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Using Solar-TiO_2 and Biocarbon to Decompose and Adsorb Amoxicillin from Polluted Waters

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Abstract

Surface water discharge of domestic sewage poses a treat mostly due to antibiotics content as amoxicillin. Its environmental presence provides the bacterial resistance enhancement and disturbance in aquatic life. The biocarbon is an organic carbon compound obtained by biomass pyrolisis at 300°C to 750°C under low oxygen environment. It is an effective adsorbent derived from agricultural and industrial solid biomass also frequently used to remove various pollutants, including dyes, pesticides, organic compounds and heavy metals from aqueous solutions. The importance of this natural material rises as low cost abundant and renewable alternative to activated carbon used on wastewater treatment application. Several technologies are employed to modify crude precursors on biocarbon preparation including chemical, physical and biological treatments with the addition of functional groups. The raw biomass material also provides some radicals and humic acids with promising water adsorbent results. The integrated process of the efficient Solar-TiO_2 photodecomposition followed by biocarbon adsorption resulted on 94% of amoxicillin removal percentage and avoids the toxic treatment sludge production.

Keywords: amoxicillin, adsorption, biocarbon, antibiotic, photodecomposition, solar

1. Introduction

In Brazil as in many countries the worthless biocarbon fine material is seeing as a work related disease and environmental problem. Its relation with suspended particle pollution and lungs disease is direct, usually is also related with infant work and slavery condition. The development of better technological use for the biocarbon can provide investments for its fine particle collection and use of this valuable high surface area renewable source on environmental conservation. Nowadays the Brazil economical condition can promote new ways for its better use and the research projects are providing a possible and feasible target for better future.

The pharmaceuticals production is essential and responsible for life quality and public health improvement, increasing the life expand and perform a significant role in prevention, diagnostic and treatment in human and veterinary medicine. Published environmental studies indicated the raw sewage discharge and urban drainage wastewater as the main routes and sources of pharmaceuticals input in the aquatic environment (Sun, Chen, Wan, & Yu, 2015).

The antibiotics presence in the environment shows direct association with chronic toxicity and the prevalence of bacterial resistance gene. Published studies confirm the presence of the amoxicillin in domestic wastewater in the range form ng L^{-1} to mg L^{-1}. Its presence, persistence and bioaccumulation in the environment may induce resistant gene contamination, toxic effects and change the natural balance of the aquatic ecosystems.

The amoxicillin has a complex chemical structure with $C_{16}H_{19}N_3O_5S$ with the molecular weight of 365.4 g $mol^{-1}$and three acids dissociation on pH 2.4 (for carboxyl), pH 7.4 (amine) and pH 9.6 (phenol) the solubility in water is 3430 mg L^{-1} at 20°C and log Kow 0.87.

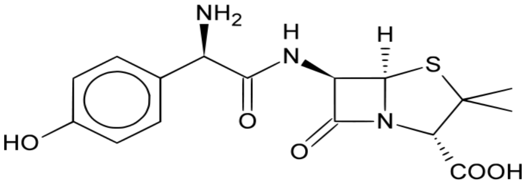

Figure 1. Amoxicillin chemical structure

There are many environmental causes of the amoxicillin presence in surface waters in small proportions. Such behavior provides excellent conditions for microorganism's changes and adapts their genetic material, to create resistance to the antibiotic and produce enzymes called beta-lactamases, which destroy penicillin base antibiotics. The resistant bacteria reproduce and multiplied, which the elimination of the weak ones, and those that have become resistant remain, posing a public health risk. Some of these threats involve the development of abnormalities and deterioration of animal reproduction. Recently published works indicate the traditional disinfection process of chlorination is not enough to deactivate such adaptation process (Lisle, 1995).

Brazil has the world largest protein production and the antibiotics use in veterinary medicine is excessive. Their application in sick animals is usually too much and also it is commonly served to healthy animals, as a ration supplement. The presence of amoxicillin contamination decrease the water quality of springs, dams and rivers, such as the Atibaia River, which supplies 90% of the drinkable water to a population of Campinas located in São Paulo state.

The photodecomposition usually involves the production of the HO* and O_2 radicals in most heterogeneous photocatalytic cases the HO* is widely regarded as the main active oxidant. The HO* production dominate the amoxicillin decomposition mechanism (Benacherine, Debbache, Ghoul, & Mameri, 2017). The photodecomposition process uses the TiO_2 as a catalyzer, generating the hydroxyl radical by many equations. However, the most commonly found in the literature are the Equation 1 and 2 summarized above:

$$TiO_2 + h\nu \rightarrow e^- + h^+ \tag{1}$$

$$H_2O + h^+ \rightarrow H^+ + HO^* \tag{2}$$

Published results indicate the stirring time for complete degradation of amoxicillin was 120 min of solar irradiation with 89% of initial amoxicillin removed. The use of solar radiation indicates does not only higher degradation efficiency but also accelerate the photocatalytic process in comparison with UV lamps (Alalm, Tawfik, & Ookawara, 2016).

There are many methods for amoxicillin and amoxicillin decomposition by products to removal from contaminated water such as nano filtration membrane, electro coagulation, electrochemical oxidation, biodegradation, reverse osmosis, ozonation, Fenton oxidation, catalytic degradation, and adsorption. Adsorption in known as an efficient process to remove various antibiotic pollutants from aqueous solutions due to simple design, flexibility, easy operation, suitability for batch and continuous processes. Additionally, all traditional water treatment processes with low pollutants concentration still result in an environmental problem as the correct disposal of the contaminated sludge. The solar energy with TiO_2promote the formation of hydroxyl radicals and increase the amoxicillin decomposition velocity possibly leading to the mineralization. The photodecomposition integrated with the fine waste biocarbon adsorption promotes the water treatment efficiency and quality polishment removing the antibiotics decomposition by-products in an efficient low cost integrated process with renewable materials.

2. Material and Methods

The eucalyptus urophilia biochar samples were a solid waste from carboniferous plant. Usually considered as an environmental problem and work related disease the low particle size material provides higher surface area for adsorption. Its natural humidity is about 5% to 7% and the total carbon is in the range of 75% to 78%. Its particle size analysis shows mostly particles from 1 to 50 µm and after micronization they reaches the average diameter lower than 37 µm (0.04 nm).

The experimental procedures used the dissolution of the amoxicillin powder brought as active medicine compound and, the preparation of the calibration curve applied the amoxicillin standard in different concentrations in the interval of 0.1 and 0.9 of adsorbance. The spectrophotometer Carry 1E allows the adsorbance measurements in $\lambda = 237$ nm (Standard Methods).The experiments design began before some exploration trials, using solar chamber and a luximeter with lux equal to one lumen per square meter.

The photodecomposition experiments used the commercial grade TiO_2 anatase and the preparation of the initial amoxicillin solutions were by the dilution of the stock solution (Ramasundaram, et al 2017). The addition of 30 mg of TiO_2 was in a 400 mL of distilled water and amoxicillin initial concentrations were in the range of 20 to 80 mg L^{-1}

accordingly with the environmental monitoring results cited in literature. The control of the temperature on 40 ℃ ± 0.5 ℃, and the pH 5.5 were during the all processes, the agitation of the solid suspension was until 120 minutes inside the solar chamber. The luximeter measurement in the solar beam allowed to measure and control the radiation incidence experimentally fixed in 1000 lumen. The collection of the solid suspensions aliquots were after 30 min each, added at Falcon flasks with 3 mg of micronized biocarbon. After the homogenization, the flasks suspensions were centrifuged at 15000 rpm for 15 min. The measurement of the clean supernatant in the spectrophotometry UV-Vis allowed quantifying the amoxicillin adsorbance and converting their values to concentration with a previously prepared calibration curve.

3. Results and Discussion

The results of the kinetics studies of photodecomposition and biocarbon sorption provide valuable insights about the kinetics models: pseudo-first-order, pseudo-second-order, and intraparticle with the determination of photodecomposition and adsorption rates.

pseudo-first-order equation:

$$\log(q_e - q_t) = \log(q_e) - \frac{\mathrm{K}_1}{2.303}\mathrm{t} \tag{3}$$

Where: K_1 is the pseudo-first-order rate (min^{-1}), and qe (mgg^{-1}) refers to the experimental adsorbed mass at equilibrium. The plotting of the calculated values of ln (qe-qt) for t (time), and the calculation of K_1 used the slope values of the line equation.

Pseudo-second order equation:

$$\frac{\mathrm{t}}{\mathrm{q_t}} = \frac{1}{\mathrm{K_2}} + \frac{1}{\mathrm{q_e}}\mathrm{t} \tag{4}$$

Where: K_2 ($g.mg^{-1}.min^{-1}$) is the kinetics adsorption rate, the values of t/qt are plotted for t (min), and the calculation predicted the adsorption capacity qe ($mg\ g^{-1}$) and the integrated adsorption rate K_2 with the slope and the intercept of the line equation, respectively.

Intraparticle equation:

$$\log(\mathrm{q_t}) = \log(\mathrm{K_{id}}) + \ \mathrm{a}\log(\mathrm{t}) \tag{5}$$

The use of the experimental results allows perform the kinetics calculations. Table 1 presents the kinetics rates calculated using the equations 3 to 5. The pseudo-first-order equation represents a logarithm of the reactant species and the reaction time, larger K_1 indicate fast reactant consumption and small time to complete the reaction, the R^2 values obtained for the pseudo-first equation indicate lower correspondence between the results and the theory. Some published results indicate the solar photodecomposition processes with goethite as pseudo-first-order kinetics with $K=0.26x10^{-2}min^{-1}$(Benacherine, Debbache, Ghoul, & Mameri, 2017).

The experimental results indicated lower correlation with pseudo-first-order, just one K_1 value was 1.6 10^{-2} (min^{-1}) with $R^2 = 0.977$, all results indicated better correlation with the pseudo-second-order.

Considering the pseudo-second-order reaction the sum of the exponents in the equation rate is equal to two. The reactant concentrations are plotted with time. The pseudo-second-order reaction depends on the initial concentration, of the two different reactants A and B combine in a single elementary step. Before the rate which A decreases they can be expressed using differential equation, rearranged, integrated and followed the linear equation which the slope value is K_2. The pseudo-second order showed better correspondence with the experimental results corroborating with published results for biocarbon adsorption and amoxicillin removal treatments, Table 2. The interparticle reaction usually point out the slow step of the adsorption reaction.

Table 1. Kinetics results of the integrated processes (solar photodecomposition and biocarbon adsorption)

Concentration ***(mg.L^{-1})***	***Pseudo-first*** ***K_1 10^{-2} (min^{-1})***	***R^2***	***Pseud-second*** ***K_2(g mg^{-1}.min^{-1})***	***R^2***	***Interparticle*** ***K_{id}***	***R^2***
21.9	1.1	0.523	17.715	0.964	1530.81	0.005
34.3	1.3	0.053	302.11	0.926	882.65	0.006
42.5	1.7	0.364	350.88	0.951	743.21	0.003
45.5	1.6	0.977	46.447	0.926	797.11	0.007
65.2	1.4	0.236	21.566	0.701	249.51	0.020
81.7	1.8	0.143	161.81	0.950	566.63	0.004

Table 2. Published results of biocarbon, methylene blue, and amoxicillin adsorption kinetics

Biocarbon	***Toxic compound***	***Adsorption capacity (mg g-1)***	***Kinetics model***	***Reference***
Eucalyptus with citric acid	Methylene Blue	178.57	Pseudo-first-order, Elovich, and intraparticle	(Sun,Chen,Wan,& Yu, 2015
Eucalyptus activated at 400^{o}C for 30 min.	Methylene Blue	9.50	Pseudo-second-order	(Sun,Wan,&Luo,2013)
Granular activated carbon PA	Amoxicillin	0.63	Pseudo-second-order	(Franco et al, 2017)
Biomass Arundo donax Linn - Microwave	Amoxicillin	196.9	Pseudo-second-order	(Chayid,&Ahmed,2015)
TiO_2 / zeolite	Amoxicillin	-	-	(Fan et al, 2016)

The concentrations of the initial amoxicillin were in the range of 28 to 83 mg L^{-1} similar with those related in literature in hospital discharge (Kanakaraju; Kockler; Motti, Glass,& Oelgemoller, 2015) (Githinji; Musey; & Ankumah, 2010) (Kavitha,& Namasivayam, 2007). The higher removal percentage was 94% for integrated process with initial amoxicillin concentration of 81.7 mg L^{-1} resulting in 825.71 mg g^{-1} higher of those systems found for eucalyptus/ citric acid (Sun, Chen, Wan,& Yu, 2015).

The use of integrated processes as solar/TiO_2 photodecomposition followed by adsorption has many advantages as a great potential for a photocatalysis with the application of solar treatment chambers and possible self-cleaning surfaces (Ramasendaram et al, 2017). However, the practical applications and continuous use demand solutions to kinetics problems, and they may rise as the adsorbent reduced surface area,TiO_2 oxidation surface and solid low stability due long term use and the potential oxide mass production.

The amoxicillin degradation with solar/TiO_2 anatase proceeds about three times faster than with ultraviolet (UV) lamp. The disproportional improvement oxidation rates may be explained by the difference between the small spectrum irradiance of UV band and the broad spectrum of solar visible light (Klauson; Babkina; Stepanova; Krichevskaya; & Preis, 2010). The intensity of radiation spectrum grows with increasing wavelength from 300 to 500 nm. The combination of solar photodecomposition and the adsorption process is actually efficient and low cost in spite some application difficulties to be overcome in near future.

The integrated process study include the adsorption isotherms, performing the calculations of Langmuir, Freundlich and Redlich-Peterson isotherms, equations 6, 7 and 8 respectively (Sampranpiboon, Charnkeitkong,& Feng,2014) (Ho, Chiu, &Wang, 2005). The Langmuir isotherm adsorption assumes an ideal solid surface composed by series of distinct sites capable of binding the adsorbate in a molecular coverage, the reaction is treated as a chemical reaction between the adsorbate molecule and the surface as a pseudo-second-order reaction. The Freundlich isotherm is empirical but widely used and the value of n is considered a measure of the adsorption intensity higher the 1 the n more favorable is the adsorption processes. The Redlich-Peterson (R-P) is more accurate than the Langmuir and Freundlich due the "g" value equals to 1 (Wu, &Tseng, 2010). Usually the R-P is in accordance with Langmuir and Freundlich isotherm equations, such behaviors could also be observed in this study

$$Ce/qe = 1/Q_0b + Ce/Q_0, \tag{6}$$

$$logqe= logKf+ 1/n\ logCe \tag{7}$$

$$\ln (Ce/qe) = g \ln Ce - \ln Kr \quad (8)$$

Where: Ce = equilibrium concentration (mgL^{-1}); qe = the amount adsorbed at equilibrium ($mg.g^{-1}$); Q_0 and b are Langmuir constants; Q_0 indicates the adsorption capacity of the material and b indicates the energy of adsorption. Kf and n are Freundlich constants. Kf indicates the adsorption capacity of the material and n indicates efficiency of adsorption. Kr and g are Redlich-Peterson constants; Kr indicates the adsorption capacity and "g" is the exponent between 0 and 1.

Table 3. Langmuir, Freundlich, and R-P isoterms for integrated processes with solar/TiO_2 and biocarbon

Langmuir	***R^2***	***K_0***	***b***
y = 0.004 + 0.001x	0.864	970.9	0.23
Freundlich	***R^2***	***Kf***	***n***
y = 2.334 + 0.377x	0.956	215.7	2.66
Radlich-Peterson	***R^2***	***Kf***	***g***
y = -6.651 + 1.002x	0.955	773.6	1.00

The RL values were in the interval from 0 to 1, with favorable adsorption accordingly with Langmuir isotherm. The Freundlich isotherm constant n was also in the interval of 2<n<10, the indication of the agreement with Freundlich model with equal adsorption heating and Redlich – Peterson parameters were also promising.

4. Conclusions

The biocarbon was efficient, low cost and renewable adsorbent material showing high efficiency (more than 95%) to remove amoxicillin and its photodecomposition by-products. The integrated process of solar/TiO_2 photodecomposition and biocarbon adsorption presented promising results and led to the better antibiotic removal process allowing the processes parameters optimization as antibiotics initial concentration, agitation time, solar radiation incidence time, TiO_2 mass, pH and temperature. The optimization of these parameters is feasible to improve the results. The combined adsorption and TiO_2solar photodecomposition of antibiotics are so far the best-integrated processes with low toxic sludge production, using the low particle biocarbon well known as worthless, an environmental risk and work related disease as high surface area solid waste, such natural renewable material showed removal capacity effectiveness and the better compromise solution for environment conservation X price.

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