

The use of electrochemically activated water in water treatment

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Many of the methods used to convert organic material in raw water to more readily biodegradable intermediate products for removal in subsequent conventional water treatment processes produce by-products harmful to human health, have limitations in application governed by water characteristics or have high capital and operational costs. There is a need to investigate new technologies capable of producing oxidants for use in pre-treatment as alternatives to pre-chlorination, pre-ozonation, hydrogen peroxide and uv-irradiation.

This thesis examines the potential use of electrochemically activated solutions to produce mixed oxidants for use in the pre-treatment of organic substances. Anolyte and Catholyte solutions were produced using a EUROSTEL electrochemical cell originating from the former USSR, which utilises a novel patented membrane to separate the anode and cathode chambers. The investigation was conducted in three phases. First, the active oxidation species which persist in the electrochemically activated solutions were characterised. Secondly, these solutions were used at laboratory scale to study their effectiveness in removing:

a) synthetic organic matter (insecticides and polyaromatic hydrocarbons) and
b) natural organic matter (humic/fulvic substances and algae) from a series of synthetic and raw waters. Thirdly, the formation of by-products (e.g. trihalomethanes) was investigated and practical constraints of using the EUROSTEL electrochemical cell at a full scale water treatment works were considered.

The research has demonstrated that EUROSTEL Anolyte solution (generated from 15% NaCl solution) has a higher oxidation potential when compared to conventional pre-chlorination (using sodium hypochlorite). This is shown to be due to the majority of the free available chlorine (FAC) existing as undissociated molecular Cl_2 (oxidation potential 1.39 V) arising from the low pH and high chloride concentrations in the anolyte, whereas in sodium hypochlorite solutions the FAC is present mainly as OCl^- (oxidation potential 0.9 V). No ozone, hydrogen peroxide or chlorine dioxide were detected in the EUROSTEL solutions 30 minutes after production. Some of these species may be present during electrochemical activation but degrade rapidly, possibly contributing decomposition products such as O^\bulletH radicals and chlorates and chlorites to the oxidation potential of the anolyte solution.

With regard to synthetic organics, the EUROSTEL anolyte solution was shown to be capable of higher removal efficiencies for some pesticides (e.g. atrazine) and PAHs (e.g. fluorene and naphthalene) when compared to pre-chlorination using hypochlorite. Other compounds such as isoproturon, benzo(a)pyrene, anthracene showed no enhanced degradation when dosed with electrochemically activated solutions as their carboxy acid bonds are readily broken down by OCl^- . Recalcitrant synthetic organics such (e.g. atrazine, fluorene, naphthalene) require a higher oxidation potential for breakdown of their ring structure and were thus only oxidised when treated with EUROSTEL Anolyte. The oxidation ability of the Anolyte solution was hindered in hard waters because of the reducing effect of OH^- ions converting Cl_2 to OCl^- and the scavenging effect of bicarbonate ions on species such as OH^\bullet radicals.

Pre-oxidation of natural organic matter (NOM) with EUROSTEL anolyte was found to aid subsequent coagulation processes when used at dosing levels that enhance bipolymer formation. However if used in excessive quantities the EUROSTEL anolyte solution was found to hinder coagulation due to the breaking up of the organic molecules into very small fragments which prevent bipolymer

formation. It was concluded that the optimum pre-oxidant dose depends on the composition of the organic matrix in the aquatic system together with factors such as hardness and pH. For hard waters containing high initial concentrations of NOM dosing with EUROSTEL Anolyte produced higher coagulation removal efficiencies than pre-treatment with hypochlorite solution.

The main by-products of atrazine oxidation (DIA and DEA) were not observed in EUROSTEL Anolyte dosed samples, although they were identified in atrazine dosed with hypochlorite, suggesting there may be fewer problems associated with breakdown products when electrochemically activated solutions are used.

THM formation in waters containing natural organics was studied and it was found that in waters containing algae and humic substances 50% less chloroform was formed when dosed with EUROSTEL Anolyte solution compared to similar waters dosed with hypochlorite. This is because OCI^- is the active reagent for THM formation, and this represents less than 12% of the FAC in Anolyte solutions, as 88% of FAC was found to be in the form of Cl_2 .

The thesis concludes that electrochemically activated solutions have benefits in the pre-treatment of natural and synthetic organics in raw waters. The practicalities of using EUROSTEL electrochemical cells at a full scale water treatment works are discussed, and the implications of dosing regimes, overall potential energy consumption and physical constraints in cell geometry suggest these cells may be impractical for widespread use in conventional plants treating large volumes of water. It is concluded that the EUROSTEL system is best used to treat waters containing specific contaminants, such as polluted groundwaters, as well as possible applications for small water supplies in developing countries. Overall the study has contributed to a better understanding of the nature of Anolyte and Catholyte solutions generated by a EUROSTEL electrochemical cell and the pre-treatment performance capabilities of such a system; recommendations are made for future work to optimise this performance on specific water types.

The work has used a series of matrix jar tests to study how the highly oxidative ionic species in the electrochemically activated solutions break down complex organic molecules such as insecticides and pesticides (atrazine and isoproturon), polyaromatic hydrocarbons (e.g. naphthalene, fluorene, anthracene, chrysene, benzo(a)pyrene). Results obtained to date suggest destruction of these compounds is very effective and the solutions are also found to be useful in dealing with algal species such as *Anabaena flos-aquae*, and *Asterionella formosa*. The work is also investigating the breakdown products of these chemicals after they have been treated. It has been found that when treating humic or algal waters THM formation is reduced by 50-60% when compared with conventional pre-chlorination techniques.