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Kinetics and Modelling of Drug Adsorption using Activated Carbon Derived from Cocoa Cob Waste

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Abstract : Residual cocoa biomass was used for the generation of low temperature activated carbon, which was prepared and characterized by scanning electron microscopy (SEM) to determine the chemical composition of cocoa, and thus evaluate its use as an adsorbent to remove amoxicillin and ibuprofen, taking as a hypothesis that activated charcoal prepared from cocoa cob waste (shell, pulp and mucilage) is a good adsorber for removing ibuprofen and amoxicillin in aqueous solution. The removal averages were compared following an experimental design 2^2, by applying a two-way ANOVA for each contaminant. The biomass was thermally pre-treated at low temperature and impregnated with a solution of $ZnCl_2$ at different concentrations (50,33.33 and 25% v $ZnCl_2$ /v H_2O). The adsorption kinetics of the batch system were determined and modeled, establishing that the best conditions of amoxicillin adsorption were given at pH 6 and impregnation of 50% v v^{-1}, reaching a removal rate of 77.4% and that the kinetic model that best fitted the experimental removal data was Elovich with an R^2 between 0.9886 and 0.9949; while for ibuprofen taking into account the impregnation of activated carbon and the initial drug concentration (20,30 and 40 ppm), it was obtained that the higher the drug concentration, the higher the removal percentage giving a maximum result of 68% removal at 40 ppm and impregnation 50% v v^{-1}, while for activated carbon with impregnation 25% v v^{-1} and 20 ppm a removal rate of 29.15% was obtained and the experimental data of adsorption kinetics at optimum conditions according to the surface response method had a good fit to the pseudo-first order model with an R^2 between 0.779 and 0.9164.
Keywords : Adsorption, activated carbon, biomaterial, removal.

1. Introduction

Antibiotics and anti-inflammatory drugs are widely used worldwide for treatments in humans, animals and the agricultural industry. Antibiotics and anti-inflammatory drugs administered are often poorly absorbed and metabolized by humans and animals, and tend to enter water bodies being difficult to recover because of their low concentration and, in large quantities, can cause damage to the ecosystem, degrading water quality [1].

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In addition, exposure to these and their by-products after transformations in the environment can cause a variety of adverse effects, including acute and chronic toxicity and micro-organisms with antibiotic resistance [2, 3, 4, 5, 6].

Amoxicillin is one of the most widely used drugs, 60-70% of which is excreted unaltered, once consumed, it therefore has a negative impact on two levels: during manufacture and during and after use [7, 8]. Bioadsorption is a technology that offers the possibility of reducing the concentration of heavy drugs present in liquid effluent, through the use of biomass as adsorbent material. In recent decades, the emphasis of research in this area has been directed towards the research and development of typical and regional biomass, which have excellent adsorbent properties [9, 10].

Activated carbons from biomass from agro-industrial waste provide the products obtained with a high affinity for the removal of substances that wish to be removed from an effluent due to the inherent characteristics of the precursor material and the chemical agent used, This is how activated carbons have multiple applications such as the synthesis of activated carbon from cocoa shells chemically impregnated with (20% lime + 40% FeCl3 + 40% $ZnCl_2$), for the efficient removal of two anti-inflammatory agents, diclofenac sodium (DFC) and nimesulide (NM), from aqueous solutions [11, 12].

Impregnation with chemical dehydrating agents has become increasingly common in the use of agro-industrial waste as precursors for the production of activated carbon, among the most commonly used chemicals are found: ZnCl2, H_3PO4[15,31,32], H_2SO_4, K_2S, KCNS[33], HNO_3, H_2O_2, $KMnO_4$, $(NH_4)_2S_2O_8$[34], NaOH, KOH[31,35], and K_2CO_3[36], These are used in order to reduce the production cost of activated carbons because they need activation temperatures lower than 600°C in contrast to the physical activation by means of water vapor and CO2, also improves their adsorption capacity, obtaining an absorbent with good mechanical and physical-chemical properties of low cost [11].

In the same sense, Iovino et al., [13]made an experimental analysis of the adsorption of ibuprofen in a granular activated carbon. The effect of ibuprofen concentration, pH and temperature on equilibrium adsorption capacity through batch testing was investigated. Experimental results show that the highest adsorption capacity is observed at low pH (acid) and high temperatures.

Mansouri et al.,[14], investigated the competitive adsorption under dynamic and equilibrium conditions of ibuprofen and amoxicillin by conducting batch adsorption experiments on nanoporous carbons of different characteristics, evaluating the adsorption balance and kinetics, as well as the validation and simultaneous elimination of mixtures. The equilibrium adsorption capabilities evaluated from pure component solutions were higher than those measured in dynamic conditions, and were found to depend on the porous characteristics of the adsorbent and the nature of the specific/dispersive interactions that are controlled by the pH of the solution, surface density change in carbon and ionization of the contaminant.

The processing of agricultural residues by pyrolysis has been studied, for the preparation of activated carbon at low temperature with the presence of air. The variables taken into account were the impregnation ratio of the activation agent ($ZnCl_2$), time and carbonization temperature. We found the best results in the range of 240-400°C. The adsorption capacity was evaluated by BET analysis and the number of iodine. The use of low carbonization temperature seeks to further improve the economy of activated carbon generation [15].

In this work, low temperature activated carbons were prepared from cocoa shells activated with zinc chloride at different concentrations, to evaluate their use in the removal of amoxicillin and ibuprofen to the conditions obtained after applying the response surface methodology taking as hypothesis that activated carbon prepared from cocoa cob waste (shell, pulp and mucilage), is a good adsorbent for removing ibuprofen and amoxicillin in aqueous solution.

2. Experimental

2.1 Design of experiments.

An experimental design of factorial type 2^2 was followed by the application of a two-way ANOVA for Amoxicillin (Factors: Ratio of impregnation and pH) and Ibuprofen (Factors: Ratio of impregnation and drug concentration). Prior to each analysis, the assumptions required for ANOVA were verified: normality of data and homogeneity of variances [16].

2.2 Preparation of biomass and activated carbon

The cocoa cob was reduced in size and washed with deionized water, then dried for 48 h at 105°C in a Esco furnace, Model Isotherm®OFA-32-8. The shells were then ground and sieved to a particle size ranging from 1 to 2 mm.

In order to increase the surface area of the coal the biomass samples were impregnated with $ZnCl_2$ for ratios 1:2,1:3 and 1:4 ZnCl2: H_2O, 50,33.33 and 25 % v v^{-1}, respectively; adding 5 g of biomass to 15 mL of the prepared solutions, in a shaker at 60°C 150 rpm for 3h. They were then heated from 150 to 350°C with a 5°C/min ramp. For activation, the coals were placed in contact with a solution of hydrochloric acid (HCl) 0.1 molar for 3 h. After taking the samples at room temperature, they were washed with hot and cold distilled water, alternating them until reaching pH between 6 and 7, finally they were allowed to dry for a period of 24 hours at 105°C.

2.3 Charcoal characterization

Prepared coals were subjected to SEM analysis to determine the surface chemical composition and morphology. Subsequently, the inspection was performed under a JEOL JSM 6490 LV model microscope in the secondary electron mode. In addition, the chemical composition of the samples was evaluated on several points or areas of inspection by means of the Oxford Instrument Model INCAPentaFETx3 EDS probe.

2.4 Preparation of aqueous solutions

To prepare the solutions initially, ibuprofen standard type was taken and a solution at a concentration of 20 mg L^{-1} at pH of 2.56 was prepared. Approximately 20mL of acetonitrile was added before the solution was calibrated with distilled water to a liter to obtain the desired concentration. to prepare the amoxicillin solution, La Santé branded amoxicillin capsules of 500 mg were taken to prepare the solution. First, sufficient amoxicillin was weighed to obtain a concentration of 20 mg L^{-1}; for the dissolution of amoxicillin in distilled water, a solution of monobasic phosphate was prepared (for this purpose, 6.8g of monobasic phosphate was weighed in 50 mL of distilled water).

2.5 Adsorption tests

The adsorption tests were performed from standard drug solutions, preparing 100 mL of the solution at a concentration of 20 ppm to which 0.5 g activated charcoal was added by stirring at 120 rpm and ambient temperature for 80 and 120 min for amoxicillin and ibuprofen, respectively. Samples were taken at different time intervals to assess the amount of drug adsorbed over time, and concentration measurements were made on the HPLC team.

3. Results and discussion

3.1 SEM analysis of coals:

Figure 1 shows a micro photograph of activated carbon impregnated with ZnCl2 in concentrations of 50,33.33 and 25%v/v at different magnifications.

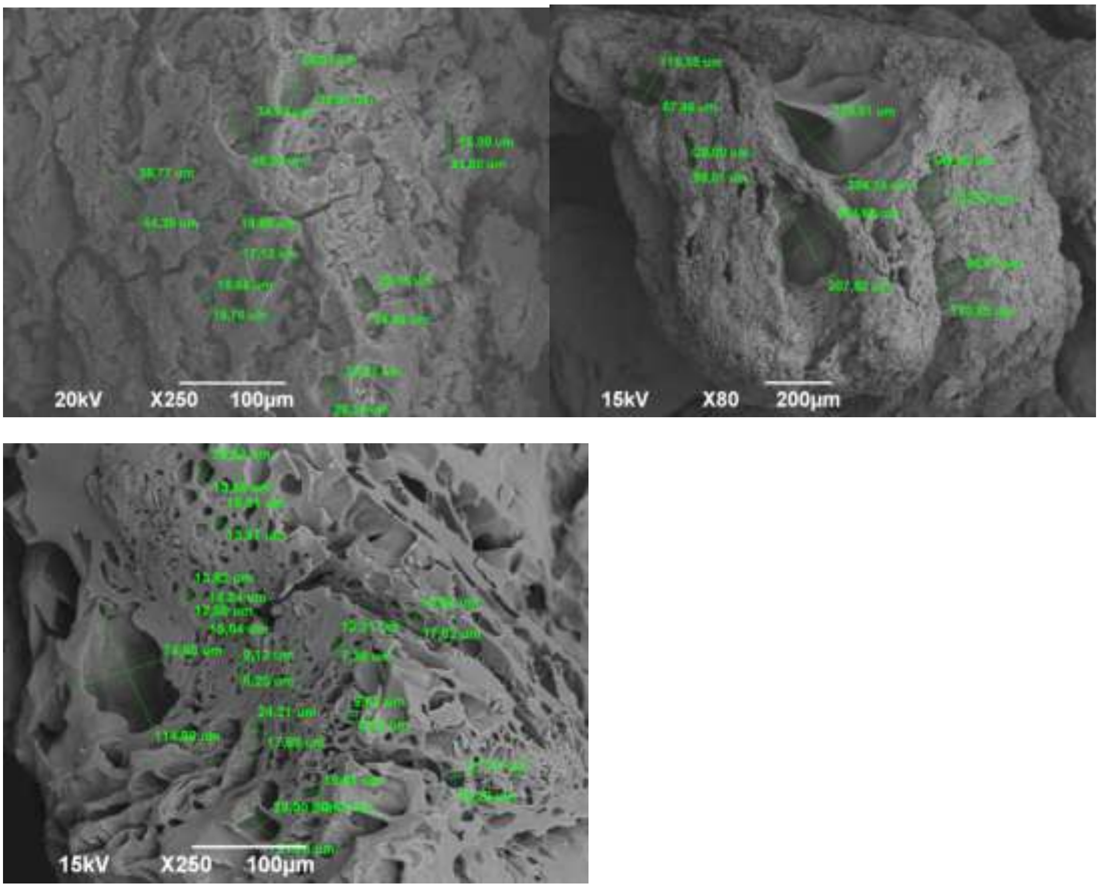


Figure 1. SEM image of carbon particles with impregnation ratio with $ZnCl_2$ (top left) 50 and 33.33% v v^{-1} (top right) and 25% v v^{-1} (bottom)

In the SEM analysis, particles with a great variety of sizes are observed (even larger than 100 µm) in which a heterogeneous solid can be observed with the presence of pores of 5 µm and others smaller than 1µm; at the same time, they present undefined forms showing crystals that can belong to $ZnCl_2$ and other larger ones that would be related to activated carbon, which when impregnated with this crystalline solid did not have appreciable increase in the amorficity and crystallinity of coal.

Wild olive tree (*Olea europea*) was used as a precursor of activated carbons, obtaining an adsorbent with morphology that attests to substantial changes caused by H_3PO_4 and with a clearly porous surface with a predominant microporous character, responsible for the developed surface and high iodine index[17]. Also, bamboo was used for the preparation of activated carbon, showing a morphology in the characteristic SEM analysis associated with cellulose fibers corresponding to the sample after thermal treatments (carbonization and activation) [18]. The activated carbon synthesized from rice husks showed in SEM images a highly developed porous structure compared to the relatively non-porous carbon of rice husks. In addition, the rice husk was found to be fibrous and had no hollow structures that eventually lead to its very low surface area. The low surface area of the rice husk could also be attributed to the fact that the pores of the coal were filled with carbon-containing products due to incomplete combustion at 400°C. However, after activation, the non-porous structure of rice husk charcoal transformed into porous activated carbon [19].

Scanning Electron Microscopy Technique (SEM) was used to investigate the physical surface morphology of activated carbons, which showed no significant differences between the superficial topographies of sour cherry pits and activated carbons, since SEM images of sour cherry pits showed the absence of micropores. Depending on the activation temperatures, the external surfaces of activated carbons have pores that were in different sizes and shapes, in this order the SEM images of activated carbons were analyzed and the pore size was observed to grow with the activation temperature increase 500-700ºC, Due to these well-developed pores, activated carbons had high surface area and adsorption capacity [20].

Table 1: Activated carbon from different plant samples with different activating agents and pore sizes

Material used to obtain coal	Activating agent	Pore size	References
Olea europea (wild olive)	H_3PO_4	Micropore (diameter <2nm), mesopore (2-50 nm) and macropore (>50 nm)	Lima et al., [17]
Rice husk	KOH	Mesopore (2-50 nm)	Kaouah et al., [19]
Bamboo species *(Guadua angustifolia, Bambusa vulgaris striata and Bambusa oldhamii).*	Water vapour	Mesopore (2-50 nm)	Muniandy et al., [18] 2014
Sour cherry	$ZnCl_2$	mesopore (2-50 nm) and macropore (>50 nm)	González y Pliego-Cuervo, [21]
Cocoa cob	$ZnCl_2$	Micropore (diameter <2nm), mesopore (2-50 nm) and macropore (>50 nm)	author

Chayid and Ahmed [22] found in the SEM analysis of the K_2CO_3 impregnated cane that its surface is dense, flat, constrained and blocked by the substance of the deposited tray, however the microwave irradiation sample showed a well developed and uniform surface, forming an orderly pore structure. In addition, previous studies assumed that KOH was reduced to metallic potassium during the carbonization process and the metallic potassium K formed during the gasification process would diffuse into the internal structure of the carbon matrix, widening existing pores and creating new porosities[23].

The hydroxyl groups of cellulosic material interact with the Cl and Zn dissolved in the solution, generating complex reactions that result in changes in the carbonaceous matrix, which is evidenced by the formation of pores. It is important to point out that for activated carbons prepared by chemical activation from lignocellulosic materials, microporous materials result, which is corroborated in Table 4 by the total volume of microprores[24].

3.2 Effects of pH on amoxicillin removal kinetics

The efficiency of the adsorption process is highly dependent on the pH of the solution, as pH variation may promote changes in the loads of adsorbent materials and adsorbate molecules [25, 26]. The removal behavior of Amoxicillin for the combination of impregnated carbon ratio factors and operating pH are shown in Figure 2.

Figure 2 shows that the highest percentages of adsorption are reached before 40 min at pH 6. In addition, it can be seen that removal occurs more quickly in treatments where the impregnation ratio is 50 and 33.33% v v^{-1}, while the lowest efficiency occurs in treatment with an impregnation ratio of 25% v v^{-1}. In addition, at pH 9 there were lower percentages of adsorption compared to pH6, which can be explained by considering that amoxicillin and carbon are negatively charged causing an electrostatic repulsion [27].

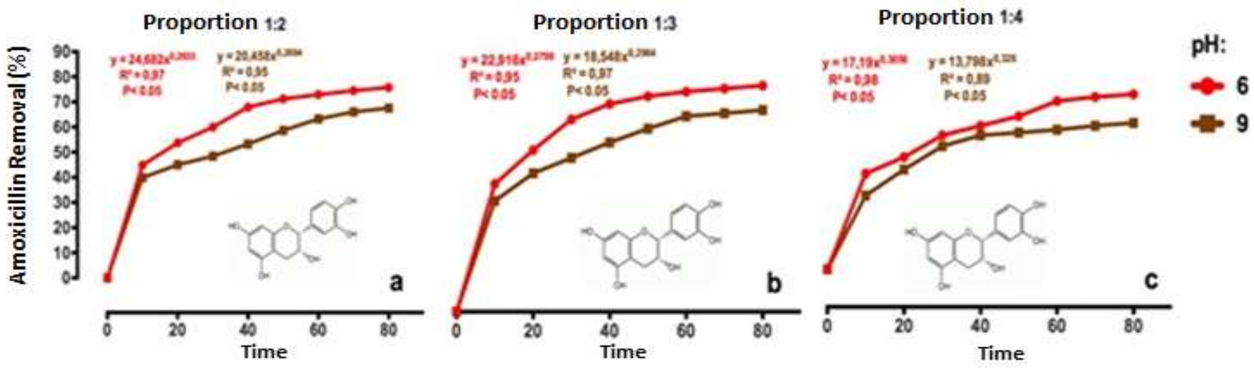


Figure 2. Kinetics of the behavior of Amoxicillin removal rate, from the use of activated carbon, using three proportions of impregnation (Proportions: a=50% v v^{-1}; b=33.33% v v^{-1} and c=25% v v^{-1})

On the other hand, the comparison of the average removal rate is a fundamental aspect in order to be able to identify in a particular way which are the treatments of both the impregnation ratio and pH, in which a higher removal rate of the analyte was presented. In this sense, the two-way ANOVA (proportion of impregnation and pH) allows us to affirm, in the case of amoxicillin, that the proportions 50 and 33.33%v v^{-1}did not present statistically significant differences (P> 0.05) between them, being these the ones with the highest rate of removal. When comparing the previous impregnation proportions with 25%v v^{-1} (Figure 3), statistically significant differences were observed (P< 0.05).

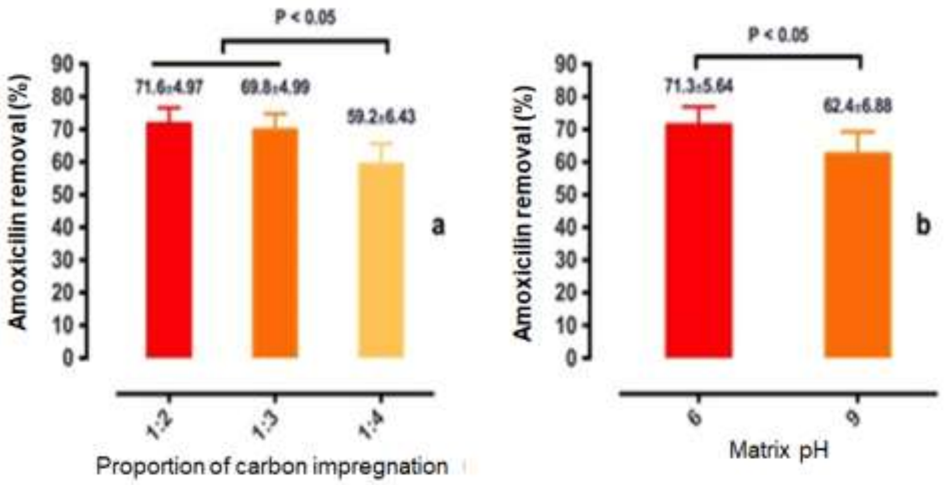


Figure 3. Comparison of Amoxicillin removal rate, from the use of activated carbon, using (left). three proportions of impregnation and (right) two pH values

With respect to the comparison of the two pH treatments, it was observed in Figure 3 that both treatments presented statistically significant differences (P< 0.05), obtaining greater removal when the pH was lower (6.0). This is because as the pH decreases the surface of the charcoal will charge positively, increasing the active sites available for the adsorption of the antibiotic amoxicillin leading to an increase in its adsorption capacity.

From Figure 3 it can be said that hydrophobic interaction mainly contributes to the adsorption of contaminant in activated carbon, since amoxicillin (AMX) will ionize under pH conditions from 9 onwards, and will become less hydrophobic, impairing the adsorption capacity. In addition, functional groups on the surface of activated carbon will take different charges under different pH conditions and can also attract or repel AMX ions [28].

Iovino and his collaborators studied the effect that the pH, temperature and speciation of ibuprofen in solution may have on the adsorption capacity of an activated carbon used to remove this drug; in addition to looking for a model that fits the adsorption of Ibuprofen from said carbon. The results showed that at acid pH and temperature increase (4-34 °C) the adsorption capacity increases, however it was shown that adsorption capacity is strictly dependent on the speciation of ibuprofen [29]. Similarly, Essandoh and collaborators showed that although the activated carbon obtained from pine wood is 1.35 m^2g^{-1}, it turns out to be a good adsorbent material of ibuprofen and acetylsalicylic acid, removing 72% and 76% respectively; high compared to commercially used carbon. It was also shown that the isothermal adsorption model is secondary [30].

3.3 Amoxicillin removal optimization

The result of adjusting the data using the response surface methodology is shown in Figure 4.

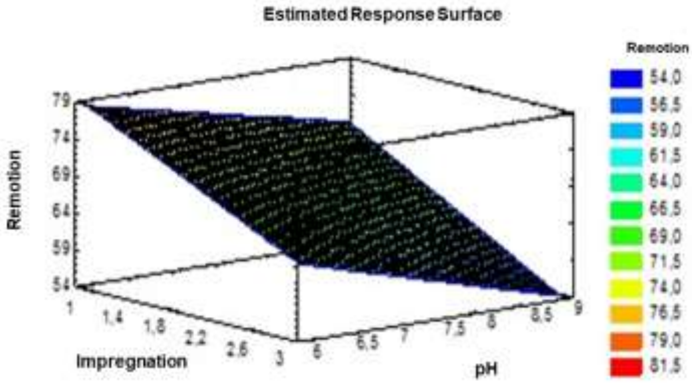


Figure 4. Fitted response surface for removal of Amoxicillin from carbon impregnation and pH of the medium

The combination of the three-dimensional response surfaces of each factor and the respective levels from which the optimized response is obtained for maximum Amoxicillin removal under the proposed experimental conditions can be identified in Figure 4; obtaining the maximum removal (78.47%), when there is a high impregnation ratio (50 % vv^{-1}) and low pH of the medium (6.0).

Dehghani et al., [31]studied the effect of pH (3-11), initial concentration (2-15 mg L^{-1}) and adsorbent dose (0.2 - 0.8 g L^{-1}) in the removal of fluorides in water using natural pumice stone (PPN), $FeCl_3$-$6H_2O$ modified pumice stone (PPMF) and hexadeciltrimethylammonium bromide (PPBH) using the surface response methodology (MSR). The results showed optimal conditions in pH = 3, initial concentration = 2 mg L^{-1} and adsorbent dosage = 0.71,0.75, 0.70 g L^{-1} with maximum removal efficiency of 9.39,76.45 and 95.09% for PPN, PPMF and PPBH, respectively, obtaining a satisfactory predictive regression model. MSR was also used to optimize adsorption conditions of Basic Blue 41 (BB41) in NaOH modified rice husk, considering pH (4,7 and 10), initial concentration of BB41 (50.75 and 100 mgL^{-1}) and adsorbent dose (0.025, 0.0875 and 0.15 g L^{-1}), showing from statistical analysis that the predicted values for BB41 adsorption were close to the experimental values and were in good agreement, on the other hand, the F value (40.48), the value p (0.0004) and R^2 (0.9865) Indicated that regression is capable of giving a good response prediction for the adsorption process in the range studied [32].

3.4 Effects of impregnation and drug concentration on ibuprofen removal kinetics

Removal of Ibuprofen from the combination of impregnated carbon ratio factors and drug concentration is shown in Figure 5.

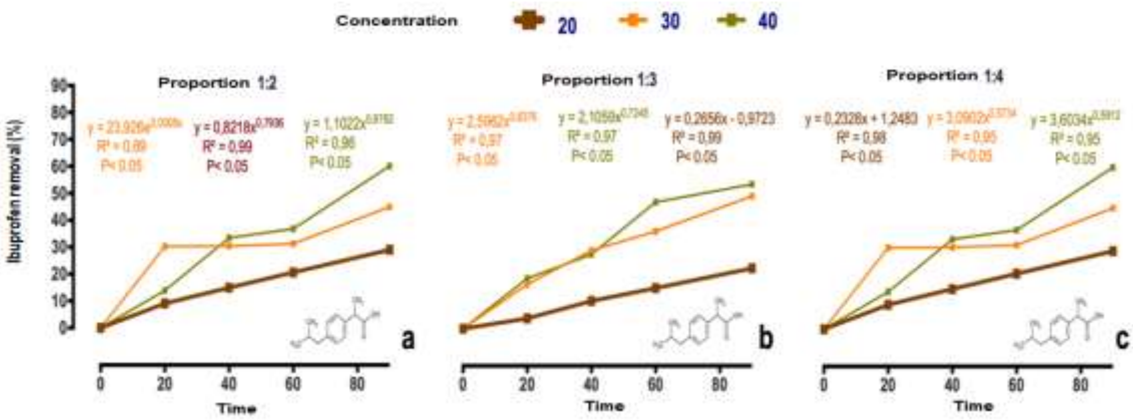


Figure 5. Kinetics of the behavior of the Ibuprofen removal rate, from the use of activated carbon, using three proportions of impregnation (Proportions: a=50% v v^{-1}; b=33.33% v v^{-1} and c=25% v v^{-1}) and drug concentration

Based on Figure 5, it could be determined that the relationship between the analyzed variables is of potential type, except for the 33.33 and 25%vv^{-1} ratio combinations, with the concentration of 20 ppm, whose adjustment was significant for the linear model. In addition, it could be seen that the greatest removal is achieved after 40 min, in treatments where the drug concentration is 40 ppm; it is also observed that the maximum removal (68).3%) occurred when the impregnation ratio was 50% v v^{-1} and the Ibuprofen concentration was highest (40 ppm); while the lowest removal was obtained when the highest impregnation ratio (25% v v^{-1}) was combined with the lowest drug concentration (Figure 5C).

Figure 6a shows the comparison of the results of the Ibuprofen removal values, which showed no statistically significant differences ($P > 0.05$), between the proportions of impregnation of activated carbon, which is due to the high variability presented by each of the treatments, however, the highest average removal rate (54.2 ± 15.25 %) was in the 50 % v v^{-1} ratio. The comparative analysis of the clearance taking into account the Ibuprofen concentration showed statistically significant differences ($P<0.05$) between the three analyzed concentrations (Figure 6b), among which the 40 ppm Ibuprofen concentration was the most effective (64.3 ± 4.78%).

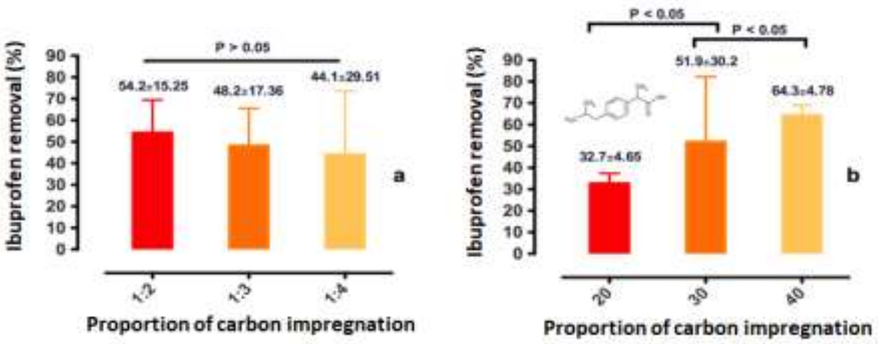


Figure 6. Comparison of Ibuprofen removal rate from the use of activated charcoal, using a. three proportions of impregnation and b. three values of drug concentration

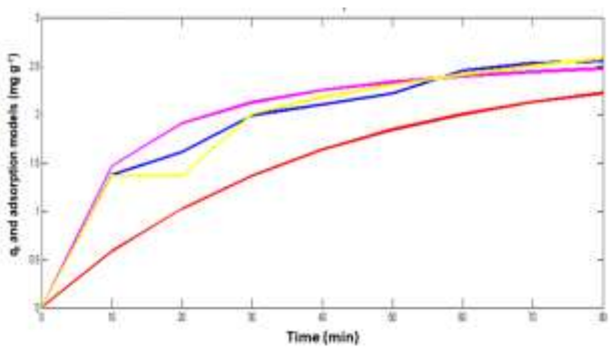
The results recorded in Figure 6 show that the removal of Ibuprofen is not significantly affected by the proportion of impregnation of activated carbon with $ZnCl_2$. Contrary to this behaviour, the concentration of Ibuprofen in the mobile phase does significantly affect its clearance rate, which is why this aspect must be taken into consideration for future projects of this type. In addition, it could be established that independently of the carbon and the concentration of the drug used, the removal for amoxicillin occurs more quickly and with a higher percentage, while for ibuprofen a slower kinetics is present. The amoxicillin molecule has shorter times to reach equilibrium, this indicates that the adsorption rate of amoxicillin is faster than for ibuprofen due to the affinity with a pH value of 6 and is also near the isoelectric point of coal. However, due to the type of molecule, it was expected that ibuprofen would have higher adsorption velocity at particle size and the variation in porosity of prepared coal.

Hu and Wang [33] prepared a coal from linseed cellulose separated and modified by ammonium salt grafting to remove amoxicillin in aqueous solution; to study the effect of the initial contaminant concentration on adsorption capacity, studies were conducted at different temperatures (303.15 K, 313.15 K and 323.15 K), found that adsorption capacity increased with the increasing AMX concentration from 30 to 100 mg L^{-1} using 0.40 g L^{-1} adsorbent in a 50 mL solution. This is because the increased AMX concentration increases the driving force responsible for removal.

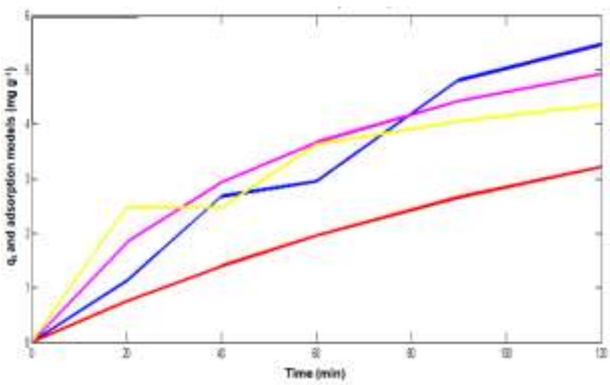
Bernardo et al.,[34] used an activated carbon with K_2CO_3 from potato shell as adsorbent in liquid phase of sodium diclofenac in parallel with a commercial activated carbon. Biomass activated carbon had an apparent surface area of 866 m^2g^{-1} and a well-developed microporous structure with a large quantity of ultramicropores; in addition, it has leaching and ecotoxicological properties compatible with its safe application to the aqueous environment. The adsorption experimental data of the commercial carbon sample and that obtained in the study were better fitted by the pseudo-second order kinetic model and by the Langmuir isotherms model, the commercial model being the one with the highest pollutant uptake, while charcoal of vegetable origin presented the highest adsorption rate associated with its greater hydrophilic nature that favoured mass transfer. Coal from potato peel and commercial coal presented adsorption monolayer capacities of 69 and 146 mg g^{-1}, and Langmuir constants of 0.38 and 1.02 L mg^{-1}, respectively. The best performance of the commercial sample was found to be associated with its slightly higher microporic volume, but the most notable effect was competition from water molecules in the carbon of biomass.

3.5 Kinetics and adsorption isotherms in batch system

Kinetics describes the adsorption rate of adsorbent adsorbent and determines the time when equilibrium is reached. The pseudo-first order, pseudo second order and Elovich models were applied in the study of adsorption of amoxicillin and ibuprofen in prepared activated carbon of cocoa cob, taking into account the optimal conditions established when applying the response methodology (pH 6 and 50%v/v impregnation).



a)



b)

Figure 7. Modelling of amoxicillin (a) and ibuprofen (b) adsorption kinetics with 50% v v^{-1} impregnated activated carbon of $ZnCl_2$ and pH 6. (▬) q_t (mg g^{-1}), (▬) First order, (▬) Second order, (▬) Elovich.

It can be seen in figure 7 that the pseudo-second order kinetic models and Elovich better fit the experimental results (with R^2 very close to the unit as shown in Table 2); however, the values of the parameter q_e obtained with the pseudo-second order model are higher than those obtained experimentally. Furthermore, with the pseudo-primer order model, despite offering a worse linearity, values are obtained that are closer to those determined experimentally. The Elovich model indicates that there is a species exchange on the non-homogeneous surface of the solid, implying different processes of isotope exchange at the same time. It can be established that the process of adsorption of amoxicillin on activated carbon from cocoa cob is controlled by chemical reaction, i. e. chemisorption, which explains the rapid adsorption of contaminant that occurred [35, 36].

Table 2. Velocity constants for the removal of adsorbed amoxicillin in equilibrium obtained with the kinetic models of pseudo-first order, pseudo second-order and Elovich

Coal with $ZnCl_2$	**Pseudo-First order model**			**Pseudo-second order model**			**Elovich Model**		
	$K_1(min^{-1})$	**R^2**	**$q_e(mg\ g^{-1})$**	**$K_2(L\ mg^{-1}\ min^{-1})$**	**R^2**	**$q_e(mg\ g^{-1})$**	**$\alpha(mg\ g^{-1}\ min^{-1})$**	**β(g/mg)**	**R^2**
AMX	0.0222	0.986	3.096	0.0470	0.988	3.271	0.772	1.405	0.9949
IBP	0.0074	0.553	5.462	0.00216	0.844	7.468	0.551	0.952	0.779

4. Conclusions

The experimental tests carried out in the batch reaction system allow a high percentage of degradation of the drugs in aqueous medium to be achieved, which favours the use of this technology in the treatment of emerging compounds such as ibuprofen and amoxicillin, using the cocoa cob as raw material with different impregnations of $ZnCl_2$ and in a maximum time of 120 min, at moderate temperature and pressure conditions.The best conditions of amoxicillin adsorption were given at pH 6 and impregnation of biomass with zinc chloride ($ZnCl_2$) of 50 %v v^{-1}, reaching a removal percentage of 77.4% coinciding with the results obtained when applying the response surface method, concluding that it is a good methodology for optimizing the adsorption process; in contrast for synthesized activated carbon. The design used for ibuprofen took into account the impregnation of activated carbon and the initial drug concentration (20,30 and 40 ppm), with the result that the higher the drug concentration, the higher the removal percentage resulting in a maximum of 68% removal at 40 ppm and impregnation of 50% v v^{-1}, while for activated carbon with impregnation of 25% v v^{-1} and 20 ppm a removal percentage was obtained. The kinetic model that best fitted the experimental data of amoxicillin removal to the optimal conditions obtained from the response surface was Elovich with an R^2 between 0.9886 and 0.9949, while for ibuprofen adsorption it was pseudo-second order with an R^2 between 0.779 and 0.9164.

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