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Supplementary information for

Title

Electrocatalytic membrane reactors for degradation of organic pollutants - a review

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Appendix A - Electrochemical oxidation pathways occurring at electrocatalytic membranes

1. Direct oxidation

A widely accepted mechanism for the direct oxidation of organics in wastewater proceeds after electro generation of hydroxyl radicals (\cdot OH)¹. The non – active electrodes such as PbO₂, SnO₂, TiO₂ loosely bound the electro generated hydroxyl radicals (\cdot OH) with the surface of electrode as per reaction 1, where MO_x is representative of anodic metal oxide². In case of active electrodes such as IrO₂, RuO₂, the electro generated hydroxyl radicals (\cdot OH) get chemically adsorbed to increase the oxidation state of these electrodes from MO_x to MO_{x+1} as per reaction 2³.

 $MO_x + H_2O \rightarrow MO_x (.OH) + H^+ + e^- (1)$

$$MO_x (.OH) \rightarrow MO_{x+1} + H^+ + e^- (2)$$

The physisorbed hydroxyl radicals in case of non – active anodic materials lead to complete combustion of organic molecule (RH) as per reactions 3 and 4⁴.

$$MO_x(.OH) + RH \rightarrow MO_x + R. + H_2O(3)$$

 $MO_x (.OH) + R. \rightarrow MO_x + CO_2 + H_2O (4)$

In case of active electrodes the chemisorbed oxygen leads to selective oxidation of organics into intermediates dependent on the reactant organic species as shown in reaction 5⁴.

$$MO_{x+1} + R. \rightarrow MO_x + intermediates (5)$$

The electrocatalytic reactions shown in reaction 3, 4 and 5 have to constantly compete with side reactions such as oxygen evolution reactions (OER) and dimerization reactions presented in reactions 6, 7 and 8 respectively.

 $MO_x (.OH) \rightarrow MO_x + \frac{1}{2}O_2 + H^+ + e^-(6)$

 $MO_{x+1} \rightarrow MO_x + \frac{1}{2}O_2 + H^+ + e^-(7)$

 $2MO_x$ (.OH) $\rightarrow 2MO_x + H_2O_2$ (8)

2. Indirect oxidation

Wastewater contains several forms of electrolytes such as Cl⁻, SO₄⁻², NO₂⁻, CO₃⁻. It is found that the presence of these ions in the solution increases the overall electro oxidation rate due to formation of oxidants that aid the degradation of organic pollutants via several side reactions⁵. For instance, the chloride ions (Cl⁻) in wastewater undergoes dimerization reactions to form chlorine (Cl₂) which lead to indirect oxidation of pollutant species in water as per reactions $9 - 12.^{6}$

 $2Cl^{-} \rightarrow Cl_2(aq) + 2e^{-}(9)$

 $Cl_2(aq) + H_2O \rightarrow HOCl + Cl^- + H^+(10)$

 $Cl_2(aq) + H_2O \rightarrow HOCl + Cl^- + H^+(10)$

 $HOCI \leftrightarrow H^+ + ClO^-(11)$

 $R + ClO^{-} \rightarrow intermediates \rightarrow CO_2 + H_2O + Cl^{-}(12)$

However, the involvement of chloride ions in electrochemical reaction can lead to the formation of undesirable chlorate (ClO_3^-) and perchlorate (ClO_4^-) ions which have detrimental impact on mankind being carcinogenic in nature⁷.



Figure S1 Schematic of electro-catalytic reactor comprising anode and cathode in the batch configuration



Figure S2 (A) Degradation pathway of phenols; (B) Degradation pathway of bisphenol



Figure S3 (A) Degradation pathway of tetracycline; (B) Degradation pathway of ibuprofen;(C) Degradation pathway of paracetamol



Figure S4 (A) Degradation pathway of tricyclazole; (B) Degradation pathway of 2, 4-Dichlorophenoxyacetic acid

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