UNIVERSITI PUTRA MALAYSIA

ELECTROCHEMICAL ACTIVATION PROCESS FOR TREATING HIGH STRENGTH WASTE

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Dedicated to daddy,

For your love and all you have done for the family

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Electrochemical Activation Process (ECA) is a method whereby electrical current is introduced to induce a chemical reaction in water containing natural salts. As a result, this process will produce a substantial electrical potential difference, leading to the generation of anolyte and catholyte. The anolyte generated by the STEL®-ECA unit system were found to contain Cl_2, Cl^-, HClO, HCl, ClO_2, O_2, O_3, and H_2O_2. As for catholyte, analyses using the ICP and IR spectroscopy showed that it contains the hydroxides of sodium, potassium, magnesium and calcium. Besides, kinetic studies on the decomposition of the components in anolyte were also studied.

Both activated solutions, anolyte and catholyte were used to treat passivation waste and landfill leachate. The studies include using anolyte and catholyte in COD reduction, the effect of contact time (of anolyte and the waste) on COD reduction, kinetics of the reaction between anolyte and the waste, using of catholyte in coagulation and

flocculation, biodegradability of the waste after treatment and others. Finally, a case study was carried out to investigate the possibility of using anolyte in combination with other treatment methods, for example, aerobic, anaerobic, sedimentation and absorption to treat chemical waste. The physical-chemical-biological treatment reactor designed for the treatment of chemical waste was closely monitored for 143 days on its COD, BOD and biodegradability.

For passivation waste, COD removal was 70% using anolyte for at least 24 hours of contact time. High efficiency on the formation and settling of floc were observed when catholyte is used together with alum and anionic polymer. In addition, the non-readily biodegradable waste was transformed to a more readily biodegradable waste after at least a 24 hours reaction with the activated solutions. As for leachate, anolyte showed good reduction in COD and ammoniacal nitrogen, whereas catholyte showed good reduction in ferum and zinc. Finally, data obtained from the case study showed that anolyte is able to convert a non-readily biodegradable waste to a more readily biodegradable waste.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PROSES ELEKTROKIMIA AKTIF UNTUK MERAWAT SISA KUAT

Oleh

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Fakulti: Kejuruteraan

Proses Elektrokimia Aktif adalah suatu proses dimana arus elektrik dibekalkan untuk merangsangkan suatu tindakbalas kimia di dalam suatu larutan bergaram. Proses ini menyebabkan suatu perubahan keupayaan elektrik lalu menghasilkan larutan 'anolyte' dan 'catholyte'. 'Anolyte' yang dijanakan oleh sistem unit STEL®-ECA didapati mengandungi Cl_2, Cl^-, HClO, HCl, ClO_2, O_2, O_3, dan H_2O_2. Untuk 'catholyte' pula, analisis menggunakan spektroskopi ICP dan IR menunjukkan bahawa ia mengandungi hidroksida natrium, kalium, magnesium dan kalsium. Selain itu, kinetik perlesapan komponen dalam 'anolyte' turut dikaji.

Kedua-dua larutan aktif, 'anolyte' dan 'catholyte' telah digunakan untuk merawat sisa pasif dan air sisa dari tempat pembuangan sampah. Kajian ini termasuk penentuan dos terbaik 'anolyte' dan 'catholyte' dalam penurunan COD, kesan masa sentuhan antara 'anolyte' dengan sisa terhadap penurunan COD, kinetik tindakbalas antara 'anolyte'

dengan sisa, penggunaan 'catholyte' dalam proses penggumpalan, biodegradasi sisa selepas rawatan dan sebagainya. Akhirnya, suatu kajian kes dijalankan untuk mengkaji pergabungan 'anolyte' dengan kaedah rawatan lain seperti aerobik, anaerobik, pemendapan dan penyerapan untuk merawat sisa kimia. Reaktor rawatan fizikal-kimia-biologi rekaan itu telah dijalankan selama 143 hari dan parameter COD, BOD dan kebolehan sisa dibiodegradasikan telahpun dikaji.

Untuk sisa pasif, penurunan COD yang dicapai adalah sebanyak 70% apabila 'anolyte' digunakan dengan masa tindakbalas sekurang-kurangnya 24 jam. Penggunaan 'catholyte' bersama-sama dengan alum dan polimer anionik telah menunjukkan keberkesanan yang tinggi dalam pembentukan 'floc' dan pemendapan 'floc'. Selain itu, sisa yang pada mulanya tidak terbiodegradasi, telah menjadi terbiodegradasi selapas rawatan dengan larutan-larutan aktif itu. Untuk 'leachate' pula, 'anolyte' menunjukkan keputusan yang baik dalam penurunan COD dan nitrogen ammonia manakala 'catholyte' pula menunjukkan keputusan yang baik dalam penurunan ferum dan zink. Akhirnya, data yang diperolehi dari kajian kes menunjukkan bahawa 'anolyte' berkebolehan menukarkan sisa tidak terbiodegradasi kepada sisa terbiodegradasi.

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LIST OF ABBREVIATIONS

ECA	Electrochemical Activation Process
FEM	Flow-through Electrochemical Modular
THM	Trihalomethanes
CIS	Commonwealth of Independent States
VAC	Voltage Alternating Current
PTFE	Polytetrafluoroethylene
COD	Chemical Oxygen Demand
BOD	Biochemical Oxygen Demand
UV	Ultraviolet
EAW	Electroactivated Water
GC-MS	Gas-Chromatography-Mass Spectroscopy
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
FTIR	Fourier Transform Infrared
TLC	Thin Layer Chromatography
min.	minutes

CHAPTER 1

INTRODUCTION

1.1 General

Coping with the improving world today i.e. industrial development, obtaining clean and hygienic water has gradually become a major concern to the entire human race. To overcome this problem, many scientists from all over the world have carried out studies and research on water and wastewater treatment. However, these serious problems did not stop. In fact, more 'water' problems were encountered. As mankind begin to develop the awareness of the importance of water, their assessments towards the value of water will be increased. One of the earliest attempt of mankind being involved in water treatment was in the nineteenth century[1]. Their efforts of using chlorine as a disinfectant to fight waterborne human diseases such as cholera and typhoid were a successful one[2]. Since then, water disinfection has created interests in mankind.

For several decades, chlorine, in different forms, has always played the role as a dominant disinfectant[3]. However, as mankind's concern on the protection of public health grows stronger, more and more questions on whether chlorination could bring a long-term, side effect to human health are often raised. This is because chlorine forms halogenated by-products, which are believed to have mutagenic and carcinogenic properties[4]. A good disinfectant must be toxic to microorganisms at concentrations well below the toxic thresholds to humans and higher animals[5]. This is true, but in order to produce an alternative disinfectant which is effective and able to fulfill the above requirements is not an easy task. Alternative disinfectants such as ozone and UV radiation have been used but due to their high operation costs and non-residual effect (do not provide long-term protection), the ideal disinfectant is yet to be found.

1.2 Electrochemical Activation (ECA)

ECA is a well-known Russian technology introduced by a Russian scientist, V.M. Bakhir in 1972. Essentially, ECA concept involves the passage of a high frequency, high voltage current through a saline solution, with a membrane interposed between the anode and cathode and resulting in a substantial electrical potential difference which leads to the formation of two types of water, namely the 'anolyte' and 'catholyte' [6,7]. The anolyte, often known as 'activated water' or 'oxidized water', is a mixture of reactive species, which contributes to special oxidizing, sterilizing and disinfecting properties of the anolyte. Despite its powerful properties, anolyte is non-toxic and harmless, both to human and the environment for it is biodegradable after some 48 hours[8]. This is because the small concentrations of free chlorine in anolyte and its low redox potential do not favor the formation of toxic trihalomethanes (THM) or other halogenated by-products[9]. STEL®, a device system designed for generation of aqueous ECA solutions specially for washing, disinfectant and sterilizing was launched in 1990 under the supervision of V.M. Bakhir, Ph.D. and Yu.G. Zadorozhny[10]. Today, thousands of the STEL® devices meant for producing electrochemically activated solutions operate in different cities of Russia and CIS countries[11]. These devices are widely used in clinical and medical preventive facilities, municipal economy institutions, health spas and swimming pools[12]. ECA research is strongly supported by the government of the Russian Federation.

1.3 Flow-through Electrochemical Modular (FEM)

The key difference between new ECA technology and traditional electrochemical processes is the incorporation of a special flow-through diaphragm-type electrochemical reactor, called FEM. The new flow-through electrolytic modular elements has no analogues in the world[11] (Figure 1.1).

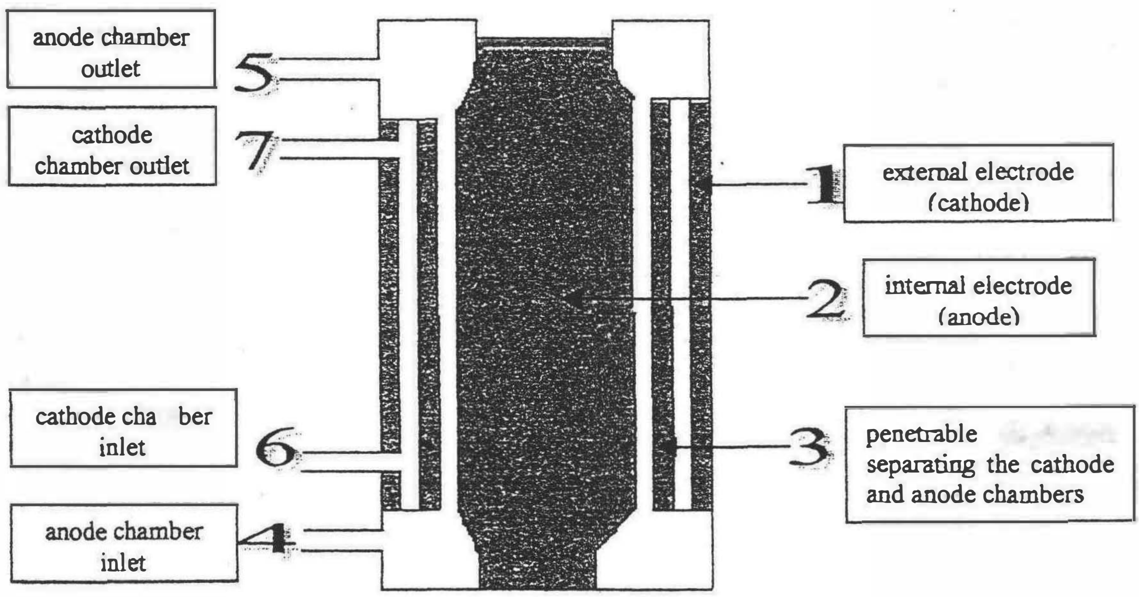

Figure 1.1: Flow-through Electrochemical Modular, FEM[13]

The electrochemical module makes use of two insulated rhodium plated, titanium electrodes where the two electrodes are separated by a patented zirconium oxide diaphragm[14]. The advantage of using FEM elements fitted in the electrochemical system is the generation of electrochemically activated, metastable solutions from low-mineralized initial solutions or natural water. This includes the anolyte, produced from the STEL® ECA system, which contains a mixture of hydrogen peroxide, chlorine dioxide, ozone, sodium hypochlorite, oxygen and other highly reactive species. The concept and theoretical aspects of this new technology in the field of applied electrochemistry was not fully and clearly discussed in any of the references obtained on this subject. The ECA technology is a sole Russian invention where all experts and specialists in this field are citizens of the former Soviet Union[11]. According to Bakhir[9], the design of FEM-3 elements (the third generation of the FEM invention) ensures the contact of all microvolumes of water flowing through the anode or cathode electrode chamber with an electrode surface, in the vicinity of which (in so-called Double Electric Layer, DEL) the electric intensity reaches few millions volts per centimeter (the effect of purification of rainwater and its saturation with vital power during spring thunderstorms). In this case, the processes of natural oxidation-reduction destruction and neutralization of toxic substances are accelerated both due to direct electrochemical reactions and as a result, highly active components electrochemically synthesized out of the water under treatment, such as ozone, atomic oxygen, peroxide compounds, active chlorine compounds, including chlorine dioxide, and short-lived free radicals.

1.4 The STEL® ECA System

1.4.1 Space Age Technology

The STEL® ECA technology was developed and patented as part of a Space Age StarWars Program over a period of 20 years at a cost of about US$20 million for the treatment and recycling of water[15]. This is because in the space program, the astronauts have a limited amount of water which they can take with them and in turn has to be continuously purified and recycled for long missions and long term orbital stays. Therefore, the ECA based water purification systems was invented and successfully supplied water to keep the astronauts in space for even up to a year.

1.4.2 Characteristics of the STEL® ECA System

The STEL® ECA system is a device system designed to generate anolyte and catholyte using the ECA process. The characteristics of the STEL® ECA system are shown in Table 1.1.