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Solar/TiO_2 Photodecomposition and adsorption of tertiary antibiotics systems

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Abstract: The antibiotic residues are present usually in mixtures in soils and rivers sediment in the range of ng L^{-1} to μg L^{-1} around the world and cause, among many things, the proliferation of super-resistant bacteria. The study analyzes the efficiency of titanium dioxide (TiO_2) and the solar photodecomposition of binary and tertiary systems of cephalexin, amoxicillin, and oxytetracicline from contaminated water discharges. The calculated kinetic constants of pseudo-first order, pseudo-second order and intraparticle diffusion confirm the better agreement with the pseudo-second-order. The isotherms parameters and constants of Langmuir, Freundlich, Redlich-Peterson (R-P) indicated the Langmuir and R-P isotherms have better correspondence, and the experimental results indicate 45% of removal percentage of antibiotics mixture in just 120 min of time stirring. The amoxicillin has the higher removal percentages followed by cephalexin and the lowest percentage was for oxytetraciclin. This behavior is explained by the chemical bond energy of the chemical structure, lower for amoxicillin increasing until the oxytetraccilin structure. The water treatment using Advanced Oxidative Processes - POA with TiO_2 and solar radiation at different concentrations an mixtures of antibiotics followed by adsorption process rises as an efficient and ready to use water treatment to reach better water quality for reuse purposes.

Keywords: adsorption, antibiotics, biocarbon, solar radiation, titanium dioxide.

I. INTRODUCTION

Tons of medicines are produced and applied in human and veterinary medicine all over the world. A study carried out in 76 countries found that although antibiotic use in developed countries decreased by 4% between 2000 and 2015, the consumption increased by 75% in the others, with significant variation even among countries with similar average incomes. Combining the data of the antibiotics consumption, its increased 65%, going from 21 billion daily doses to almost 35 billion. In 2015, Brazil antibiotics consumption raised by the veterinary medicine used as the world largest protein producer in the world

The government policies adopted in Brazil contribute to increase the medicine consumption and place the country among the world's largest consumers; consequently, the general waste still receives a greater quantity of packaging and leftover medicines. An essential cause of contamination of the environment is the improper disposal of drugs, classified as chemical substances which characteristics as corrosivity, flammability, reactivity, and toxicity. The inappropriate discharge of those substances is posing a risk to the environment and public health.

The adsorption of the antibiotics compounds for the organism is not complete. However, the overuse of these substances implies in some disposal by the excrete and destined to domestic sewage [1]. The domestic sewage is the main entry route of medicine residues in the environment, treated or not, the discard made by the final consumer presents a significant gap in Brazilian legislation. The pharmaceutical industry generates a considerable amount of waste due to the collection of medicines from the market, and to the discard of those who are rejected by quality control and lost during the process. In rural areas, the effluents present drugs originating from animal manure, even for healthy animals with are fed with antibiotics and pharmaceuticals food composition [2]. The collected contaminated manure is also contamination source when is used for soil fertilization.

The presence of drug residues in the environment is a worldwide problem and can cause adverse effects on aquatic and terrestrial organisms, such as the contribution to the development of resistant bacteria, which frequent occurrences when the pharmaceutical discharge is constant in lower concentrations into the environment [3].

Penicillin chemical structure has a thiazolidine ring fused to the β-lactam ring which binds to a side chain, any chemical changes in this nucleus reduce the antibiotic activation, Fig. 1. Amoxicillin (AMOX) and cephalexin (CEPH) are semi-synthetic penicillin, and they are among the world most clinically prescribed drug because of their high body absorption rate, allowing oral ingestion (stable in acidic conditions), and have a broad spectrum against a wide variety of bacteriological infections.

Another essential pharmacological family used worldwide is the tetracycline's, which includes the antibiotic oxytetracycline (OXY) widely used in the treatment of bacterial infections caused by chlamydia, rickettsia, mycoplasma, Brucella, and spirochaete, and in veterinary medicine, added in animal nutrition and food additives to livestock use.

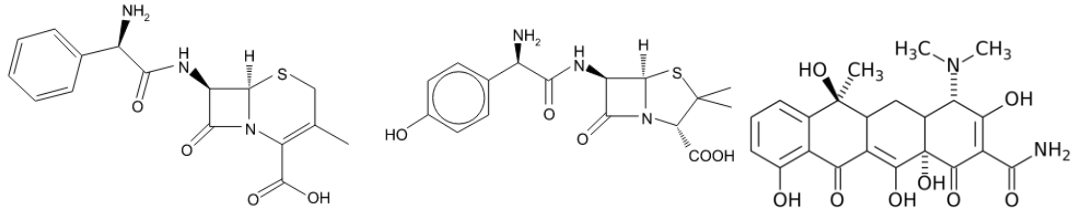

Figure 1: Chemical structure of cephalexin, amoxicillin and oxytetracycline.

CEPH AMOX OXY

Brazil imports all the active principles of these antibiotics from China and India, while Brazilian laboratories are responsible for formulating, bottling and the distribution. Such manufacture process produces a mixture of antibiotics effluents with significant variation of characteristics and volumes (depending on the productive demand) and with low biodegradability (due to the presence of biologically active and toxic compounds). This effect promotes the inactivation of the traditional water biological treatment. The Brazilian legislation with aggravates the pollution situation has not established limits for antibiotics active principles discharge in the water courses, requiring individualized studies for each substance and the effect of such antibiotics mixture [3].

The base of the Advanced Oxidative Processes (POAs) is the formation of hydroxyl radicals, with or without irradiation, that promotes the mineralization of organic compounds. Among the heterogeneous oxidative process are those using semiconductors: ZnO, WO_3, $SrTiO_3$ and Fe_2O_3, and the most used is titanium dioxide (TiO_2) because it is very active and chemically stable in photocatalysis degradation of organic substances in aqueous suspension [4]. Sunlight or artificial light must activate the semiconductors. Published results confirm the use of POAs with solar/TiO_2-graphene in a tertiary antibiotic system for E. Coli resistant gene inactivation [1]

In heterogeneous photocatalysis with solar TiO_2 is the most likely process with effectivity and low energy cost [5]. The solar lamp with 45% of the total energy instead of UV with less than 10% allows the process with high energy use [6]. The Equation 1 presents the mechanism when the inorganic semiconductor absorbs the amount of energy required to excite the electron, causing an electron transition, in which the electron is promoted from the valence band (BV) to the conduction band (BC), resulting in the formation of oxidizing sites which catalyze chemical reactions and oxidize organic compounds to carbon dioxide (CO_2) and water (H_2O). The photogenerated valency band reacts with water (2), and OH^- groups (3), producing hydroxyl radicals, and the calculation of the reactant oxygen production (4).

$$TiO_2 + hv\ (radiation) \rightarrow TiO_2\ (hBV^+ + eBC^-) \quad (1)$$

$$H_2O + TiO_2(hVB^+) \rightarrow {}^{\bullet}OH + H^+ + TiO_2 \quad (2)$$

$$OH^- + TiO_2(hVB^+) \rightarrow {}^{\bullet}OH + TiO_2 \quad (3)$$

$$O2 + TiO_2(eCB^-) \rightarrow O_2{}^{\bullet}- + TiO_2 \quad (4)$$

The generation of hydroxyl radicals has been beneficial in the decomposition of several organic pollutants through mechanisms such as hydrogen abstraction, electron transfer and electrophilic addition [5] [7].One of the most critical technologies for industrial effluents treatment is the adsorption of organic compounds using activated carbon, obtained from carbonaceous biomass, including wood, coal, lignin, coconut shells, and sugars. Activated biocarbon is microporous and has high adsorbent power because of its top surface area and a variety of functional groups on its surface.

The adsorption process can follow the solar/TiO_2 photodecomposition to complete the water treatment and removal of new pollutants as antibiotics. After photodecomposition, the saturated adsorbent will be less toxic and possibly reach the mineralization.

The present study aimed to evaluate the solar/TiO_2 photodecomposition of the individual antibiotics and the ternary mixture of amoxicillin (β-lactam), cephalexin and oxytetracycline (tetracycline)[8]. All of them have a variety of uses in human and veterinary medicine and have the same fate the sewage, industrial effluents and the water resources. To identify and quantify the interactions nature between the antibiotics the ternary multicomponent mixtures were studied, with the identification of some photodecomposition by-products.

II. MATERIAL AND METHODS

The preparation of the standard solutions of amoxicillin and cephalexin were with 0.5 g L^{-1} each, and the oxytetracycline was with 29mg L^{-1}, the experiments used the dilution of the antibiotics solutions. The experimental procedures apply the published values of the antibiotics concentration found in sewage treatment plants (ETS's) and natural waters in different world regions, and they are often in the range of μg L^{-1} and ng L^{-1}. Acknowledging that in sewage effluents there is always a wide variety of antibiotics mixtures, the experiments were carried out in 400mL aqueous systems with different compositions of the three chosen antibiotics, with initial concentration ranged from 11.81 to 42.18mg L^{-1}. Table 1 describes the antibiotics composition percentage for each mixture.

The mix of the standard solutions was kept on 900r.min^{-1} and preheated to (40,0 ± 0,5)°C using the magnetic stirrer and heating plate. The control of the temperature and pH were during the whole process, at pH 5,5 and the temperature was 40°C. The addition of 30 mg of TiO_2 was after the system stabilization in an antibiotic tertiary mixture, followed by placed under constant stirring in a solar radiation chamber for 120 minutes. The light intensity control was at 1600 lux. The collection of the 30mL of the suspension aliquots was every 20min with the addition of 3mg of micronized activated charcoal (diameter <500 mesh) to each collection tube.

Table 1: The Antibiotics percentage composition on the tertiary system

Total C_0 (mg L^{-1})	CEPH (%)	AMOX (%)	OXY (%)
11,81	9	89	2
13,69	25	74	1
16,83	9	90	1
17,82	20	79	1
22,30	44	44	12
25,95	42	42	16
28,00	26	26	48
33,26	38	38	24
42,18	25	25	50

The centrifugation step at 2000 rpm for 15 min followed the mixing of the collection tubes, and the analysis of the supernatants used the equipment Cary 13 UV-Visible Spectrophotometer at wavelengths (λ) of 272nm, 262nm, and 373nm for amoxicillin, cephalexin, and oxytetracycline, respectively. The obtained absorbances (A) were converted to antibiotic (C) concentrations using analytical curves prepared previously with standard solutions. The concentration values of the tertiary antibiotics allow to calculating the removal percentage (5), where C_0 is the initial concentration (mg L^{-1}), and Ce is the concentration at equilibrium (mg L^{-1}).

$$x = (C_0 - Ce)\, C_0 \times 100 \qquad (5)$$

The calculation of the antibiotic amount adsorbed in each instant (qt) used (6) and (7). It was possible to perform the calculation of the adsorbed mass at equilibrium (qe), both in mg of antibiotics per g of biocarbon, where Ct is the concentration at time t (mg L^{-1}), Ce is the concentration in equilibrium (mg L^{-1}), V is the volume of the solution (mL) and m is the mass of biocarbon (g).

$$qt = (C_0 - Ct)V\, m \qquad (6)$$

$$qe = (C_0 - Ce)V\, m \qquad (7)$$

The experimental data allows calculating the kinetic models of pseudo-first order (8), pseudo-second order (9) and interparticle diffusion (10) [7]. Figure 2 presents the results, the constants were determined and

appended to Table 2, where $K_1$is the kinetic constant of pseudo-first order (min^{-1}), K_2 the of pseudo-second order (g mg^{-1} min^{-1}), Kid is the constant of interparticle diffusion (mg g^{-1} $min^{-0,5}$) and t is the time in minutes [9].

$$\ln (qe - qt) = \ln (qe) - K_1 t \quad 2{,}303 \qquad (8)$$

$$t \quad qt=1 \quad K_2+t \quad qe \qquad (9)$$

$$\log (qt) = \log (Kid) + \log (t) \qquad (10)$$

III. RESULTS AND DISCUSSION

The comparison of the kinetic models best fit uses the correlation indexes (R^2) for quantitative evaluation and indicate, in all situations, the pseudo-second-order kinetics better adjustment, Figure 2. The kinetic study of the reduction rate of amoxicillin depends of the initial concentration and the stirring time [7][8]. The best kinetics correlation with pseudo-second-order mechanism is the dependency of the adsorption rate of the adsorbent mass and concentration in the equilibrium and confirms the control of the velocity mechanism by chemical adsorption[9] [10].

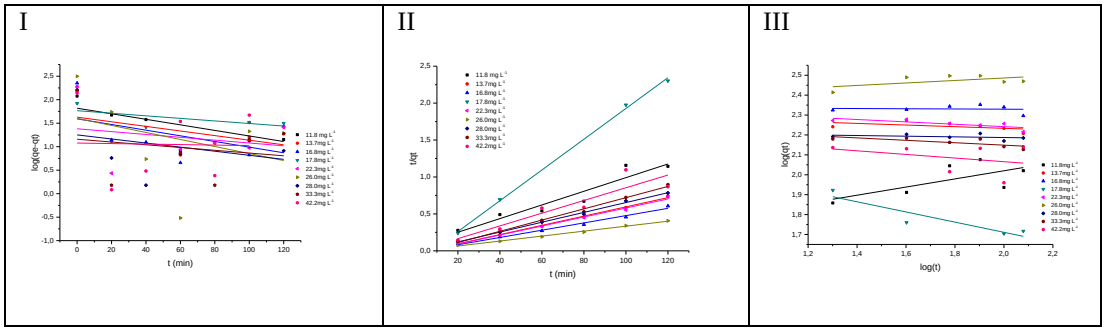

Figure 2: Pseudo first-order (I), pseudo-second-order (II) and interparticle (III).

Literature presents for TiO_2/solar photodecomposition followed by adsorption the better removal percentages for single antibiotics as amoxicillin with 94.74% and 69.45% for cephalexin. The higher removal percentage of 59.95% for binary systems corresponds in antibiotic content 69.09 % of amoxicillin and 30.92% of cephalexin. The comparison of the removal percentage for amoxicillin alone and for amoxicillin mixtures were always higher, [11][12] mostly due its chemical structure with lower energy bound and some interference of the others antibiotics presence. The Solar/TiO_2 photodecomposition process finished after 120 minutes of continuous stirring and it was measured the removal percentage, Table 2. Literature related higher removal percentages for same antibiotics compositions, but they are always for long stirring time period as 36, 48 and 52h such long process is not feasible or affordable for sewage water treatment[13][14]. The difficulty of low removal percentage can be overcome using a sequence of solar photodecomposition and adsorption processes targeting the water quality polishment.

Table 2: Pseudo-first order, pseudo-second order and interparticle diffusion parameters

C_0 (mg L^{-1})	First-Order		Second-Order		Interparticle		Removal	
	K_1	R^2	K_2	R^2	K_{id}	R^2	C_e	%
11.81	0.014	0.31	14.9	0.89	40.8	0.35	7.88	33.3
13.69	0.011	0.003	32.5	0.993	206.8	0.11	7.51	45.1
16.83	0.014	0.018	62.19	0.985	219.1	0,.24	9.40	44.2
17.82	0.006	0.156	6.47	0.998	166.8	0.77	15.1	15.5
22.30	0.007	0.186	33.78	0.991	229.8	0.50	16.0	28.1
25.95	0.017	0.105	729.9	0.993	229.8	0.157	15.6	40.0
28.00	0.010	0.137	82.8	0.995	166.2	0.090	22.7	19.0
33.26	0.007	0.210	25.48	0.992	186.4	0.445	28.2	15.2
42.18	0.001	0.249	153.4	0.799	177.0	0.109	37.6	10,.8

Table 3 presents the correlation between the antibiotics concentration and the removal percentage for tertiary systems. The high correlation was for the removal percentage and amoxicillin concentration followed by

the removal percentage and cephalexin content [15][16]. The lower removal correlation was for oxytetracycline content. The oxytetracycline chemical bonding presents higher resistance to the photodecomposition process and the adsorption in comparison with the amoxicillin and cephalexin.

The best result was 45.1% removal of antibiotics, initially with 13.69 mg L^{-1} and at equilibrium with 7.51 mg L^{-1} with 6.18 mg g^{-1}. It is clear that in solutions with a more significant presence of oxytetracycline, the removal of antibiotics decreases. This effect can be a result of the higher energy bonding and hydroxyl radicals consumption for the Oxytetracicline chemical structure.

Table 3: The correlation table for antibiotics composition and the removal percentage

	Total C_0	Cephalexin	Amoxicillin	Oxitetracyclyne	Removal
Total C_0	1				
Cephalexin	0.92	1			
Amoxicillin	0.72	0.71	1		
Oxitetracyclyne	0.87	0.71	0.36	1	
Removal	0.74	0.80	0.93	0.43	1

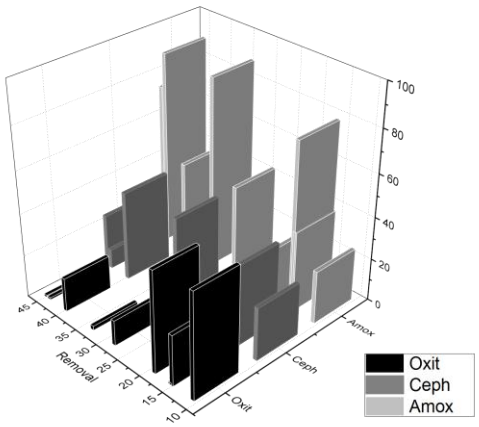

Figure 3: The comparison of Amoxicillin, Cephalexine and Oxitetracicline removal percentages

The adsorption equilibrium was compared with some isotherm models as Langmuir (11), Freundlich (12), Redlich-Peterson (13) and Temkin (14) and Fig. 3 [17]. The parameters were in Table 4, where b is the maximum adsorption capacity constant (mg g^{-1}), K_0 is the Langmuir constant corresponding to the sorption energy(L mg^{-1}), Kf ((mg g^{-1})(L mg^{-1}) and n are empirical parameters of Freundlich and measure, respectively, the adsorption capacity and the adsorption intensity, the K_R (L mg^{-1}) is a constant to Redlich-Peterson's model, and the parameter g varies between 0 and 1, $B_1$is the heat of adsorption (J mol^{-1}) and Kt is the equilibrium constant and bond (L mg^{-1}).

$$Ceqe=1\ K_0\ b+CeK_0 \quad (11)$$

$$\log (qe) = \log (Kf) + \log (Ce)\ n \quad (12)$$

$$\ln Ceqe = g \ln (Ce) - \ln (K_R) \quad (13)$$

$$qe = B_1 \ln (Kt) + B_1 \ln (Ce) \quad (14)$$

Table 4 Langmuir, Freundlich, Redlich-Peterson and Temkin constants and parameters.

Isotherms	Correlation	Constant	Parameter
Langmuir	R^2	K_0	b
y = 0.007x – 0.016	0.967	137.6	0.45
Freundlich	R^2	K_f	n
y = -0.093x + 2.33	0.106	212.0	-10.8
Redlich-Peterson	R^2	K_R	g
y = 1.09x – 5.35	0.906	209.9	1.09
Temkin	R^2	K_t	B_1
y = -18.6x + 218.6	0.064	7.77E-6	-18.6

The correlation indexes R^2 indicate better agreement with Langmuir isotherm and the R-P isotherm [18]. The Langmuir model assumes monolayer adsorption with a limited number of available sites in adsorbent surface for the antibiotic molecules and the equilibrium parameter of the Langmuir model (RL) calculated (15)[19]. The RL value corresponds to the adsorption process development from 0 to 1 is favorable for all studied systems.

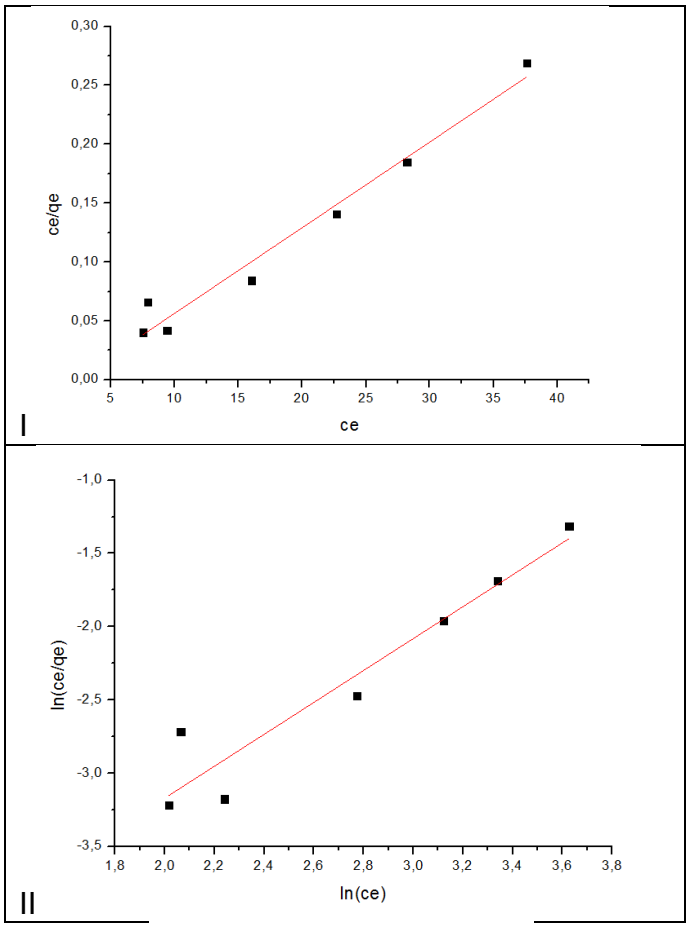

Figure 3: Langmuir (I), Redlich-Peterson(II) isotherms

IV. CONCLUSION

The TiO_2/solar photodecomposition followed by biocarbon adsorption is promising for the contaminated water treatment with the antibiotics cephalexin, amoxicillin, and oxytetracycline with the possibility of 45% removal in the tertiary systems. Literature related higher removal percentages, but they are always for long stirring time period as 36, 48 and 52h such long process is not feasible nor affordable for sewage water treatment. The difficulty of low removal percentage can be overcome using a sequence of solar photodecomposition and adsorption processes targeting the water quality polishment. The adsorption control is by chemical reaction in agreement with the kinetic model of pseudo-second-order controlled by the adsorbent mass and the antibiotics concentrations. After the antibiotic molecules decomposition the adsorption is

necessary, the rate of decomposition depends on how quickly is the hydroxyl radicals production through the Advanced Oxidative Process with TiO_2/solar. The adsorption process developed favorably because the equilibrium parameter of the calculated Langmuir model presented a value between 1 and 0. The use of solar/ TiO_2 and biocarbon in an integrated process for antibiotics decomposition and removal from contaminated water represents a low cost, natural, abundant and efficient method to threat and reduce the antibiotics presence in the environment avoiding the bacterial gene adaptation for antibiotics resistance.

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REFERENCES

[1]. Karaolia, P.; Michael-Kordatou, I.; Hapshi, E.; Drosou, C.; Bertakis, Y.; Chistofilos, D.; Armatas, G.S.; Sygellou, L.; Schwatz, T.; Xekoukoulotakis, N.P.; Fatta-Kassinos, D. Removal of antibiotics, antibiotic –resistant bacteria and their associated genes by graphene-based TiO_2 composite photocatalysts under solar radiation in urban wastewaters, 224,2018, 810-824. https://doi.org/10.1016/j.apcat.2017.11.020

[2]. Canle, M., Perez, I.F.; Santaballa, J.A. Photocatalyzed degradation/abatement of endocrine disruptors. Photocatalysis, 6, 2017, 101-136.http://dx.doi.org/10.1016/j.cogsc.2017.06.008

[3]. Trovó, A.G.; Paiva, V.A.B.; Machado, A.E.H.; Oliveira, C.A.; Santos, R.O. () Degradation of the antibiotic chloramphenicol by Photo-Fenton process at Lab scale and solar pilot plant: Kinetic, toxicity and inactivation assessment. Solar Energy, 97, 2013, 596-604. http://dx.doi.org/0.1016/j.solener.2013.09.017

[4]. Eskandarian, M.R.; Fazli, M.; Rasoulifard, M.H.; Choi, H. Decomposition of organic chemicals by zeolite –TiO_2 nanocomposite supported onto low density polyethylene film under UV-LED powered by solar radiation. Applied Catalysis B: Environmental 183,2016, 407-16. http://dx.doi.org/10.1016/j.apcatb.2015.11.004

[5]. Gimeno, O.; Garcia-Araya, J.F.; Beltran, FJ.; Rivas, F.J.; Espejo, A. Removal of emerging pollutants from primary effluent of municipal wastewater by means of sequential biological degradation-solar photocataytic oxidation processes. Chemical Engineering Journal, 290, 2016, 12-20. https://doi.org/10.1016/j.cej.2016.01.022

[6]. Wang, Y.; Tao, J.;Wang, X.; Wang, Z.;Zhang, M., Gang, H.;Sun, Z. A unique Cu_2O/TiO_2 nanocomposite with enhanced photocatalytic performance under visible light irradiation. Ceramics International,43, 2017, 4866-4872http://dx.doi.org/10.1016/j.ceramint.2016.12.130

[7]. Elmolla, E.S.; Chaudhuri, M. Comparison of different advanced oxidation processes for treatment of antibiotic aqueous solution. Desalination, 256, 2010 , 43-47. https://doi.org/10.1016/j.desal.2010.02.019.

[8]. Deng, F.; Zhao, L.; Luo, X.; Luo, S.; Dionysios, D.D. Highly efficient visible –light photocatalytic performance of Ag/AgIn5S8 for degradation of tetracycline hydrochloride and treatment of real pharmaceutical industry wastewater. Chemical Engineering Journal 333 2018, 423-433 https://doi.org/10.1016/j.cej.2017.09.022

[9]. Guilhen, S.N., Ortiz, N., Fungaro, D.A., Masek, O. Pyrolitic temperature evaluation of macauba biochar for uaranium adorption from aqueous solutions. Proceedings' of Biochar: production, characterization and applications-ECI Digital Arquives, August 20-27, 2017.http://dc.engconfinl.org/biochar

[10]. Jang, H.M.; Yoo, S.; Choi, Y., Park, S.; Kan, E. Adsoption isotherm, kinetic modeling and mechanism of tetracycline on Pinus taeda-derived activated biochar, 259, 2018, 24-31. https://doi.org/10.1016/j.biortech.2018.03.013

[11]. Sousa, M.A.; Gonçalves, C.; Vilar, V.J.P.; Boaventura, R.A.R.; Alpendurada, M.F. Suspended TiO_2 assisted photocatalytic degradation of emerging contaminants in a municipal WWTP effluent using solar pilot plant with CPCs. Chemical Engineering Journal, 198, 2012, 301-309. https://doi.org/10.1016/j.cej.2012.05.060.

[12]. Nunes, R.M., Costa, D., Ortiz, N. The use of eucalyptus activated Biocarbon for water treatment Adsorption processes. American Journal of Analytical Chemistry 8, 2017, 515-522.https://doi.org/10.4236/ajac.2017.88037

[13]. Shi, Y.; Yang, Z.; Wang, B.; An, H.; Chen, Z.; Cui, H. Adsoprtion and photocatalytic degradation of tetraciclyne hydrochloride using a palygorskite – supported Cu_2O- TiO_2. Applied Clay Science, 119, 2016, 311-320.https://doi.org/10.1016/j.caly.2015.10.033.

[14]. Ahmed, M.J. Adsorption of quinolone, tetracycline, and penicillin antibiotics from aqueous solutions using activated carbons: Review. Environmental Toxicology and Pharmacology, 50 2017, 1-10.http://dx.doi.org/10.1016/j.etap.2017.01.004

[15]. Ortiz, N., Silva, A., Lima, G.N.S, Hyppolito, F.P. using solar-TiO2 and biocarbon to decompose and adsorb amoxicillin from polluted waters. International Journal of Chemistry, 10, 2018, 1.https://doi.org/10.5539/ijc.v10n1p131

[16]. Chayid, M., Ahmed, M.J. Amoxicillin adsorption on microwave prepared activated carbon from Arundo donax Linn: Isotherms , kinetics, and thermodynamics studies, Journal of Environmental Chemical Engineering, 3, 2015, 1592-1601. https://doi.org/10.1016/j.jece.2015.05.021

[17]. Mansouri H. Carmona, R.J., Gomis-Berenguer, A., Soussi-Najar, S., Ouederni, A., Ania, C. Competitive adsorption of ibuprofen and amoxicillin mixtures from aqueous solution on activated carbons. Journal of colloid and interface science, 449, 2015, 252-260.http://dx.doi.org/10.1016/j.cis.2014.12.020

[18]. Ortiz, N. Antibiotics – Solar photodecomposition and biocarbon adsorption. In: Emerging Pollutants – Some strategies for the quality preservation of our environment. Editor Sonia Soloniska, IntechOpen-London, 2018, 20p.ISBN 978-1-78923-384-1.

[19]. Acosta, R., Fierro, V., Yuso, A.M., Nabarlatz, D., Celzard, A. Tetracycline adsorption onto activated carbons produced by KOH activation of tyre pyrolysis char. Chemosphere, 149, 168-176. https://doi.org/10.1016/j.chemosphere.2016.01.093