Abstract

Contamination of water with antibiotics has become an emerging environmental concern in current years. Antibiotics are a major group of pharmaceuticals that are extensively used for medical and non-medical purposes. Because of their broad usage, these antibiotics are continuously thrashed out in the environment due to various anthropogenic activities and are extensively noticed in industrial and domestic wastewater. In this study, the pharmaceutical industrial effluent producing Fluoroquinolones were investigated and found that the effluent was severely polluted with organic contents including residues of antibacterial compound ciprofloxacin (CIP). The concentration of CIP noticed in that effluent was very high (at mg/L). Once the CIP residues were detected in the industrial effluent, the possible environmental risks associated with CIP were evaluated using the risk quotient (RQ) mode. RQs developed for CIP residues in the current study appeared to present a severe threat to the non-targeted aquatic organisms. Also the eco-toxicological effects of the lethal concentrations of studied pharmaceutical effluent were analyzed for a short time exposure to the freshwater species; unicellular green algae (C*hlorella Vulgaris*) and fish (*Labeo Rohita*). When fish were exposed to the pharmaceutical effluent together with control for 24 to 96 h, it found that *l. rohita* was very sensitive to pharmaceutical effluent and after 96 h of exposure all exposed fish were found to be dead. The effluent was found to have toxicity unit (TU) $_{50}$ as 3.07 for fish after 96 h. However, it was also observed that effluent was found to be less sensitive for algae than fish with 1.18 TU_{50} for 72 h.

The pharmaceutical industrial effluent has been recognized as an important source for releasing antibacterial residues into the aquatic environment that severely affects the aquatic beings. The complex nature of these compounds makes it tough to remove through conventional treatment. Therefore, the present study aims to degrade an antibiotic CIP in industrial effluent utilizing advanced oxidative processes (AOPs) like photolysis, photo-catalysis, ozonation and contact glow discharge electrolysis (CGDE). For the degradation of CIP through photolysis and photo-catalytic process (UV /TiO_2), the outcomes exposed that the photo-catalytic degradation of CIP was slightly higher in alkaline environment than in acidic or neutral environment and complete degradation (99.9 %; at pH 9) was achieved in 30 min of irradiations with 1g/L of TiO_2. Also, the process led to 94.4 % removal of COD within 60 min. However, photolysis was inefficient to degrade CIP and achieve the removal of about only 74.5 % in > 2 h. The degradation rate (*k* =0.2224 min^{-1}) was found to be quicker in photo-catalytic than in photolysis. The identified degradation products showed that the CIP was degraded by the alteration of its carboxylic acid and piperazinyl ring. Furthermore, the TU_{50} of the initial pharmaceutical effluent was reduced to 0.44 and 1.57 in 150 min for algae and fish respectively during photolysis while during photo-catalysis, toxicity reduced to 0.21 and 0 for algae and fish respectively in 30 min. When the alkaline and acidic conditions were compared in the process of ozonation, it was found that the rate of CIP degradation was quicker (*k* = 0.2913 min^{-1}) under alkaline environment and complete degradation of CIP was achieved under the optimized pH (9) within 20 min. However, the reduction rate of COD was considerably lower and reached a maximum of 64% within 60 min. Besides, the impact of ozonation on the eco-toxicity of the pharmaceutical effluent was tested which showed that the TU_{50} of the initial pharmaceutical effluent was reduced to 0.21 in 120 min and 0.25 in 30 min for algae and fish respectively. Identified degradation products were rose via attack of both hydroxyl (OH*) radicals, and ozone (molecule) on the piperazinyl ring. Finally, a CGDE process alone or in combination with Fe^{2+} was applied for the degradation of CIP. The results showed that the initial concentration of CIP in the effluent was slightly reduced with an increase in exposure of the plasma discharge time and reached to 84.8 % after 3 h. The maximum *k* for CIP degradation was obtained between 45 – 90 min of treatment (*k*= 0.008– 0.015 min^{-1}). But with the addition of Fe^{2+}, the degradation of CIP was enhanced. With 15 mg/L of Fe^{2+}, degradation reached to 97.3 % within 40 min of process and it also implied that COD removal was more rapid with addition of Fe^{2+} in CGDE and reached to 78.7 % in 40 min of treatment process but without Fe^{2+} COD gradually reduced with increased process time and maximum 68.6 % removal was achieved in 180 min of process. Furthermore, the toxicity reduced to less than <1 during the CGDE process but, the combined CGDE process with Fe^{2+} did not result in a significant reduction in toxicity of the effluent to algae and reduced to 0.88 in 40 min. Besides, TU_{50} reduced to 0.81 in 180 min and 0 in 40 min during CGDE and CGDE/ Fe^{2+} respectively for fish. Also, electrical energy per order (E.E/O) was also considered for all the oxidative treatment processes and from the outcomes found the photo-catalytic process as a good opportunity for almost complete reduction of CIP and COD (> 90 %) concentrations in pharmaceutical industrial effluent by using 38.9 kWh/m^3 and 178.8 kWh/m^3 energy, respectively.