Chapter 2
Literature review

2. Literature review

2.1 Literature related to electrochemical oxidation of PhCs

The electrochemical oxidation (EO) is a proficient and flexible process applied for the water and wastewater treatment. There are two ways of oxidation in EO, direct oxidation and indirect oxidation. In direct oxidation, the hydroxyl radicals are electrochemically generated on the electrode surface; while in indirect oxidation, reactive chemical species are electrochemically generated depending upon the electrolyte and type of electrode (Ahmad et al., 2021). In the last fifteen years, there are plentiful studies carried out on the EO of PhCs with novel electrodes in the synthetic aqueous matrix. EO has predominantly appeared and has gained much attention from researchers for last decades due to the key advantages it offers: rapidity, better control, capability of complete mineralization, operation at ambient temperature and pressure, and no chemical requirement (da Silva et al., 2021; Y. Feng et al., 2016). However, the PhC removal efficiency of EO is affected by various operating parameters, such as type of electrode, electrolyte, applied current density, pH, and the initial concentration of the PhCs (J. Wang & Wang, 2020). Therefore, it is necessary to optimize these parameters to obtain required removal efficiency at a minimum operating cost. Besides, there is a possibility of formation of toxic by-products from EO of PhCs, especially in chloride rich medium where high chances are there for chlorinated by-products formation. Hence, focus of the research should also be directed to toxicity test and the identification of intermediates (Haidar et al., 2013; Xia et al., 2020). Although, EO has several benefits, such as flexibility to adjust to the fluctuating volumetric and organic load, no secondary waste generation that need further management, and significantly less power consumption for streams having high electrical conductivity, thus making the EO process suitable for the aqueous PhCs removal at the field-scale.

Literature related to various electrochemical oxidation experiments carried out for PhCs removal were reviewed and summarized in Table 1.

Table 1: Highlights of some researches on PhCs removal using electrochemical oxidation

Pharmaceutical compound	**Initial conc.**	**Electrolyte**	**pH**	**Findings**	**Author**
	Electrode material	**Electricity supplied**			
Oxytetracycline (OTC) and Chlortetracycline (CTC)	100 mg/L in 500 mL solution	1 g/L Na_2SO_4, 1 g/L NaCl	7.0 (maintained using phosphate buffer)	• Using a Ti/IrO_2 anode, OTC and CTC concentrations were decreased by more than 99.5% in six hours. While using a Ti/PbO_2 anode, OTC and CTC concentrations were decreased rapidly by 99.9% in two hours by electrochemical treatment. • With sodium sulfate electrolyte, OTC and CTC concentrations were decreased by 99.5%in six hours. With sodium chloride electrolyte, OTC and CTC concentrations were decreased by more than 99.7% only in 30 min of electrochemical treatment. • Dairy milking parlour wastewater was also spiked with 100 mg/L of OTC and similar results were achieved using a Ti/IrO_2 anode as in case with the sodium sulfate electrolyte.	Miyata et al., 2011
	Anode: Ti/IrO_2, Ti/PbO_2; 150 x 50 mm mesh anode Cathode: Ti plate Distance: 10 mm	1.5 A			

Ciprofloxacin (CIP)	10, 30, 50, 100 mg/L in 250 mL solution (@ 30^0C)	0.05 M Na_2SO_4	3, 5, 7, 9, 11 initial pH	• Electrochemical oxidation was proven to be effective for CIP degradation. After two hours of electrolysis, the CIP degradation ($[CIP]_0$=50 mg/L), COD, and TOC at 30 mA/cm^2 was almost 99.5%, 86% and 70%, respectively. • When current density was increased from ten to forty mA/cm^2, COD and CIP degradation efficiency initially increased and later decreased. • Also, when initial CIP concentrations were higher, the CIP degradation efficiency was adversely affected. • The initial pH had no significant effect.	Wang et al., 2016
	Anode: SnO_2-Sb/Ti (50 x 30 mm^2 area) Cathode: Ti plate Distance: 20 mm	10, 20, 30, 40 mA/cm^2			
Ceftriaxone sodium (CEF)	10 mg/L in 40 mL	0.1 M Na_2SO_4	7.6 to 7.8	• In comparison with Pure Nano-G and TiO_2/Nano-G anodes, RuO_2-TiO_2/Nano-G anode was more effective, as CEF removal efficiencies for these electrodes were 76.6%, 90.3%, and 97.3% respectively after 100 min. • When minute amount of RuO_2 was introduced into TiO_2/Nano-G composite, electrochemical oxidation activity was improved and charges transfer resistance of TiO_2/Nano-G anode was decreased.	Li et al., 2018
	Working electrode: RuO_2-TiO_2/Nano Graphite (Nano-G) composite Counter electrode: Pt electrode Reference electrode: Saturated calomel electrode	Constant voltages of 2.0 V (cell-voltage)			

Chlortetracycline (CTC) and Cefazolin (CFZ)	30 mg in 300 mL	1 g/L Na_2SO_4, 1 g/L NaCl	not mentioned	- More than 70 % of the CTC removal was achieved with Ti/PbO_2 anode in half an hour using electrochemical treatment at 0.25 A current. At 0.5 A current, The CTC concentration decreased to below detection limit after three hours of treatment. Alternatively, COD reduction was nearly 60 % after six hours of electrochemical treatment. - CTC removal efficiency in raw milk was different than that of the aqueous solution. Comparing with CTC degradation in water, CTC degradation in raw milk has several stages. - CFZ removal showed similar pattern to the CTC removal, but the time required was different. The reason for the difference in time requirement is because of the different activities of CFZ and CTC towards hydroxyl radical for the similar experimental condition.	Kitazono et al., 2017
	Anode: Ti/PbO_2, Ti/IrO_2 (150 x 50 mm^2 mesh) Cathode: Titanium plate Distance: 5 mm	0.25, 0.5, 1 A			
Diclofenac (DCF)	30 mg/L in 100 mL	0.1 M Na_2SO_4	neutral pH	- For the electrolysis time of four hours, DCF concentration was reduced from 30 mg/L to 1 mg/L. - The intermediates of DCF were generated at the early stage, which also got degraded when extra reaction time was given. - The % removal achieved in four hours was 6, 50, 67, 83, and 97% for applied bias potential 0.9, 1.3, 1.5, 2.5, and 4 V respectively	Zhao et al., 2009
	Working electrode: BDD electrode (area 12 cm^2), Counter electrode: Pt wire, Reference electrode: Saturated calomel electrode	0.9, 1.3, 1.5, 2.5, 4.0 V applied bias potential			

Ibuprofen (IBU)	0.2 mM in 200 mL	0.05 M Na_2SO_4 and 0.1 M NaCl	3 initial pH	• Rapid and complete removal of IBU was achieved at higher current 500 mA in sodium sulfate electrolyte. Reason could be the higher production rate of hydroxyl radical in sulfate medium. • IBU degradation follows pseudo first order kinetics, and reaction rate constants were increased with an increase in current from 50 to 500 mA. However, the increase in rate constants was not proportional to the increase in current. This may happen because of enhanced parasitic reaction of oxygen evolution. • When sodium chloride was used as an electrolyte, IBU removal was quicker due to electro-generation of active chlorine from chloride.	Ambuludi et al., 2013
	Anode: Pt mesh, BDD 25 cm^2 Cathode: Carbon felt Placed concentrically	50, 100, 200, 300, 500 mA			
Sulfamethoxazole (SMX)	0.208 mM (52.7 mg/L) in 250 mL	0.05 M Na_2SO_4	3 initial pH	• Complete abatement of SMX was observed at 1, 0.5, 0.25, and 0.12 h for 60, 120, 300, and 400 mA, respectively. • Nevertheless, SMX degradation was not enhanced when higher current was applied i.e. 450 mA. The reason could be the acceleration in the parasitic reactions of the hydrogen evolution at the carbon felt and the hydroxyl radical self-destruction at the platinum.	Dirany et al., 2010
	Anode: Platinum plate (14 x 5 cm^2) Cathode: Carbon felt Distance: not mentioned	60, 120, 300, 400, 450 mA			

Sulfamethazine (SFZ)	193, 965, 1930 mg/L in 100 mL (@35^{0}C)	0.05, 0.5 M Na_2SO_4	2 to 6 initial pH	• The EO treatment of 193 mg/L SFZ solution with 0.5 M Na_2SO_4 at regulated pH 3 in the anodic half-cell of the divided boron doped diamond/stainless steel cell gave total mineralization with 98% dissolved organic carbon reduction for current density more than 66.6 mA/cm^2. A similar mineralization degree was yielded with the undivided BDD/SS cell with 0.05 M sodium sulfate at current density more than 100 mA/cm^2, but with sluggish degradation and lesser mineralization efficiency due to the lesser oxidation ability of generated BDD and (•OH). • An identical removal rate was found in the pH range two to six. • In both undivided and divided electrolytic cells, the mineralization process increased with the increase in applied current density, however the efficiency drastically decreased due to the parasitic reactions of BDD and hydroxyl radical. • Higher concentrations of sulfamethazine inhibited the degradation % of dissolved organic carbon with a higher efficiency because of the inhibition of non-oxidizing reactions of BDD and hydroxyl radical.	El-Ghenymy et al., 2013
	Anode: Boron doped diamond-BDD (3 cm^2 area) Cathode: Stainless steel-SS plate Distance: 10 mm	33.3, 66.6, 100, 150 mA/cm^2			

Sulfachloropyridazine (SCP)	0.2 mM in 250 mL	0.05 M Na_2SO_4	3, 4.5, 8.5 initial pH	• When current was increased from 50 to 700 mA, the reaction time for complete abatement decreased from 3 hours to half an hour. • In comparison with acidic pH, for the same applied current 1000 mA, SCP degradation is apparently slow at alkaline pH (~8.5). The varied adsorption ability on the BDD surface for the protonated (at $pH < 5$) and neutral ($pH > 5$) forms explain the change between SCP oxidation rate under acidic and alkaline conditions.	Haidar et al., 2013
	Anode: BDD (25 cm^2) Cathode: Carbon felt Distance: not mentioned	50 to 700 mA, and 1000 mA			
Diclofenac (DCF), Sulfamethoxazole (SMX)	0.25, 0.5, 1, 2 mg/L in 0.15 L	0.1 M Na_2SO_4; 62, 125, 250 mg/L NaCl	Neutral pH	• DCF removal rate decreased with increase in $[DCF]_0$ from 0.5 to 2 mg/L. • DCF removal followed pseudo first order reaction kinetics. • Comparing BDD, Stainless steel (SS), and Pt-SnO_2/Ti anodes, BDD performed best in terms of DCF removal rate and the extent. However, Pt-SnO_2/Ti achieved similar DCF removal (>95%) in 60 minutes but with lower removal rate. • Increase in Chloride ion and current density resulted in higher DCF removal rate. Humic Acid inhibited the DCF removal. • UVA did not accelerate DCF removal • SMX degradation was found to be ~73% in half an hour, and simultaneous DCF removal was ~44%.	Giannakopoulos et al., 2022
	Anode: Pt-SnO_2/Ti, BDD, SS	8, 16, 32, 48 mA/cm^2			

Cyclophosphamide (CP), Carbamazepine (CBZ), Sulfamethoxazole (SMX) and Ibuprofen (IBP)	20 mg/L each in 40 mL	100 mM NaCl/$NaClO_4$ or the constituents of synthetic fresh human urine	Not mentioned	• For CBZ removal, dissolved chlorine is the responsible oxidant, while for the SMX removal HOCl is the dominant oxidant. For CP and IBP, adsorbed hydroxyl radical and IrO_3-Cl are responsible for the oxidation. • Quenching of dissolved RCS by urea, uric acid and creatinine in the solution was observed. • CBZ, CP, IBP, and SMX were degraded in synthetic fresh urine matrix at mixed kinetics and mass transfer. The reaction rate limiting step was mass-transfer and it was found to be important for both types of anodes. • Degradation rate constants for PhC removal were higher with BDD than with IrO_2.	Y. Yang et al., 2022
	BDD and Ti/IrO_2	10 mA/cm^2			

Among the advanced oxidation processes, EO is expedient because it is environmentally friendly, highly efficient, and easily automated, and there is no requirement for chemical addition (Martínez-Sánchez et al., 2022; Y. Yang, 2020). At a given current density, EO is simply a 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 on the presence of salts in the matrix and electrodes involved. In the last 15 years, many studies have been carried out on the EO of PhCs using novel electrodes in a synthetic aqueous matrix. There are few studies available that focused on real matrices such as groundwater, reverse osmosis concentrate (ROC), tertiary effluent from wastewater treatment facilities, etc. (Ganiyu & Gamal El-Din, 2020; F. Li et al., 2020; Oriol et al., 2019). ROC is generated from two ways, one from the RO unit for water use and the second from the polishing unit at the end of the effluent treatment chain. ROC has limited reuse potential because of high salinity and ROC disposal or treatment is a challenge. However, if ROC is utilized as an electrolyte medium to destruct recalcitrant organics such as PPCPs, the high salt concentration reduces energy consumption for EO considerably (Wei et al., 2021; Q. Xiang et al., 2019). Besides sulfate and hydroxide, 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 (Y. Feng et al., 2016; J. Wang et al., 2018). Mixed metal oxides coated anodes, which are called active anodes are verified to be exceptionally good because of their electro-catalytic properties for the evolution of Cl_2 along with their prolonged chemical and mechanical stability (Palma-Goyes et al., 2018; Pointer Malpass & de Jesus Motheo, 2021). Electrochemically generated in-situ reactive chlorine species are shown to be robust and resilient for oxidation of PPCPs in synthetic as well as real aqueous matrices (K. Guo et al., 2017; Y. J. Liu et al., 2019).

Keeping these facts in mind, the initial part of the present study was carried out using ROC as an electrolyte for electrochemical oxidation of model PPCP compound diclofenac sodium. Mixed metal oxides coated anode- $Ti/Ru\text{-}Sn\text{-}Sb\text{-}O_x$ was prepared and used for all the electrochemical experiments. Quantitative analysis of DCF and its intermediates were performed on HPLC. A small comparative study on commonly used quenching agents for EO samples was carried out to find the suitable quenching agent for present study. The effect of current density and reaction kinetics for EO of DCF was thoroughly studied. Effect of electrolyte composition in form of sulfate to chloride ratio on DCF degradation rate and extent of degradation was studied in synthetic electrolyte and the best performing ratio was applied to actual ROC. A phyto-toxicity study was also carried out using mung beans to check the EO effluent suitability for irrigation.

2.2 Literature related to peroxymonosulfate based processes for removal of PhCs

Of late, there has been growing curiosity in using new oxidants mainly peroxymonosulfate (PMS) and persulfate (PS) for removal of emerging contaminants. Hydroxyl radical ($^{\bullet}OH$) and sulfate radical ($SO_4^{\bullet-}$) generated through PS or PMS activation, attack the organic compounds. PS and PMS can be activated by various activation methods such as d-electron-transitional metal (e.g. Fe^{2+}, Co^{2+},and Mn^{2+}), photolysis (UV radiation, solar radiation), alkaline condition, ozonation, thermal activation, and radiolysis (Kiejza et al., 2021; Zheng et al., 2022). The sulfate radical can rapidly oxidize the emerging organic pollutants. In sulfate radical based process, organic compounds are degraded to mineralization due to its high oxidizability - 2.5 to 3 V potential, extended life (around 30 to 40 µs), and flexible pH range – 2 to 11 (Song et al., 2020). An Oxone is used as a source of PMS, which is a triple salt, consisting potassium peroxymonosulfate ($KHSO_5$), potassium hydrogen sulfate ($KHSO_4$), and potassium sulfate (K_2SO_4) at the 2:1:1 molar ratio. On the contrary, PS which is also called PDS (peroxy di-sulfate) consists of sulfate ions and positive ions. PMS is promptly activated in comparison with PS because of its asymmetric structure and lesser energy requirement for the bond dissociation (Ji et al., 2017; Kumar et al., 2021; C. Wang et al., 2021). There are three possible mechanisms for PMS activation: (i) O–O bond fission (in case of UV, thermal, and ultrasound activation), (ii) single e^- transfer (in case of activation through transition metal and carbon based materials), and (iii) hydrolysis of PMS to H_2O_2 (in case of alkaline activation) (Xia et al., 2020).

Selective research summary related to PMS based processes for aqueous PhC removal is given in Table 2.

Table 2: Highlights of some researches on PhCs removal using PMS activation

Pharmaceutical compound	Initial conc.	PMS activation method	pH	Findings	Author
	Operational parameters	**Initial PMS conc.**			
Atenolol (ATL)	0.02 mM	UV/PMS	7	• When PMS to ATL molar ratio was increased from 1 to 16, ATL % degradation was increased from 45% to 100% • When solution pH was increased from 3 to 7, the ATL degradation was more or less similar. However, when it was further increased from 7 to 9, ATL degradation was significantly improved. And when pH was increased from 9 to 11, % ATL degradation again dropped. • 7 intermediates were identified using LC-MS analysis and 4 possible pathways were proposed: dimerization, cleavage of ether bond, hydroxylation of aromatic ring, and oxidation of primary and secondary amine moieties.	X. Liu et al., 2013
	UV- 254 nm, 30 min reaction time	0.08 mM			
Sulfamerazine (SMZ)	0.2 µg/L	UV/PMS	7.5	• When $[PMS]_0$ was increased from 0.5 to 5 mg/L, SMZ removal efficiency considerably increased to 97%. • When pH was increased from 6.5 to 8.5, SMZ degraded completely. • It was found from TBA and ethanol quenching that sulfate radical dominated the degradation process and hydroxyl radical played negligible role.	Cui et al., 2016
	UV – 254 nm, 30 min reaction time	1 mg/L			

Sulfamethoxazole (SMX)	23.69 µM	UV/PMS	6.24	• When [SMX]$_0$ was increased from 6 µM to 35.5 µM, SMX degradation decreased from 0.0231 to 0.0164 min^{-1}. • When [PMS]$_0$ was increased from 0.5 mM to 5 mM, SMX degradation rate constant was increased from 0.017 to 0.0254 min^{-1}. • When pH was increased from 3 to 5, the SMX degradation rate was marginally decreased. When the pH was further increased from 5 to 11, the degradation rate remarkably increased.	Ao & Liu, 2017
	UV – 254 nm	1 mM			
Sulfamethoxazole (SMX)	0.04 mM in 60 mL	Nitrogen - doped graphene (NRGO)/ PMS	3, 7, 8, 10	• When PMS alone was used, 72% SMX removal was achieved. The SMX removal further increased to 81.5% and 92% when RGO and NRGO were added respectively. • Using NRGO, RGO, and GO, the SMX adsorption reached to its maximum in ten minutes and achieved 23, 31, and 15% SMX removal respectively. • For pH three, seven, and eight, the first order removal constant was 0.0101, 0.0129 and 0.0152 min^{-1}respectively. It showed that the increase of pH is favorable for SMX degradation. • The removal rate constants improved with the increase in temperature. When temperature was 15, 25, 35 and 45 °C, respectively removal rate constants were 0.00633, 0.0101, 0.0135 and 0.0212 min^{-1}.	S. Wang et al., 2019
	[NRGO] = 0.5 g/L (catalyst); Temp = 15, 25, 35, 45^{0}C	0.8 mM			

Carbamazepine (CBZ)	100 mg/L in 100 mL	$LaCoO_3$/ PMS	3, 4, 5, 6, 7, 8	• Initial pH, $[PMS]_0$, and initial CBZ conc. were found to be most important for CBZ removal. • The degradation was progressively enhanced with the increase in pH from three to five, but considerably hindered when pH was further increased to six and above. • CBZ degradation was in direct proportion to the PMS concentrations from 0.1 to 1 mM, in which CBZ degradation efficiency slowly improved from 57.5% in 0.5 h to 100% in 0.125 h. • Elevated $[CBZ]_0$ appreciably hindered CBZ degradation because of the competition effect between the CBZ and peroxymonosulfate for the active sites of $LaCoO_3$.	Guo et al., 2020
	$[LaCoO_3]_0$ = 0.05 g/L	0.1, 0.2, 0.3, 0.5, 0.8, 1 mM			
Diclofenac (DCF)	0.025 mM in 100 mL	$BiFeO_3$/ PMS	3, 4, 5, 7, 9	• At acidic pH (~3), the DCF degradation rate was fastest. Homogeneous reaction made a major contribution to degradation of DCF at acidic pH, hence, 65% removal efficiency was achieved. • There was no significant difference in DCF degradation rate at pH 5 and pH 7, which is lower than the rate at pH 4. At pH 9, DCF degradation was significantly repressed. • With an increase in BFO dose, DCF degradation rate was remarkably improved. DCF degradation rate was found to be 0.0351 min^{-1} at 0.6 g/L BFO dosage. • With an increase in PMS concentration from 0.1 to 0.5 mM, DCF degradation rate was increased linearly. When PMS concentration was further increased to 0.6 mM, there was not any significant improvement in DCF degradation rate constant.	Han et al., 2020
	$BiFeO_3$ (BFO)dosage : 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 g/L	0.5 mM			

Caffeine (CAF)	0.50 mM in 500 mL	Co-mesoporous silica with hexagonal order pore canal/PMS	pH was at 7.10 with 0.1 M NaOH	• CAF degradation was 98% at 600 mg/L catalyst concentration with 13.23% mineralization efficiency in an hour. • The contribution of intermediates to the mass balance kept decreasing with the increase in the reaction time. It suggested that the short-chain carboxylic acids were formed in the solution. • With the increase in catalyst dose, the CAF degradation rate linearly increased. • Rise in the PMS/CAF ratio led to the enhanced degradation and mineralization.	Qi et al., 2013
	$[\text{Catalyst}]_0$ = 20, 40, 100, 200, 400, 600 mg/L	10 mM			
Ibuprofen (IBU)	20 mg/L in 100 mL	Visible light/ $CaCu_3Ti_4O_{12}$/ PMS	Neutral pH	• Merely 3% of IBU removal was attained using the vis-light/PMS process, whereas 8% using the vis-light/$CaCu_3Ti_4O_{12}$ process. • When $CaCu_3Ti_4O_{12}$/PMS process was applied, IBU removal elevated to 35% in one and half hour, and when vis-light/$CaCu_3Ti_4O_{12}$/PMS process was applied, IBU removal elevated to 92% in one hour. • The mechanism study suggested that the availability of Cu^+ in the $CaCu_3Ti_4O_{12}$ crystal lattice could be responsible for PMS activation.	Zhu et al., 2019
	Suspensions were irradiated by 300 W xenon lamp equipped with a UV cutofflter ($\lambda \geq 420$ nm) at room temperature	0.5 mM			

Levofloxacin (LVF)	10 mg/L in 100 mL	$CoFeO_2$/ PMS	3, 5, 7, 9, 11	• When $CoFeO_2$ dosage increased from 0.05 to 0.15 g/L, the LVF degradation enhanced from 79% to 89%, however, when catalyst dosage further increased to 0.2 g/L, LVF degradation was decreased. • When PMS initial concentration was increased from 0.3 to 0.5 mM, the LVF degradation efficiency improved from 74% to 89%, but when PMS was further increased to 1 mM, the LVF degradation declined. • When reaction temperature was increased from 15 ^{0}C to 40 ^{0}C, the LVF degradation efficiency improved from 75% to 96%, also the degradation rate was accelerated at high temperatures.	Pi et al., 2020
	0.15 g/L catalyst; Temp = 15, 25, 30, 40 ^{0}C	0.05, 0.1, 0.15, 0.20 g/L			
Chloramphenicol (CRM)	30 µM	Co_3O_4/ PMS	7	• When catalyst dose increased from 0.02 to 0.4 g/L, CRM degradation remarkably improved. • When $[PMS]_0$ increased from 0.2 mM to 4 mM, CRM degradation rate constant was linearly increased. • When the reaction temperature was increased, the CRM removal rate was accelerated, which could be described by rapid PMS decomposition into active radicals under thermal activation. • Maximum CRM removal was achieved at neutral pH, below or above 7 pH, CRM removal drastically decreased.	Deng et al., 2017
	$[Co_3O_4-KIT]_0 = 0.1$ g/L dose, 1 h reaction time for complete removal	1 mM PMS			

2,4 – Dichloro phenoxy acetic acid (DPA)	20 mg/L	$CuFe_2O_4$/ Ozone/ PMS	6	• When pH was varied in the range 5 to 7, DPA degradation was efficient, below or above this range, DPA degradation was adversely affected. • When ozone dosage was increased from 0 to 20 mg/L, DPA removal was significantly increased. • When 0.5 mM PMS was added to $CuFe_2O_4$/Ozone system, DPA removal was increased to 60%. When PMS was further increased from 0.5 to 2 mM, DPA removal efficiency further increased to 89%. However, when PMS conc. was doubled to 4 mM, DPA removal decreased to 86%. This could be due to scavenging of radicals by extra PMS present.	Jaafarzadeh et al., 2017
	16 mg/L Ozone, 0.2 g/L $CuFe_2O_4$, 40 min reaction time for complete removal	2 mM PMS			
Acetaminophen (ACT)	2.5, 5, 7.5, 10 mg/L in 250 mL	Nano-scaled magnetite (Fe_3O_4)/PMS	5	• ACT degradation was not significant at pH 5 using PMS alone. • The degradation rate constant hastily improved from 0.0031 min^{-1} to 0.0134 $min^{-1}$with the increase in catalyst dosage from 0.2 g/L to 1 g/L. • When the initial PMS concentration was increased from 0 to 0.2 mM, ACT degradation rate constant was improved from 0.0023to 0.0122min^{-1}. However, further increase in initial PMS concentration from 0.2 to 0.5 mM led to slight decline in degradation rate constant. • ACT degradation rate decreased with the increase in initial ACT concentration.	Tan et al., 2014
	$[Fe_3O_4]_0$ = 0.2, 0.4, 0.6, 0.8, 1 g/L	0.02, 0.05, 0.1, 0.2, 0.4, 0.5 mM			

Ibuprofen (IBP)	0.024 mM in 0.5 L	Sonolysis (US)	5 ± 0.2	• PMS activation was compared with PDS and H_2O_2 activation applying sonolysis for IBP removal. It was observed that IBP degradation followed pseudo-first-order kinetics in all three processes. Moreover, sonolysis alone is also effective for IBP degradation. • IBP degradation rate increased with an increase in frequency from 35 to 1000 kHz. • US/PDS performed better than US/PMS for IBP removal for similar operational parameters. • IBP degradation was observed to decrease with increase in pH from 3 to 9.2.	T. Liu et al., 2023
	Input power = 70 ± 0.5 W; Frequency = 35, 72, 100, 170, 700, 1000 kHz; Temp. = 24 ^{0}C	0.03 mM			
Carbamazepine (CBZ)	25 mM in 40 mL	PMS activation by N-rich pyridyl-iron phthalocyanine derivative	3, 5, 7, 9	• FepyPc/PMS/sunlight system was developed and photocatalytic oxidation was studied for CBZ removal. • FepyPc/PMS/sunlight showed ~99% CBZ removal in 60 minutes, at neutral pH. Reusability as well as photo-catalytic activity of FepyPc was proven to be quite effective. • Higher initial PMS concentration resulted in faster CBZ removal. • Sulfate radical, hydroxyl radical, singlet oxygen, and oxygen radical are found to be responsible for CBZ removal in EPR study.	J. Li et al., 2022
	0.1 g/L Iron phthalocyanine (FepyPc)	0.7 mM			

A wide range of studies have been carried out by researchers using PMS activation for emerging contaminants such as PhCs. Amongst many activation methods, it has been found that ferrous activation is most suitable for large scale application because of its environment friendly, low cost, easily available, and most importantly, effective in activating PMS at neutral pH (Ji et al., 2017; Xiao et al., 2020). Nevertheless, high amounts of ferrous salt is required for constant activation of PMS and reverse reaction for Fe^{3+} to Fe^{2+} transformation is too frail which lower down the PMS activation efficiency (Du, Yang, et al., 2019; Govindan et al., 2015; Khan et al., 2013). Besides, iron sludge generation in bulk is also a problem with Fe^{2+}/PMS process. This shortcoming can be overcome by continuous supply of Fe^{2+} for PMS activation (EC/PMS) using iron as sacrificial anode and it also solved the recycling of Fe^{2+} from Fe^{3+} that may occur at cathode (Govindan et al., 2014; N. Yang et al., 2015). This combination EC/PMS consists of two processes: electrocoagulation (EC) and Fe^{2+}/PMS. The EC/PMS provides better control over Fe^{2+} dosing which can be adjusted with applied current density and this effectively reduces generation of iron sludge, besides PMS can also directly be activated by electricity (Govindan et al., 2014; Sun et al., 2020).

The aim of the later part of the present study is to investigate the EC/PMS process for spiked IBU removal in chloride rich reverse osmosis concentrate (ROC) matrix. Since chloride is widely present in natural water matrices, it is important to explore and understand the EC/PMS process in chloride containing matrix such as ROC. However, the treated water further require a treatment for TDS removal and it also alleviate the cost of the over-all treatment. Comparison of EC, PMS, Fe^{2+}/PMS, stepwise added Fe^{2+}/PMS, and EC/PMS were studied and chemistry of EC/PMS process was proposed. Contribution of sulfate and hydroxyl radical were evaluated by quenching experiments with tert-butyl alcohol and ethanol. To examine the effects of initial pH, initial PMS conc., and current density, for batch EC/PMS process, response surface methodology was carried out. Also, EC/PMS process was carried out in continuous flow mode and its performance was evaluated for varied flow rate (residence time). To the best of our knowledge, this study is one of its kind and of great value for researchers working with PMS based processes.