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Adsorption of pharmaceuticals in water through lignocellulosic fibers synergism

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HIGHLIGHTS

- The *Allium cepa* test showed that drugs in the water caused genotoxic and cytotoxic effects.
- Vegetable fibers decreased aquatic toxicity effects of drugs.
- The fibers used were able to retain a complex mixture of drugs in water, confirmed by the TG/DTA test.

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ABSTRACT

The contamination of water from disposal of drugs is an emerging problem due to their consequences on trophic webs. This study evaluated the ability of sugarcane and coconut fiber to reduce water toxicity contaminated by pharmaceuticals. The toxicity of solutions containing pharmaceuticals was studied by bioassay using *Allium cepa*, before and after filtration of contaminated water. The coconut and sugarcane fiber have not been satisfactory in reducing toxicity when tested separately. Despite no induction of chromosomal aberrations, our study found a reduction of the mitotic index. The mixture of fibers showed better results providing total reduction of toxicity, in addition to maintenance in the mitotic index and induction of chromosome aberrations. The interaction between fibers and drugs was confirmed by Thermogravimetry and Differential Thermal Analyses (TG/DTA) which presented differences in profile between the fibers before and after adsorption. The mixture of coconut and sugarcane proved viable for reduction of toxicity in contaminated water by a mixture of pharmaceuticals.

1. Introduction

The quality of water is one of the greatest concerns for environmental issues, and disposal of pharmaceuticals in the aquatic environment has been one of the emerging problems of this area. This may lead to different consequences throughout the trophic web, as the discharge of antibiotics may cause an increase of resistance mechanisms of various strains of micro-organisms, such as *E. coli* (Silva et al., 2011). Increase in the number of micronuclei present in blood cells was observed for *O. niloticus* (Tilapia) when exposed to non-steroidal anti-inflammatory pharmaceuticals such as 300 ng L^{-1} Ibuprofen and hormone 6 ng L^{-1} 17 β-estradiol (Ragugnetti et al., 2011; Sponchiado et al., 2010). Delay in embryonic development for *P. perna* mussel was detected when the organism was exposed to 0.1281 mg L^{-1} bacteriostatic agent Triclosan (Carvalho et al., 2011).

These contaminants reach the environment along several pathways, the most frequent resulting from inefficient removal of these contaminants in wastewater and water treatment plants. Pharmaceuticals mixed into the environment has been widely studied (Phillips et al., 2015; Beretta et al., 2014; Zenobio et al., 2014; Deschamps et al., 2012; Locatelli et al., 2011; Montagner

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and Jardim, 2011).

There are several water treatment methods for the removal of organic molecules. These treatments are effective, but also present issues related to high maintenance costs and energy consumption, the total non-removal of substances, and the formation of by-products with greater toxicity than the original product (Borowska et al., 2016; García-Galan et al., 2016; Tominaga et al., 2015). Adsorption is presented as an alternative for retaining pharmaceuticals offering a simpler, cheaper, and more versatile technique than other current options (Moreira et al., 2015; Sun et al., 2015; He et al., 2014; Mahlangu et al., 2014; Guo et al., 2012).

Biosorption is the adsorption process by biomass, which consists of waste from organic material of plant or microbial origin. It has the ability to remove dissolved substances in the aqueous environment. Its low cost makes it an ideal choice for systems requiring large volumes of effluent detoxification at low operating costs (Magalhães and Neves, 2011; Pino and Torem, 2011). Biomass may be used as the main material or as an enhancing agent in adsorption processes (Cristovão et al., 2011).

The sugarcane bagasse is an abundant agroindustrial residue in several countries and can be used as feedstock for the development of many biotechnological processes of industrial interest. This residue is obtained after sugar extraction. The polymers of sugarcane bagasse (cellulose, hemicellulose and lignin) contain hydroxyl and/or phenolic functional groups, amine, and carbonyl groups which can be chemically modified to form new compounds with various properties (Gupta et al., 2014).

Nearly the entire coconut tree is utilized, from their leaves to the fruit. It is estimated that 800 tons of green coconut shell are discarded per year in Brazil. Santos et al. (2003a, 2003b) studied the adsorption capacity of coconut fiber in liquids containing organic contaminants such as gasoline, diesel and lubricants. This study evaluated the coconut adsorption performance *in natura* and also after pre-treatment step where coconut fiber exhibited excellent results for both approaches.

According to Kyzas and Kostoglou (2014) in their critical review article, the materials coming from organic residues *(greens)* have been mainly used for the adsorption of dyes and metals, where there is limited research for adsorption of organic compounds such as petroleum derivatives, pesticides, and pharmaceuticals.

The removal studies require a method to determine if the proposed processes are effective. Among the most commonly used methods are chromatographic (Boix et al., 2016; Borowska et al., 2016) and toxicity tests with bioassays (Somensi et al., 2015; Rodríguez-Gil et al., 2010). The toxicity tests, in addition to their lower costs, present higher sensitivity since they assess not only the presence or absence of a particular molecule, but also the ecotoxicological effects generated after the removal procedure.

Among available toxicity bioassay tests, the *Allium cepa* is often used for observation of environmental genotoxicity, notably for soil and water sampling (Mazzeo et al., 2015; Arkhipchuk et al., 2004), since it is an excellent biomarker of cell mutagenic effects. This test has several advantages, which include showing the mutagenic points of the chromosome by reduction of present number ($2n = 16$), sensitive identification of pollutants, and finally its low cost and easy implementation (Kumari et al., 2011).

Genotoxic effects are estimated at meristematic cells, with different types of chromosomal and nuclear aberrations; cytotoxicity is noted by changes in the mitotic index (Mazzeo et al., 2015; Jangala et al., 2012); the mutagenic potential is evaluated by the presence of chromosomal breaks and micronuclei in meristematic cells. Mazzeo et al. (2015) have been tested *Allium cepa* and found that sewage sludge was genotoxic and mutagenic, even at very low concentrations in soil. This test evaluated that both pharmaceuticals Thiabendazole and Griseofulvin induce meristematic damage, leading to defects in microtubule such as chromosomal breakage of anaphase, metaphase C, bridged anaphase, multipolar division, and disorganized anaphases. This demonstrates the importance of such tests for ecotoxicological data collection (Andrioli et al., 2014).

The overall objective of this study was to evaluate the ability of sugarcane and coconut fibers to reduce water toxicity contaminated by pharmaceuticals, under the hypothesis that the adsorption of pharmaceuticals by these fibers may reduce the toxicity of contaminated water. For both approaches *Allium cepa* was used as a test organism.

2. Materials and methods

2.1. Compound and exposure concentration

A stock 5 $\mu g\ mL^{-1}$ solution of each drug class studied was prepared. All solutions were prepared using deionized water. The classes were: antibiotics (A) (Metronidazole, Sulfamethoxazole, Trimethoprim, and Nitrofurantoin), anti-inflammatory (B) (Naproxen), hormone (C) (17 β estradiol), analgesic (D) (Dipyrone), antilipemic (E) (Simvastatin), and stimulating (F) (Caffeine). Metronidazole (99.0%), Trimethoprim (99.0%), Nitrofurantoin (99.0%), Naproxen (99.0%), Dipyrone (99.0%), and Caffeine (99.0%) were supplied by Sigma-Aldrich, 17 β estradiol (98.0%) was supplied by Galena, Sulfamethoxazole (98.0%) was supplied by Fluka, and Simvastatin (97.0%) was supplied by All Chemistry.

From the pharmacological class of each stock solution studied, solutions were prepared with concentrations of 3.9 $\mu g\ L^{-1}$. Individual solutions of each class (A, B, C, D, E, and F) were prepared, as well as combined solutions, which contained two classes of pharmaceuticals (AB, AC, AD, AE, AF, BC, BD, BE, BF, CD, CE, CF, DE, DF, EF) and a solution containing the mixture of all the pharmaceuticals studied (MIX), since many studies have shown pharmaceuticals as a mixture in the environment (Phillips et al., 2015; Beretta et al., 2014; Zenobio et al., 2014; Deschamps et al., 2012; Locatelli et al., 2011; Montagner and Jardim, 2011). The choice of the concentration of 3.9 $\mu g\ L^{-1}$ was based on the Dalke (2013) study, since it was the lowest concentration of antibiotics which did not show toxicity to *Daphnia magna* and *Scenedesmus subspicatus.*

2.2. Adsorption tests

The tests were carried out using glass columns of 58 cm height and 4.5 cm diameter. The columns were filled with 56 g of fiber. Filled columns were tested with the coconut and sugarcane fibers individually and as a mixture 1:1 of each fiber.

Each column was eluted sequentially with 3 L of the solution containing the mixture of all pharmaceuticals in the concentration of 3.9 $\mu g\ L^{-1}$. 1 L was placed at a time, and from these 700 mL were collected for use in the *Allium cepa* test. After three elutions, the fibers were dried and taken for thermal analyses to check how the fibers have interacted with the pharmaceuticals.

2.3. Reducing toxicity evaluation after using the elution test Allium cepa

The toxicity of water contaminated with the pharmaceuticals was evaluated before and after the elution columns composed of coconut and sugarcane fiber separately and by the mixture of both. The toxicity evaluation before elution consisted of exposing the test organism to solutions of individual pharmaceuticals, as well as to combinations of the total mixture. After elution the test organism was exposed to filtrates obtained from each liter of eluted contaminated water.

The tests were carried out as described by Fiskesjö (1988) with