Electrochemical nitrate reduction at electrodeposited copper on copper substrate

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Nitrate contamination in ground and surface water is a growing environmental concern. Treatment for nitrate is typically very complicated and expensive because nitrate is a stable and highly soluble ion [1]. Current treatment methods like reverse osmosis, ion exchange and bioremediation are expensive, they often require initial pre-concentration of the contaminants and also produce secondary effluents [2]. Among the remediation methods available, electrochemical method has been employed in this work due to advantages such as environment friendliness, selectivity and high efficiency over other methods [3]. Generally, expensive noble metal-based catalysts are used as cathode for electrochemical reduction of nitrate. With an objective to find an economically alternative catalyst, in this investigation, we report on the synthesis and characterization of low-cost copper electrodeposited on copper substrate, and its applicability towards nitrate reduction.

Electrodeposition was carried out using potentiostatic technique for specific time in 0.1 M CuSO$_4$ solution + 0.5 M HClO$_4$ on a Cu foil (Alfa Aesar, 0.05 mm thickness) with 1 cm$^2$ area. At a chosen deposition potential and pH, optimum electrodeposition parameters corresponding to better catalytic activity of nitrate reduction were determined.

Electrodeposited Cu on Cu substrates (Cu/Cu) was characterized to examine the morphology and structure by Scanning Electron Microscopy and X-ray diffractometer. The electrochemical characterization was carried out to test the suitability of the catalysts for nitrate reduction. Cu/Cu prepared with different electrodeposition time was employed as the working electrode. Platinum wire and Ag/AgCl were used as counter and reference electrode, respectively. Perchloric acid (0.5 M) solution was used as the supporting electrolyte (blank) with 1 M sodium nitrate for the nitrate reduction. All solutions studied were deaerated by bubbling nitrogen prior to the electrochemical measurements.

Cyclic and linear sweep voltammograms were collected at different scan rates. As shown in Fig. 1, the increase in current density of Cu/Cu electrodes in comparison to bare Cu shows the beneficial effect of electrodeposition towards nitrate reduction. The increase in current density could be due to increase in surface area available for the nitrate reduction. A maximum catalytic activity towards nitrate reduction was observed with an electrodeposition time of 2 minutes in 0.1 M CuSO$_4$ solution.

Electrolysis was carried out using an H-cell at -0.45 V in 1 M NaNO$_3$ + 0.5 M HClO$_4$ and samples were withdrawn at regular intervals and subjected to product analysis after suitable dilution. Fig. 2 shows the concentration profile of nitrate. The nitrate removal efficiency of Cu/Cu is 58% in comparison to 48% that of Cu under identical electrolysis conditions as shown in Fig. 2 inset. Nitrate undergoes reduction following the consecutive reaction mechanism $\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NH}_3 \rightarrow \text{N}_2$ depending on the potential applied and the conversion rate vary with time. Product analysis confirmed the presence of nitrite and ammonia in addition to unreacted nitrate. The effect of electrolysis potential was studied, and it was observed that the nitrate reduction increased with increasing the electrolysis potential.

Thus electrodeposition of copper on copper substrate was carried out using constant potential technique and their catalytic activity towards nitrate reduction was studied. Based on the electrolysis results, it was observed that electrodeposited Cu/Cu exhibit higher catalytic activity towards nitrate reduction than bare copper.

References:

