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**TITLE OF THESIS: Development of Electrochemical Methods of Arsenic Removal from Groundwater.**

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# ABSTRACT

The groundwater contamination due to arsenic has received significant attention during recent years. Its distribution and toxicology in natural water is a serious environmental issue, as millions of people are affected worldwide. There are various techniques of arsenic removal such as physical, chemical and biological methods. The use of chemicals, waste disposal and low efficiency are some of the drawbacks of these methods. Besides, these methods are expensive and are not easy to handle at house hold level. There is an utmost need to develop a treatment technology, which can be used at household level economically, especially in the developing and under developed countries. Keeping these points into consideration, attempts have been made to develop fast, inexpensive, effective, efficient and reproducible electrochemical methods for the removal of both arsenite and arsenate from water. The electrochemical methods used in the present study are electrocoagulation and electrodialysis.

Chapter 1 deals with the introduction giving a brief overview of the problem followed by the objectives of the study. This chapter describes the summary of the groundwater contamination by various pollutants especially the arsenic contamination. Various methods of arsenic remediation along with their drawbacks are also summarized. Besides, a brief description of the importance of the electrochemical methods in water treatment is presented.

Chapter 2 describes materials and methodologies used in present research work. It also contains fundamentals of the electrocoagulation and electrodialysis techniques and the important parameters associated with them.

Chapter 3 of the thesis describes the removal of arsenite by electrocoagulation method using zinc-zinc and copper-copper electrode assemblies. The influence of the various parameters like initial arsenite concentration, pH, applied voltage and the processing time were studied on the removal efficiency of arsenite. The maximum removals were 99.89 and 99.56% for zinc-zinc and copper-copper electrodes, respectively. The optimum conditions for zinc-zinc electrode assembly were 2.0 mg $L^{-1}$ initial concentration, 16.0 min. processing time, 6.0 pH and 3.0 V applied voltage at 30.0 ºC temperature. On the other hand, these parameters for copper-copper electrodes were 2.0 mg $L^{-1}$, 20.0 min., 7.0 pH, 5.0 V at the same temperature. The results suggested the possibility of using electrocoagulation with either zinc-zinc or copper-copper electrodes for the effective removal of arsenite from the ground water. Adsorption isotherms models such as Langmuir, Freundlich, Temkim and Dubinin- Radushkevich were applied to know the nature of adsorption and mechanism of the removal. Moreover, kinetics and thermodynamics studies were also carried out. Freundlich model was found to best fit the isotherm data for the adsorption of arsenite with pseudo-first order kinetics. It is important to note that the removal of arsenite occurred with the conversion of arsenite into arsenate followed

by removal. The developed method was applied to the high contaminated (0.563 and 0.805 mg $L^{-1}$) real groundwater of Ballia District, U.P. India. The developed methodology showed promising results as no arsenic was detected in the treated water.

Chapter 4 deals with the investigation of removal efficiencies of aluminum-iron and iron-zinc electrode assemblies in the electrocoagulation method for arsenate. The best removal occurred at 2.0 mg $L^{-1}$ initial concentration for both the electrode systems. The optimized conditions were pH 7.0 and 3.0 volts of applied potential for both the electrode assemblies *i.e.* aluminum-iron and iron-zinc electrodes. The optimized processing times were 9.0 and 12.0 min for iron-zinc and aluminum-iron electrode assemblies, respectively. The maximum removals were 99.89 and 99.56% for aluminum-iron and iron-zinc electrodes, respectively. Moreover, iron-zinc electrodes proved better than aluminum-iron as it took less time to remove arsenate below the permissible limit prescribed by WHO (10.0 µg $L^{-1}$). The removal of arsenate occurred through the adsorption of arsenate on iron hydroxides and aluminum hydroxides; which were earlier formed by the iron and aluminum ions generated at the anode. Various isotherms models were applied to study the nature of adsorption and mechanism of the removal process. Moreover, kinetics and thermodynamics studies were also carried out. Langmuir model was found the best fit isotherm for the adsorption of arsenate with pseudo-second order kinetics. The method is simple, fast, inexpensive, easy to operate and more importantly eco-friendly in nature. The developed method was tested for the real water samples of Ballia district, U.P., India. The complete removal of arsenic from these real groundwater samples indicates the real application of the developed electrocoagulation method.

Chapter 5 discusses the removal of arsenate and arsenite from aqueous solution by electrodialysis process. The electrodialysis was carried out in cell divided into three compartments by the ion exchange membranes. The membrane was synthesized and characterized using FT-IR, SEM, XRD and TGA. The electrodialysis was carried out using the stainless steel as anode and cathode. The results indicated the maximum removal efficiency of 81.67 and 84.29% of arsenite and arsenate, respectively. The best removal of arsenate and arsenite occurred at 3.0 and 4.0 volts, 5.0 and 9.0 pH respectively, for 2.0 mg $L^{-1}$ of arsenate and arsenite contaminated water. Overall, the electrodialysis method for the removal of both the species of arsenic was quite satisfactory, but the time taken by the process was about 7.0 h; quite long in electrochemical processes. The treated water showed a small amount of the electrolyte ions *i.e.* sodium and nitrate, a source of secondary contamination in the central treated water compartment. Moreover, the effects of interfering ions has also been studied. The presence of phosphate interfered with the maximum removal of arsenate and arsenite. The developed electrodialysis method was tried to remove the arsenic from the groundwater samples of Ballia district, U.P., India. The removal of total arsenic was up to 78.8 and 80.13% from these real groundwater samples.

It can be concluded from the results presented in the thesis that electrochemical methods are effective, fast, reproducible, and selective with no or least waste material generation. Out of two methods used in the study, electrocoagulation was found more effective than the electrodialysis for both the species of arsenic as former was faster, more efficient with no secondary contamination of treated water. Briefly, it can be concluded that the developed electrocoagulation and electrodialysis methods can be applied to remove arsenic from groundwater and wastewaters for the benefit of human beings.