Integrated water treatment process with Solar/TiO_2 photodecomposition and biocarbon adsorption for enrofloxacin removal from contaminated waters.

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Abstract: Brazil is well known as the worldwide production of animal protein and there for the highest consumer of the antibiotic enrofloxacin, the most common the second generation antibiotics used in veterinary medicine. The wastewater treatment with TiO_2/solar photodecomposition natural, low-cost energy integrated with the renewable biocarbon absorbent. Such integrated process rises a possible tool to control and reduce the enrofloxacin environmental impact on soil and surface water quality loss. The process starts with the TiO_2 addition on different initial enrofloxacin concentrations, after the suspension 120 min of the stirring time inside the solar chamber the collected suspension aliquots (20 minutes each) and the addition to micronized biocarbon present in the falcon tubes. The falcon tubes are further centrifugated and the supernatant measured using spectrophotometric analysis. The maximum removal percentage was 74.63 % with higher correspondence with the kinetics of pseudo-second-order and Langmuir isotherm with RL in the range of 0 to 1and the surface coverage percentage of 92 % in the higher concentrated system.

Keywords: adsorption, titanium dioxide, solar, Langmuir, biocarbon, enrofloxacin.

Introduction

The fluoroquinolone is the antibiotic group where the enrofloxacin belongs, they are widely used in cattle and poultry production to treat the respiratory and enteric bacterial infections, after the administration most of them are excreted in urine and feces. The enrofloxacin is a second-generation quinolone which is very popular and prescribed mainly in veterinary practice due to its broad spectrum. It is also the most potent antibiotic and indeed the most used in the last two decades (Graouer-Bacart, 2013). This pharmaceutical compound has amphoteric properties tightly bounding with organic matter on feces, soil and clay materials. Those properties leads to agricultural contamination on pastures and soil fertilized with manure.

Due to its use pattern, enrofloxacin has a high potential to enter in the environment, especially the soil compartment, as the parent compound or like its metabolite. It reaches the soil through animal excretions, agricultural waste storage structures and land application of agricultural waste or sewage sludge. The enrofloxacin is also suspected to accumulate in soils and literature reports the concentrations up to 0.40 mg. kg^{-1} in agricultural land. Surface runoff and leaching soils can act as a source of the antibiotics contaminants in the aqueous environment. Another aspect to be considered is the several published works relate the antibiotics are not eliminated during conventional wastewater treatments and are introduced in different quantities into rivers streams, and as another source of soil pollution through irrigation systems (Otker, 2005).

The development of an integrated process for wastewater treatment is the need. The natural treatment, low cost abundant and using renewable sources avoiding the enrofloxacin enters in the environment and its sorption on soils is one of the critical processes governing is essential to predict its fate in soil and water mechanisms (Leal, 2017). Bridging in the environment is responsible for pharmaceuticals presence in surface water resources as rivers, water reservoirs, seas ,and groundwater. The water contamination and presence of these compounds can accelerate the process of adaptation and increase the bacteria resistance (Graouer-Bacart, 2015).

There are many interest in the application of photocatalysis in a variety of problems of ecological interest, and TiO_2 in the anatase form appears to be the most photoactive and the most practical of the semiconductors for widespread environmental application such as water purification, wastewater treatment, hazardous waste control, air purification, and water disinfection. The base of heterogeneous photocatalysis is 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. Advanced oxidation processes (AOP) are characterized by chemical oxidation reactions, mediated by the hydroxyl radical (HO •) the efficiency can increase by combination with visible irradiation usually the absorption bands of 320 to 400 nm.

Nowadays Brazil is the most responsible for protein production around the word and this study is a direct research effort to promote the enrofloxacin wastewater treatment using a naturally available energy resource and a biocarbon adsorbent low-cost renewable material minimized the antibiotics soil and water contamination.

Methods

The enrofloxacin standard solution with $0.25gL^{-1}$ was previously prepared and diluted in different initial concentrations for the experiments. The preheating of the dilutions were at 40ºC before the addition of 30mg of TiO_2, the installation of the final mixture was in the solar radiation chamber, and keeping there for 120 minutes, the pH 5.5, the temperature at $40^{o}C$ and incident radiation of 1200 lux were constant during the experiment. The collection of suspension aliquots of 30mL were after stirring 20 minutes each with the addition of 3 mg of micronized eucalyptus biocarbon (diameter < 500 mesh) using falcon tubes. The centrifugation were after the tubes agitation with biocarbon , performed at 1500 rpm for 15 minutes. The measurement of supernatants were at UV – Visible Spectrophotometer Cary 13 at λ = 275nm. The concentration conversion of the adsorbance used an analytical curve prepared with standard antibiotic solutions.

Results and Discussion

Using several different initial concentrations of the antibiotic, was possible to calculate the removal percentage, the pseudo-first-order (K_1), pseudo-second-order (K_2) and Langmuir Isotherm constants (Qo, b, RL ,and θ). The better correspondence for the kinetics calculation was the pseudo-second-order K_2 and R^2 and the isotherm constants with RL in the range of 0 and 1.

In literature is indicated the physicochemical process of surface adsorption is a rate-limiting step, and the control of the sorption capacity was the number of active sorption sites ,and they are somewhat dependent on experimental conditions of the adsorption systems including initial concentration, pH, and temperature agitation speed and particle size. The adsorption follows the photodecomposition process with biocarbon high surface area resulting in 18.26 to 74.63 % of enrofloxacin removal percentage (Berhane, 2017).

The Q_o Langmuir constant represents the total number of sorption sites. The higher correspondence of the integrated process with Langmuir isotherm confirms the adsorption favorability, predictability ,and high surface area coverage.

Conclusions

The integrated process with TiO2/solar photodecomposition and biocarbon adsorption are highly efficient in removing enrofloxacin and its decomposition by-products. However the implementation of such technologies frequently implies high energy cost using the solar chamber but in some places can be installed and use the natural solar energy and further more the photodecomposition processes hás the disadvantage of leading to newly formed by-products , these problems are avoiding by the use of biocarbon adsorption process as a result, the integrated process provides about 74.63 % for enrofloxacin removal percentage and corresponds with the pseudo-second-order kinetics and Langmuir isotherms calculations.

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