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Removal of Amoxicillin from an Aqueous Solution by Activated Carbon Prepared from Biomass

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ABSTRACT

Amoxicillin type Amox-500 is a β-lactam antibiotic belonging to the penicillin family, used to treat infections caused by bacteria. This drug has been, purified by the slow recrystallization method and characterized by RAMAN. The treatment of antibiotic-laden effluent is of interest for environmental protection, which is why the field of wastewater treatment is essential for the protection of our environment. In our research, we studied the elimination of amoxicillin as a trace pollutant in untreated wastewater discharges in an aqueous solution prepared in the laboratory, using activated carbon made from banana peel. We also showed the presence of these pharmaceutical pollutants (amoxicillin and paracetamol) in wastewater from the Dradeb area of the city of Tangier in Morocco. In this research, we took advantage of the use of activated carbon, which has been, previously treated in our laboratory for a study, which is, published [Abdellah Touijer et al, 2023]. The amount of amoxicillin adsorption is influenced by various operating parameters, and with the help of a parametric study, we have deduced the best conditions from these parameters to promote good amoxicillin adsorption yield. The amount adsorbed at equilibrium increases proportionally with amoxicillin concentration, and equilibrium is reached after the first 20 min. The maximum equilibrium amoxicillin adsorption capacity (q_e) is 35 mg/g for PBC600 (banana peel carbonized at 600 °C for 60 min) and PBC700 (banana peel carbonized at 700 °C for 60 min), and 25 mg/g for PBC500 (banana peel carbonized at 500 °C for 60 min). Under the following operating conditions: C_0 = 20 mg/l, temperature 20±5 °C, pH=6 lower than pHpzc, adsorbent/adsorbat ratio 0.5 mg/ml, stirring time 45 min. The best adsorption efficiency was 85.2% for PBC700, 79.31% for PBC600 and 12.47% for PBC500, indicating that the amount of amoxicillin adsorbed at equilibrium is proportional to the carbonization temperature. The theoretical study of the adsorption isotherm of amoxicillin on activated carbon prepared from banana peel shows that the Langmuir, Freundlich and Temkin models describe this adsorption phenomenon well, similar to the experimental results. Adsorption of amoxicillin follows a pseudo-second-order kinetic model. Thermodynamic analysis has shown that standard enthalpy ($\Delta H°$), standard free enthalpy ($\Delta G°$), and free entropy ($\Delta S°$) are negative values, allowing us to say that this adsorption process is spontaneous and favorable, meaning the decrease in disorder.

Keywords: adsorption, carbonization, activation, amoxicillin, PBC500-60, PBC600-60, PBC700-60.

INTRODUCTION

The contamination of wastewater by trace drugs has been increasing in recent years due to the rise in influenza illnesses and pharmaceutical supplementary feeds, and the total quantity consumed from the antibiotic market worldwide varies from 100,000 to 200,000 tons [Wise, 2002]. The presence of these traces in the environment, particularly aquatic environments (surface water, seawater and effluents), creates an environmental problem due to their potential toxicological risk on living beings. Amoxicillin is a β-lactam bactericide of the aminopenicillin family, used to treat sensitive bacterial infections. Amoxicillin is the world's most widely used antibiotic, especially in children, thanks to its good absorption and low cost. These antibiotics are excreted in large quantities, which are not fully metabolized by the human body [Aubry et al., 2018]. Pharmaceutical pollution arises mainly from traces of drugs in urine, from drugs disposed of in toilet bowls, and from hospital wastewater [Ternes, 2001]. The majority of drugs are polar substances, with unbiased solubility in water, [Hu and Wang, 2016]. It damages the ecology by rendering bacteria resistant, and naturally disrupts the growth, development and movement of a wide range of microorganisms [Limousy et al., 2017]. Around 90% of orally taken drugs do not break down, after this it transforms to active compounds. Unfortunately, conventional medical treatments are unable to eliminate antibiotics due to the high solubility in water, which is a major obstacle for the removal treatment [Zhu et al., 2015]. Many techniques are used to eliminate antibiotics from aqueous environment including Biological degradation [Tiwari et al., 2017], UV radiation [Rodríguez-Chueca et al., 2019], membrane filtration [Ghanbari and Amanat, 2022], photolysis [Neghi et al., 2022], and adsorption [Nasseh et al., 2019]. In wastewater, the presence of certain pharmaceuticals such as paracetamol and amoxicillin have been proven by HPLC, so we have studied the possibility of eliminating amoxicillin and others like paracetamol in previous study from wastewater and stock solutions with known concentrations using activated carbon [Touijer et al., 2023], for a clean environment free from drug contamination. The adsorption tests carried out on this activated carbon prepared by carbonization and chemical activation techniques at three different temperatures, resulting three activated carbon samples PBC500, PBC600 and PBC700, used as adsorbents. The adsorbat is amoxicillin from Amoxil-500 drug, sold in Morocco, which is purified in Laboratoiry of physical chemistry of materials, natural substances and environment (LMSNE). By slow recrystallization and characterized by the Raman technique. We tested the adsorption of Amoxicillin in aqueous solution by this activated carbon, looking for the best removal yield under the right conditions of temperature, pH, initial concentration of the aqueous solution and $m_{adsorbant}/V_{solution}$ ratio. We studied the thermodynamics of adsorption to understand the mechanism of this phenomenon.

PRODUCTS AND MATERIALS

Typical laboratory equipment

- UV-visible spectrophotometer, model "JENWAY 7205";
- ISCO-type incubator for static regime;
- HANNA HI 2550 pH meter;
- magnetic stirrer model H2A00010-BOD/6 ;
- oven type G.BOYER - Binder;
- electronic balance model KERN ABS 120-4 Readability 0,1mg;
- MORE THAN HEAT 30-3000 °C "Nabertherm" carbonization-calcination furnace;
- Bruker Raman spectrometer with microscopic configuration;
- SHIMATZU prominence-i LC-2030C 3D plus HPLC instrument.

Adsorbent preparation

Powdered activated carbon was prepared from banana peel using the pyrolysis technique under nitrogen at three different temperatures, and chemical activation with 0.5M sodium hydroxide and potassium hydroxide (1:1), at the LMSNE laboratory of FST Tangier, Morocco. This charcoal is already studied in our previous work [Touijer et al., 2023].

Preparing for adsorbat

The amoxicillin used comes from Amoxil-500 marketed in Morocco. It was purified by the method of slow recrystallization of an aqueous solution of amoxicillin. A quantity of 10g of Amoxil-500 was placed in a 250 ml beaker, to which 20 ml of distilled water was added. The mixture was heated to 30 °C under magnetic stirring until it was fully dissolved. Slow recrystallization was then carried out using an ice-cold water bath, followed by vacuum filtration and washing with a minimum of ice-cold distilled water. The crystals obtained were recovered in a watch glass, using vacuum filtration and dried at 30 °C for 2 hours.

Adsorption operating protocol

The amoxicillin stock solution was prepared by dissolving 100 mg of purified amoxicillin powder in 1000 ml of distilled water. Amoxicillin solutions were prepared by diluting the stock solution. The dilution of this stock solution leads to the preparation of different samples at various concentrations, described by a calibration curve of the standard solution of amoxicillin mixture, which shows linearity with a correlation coefficient $R^2 = 0.9987$ (Fig. 1). A series of Erlenmeyer flasks containing aqueous solutions of amoxicillin to which was added a quantity of carbonized banana peel (PBC). After determining pH values, adsorbat concentration, adsorbent mass, solution volume, stirring speed, magnet bar size and mixing temperature, the system was put under magnetic stirring. After some time, we separated the two phases using 45 µm filter paper. We determined the residual concentration of Amoxicillin by UV-vis spectrophotometry model JENWAY 7205 at a constant value of wavelength valley λ = 232 nm, and determined from this apparatus which characterizes Amoxicillin.

CHARACTERIZATION OF AMOXICILLIN BY RAMAN SPECTROSCOPY

We analyzed a sample of Amoxicillin purified by recrystallization, with the aid of a Raman apparatus in the Center for Development and Innovation (CDI), Laboratory at the University of Science and Technology in Tangier, using a Bruker-type Raman spectrometer with a microscopic configuration, with the λ = 785 nm wavelength line as the exciter line. The laser used is of 10 mW power and focused on the sample with a ×50 objective and a scan from 0 cm^{-1} to 1550 cm^{-1} with a resolution of 3.5 cm^{-1}. We have processed the data from this spectrum shown in Figure 2, (Sample 1.472) of Raman of amoxicillin (β-lactamine) by the basic data of the KnowItAll Informatics system 2020 application, which gives us the best score (85.66) for the amoxicillin trihydrate

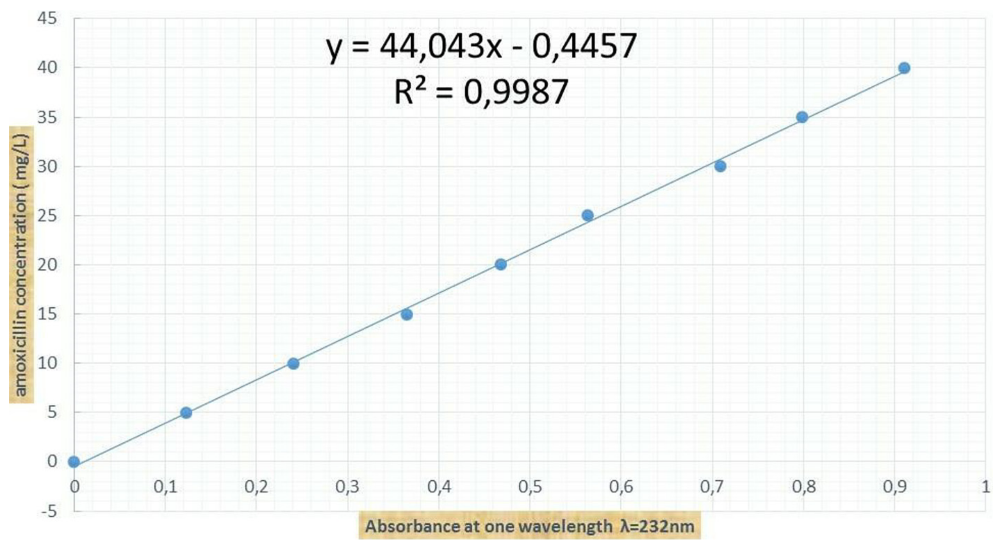

Figure 1. The amoxicillin calibration curve

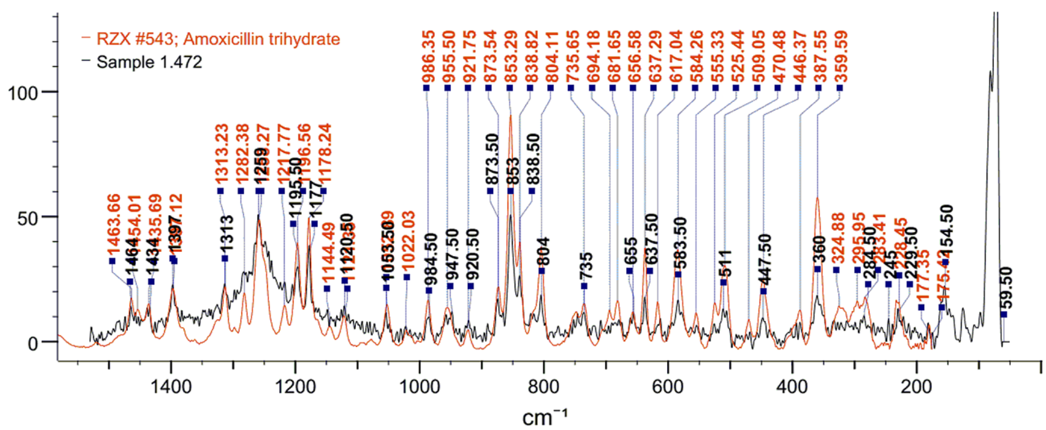

Figure 2. Raman spectrum of a sample of recrystallized amoxicillin processed by the KnowItAll Informatics analysis program

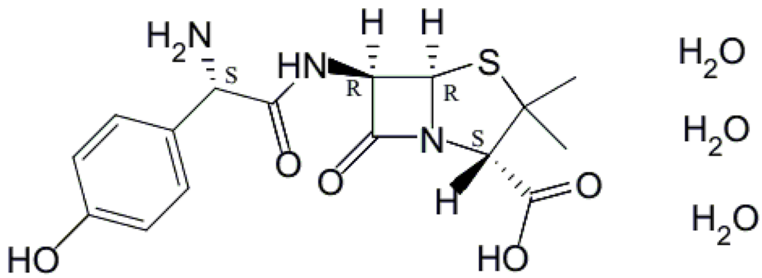

Figure 3. Amoxicillin trihydrate molecule named: (2S, 5R, 6R)-6-[[(2R)-2-amino-2-(4-hydroxyphenyl)-acetyl] amino-3, 3-dimeethyl-7-oxo-4-thia-1-azabicyclo [3.2.0] heptane-2-carboxylic acid trihydrate

Table 1. Amoxicillin sample characteristics shown by the KnowItAll Informatics system 2020 database

Name	Value
HQI resulting	60.55
Database abbreviation	RZX
Database title	Raman – Sadtler Controlled & Prescription Drugs 1 - Wiley
Registration ID	543
Nam	Amoxicillin trihydrate
CAS registry number	61336-70-7
Catalog number	46060
Compound type	Pure
Formula	$C_{16}H_{25}N_3O_8S$
InChI	InChI=1S/ C16H19N3O5S.3H2O/
InChIKey	MQXQVCLAUDMCEF-
Lot number	7346X
Molecular weight	419.450 g/mol
Polar surface area predicted	227.5
Raman corrections	Referenced to internal white light source; 180 Degree backscatter
Raman laser source	Nd: YAG
Raman laser wavelength	1064
Sadtler IR number	DW0227
Source of sample	Fluka Vetranal, Sigma-Aldrich
Source of spectrum	Forensic Spectral Research

molecule. This confirms that our amoxicillin product is well represented. Using the characteristics of this sample presented in Table 1, we have shown that this pharmaceutical product is pure of hydrated chemical formula as shown in Figure 3.

- Physical properties of amoxicillin:
  - Gross formula: $C_{16}H_{19}N_3O_5S$; $3H_2O$;
  - Molar mass: 365.4 g/mol without $3H_2O$:
    - o pKa: 2.8 and 7.2.
    - o therapeuticclass/family:antibiotic/β-lactam.
    - o melting temperature: 194 °C.
    - o Log Kow: 0.87.
    - o density: d = 1.293.
    - o solubility: water 3430 mg/L at 25 °C.
    - o λ_{max}: 232 nm.

ANALYSIS OF A WASTEWATER SAMPLE USING THE HPLC TECHNIQUE

The HPLC (High-pressure liquid chromatography) technique has been widely used for the rapid and simultaneous determination of several drug agents in pharmaceutical products [Joshi S, 2002]. We sampled a volume of wastewater flowing directly into the Mediterranean Sea, with the aim of demonstrating the existence of drug traces in this wastewater from the Tangier zone of Dradeb, Morocco (Figure 4).

We filtered this sample through 45 μm filter paper and prepared two aqueous reference solutions, one of paracetamol (5 mg/l) and the other of amoxicillin (5 mg/l). These samples were analyzed in the CID laboratory at the University of Science and Technology of Tangier using the HPLC method on a SHIMATZU prominence-i LC-2030C 3D plus instrument. The flow rate was set at 0.7 ml/min, the injection volume was carried out at 20 μl, room temperature, the eluent used was composed of 25% acetonitrile and 75% distilled water. This mixture was used as the mobile phase, while the reverse-phase C18 column was used as the stationary phase. A wavelength range from 230 nm to 240 nm for the first standard sample, which features the Amoxicillin wavelength of 232 nm, and another range from 240 nm to 250 nm for the second standard sample, which features the Paracetamol wavelength of 245 nm, and a third wastewater sample range from 200 to 260 nm. We deliberately chose a short wavelength interval to flush out the amoxicillin and paracetamol substances in the standard samples. Performance time 20 min. Figures

Figure 4. Map showing the location of the sampling point in the Dradeb zone, Markala beach in the city of Tangier, Morocco

5–7 show the results of this HPLC analysis. The HPLC chromatogram of amoxicillin shows the existence of two major peaks, an intense peak of amoxicillin trihydrate alongside another small peak of degraded amoxicillin, linked to the dissolution of amoxicillin in distilled water by the formation of these two forms. They have two different concentrations, depending on the predominance of each form in the solution at a pH of the mixture between pKa_1 and pKa_2 of amoxicillin. A comparison between the HPLC chromatograms of the reference samples (Figures 5 and 6), and those of the wastewater (Figure 7). We note that the wastewater sample shows the more or less marked presence of pharmaceutical substances such as paracetamol with a retention time of 2.337 min, a single form of amoxicillin with a retention time of 1.643 min of low intensity, which means a low concentration, but these two pharmaceutical substances influence the aquatic environment of the sea, surface and ground water.

RESULTS AND DISCUSSION

Effect of pH

The pH parameter plays an important role in the adsorption of organic or inorganic pollutants, as it directly influences the surface charge and the

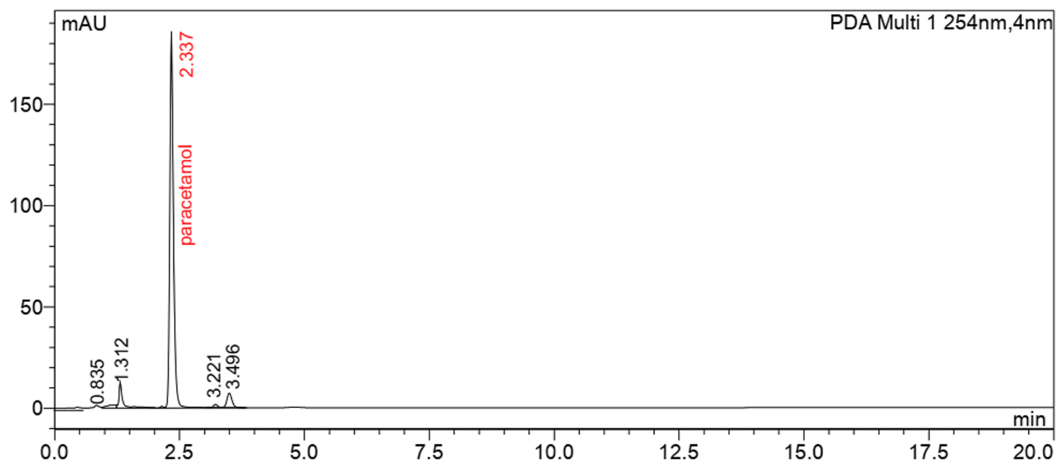

Figure 5. HPLC chromatogram of paracetamol (5 mg/l) as reference standard at a wavelength range 240 nm ≤ λ ≤ 250 nm. 0.7 ml/min, 20 µl injection, mobile phase water-acetonitrile (75–25%), pH = 6, room temperature

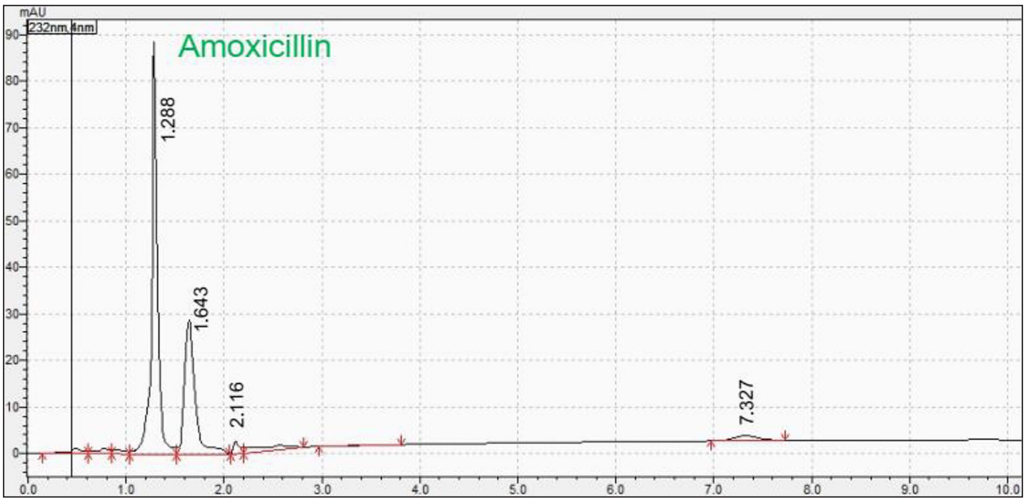

Figure 6. HPLC chromatogram of amoxicillin (5 mg/l) as reference standard at a wavelength range 230 nm ≤ λ ≤ 2 40 nm. 0.7 ml/min, 20 µl injection, mobile phase water-acetonitrile (75–25%), pH = 6.8, room temperature

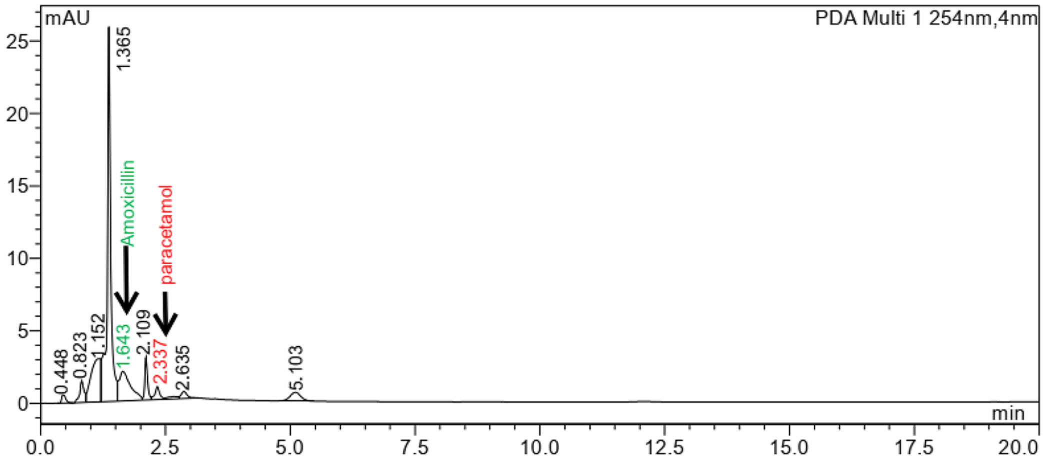

Figure 7. HPLC chromatogram of a wastewater sample from the Dradeb zone of Tangier Morocco at a wavelength range of 200 ≤ λ ≤ 260 nm. 0.7 ml/min, 20 µl injection, mobile phase water-acetonitrile (75–25%), pH=7.09, room temperature

nature of the ionic species in adsorbents. The pH of the solution is a key factor that could affect the adsorption of a pollutant on an adsorbent, as it affects the adsorbent's surface charge [Cuerda-Correa et al., 2010]. Before studying the pH effect of the aqueous amoxicillin solution on the previously prepared activated carbon, we determined the pHpcz zero charge point at which there is no positive or negative charge on the activated carbon surface. A 30 ml volume of sodium chloride solution (0.01 M) from pure NaCl crystals (99%), the pH value was adjusted from 2 to 12 by adjusting with a solution of hydrochloric acid and concentrated sodium hydroxide, then a mass of 90 mg of PBC600 was added to each Erlenmeyer flask. After 48 hours stirring, we determined the pH_f for each sample and plotted the pHi = f(pH_f) curve. The pH, which corresponds to the point of intersection between the pH_f curve and the pH_i curve, represents the pHpcz = 7.16 of the adsorbent (Figure 8).

Our experimental study concerned the effect of pH on adsorption. The pH of the initial solution was varied from 2 to 10. It was, adjusted to the desired pH and kept constant for the duration of each test by the addition of concentrated hydrochloric acid or sodium hydroxide. Adsorption of amoxicillin varied with the nature of the adsorbent, decreasing slightly with increasing pH for PBC600 and PBC700, but for PBC500 it decreased from 2 to 8 and then increased from 8 to 10 (Figure 9).

The best adsorption yield corresponds to pH values below pHpzc = 7.16 for all adsorbents. A

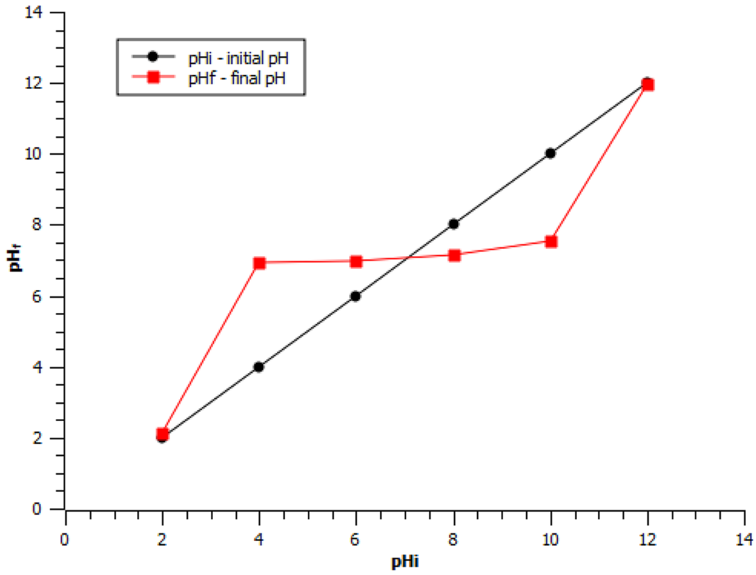

Figure 8. The final pH of an aqueous solution of PBC600 charcoal as a function of pHi of the same solution after shaking for 48H to determine pHpcz

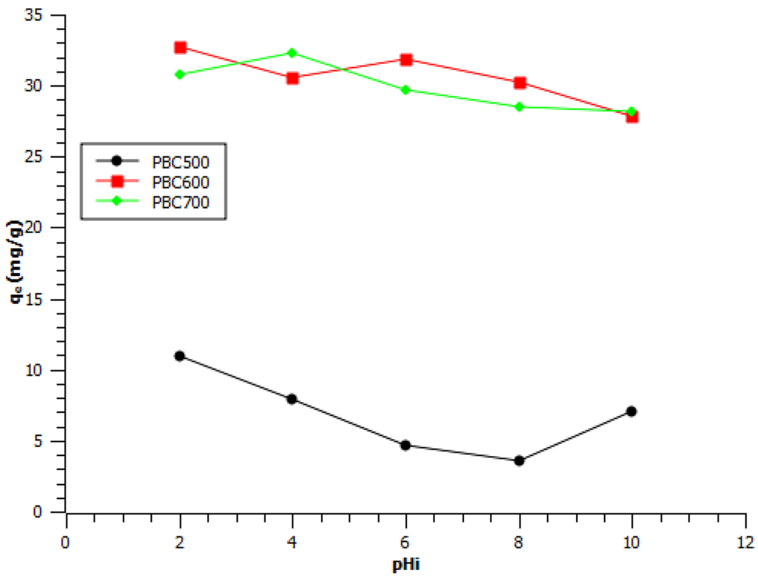

Figure 9. Evolution of the adsorbed quantity of amoxicillin as a function of pHi for the three carbons, (C_0 = 20 mg/l, Θ = 18 °C, r = 0.5 mg/ml, w = 300 tr/min, t = 45 min, Ø < 100 µm)

small increase in yield was observed for PBC500 at pH values above pHpzc (Figure 10). For this reason, all solutions were prepared at pH = 6 below pHpzc, which means that the carbon surface will be positively charged, whereas the amoxicillin ion is negatively charged. The presence of H^+ and HO^- ions in solutions can modify the surface charges of activated carbons, which contain functional groups that contribute significantly to their adsorption capacity, effectively attracting ionic or aqueous species to the carbon surface [Valix et al., 2006]. Amoxicillin has pKa_1 = 2.8 and pKa_2 = 7.2 [Riviere et al., 1996], being relatively lower than or equal to pHpzc, which means that the negative form (basic form) of the amoxicillin ion is predominant, this favors an increase in ionic strength leading to high adsorption of this pollutant [Newcombe et al., 1996].

Effect of mass/volume ratio (r) and adsorbent mass

The effect of the mass and ratio of adsorbent mass to volume of the prepared aqueous solution of amoxicillin on the adsorption capacity of activated carbon prepared from banana peel

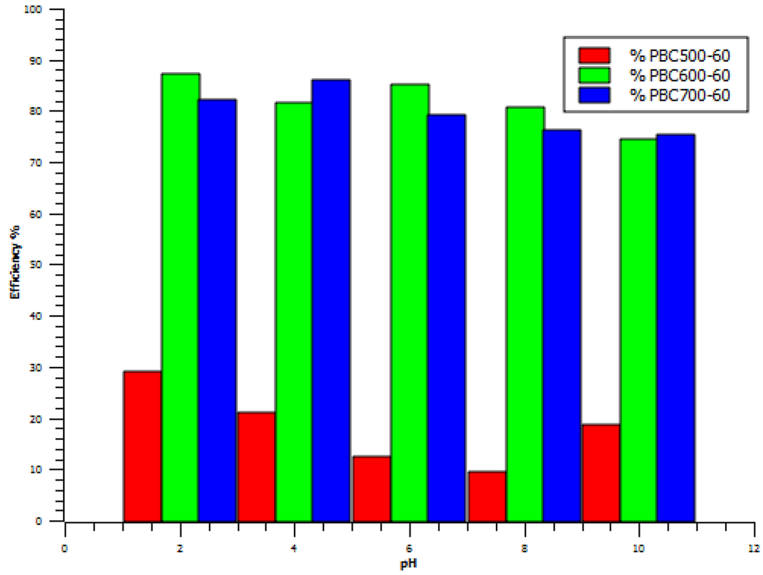

Figure 10. Yield of adsorbed amoxicillin as a function of pHi for the three carbons, (C_0 = 20 mg/l, ϴ = 18 °C, pH = 6, r = 0.5 mg/ml, w = 300 tr/min, t = 45 min, Ø < 100 µm)

was examined. For the two carbons PBC600 and PBC700, q_e was, found to decrease with increasing ratio r, whereas for PBC500 the value of q_e increased with increasing ratio r and stabilized at an almost constant value (Figure 11). The decrease in this ratio (adsorbent mass/adsorbate volume) signified an increase in active sites, and these results were confirmed by the theoretical formula for q_e, (Eq. 1). For the effect of adsorbent mass we found an optimum adsorption yield (86.21%; mads = 60 mg) for PBC600 and (82.87%; mads = 60 mg) for PBC700 in a 40 ml volume of an amoxicillin solution of concentration 20 mg/l and pH = 6 (Figure 12). The maximum yield for PBC500 was low (40.76%; mads = 80 mg), confirming that the adsorbents PBC600 and PBC700 have a higher specific surface area than PBC500, thanks to the higher thermal activation temperature during carbonization.

$$qe = (c_0 - c_e) * \frac{v}{m} = (c_0 - c_e) * \frac{1}{r} \quad (1)$$

With:

$$r = \frac{m}{v} \quad (2)$$

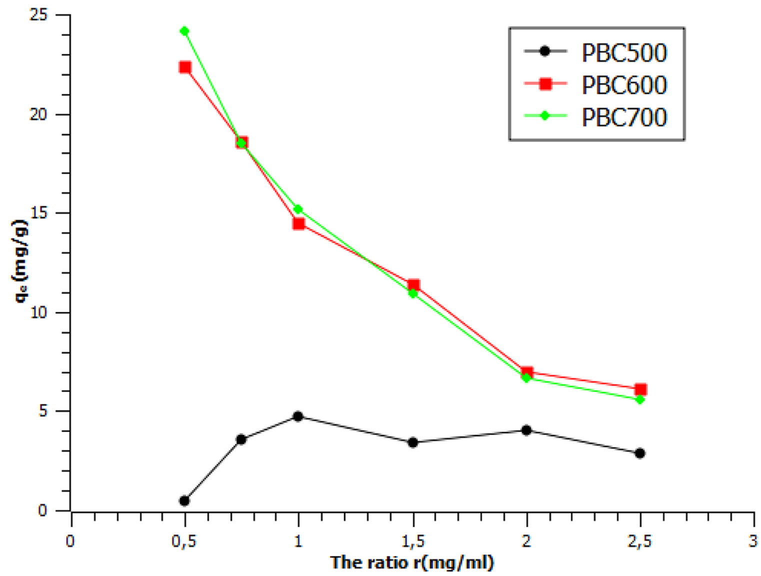

Figure 11. Evolution of the adsorbed quantity of amoxicillin as a function of the r ratio for the three carbons, (C_0 = 20 mg/l, ϴ = 18 °C, pH = 6, w = 300 tr/min, Ø < 100 µm)

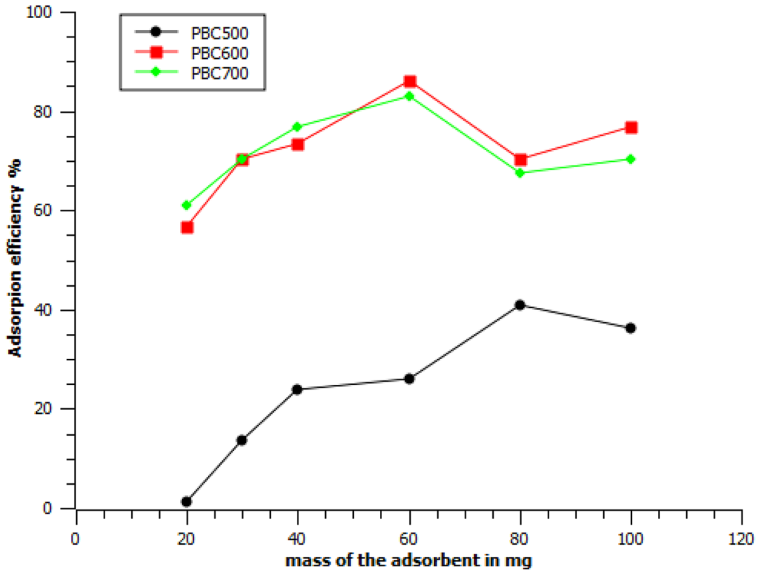

Figure 12. Evolution of the adsorbed quantity of amoxicillin as a function of adsorbent mass, for the three carbons, (C0 = 20 mg/l, Θ = 18 °C, pH = 6, r = 0.5 mg/ml, w = 300 tr/min, t = 45 min, Ø < 100 µm)

where: v – volume of solution (ml);
m – quantity of activated carbon (PBC) (g);
c_0 – initial mass concentration (mg/l);
c_e – equilibrium mass concentration (mg/l);
q_e – quantity adsorbed at equilibrium (mg/g).

Effect of contact time

The kinetic study was carried out at ambient atmospheric temperatures ranging from 15 °C to 25 °C on an amoxicillin solution with an initial concentration of 20 mg/l, a pH of 6 and an r = 0.5 mg/ml ratio. Figure 13 shows the evolution of the quantity of pollutant adsorbed (q_t) as a function of the contact time of each adsorbent. From the first 20 minutes, the pollutant was eliminated to the maximum from the solution, and after this time, the adsorption rate varied slightly over time, which is assumed to be stable at a value of q_e = 35 mg/g for PBC600 and PBC700, and a value of q_e = 25 mg/g for PBC500. This may be due in the early stages to the transfer of amoxicillin into the active sites of the charcoal, after which it reaches equilibrium after 20 to 40 min, meaning that the number of active sites available in PBC600 and PBC700 is greater than that of PBC500. So the

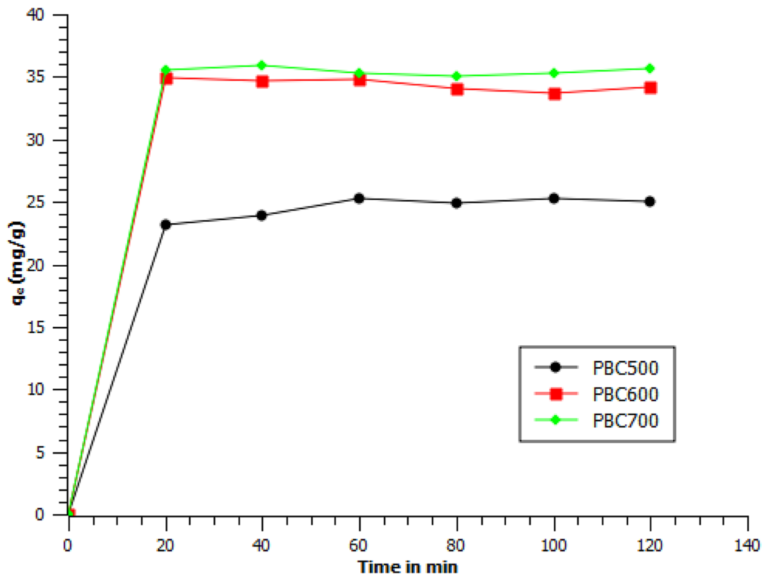

Figure 13. Evolution of the adsorbed quantity of amoxicillin as a function of stirring time, for the three carbons, (C0 = 20 mg/l, Θ = 18 °C, pH = 6, r = 0.5 mg/ml, w = 300 tr/min, Ø < 100 µm)

increase in carbonization temperature favors an increase in the number of micropores. PBC600 carbon is sufficient to remove traces of amoxicillin from urban effluents under these conditions.

Effect of initial concentration

Under the same conditions of temperature, pH, ratio r = 0.5 mg/ml and stirring time set at t = 45 min. we varied the concentration from 5 to 40 mg/L (Figure 14), we found that the amount of amoxicillin adsorbed at equilibrium increases proportionally with the increase in initial concentration. The adsorption rate of two carbons PBC600 and PBC700 is greater than that of PBC500; this is due to the abundance or availability of active sites in the activated carbons [Al-Khateeb et al., 2014]. Increasing the initial concentration promotes adsorbent-adsorbate interaction.

Effect of mixing temperature

In the temperature range from 15 °C to 40 °C, we examined the effect of temperature on the adsorption of amoxicillin in aqueous solution. Under the same conditions as the previous experiments, and using an adjustable temperature incubator for an equilibration time of 45 min. In Figure 15, we can see that the quantity adsorbed at equilibrium varies slightly over the range

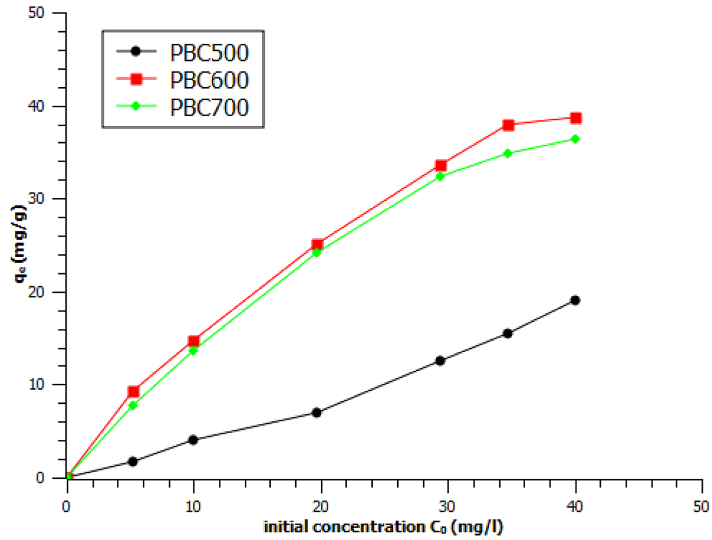

Figure 14. Evolution of the adsorbed quantity of amoxicillin as a function of initial concentration, for the three carbons, (C_0 = 20 mg/l, Θ = 18 °C, pH = 6, r = 0.5 mg/ml, w = 300 tr/min, t = 45 min, Ø < 100 μm)

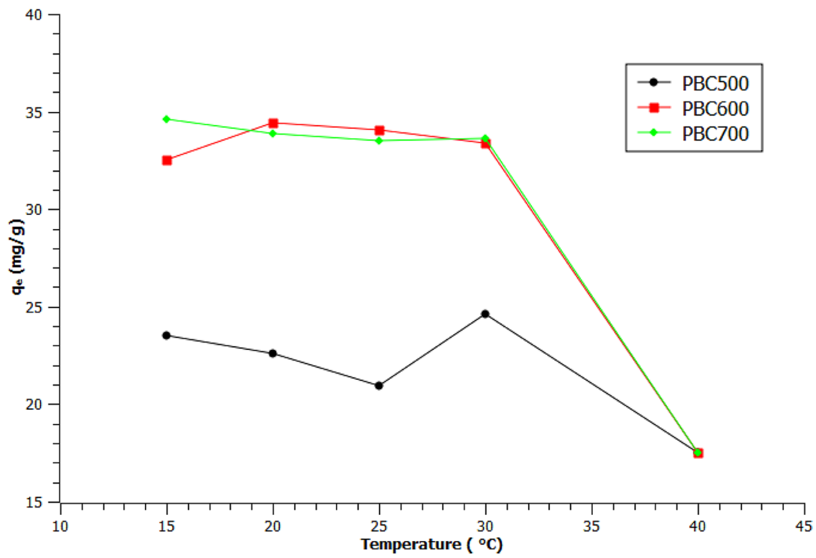

Figure 15. Evolution of the adsorbed quantity of amoxicillin as a function of temperature, for the three carbons, (C_0 = 20 mg/l, Θ = 18 °C, pH = 6, r = 0.5 mg/ml, w = 300 tr/min, t = 30 min, Ø < 100 μm)

15–30 °C, with a slight increase for PBC600 carbon, and a slight decrease for PBC700, but notably decreases for temperatures above 30 °C. In the case of PBC500, the quantity q_e varies in three temperature ranges, decreasing from 15 to 25 °C and increasing from 25 to 30 °C, then decreasing notably from 30 to 40 °C. The decrease in amoxicillin adsorption capacity with increasing temperature is due to the phenomenon of solubility, which causes amoxicillin molecules to migrate towards the solution, as the amoxicillin substance would have more affinity with the solvent than with the adsorbent [Cuerda-Correa et al., 2010, Antunes et al., 2012]. Van der Waals forces applied between the charcoal surface and the amoxicillin ion are weakened, resulting in reduced adsorption [Adak et al., 2005]. Both carbons take on the best q_e value over a range of 15 to 25 °C, which is compatible with effluent wastewater under normal conditions.

TEST FOR THE REMOVAL OF PARACETAMOL AND AMOXICILLIN FROM WASTEWATER USING PBC600-60

After filtering the wastewater taken from the Dradeb area (Figure 4), through a filter paper 45 µm, we mixed a 20 mg mass of PBC600-60 carbon with a 40ml volume of this filtrate at pH = 6.09 and a temperature of 28.8 °C. The mixture was then stirred for 40 min, after this it was filtered again using the same filter paper. This filtrate was then processed by HPLC (Figure 16). Comparison of the chromatograms in Figure 7 (before adsorption) and Figure 16 (after adsorption) revealed a decrease in the area of paracetamol from 6117 to 1245 and the absence of the amoxicillin peak (Tables 2, 3), indicating total adsorption of amoxicillin and significant adsorption of paracetamol.

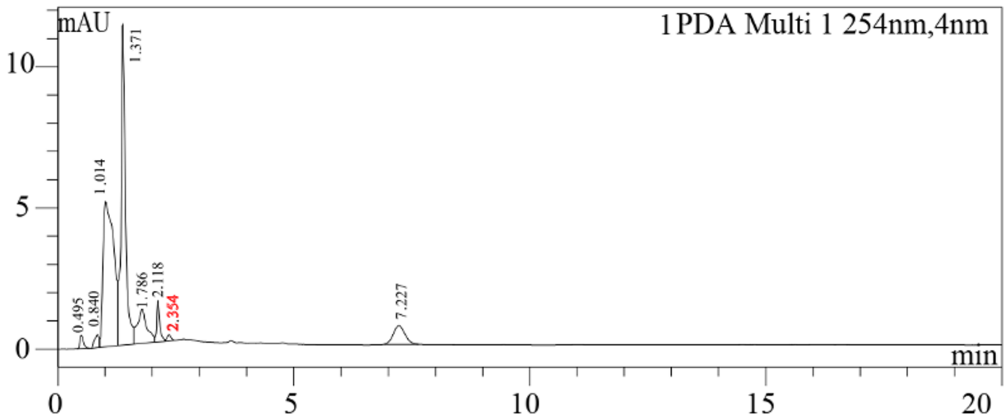

Figure 16. HPLC chromatogram of a sample of wastewater Dradeb zone Tangier Morocco, after adsorption at a wavelength range 200 ≤ λ ≤ 260 nm. 0.7 ml/min, 20 µl injection, mobile phase water-acetonitrile (75–25%), pH = 7.09, room temperature

Table 2. Heights and % areas of the chromatogram peaks in Figure 7 obtained by HPLC before adsorption

Peak#	Ret. Time	Area	Height
1	0.448	3290	547
2	0.823	9484	1526
3	1.152	39714	2983
4	1.365	128423	25847
5	1.643	32250	1937
6	2.109	11523	2967
7	2.337	6117	895
8	2.635	2487	161
9	2.868	4158	501
10	5.103	8662	595
Total		246108	37959

Table 3. Heights and % areas of the chromatogram peaks in Figure 16 obtained by HPLC after adsorption

Peak#	Ret. Time	Area	Height
1	0.495	2392	463
2	0.840	3101	450
3	1.014	81197	5135
4	1.371	75023	11327
5	1.786	17057	1215
6	2.118	6573	1455
7	2.354	1245	214
8	7.227	11227	658
Total		197815	20917

ADSORPTION ISOTHERM

Langmuir isotherm

The Langmuir adsorption isotherm quantitatively describes the formation of a monolayer of adsorbat on the outer surface of the adsorbent. The Langmuir isotherm represents the balanced distribution of ionic species between the solid and liquid phases [Hall et al, 1996]. Langmuir represented the following equation:

$$\frac{1}{q_e} = \frac{1}{q_{max}.K_L.C_e} + \frac{1}{q_{max}} \quad (3)$$

$$avec\ R_L = \frac{1}{(1 + K_l.C_0)} \quad (4)$$

where: q_e – equilibrium adsorption capacity, mg/g, determined according to the following relationship:

$$q_e = \frac{(C_0 - C_e)V}{\mathrm{m}_{ads}} \quad (5)$$

where: q_{max} – maximum adsorption capacity in mg/g;
C_0 – maximum initial concentration of dissolved paracetamol in (mg/L);
C_e – equilibrium adsorbate concentration in solution in mg/L;
K_L – Langmuir adsorption equilibrium constant in (L/mg);
R_L – the dimensionless separation factor. The value R_L indicates that adsorption is favorable if R_L<1, unfavorable if R_L>1, linear if R_L = 1, and irreversible if R_L = 0.

This isotherm is shown in Figure 17. The results given in Table 4 show that the correlation coefficient (R^2) of the Langmuir model is close to 1 for each adsorbent. The theoretical q_{max} values calculated by Langmuir q_{max} (PBC600) = 32.679 mg/g and q_{max} (PBC700)= 49.261 mg/g are close to the experimental ones, so the R_L values are less than 1, and its correlation coefficients for PBC600 and PBC700 are close to 1, which proves that these data fit Langmuir's model well only for these two adsorbents, but it is unfavorable for PBC500. The Langmuir site isotherm is valid for monolayer adsorption on a surface containing a finite number of identical sites that can be matched to uniform adsorption energies on the monolayer surface of two carbons PBC600 and PBC700.

Freundlich isotherm

The Freundlich model is commonly used to describe the adsorption characteristics of a heterogeneous surface [Thouria et al., 1018]. The empirical equation given by Freundlich:

$$Ln\ (q_e) = \frac{1}{n_F} Ln(C_e) + Ln(\ K_F) \quad (6)$$

Table 4. Isotherm parameters for amoxicillin adsorption on activated carbons at constant temperature

	PBC-500	PBC-600	PBC-700
Langmuir parameters			
R^2	0.6327	0.9004	0.9990
R_L	0.0330	0.0610	0.02509
K_L	1.2747	0.6710	0.1301
q_{max} (mg/g)	0.5761	32.6797	49.2610
Freundlich parameters			
R^2	0.9883	0.9861	0.9829
1/n	1.175	0.421	0.587
K_f (mg/g)	0.315	11.141	6.813
Temkin parameters			
R^2	0.8712	0.9355	0.9909
Bt (j/mol)	293.709	276.490	218.690
K_t (L/g)	0.2256	3.5232	1.2785

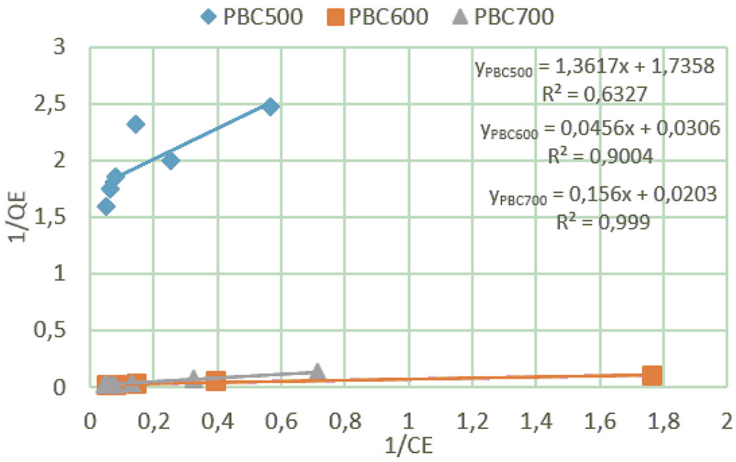

Figure 17. Linear Langmuir isotherm functions for PBC500-60, PBC600-60 and PBC700-60 adsorbents

where: K_F – Freundlich isotherm constant (mg/g);
n_F – adsorption intensity;
C_e – adsorbate concentration at equilibrium (mg/L);
Q_e – the quantity of Amoxicillin adsorbed per gram of adsorbent at equilibrium (mg/g).

The value 1/n is a function of the adsorption strength in the adsorption zone [Voudrias et al., 2002], and the results given in Table 4 show that adsorption is normal for PBC600 and PBC700 because 1/n<1, but cooperative for PBC500 because 1/n>1 [Mohan and Karthikeyan, 1997]. If n is between one and ten, this indicates a favorable adsorption process [Goldberg, 2005]. From the curve in Figure 18, we have shown the parameters represented in Table 4, the value of $1/n$ and R^2 for the two carbon samples PBC600 and PBC700 follow this condition, indicating that the removal of amoxicillin by these two samples is favorable, and due to the rise in carbonization temperature. The Freundlich model describes this phenomenon well.

Temkin isotherm

Temkin's model is given by the following equation:

$$q_e = \frac{RT}{b_t} . Ln(K_t C_e) \tag{7}$$

Or in its linear form:

$$q_e = B_t LnK_t + B_t LnC_e \tag{8}$$

where: $B_t = RT/b_t$ in (J/mol) – Temkin isothermal constant equivalent to the heat of sorption;
R – perfect gas constant (8.314 J/mol/K);
T – temperature at 291K;
K_t – Temkin isotherm equilibrium binding energy constant in (L/g).

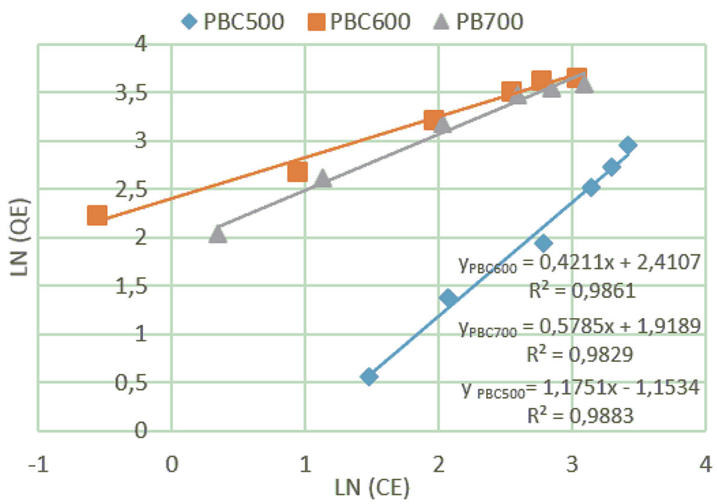

Figure 18. Linear functions of the Freundlich isotherm for the adsorbents PBC500-60, PBC600-60 and PBC700-60

From the Temkin diagrams shown in Figure 19, the kinetic parameters have been estimated and grouped together in Table 4. This model shows that the heat of adsorption due to adsorbent-adsorbat interactions decreases linearly with the rate of recovery [Mohamed et al., 2016], the surface of the three carbons is considered energetically homogeneous [Gimbert et al., 2008]. The positive values of the heat of adsorption suggest that this phenomenon is exothermic. The R^2 correlation coefficient of three coals is close to one, so this Temkin model better describes the adsorption process.

PSEUDO-SECOND-ORDER KINETICS

Ho and McKay [1999], have represented the pseudo-second-order kinetic model by equation:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{9}$$

After integrating the equation between instants 0 and t, we obtain

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \tag{10}$$

where: k_2 – pseudo-second-order apparent rate constant;
q_e^2 – adsorption capacity of amoxicillin by charcoal at saturation in mg/g;
q_t – quantity adsorbed (mg/g) by the charcoal at time t;
$v = k_2 q_e^2$ – initial adsorption rate (mg.g^{-1}.min^{-1}).

The curve of t/q_t versus time t for each carbon will give an affine line shown in Figure 20. The values obtained from this theoretical study enable the determination of the apparent rate constant K_2, and the adsorption capacity of each carbon at saturation (q_e^2), which are grouped together in Table 5.

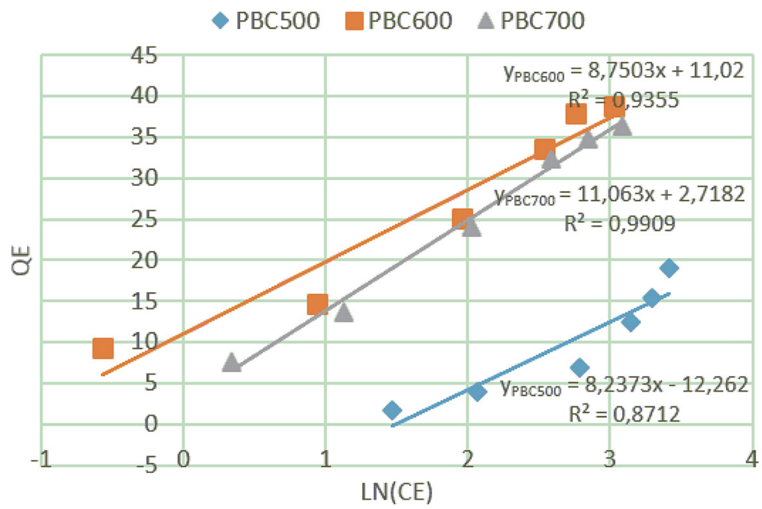

Figure 19. Linear Temkin isotherm functions for PBC500-60, PBC600-60 and PBC700-60 adsorbents

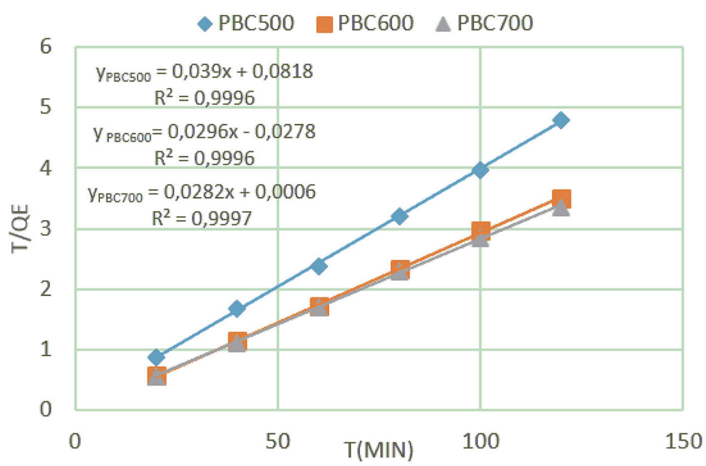

Figure 20. Pseudo-second-order kinetics of amoxicillin adsorption in aqueous media

Table 5. Pseudo-second-order kinetic parameters for amoxicillin adsorption to activated carbons

Pseudo-second-order kinetic parameters			
	PBC500	PBC600	PBC700
R^2	0.9996	0.9996	0.9997
K_2	0.0185	0.0048	1.3254
qe^2	657.462	1574.703	1257.482
q_{emax}(theo) (mg/g)	25.641	39.682	35.460
q_{emax}(exp) (mg/g)	25.220	34.926	35.927
v (mg.g^{-1}.min^{-1})	12.22	7.56	1666.66

The correlation coefficients are very close to one, and the theoretical maximum quantities adsorbed at equilibrium are very close to the experimental findings, allowing us to say that amoxicillin adsorption follows the pseudo-second kinetic model.

ADSORPTION THERMODYNAMICS

Thermodynamic quantities are determined from the VAN'T HOFF equation:

$$LnK_d = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} = \frac{-\Delta G}{RT} \quad (11)$$

With:

$$\Delta G = \Delta H - T\Delta S \quad (12)$$

where: $k_d = \frac{q_e}{C_e}$ – the distribution constant in L/g;

ΔH (KJ/mole) – standard enthalpy;

ΔS (KJ.mol^{-1}.K^{-1}) – standard entropy;

ΔG (KJ/mole) – standard free energy or enthalpy;

R = 8,314 J.mol^{-1}.K^{-1} – the perfect gas constant;

T(K) – absolute temperature of the adsorbent-adsorbate mixture.

The curve of the function of ln(kd) as a function of 1/T for the three coals represents the affine functions shown in Figure 21. We can determine the thermodynamic parameters ΔH, ΔG, ΔS and kd, which are grouped together in Table 6. All ΔG values are negative, each adsorbent shows that the adsorption of amoxicillin on these activated carbons is spontaneous and favorable [Silva et al., 2015]. It is found that the algebraic values of free enthalpy increase with increasing temperature, which are varied in the interval [0; -20 Kj/mol], this confirms the physical character of adsorption process (physical adsorption) [Ferreira et al., 2015; Allahdin et al., 2015; Singh, 2000]. Negative values of ΔH show that this adsorption process is exothermic [Ho amd McKay, 1999]. Low negative values of free entropy ΔS signify decreasing disorder [Arivoli, 2009].

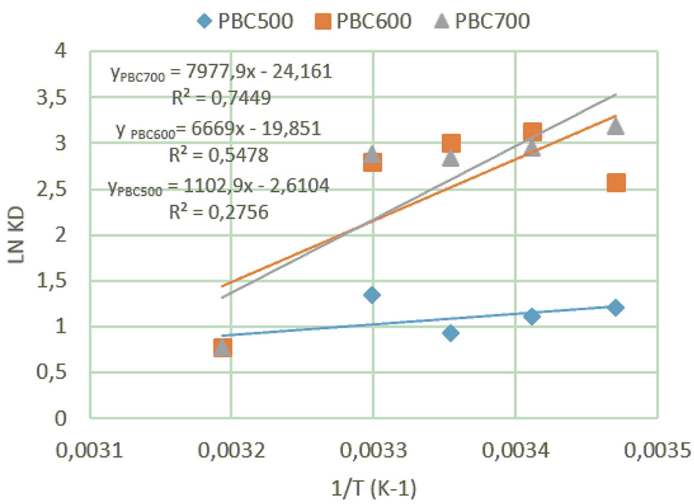

Figure 21. Linear representations of Ln(Kd) as a function of 1/T for the three prepared activated carbons

Table 6. Thermodynamic parameters of amoxicillin adsorption on these three carbons at different temperatures

Adsorption thermodynamics parameters			
	PBC-500	PBC-600	PBC-700
$\Delta H°$ KJ/mol	-9.169	-55.446	-66.328
$\Delta S°$ KJ.mol^{-1}.K^{-1}	-0.0217	-0.165	-0.200
$\Delta G°$ KJ/mol 288,15K	-2.915	-7.889	-8.446
$\Delta G°$ KJ/mol 293,15K	-2.807	-7.064	-7.441
$\Delta G°$ KJ/mol 298,15K	-2.698	-6.239	-6.437
$\Delta G°$ KJ/mol 303,15K	-2.590	-5.413	-5.433
$\Delta G°$ KJ/mol 313,15K	-2.373	-3.763	-3.424
Kd (L/g) à toutes les températures	1	1	1

CONCLUSIONS

This research, which falls within the general framework of wastewater decontamination, with the aim of removing some pharmaceutical products from wastewater, we used synthetic aqueous solutions containing the antibiotic amoxicillin trihydrate (β-lactamine). After studying the adsorption processes of this pharmaceutical product by an activated carbon prepared based on banana peel, We have shown in this work that the adsorption process is more effective for the elimination of wastewater contaminated with amoxicillin. The adsorption capacity of amoxicillin at 20 mg/l concentration at equilibrium has a value of q_e = 35 mg/g for PBC600 and PBC700, and a value of q_e = 25 mg/g for PBC500. Adsorption of amoxicillin is maximal at pH = 6 close to pHpcz = 7.16 with (adsorbent/adsorbat) ratio of around 0.5mg/ml at 18 °C. Adsorption efficiency is close to 85% under these conditions for both PBC600 carbons. However, although this work is capable of eliminating a proportion of antibiotics such as amoxicillin discharged into the household, hospital effluents at source. The Freundlich, Temkin and pseudo-second-order kinetic models best describe the adsorption phenomenon for PBC600 and PBC700, but the Langmuir isotherm is valid only for the PBC500 carbon. Thermodynamic parameters show that the adsorption of amoxicillin on these activated carbons is spontaneous and favorable. Using the HPLC method, we have shown that traces of drugs such as amoxicillin and paracetamol exist in untreated wastewater and are discharged directly into the aquatic environment full of living creatures such as the sea, requiring methodological development to eliminate or degrade these molecules in wastewater treatment plants. Our application of this process has demonstrated its effectiveness in cleaning up water contaminated with amoxicillin. However, the disadvantage of wastewater treatment is on an economic scale, as the activated carbons available are expensive. This led us to look for an inexpensive adsorbent available in abundant quantities in waste products, such as the banana peel we worked with.

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