and reduces the particle size of the adsorbent. The adsorption capacity was determined as 72.85 mg g^{-1} at 25°C and decreased to 47.36 mg g^{-1} when the temperature increased to 60°C. The value of the enthalpy change was calculated (ΔH = –2.35 kJ mol^{-1}) indicating that the removal process was exothermic and physical in nature [12].

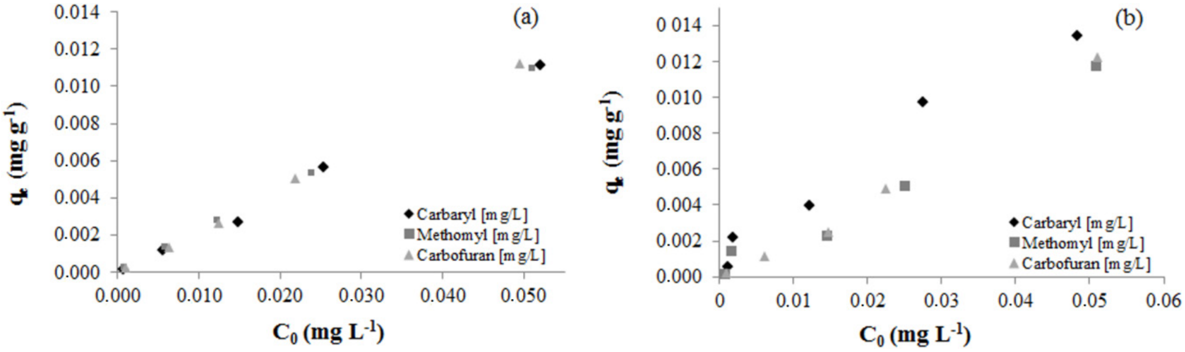


Fig. 5. Amount of carbamates adsorbed on GAC at equilibrium vs. initial concentration at 25°C. (a) Carbaryl, methomyl and carbofuran, monocomponent and (b) carbaryl, methomyl and carbofuran, multicomponent.

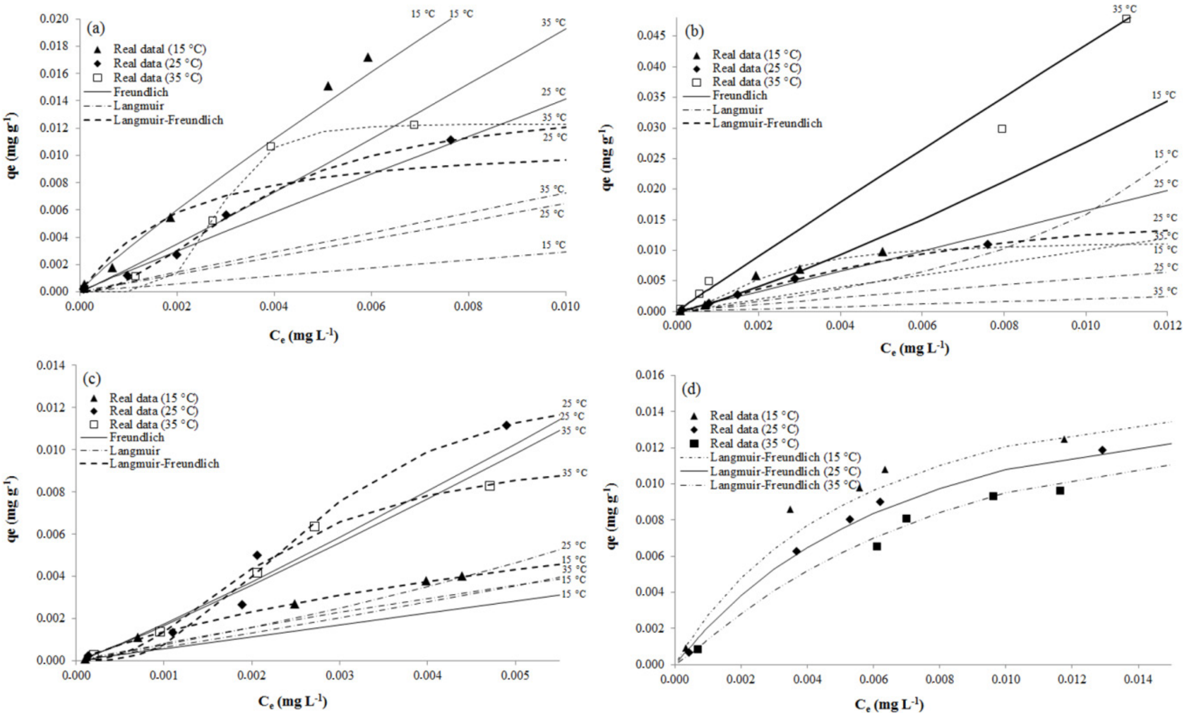


Fig. 6. Monocomponent isotherm. (a) Carbaryl, (b) methomyl, (c) carbofuran and (d) multicomponent isotherm, carbaryl, methomyl and carbofuran.

Table 5
Parameters of isotherms for removal of carbamates by GAC under three different temperatures

Adsorbate	Parameters	15°C	25°C	35°C
Carbaryl	K_L (L mg^{-1})	2.7949	0.4339	–27.2640
	Q (mg g^{-1})	0.1069	1.4950	–0.0266
	r (Langmuir)	0.136	0.0002	0.1032
	K_F (L mg^{-1})	1.5688	1.2097	2.5472
	$1/n$	0.8949	0.9662	1.0602
	r (Freundlich)	0.9881	0.9872	0.959
	K_{LF} (L mg^{-1})	46.0868	272.9182	346.2119
	Q (mg g^{-1})	0.091	0.0136	0.0123
	N	1.12	2.05	5.6043
	R (Langmuir–Freundlich)	0.9992	0.9932	0.9803
Methomyl	K_L (L mg^{-1})	–53.3192	6.2857	0.8103
	Q (mg g^{-1})	–0.0139	0.0929	0.2536
	r (Langmuir)	0.3884	0.0283	0.2387
	K_F (L mg^{-1})	6.7754	1.6590	3.9001
	$1/n$	1.1941	1.0015	0.9758
	r (Freundlich)	0.9844	0.9953	0.9906
	K_{LF} (L mg^{-1})	459.1096	149.4992	0.0229
	Q (mg g^{-1})	0.0115	0.0202	783.1399
	N	1.8218	1.2445	1.1744
	r (Langmuir–Freundlich)	0.9740	0.9999	0.9822
Carbofuran	K_L (L mg^{-1})	38.805	–43.617	–21.3832
	Q (mg g^{-1})	0.022	–0.017	–0.0298
	r (Langmuir)	0.071	0.354	0.4543
	K_F (L mg^{-1})	0.5169	3.3475	3.6107
	$1/n$	0.9820	1.1006	1.1061
	r (Freundlich)	0.9619	0.9649	0.9902
	K_{LF} (L mg^{-1})	100.8243	367.0519	452.120
	Q (mg g^{-1})	0.0124	0.0133	0.0098
	N	0.9089	2.7685	2.2768
	r (Langmuir–Freundlich)	0.9966	0.9583	0.9857
Multicomponent[a]	K_{LF}	171.6401	142.3830	120.7581
	Q (mg g^{-1})	0.019	0.0182	0.0161
	n	1.02	1.0549	1.15
	r (Langmuir–Freundlich)	0.9938	0.9925	0.9652

[a] Carbaryl, methomyl and carbofuran.

The lnK_L vs. $1/T$ plot is shown in Fig. 7, according to the Van't Hoff equation (Eq. (8)).

From the linear and angular coefficients shown in Fig. 7, the values of the calculated thermodynamic parameters of adsorption are described in Table 6.

Eqs. (8) and (9), as well as the Van't Hoff plots, allowed the determination of thermodynamic adsorption parameters for the adsorbent GAC, respectively, adsorption enthalpy ($\Delta H°_{ads}$), adsorption free energy ($\Delta G°_{ads}$) and entropy adsorption ($\Delta S°_{ads}$).

The values of the variations of $\Delta G°$, $\Delta H°$ and $\Delta S°$ are negative, these data indicate that the adsorption process between the carbamates carbaryl, methomyl and carbofuran and the GAC is spontaneous, exothermic and accompanied by a decrease in entropy, respectively.

According to a theoretical revision on the second law of thermodynamics, the spontaneous processes that result in the decrease of the entropy of the system are always exothermic. The variation of entropy (variation of disorder) affects the spontaneity of this process. The more variation of disorder will produce the entropy variation and consequently lesser spontaneity of the process [33].

3.3. Multicomponent pilot scale adsorption

WTCS fortified with carbaryl, methomyl and carbofuran (25 μg L^{-1}) had the following characteristics: no significant residual chlorine concentration; pH remained close to neutrality (6.51 ± 0.15); the temperature was 21°C ± 4°C; the turbidity and apparent color variation analyzed at the entrance of the adsorption column was 3.6 NTU (24 h) at 1.51 NTU (184 h) and 37 uH (24 h) at 6 uH (196 h), respectively; the pressure in FBAC-GAC ranged from 2 to 16 psi from 208 h of operation.

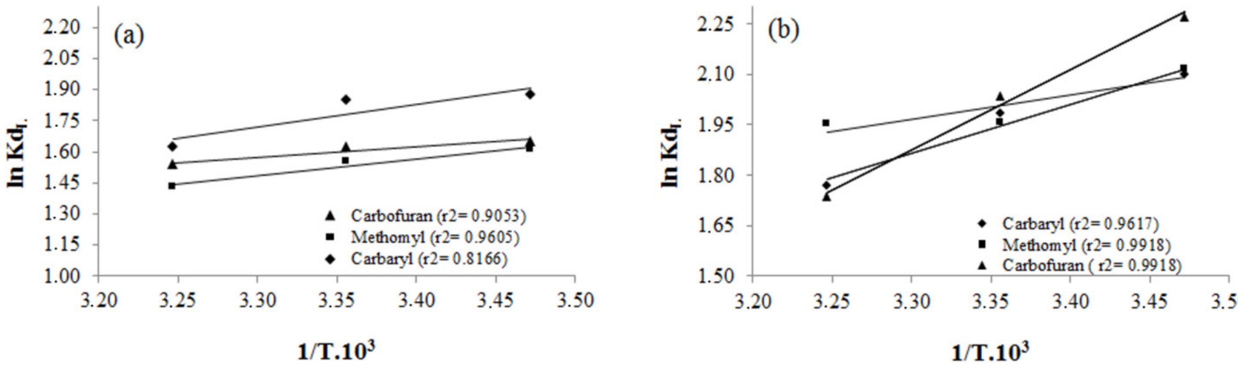


Fig. 7. Van't Hoff equation plots for GAC. (a) Carbaryl, methomyl and carbofuran, monocomponent and (b) carbaryl, methomyl and carbofuran, multicomponent.

Table 6
Thermodynamic adsorption parameters for the GAC adsorbent

Adsorbate	$\Delta S°$ (J Kmol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta G°$ (kJ mol^{-1})
Carbaryl	–16.2	–9.2	–4.583
Methomyl	–9.8	–6.7	–3.841
Carbofuran	–0.5	–4.1	–4.021

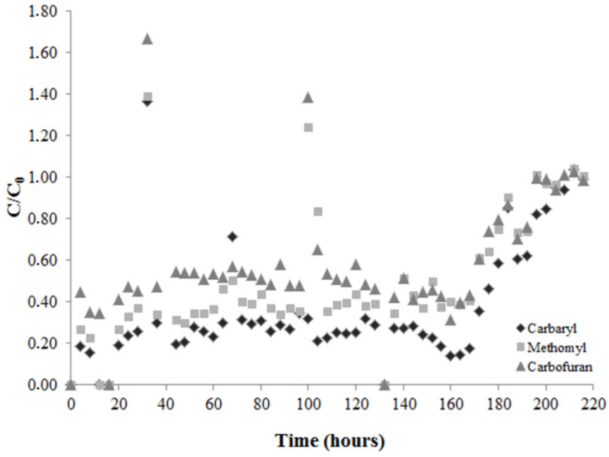


Fig. 8. Rupture curves – carbamates carbaryl, methomyl and carbofuran.

Fig. 8 shows the experimental results of the rupture curves of carbamates carbaryl, methomyl and carbofuran.

Analyzing the multicomponent adsorption of the GAC fixed bed, although the initial concentrations of the carbamates are equal to 25 µg L^{-1}, it can be seen that carbaryl is the contaminant most adsorbed by GAC. This higher adsorption tendency of carbaryl may be related to its lower solubility (0.04 g L^{-1} at 20°C), compared with carbamates methomyl (58 g L^{-1} at 20°C) and carbofuran (0.32 g L^{-1} at 20°C).

The solubility of the molecule is related to the adsorption tendency of a molecule according to its similarity to water or the adsorbent. Adsorption with GAC from water increases when the adsorbate solubility decreases in aqueous media [38]. As the molecule becomes larger with the addition of hydrophobic groups, its solubility in water decreases and adsorption increases.

However, according to the same author, the decrease in solubility does not always increase the adsorption capacity, because when the size of the molecule increases, the diffusion rate inside the GAC particle decreases, especially when the molecule reaches the size of the pore diameter of the particle. Thus, the size of the molecule will also influence its adsorption.

The higher affinity between adsorbate carbaryl and GAC shows that this result corroborates the multicomponent study in a batch reactor. Nevertheless, in the FBAC-GAC the intrinsic characteristics of the WTCS, such as color and turbidity contributed to the competitive adsorption.

The highest carbamate removal efficiency of carbaryl, methomyl and carbofuran was observed at the start of the operation (0 h), after 4 h, and thereafter at 132 h of the FBAC-GAC pilot scale operation. When monitored every 4 h, the removal efficiency tended to reduce throughout the operation of the adsorption column until reaching full saturation.

By keeping the FBAC-GAC on a pilot scale in operation (Fig. 8) after the first saturation, which occurred in 32 h, the relationship between the inlet and outlet concentrations of carbamates reduced again and reached saturation in 196 h. This result confirms that the real characteristics of the WTCS influenced the adsorption of the carbamates in GAC, that is, the desorption of the carbamates in detriment of the adsorption of compounds of greater affinity with the GAC, which are inherent to WTCS. This finding was only possible due to the use of a real matrix.

In this way, it can be verified that the saturation of the carbamates occurred after 196 h of operation of the adsorption column, from this, the exit concentration of the carbamates remained higher than the inlet concentration (25 µg L^{-1}).

Parameters such as surface application rate, adsorption process mechanism, adsorption equilibrium nature, carbamate concentration at the adsorption column inlet and adsorbent bed height will contribute to the shape of the breakthrough curve.

The adsorption rupture time in FBAC tends to decrease with decreasing bed height, increasing adsorbent particle size, increasing fluid velocity through the bed, and increasing the initial concentration of the solute [39].

The rupture curves are generally very specific in each application. Thus, in this study, the rupture curves are related to the presence of the intrinsic characteristics of the WTCS applied to the adsorption column, as well as the GAC and the carbamates removed by the adsorption process.

4. Conclusion

The adsorption study of the pesticides carbaryl, methomyl and carbofuran revealed that the commercial GAC from the babassu epicarp (*O. phalerata*) was efficient in the removal of these carbamates from the public water supply.

The activated carbon showed a large surface area and a large volume of pores, which characterizes the GAC of the babassu epicarp (*O. phalerata*) as an effective adsorbent for the adsorption of carbamates carbaryl, methomyl and carbofuran.

The equilibrium data were best suited to the Langmuir–Freundlich isotherms for monocomponent and multicomponent. The adsorption kinetics were described more precisely by the pseudo-second-order model and the adsorption process between the carbaryl carbamates, methomyl and carbofuran and the GAC was characterized as exothermic, of a physical and spontaneous nature.

Experimental results indicated that carbaryl is adsorbed in greater amounts than methomyl and carbofuran, possibly due to competition for active GAC sites between the molecules of other carbamates as well as those inherent in WTCS.

It can be concluded, therefore, that the fixed-bed adsorption technology of granular activated carbon was efficient in the removal of carbaryl, methomyl and carbofuran from the public water supply.

Acknowledgments

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