Study of antibiotics binary system treated by TiO$_2$/solar photodecomposition and biocarbon adsorption.

G.N.S. Lima[1],M.V. Macedo[1], F. P. Hyppolito[1], A. Silva[2] ,N. Ortiz[1*].
[1]Institute of Nuclear and Energy Research – IPEN
[2]Carbosolo Desenvolvimento Agrícola Ltda Cietec, São Paulo, Brazil
Av. Lineu Prestes, 2242 – USP São Paulo –Brazil

Correspondent author: * nortizbr@gmail.com

Abstract: The study presents the antibiotics TiO2/solar photodecomposition followed by adsorption using micronized biocarbon. The cephalexin and amoxicillin antibiotics are very popular in Brazil and possibly the mostly found in medical prescriptions. The adsorption process using biocarbon reduce the presence of photodecomposition by-products. The experimental project was planned to optimize the efficiency of the integrated processes (photodecomposition and adsorption) to remove the antibiotics mixture from the polluted water. The first study was only one antibiotic at the time, the amoxicillin followed by cephalexin after that was studied the binary system. The maximum single amoxicillin removal percentage was 94.74 %, the single cephalexin was 69.45%, and for the binary system the higher removal percentage after solar/TiO2 photodecomposition and biocarbon adsorption was 59.95% correspondent with 8.84% of cephalexin and 91.16% of amoxicillin. The cephalexin addition to the binary system reduces the total removal percentage. The integrated processes indicate better correspondence with the pseudo-second-order kinetics K2, and Langmuir, Freundlich, and Radlich-Peterson isotherms to amoxicillin and cephalexin experiments and the binary system.

Keywords:adsorption, titanium dioxide, solar/TiO$_2$, antibiotics, biocarbon.

Introduction

When taking medicine, the therapeutic uses has just a part of its active ingredient with the metabolization by the body, the organism eliminate the rest unchanged by excretes with 50% and 90% of a drug without any change in its formulation, and they will persist in the environment. Also improper disposal of medicines in sinks, toilets, clandestine landfills and in the environment itself means that the drugs reach the waters of rivers, seas, and groundwater, increasing contaminated with these substances. The presence of these drugs can accelerate the process of adaptation and resistance of bacteria, and the diseases caused by them become increasingly a challenge to treat.

Nowadays there is many semiconductor photocatalysis application in a variety of environmental problems. The TiO$_2$ anatase appears to be the most photoactive and the most practical of the semiconductors for ecological applications such as water purification, wastewater treatment, hazardous waste control, air purification, and water disinfection (HOFFMANN, 1995). The heterogeneous photocatalysis based on the chemical oxidation of contaminants mediated by a semiconductor activated by radiation. In general, TiO$_2$ is used, due to its high photoactivity, stability, and low cost, when compared to other available semiconductors.

The advanced oxidation processes (AOP) characterized by chemical oxidation reactions, is mediated by the hydroxyl radical (HO•) which formed from oxidants such as H$_2$O$_2$ (hydrogen peroxide) or O$_3$ (ozone), and increase their efficiency by the combination

with UV or visible irradiation. The semiconductors available for heterogeneous photocatalysis processes showed absorption bands without near UV (320-400 nm) allowing their use in solar applications.

Methods

The antibiotics standard solutions with $0,5gL^{-1}$ were previously prepared, one of amoxicillin, other of cephalexin, and diluted in different initial concentrations. The diluted solutions were preheating of 40ºC before the addition of 30mg of TiO_2 and the installation in a solar radiation chamber (solar lamp) during 120 minutes. The collection of the suspension aliquots of 30mL were every 20 minutes and in each one were added 3 mg of activated micronized charcoal (diameter < 500 mesh) using a falcon tube. After shaking the tubes, the centrifugation was at 1500 rpm for 15 minutes. The measurement of the supernatants were at UV – Visible Spectrophotometer Cary 13 at λ = 272nm and 262nm to amoxicillin and cephalexin, respectively. The adsorbance was converted to antibiotics concentration using an analytical curve prepared previously with standard antibiotics solutions.

Results

After testing various masses of titanium dioxide/solar radiation and biocarbon in different antibiotics initial concentrations, the removal percentage of single component amoxicillin was 95%. This excellent result triggered in a series of experiments using the same amount of titanium oxide and biocarbon adsorbent, changing the concentrations of amoxicillin, and subsequently replacing amoxicillin with cephalexin. Analysis of each aliquots using spectrophotometric results allowed obtaining the concentration values and the kinetics and isotherm calculations.

In literature the adsorption of the toxic metals anions by biocarbon presented for PbII $K^2 = 2.58x\ 10^{-3}\ g.mg^{-1}.min^{-1}$ and R^2= 0.904and for CrIII K_2= $0.58\ x\ 10^{-3}\ g.\ mg^{-1}\ min^{-1}$ and R^2 = 0.902. Both systems show second-order kinetics favorability. The obtained results were also favorable for pseudo-second-order with R^2 in the range of 0.734 to 0.999 for amoxicillin and cephalexin integrated processes and K^2 in the range of -1071 to 538.8. The biocarbon K_2 values are very different from one process to the other depending on the adsorbed chemical structure and composition (Singanan, 2013)(Lasheen, 2012), Table 1.

The results indicate three main isotherms models Langmuir, Freundlich and Radlich Peterson. The surface adsorbed amount is the base of Langmuir equilibrium condition with the maximum monolayer adsorption capacity, the base of Freundlich isotherm model is the equilibrium established on heterogeneous surfaces (Naeimi, 2017). The Radlich Peterson adsorption isotherm contains three parameters and incorporated the features of Langmuir and Freundlich isotherms in a single equation. The exponent between 0 and 1 presents Langmuir to g= 1 and the Henry's law with g= 0 considering the experimental results the g value is near Henry's law for amoxicillin with g = 1.002 and cephalexin with g= 1.072, Table 1 and Figure 1 (Zubaidi, 2016).

The results obtained for the binary systems indicate better removal percentage for single amoxicillin with 94,74 % of removal percentage, the maximum removal percentages for cephalexin was 69.45%. The antibiotics mixture removal percentages were higher for amoxicillin mixture with less than 30% for cephalexin. The higher cephalexine content in the binary mixture result in lower removal percentages If amoxicillin content increases the removal percentage also increases showing direct potentiality to solar TiO_2 photodecomposition and biocarbon adsorption.

Conclusions

The integrated process using TiO$_2$/solar photodecomposition and adsorption by biocarbon showed promising results on decomposing and adsorbed antibiotics as cephalexin and amoxicillin and their binary mixture. The better removal percentages were for single antibiotics as just amoxicillin with 94.74% and 69.45% for cephalexine. The better removal percentage of 59.95% for antibiotics binary systems corresponds with 69.09 % of amoxicilin and 30.92% of cephalexine. The removal percentage for amoxiciline alone and in mixture were always higher. The use of solar/ TiO$_2$ and biocarbon in na integrated process for antibiotics decomposition and removal from contaminated water reprtesents a low cost, natural, abundant and efficient process to threat and reduce the antibiotics presence in the environment avoiding the bacterial gene adaptation for antibiotics resistance.

Acknowledgements

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