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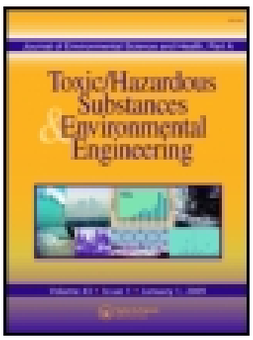

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Comparative studies in electrochemical degradation of sulfamethoxazole and diclofenac in water by using various electrodes and phosphate and sulfate supporting electrolytes

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ABSTRACT

In this study, the electro-oxidation capacities of Na_2SO_4 and potassium phosphate buffer supporting electrolytes were tested and compared for destruction of the sulfamethoxazole (SMX) and diclofenac (DCF) on platinum (Pt) electrode and graphite carbon electrode in aqueous medium. The suitability of pharmaceutical active compounds (PhACs) for electrochemical oxidation was tested by cyclic voltammetry (CV) technique performed in the potential range −1.5 to +1.5 V versus Ag/AgCl, which confirmed the electro-activity of the selected PhACs. The degradation and mineralization were monitored by ultraviolet (UV)-Vis spectrophotometry and HPLC. 0.1 M Na_2SO_4 supporting electrolyte was found to be more effective for mineralization of SMX and DCF, with efficiency of 15–30% more than the 0.1 M phosphate buffer supporting electrolyte on the platinum (Pt) and carbon electrodes. The Pt electrode showed better performance in the degradation of the two PhACs while under the same conditions than the carbon electrode for both 0.1 M Na_2SO_4 and 0.1 M potassium phosphate buffer supporting electrolytes. The SMX and DCF degradation kinetics best fitted the second-order reaction, with rate constants ranging between 0.000389 and 0.006 $mol^2\ L^{-2}\ min^{-1}$ and correlation coefficient (R^2) above 0.987. The second-order degradation kinetics indicated that the rate-determining step in the degradation could be a chemical process, thus suggesting the active involvement of electrolyte radical species in the degradation of SMX and DCF. Results obtained from a real field sample showed a more than 98% removal of the PhACs from the wastewater by electrochemical degradation.

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Introduction

Pharmaceuticals are developed and manufactured to serve human and animal health. However, after administration, these compounds are not completely metabolized in the body and trace amounts are excreted in urine and faeces in unmetabolized forms.[1] Pharmaceuticals are therefore regarded as a diverse class of emerging chemical contaminants that have been detected in all environmental matrices.[2–4] Laboratory studies have demonstrated that various PhACs can elicit responses in aquatic organisms at relatively low levels.[5] Their presence throughout the environment has impacted drinking water and groundwater, with wastewater as the main exposure route for contamination.[6] The presence of PhACs in water can be explained in terms of both their use in medicine and their inefficient water treatment systems.[7] In most cases, wastewater treatment systems are not designed to remove PhACs and other persistent organic pollutants. Therefore many wastewater treatment techniques have been developed to complement the conventional wastewater treatment systems that are mainly based on biological transformation.[8]

Various wastewater treatment methods explored by previous investigators have indicated that the option of biological treatment may not be suitable because of the inhibitory effect of chloride on microbial growth.[9] Therefore, the adoption of electrochemical oxidation technique for wastewater treatment in the past decade has been credited to its environmental friendliness, amenability to automation and its effectiveness to process a wide variety of organic pollutants.[10,11] In addition, electrochemical oxidation does not need auxiliary chemicals;[12] it is versatile, cost effective, easy to control, has great efficiency, promotes green chemistry and environmental sustainability.[13–15]

The electrochemical oxidation of pollutants from wastewater is attributed to the oxidation of the adsorbed organic compounds to CO_2. This procedure involves the oxidation of pollutants in an electrolytic cell by: (1) direct electron transfer to the anode or indirect oxidation with heterogeneous radical species formed at the anode. The existence of these radical species suggests two proposed approaches: (1) the electrochemical conversion, where the organic substances are selectively transformed into biodegradable compounds like carboxylic acids by chemisorbed "active oxygen" and (ii) the electrochemical combustion, where the organic substances are mineralized by physisorption using •OH radical.[16,17] Hydroxyl radicals can be produced in large quantity from electrolysis at platinum

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surfaces. Platinum surface does not interact with these radicals, and as a consequence, these radicals can either couple to form oxygen or oxidize the pollutants such as PhACs in the aqueous solution.

The degree of degradation varies with the anode material used. Carbon, in many respects, represents an ideal electrode because of its access to a wide anodic potential range, low electrical resistance and residual currents, and a reproducible surface structure among other advantages.[18] A study by Sopaja et al.[19] on the influence of the anode materials on the electrochemical oxidation efficiency of amoxicillin indicated that the oxidation rate constants depended mainly on applied current densities for each material. In the study, platinum anode showed a relatively good oxidation behavior compared to carbon fiber and carbon graphite. Other studies have also reported on the suitability of other electrodes used as anodes in electrochemical degradation of various pollutants. For example, Cañizares et al.[20] used diamond-based material (p-Si–boron-doped diamond) as the anode and stainless steel (AISI 304) as the cathode for the degradation of caffeine. Both electrodes were circular (100-mm diameter) with a geometric area of 78 cm^2 and an electrode gap of 9 mm. On the other hand, boron-doped diamond (BDD) was evidenced as the best anode material at high current densities due to the formation of large amounts of hydroxyl radicals and of other different oxidants such as hydrogen peroxide, ozone and persulfates that contributed to the enhancement of oxidation and mineralization of amoxicillin via mediated oxidation. BDD displays a great deal of chemical inertness hence can be used in very aggressive conditions at both anode and cathode electrodes.

The electrochemical methods use the electron as the main reagent, but also require the presence of supporting electrolytes. Supporting electrolyte ions play an active role in the oxidative degradation process. For example, when BDD anode is used, other weaker oxidizing species like peroxodisulfate, peroxodicarbonate, and peroxodiphosphate can be competitively formed from oxidation of the electrolyte ions like bisulfate, bicarbonate and phosphate, respectively.[17] Murugananthan et al.[21] observed the achievement of a complete mineralization of ketoprofen molecule using Na_2SO_4 as supporting electrolyte, on BDD and Pt anodes. The same study observed poor mineralization of ketoprofen at both BDD and Pt anodes in the presence of NaCl as supporting electrolyte. The nature of electrolyte is very crucial since the anodic reactions and its products depend on the supporting electrolyte employed. Electrochemical oxidation, frequently called anodic oxidation, for degradation of PhAC using various electrodes has been studied before. However, the performance of supporting electrolyte such as Na_2SO_4 and potassium phosphate buffer on electrochemical degradation has not been ascertained. In the present work, the electrochemical oxidation using Na_2SO_4 and phosphate buffer as supporting electrolytes was tested to achieve the complete degradation and removal of SMX, an antibiotic, and DCF, an anti-inflammatory drug, from water has been investigated. The aim of this work was therefore to explore the use Na_2SO_4 and phosphate buffer as supporting electrolytes in electrochemical degradation of SMX and DCF at Pt and graphite anodes. Diclofenac and SMX were chosen as models of the PhACs pollutant from wastewater.

Materials and methods

Chemicals, standards and reagents

High purity standards for diclofenac and sulfamethoxazole were purchased from Sigma Aldrich. Analytical grade and HPLC grade water, methanol and acetonitrile for extraction and analysis were purchased from Kobian Kenya Limited. Solid phase extraction cartridges and nylon micro filters were obtained from Estec Kenya Limited. All stock solutions were prepared using HPLC grade methanol. K_2HPO_4, KH_2PHO_4, and Na_2SO_4 used as supporting electrolyte were purchased from Sigma Aldrich through Kobian Kenya Limited (Nairobi, Kenya). Deionized water was used in all experiments. Platinum plate electrode and carbon electrode were purchased from Sigma Aldrich through Kobian Kenya Limited (Nairobi, Kenya).

Cyclic voltammetry (CV) of SMX and DCF

The Cyclic Voltammetry (CV) experiments were conducted to investigate the activity of the electrode and to evaluate the responses of the pharmaceuticals and the electroactive species present in background electrolytes. The electrochemical behaviors of SMX and DCF in the prepared solution of 0.1 M Na_2SO_4 having a concentration of background electrolytes were investigated using CV. A BASi EC epsilon version 213.77 USB Software potentiostat/galvanostat, complete with a cell stand and data processor, was used to conduct the voltammetric measurements. The CV experiments were performed in the potential scan range −1.5 to +1.5 V versus Ag/AgCl at 350 mV/s reference electrode at 25°C. Scan rate was set at 1 mV/s to 25 V/s. The working electrode was Pt, and the counter electrode was a platinum wire.

Preparation of stock standard solutions

The stock standard solutions of SMX and DCF were prepared separately in either Na_2SO_4 salt or phosphate buffer solution. Potassium phosphate buffer (0.1 M) pH 6 supporting electrolyte was freshly prepared at ambient room conditions and was used within a period of 6 h for electrolysis experiments. The 0.1 M phosphate buffer (pH 6) was prepared by mixing 6 mL of 1 M K_2HPO_4 solution and 30 mL of 1 M KH_2PO_4 solution into a 1-L volumetric flask. The solution was brought up to the mark with Milli-Q water. The conductivity range of the buffer solution was 2.5 2.7 mS at 25°C. A 1-L stock solution of 0.1 M Na_2SO_4 (pH) supporting electrolyte at 25°C, with a conductivity range of 14.28–14.94 mS at 25°C, was also prepared. The initial pH of the electrolytes was 3.48 and 6.09 for DCF and SMX. The concentrations of SMX and DCF stock solutions prepared were 52.8 and 42.5 mg/L, respectively.

Electrolytic system and electrochemical degradation of SMX and DCF

Electrochemical experiments were performed using a glass container with a working volume of 100 mL, placed in thermo-regulated water bath attached with a magnetic stirrer. The electrolysis experiments were conducted at a constant temperature of 25°C. The Pt working electrode was cut from a flat Platinum plate and had an effective surface area of 2 cm^2. The

counter electrode was its alternative. The Graphite carbon electrode was a rod with dimensions of 20 × 200 mm and 1.8 g/cm^3 density. The cathode and anode gap of 2 cm was maintained throughout the experiments. The reactor was set at a voltage of 10 V. Four-milliliter samples were collected at intervals of 0, 5, 10, 20, 40, 70 and 90 min for ultraviolet (UV)-Vis spectrophotometer and subsequent HPLC analysis.

UV-Vis spectrophotometric analysis of diclofenac and sulfamethoxazole

SMX and DCF were scanned in UV region 400–200 nm. The overlaid spectrums were obtained to determine the maximum absorbance lambda (λ max). Sequential dilutions were done using the 0.1 M phosphate buffer or 0.1 Na_2SO_4 solutions to give the concentration within Beers Law range. The λ max values obtained in the UV-Vis spectrophotometer were 275 and 254 nm for DCF and SMX, respectively. The concentration or absorbance of SMX and DCF samples were measured by UV-visible spectrophotometer with the detection wavelength at 254 and 275 nm, respectively. The experimental results are shown in Figure 1.

Extraction and HPLC analysis of DCF and SMX

Ten milliliters of the periodically obtained samples during electrochemical degradation process were extracted by passing through a Phenomenex C_{18} solid phase extraction (SPE) cartridge that had been pre-conditioned with 10 mL of methanol and distilled water, successively. Elution was carried out using 10 mL of HPLC grade methanol which were evaporated under vacuum on a rotary evaporator. Re-dissolution was done using 2 mL of HPLC-grade methanol. Residue samples were filtered using 0.45 μm nylon microfilters prior to injection to LC-MS instrument. A Shimadzu LC-20AD fitted with a SIL-20A (HT) autosampler and a SPD-20A prominence UV detector were used for HPLC analysis. A reverse phase Phenomenex (C_{18}) column (4.6 mm i.d. × 250 mm, 5 μm particle) was used for separation of the analytes. Gradient elution was carried out using a mobile consisting of (50: 50 v/v) HPLC grade acetonitrile: Methanol (A) and water with 0.1% formic acid (B) at a flow rate of 0.30 mL/min. The gradient programme was set as follows: (0–3 min) A = 90%, 8 min A = 65%, 17 min A = 50%, 20 min A = 0%, 30 min A = 90%. Quantification was done using an UV-visible detector at wavelengths of 250 and 275 nm. Analyte identification was based on comparison of chromatograms of unknowns with those of standards. Standards and blanks were measured periodically throughout the analysis for quality assurance. Quantitative analysis of pharmaceuticals was achieved through the integration of selected LC chromatograms. All analyses were carried out in triplicate.

Sampling and extraction and HPLC analysis of a real field sample

One liter of a real field wastewater sample known to be contaminated with DCF and SMX was obtained and subjected to electrochemical degradation under the optimized conditions studied. The sample was obtained from hospital wastewater treatment plant, extracted, and analyzed with HPLC prior to electrochemical degradation process to determine the original concentration of the field sample. The 1-L sample was filtered and separated into three 100-mL containers. The first sample contained the phosphate buffer electrolyte and the second sample contained Na_2SO_4 electrolyte, and the two were subjected to electrolysis on a carbon electrode. The third sample contained the phosphate buffer electrolyte and was electrolyzed on a Pt anode. The sample was subjected to electrochemical degradation for 40 min, and subsequently analyzed to obtain the resulting DCF and SMX concentrations. The analysis procedure included extraction by passing through a Phenomenex C_{18} solid phase extraction (SPE) cartridge, and eluting the sample with 10 mL of HPLC grade methanol. The method for analysis of the real field sample was as described above in this study. Attempt was not made to identify metabolites that may result from the electro-oxidation due to inadequate facilities and unavailability of metabolite standards in the market.

Results and discussion

Cyclic voltammetry of pharmaceuticals electroactive experiments

Cyclic voltammetry (CV) is usually performed as the first experiment in an electroanalytical study. This is because it is

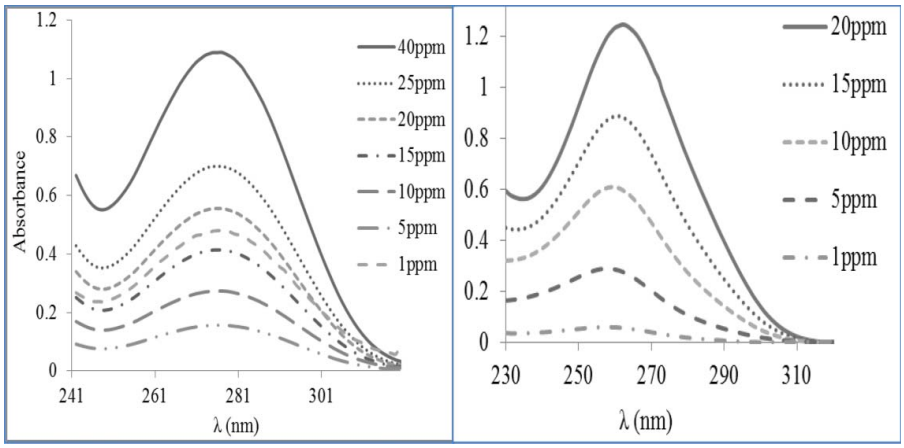

Figure 1. UV-Vis spectra for the serial dilution of the PhACs from the 42.5 mg/L stock solution for DICLOF (λ 275 nm) and the 52.8 mg/L stock solution for SMX (λ 254 nm).

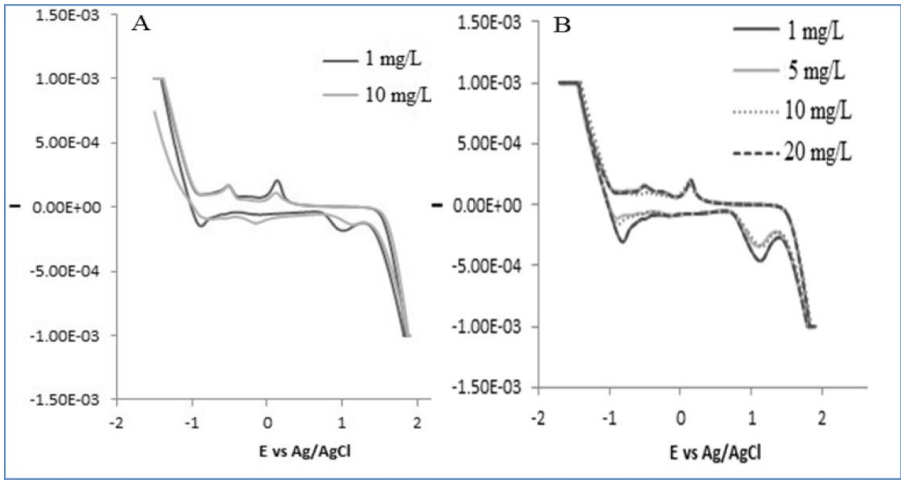

Figure 2. Cyclic voltammograms for (a) Diclofenac and (b) SMX on a Platinum electrode. (Supporting electrolyte: 0.1 M Na_2SO_4 (pH 5.0), scan rate: 320 mV S^{-1}, concentration range 1–10 mg/L and 1–20 mg/L, respectively).

the most widely used technique for acquiring both quantitative and qualitative information about electrochemical reactions. In addition, it is easy to use and offers a rapid location of reduction and oxidation potentials of the electroactive species, thus providing the chemical identity of the species under study based on the recorded peak potentials. Cyclic voltammograms were recorded to understand the redox behavior of DCF and SMX molecule on Pt electrode at a scan rate of 350 mV S^{-1} in 0.1 M Na_2SO_4 electrolyte. These experiments were conducted in a conventional, 3-electrode configuration with Ag/AgCl reference electrode and Pt wire as the auxiliary electrode. The CV experiments were performed within a potential range of −1.5 to +1.5 V versus Ag/AgCl in Na_2SO_4 having the concentration of the background electrolytes. CV entails repeatedly sweeping the potential back and forth between the initial and final potentials. In this study, reduction peaks were generated near −1 V, which were consistent to that of the background electrolytes. The reactions of the PhACs observed during cyclic voltammetry are as shown in Figure 2a and 2b for diclofenac and SMX, respectively.

The effect of the increase in concentration of SMX from 1 to 20 mg/L on the signal obtained in the CV was assessed in 0.1 M Na_2SO_4 as background electrolyte in comparison to a blank Na_2SO_4 solution. SMX has an oxidation peak near +1 V (Fig. 2), which becomes increasingly apparent in magnitude with increasing concentration. Meanwhile, no oxidation peak for the background electrolyte, but only a reduction peak at −1, is observed. This shows that SMX is electroactive and can indeed be oxidized at platinum electrode. The peaks at potentials above 1 V indicate an oxidative conversion of the compounds. The results of the UV-Vis spectrophotometric analysis of Diclofenac and Sulfamethoxazole are shown in Figures 3 and 4, respectively. The UV–Vis spectrum of DCF in phosphate buffer supporting electrolyte exhibited a peak at wavelength 275 nm. The observed peaks in UV-Vis spectrum clearly indicate a decrease in absorbance with increasing time from 0 to

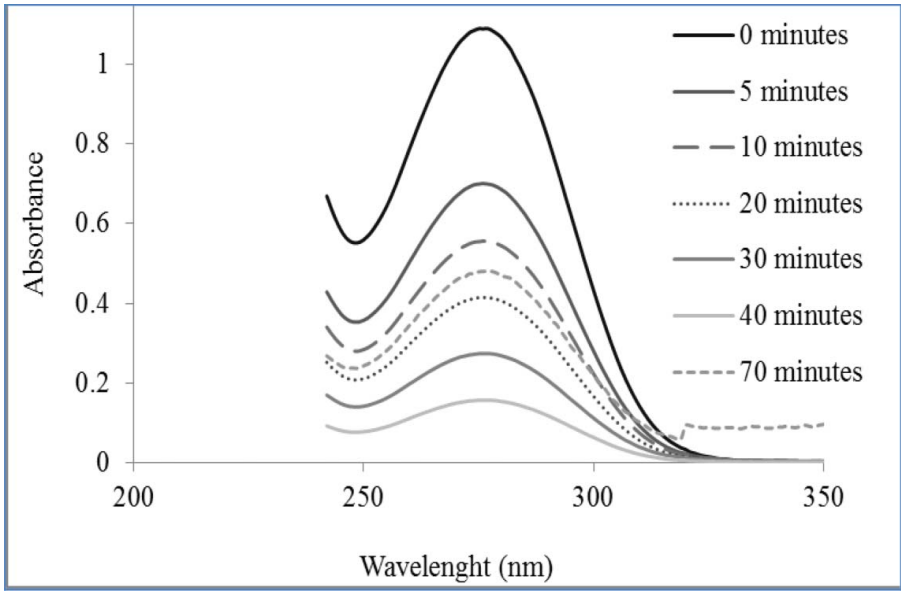

Figure 3. UV-Vis spectra for the electrochemical degradation of DCF (λ 275 nm) on Pt electrode and potassium phosphate buffer supporting electrolyte.

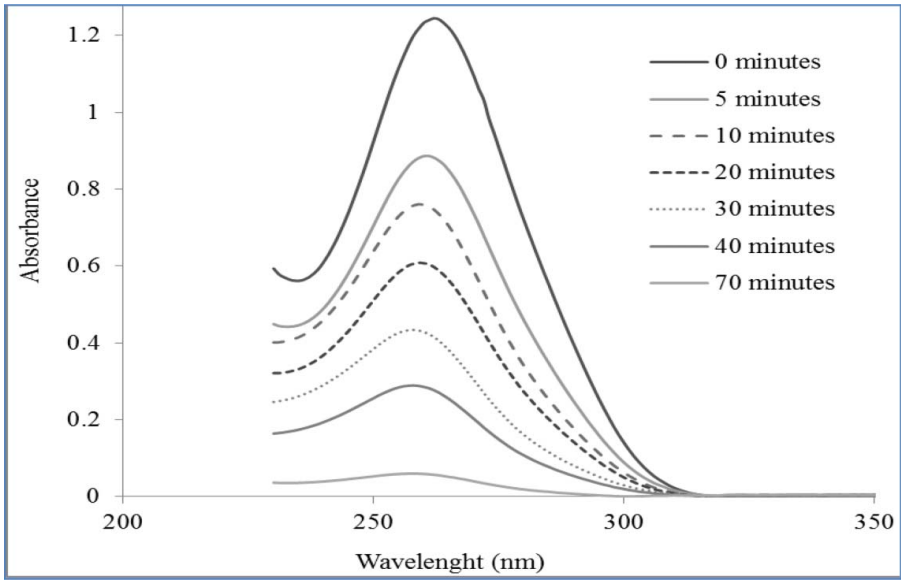

Figure 4. UV-Vis spectra for the electrochemical degradation of SMX (λ 254 nm) on Pt electrode and potassium phosphate buffer supporting electrolyte.

70 min. When Na_2SO_4 was used as a supporting electrolyte for the oxidation of DCF, the solution turned yellow, which increased in intensity over time. However, the concentrations analyzed using HPLC confirmed that DCF molecule was degraded over time in aqueous solution, at Pt and carbon anode when both supporting electrolytes were used. Figure 5 shows selected chromatograms from the HPLC instrumental analysis. It can be concluded from reduced peak intensities observed in the chromatograms that both SMX and DCF underwent oxidative degradation with Na_2SO_4 as a supporting electrolyte. The oxidation could be attributed to the various oxidants generated and reported elsewhere.[22,23]

The same decrease in absorbance over time was observed in SMX degradation at λ 254 nm when potassium phosphate buffer supporting electrolyte was used as displayed in Figure 4.

Degradation kinetics

The electrochemical degradation kinetics of SMX and DCF from their initial concentrations was determined. The degradation of SMX and DCF was found to follow second order kinetic model represented by the following equation:

$$1 / [C]_t = -kt \quad (1)$$

where C_t, t, and k represent the analyte concentration at time t, electrolysis time (min), and the second-order rate constant (mol^2 L^{-2} min^{-1}), respectively. The rate constant, k and the regression coefficients (R^2) for the degradation process using different electrodes are presented in Table 1. A good linearity was observed with R^2-values greater than 0.987. The rate

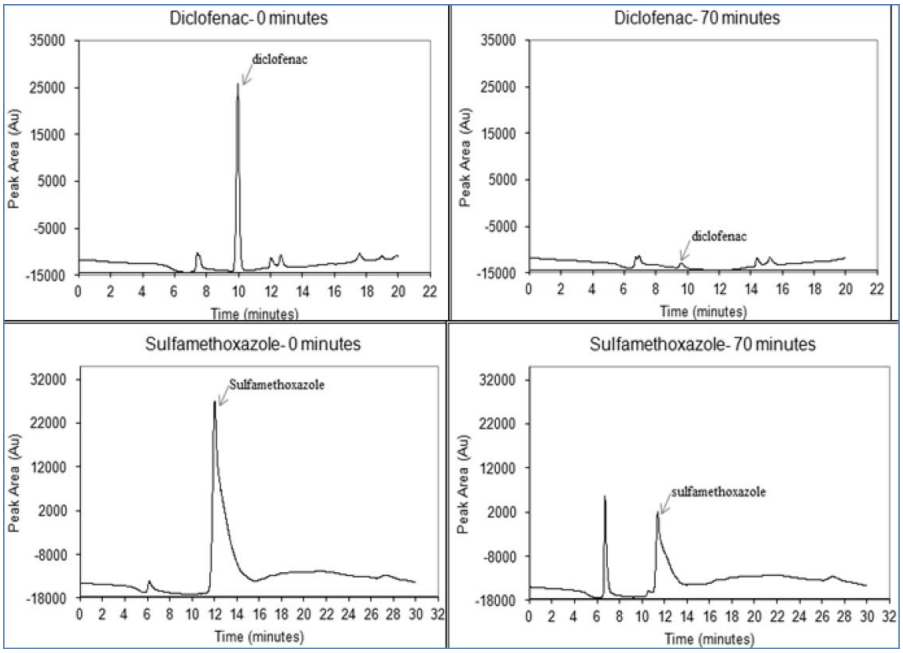

Figure 5. Chromatograms showing decreased peak intensities of both SMX and DCF.

Table 1. The values of reaction rate constants of electrochemical oxidation of SMX and DCF using various electrolytes and electrodes.

Electrode	Supporting electrolyte	PhAcs	k (mol^2 L^{-2} min^{-1})	R^2
Pt	Na_2SO_4	DCF	0.005	0.995
Pt	Na_2SO_4	SMX	0.006	0.998
Pt	*Phosphate buffer	DCF	0.001799	0.989
Pt	*Phosphate buffer	SMX	0.001514	0.998
C	Na_2SO_4	DCF	0.00417	0.999
C	Na_2SO_4	SMX	0.001875	0.989
C	*Phosphate buffer	DCF	0.000864	0.992
C	*Phosphate buffer	SMX	0.000389	0.987

* Phosphate buffer is potassium phosphate buffer.

constants, k, for the various electrodes and different electrolytes ranged between 0.000389 and 0.006 mol^2 L^{-2} min^{-1} as shown in Table 1. The results obtained from the degradation kinetics study indicated that the rate-determining step in the degradation of SMX and DCF could be a chemical process, and therefore suggest a degradation mechanism where the electrolyte species participate in the reaction.

Effect of electrolyte and type of electrode

The effect of supporting electrolytes on PhACs oxidation at carbon and Pt electrodes was studied at a constant applied current density. Figure 6 presents the results obtained from the study on the degradation of PhACs over a 90-min time. In Figure 6a, the electrochemical degradation of DCF on Pt electrode, with phosphate buffer supporting electrolytes decreased from 42.5 to 11.3 mg/L in 40 min and to 4.1 mg/L with Na_2SO_4 as supporting electrolyte. That is, a decrease of 73.4% and 90.4% of the original concentration in the two electrolytes, respectively. No significant observable change in concentration of DCF was observed after 40 min where the concentrations decreased to 9.5 and 4 mg/L for phosphate buffer and Na_2SO_4 supporting electrolytes at 90 min of contact time. The results indicated enhanced electrochemical degradation of DCF using Na_2SO_4 compared to phosphate buffer supporting electrolytes. In Figure 6b, the electrochemical degradation of DCF on carbon electrode with phosphate buffer supporting electrolytes decreased from 42.5 to 12.5 mg/L in 40 min and to 3.9 mg/L with Na_2SO_4 as supporting electrolyte representing a decrease of 70.6% and 90.8%, respectively. The results show that degradation of DCF on both electrodes (Pt and Carbon) is higher with Na_2SO_4 as the supporting electrolyte.

The degradation of SMX over 90 min contact time is shown in Figure 6c and 6d. The electrochemical degradation of SMX on Pt electrode, with Na_2SO_4 and phosphate buffer supporting electrolytes decreased from 52.8 to 6.5 mg/L and 18 mg/L in 40 min of contact time (Fig. 6c). That is a decrease of 87.7% and 65.9% of the original concentration of SMX with Na_2SO_4 and phosphate buffer electrolytes assisted degradation. Electrochemical degradation of the same PhAC gave a percentage degradation of 81.1% and 50.6% for Na_2SO_4 and phosphate buffer supporting electrolytes. The results indicated enhanced electrochemical degradation of SMX using Na_2SO_4 compared to phosphate buffer supporting electrolytes on carbon electrode and as also observed for Pt electrode. Generally, it was observed that the degradation efficiency was higher within the first 40 min of analysis time and thereafter it remained almost constant. The total time for analysis for all electro-degradation studies was 90 min. As shown in Figure 5, reduction of the initial concentration indicates that Na_2SO_4 electrolyte gives a higher performance for both SMX and DCF degradation at the tested concentration on both Pt and carbon anodes.

The effective degradation of the PhACs achieved using Na_2SO_4 could be attributed to SO_4^{2-} as an oxidant species. The SO_4^{2-} strongly influences the rate of mineralization reactions. A study by Murugananthan et al.[21] showed that the mineralization of Ketoprofen (non-steroidal anti-inflammatory drug molecule) was strongly influenced by SO_4^{2-} and a complete TOC removal was achieved using SO_4^{2-}, whereas TOC removal was just approximately 55% and 25% in the presence of other oxidant species such as NO_3^- and Cl^- media, respectively.[21] Panizza et al. (2008) documented the complex generation of active species from Na_2SO_4, where $S_2O_8^{2-}$ and sulfate radical were generated in the presence of Na_2SO_4. These

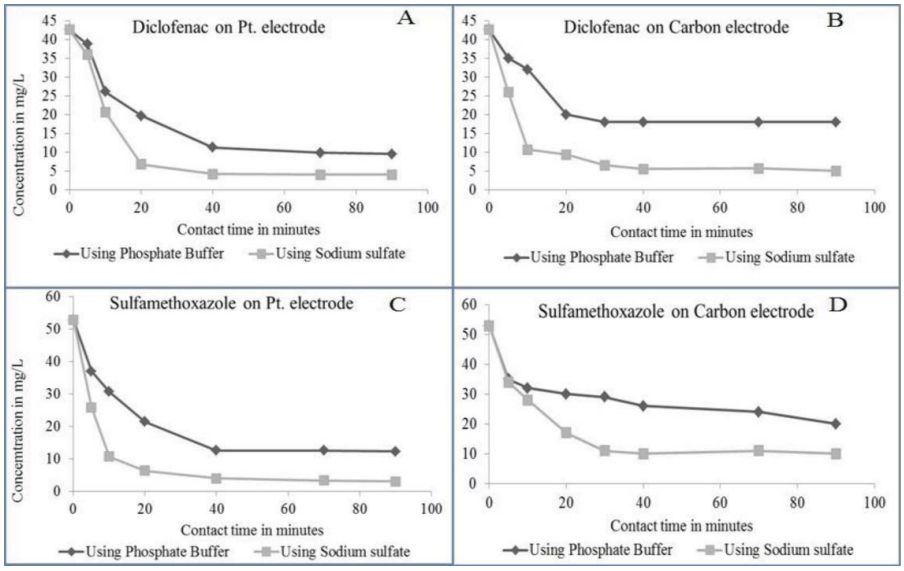

Figure 6. Degradation of PhACs over contact time. Graphical curves for DCF degradation using Phosphate buffer and Na_2SO_4 on Pt electrode and on Carbon electrode are shown in (a) and (b). SMX degradation using Phosphate buffer and Na_2SO_4 on Pt electrode and on Carbon electrode is shown in (c) and (d).

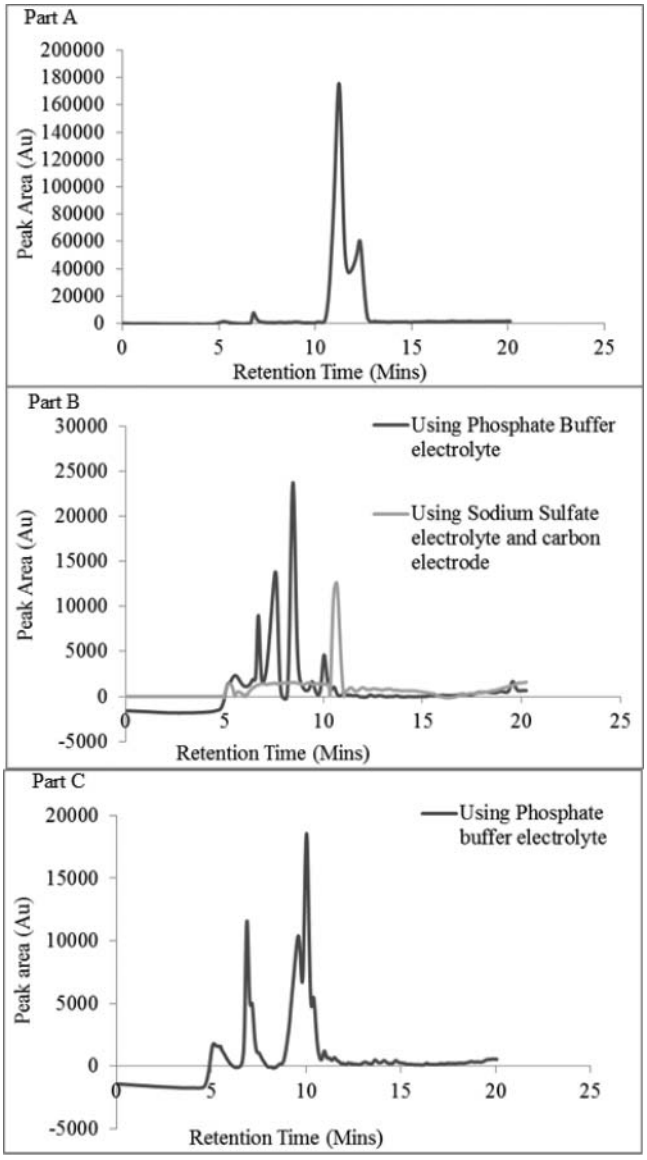

Figure 7. HPLC chromatograms for real field samples. (a) Original real field sample prior to the electrochemical degradation process. (b) Resultant chromatograph from electrochemical degradation using Phosphate buffer Electrolyte and Na_2SO_4 electrolyte with carbon electrodes. (c) Resultant chromatograph from electrochemical degradation using Phosphate buffer Electrolyte with Pt electrode.

oxidants are either consumed for the degradation as in the case of ketoprofen molecule.[21] However, some researchers have pointed out that the ability of $S_2O_8^{2-}$ ($E^0 = 2.01$ V) to oxidize refractive pollutants is comparatively less.[24]

The degradation of SMX and DCF on the tested anodes was in the order: Pt electrode greater than graphite electrode. Pt attained a SMX and DCF degradation efficiency of 76.7% and 77.6% using phosphate buffer, and 94.3% and 90.5% using Na2SO4 as supporting electrolyte respectively for 90 min electrolysis. The faster degradation of both pharmaceuticals on Pt than carbon electrode can be explained by the different adsorptions of hydroxyl radicals on these electrodes. Platinum has inert surfaces than carbon electrodes, so the hydroxyl radicals are weakly adsorbed and have a lower enthalpy of adsorption on the Pt surface. Consequently, they are very reactive and effective towards SMX and DCF oxidation because they react very rapidly with all organics arriving at the surface and in the vicinity of the anode. On the other hand, carbon electrode is less nonactive and more hydrated than Pt, with more hydroxyl radical strongly adsorbed on its surface; thus it is less reactive toward PhCAs. Figure 6 clearly shows that anodic oxidation of SMX and DCF strongly depended on the anode materials.

A real field sample

Results obtained from the analysis of a real field wastewater sample gave a concentration of 62.5 μg/L for DCF and 33.7 μg/L for SXM prior to electrochemical degradation. The results obtained after a 40-min electrochemical degradation were 0.15 μg/L and >0.1 μg/L for DCF and SXM, respectively. Figure 7 shows HPLC chromatograms obtained from these analyses, at retention times 10.5 and 12.2 min for DCF and SXM, respectively. Figure 7a shows a filtered chromatogram peak that was obtained from the original real field sample prior to the electrochemical degradation process. The peak intensities for DCF and SXM (5,860,818 and 2,246,903, respectively) were higher than those obtained for DCF (13,781)—the chromatograms are shown in Figure 7b and 7c. SXM peak was not observed in the chromatogram obtained from the resultant sample after degradation process. The chromatogram in (c) also showed a reduced peak intensity (76,972) corresponding to a concentration of 0.8 μg/L DCF. These results show a more than 98% removal of the pharmaceuticals from the wastewater by electrochemical degradation.

Conclusion

Anodic oxidation of DCF and SMX at carbon and Pt electrodes was studied, and the effects of supporting electrolytes namely Na_2SO_4 and Potassium Phosphate buffer were compared. The cyclic voltammetric studies show that DCF and SMX are electrochemically active PhACs as demonstrated by the increase in the oxidation peaks of the PhACs with increasing concentration. The significance of the supporting electrolyte on oxidative degradation of the two PhACs was compared for Na_2SO_4 and potassium buffer. The results showed that Na_2SO_4 was 15–30% more efficient in the electrochemical degradation of both SMX and DCF on Pt and Carbon electrodes than potassium phosphate buffer. The rate of mineralization of the PhACs at Pt anode was found to be better than on the carbon anode. The kinetics study shows that in all cases the degradation of SMX and DCF follow the second order reaction with correlation coefficient above 0.9. The major products expected from electro-oxidation process—simple molecules—are often in gaseous state. This work recommends an investigation on the metabolites and final product of electrochemical degradation of the PhACs. Real field samples may contain other radical electrolyte species that can participate in the electrochemical process and thus act as interferences within the electro-oxidation system. It is therefore recommended that the electrochemical degradation process be the last step in domestic water treatment because the technic also depends largely on electrolytes present in the water.

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