Biocarbon adsorption and TiO_2/solar photodecomposition of binary and tertiary antibiotics systems

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Introduction

- The medicines produced and applied at human and veterinary medicine all over the world are adsorbed and used in the organism. However, a significant quantity of these substances is still active when excreted and have the final destiny the domestic sewage and surface water resources.

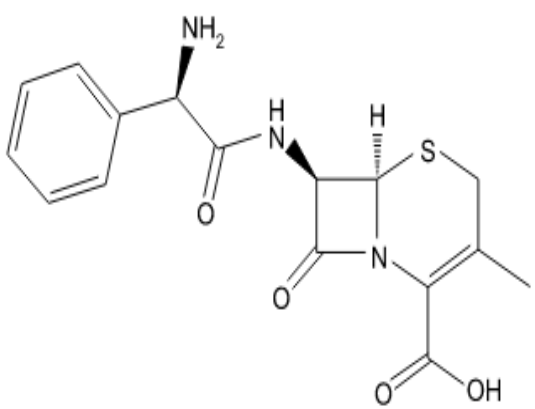
- The antibiotic residues are used and always discharged in mixtures, and they are present in soils and rivers in the range of ng L^{-1} and µg L^{-1} all around the world.

- The farmaceuticals residues in the environment can cause adverse effects on aquatic and terrestrial organisms, such as the contribution to the development of resistant bacteria.

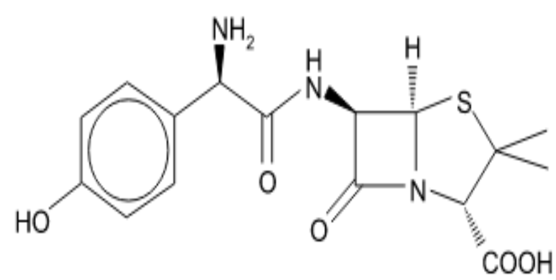
Introduction

- There are a variety of antibiotics mixture in soil and water environment providing as binary and tertiary systems.

- Amoxicillin and cephalexin are essential semi-synthetic penicillin's and are among the most clinically prescribed in the public assistance due they high absorption rate, allow oral ingestion and low cost.



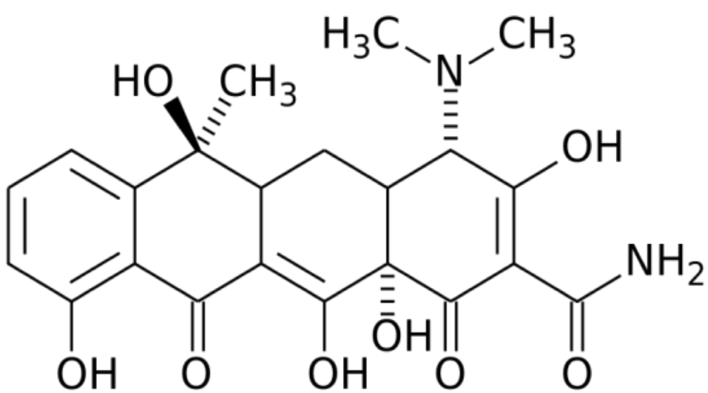
Cephalexin



Amoxicillin

Introduction

- The Oxytetracycline is widely used in the treatment of bacterial infections and veterinary medicine, animal nutrition and food additives to livestock use.



Oxytetracycline

Objective

- The study was conducted to compare the effect of methylene blue dye and Oxytetracycline ions on the removal of antibiotics from a mixture including amoxicillin and cephalexin.

- Using the photoactive titanium dioxide (TiO_2) and the artificial Solar Radiation to decompose the composts, through Advanced Oxidative Processes (AOP).

- The water polishing step performed by the biochar adsorption followed the Solar/TiO2 photodecomposition.

- The fundamentals of the Advanced Oxidative Processes (AOP) is the production of the hydroxyl radicals, with or without irradiation, and promote the mineralization of organic compounds, as some pharmaceutical compounds.

- Among the different catalyzers for photodecomposition are the semiconductors: TiO_2, ZnO, WO_3, $SrTiO_3$ and Fe_2O_3, the most used is titanium dioxide (TiO_2).

- The semiconductor absorbs the energy required to promote the electron transition, from the valence band (VB) to conduction band (CB), allowing the formation of oxidizing sites and catalyze the chemical reactions, oxidizing the organic compounds to carbon dioxide (CO_2) and water (H_2O).

$$TiO_2 + hv\ (UV) \rightarrow TiO_2\ (h_{BV}^{+} + e_{BC}^{-}) \qquad (1)$$

- The photogenerated lacuna reacts with adsorbed water, (2), and OH^- groups, (3), producing hydroxyl radicals.

$$H_2O_{(abs)} + TiO_2\ (h_{bv}^{+}) \rightarrow \bullet OH + H^+ + TiO_2 \qquad (2)$$

$$OH^- + TiO_2\ (h_{bv}^{+}) \rightarrow \bullet OH + TiO_2 \qquad (3)$$

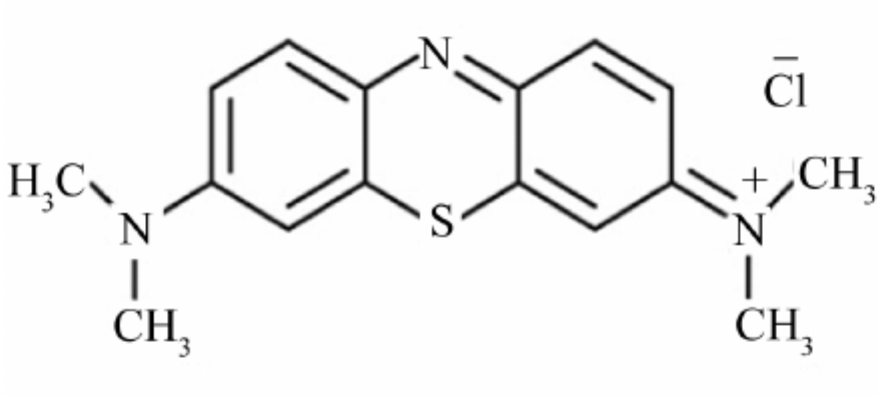
Biochar Adsorption

- One of the most important technologies for the treatment of industrial effluents is the adsorption of organic compounds on activated biocarbon.

- The biochar production use carbonaceous materials, including wood, coal, lignin, coconut shells, and sugars. It is microporous and has high adsorbent power due to its high surface area and a variety of functional groups on its surface.

- The removal of dyes such as methylene blue from industrial wastewater before discharge is of uttermost importance. Organic dyes colorize water and make them visible and aesthetically unpleasant.
- Nowadays some studies are confirming, their antagonistic effect for organics natural oxidation and photodecomposition process.

- This effect result of the dye hampered interference with sunlight penetration into water bodies, thus affecting organic decomposition, fish, and other aquatic organisms.



Chemical structure of methylene blue dye.

Material and methods

- Standard solutions of the antibiotics amoxicillin and cephalexin at 0.5g L^{-1} and oxytetracycline at 29mg L^{-1} were previously prepared and diluted in different initial concentrations for the execution of the experiments with binary and tertiary mixtures.

- The addition of the prepared standard solution of methylene blue 0.5 mg L^{-1} was in different volumes to the mixture of the antibiotics.

- It was performed to understand if the dye composition will interfere in the photodecomposition of the antibiotics tertiary mixture.

- The dilutions were subjected to the stirring of 900r/min and preheating to (40.0 ± 0.5)°C using the magnetic heater.

- The use of pHmeter and digital thermometer allows the temperature and pH control, during the process, the instruments did not indicate any essencial variations, with T=40ºC and pH 5.5.

- After preparation, the TiO_2 were weighed on the analytical balance and added to the antibiotic suspensions aliquots with and without the methylene blue dye. The solar radiation chamber kept the mixture under stirring for a total 120 minutes.

- The use of the light meter makes possible to measure and control the artificial solar intensity and kept constant on 1600lux.

- Aliquots of 30mL of the suspension were collected every 20min and added to the micronized activated charcoal (diameter <500 mesh)in Falcon tubes for further centrifugation.

- After shaking, the aliquots were centrifuged at 1500 rpm for 15 minutes.

- The supernatants were measured at UV – Visible Spectrophotometer Cary 13 at λ = 273nm, 261nm, 663nm and 373nm to amoxicillin, cephalexin, methylene blue dye and oxytetracycline, respectively.

- The adsorbance (A) was converted to antibiotics concentration (C) using an analytical curve prepared with standard solutions.

$$C_{amoxicillin} = \frac{(A - 0{,}011)}{2{,}370} \quad (4); \quad C_{cephalexin} = \frac{(A + 0{,}001)}{0{,}015} \quad (5); \quad C_{oxytetracycline} = \frac{(A + 0{,}051)}{0{,}045} \quad (6)$$

Results and Discussion

- The results obtained allowed to elaborate graphs of pseudo first-order and pseudo second-order to experiments and to determine in which of them the systems fit better.

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (7); \qquad\qquad q_e = \frac{(C_0 - C_e)V}{m} \qquad (8)$$

- Through Equation 7 it was possible to calculate the amount of antibiotic adsorbed at each instant (q_t), and using Equation 8, it was possible to perform the calculation of the amount adsorbed at equilibrium (q_e).

C_t - concentration at time t (mg L^{-1})

C_e - concentration in equilibrium (mg L^{-1})

V - volume of the solution (mL)

m - mass of biocarbon and TiO_2 (g)

- In order to analyze the experimental data, graphs for the kinetic models of pseudo-first order (Equation 9) and pseudo-second order (Equation 10) were constructed.

$$\ln(q_e - q_t) = \ln(q_e) - \frac{K_1 t}{2,303} \qquad (9); \qquad \frac{t}{q_t} = \frac{1}{K_2} + \frac{t}{q_e} \qquad (10)$$

K_1 - kinetic constant of pseudo-first order (min^{-1})

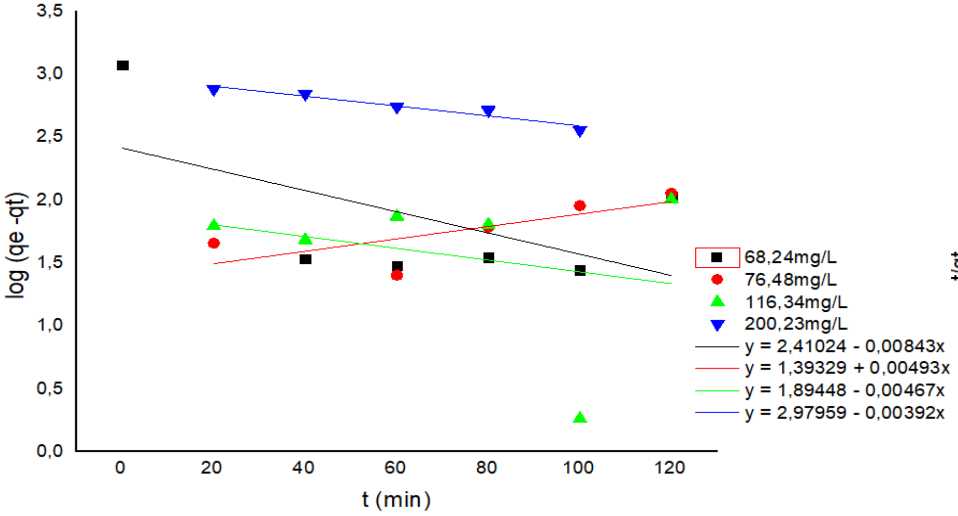
K_2 - kinetic constant of pseudo-second order ($g\ mg^{-1}\ min^{-1}$)

t – time (min)

Kinetics Tertiary - Methylene Blue Dye								
Concentration ($mg.L^{-1}$)	First-Order		Second-Order		Ce ($mg.L^{-1}$)	Removal percentage (%)		
	K_1	R^2	K_2	R^2		Methylene Blue	Cephalexin	Amoxicillin
68.24	0.019	0.159	-371.75	0.995	29.36	30	57.81	56.86
76.48	-0.011	0.397	-286.53	0.995	76.48	0	0	0
116.34	0.011	-0.159	-161.12	0.972	116.34	0	0	0
200.23	0.009	0.918	50.94	0.921	200.13	38.1	0	0
Kinetics Tertiary - Oxytetracycline								
Concentration ($mg.L^{-1}$)	First-Order		Second-Order		Ce ($mg.L^{-1}$)	Removal percentage (%)		
	K_1	R^2	K_2	R^2		Oxytetracycline	Cephalexin	Amoxicillin
80.62	0.007	-0.058	-176.06	0.986	36.05	14.08	50.47	53.59
99.09	0.017	0.151	-719.42	0.983	47.56	1.63	30.43	31.79
128.30	0.008	0.112	-93.46	0.988	88.31	13.45	53.00	57.36
201.36	0.002	-0.249	-145.56	0.990	169.26	7.31	16.34	16.10

Pseudo-first order, pseudo-second order and interparticle diffusion parameters

Results



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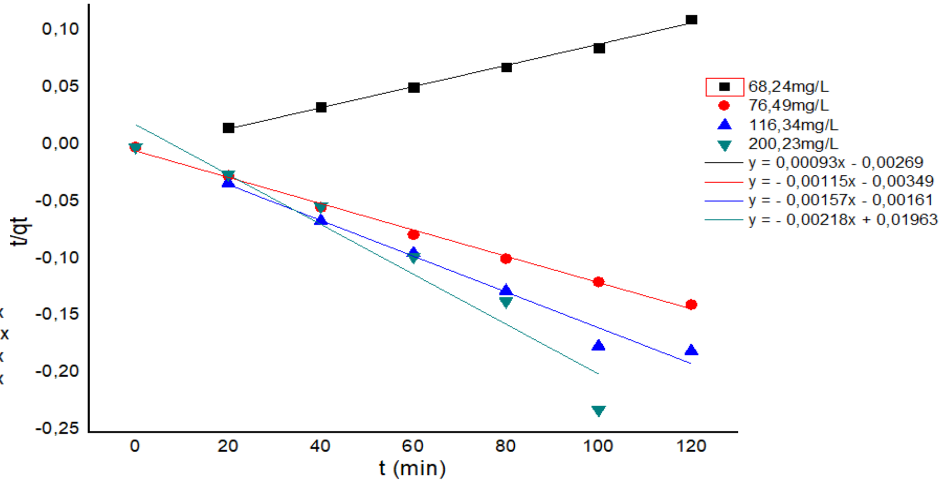
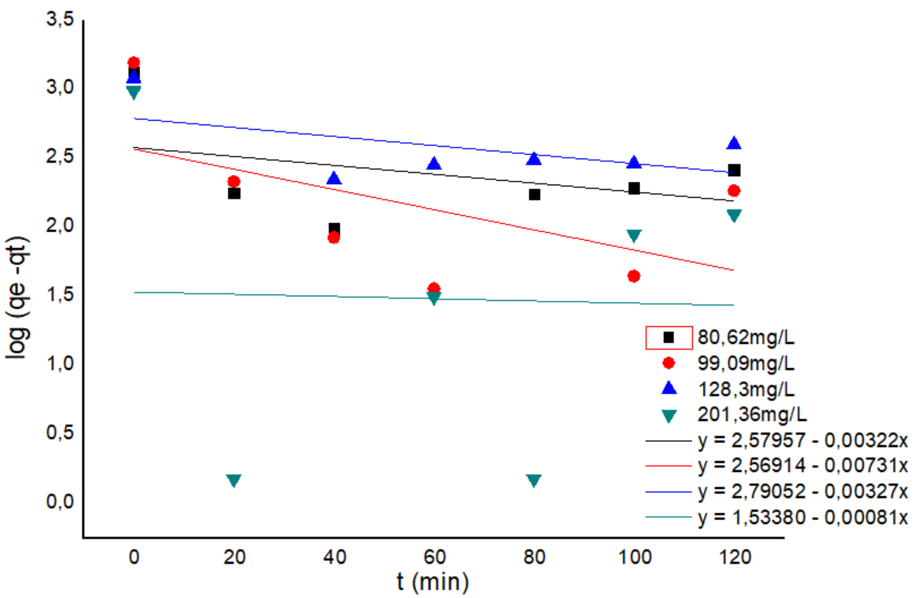


II

Pseudo First Order (I) and Pseudo Second Order (II) to the Tertiary mixture and Methylene Blue Dye

Results



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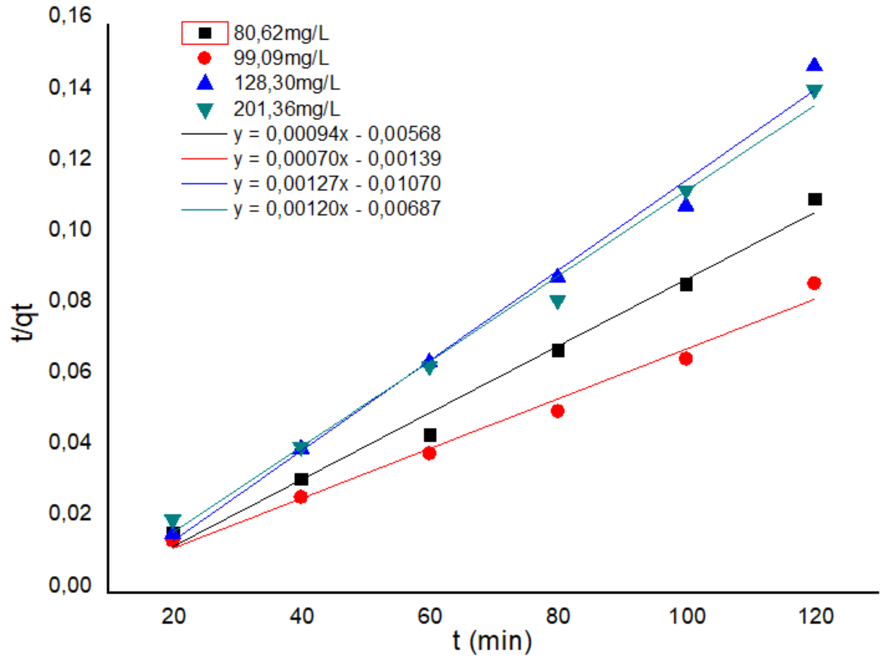

II

Pseudo First Order (I) and Pseudo Second Order (II) of Tertiary mixture and Oxytetracycline

- All results indicate the TiO_2/solar photodecomposition followed by biocarbon adsorption have better agreement with pseudo-second-order kinetics with higher dependence from the reactants concentration.

- The comparison between the antibiotics photodecomposition removal percentages of the binary mixtures indicates higher decomposition for amoxicillin (57.38%), followed by cephalexin (48.04%) and considering the tertiary antibiotic systems the oxytetracycline (14.63 %).
- The presence of **Oxytetracycline** and the methylene blue reduces the antibiotics photodecomposition by Solar/TiO2 indicating an antagonistic effect.

Conclusion

- The use of Solar/TiO_2 photodecomposition for water treatment and pollutants decomposition is promising when is applied to the antibiotics mixtures
- The presence of the methylene blue dye in the antibiotics photodecomposition reaction promote de antagonistic effect consuming the free hydroxyl radicals and reducing the antibiotics decomposition drastically.
- The decomposition order is AMOX>Ceph>Oxyt such removal difference is a result of the antibiotics chemical structure and bounding energy by the hydroxyl radicals produced by solar/TiO_2 photodecomposition reaction.
- For amoxicillin, the decomposition results refer to break the weak thiophene sulfur bond, for the cephalexin and Oxytetracycline they have to break the strong hydrogen bonding of amide (amino carbonyls group) and the benzamide bond.
- The antagonistic effect is related with the methylene blue and oxytetracycline presence. Further studies are performed to analyse the main responsible for such effect.
- The use of the biocarbon adsorption in the water treatment is the final stage to ensure the water quality polishing results. The satured biochar also acts as time break allowing the decomposition and mineralization reaction continues out of the water treatment system.

Acknowledgments

National Council for Scientific and Technological Development (CNPq)
PIBIC program

São Paulo Research Foundation (Fapesp).

References

- ANIKA, Z. M. R.; ABDULLAH, N. ABDULLAH, M. F. L. **Characterization and Treatment of Titanium Dioxide via Ultrasonic Process with Melastoma malabathricum as Sustainable Sensitizer for Photovoltaic Solar Cell.** Journal of Chemistry, 2013.
- APPUSAMY, A.; PURUSHOTHAMAN, P.; PONNUSAMY, K.; ANANTHARAJ, R. **Separation of Methylene Blue Dye from Aqueous Solution Using Triton X-114 Surfactant.** Journal of Thermodynamics, 2014.
- BILA, D. M.; DEZOTTI, M. **Fármacos no meio ambiente.** Química Nova, v. 26, n. 4, p. 523-530, 2003.
- BRITO, N. N.; SILVA, V. B. M. **Processo oxidativo avançado e sua aplicação ambiental.** REEC-Revista Eletrônica de Engenharia Civil, v. 3, n. 1, 2012.
- ELMORSI, T. **Equilibrium Isotherms and Kinetic Studies of Removal of Methylene Blue Dye by Adsorption onto Miswak Leaves as a Natural Adsorbent**. Journal of Environmental Protection, 2011.

- FERREIRA, I. V. L. **Fotocatálise heterogênea com TiO2 aplicada ao tratamento de esgoto sanitário secundário**. 2005. Tese (Doutorado em Hidráulica e Saneamento) - Escola de Engenharia de São Carlos, Universidade de São Paulo, São Carlos, 2005.
- GUILARDUCI, V. V. da S. et al. **Adsorção de fenol sobre carvão ativado em meio alcalino.** Quim. Nova, v. 29, n. 6, p. 1226-1232, 2006.
- KLEIN, E. Y., VAN BOECKEL, T. P., MARTINEZ, E. M., PANT, S., GRANDA, S., LEVIN, S. A., HERMAN, G., LAXMINARAYAN, R. **Global increase and geographic convergence in antibiotic consumption between 2000 and 2015**. Proceedings of the National Academy of Sciences. 2018.
- LI, C.; WANG, F.; YU, J. C. **Semiconductor/biomolecular composites for solar energy applications.** The Royal Society of Chemistry, *2010.*
- PEREIRA, S. C. et al. **Inovações na síntese enzimática de amoxicilina.** 2012.

- RUELA, I. C., LIMA, J. A., SOUZA, S. V. C., JUNQUEIRA, R. G.. **Otimização e validação de método para determinação de resíduos de oxitetraciclina, tetraciclina e clortetraciclina em leite por cromatografia líquida de alta eficiência.** Cienc Tecnol Aliment, v. 25, n. 1, p. 139-46, 2005.
- SANTANA, H. de; BONANCÊA, C. E.; TAKASHIMA, K. **Fotocatálise eletroquímica de atrazina sobre dióxido de titânio: efeito de diferentes parâmetros experimentais.** Química Nova, v. 26, n. 6, p. 807-811, 2003.
- TAN, X.; LIU, Y.; ZENG, G.; WANG, X.; HU, X.; GU, Y.; YANG, Z. **Application of biochar for the removal of pollutants from aqueous solutions: a review to establish current knowledge status and research needs.** Chemosphere, 2015.