Treatment of domestic wastewater from northern Mexico City including recalcitrant compounds using coagulation/flocculation and UV254 photo-assisted electrochemical process

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Wastewater

Coagulation/ Flocculation

AOP

The treatment of raw wastewater from a treatment plant (WWTP) in Mexico City (CDMX) is evaluated at the bench scale, in which the presence of the following emerging pollutants: Ciprofloxacin (CIP), Cefadroxil (CFX), Sulfamethoxazole (SMX) and Carbamazepine (CBZ) was determined. The treatment consisted of coagulation/flocculation, and an electrochemical process of active chlorine production photo-assisted by UV254, to generate hydroxyl radicals. The original sample presented a total organic carbon (TOC) content of 1317 mg L^{-1}, while it decreased to 212.1 mg L^{-1} after the primary treatment, and 69.85 mg L^{-1} after the advanced oxidation process (AOP). The first treatment did not significantly remove the drugs, but only solids and biodegradable matter, which allowed the efficient mineralization of 94.8% of all contaminants after 1 h of AOP treatment.

Introduction

The great water stress existing in CDMX promotes the maximum use of WWTP effluents. At the national level, these circuits do not have the capacity to remove recalcitrant contaminants, which constitute a restriction to generate drinking water [1]. In addition to being toxic, there are no detailed studies of the purification capacity of each of the stages of a treatment train for this type of contaminants. Most of this type of effluent presents numerous emerging contaminants, among which the pharmaceutical compounds used in daily life stand out [2], such as analgesics, anti-staminics and antibiotics. The presence of this type of contaminants constitutes the last step to achieve the recycling of this resource [3]. Accordingly, this study evaluates the efficiency of a bench-scale treatment train composed of a coagulation/flocculation process with a ferric chloride salt/biopolymer, and an advanced oxidation process where active chlorine is generated by an electrochemical process, which is transformed into radicals through the application of UV254 radiation.
The development of this proposal aims to generate elements that facilitate decision-making by stakeholders to establish operational and legislative measures in the medium and long terms, which allow the sustainable use of treated water at CDMX.

Material and Methods

Chemical reagents
The following analytical reagents were purchased from Merck and used as received: sodium chloride (NaCl, 98 %), sulfuric acid (H_2SO4, 96 % v/v). While ciprofloxacin, carbamazepine, cefadroxil and sulfamethoxazole were pharmaceutical grade.

Coagulation/flocculation and UV254 photo-assisted electrochemical process
In the coagulation flocculation process, jar tests were conducted at different volumes and concentrations of coagulant ($FeCl_3$) and flocculant (biopolymer); the optimized conditions were selected to carry out this primary treatment. Subsequently, macro-electrolysis experiments were carried out in a filter-press FM01-LC reactor at ~25 °C using a Ti/RuO_2-ZrO_2-Sb_2O_3 anode, at the following optimized experimental conditions: 0.1 and 0.2 mol L^{-1} NaCl, 20 and 30 mA cm^{-2}, 1 and 5 L min^{-1}. The active chlorine (i.e. HOCl) was fragmented using two UV254 lamps, one placed in the reservoir tank, and the other one in the central channel of the electrochemical reactor. During the degradation process, aliquots were sampled in the reactor and analyzed by UV-Vis spectrometry, High-performance liquid chromatography (HPLC), TOC, and other basic physicochemical parameters.

Results and Discussion

The effluent used in this research was collected from the San Juan Ixhuatepec plant located at “La Presa 63, 54187 Tlalnepantla de Baz, Méx.“; which possesses a domestic origin without undergoing any type of treatment.

In **Figure 1**, the chromatographic analysis are described for a real raw sample from the WWTP, where four well-defined peaks are shown representing each of the contaminants detected.

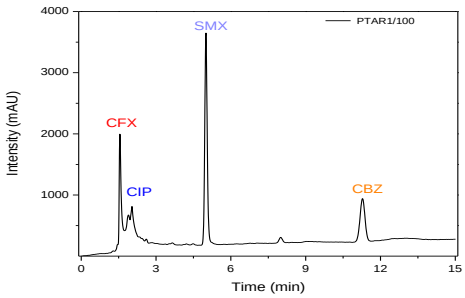

Figure 1. HPLC analysis performed to the raw wastewater from the WWTP.

The sample from the WWTP was fortified with 20 mg L^{-1} of each pharmaceutical compound to evaluate its effects in the primary treatment, and facilitate its detection in the AOP. In the first treatment, tests were carried out at a 50 mL volume to determine the optimal concentration of coagulant (ferric chloride) and biopolymer (chitosan), revealing an optimized 1:1 ratio.

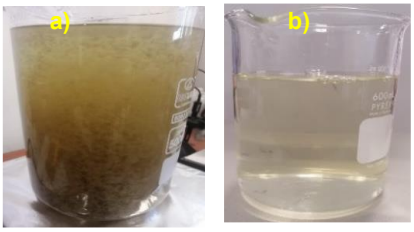

Figure 2a. Coagulation/flocculation process in a sample fortified with pharmaceutical compounds, using a 1:1 ratio of coagulant: flocculant. **Figure 2b.** Clarified solution obtained from the coagulation/flocculation process.

Figure 2a shows the coagulation/flocculation process in a volume of 2 L of real sample from the WWTP, while **Figure 2b** shows the clarified product (supernatant) obtained after removing the coagulated matter by filtration.

Subsequently, the clarified solution obtained in the primary treatment was used for the electrochemical process assisted by photolysis, where the production of HOCl was evaluated by varying volumetric flow, NaCl concentration, pH, current density. The best degradation and mineralization results were obtained for the following conditions: 30 mA cm^{-2}, 0.2 mol L^{-1} NaCl, 5 L min^{-1}, pH adjustment during the process between 4.5 to 5, and 60 min of treatment. **Figure 3** shows the HPLC analysis carried out on the wastewater sample from the WWTP after being fortified with 20 mg L^{-1} of each contaminant at different AOP treatment times. The presence of each emerging contaminant is indicated at different retention times. It is evident that after 30 min of treatment, the drugs have been significantly degraded, mainly due to the production of hydroxyl radicals ($^{\bullet}OH$), from the homolytic reaction of UV254 radiation with the HOCl species, predominant at the pH of the effluent. Therefore, it was overriding to control the pH to guarantee the formation of hydroxyl radicals, which would otherwise formed $^{\bullet}O$ if the pH increases, as a result of the oxidation of water on the anode, and H^{+} reduction on the cathode. These optimized conditions generated a degradation of ~94.8% (TOC = 69.85 mg L^{-1}) of all the contaminants present in the real fortified WWTP sample after 60 min of AOP treatment.

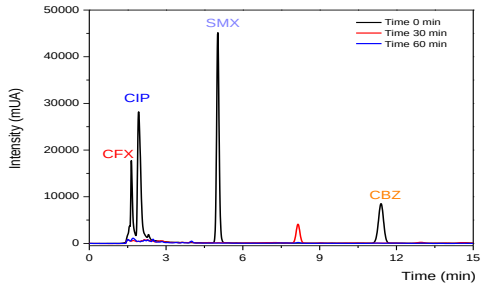

Figure 3. HPLC analysis on real samples fortified with 20 mg L^{-1} of CFX, CIP, SMX and CBZ subjected to coagulation/flocculation, and UV254 photo-assisted electrochemical process in chloride medium at different treatment times.

Conclusions

The treatment of crude domestic wastewater from a WWTP in the north of CDMX was carried out, detecting the presence of CFX, CIP, SMX and CBZ, which was also fortified to account for the removal efficiency of each treatment. The optimized coagulation/flocculation only removed biodegradable matter and solids, thus, increasing the efficiency of the AOP. Thus, 94.8% mineralization of all contaminants was achieved in the electrochemical process assisted by photolysis, which generated HOCl and $^{\bullet}OH$ at the following optimized conditions: 30 mA cm^{-2}, 0.2 mol L^{-1} NaCl, 5 L min^{-1}, pH adjustment, and 60 min of treatment.

Acknowledgments

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