ABSTRACT

Pharmaceuticals (PhCs) have been identified as emerging pollutants for the last two decades. Usage of these chemicals is extensive, on the other hand, their degradability is limited. This leads to the accumulation of such compounds in our environment. These emerging pollutants are potentially hazardous for all living beings even at a small concentration such as ng/L to mg/L. Conventional treatment methods are not sufficient to degrade these compounds to Mineralization. Advanced oxidation processes (AOPs) are proven to be capable of degrading pharmaceuticals to Mineralization. AOPs such as Ozonation, Fenton and Fenton-like oxidation, electrochemical oxidation, photo-catalytic oxidation, and the combination of these processes are broadly reported as an effective treatment for complete degradation of PhCs.

Among these treatment methods, electrochemical oxidation (EO) is an expedient as it is environment-friendly, easily automated, efficient, and there is no requirement of chemical addition. At a given current density, EO is a mere function of the types of electrodes involved and the composition of the electrolyte matrix. Reactive species responsible for oxidation attack are in situ generated, depending upon the presence of salts in the matrix and electrodes involved. Of late, sulfate radical based processes are also confirmed as promising treatment methods owing to the exceptional performance in destruction of various PhCs. In sulfate radical based process, PhCs are degraded to mineralization due to its high oxidizability, extended life, and flexible pH range. Commonly, sulfate radicals are produced by means of transition metals, high temperature, and ultra-violet radiation activation of peroxymonosulfate or persulfate, which are considered as environment friendly oxidants.

Most of the PhC removal studies are carried out in synthetic matrix prepared with distilled water. There are few studies available that focused on real matrices such as groundwater, reverse osmosis concentrate (ROC), tertiary effluent from wastewater treatment facilities, etc. ROC has limited reuse potential because of high salt content and its disposal or treatment is a challenge. Nonetheless, if ROC is utilized as an electrolyte medium to destruct recalcitrant organics such as PhCs, the high salt concentration reduces energy consumption for

electrochemical processes considerably. Besides sulfate ions, an enormous amount of chlorides in ROC attracts the application of ROC for indirect electro-oxidation which involves the in-situ generation of Cl_2, HOCl, and OCl^- also known as reactive chlorine species.

Keeping these facts in mind, the first part of the present study was carried out using ROC as an electrolyte for electrochemical oxidation of model PhC compound Diclofenac sodium (DCF). Mixed metal oxides coated anode- Ti/Ru-Sn-Sb-O_x was indigenously prepared and used for the most EO experiments. The graphite and Ti/Ru-Ir-O_x were also used as anodes for comparative study. Quantitative analysis of DCF and its intermediate products (IPs) were performed on High Performance Liquid Chromatography (HPLC). The Liquid Chromatography – Mass Spectroscopy (LC-MS) study was also carried out to identify the intermediates generated during EO for different anodes. A study on commonly used quenching agents for EO samples was carried out to find a suitable quenching agent to prevent the action of reactive chlorine species on samples during storage. The p value 0.005 obtained using paired t-test indicated that the results obtained using methanol as a quenching agent matches with those obtained by immediate analyses (without quenching) with 99.5% confidence level. Thus, methanol is found to be the most suitable quenching agent in the present study. The effect of current density and reaction kinetics for EO of DCF was thoroughly studied. The removal rate increased with an increase in current density from 5 to 10 mA/cm^2 for DCF and IPs both. Effect of electrolyte composition in form of sulfate to chloride ratio on DCF degradation rate and extent of degradation was studied in synthetic electrolyte. The maximum removal (~95%) of DCF was obtained in the presence of sulfate to chloride mass ratio ranging from 0.85 to 1.35. In comparison with Graphite anode, MMO anodes Ti/Ru-Sn-Sb-O_x and Ti/Ru-Ir-O_x were found to be more efficient for DCF and IPs removal. DCF degradation rate was fastest while using indigenously prepared MMO anode Ti/Ru-Sn-Sb-O_x. A phytotoxicity study was also carried out using mung beans to check the EO effluent suitability for irrigation. The phytotoxicity level marginally increased after 120 min of EO; however, not significant enough compared with similar previous studies.

In the second part of the study, Ibuprofen (non-steroidal anti-inflammatory drug) removal

is investigated by means of electrochemically activated peroxymonosulfate (EC/PMS) using iron as sacrificial anode in reverse osmosis concentrate (ROC). Complete ibuprofen (IBU) removal was achieved in 30 min at near neutral pH with $[PMS]_0$=500 mg/L and current density (CD)=2.5 mA/cm^2 using EC/PMS process. EC/PMS performed extremely well in comparison with PMS alone, electrocoagulation (EC) alone and $FeSO_4$/PMS when $FeSO_4$ was added in the beginning. However, when $FeSO_4$ was added stepwise, PMS activation turned out to be more efficient and IBU removal rate was near to that of EC/PMS. Intermediate products formed from IBU during EC/PMS process were also identified using LC/MS. Quenching experiments using tert-butyl alcohol and ethanol indicated that the contribution of sulfate radical is quite higher than hydroxyl radical for IBU removal in ROC using EC/PMS process. Response surface methodology was carried out to determine the effect of initial pH, $[PMS]_0$, and CD on the % IBU removal in 30 min and pseudo first order removal rate constants. It was observed that acidic initial pH, lesser $[PMS]_0$, and highest CD were favorable conditions for higher removal rate constants. Nevertheless, higher removal rate constant did not necessarily lead to complete removal. $[PMS]_0$ to CD ratios significantly affected both % IBU removal and removal rate constant in batch EC/PMS process. EC/PMS process functioned quite well% in continuous flow mode. The increase in flow rate from 2 to 4 L/h gave higher % IBU removal 96.5% to 99.5% and residual Fe^{2+} was reduced from 10 to 3 mg/L, indicating better utilization of Fe^{2+}. Conclusively, EC/PMS was found to be a promising green treatment method for complex organic compound such as IBU. At last, LC-MS analysis was carried out to identify the intermediates formed during ECO of DCF and EC/PMS of IBU. LC-MS results showed that DCF and IBU intermediates were hydroxylation products due to indirect oxidation.