INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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SHORT ABSTRACT

Environment friendly reagent Hydrogen peroxide (H_2O_2) has wide applications in chemical synthesis, food, clinical, biological, and environmental processes. One of the common applications of H_2O_2 is its use as a precursor for the hydroxyl radicals ($^{\bullet}OH$) formation in the advanced oxidation processes (AOPs) for the wastewater treatment. Therefore, H_2O_2 electrogeneration is usually carried out through the reduction of dissolved O_2 (DO) in an acidic solution at a low cathodic potential. The present study comprises of three parts.

The first part of this work is undertaken to investigate on H_2O_2 decomposition over a broad range of its concentration which is typically employed in water treatment. Various parameter such as pH and reaction temperature and also trace metals (Na^+, Ca^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, etc) effect H_2O_2 decomposition. H_2O_2 became essentially unstable at a higher pH in the presence of these trace metal ions except Co^{2+} and Ni^{2+} due to low catalytic effect. This work also focused on the role of common supporting electrolytes (SEs) in the electro-chemical inertness of Ti-based materials employed for the anodic (direct) oxidation coupled with H_2O_2 electrogeneration at the graphite cathode for the concurrent decomposition of organic contaminants. It was found that ClO_4^- corroded TiO_2 coated Ti (TiO_2–Ti) anode very fast (>60 min), and Ti^{4+} ions formed a yellow color complex (λ_{max} = 380 nm) with H_2O_2. The influence of Cl^-, NO_3^-, and SO_4^{2-} was insignificant on the stability of TiO_2–Ti. The cell current efficiency of H_2O_2 formation dropped sharply with ClO_4^- in the case of TiO_2–Ti anode. The TiO_2–Ti corrosion also reduced the mass transfer co-efficient of DO transport from bulk to the cathode surface because of Ti^{4+} adsorption on graphite cathode.

In the second part, the NiO and Co_3O_4 NPs were successfully synthesized by a green synthesis pathway at higher pH using the analytes (ascorbic acid (AA)) extracted from *Sechium edule*, the fruit of a perennial climber, for electrocatalytic applications of these NPs in H_2O_2 generation and sensing. It was found that Ni(II)-AA complex was formed in an aqueous solution near the neutral pH. At a higher pH, $Ni(OH)_2$ could be formed by the ligand exchange between AA^- and OH^-. At pH>10, AA^- is converted to 2,3-diketogulonic acid (2,3-DKG). Similarly, AA mediated CoOOH transformation to $Co(OH)_2$, and CoOOH was abundant with Co_3O_4 NPs synthesized in the control condition without the use of the bio-extract. The as-obtained oxide were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Atomic force

microscopy (AFM), Field emission scanning electron microscopy (Fe-SEM), Transmission electron microscopy (TEM) and Vibrating sample magnetometer (VSM).

The synthesized NiO NPs were immobilized on the graphite surface and tested for its electrocatalytic activity for the production of H_2O_2 in an acidic pH (1.5≤pH≤4.5, 0.5 M Na_2SO_4 and O_2 flow rate 1.0 LPM). From the cyclic voltammetric (CV) tests (vs. Ag/AgCl), it was found that O_2 reduction took place at a low overpotential which was independent on the solution pH, but the cell current was diminishing beyond the optimal pH of 2.5. There was a remarkable increase in the cell current (3.5 times) and current efficiency (CE_f) (61 % higher) of H_2O_2 formation with graphite/NiO NPs cathode than the bare graphite, and the CE_f didn't decrease (5-7 %) much during electrolysis. It was even higher with the graphite/Co_3O_4 NPs electrode. The limiting current density (1.42 A/m^2) was independent on the surface area of graphite/NiO NPs cathodes, and the mass transfer coefficient (k_m) and thickness (δ) of O_2 diffusion layer were 0.955×10^{-5} m/s and 209 µm, respectively. But, marginally higher mass transfer coefficient and thickness of the diffusion layer were found as 1.1.3×10^{-5} m/s and 177 µm, respectively, due to higher limiting current density (1.60 A/m^2) in the case of graphite/Co_3O_4 NPs electrode.

The degradation of CIP was quite impressive (71-78 %) in the electro-Fenton process (EFP) where H_2O_2 generation was catalyzed by NiO and Co_3O_4 NPs. However, the mineralization efficiency was notably lower due to the formation of the refractory intermediates attached to the quinolone structure. The degradation of the CIP molecule mainly took place through three different pathways such as piperazine moiety breaking, cyclopropyl group cleavage, and decarboxylation reaction. The proposed mechanisms were well supported by the fragments appeared in the mass spectra, and most of the fragments were originated from the cleavage of piperazine ring moiety. The pseudo 1st order kinetic model well fitted the experimental data of CIP cleavage.

In the last part of the work for the electrocatalytic H_2O_2 sensing, the Co_3O_4 and NiO NPs were tailored on a graphite electrode with an average concentration of 5.92×10^{-13} and 5.19×10^{-13} mol/cm^2 in a deaerated phosphate buffer media (pH 7.2). The CV at -E_{cat}= 0.5 to −0.5 V vs. Ag/AgCl showed a low H_2O_2 reduction peak at –0.117 V vs. Ag/AgCl for the graphite/Co_3O_4 NPs and at −0.129 V vs. Ag/AgCl for the graphite/NiO NPs electrode with a quasi-reversible electrochemical system. The modified electrode was exhibited a quick amperometric response (< 5 s), a low limit of detection (LOD) of H_2O_2 of 0.0217 µM, and a high electrode sensitivity of 65.32 nA/µM/cm^2 compared to the graphite/NiO NPs electrode (LOD of 0.0271 µM with electrode sensitivity of 62 nA/µM/cm^2). No alteration of the amperometric responses was noted in the presence of common interferents.