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DESIGN OF AN ELECTROCHEMICAL REACTOR FOR THE REMOVAL OF PHARMACEUTICAL POLLUTANTS IN SOURCE-SEPARATED BLACKWATER FROM A HOSPITAL OF 1,000 BEDS

AUTOR: Jennifer Bain

TUTOR: María Teresa Montañés Sanjuan

COTUTORE: Montserrat García Gabaldón
Jordi Carrillo Abad

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ABSTRACT

Water pollution by toxic pharmaceutical pollutants has been highlighted as a global environmental issue in recent years. As conventional wastewater treatment is inefficient at degrading recalcitrant organics, there is a demand for technologies to remove pharmaceutical residues in wastewaters. Studies have shown that electrochemical oxidation can fully mineralise pharmaceuticals into biodegradable, non-toxic compounds, however, this technology has not yet been implemented on a large-scale. This work concerns the design of a treatment process for the electrochemical oxidation of a relatively low volume, high concentration blackwater stream from a typical Scottish hospital of 1,000 beds.

The proposed process was designed to handle a maximum blackwater flowrate of 60 m^3 day^{-1} containing a pharmaceutical pollutant concentration of 1 mg L^{-1}. It was concluded that a batch-recirculated electrochemical reactor with BDD anodes operated at a current density of 100 mA cm^{-2} was optimal for the process. The electrochemical reactor module comprises a stack of 24 filter-press cells corresponding to an active anode area of 10.1 m^2, a 7.8 m^3 external reservoir tank and a recirculation pump. A batch treatment time of 2.5 hours was determined to be sufficient for 80% mineralisation of pollutants to yield biodegradable, non-toxic compounds. The reactor performance parameters, instantaneous current efficiency and specific energy consumption, were calculated to be 15.8% and 0.501 kWh g_{COD}^{-1}, respectively.

To determine the feasibility of implementing the proposed process on a large-scale, an economic assessment was performed. Total equipment capital and energy consumption costs were calculated to be €964,000 and €389,000 yr^{-1}, respectively. Due to excessive energy consumption and lack of revenue generation, large-scale implementation is unlikely. However, if legislation is introduced to impose restrictions on pharmaceutical concentrations in the environment, this process may be implemented to minimise the discharge of toxic pollutants to surface waters and ensure regulatory compliance.

Keywords: Pharmaceutical pollutants, electrochemical oxidation, hospital wastewater treatment, aquatic environment

RESUMEN

La contaminación del agua por contaminantes farmacéuticos tóxicos se ha considerado un problema ambiental global en los últimos años. Dado que el tratamiento convencional de aguas residuales es ineficaz para degradar los compuestos orgánicos recalcitrantes, hoy en día existe una demanda de tecnologías que permitan eliminar los residuos farmacéuticos de las aguas residuales. Los estudios efectuados han demostrado que la oxidación electroquímica puede mineralizar completamente los productos farmacéuticos en compuestos biodegradables y no tóxicos; sin embargo, esta tecnología aún no se ha implementado a gran escala. En este trabajo se pretende diseñar un proceso para tratar mediante oxidación electroquímica una corriente de aguas negras, de alta concentración y caudal relativamente bajo, procedentes de un hospital típico escocés de 1.000 camas.

El proceso propuesto se ha diseñado para tratar un caudal máximo de aguas negras de 60 m^3/día, las cuales tienen una concentración de contaminantes farmacéuticos de 1 mg/L. Se ha concluido que el reactor óptimo para llevar a cabo el proceso es un reactor electroquímico discontinuo con recirculación, el cual utilizará ánodos BDD y trabajará a una densidad de corriente de 100 mA/cm^2. El módulo del reactor electroquímico propuesto está constituido por una pila de 24 celdas del tipo filtro prensa correspondientes a un área de ánodo activo de 10,1 m^2, un tanque de reserva externo de 7,8 m^3 y una bomba de recirculación. Se determinó que un tiempo de tratamiento de 2,5 horas es suficiente para que la mineralización alcanzada sea del 80% de los contaminantes produciendo compuestos biodegradables y no tóxicos. Además, se calcularon los parámetros de rendimiento del reactor obteniéndose una eficiencia de corriente instantánea del 15,8% y un consumo específico de energía de 0,501 kWh/g_{COD}.

Por último, para determinar la viabilidad de implementar el proceso propuesto, se realizó una evaluación económica. Se calcularon los costes totales de inversión y los correspondientes al consumo de energía, obteniéndose 964.000 € y 389.000 €/año, respectivamente. Debido al excesivo consumo energético y a la falta de generación de ingresos, es poco probable una implementación del proceso a gran escala. Sin embargo, si en un futuro se aprueba legislación

para imponer restricciones a las concentraciones de compuestos farmacéuticos en las aguas residuales, este proceso puede implementarse para minimizar la descarga de dichos contaminantes tóxicos a las aguas superficiales y garantizar el cumplimiento normativo.

Palabras clave: Contaminantes farmacéuticos, oxidación electroquímica, tratamiento de aguas residuales hospitalarias, medio acuático

RESUM

La contaminació de l'aigua per contaminants farmacèutics tòxics s'ha considerat un problema mediambiental mundial als darrers anys. Com que el tractament convencional de les aigües residuals és ineficient per degradar els compostos orgànics recalcitrants, hui en dia hi ha una demanda de tecnologies per eliminar els residus farmacèutics de les aigües residuals. Els estudis efectuats han demostrat que l'oxidació electroquímica pot mineralitzar completament els productes farmacèutics en compostos biodegradables i no tòxics, però aquesta tecnologia encara no s'ha implementat a gran escala. En aquest treball es pretén dissenyar un procés per a tractar mitjançant oxidació electroquímica un corrent d'aigües negres, d'alta concentració i cabal relativament baix, provinents d'un típic hospital escocès de 1.000 llits.

El procés proposat s'ha dissenyat per tractar un cabal màxim d'aigües negres de 60 m^3/dia, les quals tenen una concentració de contaminants farmacèutics d'1 mg/L. S'ha conclòs que el reactor òptim per dur a terme el procés, és un reactor electroquímic discontinu amb recirculació, el qual utilitzarà ànodes BDD i treballarà a una densitat de corrent de 100 mA/cm^2. El mòdul del reactor electroquímic proposat està constituït per una pila de 24 cel·les del tipus filtre de premsa que corresponen a una àrea d'ànode actiu de 10,1 m^2, un dipòsit extern de 7,8 m^3 i una bomba de recirculació. Es va determinar que un temps de tractament de 2,5 hores és suficient per aconseguir la mineralització del 80% dels contaminants i així produir compostos biodegradables i no tòxics. A més, es calcularen els paràmetres de rendiment del reactor i s'obtingué una eficiència instantània de corrent del 15,8% i un consum d'energia específic de 0,501 kWh/g_{COD}.

Per últim, per determinar la viabilitat d'implementar el procés proposat, es va realitzar una avaluació econòmica. Es calcularen els costos totals d'inversió i els corresponents al consum d'energia; el resultat és de 964.000 € i 389.000 €/any, respectivament. A causa del consum excessiu d'energia i de la manca de generació d'ingressos, és improbable la implementació del procés a gran escala. No obstant això, si en un futur s'aprova legislació per imposar restriccions a les concentracions de compostos farmacèutics a les aigües residuals, aquest

procés es pot implementar per minimitzar l'abocament d'aquests contaminants tòxics a les aigües superficials i garantir el compliment normatiu.

Paraules clau: contaminants farmacèutics, oxidació electroquímica, tractament d'aigües residuals hospitalàries, medi aquàtic

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DOCUMENT I: MEMORY

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LIST OF ABBREVIATIONS

Abbreviation	
AOP	Advanced oxidation process
BDD	Boron-doped diamond
BOD	Biological oxygen demand
COD	Chemical Oxygen Demand
EAOP	Electrochemical advanced oxidation process
ELOX	Electrochemical oxidation
EQS	Environmental quality standards
HBW	Hospital blackwater
HWW	Hospital wastewater
ICE	Instantaneous current efficiency
MCE	Mineralisation current efficiency
TOC	Total organic carbon
TSS	Total suspended solids
WWTP	Wastewater treatment plant

LIST OF NOMENCLATURE

Symbol

A	Available anode area
B	Electrochemical cell channel breadth
C_P	Pollutant concentration
D_a	Active species diffusion coefficient
d_e	Electrochemical cell equivalent diameter
δ	Diffusion layer thickness
$E_{specific}$	Specific energy consumption
F	Faraday's constant
I	Current
i	Current density
k	Rate constant
k_m	Mass transfer coefficient
L	Electrochemical cell channel length
m	Number of carbon atoms per pollutant molecule
n	Number of electrons consumed in mineralisation
P	Pressure
ρ	Density
$\dot{Q}$	Volumetric flowrate
Re	Reynolds number
s	Electrochemical cell electrode-wall separation
Sc	Schmidt number
Sh	Sherwood number
t	Time
T	Temperature
u	Linear flow velocity
U	Voltage
μ	Dynamic viscosity
V	Volume

DOCUMENT I: MEMORY

1. Introduction

Wastewater treatment and reuse is fundamental to ensure that the water demands of current and future generations are met. However, many toxic organics present in wastewaters, including pharmaceutical residues, are resistant to degradation by conventional treatment methods thus emerge in effluents and are discharged to the aquatic environment. Owing to their persistence and potential to impose significant harm to living organisms, pharmaceuticals have been highlighted as an essential class of emerging contaminants [1].

Despite trace quantities of over 630 pharmaceutical compounds having been detected in surface waters, worldwide, it is generally accepted that dilution is sufficient to reduce environmental concentrations to non-toxic levels [1, 2]. However, extensive research into the ecotoxicological potential of pharmaceuticals in recent years has concluded that even concentrations in the low μg L^{-1} range can have severe detrimental effects on aquatic organisms [3]. Furthermore, the presence of pharmaceuticals in the aquatic environment is expected to increase as a result of the growing dependence on medicines in modern day healthcare systems [2]. In Scotland, alone, over 103 million items were prescribed in 2018-2019, representing an increase of over 20% in just ten years [4]. This excessive use is attributable to ageing populations, technological advancements and tendency to prescribe pharmaceuticals for conditions that were previously not medicalised [2].

Water pollution by pharmaceuticals has been recognised as an environmental issue of serious concern in recent decades therefore significant research efforts have been made for the development of technologies for the removal of recalcitrant pharmaceuticals in wastewater. Such technologies have not yet been implemented on a large-scale due to lack of economic and legislative incentive.

The application of electrochemical techniques for the degradation of pharmaceuticals in wastewater matrices has been researched extensively and electrochemical oxidation (ELOX), in particular, has gained attention due to its simplicity and environmental compatibility [5]. ELOX process and cost efficiencies are enhanced when treating waters with high pollutant

concentrations therefore treatment of relatively low volume, high concentration hospital blackwater has been identified as a promising method for minimising the discharge of pharmaceuticals to aquatic environments [6]. This work comprises a proposal for the treatment of source-separated hospital blackwater using electrochemical oxidation and includes a discussion on the economic feasibility of large-scale process implementation.

1.1 Project Objectives

The overall objective of this project was to develop a design proposal for an electrochemical reactor capable of removing pharmaceutical pollutants in source-separated blackwater from a typical Scottish hospital of 1,000 beds. Specific project objectives included:

- Analysing hospital wastewater data to determine key process parameters and identify priority pharmaceutical pollutants.
- Reviewing experimental work on the ELOX of priority pharmaceuticals to determine an optimal reactor configuration and operating conditions.
- Developing a proposal for the overall blackwater treatment process.
- Producing a detailed design proposal for the electrochemical reactor module in addition to the preliminary design of additional equipment.
- Evaluating process economics to determine the feasibility of large-scale implementation.
- Developing a deeper understanding of the detrimental impacts of pharmaceuticals in the environment and gaining an awareness of the need for technology development for the removal of toxic organics in wastewater.

1.2 Thesis Structure

This thesis is comprised of 10 sections, including the introduction. Background information concerning the presence of pharmaceuticals in the environment and the basic principles of ELOX are presented in *Sections 2-3*. *Sections 4-5* contains a basic overview of the proposed process and details of hospital blackwater analytics. Conclusions from the review of experimental work are discussed in *Section 6* and basic design proposals for preliminary equipment are presented in *Section 7.* The primary part of this work is presented in *Section 8*

which includes the detailed design proposal for the electrochemical reactor module and a discussion of the findings and limitations of this project are presented in *Section 9*. *Section 10* contains the key conclusions of this project and information regarding the budget and proposed plans are presented in subsequent documents, Document II: Budget and Document III: Plans, respectively.

2. Pharmaceutical Pollutants in the Environment

2.1 Classification of Pharmaceuticals

Pharmaceuticals are used extensively in modern healthcare for the treatment, diagnosis, curing and prevention of medical conditions. Significant variations exist between the chemical structures, physiological effects and action mechanisms of pharmaceuticals therefore classification systems are in place for ease of identification and comparison. Pharmaceuticals are most commonly grouped by therapeutic class which describes the intended pharmacologic action and use. Therapeutic classes of pharmaceuticals include but are not limited to [7]:

- Analgesics and anti-inflammatories such as acetaminophen and ibuprofen.
- Antibiotics which include macrolides such as clarithromycin and fluoroquinolones such as norfloxacin.
- Beta blockers such as atenolol and sotalol.
- Psychiatric drugs such as carbamazepine and venlafaxine.

An exhaustive list of the therapeutic drug classes used in this study is presented in *Annex 1.*

2.2 Source of Pharmaceuticals in the Environment

Sources of pharmaceuticals in the environment include: human excretion, application in farming and fishing industries and improper disposal of excess medicines [1]. Human excretion is recognised as a primary source of pharmaceutical pollutants in the aquatic environment; after consumption, a significant proportion of pharmaceuticals are excreted as a mixture of the drug's parent compound and its metabolites in urine and faeces. Blackwater, containing urine, faeces and flush water is discharged to the sewer network and comprises a fraction of the total wastewater stream. The majority of pharmaceuticals, hormones and pathogens present in domestic wastewater originates from blackwater [8].

Pharmaceutical consumption is considerably greater in hospital environments than in the wider community; it is estimated that up to 14% of total pharmaceutical consumption in Europe occurs in hospitals [9]. Consequently, hospital blackwater contains pharmaceutical

pollutants in comparatively high concentrations. Wastewater, including blackwater from hospitals, is processed in conventional wastewater treatment plants (WWTP) before return to the aquatic environment. This process is illustrated in *Figure 1*.

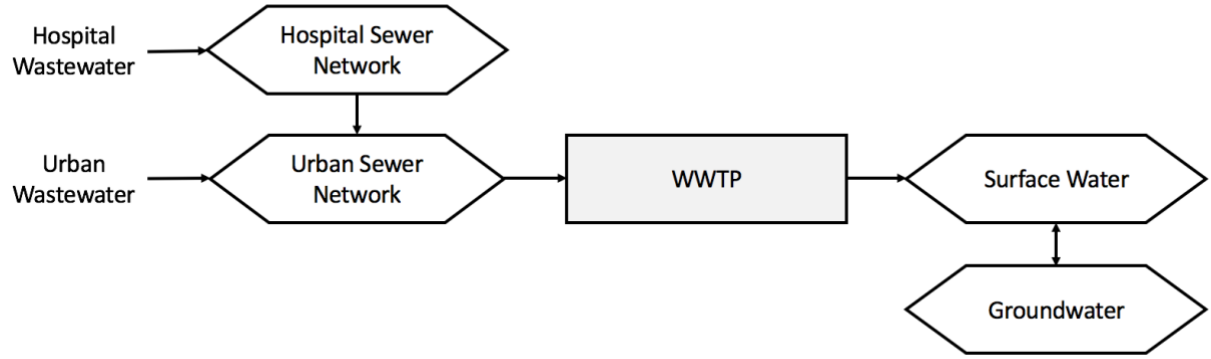


Figure 1 - Simplified schematic of hospital wastewater treatment (adapted from [10])

The fundamental objective of wastewater treatment is to prevent environmental harm. Release of untreated wastewater can cause oxygen depletion in receiving waters due to organics biodegradation, promote the spread of water-borne pathogens and damage ecosystems by eutrophication [11]. The degree of treatment in conventional WWTPs is dependent on the sensitivity of receiving waters and the population equivalent of the area it serves. WWTPs may comprise the following stages [11]:

1. Preliminary treatment: Screening of large solids and removal of grit and gravel.
2. Primary treatment: Settling of larger, typically organic, suspended matter.
3. Secondary treatment: Biological degradation of organic matter using either biological filtration or activated sludge processes.
4. Tertiary treatment: Additional treatment to address specific pollutants and pathogens.

The majority of WWTPs in Scotland are, at minimum, secondary treatment facilities; tertiary treatment is applied only when discharging to sensitive areas [11].

The occurrence of pharmaceutical residues in WWTP effluents can be attributed to poor microbial degradation and low or null potential for adsorption to sludge [12]. Pollutant removal efficiencies vary significantly depending on factors including: type of pharmaceutical and their degradation kinetics, temperature, retention times, influent composition and sludge characteristics [12]. High removal efficiencies of up to around 90% are commonly observed for non-steroidal anti-inflammatory drugs like acetaminophen, however, much lower removal efficiencies are typical for macrolide and fluoroquinolone antibiotics, lipid regulators and steroid hormones [12]. For example, fluoroquinolone antibiotic, norfloxacin, is extremely resistant to biodegradation; it possesses a very stable, complex structure and its antimicrobial activity is detrimental to microorganisms in biological treatment [13].

At present, conventional WWTPs are not designed specifically for the elimination of pharmaceutical residues, however, to combat potential environmental issues, it is fundamental to implement innovative pollutant removal solutions.

2.3 Environmental Impact

The presence of recalcitrant pharmaceuticals in the environment poses a serious threat to local ecosystems. Many pharmaceuticals are extremely resistant to biodegradation therefore persist in the environment and evoke biological responses in non-target organisms existing in polluted waters [3]. Adverse effects to organisms include: direct toxicity, endocrine system disruption and potentially induced drug resistance in pathogenic organisms [3]. The ecotoxicological potential of different pharmaceuticals has been reported extensively in literature; toxic effects are reported as acute or chronic. Acute toxicity describes short-term effects whilst chronic toxicity describes the long-term effects after exposure.

Endocrine-disrupting pharmaceutical pollutants such as steroid hormone, 17α–ethinylestradiol, can induce severe adverse effects to the hormonal functions of non-target organisms which can result in: feminisation of male species, reduced fertility and inhibited sexual organ development [3]. It has been reported that the presence of sex hormones, estrogen and progestogen, in waters at concentrations as low as 1 μg L^{-1} can promote the feminisation of male fish [14]. Antibiotic resistance is regarded as a major threat

to global health; there is concern that the presence of antibiotic residues in the aquatic environment may contribute to this issue. Antibiotic resistance occurs when pathogenic organisms such as bacteria alter their response to specific pharmaceuticals after being subjected to continuous exposure [15].

2.4 Environmental Legislation

In Scotland, hospital blackwater is discharged to the foul sewer network where it is combined with urban wastewater prior to treatment. Discharge to the foul sewer network is regulated by sewerage undertakers, Scottish Water, and must be in compliance with the Sewerage (Scotland) Act 1968 [16]. Entry requirements to sewer networks include a maximum temperature of 43.3^{o}C and pH between 6-10; maximum organic loading conditions are imposed only to non-domestic trade effluents [17].

Under regulations outlined by Scottish Water and the Scottish Environment Protection Agency, pollutant monitoring in surface water is compulsory, however, there are currently no environmental quality standards (EQS) for pharmaceuticals [2]. Under the EU Water Framework Directive, EQS have been established for a number of priority substances which impose maximum allowable surface water concentrations. Amendments to this directive in 2015 included a watch list mechanism for the temporary monitoring of pollutants which may pose an environmental risk. Pharmaceutical pollutants highlighted in amended watch lists include [18, 19]:

- 17α–ethinylestradiol
- 17β–estradiol
- Macrolide antibiotics
- Amoxicillin
- Ciprofloxacin
- Sulfamethoxazole
- Trimethoprim
- Venlafaxine and O-desmethylvenlafaxine
- Azole compounds

Despite appearing frequently on amended watch lists, no pharmaceuticals have been promoted to priority substance status hence there remains no legislation in place to restrict the concentration of pharmaceuticals in the aquatic environment.

2.5 Emerging Pollutant Removal Techniques

Growing concern about the presence of pharmaceuticals in global waters has encouraged the development of removal techniques including advanced oxidation processes (AOPs) and physical treatment methods. Advanced pollutant removal techniques should be used in combination with conventional wastewater treatment.

2.5.1 Physical Treatment

Physical treatment methods such as adsorption and membrane technologies are efficient at isolating diluted pollutants from wastewater [1]. Adsorption techniques are implemented in various industries and involve the use of solid adsorbents which, when in contact with wastewater, interact with dissolved contaminants, removing them from the bulk liquid [20]. Activated carbon adsorbents have been studied extensively for wastewater treatment; high removal efficiencies have been attained for a range of pharmaceuticals including ibuprofen, fluoroquinolones and floxacins using powdered activated carbon adsorbents [1]. Use of this adsorbent in industrial-scale wastewater treatment is restricted due to high manufacturing costs and poor regeneration efficiency [3].

Numerous membrane processes have also been investigated for pollutant removal including: forward and reverse osmosis, nanofiltration and ultrafiltration [1]. It has been shown that pharmaceutical pollutants, namely anti-inflammatory drugs and fluoroquinolones, can be removed using a combination of bioreactor membranes and reverse osmosis at elimination levels exceeding 99% [21]. The fundamental issue with both adsorption and membrane technologies is that pollutants are simply transferred from one phase to another; pharmaceuticals are not degraded therefore may still find a pathway into the environment.

2.5.2 Advanced Oxidation Processes

AOPs have been identified as extremely promising for the degradation of complex organic pollutants. AOPs are based on the *in situ* production of strong oxidants such as the hydroxyl radical, •OH, which are capable of mineralising organics into non-toxic compounds, CO_2 and water [22]. A summary of the different AOP classes including examples of each is presented in *Figure 2*.

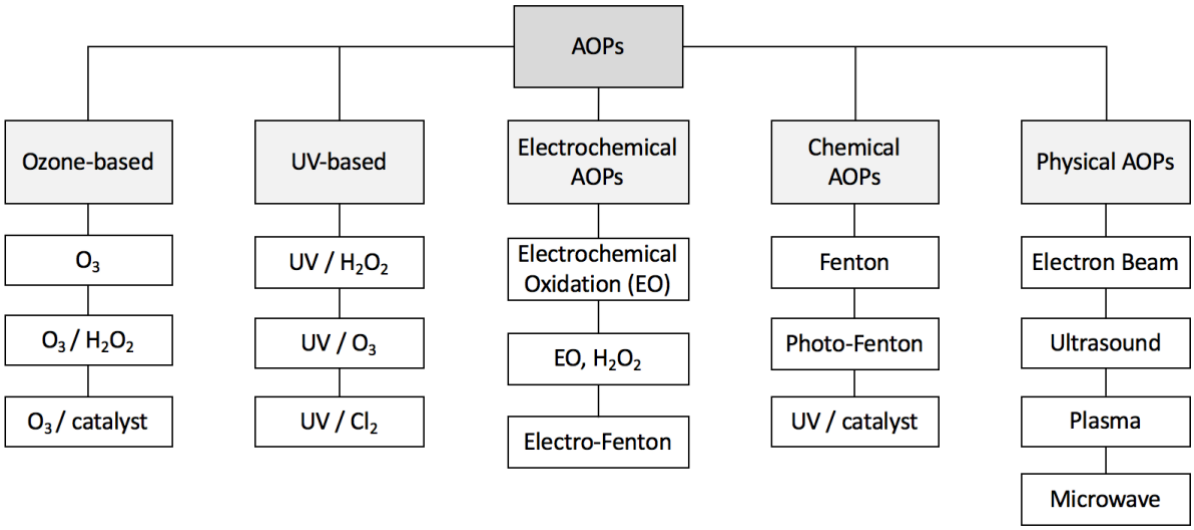


Figure 2 - Overview of advanced oxidation processes (adapted from [23])

Ozone-based AOPs involve the addition of ozone, O_3, to contaminated wastewaters for the degradation of microorganisms and organics. As ozone is particularly powerful and highly unstable, it is commonly generated *in situ* prior to use. Commercial ozone generation is based on the corona discharge process which involves applying a high voltage discharge to ambient air or oxygen gas [24]. Ozonation is a well-established technique; it is efficient for degrading a wide range of organics and does not result in chemical residues, however, it requires expensive equipment, can result in the formation of unwanted intermediates and requires large amounts of energy [3].

The use of Fenton's reagent is recognised as one of the most effective AOPs for wastewater treatment [25]. The addition of Fenton's reagent, comprised of aqueous Fe^{2+} ions and H_2O_2, results in the generation of powerful oxidants; Fe^{2+} ions catalyse the decomposition of H_2O_2 into hydroxyl radicals which subsequently react with and destroy organic pollutants [25].

Despite high pollutant removal efficiencies attained using Fenton's reagent, disadvantages restricting its application include: requirement of a strict acidic environment, generation of ferric sludge and high H_2O_2 consumption [25].

In recent decades, electrochemical advanced oxidation processes (EAOPs) have been identified as a promising class of AOP thus significant research efforts have been made for their development. In EAOPs, energy is supplied to promote the *in situ* electrochemical generation of powerful oxidants. EAOPs include: electrochemical oxidation, electrochemical oxidation with electrogenerated H_2O_2 and the electro-Fenton process [22]. Electrochemical oxidation (ELOX), the simplest and most common EAOP, is the technique proposed for pharmaceutical pollutant removal in this work and is discussed in depth in *Section 3.*

3. Electrochemical Oxidation

3.1 Basic Principles of Electrochemical Treatment

Electrochemical treatment involves the application of electrical current to a medium to promote chemical reactions. With regards to the removal of recalcitrant pollutants in wastewater by ELOX, current is applied to promote the breakdown of organic matter.

Electrochemical processes are conducted in specialised reactors; a simplified electrochemical reactor model for the ELOX of wastewater is presented in *Figure 3.*

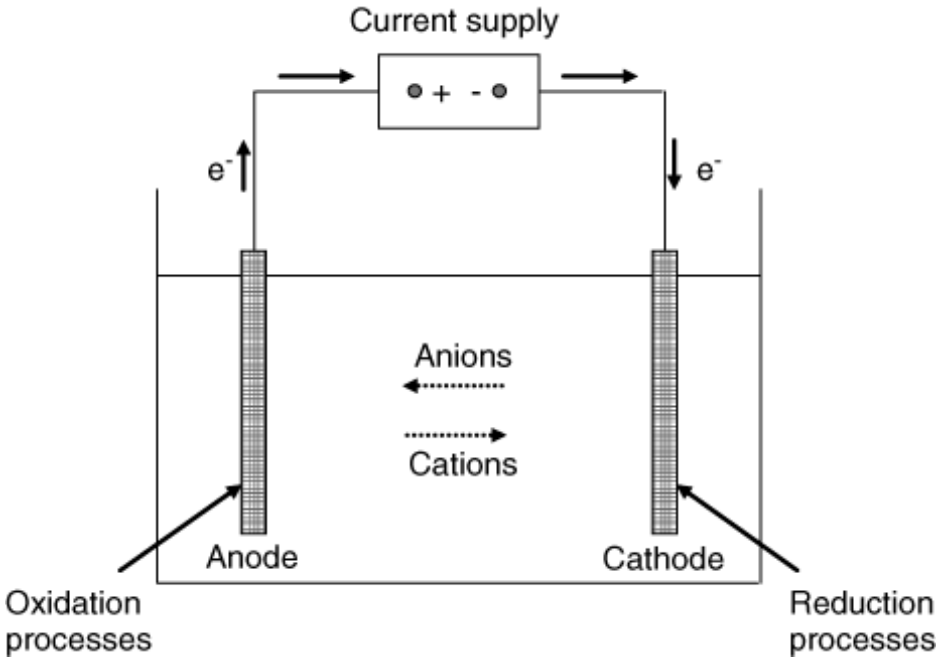


Figure 3 - Conceptual model of reactor for wastewater ELOX [26]

Electrochemical reactors comprise the following fundamental components [27]:

- ***Power Supply**:* A direct current power supply provides electrical current to the system thus supplies the energy required to drive nonspontaneous reactions.
- ***Anode(s)**:* Electrochemical reactors must contain a minimum of one positively charged anode at which species are oxidised via the transfer of electrons to the anode surface, as shown in *Eq. (1)*, where *Red* and *Ox* represent reduced or oxidised species, respectively, and *z* is the number of electrons exchanged [27]:

$$Red \rightarrow Ox + ze^{-} \qquad \textit{Eq. (1)}$$

- ***Cathode(s)**:* Electrochemical reactors must contain a minimum of one negatively charged cathode at which species are reduced via the transfer of electrons from the cathode surface, as shown in *Eq. (2)* [27]:

$$Ox + ze^{-} \rightarrow Red \qquad \textit{Eq. (2)}$$

- ***Electrolyte**:* The intermediate space between the anode and cathode is occupied by an electrolyte. In *Figure 3,* this is the liquid in which both electrodes are immersed. Electrolytes, typically in solution form, conduct charged species to their respective electrodes; positively charged cations migrate to the cathode whilst negatively charged anions migrate to the anode [28]. For wastewater ELOX, the electrolyte is the polluted wastewater itself.
- ***External path for current flow**:* External electrical connections between electrodes and the power supply closes the circuit thus allowing current to flow.

3.2 Advantages of Electrochemical Oxidation

In comparison to other pharmaceutical removal techniques, ELOX presents many advantages. Above all, ELOX is an environmentally compatible process as the primary reagent, the electron, is clean; there is no requirement for chemical addition thus no need for subsequent steps to eliminate potentially hazardous by-products [5]. Electrochemical processes, in general, are extremely versatile; they are applicable to systems handling a range of organic pollutants and fluctuating volumetric flowrates [29]. Moreover, unlike techniques such as adsorption and membrane processes in which pollutants are simply transferred from one phase to another, ELOX may be employed to achieve total mineralisation, and therefore completely eliminating environmental risk [30].

3.3 Mineralisation of Organic Pollutants by Electrochemical Oxidation

ELOX is recognised as an extremely promising technique for the mineralisation of complex organics therefore has been extensively researched for the removal of recalcitrant pharmaceutical pollutants in wastewater. Complete mineralisation constitutes the breakdown of organic matter into non-toxic compounds, CO_2 and water, in addition to other products such as NH_4^+ and Cl^- depending on initial composition [31]. For complex pharmaceutical pollutants, this involves breakdown into a series of intermediate compounds first which are then further mineralised into shorter-chain compounds, as shown by the general reaction in *Figure 4.*

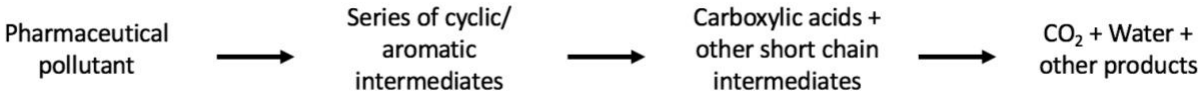


Figure 4 - Generalised pathway for pharmaceutical pollutant mineralisation (interpreted from [32])

Incomplete mineralisation of toxic pharmaceuticals yields numerous metabolites [31]; so long as these are biodegradable and have reduced toxicity, biological treatment can be applied to the electrochemical reactor product stream for complete removal.

3.3.1 Direct and Indirect Oxidation Mechanisms

During ELOX, organic pollutants can be oxidised via direct or indirect mechanisms, as shown in *Figure 5.* Direct oxidation involves the transport of pollutants to the anode surface at which the pollutant is oxidised via direct electron transfer to the anode [22]. Indirect oxidation involves the interaction between the pollutant and mediated oxidant species which include electro-generated oxidants adsorbed at the anode surface and oxidants pre-existing in solution [22].

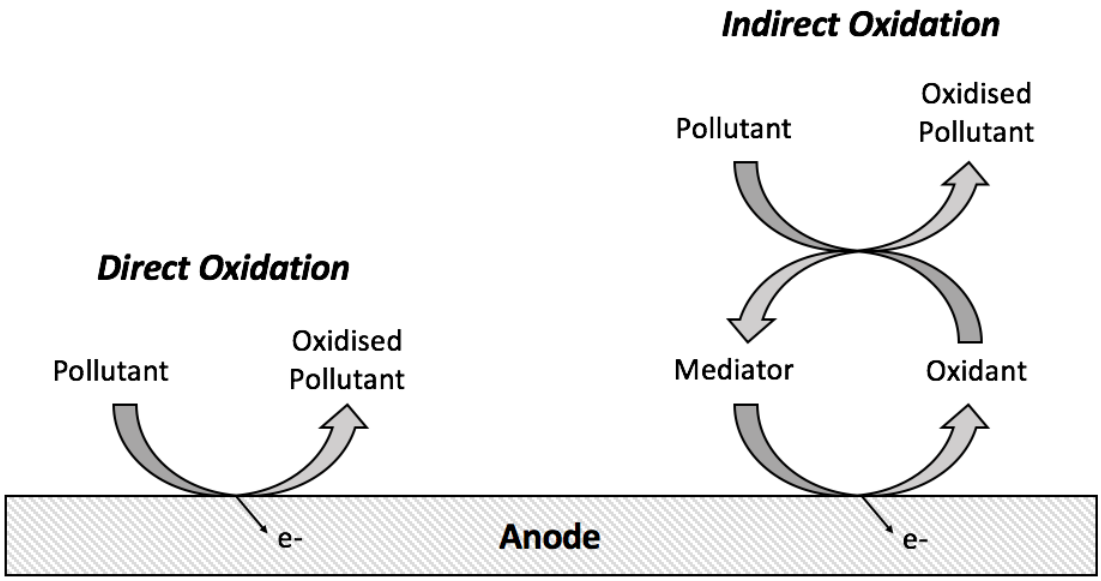


Figure 5 - Schematic of direct and indirect oxidation mechanisms (adapted from [33])

The primary electro-generated oxidant in ELOX is the hydroxyl radical (•OH) which is generated and subsequently adsorbed at the anode surface (M) via the direct oxidation of water and hydroxyl ions as shown in *Eq. (3)* and *Eq. (4)* [31]:

$$M + H_2O \rightarrow M(\bullet OH) + H^+ + e^- \qquad \textit{Eq. (3)}$$

$$M + OH^- \rightarrow M(\bullet OH) + e^- \qquad \textit{Eq. (4)}$$

Hydroxyl radicals are strong, non-selective oxidant species capable of degrading the majority of organics including highly recalcitrant pharmaceuticals [22]. The type of interaction between electro-generated hydroxyl radicals and the anode surface significantly impacts the performance of ELOX processes.

3.3.2 Active and Non-Active Anodes

Active anodes, such as platinum, have low oxidation power and yield strongly chemisorbed "active oxygen" at their surface [30]. Interaction with the anode material results in the transformation of adsorbed hydroxyl radicals into higher state oxides (MO), as shown in *Eq.*

(5) [22]. The higher state oxide, in combination with the anode surface, act as the mediator for organics oxidation, shown in *Eq. (6)*, where *R* represents the organic pollutant [31]:

$$M(\bullet OH) \rightarrow MO + H^+ + e^- \qquad \textit{Eq. (5)}$$

$$MO + R \rightarrow M + RO \qquad \textit{Eq. (6)}$$

ELOX using active anodes cannot achieve complete mineralisation of organics and yields numerous refractory products [30].

Higher degrees of organics mineralisation with the production of less or null amounts of recalcitrant intermediate products can be achieved using non-active anodes [22]. Non-active anodes, such as boron-doped diamond (BDD), have high oxidation power and yield weakly physisorbed hydroxyl radicals at their surface which mediate the oxidation of organics [30]. Complete mineralisation is possible using non-active anodes, as shown in *Eq. (7)*, where *R* represents an organic compound comprising only of carbon and hydrogen which requires one oxygen atom for total oxidation [31]:

$$M(\bullet OH) + R \rightarrow M + mCO_2 + nH_2O + H^+ + e^- \qquad \textit{Eq. (7)}$$

Typically, the interaction between the anode surface and adsorbed hydroxyl radicals is weaker for higher oxidation power anodes and as a result, chemical reactivity towards organic pollutants is greater [22]. Oxidation power is explicitly related to oxygen evolution overpotential, thus, BDD anodes, with high potentials for oxygen evolution of 2.2 – 2.6V, are considered optimal for ELOX [22].

3.4 Measuring the Performance of Electrochemical Oxidation

The performance of ELOX processes can be assessed using a variety of measurements. Quantifying percentage degradation and mineralisation indicates the degree to which target organic pollutants are broken down. Percentage degradation is a measure of the reduction in pollutant concentration, C_p, whilst percentage mineralisation quantifies the reduction in total

organic carbon (TOC) where TOC is the amount of carbon bound in all organic compounds [30]. The equations used to determine percentage degradation and mineralisation are presented in *Eq. (8)* and *Eq. (9),* respectively.

$$\%\ Pollutant\ Degradation = \frac{C_{p,initial} - C_{p,final}}{C_{p,initial}} \times 100 \qquad \textit{Eq. (8)}$$

$$\%\ Pollutant\ Mineralisation = \frac{TOC_{initial} - TOC_{final}}{TOC_{initial}} \times 100 \qquad \textit{Eq. (9)}$$

Pollutant destruction may also be expressed in terms of the reduction in chemical oxygen demand (COD) where COD is the oxygen required for total pollutant decomposition by chemical reaction.

As discussed in *Section 3.3*, organic pollutants are mineralised via a series of intermediates which may vary in terms of both toxicity and biodegradability [34, 35]. It is fundamental to understand pollutant mineralisation pathways in order to identify potential intermediate products. This dictates what mineralisation percentage is required to improve the overall biodegradability of wastewater whilst minimising its toxicity.

Process performance can also be assessed by determining specific energy consumption and mineralisation current efficiency (MCE). MCE quantifies what percentage of current supplied to the system is utilised for pollutant mineralisation and can be calculated using *Eq. (10)* [35]:

$$MCE\ \% = \frac{nFV(\Delta TOC)}{4.32 \times 10^7 mIt} \times 100 \qquad \textit{Eq. (10)}$$

Where *n* is the number of electrons consumed for each pollutant molecule, *F* is Faraday's constant (96,485 C $mol_{e^-}^{-1}$), *V* is the solution volume (L), *ΔTOC* is the change in TOC (mg L^{-1}), *4.32 x* 10^7 is a conversion factor, *m* is the number of carbon atoms in each pollutant molecule, *I* is the applied current (A) and *t* is the electrochemical treatment time (hr).

Specific energy consumption, $E_{specific}$, is the energy required for the electrochemical treatment of a unit amount of polluted water which may be expressed in terms of kWh g_{COD}^{-1} or kWh $m_{solution}^{-3}$ [36]. $E_{specific}$, in terms of kWh g_{COD}^{-1}, can be calculated using *Eq. (11).*

$$E_{specific} = \frac{IU\Delta t}{V\Delta COD} \qquad \textit{Eq. (11)}$$

Where I is applied current (A), U is total voltage (V), Δt is treatment time, V is volume (m^3) and ΔCOD is change in COD (g m^{-3}).

4. Hospital Blackwater Treatment

4.1 Electrochemical Oxidation as Pre-Treatment

Wastewater ELOX can be implemented as pre-treatment before discharge to sewers or as tertiary treatment in conventional WWTPs. The former is recognised as very promising as it can be used to treat smaller volumes of more concentrated wastewaters thus reducing required equipment capacities and associated costs. ELOX pre-treatment serves to partially mineralise pollutants into biodegradable compounds which can be removed entirely in conventional WWTPs, however, for tertiary treatment, complete mineralisation is required for removal which requires longer treatment times. Another disadvantage of using tertiary treatment is that pharmaceuticals may accumulate in the sludge commonly re-used as fertiliser, presenting an alternate route into the environment [37].

As a relatively large proportion of pharmaceuticals are consumed in hospitals, it is recognised that ELOX pre-treatment of hospital wastewaters offers a promising solution to reduce the presence of toxic pollutants in the aquatic environment.

4.2 Source Separation of Blackwater

Source separation has been explored extensively for wastewater treatment. Separation methods can be implemented to yield three streams: blackwater, grey water and rain water. As they vary significantly in terms of quantity and quality, each can be treated using optimal, stream specific methods. Blackwater, comprised of urine, faeces and flush water, presents a relatively concentrated, low volume stream containing the majority of pharmaceutical residues [8] therefore ELOX of blackwater is more effective in comparison to treating the entire wastewater stream. Furthermore, this reduces the cost of both implementation and operation of the technology.

Treatment of source-separated urine has been proposed in literature for the removal of pharmaceuticals; micropollutant concentrations in urine are 100-500 times greater than in conventional wastewater streams, providing optimal treatment conditions [38]. Approximately 70% of pharmaceuticals and their metabolites are excreted in urine with the

remaining in faeces [39]. The excretion of metabolites in faeces is often negligible, however, it typically contains non-metabolised parent drugs with high toxic potentials [39]. Therefore, treatment of less concentrated blackwater in comparison to source-separated urine was concluded to be more beneficial in terms of reducing overall toxicity.

4.3 Overview of Proposed Process

The proposed process is designed to treat source-separated hospital blackwater. It is assumed that source separation methods are already in place and blackwater is directed to the treatment facility. Electrochemical reactor effluent will be discharged to the sewer network and transported to a nearby WWTP where it is treated using conventional methods. A block flow diagram of the proposed process is presented in *Figure 6.* It should be noted that the three-way valve and recirculation pump are included to aid with the understanding of the overall process.

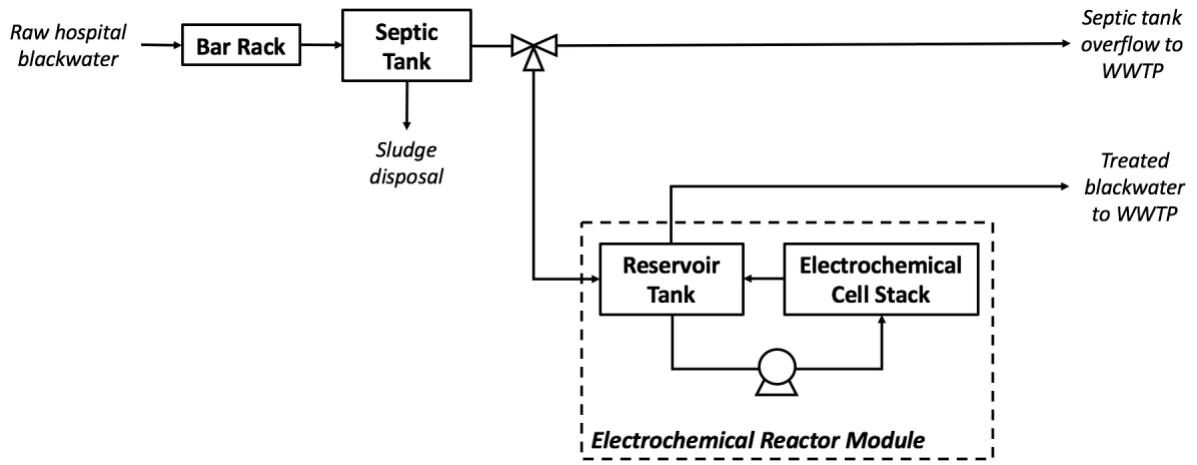


Figure 6 – Block flow diagram of proposed hospital blackwater treatment process

The function of each major piece of equipment in the process is discussed below:

- *Bar rack:* A bar rack is in place for the initial screening of unwanted solids such as wipes or medical swabs that may cause pipeline blockages or damage to downstream equipment.

- *Septic tank:* The septic tank has two primary functions: to segregate suspended solids and digest readily biodegradable organic matter in the incoming stream. This prevents solids entering the electrochemical reactor downstream and reduces the COD of blackwater. The tank also transforms flow from being continuous to discontinuous; septic tank effluent is discharged intermittently for the filling of the batch operated electrochemical reactor. The three-way valve at the outlet allows blackwater to be expelled to the sewer in the case of tank overfill. The sludge accumulated at the bottom of the septic tank will be removed periodically (every 3 months), disposed of to the foul sewer network and subsequently processed at a nearby WWTP.

- *Electrochemical reactor:* The electrochemical reactor module, comprised of an external reservoir tank and stack of filter-press electrochemical cells, operates in batch recirculation mode. The fundamental purpose of the reactor is to mineralise pharmaceutical pollutants in hospital blackwater thus reducing toxicity and enhancing biodegradability before discharge to the sewer network. It should be noted that two additional pumps, not pictured in *Figure 6,* are required for the filling and emptying of the reservoir tank.

It is proposed that the septic tank is installed in the hospital grounds and is buried such that the lid is at ground level to allow easy access for inspections and sludge clearing. The electrochemical reactor module, including all associated pumps and piping, will be housed in a separate building located within close proximity to the septic tank and hospital. It is assumed that the building will be located such that the electrochemical reactor effluent can be discharged to the foul sewer without requiring the construction of an excessive and complicated piping system. Additionally, it is proposed that the air within the building containing the reactor module is vented to the atmosphere via a bio filter as this will help to prevent unwanted odours escaping. An example hospital site map and a proposed floor plan for the blackwater treatment plant are provided in plans 1 and 2, respectively.

5. Hospital Blackwater Analytics

Data on hospital wastewater available in literature was analysed to determine the characteristics of source-separated blackwater from a typical Scottish hospital of 1,000 beds. Properties of hospital wastewater vary considerably depending on factors including: number and type of wards, geographical and cultural factors, general services on offer and management policies [40]. To minimise errors arising due to this variability, data was primarily collected from reports on similarly sized hospitals located in Europe.

5.1 Blackwater Characteristics

The properties of hospital blackwater required to proceed with the design of the waste treatment system were determined and are presented in *Table 1* below. The daily volumetric flow of blackwater was estimated based on the average consumption of water in Scottish hospitals; in an acute hospital housing over 100 beds, between 0.531 and 0.710 m^3 bed^{-1} day^{-1} of water are used [41]. It was assumed that 80% of the water consumed is released and that blackwater comprises approximately 10% of the total wastewater stream. To account for variability, the system was designed to handle maximum flow. Other parameters presented in *Table 1* were estimated using data from reports on hospital wastewater.

Table 1 - Hospital blackwater characteristics (adapted from [42, 43, 44])

Parameter	Value
Volumetric Flowrate	60 m^3 day^{-1}
Average Temperature	15 °C
pH	7.4
Conductivity	1700 µS cm^{-1}
COD	650 mg L^{-1}
BOD	260 mg L^{-1}
TSS	330 mg L^{-1}

5.2 Pharmaceutical Pollutant Concentrations

Concentrations of pharmaceutical pollutants in hospital blackwater were approximated using available data on typical hospital wastewater compositions. This analysis highlighted priority

pharmaceutical pollutants which was fundamental in forming the basis of the electrochemical reactor design.

Composition data on 20 hospital wastewater matrices was collected and stored in a database. An average concentration of each pollutant was calculated, omitting extreme outliers, and additional findings including the therapeutic class, frequency of detection and environmental impact of each pharmaceutical were recorded. To convert to concentrations in hospital blackwater, it was assumed that all pharmaceuticals present in the total wastewater stream were excreted in the urine and faeces of patients [8]. Average concentrations of pharmaceuticals by therapeutic class are presented in *Table 2* and a simplified blackwater analytics database is provided in *Annex 2 (Table 17).*

Table 2 - Concentrations of pharmaceuticals by therapeutic class in hospital blackwater (adapted from [7, 43, 45, 46, 47])

Therapeutic Class of Pharmaceutical	Average Concentration in HBW [µg L^{-1}]
Antibiotics	402
Analgesics/ Anti-inflammatories	341
Diuretics	115
Beta Blockers	61
Receptor Antagonists	26
Psychiatric Drugs	25
Lipid Regulators	15
Anti-hyperintensives	4
Barbiturates	3
Anti-diabetics	1
Beta Agonists	1
Hormones	1
Total	**995**

As shown in *Table 2*, the total concentration of pharmaceutical pollutants in hospital blackwater was estimated to be 995 µg L^{-1}. To proceed with the design of equipment, this was rounded to 1 mg L^{-1}.

5.2.1 Priority Pollutants

A small number of priority pollutants were identified and assumed to be representative of all pharmaceuticals in hospital blackwater in order to reduce the complexity of the electrochemical reactor design process.

To determine priority pollutants, a number of criteria were established including: average concentration in blackwater, environmental impact and availability of experimental data. The environmental impact of each pollutant was assessed based on: persistence in the environment, potential for bioaccumulation and toxicity. Pollutant concentration was established as the primary selection criterion as pollutants present in greater quantities are most likely to impact the electrochemical reaction kinetics and, consequently, the overall reactor design. The concentrations and environmental impacts of the priority pollutants identified are presented in *Table 3*. It should be noted that the average concentrations of receptor agonist, ranitidine, and macrolide antibiotics, azithromycin and clarithromycin, are relatively high, however, they were not classified as priority pollutants due to lack of experimental data. Additionally, estrogen hormones, 17α-ethinylestradiol and 17β-estradiol were not considered; despite their high levels of ecotoxicity and capacity to disrupt organism endocrine systems, they exist in very low concentrations therefore do not accurately represent all pharmaceutical pollutants present in blackwater.

Table 3 - Priority pharmaceutical pollutants in hospital blackwater

Pharmaceutical Pollutant	Therapeutic Class	Concentration in Hospital Blackwater [µg L^{-1}]	Environmental Impact
Acetaminophen	Analgesics/ Anti-inflammatories	208	• *Persistence:* Inherently biodegradable. • *Bioaccumulation:* Low potential for bioaccumulation. • *Toxicity:* Moderate acute toxicity towards aquatic organisms.
Ofloxacin	Antibiotic (Fluoroquinolone)	160	• *Persistence:* Potentially persistent in the environment. • *Bioaccumulation:* Potential for bioaccumulation (limited data). • *Toxicity:* Very high acute toxicity towards aquatic organisms and potential to promote antibiotic resistance.
Ciprofloxacin	Antibiotic (Fluoroquinolone)	151	• *Persistence:* Potentially persistent in the environment. • *Bioaccumulation:* Low potential for bioaccumulation. • *Toxicity:* Very high acute toxicity towards aquatic organisms and potential to promote antibiotic resistance.
Furosemide	Diuretic	101	• *Persistence:* Potentially persistent in the environment. • *Bioaccumulation:* Low potential for bioaccumulation. • *Toxicity:* Low toxicity towards aquatic organisms.
Ibuprofen	Analgesics/ Anti-inflammatories	41	• *Persistence:* Inherently biodegradable. • *Bioaccumulation:* Low potential for bioaccumulation. • *Toxicity:* Moderate toxicity towards aquatic organisms.
Atenolol	Beta Blocker	28	• *Persistence:* Potentially persistent in the environment. • *Bioaccumulation:* Low potential for bioaccumulation. • *Toxicity:* Low toxicity towards aquatic organisms.
Sufamethoxazole	Antibiotic	27	• *Persistence:* Potentially persistent in the environment. • *Bioaccumulation:* Low potential for bioaccumulation. • *Toxicity:* Moderate chronic toxicity and potential to promote antibiotic resistance.
Trimethoprim	Antibiotic	8	• *Persistence:* Potentially persistent in the environment. • *Bioaccumulation:* Low potential for bioaccumulation. • *Toxicity:* Moderate chronic toxicity towards aquatic organisms and potential to promote antibiotic resistance.
Norfloxacin	Antibiotic (Fluoroquinolone)	2	• *Persistence:* Potentially persistent in the environment. • *Bioaccumulation:* Low potential for bioaccumulation. • *Toxicity:* Moderate to high acute toxicity towards aquatic organisms and potential to promote antibiotic resistance.

6. Review of Experimental Work on Electrochemical Oxidation

For each priority pollutant, a review of lab-scale ELOX experiments was conducted to investigate the effect of varying certain parameters on kinetics and overall process performance. Performance was primarily assessed based on MCE and the degree of pollutant degradation and mineralisation in a specified time. An investigation into the reaction pathways of each pollutant and the impact of competitive oxidation between all organics present in blackwater was also performed. Conclusions from this review were fundamental in aiding with the selection of an optimal reactor configuration and operating conditions for the full-scale electrochemical reactor.

6.1 Electrochemical Reaction Kinetics

The ELOX of all pharmaceuticals investigated exhibit pseudo-first order reaction kinetics, irrespective of configuration and operating conditions [48]. The rate expression for pharmaceutical degradation is provided in *Eq. (12)* where [PP] and [•OH] are the pharmaceutical pollutant and •OH concentrations, respectively, k is the rate constant and k_{app} is the pseudo-first order rate constant [48].

$$\frac{-d[PP]}{dt} = k[PP][\cdot OH] = k_{app}[PP] \qquad \textit{Eq. (12)}$$

Pseudo-first order kinetic behaviour is typical of mass-transfer controlled processes which are achieved when the current applied exceeds the limiting current required for the reaction [49]. In agreement with reaction kinetics, pharmaceutical degradation follows an exponential trend. Pollutant mineralisation exhibits a similar trend, however, due to proceeding via a series of complex intermediates, mineralisation demands much longer treatment times. The relationship between pollutant degradation and mineralisation over time is illustrated in *Figure 7.*

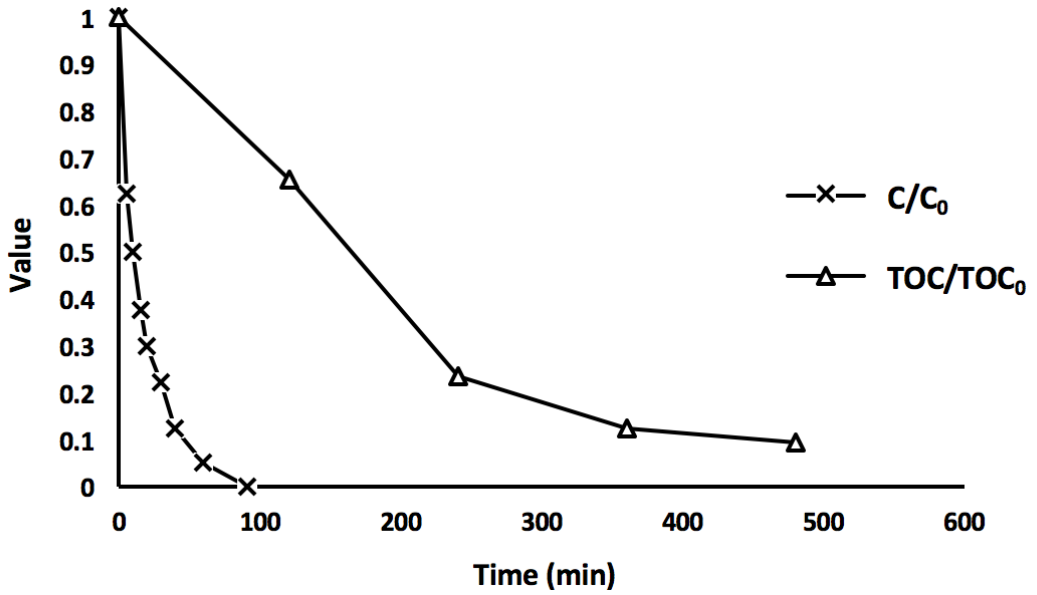


Figure 7 – Degradation (C/C_0) and mineralisation (TOC/TOC_0) of 0.2 mM ibuprofen at BDD anodes at 500 mA in 0.05 M Na_2SO_4 [50]

6.2 Impact of Varying Operating Parameters

The impact of varying the following parameters on ELOX performance was investigated: anode material and reactor configuration, current density, initial pollutant concentration, temperature and pH.

6.2.1 Reactor Configuration and Anode Material

All experimental work reviewed involved ELOX in parallel plate reactors operating in batch or recirculated batch mode. Operating in recirculated batch mode enhances flow velocities thus increases active species mass transfer and degradation rates [51]. Experiments conducted in reactors divided by a cation exchange membrane exhibited better performance compared with undivided reactors. The degree of atenolol degradation attained in 90 minutes at BDD anodes was 75% and 100% in an undivided and divided reactor, respectively [52]. A membrane results in improved performance as it prevents the reduction of intermediate products at the cathode, however, operating divided reactors requires the presence of an electrolyte such as Na_2SO_4 in the reactor's cathodic compartment [30]. The resulting oxidation of sulphates yields persulphates which increases solution toxicity [53]. Operating a

divided cell also requires greater energy input due to the increased ohmic drop across the membrane [30].

Varying anode material impacts pollutant degradation significantly; as predicted, non-active anodes were optimal. This is illustrated in the graph in *Figure 8* showing the mineralisation of acetaminophen at BDD and platinum anodes.

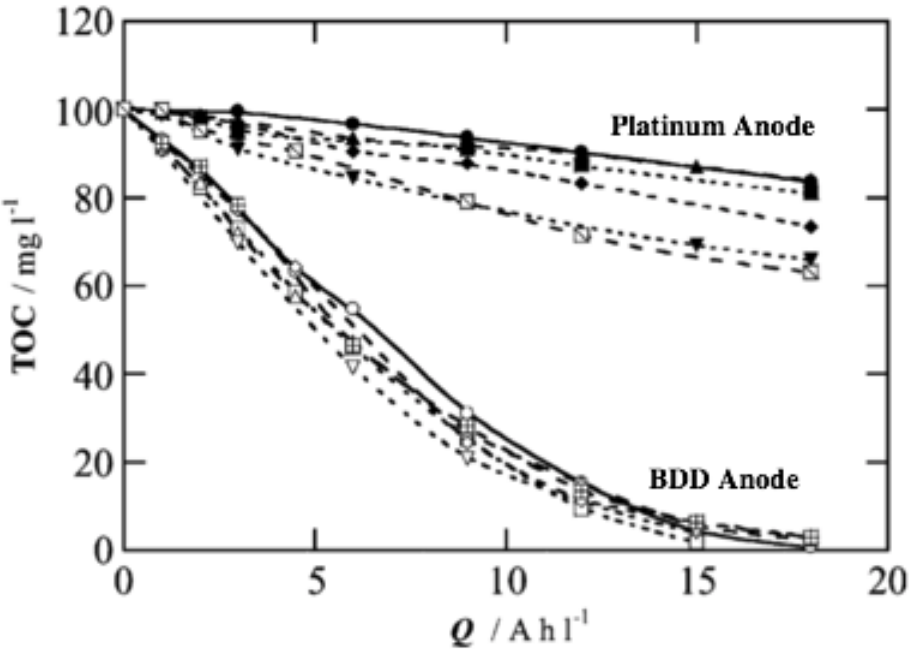


Figure 8 - TOC removal vs. specific charge for electrochemical oxidation of a 157 mg L^{-1}acetaminophen solution in 0.05M Na_2SO_4 at 300 mA and 35°C using Pt or BDD anodes at different pH values [54]

The results presented in *Figure 8* highlight non-active BDD anode as optimal for rapid and complete organics mineralisation. This corroborates the results of numerous reports on the ELOX of pharmaceuticals in which BDD is recognised as the best non-active anode. For example, the apparent degradation constants for 100 mg L^{-1} norfloxacin in an undivided batch reactor at current density of 50 mA cm^{-2} were 4.5 x 10^{-4} s^{-1} and 2 x 10^{-4} s^{-1} for BDD and ceramic anodes, respectively [30].

6.2.2 Current Density

Current density was identified as the most influential operating parameter on performance; the rate of pollutant degradation is approximately linearly dependent on applied current

density. Complete degradation of 50 mg L^{-1} ofloxacin in a divided batch reactor required only 60 minutes at i = 100 mA cm^{-2} compared with more than 150 minutes at i = 20 mA cm^{-2} [48]. The overall effect of current density on degradation is illustrated in *Figure 9* and the general relationship shown was observed for all pollutants investigated.

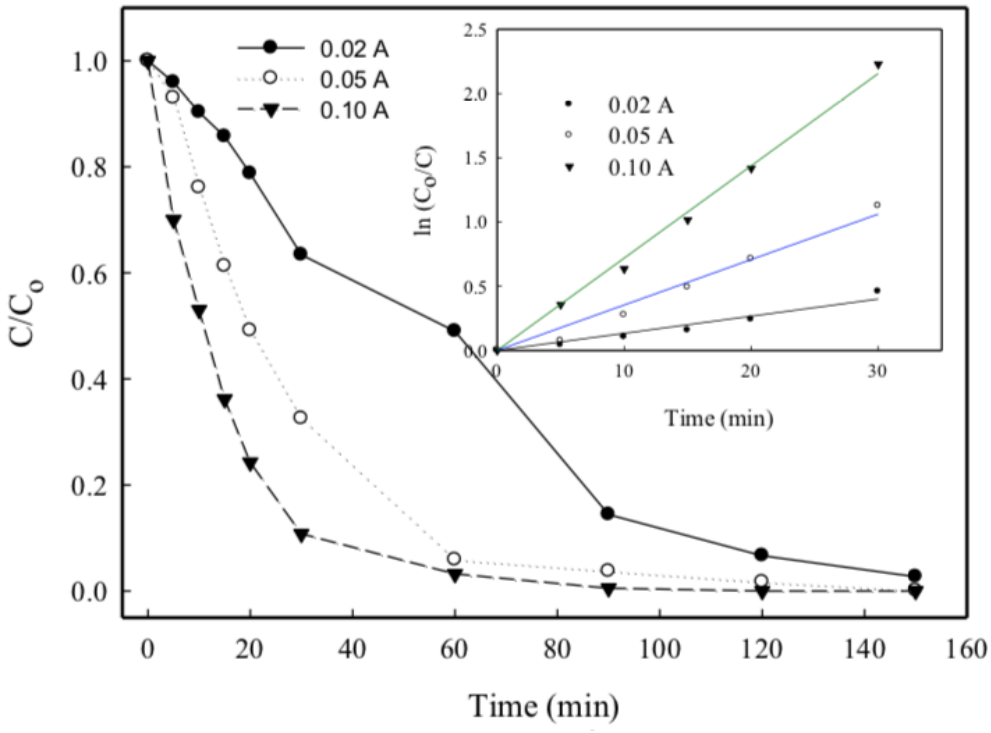


Figure 9 - Effect of current density (20-100 mA cm^{-2}) on ofloxacin degradation at BDD anode. (projected anode surface area, $1cm^2$; ofloxacin, 50 mg L^{-1}; electrolyte, 0.1M Na_2SO_4; T, 30°C; separator, AMI-7002] *[48]*

Increased pollutant degradation rate with current density is primarily due to enhanced production of active oxidant, •OH [30]. Operating at high current densities reduces treatment times for total degradation, however, is also associated with lower MCE therefore more energy is needed to achieve the same degree of degradation. For example, increasing current density from 33 mA cm^{-2} to 83 mA cm^{-2} in an experiment on the ELOX of 100 mg L^{-1} norfloxacin at BDD anodes resulted in MCE decreasing from 7.8% to 2.4% [30].

6.2.3 Pollutant Concentration

With all other parameters remaining constant, increasing initial pollutant concentration results in poorer degradation kinetics. This relationship is illustrated in *Figure 10* showing

ibuprofen degradation at non-active Ti/SnO_2-Sb/Ce-PbO_2 anode at different pollutant concentrations. The general relationship depicted in *Figure 10* was observed for all priority pollutants.

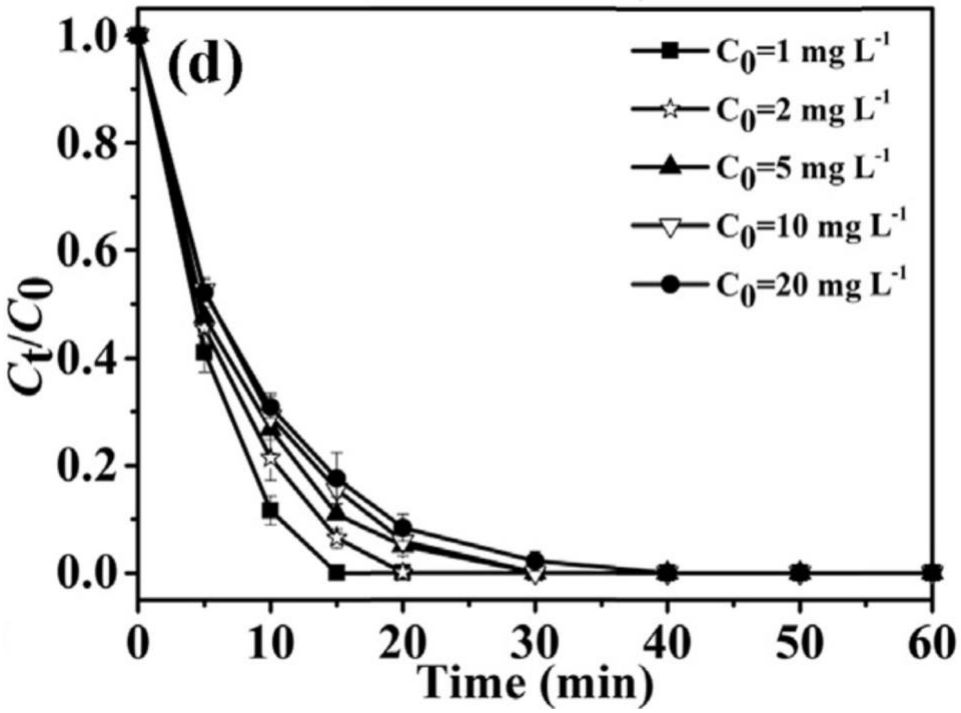


Figure 10 - Effect of initial concentration (1-20mg L^{-1}) on ibuprofen degradation at Ti/SnO2-Sb/Ce-PbO2 anode. (current density, 10 mA cm^{-2}; electrolyte, 10mM Na_2SO_4, T, 25°C) [55]

The relationship shown in *Figure 10* is explained by the greater ratio of •OH radicals to pollutant molecules; at a given current density, •OH generation is the same, however, when pollutant concentrations are low, there is a higher probability of •OH-pollutant interaction [55].

6.2.4 Temperature and pH

Degradation rates were found to increase with temperature; the degradation constant for 50 mg L^{-1} ofloxacin at a BDD anode increased from 1.2 x 10^{-3} s^{-1} to 1.5 x 10^{-3} s^{-1} upon increasing the temperature from 30°C to 70°C [48]. At higher temperatures, active species mass transfer is enhanced and kinetic rate constants increase according to the Arrhenius expression [48]. Dependence of degradation kinetics on initial pH was found to vary; the rate of

sulfamethoxazole degradation at BDD anodes was highest at neutral pH and lowest at alkaline pH whereas for ciprofloxacin, an acidic initial pH was optimal [56]. The variation in kinetics with pH and temperature is relatively insignificant compared with current density.

6.3 Reaction Pathways and Toxicity of Intermediates

For successful ELOX of pharmaceuticals, it is necessary to reduce overall toxicity whilst enhancing biodegradability. An investigation into mineralisation pathways and the variation of toxicity with intermediates production enabled the determination of a suitable mineralisation % to achieve these criteria. In the work reviewed, toxicity was measured in terms of the inhibition of bioluminescence in *Vibrio fischeri* and *Escherichia coli*. It was concluded that initial intermediate oxidation products typically present greater toxicity towards organisms, however, if mineralisation is completed to a degree where only carboxylic acids remain, toxicity is reduced and biodegradability is enhanced [56]. Variation of intermediate product toxicity is shown in *Figure 11* which represents the ELOX of furosemide at BDD anodes. The general trend depicted in *Figure 11* where toxicity initially increases and then declines at approximately 80-90% mineralisation was observed for all pollutants with available toxicity data.

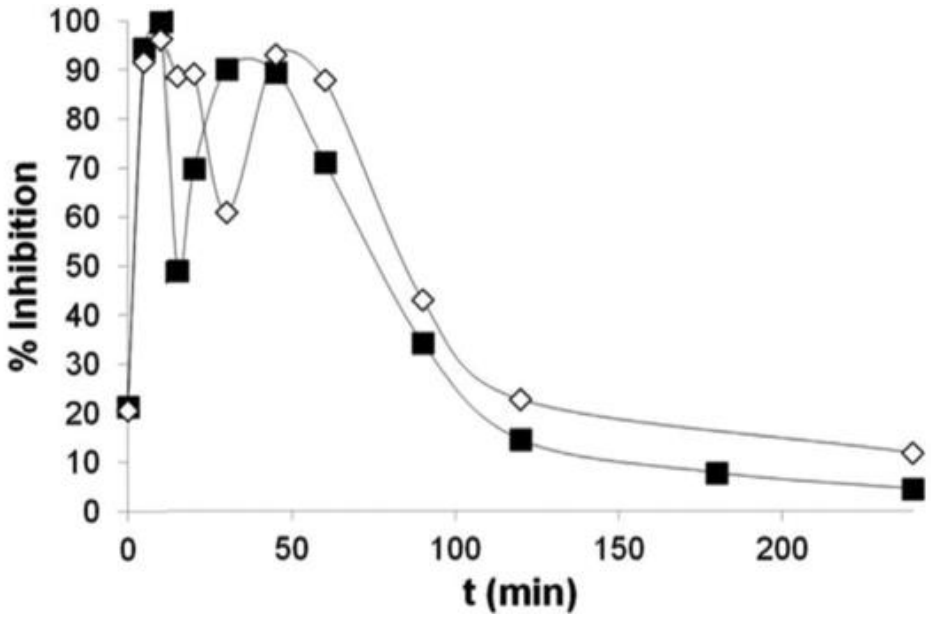


Figure 11 – Toxicity towards V. fischeri during mineralisation of 0.1mM furosemide in 0.05M Na_2SO_4 at 500 mA (diamond) and 1000 mA (square) using EF-BDD [35]

6.4 Competitive Oxidation

In addition to pharmaceuticals, there exists a vast range of organic compounds in hospital blackwater which undergo oxidation by •OH radicals. This competitive oxidation between organics was investigated to determine the impact of additional components on target pollutant mineralisation. Experimental work on the urine of polymedicated patients concluded that pharmaceuticals are oxidised at a much faster rate compared with simple components of urine, urea and creatinine. However, the third primary component of urine, uric acid, is oxidised at the greatest rate. Degradation rate constants determined for the ELOX of urine contaminated with 1 mg L^{-1} ibuprofen and 10 mg L^{-1} cloxacillin at diamond anodes were $k_{uric\ acid}$ = 0.0396 min^{-1} > k_{CLX} = 0.0132 min^{-1} > k_{IBP} = 0.0117 min^{-1} > k_{urea} = 0.005 min^{-1} ~ $k_{creatinine}$ = 0.0047 min^{-1} [6]. It was concluded that competition from other organics has the effect of decreasing the rate of target pharmaceutical pollutant degradation.

6.5 Conclusion

Conclusions from the review were fundamental in forming design decisions for the full-scale electrochemical reactor. It was concluded that a reactor operating in recirculated batch mode is most suitable for the specific application and that BDD anodes are optimal. Additionally, an undivided reactor was identified as the most appropriate reactor type; despite exhibiting higher efficiencies, divided reactors require additional electrolytes which increases both process complexity and operating costs.

It was concluded that an applied current density of 100 mA cm^{-2} is sufficient to achieve high degrees of pollutant mineralisation in relatively short treatment times and a moderate temperature and unchanged neutral pH is most suitable. Varying temperature and pH does not enhance degradation significantly, however, requires reagents, energy and potentially additional treatment to meet sewer entry requirements. Approximately 80% pollutant mineralisation is necessary to decrease toxicity and enhance biodegradability and competitive oxidation from other organics demands longer required treatment times. A summary of some of the results extracted from experimental work is presented in *Annex 3*,

however, it should be noted that comparison of the ELOX of pharmaceuticals was complex due to dependence on a wide range of operating parameters.

7. Design of Preliminary Equipment

Preliminary equipment for the proposed process includes the bar rack and septic tank, as depicted in the block flow diagram in *Figure 12.* Presented in this section are basic design proposals for the preliminary equipment which were produced using methodologies proposed in literature.

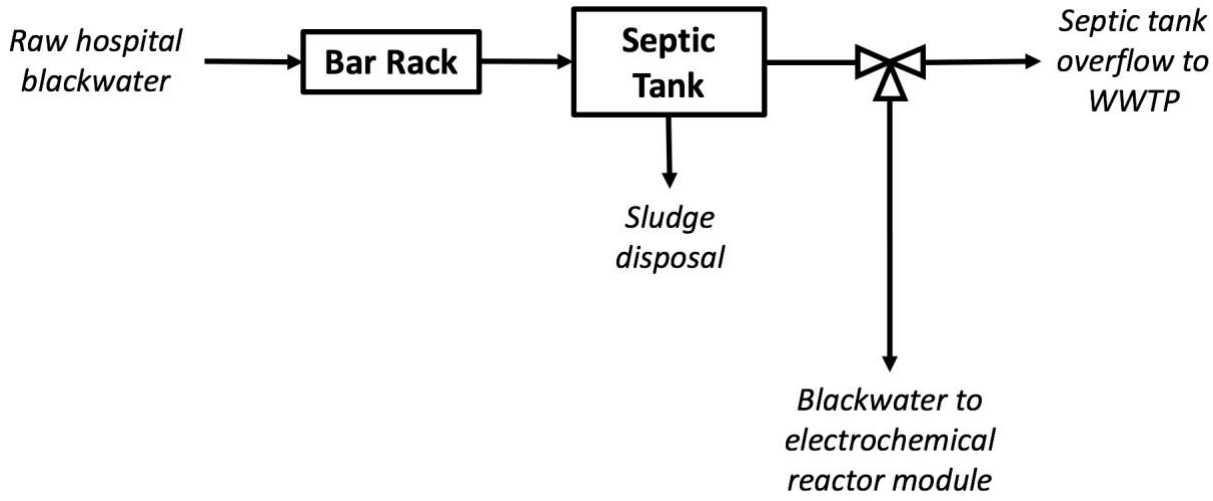


Figure 12 - Block flow diagram of preliminary equipment

7.1 Bar Rack

Hospital blackwater is first passed through a bar rack which comprises a set of parallel metal bars for the screening of large, suspended objects that may cause downstream blockages and impact treatment efficiencies. It is assumed that a bar spacing of 15 mm is sufficient for unwanted solids removal; a smaller spacing is not suitable due to potential clogging issues [57]. The bar rack will be fitted at a 60^{o} angle from the direction of flow to ensure easy removal for cleaning. Bar rack parameters are summarised in *Table 4* and the method for head loss determination is presented in *Annex 4.*

Table 4 - Bar rack properties

Parameter	Value
Bar spacing	15 mm
Number of bars	10
Inclination angle from horizontal	60°
Bar width	5 mm
Material of construction	Stainless steel
Head loss across screen (clear)	0.002 m

7.2 Septic Tank

The function of the septic tank is to settle suspended solids and digest readily biodegradable matter in the incoming blackwater. A rectangular two-compartment septic tank was selected for the purpose of maximising available space and improving solids removal efficiencies [58]. It is assumed that it is feasible to construct the septic tank underground with the lid at ground level to minimise unwanted odours and ensure easy access to existing piping.

7.2.1 Performance

For adequate solids removal, minimum retention times range between 6 to 24 hours with shorter times being more appropriate for higher flowrates [58, 59]. Based on the maximum flowrate of 60 m^3 day^{-1}, a retention time of 8 hours was selected. It was assumed that inlet and outlet volumetric flowrates are equal and that pharmaceuticals are not degraded in the septic tank. COD and TSS removal efficiencies were determined based on typical septic systems and are presented in *Table 5* [59].

Table 5 - Septic tank performance parameters

Parameter	Value
Hydraulic retention time	8 hr
Inlet flowrate	60 m^3 day^{-1}
Outlet flowrate	60 m^3 day^{-1}
COD removal	50%
TSS removal	65%
Inlet COD	650 mg L^{-1}
Outlet COD	325 mg L^{-1}
Inlet TSS	330 mg L^{-1}
Outlet TSS	115.5 mg L^{-1}

7.2.2 Tank Volume

The required septic tank volume was determined using the following expression in which total volume, V_t, is equal to the sum of individual zone volumes [59]:

$$V_t = V_r + V_{oa} + V_{cz} + V_{sc} + V_{sl} \qquad \textit{Eq. (13)}$$

V_r is the reserve zone volume which allows for ventilation and additional storage in the case of malfunction; it typically occupies between 10-20% of total volume [59]. V_{cz} provides a clear zone for the retention of incoming blackwater and was determined on the basis of flowrate and retention time. V_{oa} is the operating zone volume which allows space for flow surges. V_{sc} and V_{sl} provide storage capacity for scum and sludge; scum floats to the surface whilst sludge accumulates at the bottom [59].

The volumes of the individual zones are presented in *Table 6.* All assumptions and calculations performed for the septic tank volume determination are presented in *Annex 5.*

Table 6 - Septic tank zone volumes

Septic Tank Zone	Volume
Reserve zone	5 m^3
Operating zone	5 m^3
Clear zone	20 m^3
Sludge layer	13.3 m^3
Scum layer	6.7 m^3
Total	**50 m^3**

7.2.3 Tank Dimensions

Septic tank dimensions were determined using literature recommendations and typical dimension ratios used in commercial systems. Key requirements included [58, 59]:

- Provision of inspection ports and access for sludge removal.
- Tank length must exceed width and depth to prevent short-circuiting; optimal results are achieved when the first compartment length is double that of the second.

- Turbulence must be minimised by directing influent to the liquid mid-depth and providing a suitable pass-through diameter for liquid to flow into the second compartment.

Key dimensions are provided in *Table 7* with all dimensions outlined in the septic tank drawings in *Figure 13*. The dimension ratios used are given in *Annex 6.*

Table 7 - Key septic tank dimensions

Dimension	Value
Compartment 1 internal length	4.3 m
Compartment 2 internal length	2.2 m
Internal height	2.8 m
Internal width	2.8 m
Diameter of inlet, outlet and pass through	0.2 m
Diameter of access points	0.8 m
Wall thickness	0.3 m

7.2.4 Construction Materials and Maintenance

The proposed tank construction material is reinforced concrete which is suitable for made to order designs. Concrete tanks are resistant to corrosion, watertight and easy to install [59]. With regards to tank cleaning, accumulated sludge should be removed every three months and disposed of correctly; a fraction of sludge should be left to ensure sufficient bacteria for digestion. Regular inspections of tank contents should be performed to ensure no significant build-up of sludge and scum.

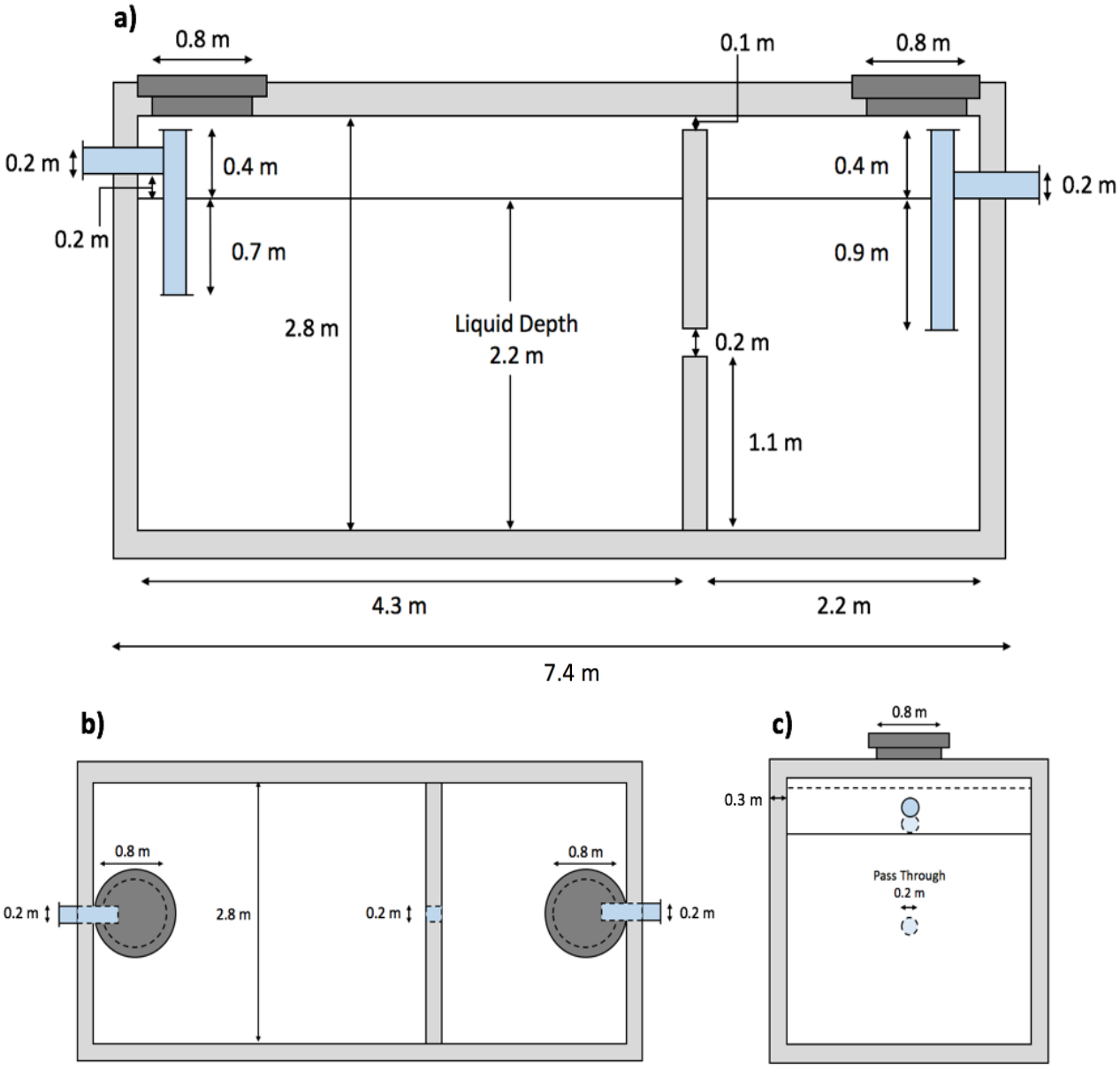


Figure 13 – Septic tank schematics - a) side view b) top view c) end view

8. Electrochemical Reactor Design

8.1 Reactor Configuration

The proposed reactor module comprises a stack of electrochemical cells, an external reservoir tank and a recirculation pump, as illustrated in *Figure 14.*

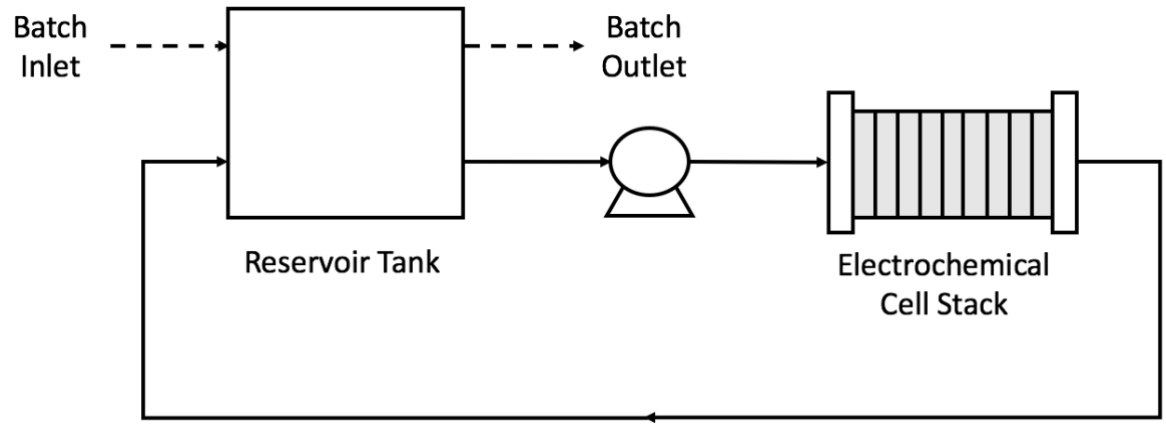


Figure 14 - Schematic of electrochemical reactor module

8.1.1 Batch Recirculation Operation

The electrochemical reactor will operate in batch recirculation mode; the reservoir tank will be filled and, once full, blackwater will be recirculated through the system for a total of 2.5 hours. Upon completion, reservoir contents will be discharged to the sewer before commencing treatment of a new batch. Operating in batch recirculation mode offers many advantages including: enhanced pollutant degradation, operational flexibility and improved system monitoring and control [51].

8.1.2 Filter-Press Type Reactor

Filter-press cells were selected for the reactor design as they are a versatile, robust technology used extensively in a range of electrochemical processes. A typical filter-press cell comprises of fixed electrodes arranged in a parallel plate assembly. Additional cell components include: end plates, gaskets and spacers as shown in the diagram provided in *Figure 15.*

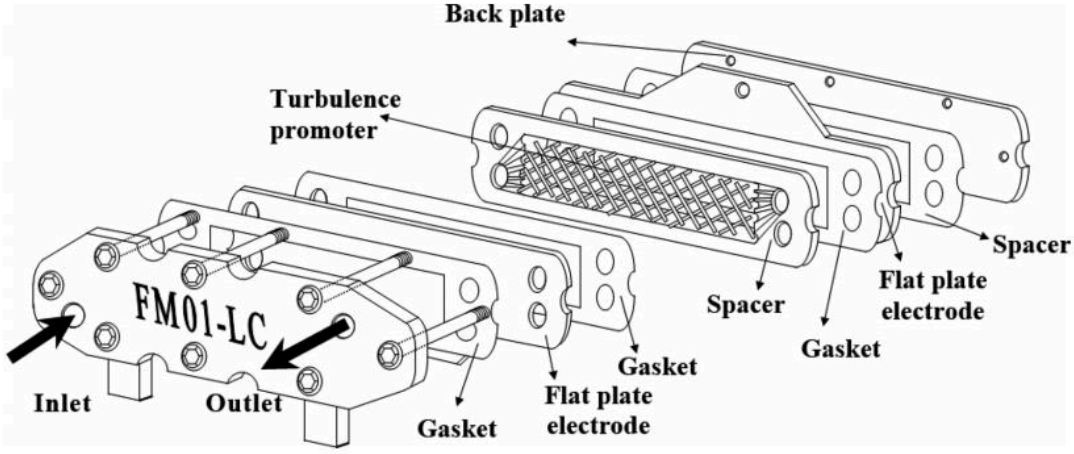


Figure 15 - Components of FM01-LC filter-press cell [60]

A major advantage of filter-press type reactors is their ease of scalability; scale-up is achieved by increasing electrode area or assembling multiple cells in stack [61]. The proposed reactor will comprise a stack of filter-press cells to achieve the total anode area required for pollutant removal.

Dimensions of the commercially available *FM21-SP* filter-press cell were used to form the basis of the reactor design. The *FM21-SP* electrolyser was originally designed for the chlor-alkali industry, however, has since been adapted for other applications [61]. The properties of the *FM21-SP* cell used for the filter-press stack design are presented in *Table 8.*

Table 8 - FM21-SP cell dimensions [62]

Parameter	Symbol	Value
Available electrode area (double sided planar)	A	2 x 0.21 m^2
Channel breadth	B	0.24 m
Channel length	L	0.93 m
Electrode-wall separation	s	0.008 m
Equivalent diameter of rectangular flow channel	d_e	0.015 m
Electrical connection	-	Monopolar

8.1.3 Electrode Materials

The proposed filter-press cell design contains flat plate BDD anodes and stainless-steel cathodes. BDD was identified as the optimal material for the ELOX of hospital blackwater due to the high pharmaceutical degradation rates attained. Stainless steel was selected due to its high durability, corrosion resistance and frequency of use in commercial cathode construction [62].

8.2 Operating Conditions and Target Pollutant Degradation

Conclusions from experimental work were used to identify optimal operating conditions for the ELOX of hospital blackwater containing 1 mg L^{-1} pharmaceuticals and 325 mg L^{-1} COD. Selected operating conditions are summarised in *Table 9.* It should be noted that pH and temperature will not be altered, however, it is expected that a slight temperature rise will occur in the reactor.

Table 9 - Electrochemical reactor operating conditions

Operating Parameter	Symbol	Value
Applied current density	i	1000 A m^{-2}
pH	-	~ 7.8
Temperature	T	~ 15-20°C

To achieve reduced toxicity and enhanced biodegradability, approximately 80% mineralisation of pharmaceutical pollutants is required. This corresponds to complete pollutant degradation and an approximated COD removal of 65% [6]. The electrochemical reactor was designed on the basis that a treatment time of 2.5 hours is sufficient to meet these performance criteria.

8.3 Total Anode Area

To determine the total active anode area required, the following equation was used [63]:

$$A = \dot{Q}\frac{\Delta C_P}{C_P}\frac{\delta}{D_a} \qquad \textit{Eq. (14)}$$

Where the parameters required for area determination are presented in *Table 10.*

Table 10 - Design parameters for anode area calculation

Parameter	Symbol	Value
Volumetric flowrate	$\dot{Q}$	60 m^3 day^{-1}
Target pollutant degradation	$\Delta C_P/C_P$	100 %
Diffusion layer thickness	δ	6 x 10^{-6} m
Active species diffusion coefficient	D_a	4.14 x 10^{-10} m^2 s^{-1}

Diffusion layer thickness describes the zone surrounding the anode in which pollutant concentration drops from the bulk solution value to the value at the anode surface [63]. δ was assumed to be 0.0006 cm which is typical of pollutant ELOX occurring via hydroxyl radicals [63]. Diffusion coefficients were determined for each priority pollutant in blackwater and the calculated limiting value was used. It was determined that pharmaceutical, norfloxacin, has the lowest diffusion coefficient of 4.14 x 10^{-10} m^2 s^{-1} therefore this value was used for all subsequent design calculations. Calculations performed for the determination of D_a are presented in *Annex 7.* It should be noted that the time required for tank filling and emptying was neglected therefore the reactor was designed based on the daily volumetric flowrate.

The total anode area required and associated number of electrochemical cells are presented in *Table 11*, assuming that cell dimensions are equal to that of the commercially available *FM21-SP* cell.

Table 11 - Total anode area requirements

Parameter	Value
Total active anode area	10.1 m^2
Anode area per cell	0.42 m^2 $cell^{-1}$
Number of cells	24 cells

8.4 External Reservoir Tank

The volume of the external reservoir tank was determined using *Eq. (15)* [63]:

$$V = D_a \frac{A}{\delta} t_c \qquad \textit{Eq. (15)}$$

Where V is volume, t_c is the reaction characteristic time (s) and all other parameters are described in *Table 10*. The reaction characteristic time is the time required for complete reaction hence was taken as 2.5 hours. The minimum required tank volume was calculated to be 6.3 m^3. Assuming that the contents occupy 80% of the total volume, the total tank volume is 7.8 m^3.

8.5 Mass Transport

In electrochemical flow cells, performance is highly dependent on mass transport rates which can be enhanced through optimising the rate of recirculation [61]. A suitable recirculation rate was selected on the basis that it enhances mass transport without demanding excessive pumping requirements. A suitable recirculation flowrate of 1.25 m^3 min^{-1} was selected which corresponds to the total tank volume being passed through the reactor every 5 minutes. The corresponding mass transfer coefficient was determined using the dimensionless number correlation for turbulent flow in parallel plate geometries [64]:

$$Sh = 0.023\, Sc^{1/3}\, Re^{4/5} \qquad \textit{Eq. (16)}$$

$$\frac{k_m d_e}{D_a} = 0.023 \left(\frac{\mu}{\rho D_a}\right)^{1/3} \left(\frac{\rho u d_e}{\mu}\right)^{4/5} \qquad \textit{Eq. (16a)}$$

Where k_m is mass transfer coefficient (m s^{-1}), μ is dynamic viscosity (Pa s), ρ is density (kg m^{-3}), D_a is active species diffusion coefficient (m^2 s^{-1}), u is linear flow velocity (m s^{-1}) and d_e is equivalent diameter (m). The calculated dimensionless numbers and mass transfer coefficient are presented in *Table 12* and the corresponding calculations are provided in *Annex 8.*

Table 12 - Dimensionless numbers and mass transfer coefficient

Parameter	Symbol	Value
Reynolds number	Re	6150
Schmidt number	Sc	2750
Sherwood number	Sh	346
Mass transfer coefficient	k_m	9.2 x 10^{-6} m s^{-1}

8.6 Recirculation Pump Duty

To determine the duty of the recirculation pump, the pressure drop across the stack was first calculated using the correlation for filter-press cells in *Eq. (17)* [65]:

$$\Delta P_{cell} = aRe^{b} \qquad \textit{Eq. (17)}$$

Where ΔP_{cell} is the pressure drop per cell (Pa), Re is Reynolds number and a and b are coefficients with values of 0.0069 and 1.39, respectively [65]. The pressure drop across an individual filter-press cell was calculated to be 1274 Pa therefore the pressure drop across the whole stack is 30.6 kPa.

Pump duty was calculated using the energy conservation equation; the energy supplied is sufficient to overcome the pressure drop across the cell stack, the difference in elevation between the stack and reservoir tank and frictional losses across pipe length and fittings. A pipe length of 5 m and an internal pipe diameter of 10 cm were selected for the system design. The calculated pump duty and all elements contributing to pressure loss in the system are presented in *Table 13* and the corresponding calculations are presented in *Annex 9.*

Table 13 - Recirculation pump duty

Parameter	Value
Pressure drop across stack	30.6 kPa
Pressure drop due to friction	75.4 kPa
Type of pump	Centrifugal
Pump efficiency	70 %
Pump duty	3.74 kW

8.7 Reactor Performance

Two important global parameters used to quantify and compare electrochemical treatment process efficiencies are instantaneous current efficiency (ICE) and specific energy consumption ($E_{specific}$). ICE quantifies what percentage of current supplied to the system is utilised for COD degradation whilst specific energy consumption provides information about the energy required to remove a unit mass of COD. ICE and $E_{specific}$ were calculated using E*q.*

(18) and *Eq. (19)* [49], respectively, and all parameters required to perform the calculations are presented in *Table 14.*

$$ICE = \frac{v_e F V \Delta COD}{I \Delta t M_{O_2}} \qquad \textit{Eq. (18)}$$

$$E_{specific} = \frac{IU\Delta t}{3.6 \times 10^6 V \Delta COD} \qquad \textit{Eq. (19)}$$

Table 14 - Parameters for ICE and $E_{specific}$ determination

Parameter	Symbol	Value
Number of electrons per mole O_2	v_e	4 mol_{e^-} mol_{O2}^{-}
Faraday's constant	F	96485 C $mol_{e^-}^{-1}$
Volume	V	6.25 m^3
Change in COD	ΔCOD	211 g m^{-3}
Total applied current	I	11.2 x 10^3 A
Batch time	Δt	9000 s
Molar mass of oxygen	M_{O2}	32 g mol_{O2}^{-1}
Total voltage	U	23.68 V

It should be noted that the total applied current was calculated using current density and the total anode area of 11.2 m^2 which was calculated using the assumption that 90% of the total anode surface is active. The applied voltage was taken to be 23.68 V; this value was estimated using correlated I-U values available in literature [66].

The calculated values of ICE and $E_{specific}$ are presented in *Table 15.*

Table 15 - Electrochemical reactor global performance parameters

Performance Parameter	Symbol	Value
Instantaneous current efficiency	ICE	15.8 %
Specific energy consumption	$E_{specific}$	0.501 kWh g_{COD}^{-1}

9. Discussion

9.1 Equipment Design

The equipment designs proposed in this work were based on the average properties of blackwater as determined in the analysis of hospital wastewater data. However, as wastewater characteristics vary significantly between hospitals, the process equipment requirements also vary; large-scale implementation of the proposed process would require an in-depth assessment into the properties of blackwater from the specified hospital.

Parameters specific to the ELOX of 9 priority pollutants were used to form the basis of the electrochemical reactor design. These parameters, including degradation rate kinetics and diffusion coefficients, were extracted from experimental data and calculated using correlations proposed in literature. It was concluded that the degradation behaviours of all 9 priority pollutants were very similar and diffusion coefficients varied in a small range of 4.14 x 10^{-10} – 6.36 x 10^{-10} m^2 s^{-1} therefore the assumption that priority pollutants are representative of all pharmaceuticals in hospital blackwater is reasonable. However, certain parameters including diffusion layer thickness, δ, and total voltage, U, were approximated based on similar processes discussed in literature. It is recommended that these parameters are determined for the specific process to improve the reactor design accuracy. Furthermore, neglecting batch filling and emptying times is not practically feasible therefore it is suggested that this is taken into consideration in future.

The anode area calculated for pollutant degradation corresponds to 24 *FM21-SP* cells which was concluded to be feasible through comparison to commercial reactors; a typical electrochemical cell stack for the chlor-alkali process comprises up to 60 *FM21-SP* cells [62]. In addition, the calculated mass transfer coefficient, k_m = 5.3 x 10^{-6} m s^{-1}, aligns with values observed in commercial reactors [62] and the pressure drop across the cell stack does not demand excessive pumping requirements. It is proposed that a sensitivity analysis is carried out to investigate the effects of varying recirculation rate on the mass transfer coefficient, reactor performance and pressure drop as this will enable an optimal recirculation rate to be realised. With regards to reactor performance, the value obtained for ICE also complies with

those provided in literature; when operating at high current densities, in the mass transport-control region, a significant proportion of current is wasted and does not contribute to pharmaceutical degradation [49].

9.2 Proposed Future Work

This work illustrates a potential treatment process for the degradation of pharmaceuticals in hospital blackwater, however, prior to large-scale implementation, further research into the ELOX of real wastewater matrices is recommended. It is crucial to determine pharmaceutical degradation rates in the presence of competing organics in hospital blackwater as this will allow for a more accurate determination of the required electrochemical treatment times and the identification of potential toxic products.

The reactor proposed in this work is based on commercially available *FM21-SP* cells. To determine an optimal system design, it is recommended that a pilot-scale filter-press type reactor for the ELOX of hospital blackwater is constructed. This will allow parameters such as cell dimensions, recirculation rate and electrode-separation to be optimised. Due to the high production costs of BDD anodes, further research into the development of low-cost, non-active anode materials is also necessary. Furthermore, it was assumed that suspended solids present in the septic tank effluent do not pose a threat to the function of the electrochemical cell stack. However, potential solids deposition may cause blockages and damage cell components. To prevent this, a recommendation is to include a filter at the septic tank outlet for further solids removal.

10. Conclusion

In line with the objectives of this project, a proposal for the electrochemical oxidation of blackwater from a typical Scottish hospital of 1,000 beds was developed. An analysis of hospital wastewater data was conducted for the estimation of key process parameters. It was concluded that a maximum blackwater flowrate of 60 m^3 day^{-1} is expected and the approximated COD, TSS and pharmaceutical pollutant concentrations are 650 mg L^{-1}, 330 mg L^{-1} and 1 mg L^{-1}, respectively. An analysis of composition data enabled the identification of 9 priority pharmaceutical pollutants. A review of experimental work on the ELOX of these pollutants was performed to identify an optimal reactor configuration and operating conditions. It was concluded that a batch recirculated, undivided electrochemical reactor with BDD anodes operated at a current density of 100 mA cm^{-2} and unchanged temperature and pH was optimal.

The electrochemical reactor module was designed using experimental data and design methodologies proposed in literature. The module comprises a stack of electrochemical cells, an external reservoir tank and a recirculation pump. It operates in batch recirculation mode with a treatment time of 2.5 hours which is assumed to be sufficient for 80% mineralisation of pharmaceutical pollutants. The stack is comprised of 24 electrochemical cells containing double-sided planar BDD anodes and the required external reservoir tank volume was determined to be 7.8 m^3. The entire tank contents are recirculated through the reactor every 5 minutes which requires a recirculation pump duty of 3.74 kW. Global performance parameters, ICE and $E_{specific}$, were calculated to be 15.8 % and 0.501 kWh g_{COD}^{-1}, respectively.

Overall, the proposed treatment process can be implemented to degrade pharmaceutical residues into non-toxic, biodegradable compounds. As up to 14% of pharmaceuticals are consumed in hospitals, treatment of all hospital blackwater could significantly reduce the presence of pharmaceuticals in the aquatic environment [9]. A major drawback of the process is the excessive energy consumption which can be attributed to the relatively high volumetric flowrates handled and competitive oxidation between other organics present in blackwater. Further work may involve assessing the feasibility of the separation and treatment of urine

and faeces, only, or developing methods to increase pharmaceutical concentrations prior to electrochemical oxidation.

Bibliography

[1] B. Rathi et al., "A review on effective removal of emerging contaminants from aquatic systems: Current trends and scope for further research," *Journal of Hazardous Materials,* vol. 409, 2020.

[2] L. Niemi, "Pharmaceuticals in the environment: Introduction and cross-sector partnership addressing the issue in Scotland," The Scottish Parliament Information Centre , 2 June 2020. [Online]. Available: https://spice-spotlight.scot/2020/06/02/pharmaceuticals-in-the-environment-introduction-and-cross-sector-partnership-addressing-the-issue-in-scotland/. [Accessed 1 April 2021].

[3] A. Oluwole et al., "Pharmaceuticals and personal care products in water and wastewater: a review of treatment processes and use of photocatalyst immobilized on functionalized carbon in AOP degradation," *BMC Chemistry,* vol. 14, 2020.

[4] M. Mikulic, "Number of pharmaceutical prescription items dispensed in Scotland 2008-2019," 27 August 2019. [Online]. Available: https://www.statista.com/statistics/886592/prescription-items-dispensed-in-scotland/. [Accessed 8 April 2021].

[5] A. Hassani et al., "Activated carbon fiber for environmental protection," in *Activated Carbon Fiber and Textiles*, Woodhead Publishing, 2017, pp. 245-280.

[6] S. Cotillas et al., "Removal of pharmaceuticals from the urine of polymedicated patients: A first approach," *Chemical Engineering Journal,* vol. 331, pp. 606-614, 2018.

[7] P. Verlicchi et al., "Hospital effluent: Investigation of the concentrations and distribution of pharmaceuticals and environmental risk assessment," *Science of the Total Environment,* vol. 430, pp. 109-118, 2012.

[8] K. Kujawa-Roeleveld et al., "Anaerobic Treatment in Decentralised and Source-Separation-Based Sanitation Concepts," *Reviews in Environmental Science and Bio/Technology,* vol. 5, pp. 115-139, 2006.

[9] S. Vogler et al., "PHIS Hospital Pharma Report 2010," Pharmaceutical Health Information System, 2010.

[10] E. Emmanuel et al., "Ecotoxicological risk assessment of hospital wastewater: a proposed framework for raw effluents discharging into urban sewer network," *Journal of Hazardous Materials ,* vol. 117, 2005.

[11] Department for Environment, Food and Rural Affair, "Waste water treatment in the United Kingdom - 2012: Implementation of the European Union Urban Waste Water Treatment Directive - 91/271/EEC," 2012.

[12] M. Gros et al., "Removal of pharmaceuticals during wastewater treatment and environmental risk assessment using hazard indexes," *Environment International,* vol. 36, pp. 15-26, 2010.

[13] S. Jojoa-Sierra et al., "Elimination of the antibiotic norfloxacin in municipal wastewater, urine and seawater by electrochemical oxidation on IrO2 anodes," *Science of the Total Environment,* vol. 575, pp. 1228-1238, 2017.

[14] M. Solé et al., "Feinization of wild carp, Cyprius carpio, in a polluted environment: plasma steroid hormones, gonadal morphology and xenobiotic metabolizing system," *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology,* vol. 136, pp. 145-156, 2003.

[15] World Health Organization, "Antibiotic resistance," 31 July 2020. [Online]. Available: https://www.who.int/news-room/fact-sheets/detail/antibiotic-resistance. [Accessed 1 April 2021].

[16] Water UK, "National Guidance for Healthcare Waste Water Discharges," UK Water and Sewerage Services, 2011.

[17] United Utilities, "Trade effluent infromation leaflet: An overview of United Utilities trade effluent control," 2020.

[18] European Commission, "Updated surface water Watch List adopted by the Commission," EU Science Hub, 3 July 2018. [Online]. Available: https://ec.europa.eu/jrc/en/science-update/updated-surface-water-watch-list-adopted-commission. [Accessed 1 April 2021].

[19] European Commission, "Establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council," *Official Journal of the European Union,* 2020.

[20] J. de Andrade et al., "Adsorption of Pharmaceuticals from Water and Wastewater Using Nonconventional Low-Cost Materials: A Review," *Industrial & Engineering Chemistry Research,* vol. 57, pp. 3103-3127, 2018.

[21] D. Dolar et al., "Removal of emerging contaminants from municipal water with an integrated membrane system, MBR-RO," *Journal of Hazardous Materials,* vol. 239, pp. 64-69, 2012.

[22] F. Moreira et al., "Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters," *Applied Catalysis B: Environmental,* vol. 202, pp. 217-261, 2017.

[23] D. Miklos et al., "Evaluation of advanced oxidation processes for water and wastewater treatment - A critical review," *Water Research,* vol. 139, pp. 118-131, 2018.

[24] C. Rekhate et al., "Recent advances in ozone-based advanced oxidation processes for treatment of wastewater - A review," *Chemical Engineering Journal Advances,* vol. 3, 2020.

[25] M. Xu et al., "Advancements in the Fenton Process for Wastewater Treatment," in *Advanced Oxidation Processes - Applications, Trends, and Prospects*, Intech , 2019.

[26] Á. Anglada et al., "Contributions of electrochemical oxidation to waste-water treatment: fundamentals and review of applications," *Emerging Technologies,* vol. 84, pp. 1747-1755, 2009.

[27] T. Muddemann et al., "Electrochemical Reactors for Wastewater Treatment," *ChemBioEng Reviews,* vol. 6, pp. 142-156, 2019.

[28] J. Moore et al., "Electrolysis," Chemistry LibreTexts, 5 November 2020. [Online]. Available: https://chem.libretexts.org/@go/page/49549. [Accessed 17 March 2021].

[29] A. Sulaymon et al., "Scale-Up of Electrochemical Reactors," in *Electrolysis*, IntechOpen, 2012.

[30] J. Mora-Gomez et al., "Electrochemical degradation of norfloxacin using BDD and new Sb-doped SnO2 ceramic anodes in an electrochemical reactor in the presence and absence of a cation-exchange membrane," *Separation and Purification Technology,* vol. 208, pp. 68-75, 2019.

[31] C. Martínez-Huitle et al., "Electrochemical oxidation of organic pollutants for the wastewater treatments: direct and indirect processes," *Chemical Society Reviews,* vol. 35, pp. 1324-1340, 2006.

[32] A. Pieczyńska et al., "Insights into Mechanisms of Electrochemical Drug Degradation in Their Mixtures in the Split-Flow Reactor," *Molecules,* vol. 24, 2019.

[33] A. Fernandes et al., "Review on the electrochemical process for the treatment of sanitary landfill leachates: Present and future," *Applied Catalysis B: Environmental,* vol. 176, pp. 183-200, 2015.

[34] L. Zhu et al., "Electrochemical oxidation of fluoroquinolone antibiotics: Mechanism, residual antibacterial activity and toxicity change," *Water Research,* vol. 102, pp. 52-62, 2016.

[35] H. Olvera-Vargas et al., "Electro-oxidation of the Pharmaceutical Furosemide: Kinetics, Mechanism, and By-Products," *CLEAN - Soil, Air, Water,* vol. 43, pp. 1455-1463, 2015.

[36] A. Regalado-Méndez et al., "Electrochemical Mineralization of Ibuprofen on BDD Electrodes in an Electrochemical Flow Reactor: Numerical Optimization Approach," *Processes,* vol. 8, 2020.

[37] V. Frade et al., "Environmental contamination by fluoroquinolones," *Brazilian Journal of Pharmaceutical Sciences,* vol. 50 , pp. 43-54, 2014.

[38] T. Larsen et al., "How to avoid pharmaceuticals in the aquatic environment," *Journal of Biotchenology,* vol. 113, pp. 295-304, 2004.

[39] J. Lienert et al., "Screening Method for Ecotxociological Hazard Assessment of 42 Pharmaceuticals Considering Human Metabolisms and Excretory Routes," *Environmental Science & Technology,* vol. 41, pp. 4471-4478, 2007.

[40] A. Kumari et al., "Hospital wastewater treatment scenario around the globe," in *Current Developments in Biotechnology and Bioengineering*, Elsevier, 2020, pp. 549-570.

[41] Great Britain Department of Health, "Health Technical Memorandum 07-04: Water management and water efficiency - best practice advice for the healthcare sector," London, 2013.

[42] T. Oliveira et al., "Occurrence of Common Pollutants and Pharmaceuticals in Hospital Effluents," *Hospital Wastewaters,* pp. 17-32, 2017.

[43] L. Niemi et al., "Assessing hospital impact on pharmaceutical levels in a rural 'source-to-sink' water system," *Science of the Total Environment,* vol. 737, 2020.

[44] P. Verlicchi et al., "Hospital effluents as a source of emerging pollutants: An overview of micropollutants and sustainable treatment options," *Journal of Hydrology,* vol. 389, pp. 416-428, 2010.

[45] A. Galetti, "Pharmaceutical compounds in waters. Investigations on hospital effluents as a source of environmental contamination and on their treatability," University of Ferrara, 2010.

[46] L. Santos et al., "Contribution of hospital effluents to the load of pharmaceuticals in urban wastewaters: Identification of ecologically relevant pharmaceuticals," *Science of the Total Environment,* vol. 461, pp. 302-316, 2013.

[47] Y. Ouarda et al., "Electrochemical treatment of real hospital wastewaters and monitoring of pharmaceutical residues by using surrogate models," *Journal of Environmental Chemical Engineering,* vol. 7, 2019.

[48] T. Chen et al., "Anodic Degradation of Ofloxacin on a Boron-Doped Diamond Electrode," *International Journal of Electrochemical Science,* vol. 8, pp. 7625-7633, 2013.

[49] A. Savall, "Electrochemical Reactor Design for the Oxidation of Organic Pollutants," in *Encyclopedia of Applied Electrochemistry*, Springer, 2014, pp. 577-585.

[50] S. Ambuludi et al., "Kinetic behaviour of anti-inflammatory drug ibuprofen in aqueous medium during its degradation by electrochemical advanced oxidation," *Environmental Science and Pollution Research,* vol. 20, pp. 2381-2389, 2013.

[51] F. Walsh et al., "Conversion Expressions for Electrochemical Reactors which Operate under Mass Transfer Controlled Reaction Conditions - Part 2: Batch Recycle, Cascade and Recycle Loop Reactors," *International Journal of Engineering Education,* vol. 21, pp. 981-992, 2005.

[52] J. Mora-Gómez et al., "Influence of the reactor configuration and the supporting electrolyte concentration on the electrochemical oxidation of Atenolol using BDD and SnO2 ceramic electrodes," *Separation and Purification Technology,* vol. 241, 2020.

[53] M. Montañés et al., "Analysis of norfloxacin ecotoxicity and the relation with its degradation by means of electrochemical oxidation using different anodes," *Ecotoxicology and environmental Safety,* vol. 188, 2020.

[54] E. Brillas et al., "Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode," *Chemosphere,* vol. 58, pp. 399-406, 2005.

[55] C. Wang et al., "Insights of ibuprofen electro-oxidation on metal-oxide-coated Ti anodes: Kinetics, energy consumption and reaction mechanisms," *Chemosphere,* vol. 163, pp. 584-591, 2016.

[56] H. Hai et al., "Electrochemical oxidation of sulfamethoxazole in BDD anode system: Degradation kinetics, mechanisms and toxicity evaluation," *Science of the Total Environment,* vol. 738, 2020.

[57] A. Butler et al., "Waste Water Treatment Manuals: Preliminary Treatment," Environmental Protection Agency, 1995.

[58] B. Reed, "Septic tank and aqua privy design," Water, Engineering and Development Centre, 2011.

[59] T. Bounds, "Design and Performance of Septic Tanks," in *Site Characterization and Design of On-Site Septic Systems*, ASTM International, 1997, pp. 217-234.

[60] D. Pletcher et al., "Flow Electrolysis Cells for the Synthetic Organic Chemistry Laboratory," *Chemical Reviews,* vol. 118, pp. 4573-4591, 2018.

[61] F. Rivera et al., "The filter-press FM01-LC laboratory flow reactor and its applications," *Electrochimica Acta,* vol. 163, pp. 338-354, 2015.

[62] L. Arenas et al., "Critical Review - The Versatile Plane Parallel Electrode Geometry: An Illustrated Review," *Journal of The Electrochemical Society,* vol. 167, 2020.

[63] M. De Francesco et al., "On the design of electrochemical reactors for the treatment of polluted water," *Journal of Cleaner Production,* vol. 12, pp. 159-163, 2004.

[64] K. Rajeshwar et al., "Mass Transport under Forced Convection in an Electrochemical Cell," in *Environmental Electrochemistry: Fundamentals and Applications in Pollution Abatement*, Elsevier, 1997, pp. 101-104.

[65] Rivera et al., "The reaction environment in a filter-press laboratory reactor: the FM01-LC flow cell," *Electrochimica Acta,* vol. 161, pp. 436-452, 2015.

[66] A. Urtiaga et al., "BDD anodic treatment of 6:2 fluorotelomersulfonate. Avaluation of operating variabls and by-product formation," *Chemosphere,* vol. 201, pp. 571-577, 2018.

[67] E. Mousset et al., "Advanced Electro-Oxidation with Boron-Doped Diamond for Acetaminophen Removal from Real Wastewater in a Microfluidic Reactor: Kinetic and Mass-Transfer Studies," *ChemElectroChem,* vol. 6, pp. 2908-2916, 2019.

[68] G. Li et al., "Electrochemical degradation of ciprofloxacin on BDD anode using a differential column batch reactor: mechanisms, kinetics and pathways," *Environmental Science and Pollution Research,* vol. 26, pp. 17740-17750, 2019.

[69] M. Ghangrekar et al., "Industrial Water Pollution Control: Screens," 2016.

[70] R. Schultheis, "Septic Tank/ Absorption Field Systems: A Homeowner's Guide to Installation and Maintenance," MU Extension, University of Missouri-Columbia.

[71] Inland Northwest Precast, "1000 Gallon Double Compartment Septic Tank," 2021. [Online]. Available: https://inwprecast.com/tanks/. [Accessed 06 April 2021].

[72] R. Sitaraman et al., "A Generalized Equation for Diffusion in Liquids," *Journal of Chemical and Engineering Data,* vol. 8, pp. 198-201, 1963.

[73] R. Sinnott and G. Towler, "Piping and Instrumentation," in *Chemical Engineering Design*, Butterworth-Heinemann, 2009, pp. 229-289.

Annexes

Annex 1 – Therapeutic Drug Classification

Presented in *Table 16* is a complete list of the therapeutic drug classes investigated in this project.

Table 16 - Therapeutic classification of pharmaceuticals [7]

Therapeutic Drug Class	Use	Example
Antibiotics	Treat or prevent bacterial infections.	Ofloxacin
Analgesics/ Anti-inflammatories	Relieve pain and reduce inflammation.	Acetaminophen
Diuretics	Increase the amount of water and salt released in urine.	Furosemide
Beta Blockers	Prevent the release of stress hormones.	Atenolol
Receptor Antagonists	Prevent or minimise biological response by blocking receptors.	Ranitidine
Psychiatric Drugs	Alter the chemical make-up of the brain and nervous system.	Carbamazepine
Lipid Regulators	Decrease lipoprotein or cholesterol production, increase lipoprotein degradation or increase cholesterol removal.	Bezafibrate
Anti-hyperintensives	Treat hypertension (high blood pressure).	Enalapril
Barbiturates	Depress central nervous system; used for anaesthesia and seizure prevention, for example.	Butalbital
Anti-diabetics	Control and stabilise glucose levels in blood.	Glibenclamide
Beta Agonists	Relax the muscles in airways.	Salbutamol
Hormones	Control bodily functions; used for contraceptive purposes, for example.	17α-ethinylestradiol

Annex 2 – Hospital Blackwater Analytics Database

Table 17 – Simplified hospital blackwater analytics database

Therapeutic Class	Pharmaceutical Pollutant	Concentration Range in Hospital Wastewater [µg L^{-1}]	Average Concentration in Hospital Wastewater [µg L^{-1}]	Average Concentration in Hospital Blackwater [µg L^{-1}]
Analgesics/ Anti-inflammatories	Codeine	0.30 - 1.90	0.75	7.51
	Diclofenac	0.08 - 0.51	0.26	2.56
	Ibuprofen	0.14 - 20.0	4.14	41.37
	Indomethacin	0.53 - 2.50	1.77	17.74
	Ketoprofen	0.10 - 5.03	2.15	21.46
	Mefenamic Acid	0.12 - 0.55	0.34	3.42
	Naproxen	0.41 - 4.90	2.21	22.15
	Acetaminophen	2.50 - 62.3	20.81	208.13
	Phenylbutazone	0.04 - 0.14	0.08	0.77
	Propyphenzanone	0.01 - 0.10	0.04	0.41
	Salicylic Acid	1.00 - 2.22	1.52	15.23
Antibiotics	Azithromycin	0.03 - 3.75	0.90	8.96
	Chloramphenicol	0.01 - 0.08	0.05	0.45
	Chlortetracycline	0.04 - 0.08	0.06	0.58
	Ciprofloxacin	0.50 - 62.6	15.10	150.95
	Clarithromycin	0.01 - 11.0	1.75	17.53
	Doxycycline	0.08 - 0.17	0.12	1.24
	Enoxacin	0.08 - 0.41	0.27	2.73
	Erithromycin	0.08 - 0.21	0.15	1.51
	Metronidazole	0.03 - 1.64	0.71	7.13
	Nifuroxazide	0.14 - 1.40	0.69	6.91
	Norfloxacin	0.03 - 0.35	0.15	1.48
	Ofloxacin	3.70 - 31.0	15.98	159.80
	Oxytetracycline	0.09 - 0.78	0.43	4.35
	Spiramycin	0.01 - 0.07	0.05	0.47

Therapeutic Class	Pharmaceutical Pollutant	Concentration Range in Hospital Wastewater [µg L^{-1}]	Average Concentration in Hospital Wastewater [µg L^{-1}]	Average Concentration in Hospital Blackwater [µg L^{-1}]
	Sulfadiazine	0.03 - 0.33	0.15	1.46
	Sulfamethazine	0.01 - 0.02	0.02	0.17
	Sulfamethoxazole	0.03 - 9.80	2.68	26.81
	Tetracycline	0.01 - 0.02	0.02	0.17
	Tilmicosin	0.02 - 0.26	0.11	1.12
	Trimethoprim	0.18 - 1.85	0.85	8.49
Anti-diabetics	Glibenclamide	0.07 - 0.10	0.08	0.80
Anti-hyperintensives	Enalapril	0.13 - 0.31	0.22	2.16
	Lisiniopril	0.12 - 0.25	0.23	2.32
Barbiturates	Butalbital	0.02 - 0.36	0.14	1.40
	Pentobarbital	0.02 - 0.13	0.06	0.61
	Phenobarbital	0.01 - 0.25	0.09	0.91
Beta Agonists	Salbutamol	0.04 - 0.38	0.13	1.26
Beta Blockers	Atenolol	0.33 - 5.80	2.80	28.00
	Betaxolol	0.01 - 0.02	0.01	0.12
	Metoprolol	0.04 - 1.10	0.65	6.46
	Pindolol	0.04 - 0.12	0.08	0.81
	Propanolol	0.02 - 0.09	0.04	0.42
	Sotalol	0.05 - 5.10	2.58	25.83
Diuretics	Furosemide	5.80 - 14.4	10.10	100.99
	Hydrochlorothiazide	0.68 - 2.20	1.36	13.63
Hormones	17A-Ethinylestradiol	0.00 - 0.03	0.01	0.11
	17B-Estradiol	0.02 - 0.09	0.04	0.40
Lipid Regulators	Atorvastatin	0.01 - 0.27	0.13	1.31
	Bezafibrate	0.09 - 0.95	0.44	4.40

Therapeutic Class	Pharmaceutical Pollutant	Concentration Range in Hospital Wastewater [µg L^{-1}]	Average Concentration in Hospital Wastewater [µg L^{-1}]	Average Concentration in Hospital Blackwater [µg L^{-1}]
	Gemfibrozil	0.02 - 0.03	0.03	0.28
	Mevastatin	0.02 - 1.10	0.58	5.80
	Pravastatin	0.08 - 0.62	0.29	2.86
Psychiatric Drugs	Carbamazepine	0.01 - 0.97	0.60	6.02
	Diazepam	0.01 - 0.03	0.02	0.20
	Fluoxetine	0.01 - 0.07	0.03	0.34
	Lorazepam	0.06 - 0.67	0.39	3.94
	Venlafaxine	0.23 - 3.87	1.47	14.74
Receptor Agonists	Cimetidine	0.01 - 0.11	0.05	0.48
	Famotidine	0.01 - 0.16	0.08	0.82
	Loratadine	0.01 - 0.02	0.01	0.11
	Ranitidine	1.30 - 4.16	2.42	24.17

Annex 3 – Summary of Review on Experimental Work

Table 18 - Summary of results from review on experimental work (adapted from [30, 35, 48, 50, 52, 67, 68])

Operating Parameter	Pharmaceutical							
	Acetaminophen	**Ofloxacin**	**Ciprofloxacin**	**Ibuprofen**	**Sulfamethoxazole**	**Furosemide**	**Norfloxacin**	**Atenolol**
Reactor configuration	Recirculated Batch/ Undivided	Batch/ Divided	Recirculated Batch/ Undivided	Batch/ Undivided	Batch/ Undivided	Batch/ Undivided	Batch/ Undivided	Batch/ Undivided
Anode material	BDD (50 cm^2)	BDD (1 cm^2)	BDD (10 cm^2)	BDD (25 cm^2)	BDD (2 cm^2)	BDD (25 cm^2)	BDD (12 cm^2)	BDD (12 cm^2)
Temperature	25°C	30°C	25°C	20°C	23°C	25°C	25°C	25°C
pH	7.7	N/A	7	3	7	3	N/A	7
Initial concentration	15 mg L^{-1}	25 mg L^{-1}	10 mg L^{-1}	10 mg L^{-1}	30 mg L^{-1}	33 mg L^{-1}	100 mg L^{-1}	100 mg L^{-1}
Current density	4 mA cm^{-2}	100 mA cm^{-2}	30 mA cm^{-2}	20 mA cm^{-2}	30 mA cm^{-2}	20 mA cm^{-2}	83 mA cm^{-2}	50 mA cm^{-2}
Electrochemical treatment time	90 minutes	60 minutes	120 minutes	480 minutes	180 minutes	60 minutes	30 minutes	90 minutes
Degradation %	67% (after 90 minutes)	100%	100% (after 20 minutes)	100% (after 90 minutes)	100% (after 90 minutes)	100% (after 30 minutes)	64%	75%
Mineralisation %	87% (after 240 minutes)	N/A	50%	N/A	66%	95% (after 240 minutes)	14%	50%
Degradation rate constant	0.015 min^{-1}	0.023 min^{-1}	0.079 min^{-1}	0.042 min^{-1}	0.078 min^{-1}	N/A	0.035 min^{-1}	0.012 min^{-1}
MCE %	7.4 %	N/A	N/A	5%	N/A	N/A	2.4%	8%
Specific energy	0.49 kWh g_{TOC}^{-1}	N/A	N/A	N/A	72 kWh kg_{COD}^{-1}	N/A	N/A	N/A

Annex 4 – Pressure Drop Across Bar Rack

The following calculations adapted from [69] were performed to determine the head loss across the bar rack when it is completely clear. Using a bar width of 5 mm and bar spacing of 15 mm, the net submerged area of the screen opening required to achieve the recommended normal approach velocity of 0.3 m s^{-1} is 0.0023 m^2 according to:

$$A_N = \frac{\dot{Q}}{v_N} \qquad \textit{Eq. (20)}$$

Where A_N is net submerged area, $\dot{Q}$ is volumetric flowrate and v_N Is normal flow velocity.

The gross submerged area of the screen was calculated using the ratio of open space to gross width of the bar rack:

$$ratio = \frac{15(n+1)}{15(n+1)+5n} = 0.77 \qquad \textit{Eq. (21)}$$

Where n is the number of bars, 15 is the bar spacing and 5 is the bar width. Using this ratio, the gross submerged screen area was calculated to be 0.003 m^2 which was used to determine the submerged vertical screen area and the flow velocity the through the screen:

$$A_V = 0.003 \times \sin\theta = 0.0026\, m^2 \qquad \textit{Eq. (22)}$$

$$v_F = \frac{\dot{Q}}{A_V} = 0.27\, m\, s^{-1} \qquad \textit{Eq. (23)}$$

Where A_V is the submerged vertical screen area, θ = 60° is the angle of inclination and v_F is the flow velocity.

Using the calculated flow velocity, head loss through the screen was calculated to be 0.0017 m using:

$$h = \beta \left(\frac{W}{b}\right)^{4/3} \left(\frac{v_F^2}{2g}\right) sin\theta \qquad \textit{Eq. (24)}$$

Where h is head loss, $\beta = 2.42$ is the bar shape factor, W is bar width, b is bar spacing and g is the gravitational constant.

Annex 5 – Septic Tank Volume Determination

The volumetric capacity of the septic tank was determined using *Eq. (13)* as presented in *Section 7.2* where total volume is expressed as the sum of individual tank zones.

The clear zone volume, V_{CZ}, was calculated utilising the daily volumetric flowrate of blackwater, $\dot{Q}$, and the defined hydraulic retention time, t_h:

$$V_{cz} = \dot{Q} \times \frac{t_h}{24} = 60 \times \frac{8}{24} = 20\ m^3 \qquad \textit{Eq. (25)}$$

The operating volume, V_{OA}, which accounts for flowrate fluctuation was calculated based on a 25% increase in flowrate therefore was calculated to be 5 m^3. The maximum volume occupied by sludge and scum was calculated using the following relationship where P is the number of people served, N is the number of years between desludging, F is the factor for sludge digestion rate and S_d is the annual rate of sludge and scum production per person annually [58]:

$$V_{sc} + V_{sl} = P \times N \times F \times S_d \qquad \textit{Eq. (26)}$$

S_d for WC wastes was taken to be 0.025 m^3 $person^{-1}$ $year^{-1}$ [58]. It was approximated that there are 1600 permanent users of the septic tank and the tank is cleaned every 3 months. The sludge accumulation factor was assumed to be 2 based on the average temperature and time between desludging.

$$V_{sc} + V_{sl} = 1600 \times 0.25 \times 2 \times 0.025 = 20\ m^3$$

It was approximated that 2/3 of this volume is sludge and the remainder is scum [58]. The reserve volume typically comprises 10-20% of the total tank volume [59]. Assuming 10% of the total volume is reserve space, V_r = 5 m^3.

The total internal volume of the septic tank was therefore calculated to be:

$$V_t = V_r + V_{oa} + V_{cz} + V_{sc} + V_{sl} = 5 + 5 + 20 + 20 = 50\ m^3$$

Annex 6 – Septic Tank Dimension Ratios

To determine the dimensions of the septic tank, recommendations provided in literature and typical dimension ratios of commercial septic tank systems were used. The tank was designed using the dimension ratios presented in *Table 19* such that it met the criteria listed below:

- To minimise disturbance to the system and ensure optimal solids settlement, inlet and outlet tees are used. Mouths of the tee pieces are situated at around the mid-depth of the liquid level to prevent mixing with sludge and scum [59].
- The pass-through diameter was designed such that the average flow through velocity does not exceed 0.1 m s^{-1} to prevent turbulence [58].
- The tank inlet pipe is at minimum 3” above liquid level [70].
- A minimum of one manhole is provided with a diameter sufficient for tank access for cleaning and inspections.
- The divider height is not equal to total internal height to ensure ventilation.
- The pass through height is located to ensure sufficient separation from scum and sludge layers; minimum recommended scum and sludge clear spaces are 3” and 6”, respectively [59].
- Wall thickness is sufficient to support large volumes of liquid and was selected based on similarly sized water tanks used in industry.

Table 19 - Septic tank dimension ratios (adapted from [59, 70, 71])

Dimension Ratio	Value
Internal length: Liquid depth	1– 3 (designed at 2.8)
Length compartment 1: Length compartment 2	2
Height: Width	1
Inlet pipe height: Liquid level	1.06
Outlet pipe height: Liquid level	1
Influent discharge height: Liquid depth	0.7
Pass-through height: Liquid depth	0.6
Effluent withdrawal height: Liquid depth	0.6
Height divider: Internal height	0.96
Inlet baffle height: Liquid depth	1.2
Outlet baffle height: Liquid depth	1.2

Annex 7 – Determination of Active Species Diffusion Coefficients

As detailed in *Section 8.3*, the diffusion coefficients of all priority pollutants were determined and the limiting value was selected for the electrochemical reactor design. Active species diffusion coefficients were calculated using the correlation proposed by Wilke and Chang [72]:

$$D_a = \frac{7.4 \times 10^{-8}(XM)^{1/2}T}{\mu V_m^{0.6}} \qquad \textit{Eq. (27)}$$

Where D_a is active species diffusion coefficient ($cm^2\ s^{-1}$), X is the association parameter which defines the association between solute and solvent molecules, M is the solvent molecular weight ($g\ mol^{-1}$), T is temperature (K), μ is liquid viscosity (cP) and V_m is molal pollutant volume ($cm^3\ g^{-1}$).

A temperature of 293.15K was assumed; despite the incoming blackwater existing at an average temperature of 288.15 K, it is expected that there will be a slight temperature increase within the reactor. Additionally, an association factor of 1.5 was assumed for all pollutants through comparison of calculated diffusion coefficients to data available in literature. Calculated diffusion coefficients for each priority pollutant are presented in *Table 20.*

Table 20 - Active species diffusion coefficients

Priority Pollutant	Diffusion Coefficient
Acetaminophen	$6.36 \times 10^{-10}\ m^2\ s^{-1}$
Ofloxacin	$4.19 \times 10^{-10}\ m^2\ s^{-1}$
Ciprofloxacin	$4.41 \times 10^{-10}\ m^2\ s^{-1}$
Furosemide	$4.59 \times 10^{-10}\ m^2\ s^{-1}$
Ibuprofen	$4.68 \times 10^{-10}\ m^2\ s^{-1}$
Atenolol	$4.18 \times 10^{-10}\ m^2\ s^{-1}$
Sulfamethoxazole	$5.18 \times 10^{-10}\ m^2\ s^{-1}$
Trimethoprim	$4.38 \times 10^{-10}\ m^2\ s^{-1}$
Norfloxacin	$4.14 \times 10^{-10}\ m^2\ s^{-1}$

Annex 8 – Determination of Mass Transfer Coefficient using Dimensionless Numbers

To identify an appropriate dimensionless number correlation for the calculation of mass transfer coefficient, the Reynolds number was first calculated to determine the flow regime:

$$Re = \frac{\rho u d_e}{\mu} \qquad \textit{Eq. (28)}$$

Where the density and dynamic viscosity were assumed to be that of water (ρ= 999 kg m^{-3} and μ = 0.00114 Pa s). The equivalent diameter of the rectangular flow channel, d_e, was calculated to be 0.015 m where d_e = 2Bs/(B+s) [65].

Linear velocity, u, was calculated using the fluid recirculation rate and channel dimensions:

$$u = \frac{\dot{Q}_{recirc}}{N_{cells} \times B \times s} = 0.452\ m\ s^{-1} \qquad \textit{Eq. (29)}$$

Using the linear flow velocity, Reynolds number was calculated to be 6150 therefore a turbulent flow regime is exhibited and the correlation presented in *Eq. (16)* in *Section 8.5* is applicable and was used for the determination of k_m.

Annex 9 – Recirculation Pump Duty Determination

The duty of the recirculation pump was calculated using the energy conservation equation [73]:

$$W = g\Delta z - \frac{\Delta P}{\rho} - \frac{\Delta P_f}{\rho} \qquad \textit{Eq. (30)}$$

Where W is work done by fluid (J kg^{-1}), g is the gravitational constant (9.81 m s^{-2}), Δz is the difference in elevation (m) ΔP is the pressure drop across the cell stack (Pa), ΔP_f is the pressure drop due to friction (Pa) and ρ is fluid density. The maximum difference in elevation between the stack and reservoir tank was assumed to be -2 m.

The pressure drop due to frictional losses was determined using *Eq. (31):*

$$\Delta P_f = 4f\left(\frac{L}{d_i}\right)\rho u^2 \qquad \textit{Eq. (31)}$$

Where all parameters are presented in *Table 21.*

Table 21 - Parameters for pressure drop due to frictional losses

Parameter	Symbol	Value
Friction factor	f	0.0037
Pipe length	L_1	5 m
Equivalent pipe length due to miscellaneous losses	L_2	67.5 m
Total pipe length (inc. losses)	L	72.5 m
Pipe internal diameter	d_i	0.1 m
Fluid density	ρ	999 kg m^{-3}
Fluid velocity	u	2.65 m s^{-1}

The total work done by the fluid was calculated to be -125.7 J kg^{-1}. The pump duty was then calculated using *Eq. (32)* where η is pump efficiency and m is fluid mass flowrate.

$$P = \frac{-W \times m}{\eta} \qquad \textit{Eq. (32)}$$

DOCUMENT II: BUDGET

1. Introduction

To determine the feasibility of large-scale implementation, an economic evaluation of the proposed hospital blackwater treatment process was conducted. Preliminary cost estimates were calculated for the installation of major equipment and the predicted yearly energy consumption. In addition, the engineering cost of this work was determined. It should be noted that VAT is included in all costs presented in this section.

2. Engineering Cost

The engineering costs associated with this work were evaluated and will comprise part of the total cost of the project. Engineering costs cover the research conducted and the development of the process design proposal presented in this work. Assuming a typical engineering cost of €30 per hour of work and taking into consideration that 300 hours have been dedicated to this project thus far, the total engineering cost of this work is €9,000.

3. Equipment Capital Costs

Equipment costs were calculated using the Class 4 costing correlation provided in *Eq. (33)* which gives an accuracy of approximately ± 30% [1].

$$C_e = a + bS^n \qquad \textit{Eq. (33)}$$

Where C_e is the equipment purchase cost, S is an equipment size parameter and a, b and n are constants specific to each piece of equipment [1].

To determine the equipment capital costs using data provided in [1], the following parameters were required:

- US inflation from 2007: $1 (2007) = $1.28 (2021) [2]
- US dollar to UK pound conversion: £1 = $1.37 [3]
- UK pound to EU euro conversion: £1 = €1.15 [4]

The cost of all equipment was calculated using *Eq. (33)* with the exception of the electrochemical cell stack which was determined using the cost per unit anode area of a typical *FM21-SP* cell. Using cost correlation data available from [5], the cost of *FM21-SP* cells was estimated at \$20,000 m^{-2} in terms of 1998 US dollars. Accounting for the rate inflation and the installation factor, the total cost of the electrochemical cell stack was calculated to be €756,000 which comprises the majority of the total equipment cost.

To account for the cost of installation, equipment costs were multiplied by the relevant parameters proposed by Hand [1]. A summary of major equipment capital costs is presented in *Table 22.* It should be noted that the cost of the bar rack was neglected as it was assumed to be negligible in comparison to the other more major pieces of equipment.

Table 22 – Equipment capital costs

Equipment	Cost
Septic tank	€72,000
Reservoir tank (reactor)	€35,000
Filter-press cell stack (reactor)	€756,000
Centrifugal pumps	€101,000
TOTAL	**€964,000**

In total, the initial investment required to cover the cost of major pieces of equipment was calculated to be *nine hundred sixty-four thousand euros*.

4. Cost of Energy Consumption

The total annual energy cost was determined by considering the calculated power requirements of each piece of equipment which included: the electrochemical cell stack and centrifugal pumps for recirculation, filling and emptying the reservoir tank. The energy consumption of the filling and emptying pumps was calculated using the same method as for the recirculation pump. The filling and emptying pump duties were calculated to be 1.65 kW and 0.38 kW, respectively, and it was determined that they are in operation for 146 hours per year, assuming that they are switched on intermittently for tank filling and emptying.

The total annual energy consumption and associated costs are presented in *Table 23* where the cost of electricity was taken as €0.1653 kWh^{-1} [6].

Table 23 – Cost of annual energy consumption

Energy Consumer	Annual Energy Consumption	Annual Energy Cost
Centrifugal pumps	33 MWh	€5,500
Electrochemical cell stack	2320 MWh	€383,500
TOTAL	**2353 MWh**	**€389,000**

The cost of annual energy consumption, which accounts for the operation of all centrifugal pumps and the electrochemical cell stack, was determined to be *three hundred eighty-nine thousand euros* per year.

5. Discussion

The sum of major equipment capital costs for the proposed process was calculated to be €964,000 with the stack of electrochemical cells comprising 78% of the total. Due to the relatively high flowrates of blackwater in combination with long residence times, large equipment volumes are required therefore an investment of this magnitude was expected.

A major limitation of the economic assessment is with regards to the cell stack as cost data for typical *FM21-SP* cells from 1998 was used; it is probable that manufacturing costs for simple filter-press type cells have decreased in recent years due to technological advancements. The cost estimate was based on cells containing low-cost platinum anodes, however, production costs for the proposed BDD anodes are significantly higher therefore it is probable that the cell stack cost was underestimated [7]. Current cost data for large-scale BDD anode manufacture is required to improve the cost estimate accuracy.

As shown in *Table 23,* the primary energy consumer in the process is the electrochemical cell stack which has an annual energy requirement of 2320 MWh. This contributes to 99% of the annual energy consumption which is estimated to cost €389,000 yr^{-1}. Despite appearing excessive, this equates to approximately €17 m^{-3} of treated blackwater which is consistent with values presented in literature; the cost of BDD-ELOX of wastewaters contaminated with organic pollutants in concentrations of 100-2000 g m^{-3} was determined to range between €10 m^{-3} and €35 m^{-3} [8].

From an economic perspective, large-scale implementation of the proposed blackwater treatment process is unlikely due to excessive energy costs and lack of revenue generation. As there are no economic incentives to reduce pharmaceutical presence in the environment, upgrading wastewater treatment is primarily dependent on environmental incentives. At present, environmental legislation does not impose restrictions on pharmaceutical concentrations in surface waters, however, if introduced in future, large-scale implementation of the treatment process proposed in this work could help ensure regulatory compliance.

Bibliography

[1] R. Sinnott and G. Towler, "Costing and Project Evaluation," in *Chemical Engineering Design*, Butterworth-Heinemann, 2009, pp. 291-388.

[2] I. Webster, "$1 in 2007 -> 2021 Inflation Calculator," Alioth Finance, 12 April 2021. [Online]. Available: https://www.officialdata.org/us/inflation/2007?amount=1. [Accessed 12 April 2021].

[3] "1 British Pound Sterling to US Dollar," Wise, 12 April 2021. [Online]. Available: https://wise.com/us/currency-converter/gbp-to-usd-rate?amount=1. [Accessed 12 April 2021].

[4] "1 British Pound Sterling to Euro," Wise, 12 April 2021. [Online]. Available: https://wise.com/gb/currency-converter/gbp-to-eur-rate?amount=1. [Accessed 12 April 2021].

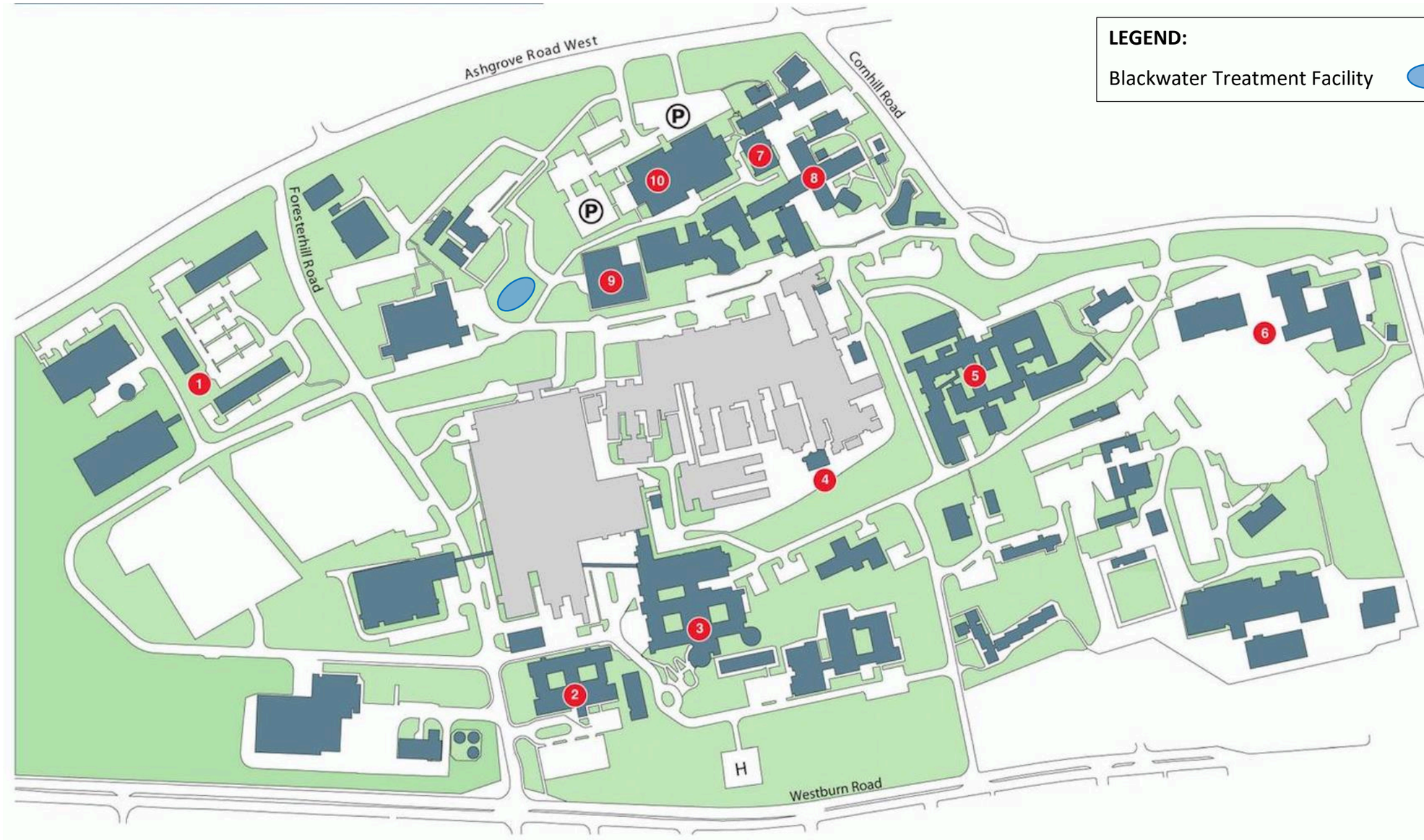
[5] S. Demuth et al., "Cost Benefit of Caustic Recycle for Tank Waste Remediation at the Hanford and Savannah River Sites," Environmental Technology Cost-Savings Analysis Project, 1998.

[6] UK Power, "Compare energy prices per kWh," 13 April 2021. [Online]. Available: https://www.ukpower.co.uk/home_energy/tariffs-per-unit-kwh. [Accessed 13 April 2021].

[7] J. Mora-Gómez et al., "Influence of the reactor configuration and the supporting electrolyte concentration on the electrochemical oxidation of Atenolol using BDD and SnO2 ceramic electrodes," *Separation and Purification Technology,* vol. 241, 2020.

[8] P. Cañizares et al., "Costs of the electrochemical oxidation of wastewaters: A comprarison with ozonation and Fenton oxidation processes," *Journal of Environmental Management ,* vol. 90, pp. 410-420, 2009.

DOCUMENT III: PLANS



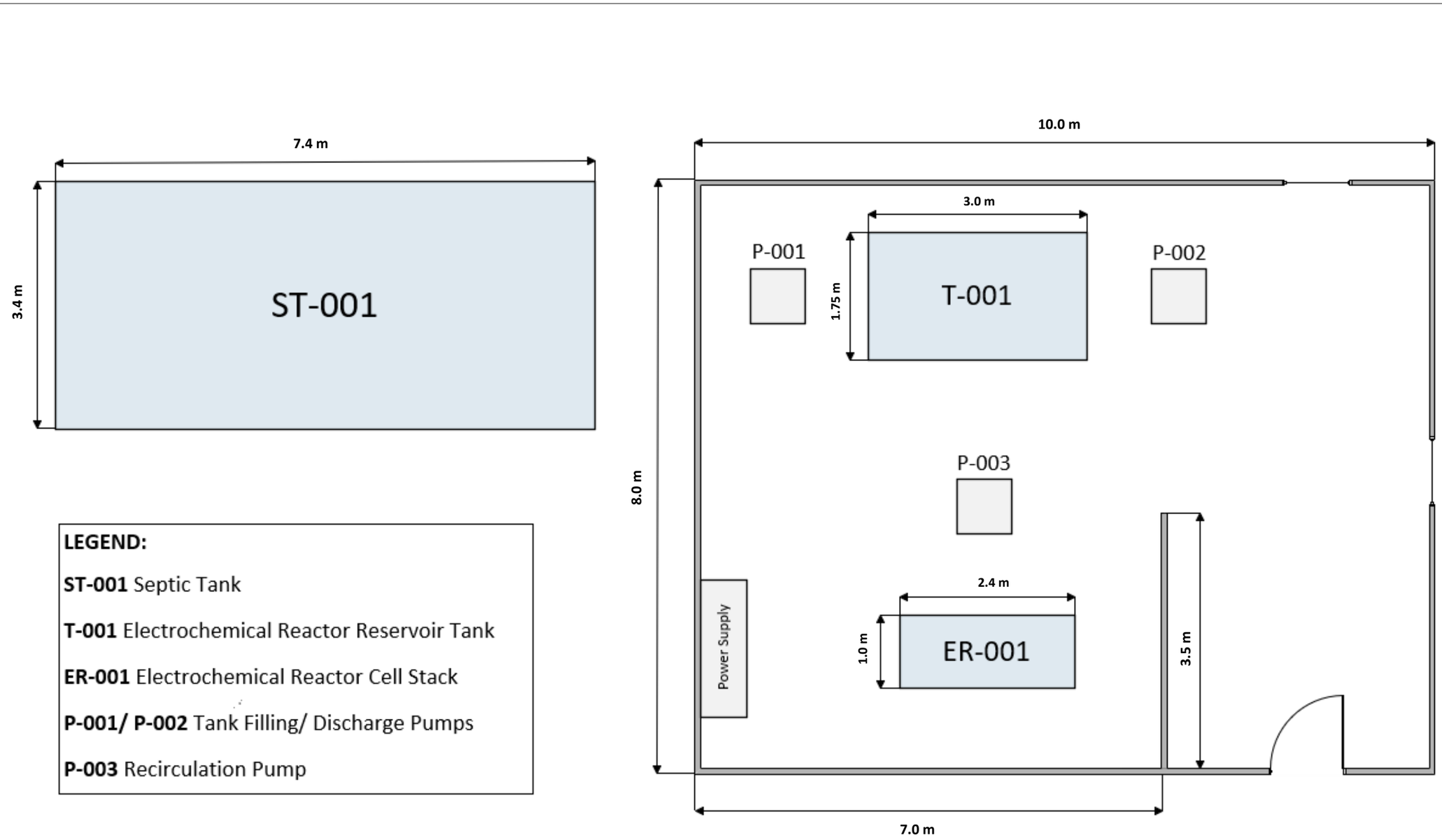
SCHOOL OFFICES & BUILDINGS

Liberty Safe Work Research Centre	1	Royal Aberdeen Maternity Hospital/ Dugald Baird Centre	5	Polwarth	8
Foresterhill Health Centre	1	Dental School/Argyll House	6	Suttie Centre	9
Royal Aberdeen Children's Hospital	3	School of Medicine and School of Medical Sciences	7	Institute of Medical Sciences	10
Lilian Sutton Building	4				

TRABAJO FIN DE MASTER EN INGENIERIA INDUSTRIAL

UNIVERSITAT POLITÈCNICA DE VALÈNCIA — ESCUELA TÉCNICA SUPERIOR INGENIEROS INDUSTRIALES VALENCIA

Proyecto: DESIGN OF AN ELECTROCHEMICAL REACTOR FOR THE REMOVAL OF PHARMACEUTICAL POLLUTANTS IN SOURCE-SEPARATED BLACKWATER FROM A HOSPITAL OF 1,000 BEDS	Plano: Example hospital site plan (Foresterhill Hospital, Aberdeen, Scotland) with blackwater treatment plant location highlighted	Fecha: April 2021	N° Plano: 1
	Autor: Jennifer Bain	Escala: 1:3900	



LEGEND:

ST-001 Septic Tank

T-001 Electrochemical Reactor Reservoir Tank

ER-001 Electrochemical Reactor Cell Stack

P-001/ P-002 Tank Filling/ Discharge Pumps

P-003 Recirculation Pump

TRABAJO FIN DE MÁSTER EN INGENIERÍA INDUSTRIAL UNIVERSITAT POLITÈCNICA DE VALÈNCIA · ESCUELA TÉCNICA SUPERIOR INGENIEROS INDUSTRIALES VALENCIA	Proyecto: DESIGN OF AN ELECTROCHEMICAL REACTOR FOR THE REMOVAL OF PHARMACEUTICAL POLLUTANTS IN SOURCE-SEPARATED BLACKWATER FROM A HOSPITAL OF 1,000 BEDS	Plano: Floor plan of hospital blackwater treatment facility	Fecha: April 2021	Nº Plano: 2
		Autor: Jennifer Bain	Escala:	