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Aplicação de tratamentos eletroquímicos integrados
para remediação de solos e águas contaminadas
com petróleo e pesticidas

Elisama Vieira dos Santos

Tese de Doutorado
Natal/RN, julho de 2015

Elisama Vieira dos Santos

**Aplicação de tratamentos eletroquímicos integrados para remediação de solos e
águas contaminadas com petróleo e pesticidas**

Tese de Doutorado apresentada ao Programa de Pós-Graduação em Química PPGQ, da Universidade Federal do Rio Grande do Norte, como parte dos requisitos para obtenção do título de Doutor em Química.

Orientador: Carlos Alberto Martinez Huitle
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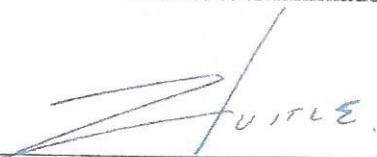
Elisama Vieira dos Santos

APLICAÇÃO DE TRATAMENTOS ELETROQUÍMICOS INTEGRADOS PARA
REMEDIAÇÃO DE SOLOS E ÁGUAS CONTAMINADAS COM PETRÓLEO E
PESTICIDAS

Tese apresentada ao Programa de Pós-
graduação em Química da Universidade
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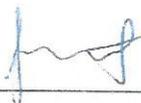
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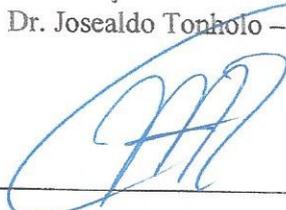
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“A mente que se abre a uma
nova ideia jamais voltará ao
seu tamanho original. ”

Albert Einstein

RESUMO

Tecnologias eletroquímicas têm sido propostas como uma alternativa promissora para o tratamento de águas residuais e solos contaminados. Portanto, este trabalho teve como objetivo estudar o tratamento de solos e águas contaminadas usando tecnologias eletroquímicas. A fim de avaliar o processo em modo contínuo foram empregados eletrodos de platina suportada em titânio (Ti/Pt) e Diamante Dopado com Boro (DDB). Os resultados mostraram que sob as condições operacionais estudadas e os materiais eletrocatalíticos empregados, a melhor eficiência de remoção foi atingida com o eletrodo de DDB reduzindo a demanda química de oxigênio (DQO) de 2746 mg L⁻¹ para 200 mg L⁻¹ em 5 h, consumindo 56.2 kWh m⁻³. A descontaminação de solos foi avaliada mediante remediação eletrocínética para remoção de Hidrocarbonetos Totais de Petróleo (HTP) em solos contaminados com diesel. A eficiência deste processo foi dependente dos eletrólitos usados Na₂SO₄ (96,46%), ácido cítrico (81,36 %) e NaOH (68,03%) durante 15 dias. O efluente gerado após o tratamento do solo foi tratado mediante oxidação eletroquímica com anodos de Ti/Ru_{0,3}Ti_{0,7}O₂, atingindo a eliminação da matéria orgânica. Em função do comportamento físico dos efluentes contaminados com petróleo (estado emulsionado); efluentes emulsionados com atrazina foram investigados. As principais características dos efluentes produzidos durante a lavagem de solos contaminados COT, potencial zeta, tamanho médio das partículas, sendo dependentes da dosagem de surfactante usado; o que influenciou no tratamento eletroquímico com DDB. A oxidação eletroquímica do efluente emulsionado com atrazina.

Palavras-Chaves: Água produzida. Pesticidas. Oxidação eletroquímica. Remediação de solo. Tecnologia integrada.

ABSTRACT

Electrochemical technologies have been proposed as a promising alternative for the treatment of effluents and contaminated soils. Therefore, the objective of this work was to study the treatment of contaminated soils and wastewaters using electrochemical technologies. Thus, the study regarding the scale-up of the electrochemical system with continuous flow treatment of wastewater of the petrochemical industry was investigated using platinum electrodes supported on titanium (Ti / Pt), and boron-doped diamond (BDD). The results clearly showed that under the operating conditions studied and electrocatalytic materials employed, the better removal efficiency was achieved with BDD electrode reducing the chemical oxygen demand (COD) from 2746 mg L⁻¹ to 200 mg L⁻¹ in 5 h consuming 56.2 kWh m⁻³. The decontamination of soils and effluents by petrochemical products was evaluated by studying the effects of electrokinetic remediation for removal of total petroleum hydrocarbons (HTP) from contaminated soil with diesel. The efficiency of this process was dependent on the electrolyte used Na₂SO₄ (96.46%), citric acid (81.36%) and NaOH (68.03%) for 15 days. Furthermore, the effluent after treatment of the soil was treated by electrochemical oxidation, achieving a good elimination of the organic polluting load dissolved. Depending on the physical behavior of wastewater contaminated with oil (emulsified state); atrazine emulsified effluents were investigated. The main characteristics of the effluent produced during the washing of contaminated soil were studied, being dependent on the surfactant dosage used; which determined its electrolytic treatment with BDD. The electrochemical oxidation of emulsified effluent of atrazine was efficient, but the key to the treatment is reducing the size of micelles.

Keywords: Produced water. Pesticides. Electrochemical oxidation. Soil remediation. Integrated technology.

LISTA DE FIGURAS

Figura 2.1-	Esquema da oxidação eletroquímica de compostos orgânicos com ânodos ativos (reações a, b, c, d) e não-ativos (reações a, e, f). M representa um sítio ativo do ânodo.	28
Figura 2.2-	Mecanismo da remediação Eletrocinética.....	31
Figura 2.3-	Dodecil sulfato de sódio.....	32
Figure 3.1-	Main methods used for the removal of organic pollutants from PWs.....	42
Figure 3.2-	Mechanisms during electrochemical coagulation.....	44
Figure 3.3-	(a) Comparison of the COD decay, as a function of time, between Pt and BDD anodes during electrochemical treatment of PW containing with 5 g of Na ₂ SO ₄ dissolved by applying 15 and 60 mA cm ⁻² of current density at 60 °C. (b) Evolution of the energy consumption against % of COD removal during electrochemical treatment of petrochemical wastewater on Pt and BDD anodes. Conditions: applied current density: 15 and 60 mA cm ⁻² ; T=60 °C; agitation rate: 400 rpm and 5 g of Na ₂ SO ₄ dissolved in PW effluent.....	49
Figure 3.4-	Scheme of the electrolytic cell used in the experiments. A) effluent entrance; B) effluent exit; C) cathode: titanium plate; D) anode: Ti/RuO ₂ plate; E) SEM micrographs of Ti/RuO ₂ anode. Graphics: Influence of electrolysis time on COD removal from effluents before filtration (BF) and after filtration (AF) for different current densities. Anodic area: 107 cm ² , flow rate: 0.54 mL s ⁻¹ , T: 25 °C.....	52
Figure 4.1-	Electrochemical flow cell for the oxidation of PW at Ti/Pt and BDD anodes. (a) Set-up used: (1) thermoregulated reservoir; (2) electrochemical cell; (3) power supply; (4) pump. (b) Electrochemical cell: (1) inlet; (2) anode; (3) cathode; (4) electrolysis compartment; (5 and 6) electrical contacts and (7) outlet.....	61
Figure 4.2-	Influence of applied current density on the COD removal as a function of time and total current efficiency (inset) during PW	

	anodic oxidation using (a) Ti/Pt and (b) BDD anodes. Operating conditions: PW sample, as obtained from Brazilian platform, applied current density = 20, 40 and 60 mA cm ⁻² , Temperature=25 °C, flow rate: 151 L h ⁻¹	65
Figure 4.3-	Influence of temperature on the evolution of COD, as a function of time, during electrochemical treatment of actual petrochemical wastewater on (a) Ti/Pt and (b) BDD anodes by applying 40 mA cm ⁻² (flow rate: 151 L h ⁻¹). Inset: % TCE as a function of temperature.....	67
Figure 4.4-	Influence of amount of Na ₂ SO ₄ dissolved on the COD decay, as a function of time and total current efficiency (inset) during oxidation of PW effluent using (a) Ti/Pt and (b) BDD anodes, applying 40 mA cm ⁻² at 25°C.....	70
Figure 4.5-	Influence of amount of Na ₂ SO ₄ dissolved/temperature on the evolution of COD, as a function of time, during electrochemical treatment of actual petrochemical wastewater using (a) Ti/Pt and (b) BDD anodes at 40 mA cm ⁻²	71
Figure 5.1-	TOC removal during EK process in three soil sections using as supporting electrolyte (a) NaOH, Na ₂ SO ₄ and (c) citric acid by applying 2.0 mA cm ⁻² for 15 days. Anode was Ti/Ru _{0.3} Ti _{0.7} O ₂ and as cathode, titanium (Ti).....	82
Figure 5.2.	pH variation, as a function of time, during electrokinetic tests at different supporting electrolytes: (a) NaOH (b) Na ₂ SO ₄ and (c) citric acid.....	84
Figure 5.3-	TPH removal efficiency using different supporting electrolytes in EK treatment.....	85
Figure 5.4-	Electrochemical degradation of wastewater produced after EK treatment. Anode was Ti/Ru _{0.3} Ti _{0.7} O ₂ by applying 20 mA cm ⁻² ..	86
Figure 6.1-	Changes during the CDEO of surfactant-soil-washing effluent (a) (▲) TOC: (■) COD (Δ) Atrazine: (□) SDS concentration. (b) total amount of intermediates (▲) quantified as total chromatographic area and (■) concentration of SO ₄ ²⁻	94
Figure 6.2-	Changes in z-potential (▲) and mean particle size (■) during the CDEO of surfactant soil-washing effluent. Size limits	

	including (---) 50% of the particles; size limits including 80% of the particles (.....)	96
Figure 7.1-	Surplus concentration of SDS (■) and atrazine (▲) after the soil washing treatment	108
Figure 7.2-	Soil-washing effluent polluted with atrazine. (a) z-potential (▲), mean particle size (■), size limits including 50% of the particles (---), size limits including	109
Figure 7.3-	Changes in the mean particle size (a) and z-potential (b) during the electrolysis at $j: 30 \text{ mA cm}^{-2}$ of the effluents produced during soil washing with the following [SDS]/soil ratios: 0.5 (▲), 2.5 (◆), 5.0 (●), 12.5 (x) and 25.0 (■)	110
Figure 7.4-	SDS (a) and atrazine (b) removal profiles during the electrolysis at $j: 30 \text{ mA cm}^{-2}$ of the effluents produced during soil washing with the following [SDS]/soil ratios: 0.5 (▲), 2.5 (◆), 5.0 (●), 12.5 (x) and 25.0 (■)	111
Figure 7.5-	TOC and COD removal profiles during electrolysis at $j: 30 \text{ mA cm}^{-2}$ of the effluents produced during soil washing with the following [SDS]/soil ratios: 0.5 (▲), 2.5 (◆), 5.0 (●), 12.5 (x) and 25.0 (■)	112
Figure 7.6-	Sulphate ions produced during the electrolysis at $j: 30 \text{ mA cm}^{-2}$ of the effluents produced during soil washing with the following [SDS]/soil ratios: 0.5 (▲), 2.5 (◆), 5.0 (●), 12.5 (-) and 25.0 (■)	113

LISTA DE TABELAS

Tabela 2.1-	Máximo permitido em água de hidrocarbonetos Policíclicos Aromáticos.....	25
Tabela 2.2-	Tipos de pesticidas.....	26
Table 3.1-	Electrochemical characteristics of electrocoagulation process.....	43
Table 3.2-	Percentage petroleum pollutants removals and energy consumption determined for the EO, IEO and EF with different anodes of selected petrochemical wastewaters...	50
Table 4.1-	Average concentration of inorganic species in the produced water samples.....	60
Table 4.2-	Average concentration of inorganic species in the produced water samples after electrochemical treatment applying 60 mA cm^{-2} of current density, 60°C and 5 g of Na_2SO_4	63
Table 4.3-	Total current efficiencies and energy requirements for electrochemical treatment of petrochemical wastewater at different applied current densities.....	72
Table 7.1-	Maximum concentration of intermediates (expressed as chromatographic area) measured during the electrolysis of the soil washing effluents.....	111

LISTA DE ABREVIATURAS

Ap	Água Produzida
Pw	Produced Water
Mbpd	Million Barrels Per Day
BTEX	Benzene, Toluene, Ethylbenzene, And Xylenes
PAHS	Polyaromatic Hydrocarbons
AOPS	Advanced Oxidation Processes
ER	Electroreduction
EC	Electrocoagulation
EF	Electro-Fenton
PEF	Photoelectro-Fenton
PEC	Photoelectrocatalysis
COD	Chemical Oxygen Demand
BOD	Biochemical Oxygen Demand
IEO	Indirect Electrochemical Oxidation
BDD	Boron Doped Diamond
TCE	Total Efficacy Of Current
TPH	Total Petroleum Hydrocarbon
EK	Electrokinetic
CEC	Cation Exchange Capacity
TOC	Total Organic Carbon
CDEO	Conductive - Diamond Electrochemical – Oxidation
SASW	Surfactant-Aided Soil Washing

SUMÁRIO

1	INTRODUÇÃO.....	15
1.2	OBJETIVOS.....	17
1.2.1	Gerais.....	17
1.2.2	Específicos.....	17
2	ASPECTOS TEÓRICOS.....	18
2.1	CONTAMINAÇÃO POR PETRÓLEO.....	18
2.2	IMPACTO AMBIENTAL.....	18
2.3	PESTICIDAS E SUAS CLASSIFICAÇÕES.....	20
2.4	TRATAMENTO ELETROQUÍMICO.....	21
2.5	TRATAMENTO DE SOLOS.....	24
3	DECONTAMINATION OF PRODUCED WATER CONTAINING PETROLEUM HYDROCARBONS BY ELECTROCHEMICAL METHODS: A MINIREVIEW.....	28
3.1	INTRODUCTION.....	28
3.1.1	Petrochemical industry.....	28
3.2	PRODUCED WATER.....	28
3.3	TREATMENT OF PW.....	30
3.4	APPLICABILITY OF ELECTROCHEMICAL TECHNOLOGIES FOR TREATING PW.....	31
3.5	ELECTROCHEMICAL REDUCTION.....	32
3.6	ELECTROCOAGULATION.....	33
3.7	DIRECT AND INDIRECT ELECTROCHEMICAL OXIDATION.....	35
3.7.2	Application of electrochemical technology (EO and IEO) for treating petroleum wastewater.....	36
3.8	PETROCHEMICAL WASTEWATERS TREATMENT BY EMERGING TECHNOLOGIES.....	43
3.9	CONCLUSIONS AND TRENDS.....	44
4	SCALE-UP OF ELECTROCHEMICAL OXIDATION SYSTEM FOR TREATMENT OF PRODUCED WATER GENERATED BY BRAZILIAN PETROCHEMICAL INDUSTRY.....	48
4.1	INTRODUCTION.....	48
4.2	EXPERIMENTAL.....	50

4.2.1	Description of the produced water.....	50
4.2.2	Chemicals.....	51
4.2.3	Electrolytic systems.....	51
4.2.4	Analytical methods.....	57
4.3	RESULTS AND DISCUSSIONS.....	54
4.3.1	Electrochemical treatment of PW using the Ti/Pt and BDD anodes.....	54
4.3.2	Influence of Na ₂ SO ₄ concentration.....	61
4.3.3	Electrochemical treatment of petrochemical effluent adding Na ₂ SO ₄ varying the temperature.....	62
4.3.4	Comparison of the electrode materials.....	64
4.4	CONCLUSIONS.....	65
5	APPLICATION OF ELECTROCHEMICAL TECHNOLOGIES TO TREAT POLLUTED SOIL BY DIESEL.....	71
5.1	INTRODUCTION.....	71
5.2	MATERIALS AND METHODS.....	73
5.2.1	Preparation of soil samples.....	73
5.2.2	Analysis of organic matter removal from soil and Diesel removal.....	73
5.3	ELECTROKINETIC CELL.....	74
5.4	ELECTROCHEMICAL OXIDATION EXPERIMENTS.....	74
5.5	RESULTS AND DISCUSSION.....	75
5.5.1	Efficiency carbon organic total removal and electrical power consumption.....	75
5.5.2	Concentration of TPH in soil.....	78
5.5.3	Electrochemical oxidation.....	79
5.6	CONCLUSIONS.....	80
6	THE ROLE OF PARTICLE SIZE ON THE CONDUCTIVE DIAMOND ELECTROCHEMICAL OXIDATION OF SOIL- WASHING EFFLUENT POLLUTED WITH ATRAZINE.....	82
6.1	INTRODUCTION.....	83
6.2	MATERIALS AND METHODS.....	84
6.2.1	Chemicals.....	84
6.2.2	Analytic techniques.....	84

6.2.3	Preparation of spiked soil.....	85
6.2.4	Surfactant-aided soil washing procedure.....	85
6.2.5	CDEO procedure.....	85
6.3	RESULTS AND DISCUSSION.....	86
6.4	CONCLUSIONS.....	90
7	COMBINED SOIL WASHING AND CDEO FOR THE REMOVAL OF ATRAZINE FROM SOILS.....	95
7.1	INTRODUCTION.....	96
7.2	MATERIALS AND METHODS.....	98
7.2.1	Preparation of spiked soil.....	98
7.2.2	Soil washing procedure.....	98
7.2.3	Electrochemical oxidation of the soil washing effluents.....	99
7.2.4	Analyses.....	99
7.2.5	Results and Discussions.....	100
7.3	SOIL WASHING.....	100
7.3.1	Electrolysis of the soil washing effluent.....	102
7.3.2	Conclusions.....	114
8	CONSIDERAÇÕES FINAIS.....	116
9	REFERÊNCIAS.....	114

1 INTRODUÇÃO

O impacto ambiental provocado pelo descarte de poluentes e efluentes em solos é geralmente analisado pela toxicidade dos constituintes e pela quantidade de compostos orgânicos e inorgânicos presentes. Estes contaminantes podem provocar diversos efeitos nos solos e águas, devido a presença de alguns constituintes serem solúveis em água e outros serem insolúveis; entretanto, alguns poluentes são adsorvidos e fixados permanentemente quando se discute sobre solos. Acredita-se que os efeitos mais nocivos ao meio ambiente são aqueles relacionados aos compostos que são solúveis após o descarte.

O desenvolvimento de tratamentos alternativos para descontaminação de solos e efluentes se faz necessários, a fim de atender as legislações governamentais e evitar (em alguns casos prevenir) impactos ambientais irreversíveis em ecossistemas de solos ou aquáticos.

Em função da problemática relacionada com a produção de efluentes contaminados por parte da indústria petroquímica, o tratamento de água produzida é um dos temas atuais de maior discussão no que se refere a metodologias alternativas para sua descontaminação ou diminuição da sua toxicidade. Esta tese está organizada em forma de capítulos sendo o **capítulo 1** referente a introdução do trabalho desenvolvido e o **capítulo 2** aspectos teóricos das tecnologias empregadas nesta tese. O **capítulo 3** apresenta uma revisão bibliográfica sobre os tipos de tratamentos usados na remoção de compostos orgânicos em água produzida derivada da indústria petrolífera, enfatizando as tecnologias eletroquímicas empregadas (oxidação eletroquímica, eletrocoagulação, eletro-fenton, etc.). Esta revisão foi publicada no jornal internacional indexado: *Environmental Science and Pollution Research*.

Baseados nos resultados promissores da literatura referentes a implementação do tratamento eletroquímico para remoção da matéria orgânica em água produzida derivada da indústria do petróleo, investigou-se a aplicação da oxidação eletroquímica para a descontaminação de um efluente real da indústria petrolífera do estado do Rio Grande do Norte, Brasil. No **capítulo 4** são apresentados resultados dessa investigação visando o emprego de eletrodos anódicos do tipo Ti/Pt e DDB (Diamante Dopado com Boro), ativos e não ativos respectivamente, considerados os mais utilizados na oxidação eletroquímica. Estes resultados foram publicados no jornal internacional indexado: *Environmental Science and Pollution Research*.

No intuito de continuar avaliando as técnicas de descontaminação de efluentes e solos contaminados por derivados de petróleo, a aplicação de tecnologias eletroquímicas tornou-se o nosso objetivo de interesse no **Capítulo 5**. Assim, a remediação eletrocinética bem como a oxidação eletroquímica foram aplicadas para a remoção dos compostos orgânicos derivados do petróleo (diesel) em solo. O objetivo foi investigar a influência dos tipos de eletrólitos usando eletrodos de $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$, classificado como ADE (Anodo Dimensionalmente Estável) durante a remediação eletrocinética de solos coletados em postos de combustível (contaminados com diesel) na cidade de Natal, visando avaliar a eficiência para descontaminação do solo, removendo a matéria orgânica e os hidrocarbonetos totais de petróleo (HTPs). Além disso, o uso da oxidação eletroquímica foi proposto como alternativa viável no tratamento dos efluentes gerados após o tratamento eletrocinético do solo, a fim de oxidar os compostos orgânicos das águas contaminadas. Os achados científicos oriundos da investigação foram publicados no jornal internacional indexado: *Chemical Engineering Transactions*.

Neste contexto, o tratamento de solos e efluentes (águas poluídas como resultado do tratamento do solo) foi objeto de interesse da nossa pesquisa, já que a tecnologia eletroquímica empregada dependia do tipo de poluente a ser eliminado. O **Capítulo 6** apresenta os resultados de experimentos que visavam avaliar o comportamento eletroquímico e tamanho das partículas do efluente de lavagem de solo contaminado com atrazina (pesticida). Este estudo foi realizado como parte de uma colaboração científica entre a UFRN e a *Universidad de Castilla La-Mancha* (UCLM), em Espanha. A pesquisa foi desenvolvida sob orientação do Prof. Dr. Manuel Andres Rodrigo a fim de comprovar o comportamento do ataque eletroquímico a micelas geradas durante o processo de lavagem de solo. O artigo científico referente deste capítulo desta tese, também já se encontra publicado no jornal internacional indexado: *Electrochemistry Communications*.

Finalmente, distintas concentrações de surfactante foram propostas a fim de verificar como se comportava as micelas formadas durante o processo de lavagem de solo, durante a remoção do pesticida em solo (**Capítulo 7**). Foi possível evidenciar os tamanhos das diferentes micelas formadas que posteriormente foram submetidas ao processo eletroquímico, no qual foi observada a produção de espécies iônicas que favoreceram a remoção da matéria orgânica. Os resultados oriundos deste capítulo foram publicados no jornal internacional indexado: *Journal of Hazardous Materials*.

1.2 OBJETIVOS

1.2.1 Gerais

Avaliar a eficiência do tratamento eletroquímico na remediação de água e solo contaminados por compostos orgânicos derivados do petróleo e com pesticidas.

1.2.2 Específicos

- ✓ Avaliar corpos hídricos contaminados por derivados do petróleo e pesticidas;
- ✓ Realizar oxidação eletroquímica usando uma célula eletroquímica em fluxo para determinar a taxa de remoção de matéria orgânica presente na água produzida e o efeito do tipo de material anódico (Pt, DDB e $\text{Ti/Ru}_{0,3}\text{Ti}_{0,7}\text{O}_2$);
- ✓ Emprego da remediação eletrocínética para remediação de solo contaminado com diesel e aplicabilidade da oxidação eletroquímica para descontaminação do efluente gerado durante a descontaminação do solo;
- ✓ Avaliação do processo de lavagem de solo contaminados com atrazina empregando dodecil sulfato de sódio;
- ✓ Aplicação da oxidação eletroquímica para remediar o efluente gerado após o processo de lavagem de solo;
- ✓ Avaliação da influência do dodecil sulfato de sódio no comportamento físico-químico do efluente gerado.

2 ASPECTOS TEÓRICOS

2.1 CONTAMINAÇÃO POR PETRÓLEO

O petróleo pode contaminar a água e o solo durante o processo de exploração, produção e injeção. Durante a produção do petróleo é produzido concomitantemente água sendo denominada Água Produzida (AP) que consiste na água aprisionada nas formações subterrâneas que é trazida à superfície juntamente com petróleo e gás durante as atividades de produção desses fluidos. Entre os aspectos da AP que merecem atenção estão os seus elevados volumes e a complexidade da sua composição. Esses aspectos fazem com que o gerenciamento da AP requeira cuidados específicos, não apenas relacionados com aspectos técnicos e operacionais, mas, também, os ambientais. Como consequência, o gerenciamento da AP resulta em custos consideravelmente elevados representando um percentual significativo dos custos de produção (AMINI et al, 2012).

O controle desse resíduo constitui um embate tecnológico para o mundo petrolífero. Tendo como destino o descarte ou reutilização, é necessário o tratamento dessa água, de modo que não venha a causar efeitos deletérios ao meio ambiente, ou efeitos prejudiciais à produção, na qual ela venha ser reaproveitada. A reutilização tem sido foco de vários grupos de pesquisa, devido à escassez de recursos hídricos. No cenário mundial é notória a preocupação em melhorar a qualidade desses efluentes. Dentro deste contexto verifica-se a necessidade do desenvolvimento de novas tecnologias que permitam, de forma eficiente, o tratamento de solos e corpos hídricos (SILVA et al, 2005b).

2.2 IMPACTO AMBIENTAL

A água produzida pode também ter uma série extensa de hidrocarbonetos policíclicos aromáticos (HPAS), compostos com anéis aromáticos com ou sem ramificações saturadas, que configuram uma classe importante de compostos orgânicos presente na composição do petróleo, apesar da sua baixa concentração em relação aos outros hidrocarbonetos.

Dos mais de 100 diferentes HPAs conhecidos, apenas 16 deles foram considerados prioritários pela USEPA (“United State Enviromental Protection Agency”) para monitoramento, sendo 7 classificado pela IARC (“International Agency

for Research on Cancer”) como cancerígenos para animais e potencialmente cancerígenos para seres humanos. A resolução n° 357 do CONAMA (“Conselho Nacional do Meio Ambiente”), dispõe sobre a classificação dos corpos de água e diretrizes ambientais para seu enquadramento, bem como estabelece as condições e padrões de lançamentos de efluentes, classificando os valores máximos permissíveis para metais e compostos orgânicos presente em água doce, potável, salobra, salgada e para descarte em meio ambiente. A água produzida pode ser descartada em corpo receptor ou ser utilizada na injeção de poços de petróleo maduros. Mas para essa disposição é necessário o tratamento adequado dessa fase líquida. Para a utilização na forma de descarte corpos receptores, o limite é de até 20 mg L⁻¹ de óleos e graxas na água produzida, segundo a Resolução 357/ 2005 do CONAMA. Para o descarte em plataformas marítimas de petróleo a Resolução 393/2007 do CONAMA, que estabelece a média aritmética simples mensal do teor de óleos e graxas até 29 mg L⁻¹, com valor máximo diário de 42 mg L⁻¹ (CONAMA, 2009). A Tabela 2.1 apresenta os 16 compostos orgânicos prioritários e seus limites máximos permissíveis.

Durante o processo de perfuração e extração são necessárias operações para maximizar a produção de óleo principalmente pelo contra-balanceamento com a contaminação da água produzida por poluentes, tal como metais pesados, compostos orgânicos e sólidos suspensos dissolvidos. Correspondente aos compostos orgânicos: benzeno, tolueno, xileno, fenol, compostos aromáticos halogenados, hidrocarbonetos policíclicos aromáticos (HPAs), clorofórmio e tricloroetileno são os principais compostos presentes em água produzida (DUARTE et al, 2011). Neste caso os HPAs, são compostos lipofílicos, contendo uma mistura mais facilmente solúvel em óleo que é em água. Os compostos com cadeias carbônicas maiores são menos solúvel em água e menos voláteis. Portanto, devido às propriedades dos HPAs no meio ambiente eles são encontrados principalmente em solo, sedimentos e substâncias oleosas. Entretanto, em alguns casos os HPAs podem ser encontrados em ecossistemas aquáticos em altas concentrações sob condições específicas de temperatura e pressão (PAZOS et al, 2010).

Tabela 2.1- Máximo permitido em água de hidrocarbonetos Policíclicos Aromáticos

<i>Hidrocarbonetos Policíclicos Aromáticos</i>	Valor Máximo
<i>Benzo(a)pireno</i>	0,018 $\mu\text{g L}^{-1}$
<i>Benzo(b)fluoranteno</i>	0,018 $\mu\text{g L}^{-1}$
<i>Benzo(k)fluoranteno</i>	0,018 $\mu\text{g L}^{-1}$
<i>Crisceno</i>	0,018 $\mu\text{g L}^{-1}$
<i>Acenaftileno</i>	0,012 $\mu\text{g L}^{-1}$
<i>Fluoreno</i>	0,014 $\mu\text{g L}^{-1}$
<i>Antraceno</i>	0,018 $\mu\text{g L}^{-1}$
<i>Benzo(g,h,i)perileno</i>	0,05 $\mu\text{g L}^{-1}$
<i>Fenantreno</i>	0,018 $\mu\text{g L}^{-1}$
<i>Dibenzo(a,h)antraceno</i>	0,018 $\mu\text{g L}^{-1}$
<i>Indeno(1,2,3cd)pireno</i>	0,018 $\mu\text{g L}^{-1}$
<i>Pireno</i>	0,018 $\mu\text{g L}^{-1}$
<i>Acenafteno</i>	0,01 $\mu\text{g L}^{-1}$
<i>Fluoranfteno</i>	0,018 $\mu\text{g L}^{-1}$
<i>Naftleno</i>	0,05 $\mu\text{g L}^{-1}$
<i>Benzo(a)antraceno</i>	0,018 $\mu\text{g L}^{-1}$

Fonte: DUARTE et al, 2011

2.3 PESTICIDAS E SUAS CLASSIFICAÇÕES

Os pesticidas são substâncias químicas destinadas a exterminar, controlar ou combater algumas espécies de praga que atacam, lesam ou transmitem doenças às plantas, animais e ao ser humano. No Brasil, os pesticidas foram primeiramente utilizados em programas de saúde pública, no combate a vetores e controle de parasitas, passando a ser usados na agricultura em 1960. Do ponto de vista toxicológico podem ser mais ou menos tóxicos ao homem. Em decorrência da sua toxicidade tem surgido leis que regulamentam os limites máximos em alimentos, solos e águas (SANTOS, et al., 2007).

Os limites máximos desses componentes nocivos à saúde humana e ao meio ambiente é regulamentada no Brasil para ambientes aquáticos, pela Resolução CONAMA 357/05 e pela Portaria 2.914/11, que estabelece os limites de substâncias tóxicas (como os pesticidas) nas águas superficiais, abaixo dos quais é garantida a saúde humana e o equilíbrio ecológico aquático.

Os pesticidas podem ser classificados de muitas maneiras diferentes, dependendo de suas aplicações: herbicidas, inseticidas, fungicidas, acaricidas, etc.), sua aplicabilidade (espectro amplo ou seletivo), os principais ativos químicos (organoclorados, organofosforados, carbamatos, piretróides, triazinas, etc.), sua mobilidade nas plantas, (sistêmica e não sistêmica), ou suas fontes (mineral, orgânica e

sintética). Há uma grande variedade de pesticidas que possuem características nocivas ao meio ambiente. A tabela 2.2 é uma classificação simplificada de pesticidas, representando seus exemplos e aplicações como pesticida (RODRIGO et al, 2014)

Tabela 2.2- Tipos de pesticidas

<i>Tipos de pesticidas</i>	<i>Uso primário</i>	<i>Tipo</i>	<i>Exemplos</i>
<i>Carbamatos</i>	Herbicidas, pesticidas, fungicidas	Não-iônico	Carbaryl, cabofuran, carbedazim, aldicarb e fenoxcar
<i>Cloroacetanilidas</i>	Herbicida pre-emergente	Não-iônico	Metolachlor, alachlor
<i>Clorofenoxi</i>	Inseticidas	Não-iônico	DDT, dieldrin, lindano, endosulfan e methoxychlor
<i>Organofosforados</i>	Pesticidas	Não-iônico	Biphentrin etofenprox, dentametrin, cipermetrina e esfenvalente
<i>Trazina</i>	Herbicida seletivo	Iônico	Não-ionico (Diuron, isoproturon), ácido iônica (mecotrop), iônico básico (prometone) catiônica (clormequat)
<i>Outros pesticidas</i>	Micelas	Iônico ou não-iônico	Ureas não-iônicas (diuron, isoproturon), ácido iônico (mecotrop), iônico básico (prometone), cationic (chlormequat)

Fonte: Adaptado de Rodrigo et al., 2014.

2.4 TRATAMENTO DE ELETROQUÍMICO

O tratamento Eletroquímico mostra-se como uma técnica inovadora, por ser bastante eficiente e limpa, podendo ser aplicada como uma alternativa atrativa para o tratamento de efluentes contendo compostos orgânicos via eletroxidação na superfície do ânodo (PELEGRINO et al, 2002; MARTÍNEZ-HUITLE et al, 2006 e 2009). Suas vantagens são: relativa disponibilidade de energia elétrica, condições energéticas

reacionais reduzidas (processo a frio), sistemas altamente reprodutíveis e facilmente controláveis permitindo a automação e facilidade de montagem de plantas relativamente compactas. Dois diferentes mecanismos podem ser distinguidos na oxidação de moléculas orgânicas: a oxidação direta e a indireta (MARTÍNEZ-HUITLE et al, 2006 e 2009). A oxidação direta ocorre em eletrodo com alta atividade eletrocatalítica, como a platina. Por outro lado, a oxidação eletroquímica indireta ocorre *via* mediadores que se mantêm aderidos à superfície do ânodo, onde eles são continuamente gerados. Eletrodos de óxidos de metais são comumente usados para a oxidação indireta (SIMOND et al, 1997). Na oxidação indireta, o primeiro passo consiste na descarga da água, formando radicais hidroxila (OH^\bullet) adsorvidos sobre a superfície do eletrodo Figura 1:



Os radicais hidroxilas irão reagir e formar os superóxidos MO_{x+1} sobre os sítios ativos do óxido MO_x , de acordo com :



O superóxidos fisissorvidos oxidarão então as moléculas orgânicas de acordo com:



A espécie MO_{x+1} também será responsável pela formação de oxigênio, num processo competitivo:



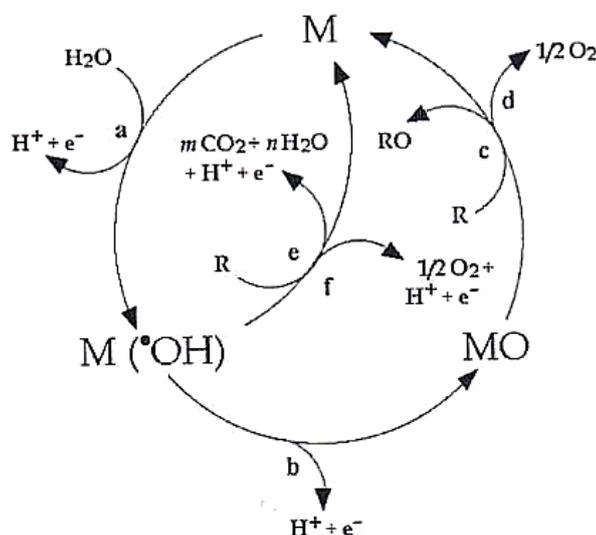
Um segundo caminho para a reação, em que o composto orgânico é mineralizado, deve também ser considerado:



A reação de combustão é mais provável que ocorra em condições de altos sobrepotenciais para a reação de desprendimento de oxigênio em superfícies de PbO_2 , SnO_2 ou Sb_2O_5 . Nestas condições, também será formado oxigênio:



Figura 2.1- Esquema da oxidação eletroquímica de compostos orgânicos com ânodos ativos (reações a, b, c, d) e não-ativos (reações a, e, f). M representa um sítio ativo do ânodo.



Fonte: Adaptada de Comninellis (1994).

Durante a eletroxidação de moléculas orgânicas, é provável que todas as reações exerçam influência sobre o processo total. De maneira geral, os ânodos são divididos em duas categorias (BOCK; MacDOUGALL, 2000, MARTÍNEZ-HUITLE et al, 2009):

- 1) Bons eletrocatalisadores da reação de desprendimento de oxigênio (RDO). São exemplos desta classe os óxidos de irídio, rutênio, tântalo, titânio e seus óxidos mistos.
- 2) Pobres eletrocatalisadores da RDO. Nesta classe estão os ânodos de PbO_2 e Pt.

A primeira categoria de ânodos é geralmente utilizada em aplicações em que a reação de desprendimento de oxigênio é de interesse primordial. Dentre os óxidos da

segunda categoria, tem destaque os ânodos de PbO_2 e Pt. Diversos autores que dedicaram seus estudos somente à comparação entre os diferentes materiais anódicos concluíram que estes apresentam o melhor desempenho na oxidação de compostos orgânicos em termos de eficiência, tempo de processo e consumo energético (KÖTZ et al, 1991; STUCKI et al, 1991; GRIMM et al, 1998, POLCARO et al, 1999, MARTÍNEZ-HUITLE et al, 2009).

A oxidação eletroquímica é uma técnica que vem sendo utilizada para remoção de compostos orgânicos em águas residuais (MONTILA et al, 2002; ZHU et al, 2009; PANIZA et al, 2010; ZHU, 2011; SIRÉS, 2012). Nos últimos anos vários grupos científicos têm investigado a aplicação da oxidação eletroquímica como alternativa para remoção de compostos orgânicos a partir de água contaminada. O capítulo 2 comenta com mais informação a aplicabilidade da tecnologia eletroquímica para remoção de compostos orgânicos em águas derivadas da indústria petrolífera.

2.5 TRATAMENTO DE SOLOS

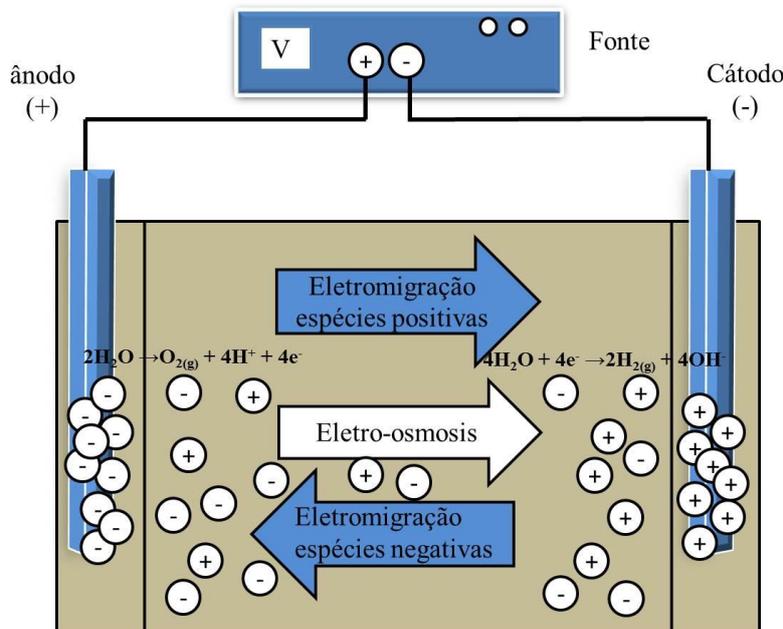
Hoje em dia, a descontaminação de solos, tornou-se uma questão ambiental de maior importância (RODRIGO et al, 2014). Além do impacto negativo sobre os ecossistemas, o transporte de poluentes para reservatórios de água pode diminuir a qualidade e até mesmo impedir a sua utilização para o abastecimento humano. Por esta razão, é muito importante a rápida atuação contra descargas acidentais de espécies perigosas, com tecnologias eficientes para remediação do solo e água evitando a poluição difusa. A contaminação de solo vem se tornando um problema ambiental e econômico nos últimos anos, em virtude da influência na produção agrícola e contaminação de lençóis freáticos. Diversas são as tecnologias para remediação de solo contaminados com compostos orgânicos tais como, processos biológicos e não biológicos (ZHANG et al, 2014), Processos Oxidativos Avançados (POA)(HUGUENOT et al, 2015), lavagem de solo (SANTOS et al, 2015) e remediação eletrocinética (SAICHEK et al, 2005; LÓPEZ-VIZCAÍNO et al, 2014). Neste trabalho será dada ênfase aos processos de remediação eletrocinética e lavagem de solo.

A remediação eletrocinética (EK) de solos contaminados com derivados do petróleo surge como uma alternativa para descontaminação, esta técnica, usada principalmente para extração de metais pesados e compostos orgânicos é fundamentada na aplicação de uma corrente elétrica para promover a movimentação dos

contaminantes (MATURI et al, 2006). Hoje em dia, a aplicação da técnica está sendo aplicada isolada (SAICHEK et al, 2003) ou combinada (MENA et al, 2014; 2015) com outras técnicas. A remoção de compostos derivados de petróleo em solo embora esteja em fase inicial, alguns pesquisadores vêm demonstrando sua eficiência e aplicabilidade (Roulier et al, 2000; TZAI et al, 2010; MENA et al, 2011; WAN et al, 2011; SEO et al, 2015). A remediação eletrocinética é uma tecnologia *in situ* que se constitui na aplicação controlada de corrente contínua de baixa intensidade, através do solo entre os eletrodos distribuídos apropriadamente. Uma das vantagens mais importantes da tecnologia é a eficácia para o tratamento de solos de baixa permeabilidade hidráulica, onde outras técnicas de atenuação natural ou tradicional não são adequadas.

A remediação eletrocinética tem seus mecanismos teóricos de aplicação baseados na *eletromigração*: é o movimento dos íons na água retida no solo sob ação de um campo elétrico gerado entre o ânodo e o cátodo. Os ânions (íons negativamente carregados) movem-se em direção ao ânodo (eletrodo carregado positivamente), ao mesmo tempo em que os cátions (íons positivamente carregados) movem-se em direção cátodo (eletrodo carregado negativamente); *Eletroforese*: é o movimento de partículas carregadas no solo (ou surfactantes adicionadas para tratar o solo), sob ação de um campo elétrico; *Eletro-osmose*: é o movimento das águas subterrânea, ou uma solução aquosa que tenha sido acrescentada para promover o movimento dos poluentes, o líquido flui tipicamente a partir do ânodo para o cátodo. *Eletrólise*: é um conjunto de processos reativos que ocorrem em superfícies anódicas e catódicas colocados no solo, diretamente ou dentro de uma solução eletrolítica em contato com o solo. Os processos mais importantes são oxidação da água sobre a superfície anódica e a redução da água sobre a superfície catódica. De uma perspectiva de recuperação do solo, a principal consequência da oxidação da água é a formação de uma “frente ácida” decorrentes da formação dos íons H^+ que se move em direção ao cátodo principalmente por eletromigração, libertando assim os poluentes fixos no solo. A redução da água na superfície catódica gera uma frente básica sentido contrário à frente ácida, decorrentes da formação dos íons OH^- , ambas as frente podem ser modificadas pela adição de reagentes adequados ao solo. *Aquecimento elétrico*: aumento da temperatura do solo, especialmente na vizinhança dos eletrodos. Esse aumento de temperatura é causado por quedas ôhmicas que são geradas por grandes resistências iônicas de solo (ou seja, o que corresponde a uma baixa condutividade iônica do solo) (ACAR, 1993; RODRIGO et al, 2014; LOPEZ-VIZCAINO et al, 2011; 2012).

Figura 2.2- Mecanismo da remediação eletrocinética.



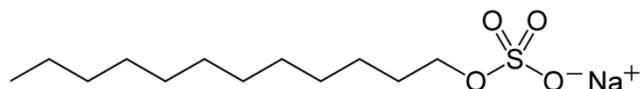
Fonte: autor, 2015.

A lavagem de solo é tida como uma tecnologia convencional para remoção de compostos orgânicos em solo (LIN, 2014; DOMBEK, 2004). Ela consiste na extração de poluentes contidos no solo com uma solução que ajuda a obter uma eficiente transferência da poluição do solo para a fase líquida. É uma tecnologia off-site, que requer escavação e transformação do solo em unidades extratoras especiais. Na verdade, ela pode ser considerada como uma unidade de operação de extração de líquido no solo, em que o poluente é transferido a partir do solo para o líquido de lavagem. No caso de produtos orgânicos, o uso de soluções contendo tensoativo é a aplicação mais abrangente. Empregando este processo, o solo contaminado pode ser descontaminado do ponto de vista químico. No entanto, um dos resíduos altamente poluidores é obtido com uma elevada carga orgânica e mistura complexa de poluentes que consiste de poluente orgânico dissolvido, e micelas (surfactante com ambas as espécies), em adição aos sais inorgânicos dissolvidos e trocados a partir do solo durante o processo de extração.

Os surfactantes empregados podem ser classificados como catiônicos, aniônicos ou surfactantes não iônicos. São compostos anfifílicos contendo tanto os grupos hidrofílicos (cabeças) e grupos hidrofóbicos (caudas) (figura 2.3). Os surfactantes podem ser classificados como sintéticos ou naturais: surfactantes naturais são também conhecidos como biossurfactantes, eles são biologicamente produzidos a partir de leveduras ou de

bactérias a partir de várias maneiras incluindo substrato açúcares, óleo, alcanos e resíduos.

Figura 2.3- Dodecil sulfato de sódio.



Fonte: autor, 2015.

Os surfactantes podem baixar a tensão superficial de um líquido, para permitir mais fácil espalhamento, a tensão interfacial entre dois líquidos, ou entre um líquido e um sólido. Assim, podem atuar como adesivos, agentes de floculação, agentes de molhagem, agentes de formação de espuma, detergentes, de emulsões, agentes de penetração e agentes dispersantes. Funções desejáveis típicas dos surfactantes incluindo aumento de solubilidade, a redução da tensão superficial, a concentração micelar crítica, habilidade de molhamento, e formação da capacidade de espumas.

3. DECONTAMINATION OF PRODUCED WATER CONTAINING PETROLEUM HYDROCARBONS BY ELECTROCHEMICAL METHODS: A MINI-REVIEW

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Abstract: Produced water (PW) is the largest waste stream generated in oil and gas industries. The drilling and extraction operations that are aimed to maximize the production of oil may be counterbalanced by huge production of contaminated water (called PW) with pollutants, such as heavy metals, dissolved/suspended solids and organic compounds. PW is conventionally treated through different physical, chemical, and biological methods. In offshore platforms because of space constraints, compact physical and chemical systems are used. However, major research efforts are being developed with innovative technologies for treating PW in order to comply with reuse and discharge limits. Among them, electrochemical technologies have been proposed as a promising alternative for the treatment of this kind of wastewaters. Then, this paper presents a mini-review of efficient electrochemical technologies used until now for treating PW generated by petrochemical industry.

3.1 INTRODUCTION

3.1.1 Petrochemical industry

The significance of oil and natural gas in modern civilization is well known. The process of refining crude oil consumes large amounts of water. Consequently, significant volumes of wastewater are generated. Oilfield wastewater or PW contains various organic and inorganic components that can pollute surface and underground water and soil (AHMADUNA et al, 2009). Coelho et al. reported that the volume of petroleum refinery effluents generated during processing is 0.4–1.6 times the amount of

the crude oil processed. Thus, based on the current yield of 84 million barrels per day (mbpd) of crude oil, a total of 33.6 mbpd of effluent is generated globally (DIYA'UDDEEN et al, 2011). World oil demand is expected to rise to 107 mbpd over the next two decades, and oil will account for 32% of the world's energy supply by 2030. Whereas, biofuels (including ethanol and biodiesel) are expected to account for 5.9 mbpd by 2030, and the contributions from renewable energy sources like wind and solar power are estimated to be 4–15% (DIYA'UDDEEN et al, 2011; DOGGETT 2009; MARCILLY, 2003). These data clearly indicate that effluents from the oil industry will continually be produced and discharged into the world's main water bodies. As regards the significant matter of environmental concern, many countries have implemented more stringent regulatory standards for discharging PW. On the other hand, because large volumes of PW are being generated, many countries with oilfields, which are also generally water-stressed countries, are increasingly focusing on efforts to find efficient and cost-effective treatment methods to remove pollutants as a way to supplement their limited fresh water resources.

3.2 PRODUCED WATER

Naturally occurring rocks, in subsurface formations are generally permeated by different underground fluids such as oil, gas, and saline water. Before trapping hydrocarbon compounds in rocks, they were saturated with saline water. Hydrocarbons with lower density migrated to trap locations and displaced some of the saline water from the formation. Finally, reservoir rocks absorbed saline water and hydrocarbons (oil and gas). There are three sources of saline water: (i) flow from above or below the hydrocarbon zone, (ii) flow from within the hydrocarbon zone and (iii) flow from injected fluids and additives resulting from production activities (AHMADUNA et al, 2009).

The last category is called “connote water” or “formation water” and becomes “PW” when saline water mixed with hydrocarbons comes to the surface (AHMADUNA et al, 2009; VEIL et al, 2004). In oil and gas production activities, additional water is injected into the reservoir to sustain the pressure and achieve greater recovery levels. Both formation water and injected water are produced along with hydrocarbon mixture. At the surface, processes are used to separate hydrocarbons from the produced fluid or PW (EKINS et al, 2007). Then, PW is considered to be one of the largest waste streams

in the petroleum, oil and gas industry. Effects of PW components on the environment are (AHMADUNA et al, 2009): (i) increase in the salinity, (ii) dispersed and soluble oil contribution in marine ecosystems, (iii) inclusion of other compounds from treating chemicals, (iv) higher concentration of heavy metals than in seawater and (v) presence of radionuclides.

PW characteristics depend on the nature of the producing/storage formation from which they are withdrawn, the operational conditions, and chemicals used in process facilities. The composition of PWs from different sources can vary by order of magnitude. However, PW composition is qualitatively similar to oil and/or gas production (FILLO et al, 1992). The major compounds of PW include: (i) Dissolved and dispersed oil compounds (a mixture of hydrocarbons including benzene, toluene, ethylbenzene, and xylenes (BTEX), naphthalene, phenanthrene, dibenzothiophene (NPD), polyaromatic hydrocarbons (PAHs) and phenols), (ii) Dissolved formation minerals, (iii) Production chemical compounds (include some chemicals that are added to treat or prevent operational problems. Treatment chemicals (production treating, gas processing, and stimulation) and production treating chemicals (scale and corrosion inhibitors, biocides, emulsion breakers, antifoam and water treatment chemicals)), (iv) Production solids (including formation solids, corrosion and scale products, bacteria, waxes, and asphaltenes), (v) Dissolved gases (VEIL et al, 2004). Water cannot dissolve all hydrocarbons, so most of the oil is dispersed in water (EKINS et al, 2007); and dissolved and suspended oil present in PW (prior to treatment) depend on several factors (AHMADUNA et al, 2009; HANSEN et al, 1994).

3.3 TREATMENT OF PW

Considerable studies have been conducted to investigate new treatment technologies in order to treating PW. Figure 1 summarizes the main technologies utilized. An extensive literature reporting the characteristics and applications of most important conventional technologies developed for this purpose including physical-chemical and chemical methods, advanced oxidation processes (AOPs), microbiological treatments and biological decomposition, has been collected in an authoritative review (AHMADUNA et al, 2009). Fakhrul-Razi et al. have indicated that oil content and salinity of PW from offshore and onshore activities can be reduced through various physical, chemical, and biological methods (AHMADUNA et al, 2009). In offshore

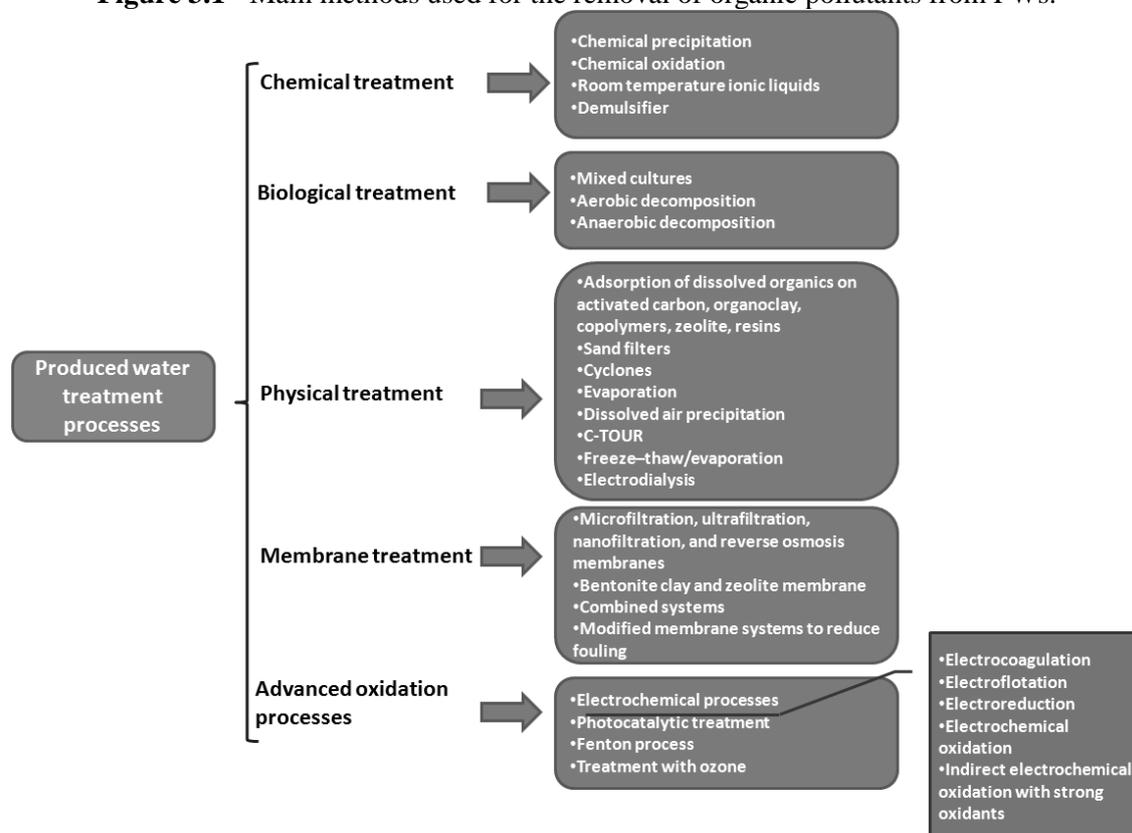
extraction facilities due to space constraints, compact physical and chemical treatment technologies are preferred. However, as capital cost of physical methods and cost of chemicals for chemical treatment of hazardous sludge is high, the application of these methods is limited. Current methods cannot remove minute suspended oil and/or hazardous dissolved organic and inorganic components. In contrast, biological treatment is a cost-effective method for removing dissolved and suspended compounds from oilfield wastewater in onshore extraction facilities. Nevertheless, electrochemical technologies for destroying petrochemical pollutants from PW have showed great attention in the last years (RAJKUMAR et al, 2004; LI et al, 2006; SANTOS et al, 2006; MA et al, 2006; DE LIMA et al, 2009; ABDELWAHAB et al, 2009; TRAN et al, 2009; TRAN L.- et al, 2009; TRAN L.-H. et al, 2010; KÖRBAHTI 2010; YAVUZ et al, 2010; ZANBOTTO RAMALHO et al, 2010; WOYTOWICH et al, 1993; MEDEL et al, 2012; WU et al, 2011; YAN et al, 2011; ZHOU et al, 2011; ROCHA et al, 2012; HE et al, 2013; SANTOS et al, 2013; LI et al, 2006; LI et al, 2006a; LI et al, 2007). Therefore, a general overview of lab and pilot plant experiments related to the most relevant applications of electrochemical methods for removing petroleum hydrocarbons from PWs will be presented.

3.4 APPLICABILITY OF ELECTROCHEMICAL TECHNOLOGIES FOR TREATING PW

Electrochemistry can be considered an alternative for the prevention of pollution problems and intensive research proceeds with the goal of discovering more efficient techniques, processes, materials, technologies and applications of electrochemistry for removing organic pollutants from water (RAJESHWAR et al, 1994; MARTÍNEZ-HUITLE et al, 2006; MARTINEZ-HUITLE et al, 2009; SALES SOLANO et al, 2013; ROCHA et al, 2012). Electroreduction (ER), Electroflotation, Electrocoagulation (EC), Electrochemical Oxidation or electro-oxidation (EO) with different anodes and Indirect Electro-oxidation (IEO) with active chlorine are the main methods for treating petrochemical wastewaters. Also, the treatment by emerging technologies such as electro-Fenton (EF) and photoassisted systems like photoelectro-Fenton (PEF) and photoelectrocatalysis (PEC) has recently received great attention. Fundamentals of each technology will be briefly commented to better understand its advantages and

limitations for the environmental prevention of pollution by petroleum hydrocarbons from PW.

Figure 3.1 - Main methods used for the removal of organic pollutants from PWs.



Fonte: Autor, 2014.

3.5 ELECTROCHEMICAL REDUCTION

A limited number of papers have been published dealing with the direct ER of petroleum hydrocarbons in aqueous solution on suitable cathodes (TRAN et al, 2009). The reason of the low interest for this conventional electrochemical technique is that it offers poor decontamination of wastewaters in comparison to more potent direct and IEO methods. An example is the elimination of polycyclic aromatic hydrocarbons (PAHs) (TRAN et al, 2009; TRAN et al, 2009; TRAN et al, 2010), where the principal degradation mechanism is due to the EO; however, an amount of the PAHs is degraded by ER at the cathode surface. The abatement of these organic compounds is the high priority because these cause serious disequilibrium in the aquatic environments, even dissolved in lower concentrations.

3.6 ELECTROCOAGULATION

EC promotes the production of coagulating agents using a current to dissolve Fe (or steel) or Al sacrificial anodes immersed in the polluted water, giving rise to the corresponding metal ions that yield different Fe(II) (and/or Fe(III)) or Al(III) species with hydroxide ion depending on the medium pH (see Figure 2, adapted from (HOLT et al, 2002). In general, the EC has important advantages and disadvantages, as indicated in Table 1 (MARTINEZ-HUITLE et al, 2009).

Apart from the electrolytic system and anode material used, petrochemical hydrocarbons removal mainly depends on solution pH, retention time (t_r), stirring or flow rate and applied current density (or cell voltage) (MA et al 2006; ABDELWAHAB et al, 2009; KÖRBAHTI 2010; YAVUZ et al, 2010). For example, EC process of phenol using Al screen as a scarified anode was studied by Abdelwahab et al, 2009. Experimental parameters such as pH, time, current density, electrolyte concentration, initial phenol concentration and an array of closely packed Al screen anode were investigated. Subsequently, under optimal experimental conditions, after 2 h of EC, 94.5% of initial phenol concentration was removed from the petroleum refinery wastewater (volume 3.5 L containing 13 mg L⁻¹ phenol, 2 g L⁻¹ of NaCl and pH 8). Practically, the effluent achieved the discharged standards after 2 h of EC time with energy consumption of 1.8 kWh g⁻¹ phenol and electrode consumption of 0.091 g Al g⁻¹ phenol.

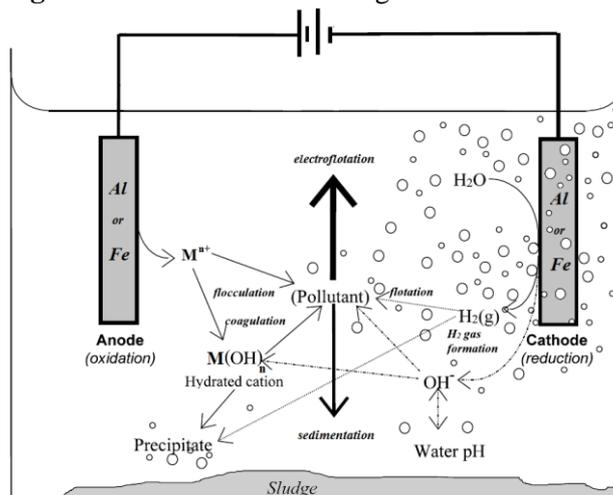
Table 3.1- Electrochemical characteristics of electrocoagulation process

Advantages	(i) more effective and rapid organic matter separation than in coagulation, (ii) pH control is not necessary, except for extreme values, (iii) the amount of chemicals required is small, (iv) the amount of sludge produced is smaller when compared with coagulation. For example, the sludge formed in the EC method with Fe contains higher content of dry and hydrophobic solids than that produced in coagulation by the action of FeCl ₃ followed by the addition of NaOH or lime, (v) the operating costs are much lower than in most conventional technologies.
Disadvantages	(i) anode passivation and sludge deposition on the electrodes that can inhibit the electrolytic process in continuous operation mode, (ii) high concentrations of iron and aluminum ions in the effluent that have to be removed.

Fonte: Autor, 2014.

Ma, 2006 and Yavuz et al, 2010 studied coupled processes (EC and EO) where the oil field PW was treated in laboratory pilot-scale plant, using double anodes with active metal (M) and graphite (C) with iron as cathode and a noble metal content catalyst with big surface. Due to the strong oxidizing potential of the chemicals and coagulants produced, when the wastewater passes through the pilot plant, the organic pollutants were oxidized and coagulated. Both chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were reduced by over 90% in 6 min, suspense solids (SS) by 99%, Ca²⁺ content by 22%, corrosion rate by 98% and bacteria by 99% in 3 min under 15 V/120 A. However, EC process was found to be ineffective for the treatment of petroleum refinery wastewater, achieving removal efficiencies of 8.23% and 6.27% for phenol and COD, respectively. Also, an average energy consumption value of 32 kWh g⁻¹ was obtained, and it is approximately 5 times higher than the energy consumption values obtained in other methods. Woytowich et al. 1993, investigated the treatment of ship bilge water contaminated with high concentrations of oil, suspended solids, and heavy metals in a continuous EC system using iron and aluminum electrodes, and this process was effective in destabilizing oil emulsions and in removing heavy metals, obtaining modest efficiencies on COD removal.

Figure 3.2 - Mechanisms during electrochemical coagulation.



Fonte: Adapted from (Holt, et al., 2002).

3.7 DIRECT AND INDIRECT ELECTROCHEMICAL OXIDATION

EO is the most popular electrochemical technology for removing organic pollutants from wastewaters (RAJESHWAR 1994; MARTÍNEZ-HUITLE 2006; MARTÍNEZ-HUITLE 2009; SALES SOLANO et al, 2013; ROCHA et al, 2012). It consists in the oxidation of pollutants in an electrolytic cell by: (i) direct anodic oxidation (or direct electron transfer to the anode), which yields very poor decontamination, and (ii) chemical reaction with electrogenerated species from water discharge at the anode such as physically adsorbed “active oxygen” (physisorbed hydroxyl radical ($\bullet\text{OH}$)) or chemisorbed “active oxygen” (oxygen in the lattice of a metal oxide anode (MO)). The action of these oxidizing species leads to total or partial decontamination, respectively. Considering the above electrocatalytic fundamentals, two main approaches for the pollution abatement in wastewaters by EO (MARTÍNEZ-HUITLE, 2006) has been proposed: (i) the electrochemical conversion method, in which refractory organics are selectively transformed into biodegradable compounds, usually carboxylic acids, with chemisorbed “active oxygen”, and (ii) the electrochemical combustion (or electrochemical incineration) method, where organics are completely mineralized, i.e., oxidized to CO_2 and inorganic ions, with physisorbed $\bullet\text{OH}$.

Based on the existing literature, the nature of the anode materials as well as the electrochemical reactor configuration influence strongly the selectivity and efficiency of the EO process due to the significant cell voltages that are applied to the electrochemical cell for the simultaneous oxidation of pollutants and water. It is important to note that, EO via OH radicals is not the only oxidation mechanism that occurs by electrochemical technologies use; other oxidants can be also generated on anode surface, and consequently oxidizing organic matter, commonly known as indirect electrochemical oxidation (IEO). In the case of IEO, two approaches are mainly utilized: (i) the EO with active chlorine, where direct anodic oxidation of chloride ion present in the effluent leads to the formation of free chlorine and/or chlorine-oxygen species that can oxidize organic pollutants in the bulk until overall mineralization (ZANBOTTO RAMALHO et al, 2010), and (ii) the EF process in which organics can be mineralized with homogeneous $\bullet\text{OH}$ formed from Fenton's reaction between added catalytic Fe^{2+} and H_2O_2 electrogenerated from O_2 reduction at a suitable cathode (YAVUZ et al, 2010).

In both cases petroleum pollutants are also competitively destroyed by direct anodic oxidation and by reaction with heterogeneous $\bullet\text{OH}$ and other reactive oxygen species and weaker oxidants produced from anodic oxidation of water and anions of the wastewater (YAVUZ et al, 2010; ZANBOTTO RAMALHO et al, 2010; MARTÍNEZ-HUITLE 2006; MARTÍNEZ-HUITLE, 2009). In EO with active chlorine, however, a special attention merits the kind of anode material chosen, because it determines the predominant oxidants produced during the electrolysis of chloride solutions.

3.7.1 Application of electrochemical technology (EO and IEO) for treating petroleum wastewater

A limited number of reports have published concerning the application of EO and IEO for removing petroleum hydrocarbons from waters (RAJKUMAR 2004; SANTOS et al, 2006; DE LIMA et al., 2009; TRAN et al., 2009; TRAN 2010; MEDEL et al, 2012). Table 2 summarizes the most relevant results obtained for the degradation of petroleum hydrocarbons by EF, direct and indirect EO process. An inspection of Table 2 corroborates the great mineralization attained for petroleum pollutants in EO with different anodes. For example, Santos et al, 2006, investigated the electrochemical remediation of oil extraction industry wastewater using $\text{Ti/Ru}_{0.34}\text{Ti}_{0.66}\text{O}_2$ anode. The

authors obtained the best COD reduction (57%) of an oily sample for 70 h at 50°C with a current density of 100 mA cm⁻² (Santos et al, 2006), but the slow rate of COD reduction could be attributed to the occurrence of secondary reactions involving O₂, Cl₂ and H₂ evolution. Also, 24%, 48% and 57% COD reduction after 70 h of electrolysis at 10 °C, 25 °C and 50 °C were achieved, respectively. The electrochemical purification of bilge water using Pt/Ir electrodes were investigated by Körbahti and Artut 2010, where the optimized conditions under specified constraints were obtained for the highest desirability at 100% bilge water composition (COD₀ = 3080 mg/L), 50/50% seawater/fresh water composition, 12.8 mA cm⁻² current density and 32°C reaction temperature, obtaining COD removals ranging from 85-100%.

On the other hand, EO and IEO by using boron doped diamond anode (BDD), EO by using ruthenium mixed metal oxide (Ru-MMO) electrode, and EF by using iron electrode were investigated for the treatment of petroleum refinery wastewater (PRW) by Yavuz et al, 2010. Under best operational conditions, complete phenol and COD removal can be achieved in almost all electrochemical methods (Table 1). The most efficient method was the EF process followed by the EO using BDD anode. Phenol removal of 98.74% was achieved in 6 min of electrolysis and COD removal of 75.71% was reached after 9 min of electrolysis in EF. Whereas, 99.53% phenol and 96.04% COD removal were obtained in EO at the current density of 5 mA/cm² and in IEO, in the presence of 0.05 M NaCl, 98.9% phenol removal at 60th min, and 95.48% COD removal at 90th min were reached at the current density of 3 mA/cm².

Zanbotto Ramalho et al, 2010 studied the anodic oxidation of organic pollutants from PW generated by petroleum exploration of the Petrobras plant-Brazil using an electrochemical reactor with a Ti/RuO₂-TiO₂-SnO₂ electrode. Under galvanostatic conditions ($j = 89 \text{ mA cm}^{-2}$), it was found that the organic pollutants degradation, using different flow rates (0.25, 0.5, 0.8 and 1.3 dm⁻³ h), achieved distinct removal efficiencies (98%, 97%, 95% and 84% were achieved, respectively). Significantly, under the same conditions, EO process achieved poor degradation of phenol and ethyl benzene: 20–47% (at 0.25, 0.8 and 1.3 dm⁻³ h) and 17–47% (at 0.25, 0.5, 0.8 dm⁻³ h), respectively. Complete elimination of pollutants was obtained after 0.5–2.5 h of electrolysis, with energy consumption values ranging from 4.84 to 0.97 kWh m⁻³ and removal prices from 0.14 to 0.61 US\$ (from 0.11 to 0.5 Euros).

Other organic compound that is considered an important pollutant is the methyl tert-butyl ether (MTBE); it is always the most likely found compound at the front of a

gasoline plume due to its chemical characteristics. Wu 2011, studied the electrochemical removal of MTBE in a lab-scale bath electrolyzer, using an iridium dioxide (IrO_2) coated electrode. The results demonstrated that depending on the constant-potential controls, electrochemical removal of MTBE can be conducted either through direct oxidation, water electrolysis competition, or indirect oxidation. Direct oxidation mechanism performed MTBE removal up to 39% as electrolyzing below 1.2 V, and the occurrence of water electrolysis competition dropped MTBE removal as increasing the operative potential up to 2.0 V. The continual increase of operative potential above 2.0 V brought about indirect oxidation of MTBE through the chain reactions of the redox mediator $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$. The matrix effect of iron enhances electrochemical oxidation of MTBE to provide about 2 times improvement on MTBE removal. The products of MTBE degradation were identified as tert-butyl alcohol (TBA), acetone, and CO_2 by GC/MS, and the distributions of carbon atoms in TBA, acetone, CO_2 , and MTBE were found 18, 12, 62, and 8% through the optimum control of electrochemical oxidation (WU, 2011).

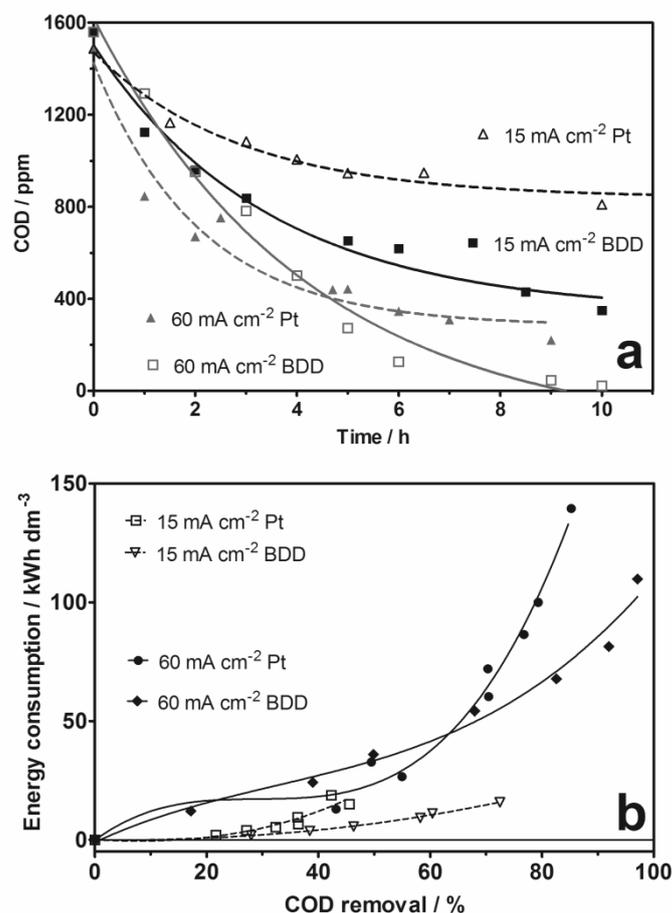
On the other hand, Yan et al, 2011, treated a petroleum refinery wastewater by an electrochemical process with three dimensional multi-phase electrodes, which introduced Fe particle and air into a traditional two-dimensional reactor. The experimental results showed that the effluent with higher COD removal efficiency (92.8%) and low salinity ($84 \mu\text{S cm}^{-1}$) was obtained when the initial pH was 6.5, cell voltage was 12 V and fine Fe particle was introduced in the reactor. The main organic compounds in the refineries wastewater, identified by GC-MS, UV spectrum and conductivity, were phenols as well as little amount of phthalate, paraffin, unsaturated acid and halogenated hydrocarbons, which contribute to the COD value and pollute the environment. Based on these results, the electrochemical system with three-dimensional multi-phase electrode can be proposed as an effective approach to treat petroleum refinery wastewater.

Electrochemical oxidation approach for the treatment of a high-salinity reverse osmosis (RO) concentrate on BDD, $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ and $\text{Ti}/\text{IrO}_2\text{-RuO}_2$ anodes was investigated by Zhou et al, 2011. Both direct oxidation and indirect oxidation by active chlorines played a role on the treatment of RO concentrate, but the contribution was different on three anodes. A highest COD removal (>98%) was observed on BDD electrode at the same current density (25, 50 and 75 mA), and a least energy consumption was obtained on $\text{Ti}/\text{IrO}_2\text{-RuO}_2$ electrode (ranging from 0.048 to 0.066

kWh/g COD), while only partial COD removal (<50%) was achieved on Ti/IrO₂-Ta₂O₅ electrode. The feasibility of the electrochemical treatment of RO concentrate was validated, and the Ti/IrO₂-RuO₂ electrode showed the greatest potential for industrial application owing to its comparably large removal efficiency, low energy consumption and suitability in wide pH ranges.

Bezerra Rocha et al, 2012, investigated the anodic oxidation of real PW, generated by petroleum exploration of the Petrobras plant from Brazil, using platinum supported on Ti (Ti/Pt) and boron-doped diamond (BDD) anodes in an electrolytic batch cell. The influence of several operating parameters such as current, supporting electrolyte, agitation rate and temperature on the performance was studied and the energy consumption was also evaluated. Results clearly showed that BDD promotes complete COD removal (98%) due to the high amounts of effective hydroxyl radicals and peroxodisulfates generated from water oxidation. COD removal rate increased notoriously when an increase on current density (from 15 to 60 mA cm⁻²) was applied (Figure 3a). Conversely, at Pt electrode, about 50% of COD removals were achieved by applying 15 and 30 mA cm⁻² of current density, and 80% of COD removal at 60 mA cm⁻². When GC-MS analysis was performed to determine the concentration of the principal petroleum hydrocarbons eliminated; a comparison between the elimination of these organic pollutants as a function of applied current densities (15 and 30 mA cm⁻²) and experimental conditions (real discharged conditions, Na₂SO₄ dissolved in the effluent and temperature) demonstrated that more than 95% of the organic compounds were completely oxidized as well as heavy metals were removed (ROCHA et al, 2012). However, higher energy consumption and longer process time were accomplished, limiting the applicability of this technology for complete treatment of petrochemical wastewaters (Figure 3b).

Figure 3.3- (a) Comparison of the COD decay, as a function of time, between Pt and BDD anodes during electrochemical treatment of PW containing with 5 g of Na_2SO_4 dissolved by applying 15 and 60 mA cm^{-2} of current density at 60 °C. (b) Evolution of the energy consumption against % of COD removal during electrochemical treatment of petrochemical wastewater on Pt and BDD anodes. Conditions: applied current density: 15 and 60 mA cm^{-2} ; $T=60$ °C; agitation rate: 400 rpm and 5 g of Na_2SO_4 dissolved in PW effluent.



Fonte: Rocha, et al., 2012.

Electrochemical removal of bisphenol A using a carbon nanotubes-covered polyester yarn electrode was studied by He and co-workers 2013, demonstrating that carbon nanotubes-based electrode with a carbon nanotubes (CNT) network on surface, has a high special surface area and a high electrochemical activity, making it useful for the removal of phenolic compounds from the contaminated water. Through electrochemical polymerization and degradation on this electrode, high removal efficiency of bisphenol A was obtained, at levels as high as 8.1×10^{-5} mol/g with 0.75 V applied potential.

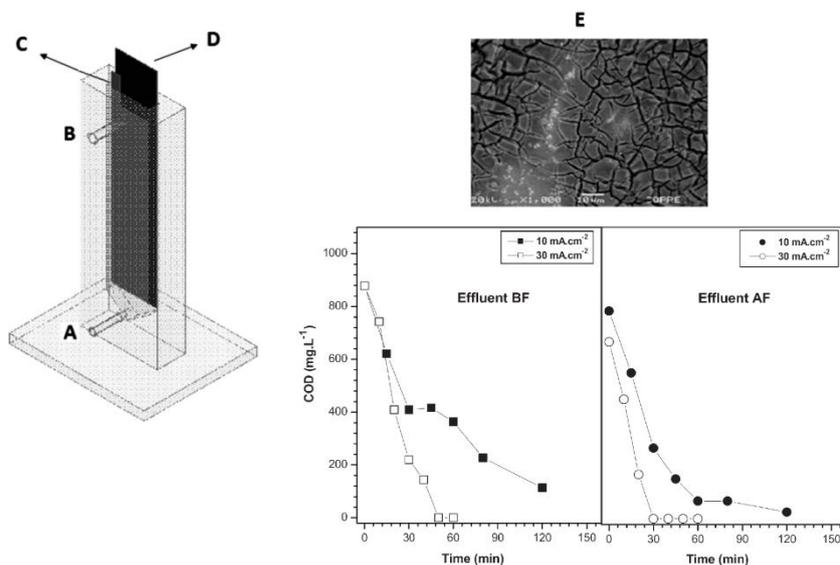
Table 3.2- Percentage petroleum pollutants removals and energy consumption determined for the EO, IEO and EF with different anodes of selected petrochemical wastewaters.

Anode used* Wastewater	C_0 / mg dm ⁻³	j^d / mA cm ⁻²	Electrolysis time / h	Current efficiency/ %	COD decay / %	Energy consumption/ Cost
<i>Ti/TiO₂-RuO₂- IrO₂</i> Oil refinery	602 ^a 141 ^b 112 ^c	54	20 ^d	7.5	92	105.8 kWh m ⁻³
<i>Ti/Ru_{0.34}Ti_{0.66}O₂</i> Oil extraction industry	315 ^a 887 ^c	100	70	5	57	- ^f
<i>Ti/RuO₂-TiO₂</i> Produced water	103 ^g 1.8 ^b	8.6-17.8	2	65	99 ^h	- ^f
<i>Ti/RuO₂</i> Creosote oil solution containing PAHs	2102 ^a 237 ⁱ	9.23	1.5	70	61 26 ^j	42 kWh m ⁻³
Industry waste containing PAHs	18440- 7709 ^k	9.23	1.5 6.5	67 100	65-95 ^l	1680-735 kWh t ⁻¹
Amphoteric surfactant solution containing PAHs	418 ^k	4-13	1.5	45	80-82 ^l	5.11 US\$ m ⁻³ (3.8 Euros m ⁻³)
<i>Pt/Ir</i> Bilge water (seawater + petroleum pollutants)	3080 ^a 23916 ^b	12.8	4	79	85-100	13.9-50.9 kWh kg ⁻¹
<i>Nb/BDD</i> Petroleum refinery (EO process)	590 ^a 193 ^b 1775 ^c	3	1	90	95 98 ^m	4 kWh g ⁻¹
Petroleum refinery (IEO process)	3471 ^b	320	2	70	98 ^j	2 kWh g ⁻¹
<i>Si/BDD</i> Phenolic compounds from the hydrocarbon industry	590 ^a 193 ^b	1	0.25	70	98 75 ^m	- ^f
<i>Iron</i> Petroleum refinery (EF process)	590 ^b 193 ^c	20	3.5	76	70 94 ^m	0.15 kWh g ⁻¹
<i>Ru mixed metal oxide</i> Petroleum refinery						7 kWh g ⁻¹

^a Initial COD (mg L^{-1}); ^b Phenolics initial concentration (mg L^{-1}); ^c Chloride dissolved (mg L^{-1}); ^d Applied current density; ^e Specific charge passed (Ah dm^{-3}); ^f Not determined; ^g NH_4^{4+} concentration; ^h % NH_4^{4+} of removal; ⁱ initial TOC; ^j %TOC of removal; ^k mg Kg of PAHs; ^l % of PAHs removal; ^m % of phenol removal.

Recently a study has evaluated the efficiency of Ti/RuO₂ anode in degrading organic substances, present in wastewaters from petroleum industry, before their discharge or reuse (SANTOS et al, 2013) using an electrochemical flow reactor with higher anode area (Figure 4). The COD removals, after 120 min of electrolysis, with a current density of 10 mA cm^{-2} , anodic area of 107 cm^2 , flow rate of 0.54 mL s^{-1} and at 25°C , were above 96%, for effluent after flotation, with 712 mg L^{-1} COD, and 87% for effluent before flotation, with 833 mg L^{-1} COD. Partial COD removal from both effluents was achieved when current density was increased from 10 to 30 mA cm^{-2} . The increase of current density also favored a decrease of the electrolysis time necessary to achieve a complete COD removal from both effluents. However, current density increase also led to higher specific energy consumption. For example, for the effluent before flotation treatment, the cost of the energy necessary to achieve a complete COD removal in 60 min was around $38 \text{ US\$ kg}_{\text{COD}}^{-1}$ ($28.5 \text{ Euros kg}_{\text{COD}}^{-1}$), while that for effluent after flotation treatment, under similar conditions after 30 min of electrolysis was only $28 \text{ US\$ kg}_{\text{COD}}^{-1}$ ($21 \text{ Euros kg}_{\text{COD}}^{-1}$). Results showed that Ti/RuO₂ electrode can be an efficient alternative for the treatment of effluents containing residues of petroleum and petroleum products (SANTOS et al, 2013).

Figure 3.4- Scheme of the electrolytic cell used in the experiments. A) effluent entrance; B) effluent exit; C) cathode: titanium plate; D) anode: Ti/RuO₂ plate; E) SEM micrographs of Ti/RuO₂ anode. Graphics: Influence of electrolysis time on COD removal from effluents before filtration (BF) and after filtration (AF) for different current densities. Anodic area: 107 cm², flow rate: 0.54 mL s⁻¹, T: 25 °C.



Fonte: Adapted from WU, 2011.

3.8 PETROCHEMICAL WASTEWATERS TREATMENT BY EMERGING TECHNOLOGIES

Recently, the emerging electrochemical treatments have received increasing attention, such as electro-Fenton (EF) and photoassisted systems like photoelectro-Fenton (PEF) and photoelectrocatalysis (PEC) (TRAN et al, 2009; MEDEL et al, 2012; Wu 2011). Li et al. found that the COD removal efficiency of PW by PEC process was much higher than that of by photocatalytic or EO. They also observed an increase in COD removal at concentrations of 316.9 mg/L and a decrease in COD removal at twofold concentrations (645.0 mg/L) (LI, et al., 2006a). Li et al. 2007 also compared treatment of PW by photocatalysis, EO, and PEC. Results showed that at equivalent doses, PEC exhibited the greatest capability to reduce genotoxicity, whereas photocatalysis was the least effective and did not cause appreciable change in mutagenicity, but results of both biological and chemical analysis indicated that PEC was the most effective technology for degradation of oilfield wastewater. Also, a recent report published by Yavuz et al. 2010, demonstrated the efficiency of EF for removing organic pollutants from petroleum refinery wastewater (see Table 1).

4 CONCLUSIONS AND TRENDS

Electrochemical technologies to remove organic pollutants from PWs were investigated by some authors. The present findings show the applicability of electrochemical technology for the treatment of organic petroleum wastewater, and they point to the EO and IEO as promising alternatives for organic/inorganic pollutants removal from PWs generated in petrochemical industries. At the same time, these technologies are suitable for the elimination of several petroleum pollutants from water, under different environmental conditions; and coupled to other electrochemical technologies could be applied to reduce the environmental disaster as occurred in Mexico Gulf with the oil massive spill.

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4. SCALE-UP OF ELECTROCHEMICAL OXIDATION SYSTEM FOR TREATMENT OF PRODUCED WATER GENERATED BY BRAZILIAN PETROCHEMICAL INDUSTRY

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Abstract

Scale-up of anodic oxidation system is critical to the practical application of electrochemical treatment in bio-refractory organic wastewater treatment. In this study, the scale-up of electrochemical flow system was investigated by treating petrochemical wastewater using Ti/Pt and BDD anodes. It was demonstrated that flow cell was successfully scaled up because when it was compared with batch mode (BEZERRA-ROCHA et al., 2012), higher performances on organic matter removal were achieved. Under the suitable operating conditions and better anode material, the COD of petrochemical wastewater was reduced from 2746 mg L⁻¹ to 200 mg L⁻¹ within 5 h with an energy consumption of only 56.2 kWh m⁻³ in the scaled-up BDD anode system. These results demonstrate that anode flow system is very promising in practical bio-refractory organic wastewater treatment.

Keywords: produced water; water treatment; electrochemical oxidation; petrochemical pollution.

4.1 INTRODUCTION

Many industrial processes generate bio-refractory organic wastewaters, i.e., the production of pesticide and herbicide, dyes and textiles, pharmaceuticals, pulp and

paper, plastics and detergents coking, oil refineries and petrochemical industries (BEZERRA-ROCHA et al, 2012; LAI et al, 2008; KIM et al, 2002; CHEN et al, 2007; CHELLIAPAN et al, 2006; POKHREL et al, 2004). These wastewaters usually contain many toxic organic pollutants, and thus are difficult to be effectively treated by conventional biological methods. Advanced oxidation processes (AOPs), including Fenton oxidation (BRILLAS et al. 2009), ozonation (LIN et al, 2001), wet air oxidation (GOGATE et al, 2004), photocatalytic oxidation (CHONG et al, 2010), supercritical water oxidation (DING et al, 1996) and electrochemical oxidation (BEZERRA-ROCHA et al, 2012; MARTÍNEZ-HUITLE et al, 2006; RAJKUMAR et al, 2004), have been developed to treat these bio-refractory organic wastewaters.

In recent years, electrochemical oxidation (EO) of refractory effluents has received a great deal of attention thanks to its attractive characteristics, such as versatility, energy efficiency, amenability of automation and environmental compatibility (free-chemical reagents). And, so far, many papers reported that electrochemical treatment has been applied successfully for the complete oxidation of various organic pollutants (MARTÍNEZ-HUITLE et al, 2006; MARTINEZ-HUITLE et al, 2009; PANIZZA et al, 2009). Moreover, a wide variety of electrode materials have been suggested, such as dimensionally stable anodes, noble metals (e.g. platinum), carbon-based anodes, PbO_2 and BDD; obtaining different removal organic matter efficiencies. At the same time, a large variety of electrochemical systems have been tested for the treatment of wastewaters by EO (MARTÍNEZ-HUITLE et al, 2006; MARTINEZ-HUITLE et al, 2009; PANIZZA et al, 2009). Conventional three-electrode cells with two-compartment or one-compartment and divided or undivided two electrode cells or tank reactors have been widely utilized. Other authors have employed flow cells with parallel electrodes and flow plants with a three-phase three-dimensional electrode reactor or a bipolar trickle tower reactor.

However, the scale-up of electrochemical systems is the next critical step that would make electrochemical oxidation to be a practical technology for wastewater treatment. Only a few researches on the scale-up anodic systems have been reported (TRÖSTER et al, 2002; URTIAGA et al, 2009; ANGLADA et al, 2010; ANGLADA et al, 2009; ZHU et al, 2010; ZHU et al, 2011). Therefore, in this study, the scale-up of anode oxidation systems was investigated on flow mode electrochemical oxidation of produced water (wastewater produced by Brazilian petrochemical industry) at different volume value, current density, temperature, initial COD concentration and supporting

electrolyte concentration than those used to batch mode. Moreover, the perspective of electrochemical oxidation using BDD and Ti/Pt electrodes is discussed based on the scaled-up results, compared with the results obtained on batch mode in our previous work (BEZERRA-ROCHA et al, 2012). Produced water (PW) wastewater was chosen as the studied object since it is the most important effluent generated by Brazilian petrochemical industry.

PW is considered to be one of the largest waste streams in the petroleum, oil and gas industry. The drilling and extraction operations that are aimed to maximize the production of oil may be counterbalanced by huge production of contaminated water (called PW) with pollutants, such as heavy metals (Cd, Cr, Cu, Pb, Hg, Ag, Ni, Zn), organic compounds, and dissolved/suspended solids (BEZERRA-ROCHA et al, 2012; YAVUZ et al, 2010; RAMALHO et al, 2010). Benzene, toluene, xylene, phenol, halogenated aromatic compounds, chloroform and trichloroethylene are the major organic pollutants present in PW, which were generated by oil refineries and fine chemical industries (RAMALHO et al, 2010). Also, the PW generally presents high amounts of other toxic chemicals added during oil recovery such as: corrosion and incrustation inhibitors, de-emulsifiers, methanol, glycol, poly-electrolytes, as well as a complex mixture of organic and inorganic compounds, whose composition varies along the lifetime of the oil source. The environmental impact due to disposal of the PW is determined by the toxicity and the amount of its constituents. Some of them remain dissolved, while others tend to disappear due to decomposition, evaporation, transformation in another less toxic compound, deposition in the deep sea, etc. The most harmful effect is associated to the compounds that remain soluble in water, as they interact, consequently, directly with life (AHMADUNA et al. 2009).

4.2 EXPERIMENTAL

4.2.1 Description of the produced water

PW samples were supplied by Petrobras plant in Rio Grande do Norte. The oil is separated from the produced water in that terminal. Its pH is around 7.59 and electric conductivity around $63.88 \mu\text{S cm}^{-1}$. It contains 4.38 g L^{-1} of total dissolved solids and 15 mg L^{-1} of oils and greases. Chemical oxygen demand (COD) was about 2746 mg

L⁻¹. Table 1 reports the average composition of the produced water as received in the terminal, concerning to inorganic species.

Table 4.1- Average concentration of inorganic species in the produced water samples.

Ion	mg L ⁻¹
Cl ⁻	22441
Na ⁺	5857
Ca ²⁺	1635
Br ⁻	215
Mg ²⁺	248
K ⁺	156
Sr ²⁺	148
NH ⁴⁺	98
S ²⁻	120
Ba ²⁺	5
Cr ³⁺	<0.1
SO ₄ ²⁻	120
Fe ³⁺	3.4
Cd ²⁺	<0.1
Mn ²⁺	1.2
Li ⁺	2.0
Zn ²⁺	0.7
Cu ²⁺	<0.1
Ni ²⁺	0.14
Pb ²⁺	0.08
Ag ⁺	<0.5
Al ³⁺	<0.1
Sn ⁴⁺	<0.1
F ⁻	4.1
Co ²⁺	<0.1
CN ⁻	<0.1

Fonte: Autor, 2014.

4.2.2 Chemicals

Chemicals were of the highest quality commercially available, and were used without further purification. Na₂SO₄ was purchased from Fluka.

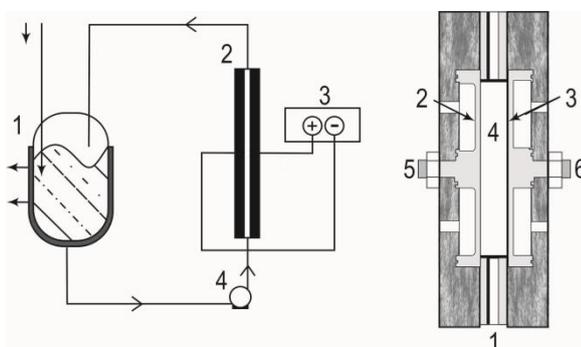
4.2.3 Electrolytic systems

Bulk oxidations were performed in a single-compartment, electrolytic flow cell with parallel plate electrodes (Fig. 1). Circular electrodes (Ti/Pt or BDD electrode) were used, as anodes; exposing to the effluent a nominal surface area of 63.5 cm²; in all

cases, a Ti disc was used as the cathode. The inter-electrode gap was 10 mm. Ti-supported Pt anode was supplied by Industrie De Nora S.p.A. (Milan, Italy). Whereas, the boron-doped diamond (BDD) thin-film electrode was supplied by CSEM (Centre Swiss d'Electronique et de Microtechnique, Neuchatel, Switzerland). It was synthesized by the hot filament chemical vapor deposition technique (HF-CVD) on single-crystal *p*-type Si $\langle 1\ 0\ 0 \rangle$ wafers (1–3 m Ω cm, Siltronix). The doping level of boron in the diamond layer, expressed as B/C ratio, was about 3500 ppm. The resulting diamond film thickness was about 1 μm with a resistivity of 10–30 m Ω cm.

For the electrochemical flow cell, inlet and outlet were provided for effluent circulation through the reactor; the PW was stored in a thermoregulated glass tank (5 L) and circulated through the cell using a peristaltic pump (inset in Fig. 1), at a flow rate of 151 dm³ h⁻¹, which allowed a mass transfer coefficient (determined using the ferri/ferro-cyanide redox couple) of 2.0×10^{-5} m s⁻¹.

Figure 4.1- Electrochemical flow cell for the oxidation of PW at Ti/Pt and BDD anodes. (a) Set-up used: (1) thermoregulated reservoir; (2) electrochemical cell; (3) power supply; (4) pump. (b) Electrochemical cell: (1) inlet; (2) anode; (3) cathode; (4) electrolysis compartment; (5 and 6) electrical contacts and (7) outlet.



Fonte: Autor, 2014.

The oxidation experiments of PW were performed under galvanostatic conditions (using a power supply MINIPA-3305M) at 25 °C for studying the role of applied current density ($j = 20, 40$ and 60 mA cm⁻²) adding or not Na₂SO₄ for increase effluent conductivity (as already observed in previous work (BEZERRA-ROCHA et al, 2012), while the temperature effect (25, 40 and 60°C) was studied under a current density of 40 mA cm⁻².

4.2.4 Analytical methods

Experimentally, decontamination of petrochemical wastewaters was monitored from the abatement of their COD. Values were obtained, using a HANNA HI 83099 spectrophotometer after digestion of samples in a HANNA thermo-reactor, in order to estimate the Total Current efficiency (TCE) for anodic oxidation of PW, using the following relationship (BEZERRA-ROCHA et al. 2012):

$$\%TCE = FV \left(\frac{[COD_0 - COD_f]}{8I\Delta t} \right) \times 100 \quad (1)$$

where COD_0 and COD_f are chemical oxygen demands at times $t=0$ (initial) and f (final time) in $g\ O_2\ dm^{-3}$, respectively; I the current (A), F the Faraday constant ($96,487\ C\ mol^{-1}$), V the electrolyte volume (dm^3), 8 is the oxygen equivalent mass ($g\ eq.^{-1}$) and Δt is the total time of electrolysis, allowing for a global determination of the overall efficiency of the process.

Additionally, the limiting current can be estimated from the value of COD using the equation 2 for anodic oxidation of a real wastewater (BEZERRA-ROCHA et al, 2012; PANIZZA et al, 2010; MARTÍNEZ-HUITLE et al, 2012).

$$I_{lim}(t) = 4FAk_m COD(t) \quad (2)$$

where $I_{lim(t)}$ is the limiting current (A) at a given time t , 4 the number of exchanged electrons, A the electrode area (m^2), F the Faraday's constant, k_m the average mass transport coefficient in the electrochemical reactor ($m\ s^{-1}$) and $COD(t)$ the chemical oxygen demand ($mol\ O_2\ m^{-3}$) at a given time t .

The energy consumption (EC) per volume of treated effluent was estimated and expressed in $kWh\ dm^{-3}$. The average cell voltage, during the electrolysis, is taken for calculating the energy EC, as follows (BEZERRA-ROCHA et al, 2012):

$$Energy\ consumption = \left(\frac{\Delta E_c \times I \times t}{3600 \times V} \right) \quad (3)$$

where t is the time of electrolysis (s); ΔE_c (V) and I (A) are the average cell voltage and the electrolysis current, respectively; and V is the sample volume (dm^3).

The concentration of inorganic species in the petrochemical wastewater before and after the electrochemical treatment (Table 1 and 2) was measured using a Varian AA 340 Atomic Absorption Spectrometer. On the other hand, during each some electrolysis, samples of anolyte were extracted into non-aqueous medium and were subjected to GC-MS analysis using GC-MS-QP Shimadzu Mass Spectrometer to confirm the elimination of most important petroleum hydrocarbons during the course of the reaction.

Table 4.2- Average concentration of inorganic species in the produced water samples after electrochemical treatment applying 60 mAcm^{-2} of current density, 60°C and 5 g of Na_2SO_4 .

Using Pt electrode		Using BDD electrode	
Ion	mgL^{-1}	Ion	mgL^{-1}
Cl^-	13658	Cl^-	18345
Na^+	5199	Na^+	5684
Br^-	<0.1	Br^-	<0.1
F^-	1.71	F^-	1.48
NO_3^-	30.20	NO_3^-	70808
SO_4^{2-}	840.1	SO_4^{2-}	50.4
K^+	158.5	K^+	175.7
Mn	<0.1	Mn	<0.1
Mg^{2+}	227.5	Mg^{2+}	237.5
Fe	2.37	Fe	1.57
Sr	254.7	Sr	157.8
Ca^{2+}	1325	Ca^{2+}	1448
B	12.28	B	8.88
Ba	<0.1	Ba	<0.1
Cl^-	13658	Cl^-	18345
Na^+	5199	Na^+	5684

Fonte: Autor, 2014.

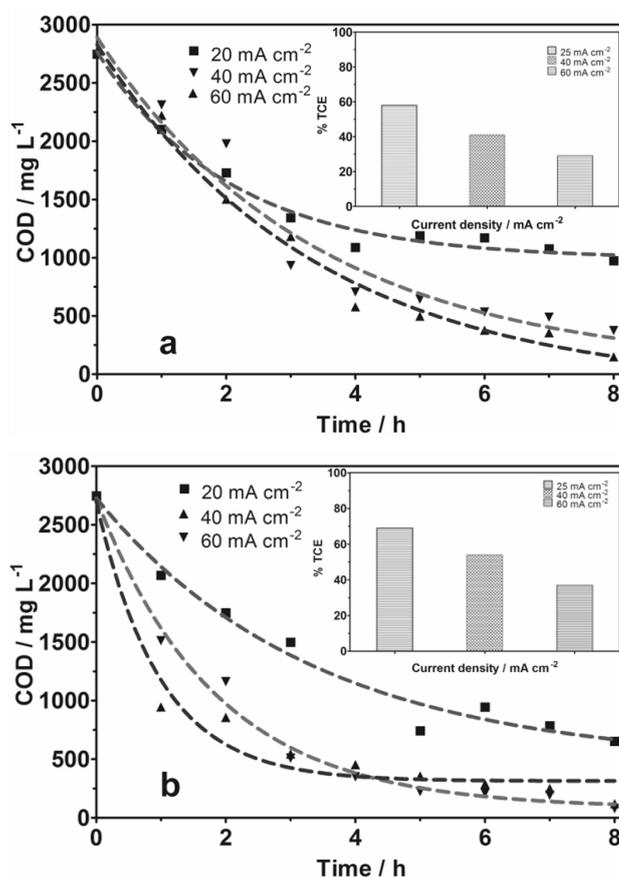
4.3 RESULTS AND DISCUSSIONS

4.3.1 Electrochemical treatment of PW using the Ti/Pt and BDD anodes

As it was evidenced in our previous work (BEZERRA-ROCHA et al, 2012), Ti/Pt and BDD anode had great oxidation ability to remove organic pollutants from PW

in batch mode, requiring modest electrolyses times to reach overall mineralization, thus leading to remarkably current efficiency and relative energy consumptions. For these reasons, the good removal efficiencies suggest the possibility of using EO as treatment technology for treating real petrochemical effluents (ABDELWAHAB et al, 2009; TRAN et al, 2009; TRAN et al, 2010; KÖRBAHTI et al, 2010; YAVUZ et al, 2010; RAMALHO et al, 2010). However, the scale-up of electrochemical systems is the next critical step that would make EO to be a practical technology for wastewater treatment. Consequently, an electrochemical flow cell was used in order to find the best condition for the anodic treatment of the petrochemical wastewater (employing the PW samples as received from petrochemical industry), preliminary experiments were performed at 25°C for studying the role of anode material (Ti/Pt and BDD anodes with 63.5 cm²) and applied current density ($j=20, 40$ and 60 mAcm⁻²). Fig. 2a and 2b show the trend of the COD as a function of time and %TCE (insets) during the anodic treatment by applying 20, 40 and 60 mAcm⁻² of current density at Ti/Pt and BDD anodes, respectively. Results clearly indicate that higher COD removals were achieved at different applied current densities, using Ti/Pt and BDD anodes. At 20, 40 and 60 mAcm⁻² using Ti/Pt electrode, 64.5% 90.7% and 93.6% of COD removals were achieved, respectively. Under similar conditions, at BDD anode, 76.2%, 94.5% and 97.1% of COD elimination were obtained in 8 h of treatment.

Figure 4.2- Influence of applied current density on the COD removal as a function of time and total current efficiency (inset) during PW anodic oxidation using (a) Ti/Pt and (b) BDD anodes. Operating conditions: PW sample, as obtained from Brazilian platform, applied current density = 20, 40 and 60 mA cm⁻², Temperature=25 °C, flow rate: 151 L h⁻¹.



Fonte: Autor, 2014.

The higher COD removal efficiencies obtained at both anodes are related to the production of strong oxidant species. For Ti/Pt, hydroxyl radicals are formed on its surface ($\text{Pt} + \text{H}_2\text{O} \rightarrow \text{Pt}(\cdot\text{OH}) + \text{H}^+ + \text{e}^-$) and these $\cdot\text{OH}$ radicals participate on organic matter degradation. However, $\text{Pt}(\cdot\text{OH})$ favors the formation of metal oxide ($\text{Pt}(\cdot\text{OH}) \rightarrow \text{PtO}_x + \text{H}^+ + \text{e}^-$), decreasing $\cdot\text{OH}$ radicals concentration on its surface and passivating the electrocatalytic material, as already observed in previous work (BEZERRA-ROCHA et al, 2012). Also, the adsorption of by-products formed during anodic oxidation may contribute to decrease the degradation efficiency using Ti/Pt. Conversely, using BDD anodes, it is expected that it do not provide any catalytically active site for the adsorption of reactants and/or products in aqueous media (MARTÍNEZ-HUITLE et al, 2006; MARTÍNEZ-HUITLE et al, 2009; PANIZZA et al, 2009). Hydroxyl radical

(BDD(\bullet OH)) formed from water discharge on its surface from reaction: ($\text{H}_2\text{O} \rightarrow \bullet\text{OH} + \text{e}^- + \text{H}^+$), is then considered the responsible species for the electrochemical combustion of organic pollutants (close to anode surface and in the reaction cage), although additional reactions with other reactive oxygen species (H_2O_2 and O_3) and electrogenerated oxidants (active chlorine, peroxodisulphate, peroxodicarbonate or peroxodiphosphate) are also feasible (MARTÍNEZ-HUITLE et al, 2012; SALES et al, 2013). Based on above information, more efficient COD removal rate was attained using BDD anode (diminishing electrolysis time) by applying higher current densities because of there is a greater charge passing into the cell that favors the electrogeneration of more hydroxyl radicals that those formed on Ti/Pt as well as no adsorption phenomena are observed.

To understand the efficacy of current used for EO of PW, from COD values (insets in Figure 2a and 2b), different TCE values were estimated, depending on anode material and current density used. For Pt anode by applying 20, 40 and 60 mAcm^{-2} , 58%, 41% and 29% were achieved respectively, whereas at BDD anode, 70%, 54% and 39% were obtained, respectively. These values confirm that an amount of current is employed in oxygen evolution reaction (undesired reaction) after the first hours of treatment, decreasing the total efficiency of EO reaction.

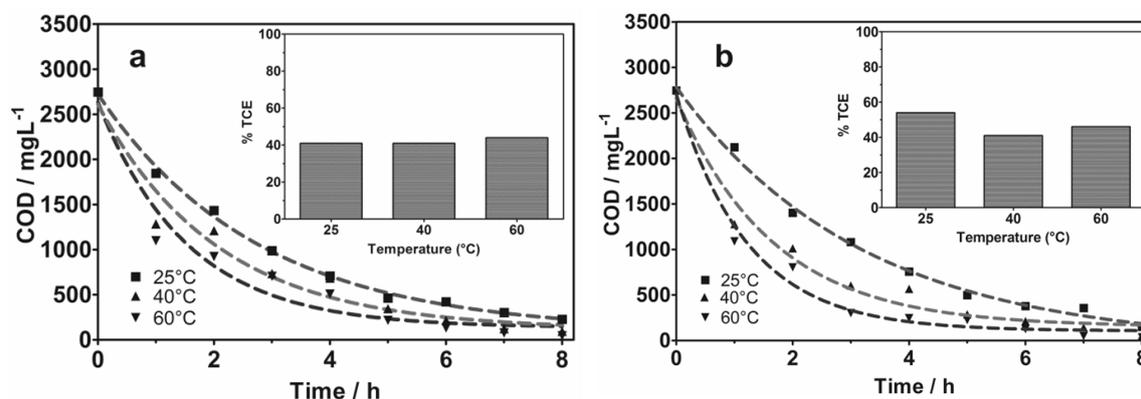
It is also important to remark that, a particular trend of COD removal was observed for higher applied current densities (40 and 60 mAcm^{-2}) using BDD anodes where COD decreases at the beginning of electrolysis; after that, it remains almost stable forming a plateau (ranging from 84% to 92% of COD removal) since the 4 h of electrolysis time. Nevertheless, the plateau observed at BDD was less noticeable at Ti/Pt anode by applying higher current densities. These behaviors are frequently characteristic of electrolysis under mass transport control when the electrolysis are performed applying a current higher than the limiting one. For the electrochemical flow cell used in this study, the mass transfer coefficient was $2.0 \times 10^{-5} \text{ m s}^{-1}$ and the limiting current (for both anodes) results in an average value of 0.45 A, according to Eq. 2. This current is lower than all the currents applied in this work (1.27–3.81A), suggesting that the oxidation under these experimental conditions could be occurring under mass transport control since the 4 h of electrochemical treatment. These assumptions, treating a real effluent, are in agreement with the studies recently published by (BEZERRA- ROCHA et al. 2012), (PANIZZA and CERISOLA 2010) and (MARTINEZ-HUITLE et al, 2012).

Low COD depletion achieved at Ti/Pt and BDD anodes, after 7 h and 4 h of treatment, respectively, using electrochemical flow cell did not affect the efficient elimination of the organic matter dissolved in the real wastewater. Contrary to the figures obtained in our previous work (BEZERRA- ROCHA et al, 2012) where the results clearly indicated that a modest COD removal was achieved at different applied current densities, using Ti/Pt and BDD anodes, in batch mode. At 15 and 30 mA cm⁻² using Pt electrode, 33.8% and 46.5% of COD removals were achieved, respectively. Under similar conditions, at BDD anode, 50.3% and 57.5% of COD elimination were obtained after 10 h of treatment. These lower efficiencies were due to the presence of surfactants and corrosion inhibitors in the petrochemical wastewaters and poor conductivity of this real effluent. In the first case, these surfactants and corrosion inhibitors may produce a polymeric film adsorbed in the anode surface avoiding an efficient elimination of organic matter dissolved in the real wastewater. On the second case, the poor conductivity for this real effluent avoids the efficient production of •OH on anode surfaces, limiting the oxidation of organic pollutants. However, we can infer that in the present study, the electrochemical flow cell avoided the formation of polymeric film thanks to its hydrodynamic configurations while the effluent used offered higher conductivity due to higher amount of salts dissolved (see Table 1). Then, the scale-up of anodic oxidation system improves its treatment capacity (volume) with higher removal efficiencies due to its hydrodynamic configuration.

The effect of temperature during the electrochemical treatment of petrochemical effluent (employing the PW samples as received) was also studied by applying 40 mA cm⁻², varying the temperature (25, 40 and 60°C). These temperatures were selected; because these mimic the real temperatures of the petroleum platform discharges. It was observed (Fig. 3) that changes in temperature have a strong influence on oxidation rate by applying 40 mA cm⁻² at Ti/Pt anode, reducing treatment times. COD removals after 5 h of treatment were of 83.2%, 87.4% and 92.1% at Ti/Pt (Fig 3a); while for BDD the influence on temperature contributes with a modest increase on oxidation rate, COD removals of 81.9%, 91.8% and 94.5% were achieved (Fig. 3b). As well-know from literature (BEZERRA-ROCHA et al, 2012; MARTINEZ-HUITLE e BRILLAS, 2009; PANIZZA e CERISOLA, 2009; MICHAUD et al, 2000; CAÑIZARES et al, 2005), changes in temperature have an important influence on oxidation rate. However, this behavior has been attributed not to an increase of the activity of the anodes but to an increase of the indirect reaction of organics with electrogenerated oxidizing agents from

electrolyte oxidation. In fact, electrolysis with BDD anodes at higher temperatures, in aqueous media containing chloride or sulphate ions generates chlorine ($2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$), peroxodisulfate ($2\text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} + 2\text{e}^-$) and hydrogen peroxide ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$). These powerful oxidizing agents can oxidize organic materials by a chemical reaction whose rate increases with temperature.

Figure 4.3- Influence of temperature on the evolution of COD, as a function of time, during electrochemical treatment of actual petrochemical wastewater on (a) Ti/Pt and (b) BDD anodes by applying 40 mA cm^{-2} (flow rate: 151 L h^{-1}). Inset: % TCE as a function of temperature.



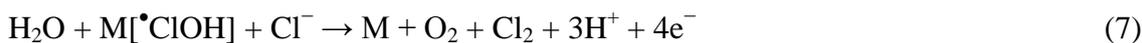
Fonte: Autor, 2014.

Generally, under high concentrations of NaCl in solution (such as observed in our PW samples), EO via OH^\bullet radicals are not the only oxidation mechanism that occurs on the BDD and DSA anodes. In this case, chlorohydroxyl radicals are also generated on anode surface, and consequently oxidizing organic matter (SALES et al, 2013; BONFATTI et al, 2000; BONFATTI et al, 2000):



Reactions between water and radicals near to anode surface can yield molecular oxygen, free chlorine and hydrogen peroxide:

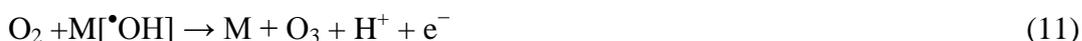
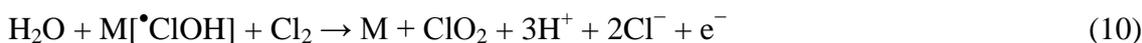




Furthermore, hypochlorite can be formed as follows:



Therefore, direct anodic oxidation, through the reaction (5), results in reduction of organic pollutants on PW as well as formation of primary oxidants, such as oxygen, chlorine, hypochlorite and hydrogen peroxide. Free chlorine and oxygen can further react on anode surface, thus yielding secondary oxidants, such as chlorine dioxide and ozone, respectively:



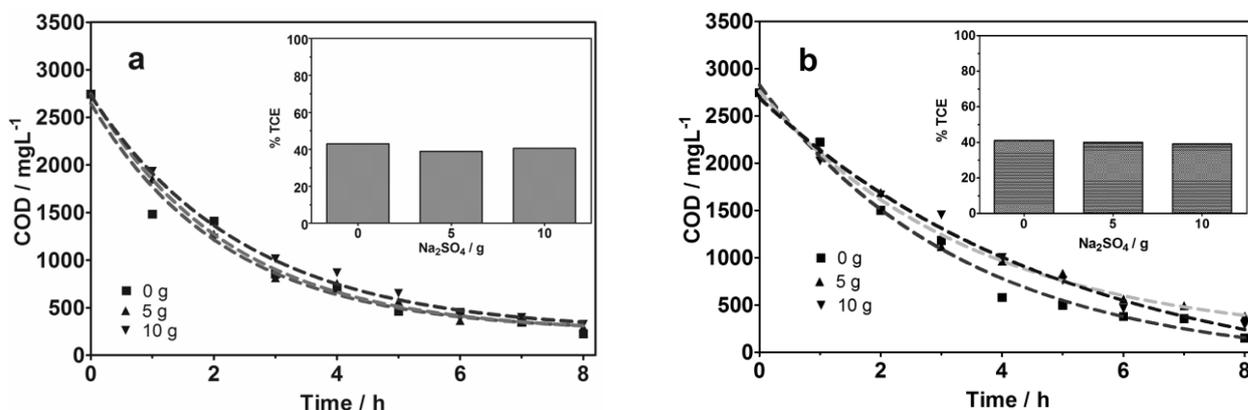
Primary and secondary oxidants are quite stable and migrate in the solution bulk, favored by hydrodynamic configuration of electrochemical cell, which indirectly oxidize the effluent. The efficiency of indirect oxidation depends on the diffusion rate of oxidants in the solution, concentration produced and pH value (SALES et al, 2013; BONFATTI et al, 2000; BONFATTI et al, 2000): at BDD and Pt anodes. In acidic conditions, free chlorine is the dominant oxidizing agent, while in slightly alkaline conditions hypochlorite, chloride ions and hydroxyl radicals are all generated in relevant concentrations. Most of the experiments in this study were performed at pH=7.5, although it is known that the pH increases during this process. In fact, pH typically varies between 7.0 and 8.5 throughout the course of the reaction for the runs with PW. Then, this pH behavior suggests the participation of active chlorine oxidants, confirming the increase on COD removal rate. Assuming that, in the case of chloride mediation, incineration reactions should be mainly a set of volume rather surface reactions, the change from Pt (by the way also a “bad” catalyst for oxygen evolution

reaction (o.e.r.)) to BDD should not involve dramatic changes in the incineration mechanism. However, the COD decay observed at BDD anodes was partially significant than that observed at Pt because the presence of sulphates ions favors the production of peroxodisulphates (Rocha et al, 2012) that together to reactive oxygen species (such as, hydroxyl radicals) plus active chlorine promote a faster oxidation of dissolved organic matter in real effluent (close to anode surface and in the reaction cage). However, TCE values decreased after an increase on the temperature at both electrodes (Figure 3a and 3b) respect to 25°C due to the promotion of undesired reactions, such as oxygen and chlorine gas. Nevertheless, in terms of stability and organic matter removal, better performances were observed at Pt electrode, see Figure 3a.

4.3.2 Influence of Na₂SO₄ concentration

Based on the existing literature, an increase on the sulphates concentration in the effluent favors the production of peroxodisulphates (BEZERRA-ROCHA et al, 2012). Then, Figures 4a and 4b show the influence of adding Na₂SO₄ concentration (in g L⁻¹) as a function of the time and TCE (inset) values during galvanostatic electrolyses of petrochemical wastewater by applying 40 mA cm⁻² at 25°C, using Pt and BDD anodes, respectively. As can be observed, the trends of COD decay present reasonably similar behavior and comparable electrolysis-times are required to achieve complete COD abatement, employing 5 or 10 g of Na₂SO₄ in PW wastewater. In fact, higher concentrations of sulphates are presented in PW (see Table 1), then, adding Na₂SO₄, no remarkable effect on the elimination of COD was achieved. On the other hand, this behavior did not affect the TCE values achieved at both anodes, because no significant current efficiencies were accomplished (see inset on Figure 4a and 4b). It was confirmed that the flow regimen diminishes mass transport limitations as well as the secondary reaction of oxygen evolution, maintaining modest current efficiencies during anodic oxidation of organic matter.

Figure 4.4- Influence of amount of Na_2SO_4 dissolved on the COD decay, as a function of time and total current efficiency (inset) during oxidation of PW effluent using (a) Ti/Pt and (b) BDD anodes, applying 40 mA cm^{-2} at 25°C .

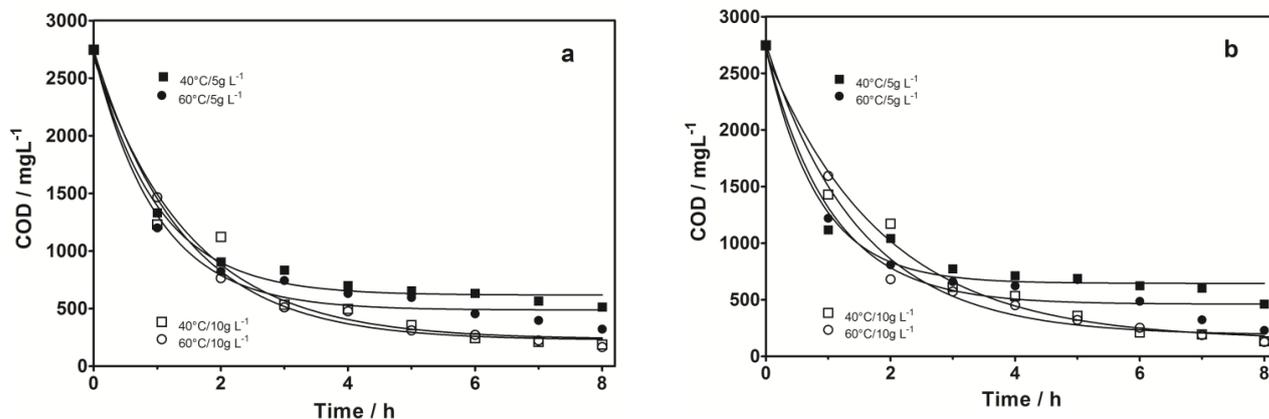


4.3.3 Electrochemical treatment of petrochemical effluent adding Na_2SO_4 varying the temperature.

Therefore, a new set of experiments were performed by applying 20, 40 and 60 mA cm^{-2} of current density at different temperatures (25 , 40 and 60°C), but dissolving a known-amount of Na_2SO_4 in 5 L of PW sample. As mentioned above, peroxodisulphates can be electrochemically formed in solutions containing sulphates (Eq. (6)), especially at higher temperatures (MICHAUD et al, 2000). For this reason, petrochemical wastewaters were treated electrochemically using Pt and BDD employing these experimental conditions.

The influence of the current density on the COD decay during the EO of the petrochemical wastewater at 25°C using Pt and BDD anodes is shown in Figures 5a and 5b. These results clearly indicate that the COD elimination rate and %COD removal are strongly influenced by the anode material and applied current density. At Pt electrode (Figure 5a), good performances of elimination was achieved by applying 40 mA cm^{-2} at 40 and 60°C , adding 5 or 10 g of Na_2SO_4 in the effluent. The low COD depletion at the final stages of electrolysis (the rapid decrease of the reaction rate), with a consequent low value of current efficiency could be explained by the accumulation of oxidation intermediates or the mass transport limitations under lower organic matter concentrations.

Figure 4.5- Influence of amount of Na_2SO_4 dissolved/temperature on the evolution of COD, as a function of time, during electrochemical treatment of actual petrochemical wastewater using (a) Ti/Pt and (b) BDD anodes at 40 mA cm^{-2} .



Conversely, using BDD anodes (Figure 5b), the COD depletion was improved respect to the attained at 25°C . COD decreased efficiently at 60°C , meaning the complete oxidation of organic pollutants contained in PW and all its intermediates by means of the electrogenerated oxidant species (Figure 5b). In fact, increasing the temperature resulted in an enhancement of the oxidation rate but also in an increase of charge consumed due to the improvement of the side reaction of oxygen evolution.

Using the BDD anode instead of the Pt anode, higher % of COD removal were achieved by applying 40 mAcm^{-2} (Figure 5a and 5b) at different temperatures, probably because the oxidation was faster due to the higher amount of oxidant species, principally peroxodisulphates electrogenerated on BDD surface (ROCHA et al, 2012), increasing sulphates-concentration in the effluent. In fact, no passivating film was observed on BDD surface after all electrolysis treatments under these conditions. This result indicated that the peroxodisulphates electrochemically generated contributes in the oxidation of organic pollutants and avoid the probable formation of passivating film by corrosion inhibitors or surfactants present in petrochemical wastewater. Additionally, no formation of this passivating film also favors the production of $\bullet\text{OH}$ radicals on BDD surface through the electrochemical oxidation of water, allowing the oxidation of organic molecules in the proximity of the surface layer of hydroxyl radicals, increasing the COD removal (MARTÍNEZ-HUITLE et al, 2012; SALES et al, 2013). On the contrary, Pt is hydrated and hydroxyl radicals are expected to be more strongly adsorbed on its surface and consequently less reactive, but at higher temperatures the reaction of oxygen evolution is also favored (PANIZZA et al, 2010; SALES et al, 2013).

4.3.4 Comparison of the electrode materials

Comparison between the trend of COD removal, as a function of time, for Pt and BDD anodes by applying different values of current density, is necessary (see Figures 2a and 2b). The results clearly evidence that BDD anode allows significantly faster COD removal than Pt, thanks its greater oxidation ability with high reactivity of the strong oxidant species (hydroxyl radicals and peroxodisulphates) electrogenerated on this electrode. Lower removal efficiencies achieved in the final stages of electrochemical processes take place as a result of the mass transfer limitations due to that the oxidation of petroleum compounds to other more simple organic compounds occurs by chemical structure fragmentation. Then, EO is controlled by the rate at which organic molecules are carried from the bulk liquid to the electrode surface; but when the concentration of final intermediates increase (generally aliphatic carboxylic acids) their rate to the electrode surface are limited by diffusion control, which justify the COD values obtained, increasing the electrochemical treatment time (see, Figure 2a and 2b).

It is very important to estimate the treatment costs, and thus Table 3 reports the EC (kWh dm^{-3}) and costs at 20, 40 and 60 mAcm^{-2} , after 8 h of electrochemical treatment. As can be observed, Pt consumed relatively less energy than BDD anode, but similar COD removals were achieved after 8 h of electrolysis at both anode materials. Nevertheless, the electrochemical treatment time could be substantially reduced using BDD system because 90% of COD decay is accomplished, at 40 and 60 mAcm^{-2} , after 5 h. Similar performances are observed, at BDD flow cell, when an increase in the temperature was attained.

Table 4.3- Total current efficiencies and energy requirements for electrochemical treatment of petrochemical wastewater at different applied current densities.^a

Current density (mA cm^{-2})	TCE (%)		EC (kW h dm^{-3})		Cost (USD)	
	Pt	BDD	Pt	BDD	Pt	BDD
20	58	70	56	71	5	7
40	41	54	140	191	14	19
60	29	39	300	314	30	32

^a Temperature = 25 °C, flow rate of 151 L h^{-1} , electrolysis time of 8 h.

Alternatively, the variation of inorganic species concentration (heavy metals) dissolved in the PW after electrochemical process using Pt and BDD anodes, at a

constant applied current density of 40 mAcm^{-2} and 25°C (under discharged conditions), is present in Table 2. As can be observed, the almost total heavy metal concentrations were removed from petrochemical wastewater after the electrochemical treatment. It appears that the OH^- species produced during electrolysis of water, favor the formation of hydroxides with some heavy metals. These inorganic compounds are deposited on the cathode, as observed at this electrode after electrolysis treatment; and confirmed by the decrease of heavy metals dissolved (Table 2). These outcomes are confirmed by pH solution measured during the electrochemical treatment, which change from neutral to alkaline (from 7 to 8.5). These results indicated that electrochemical treatment technology could be also used for removing heavy metals from petrochemical wastewaters. However, an integrate treatment (anodic oxidation and electrocoagulation) could be planned in order to increase the efficiency and decrease the EC.

4.4 CONCLUSIONS

This study demonstrated that anodic oxidation can be used successfully to remove completely organic pollutants from petrochemical wastewaters as well as that electrochemical oxidation system could be scaled up as large as required without performance deterioration by increasing the total anode area and modifying the hydrodynamic configuration of cell. In the case of PW, the efficiency decontamination and time process depend on the operating conditions, such as current density, electrolyte, temperature and nature of material.

Restricting now our analysis to the comparison between batch and flow modes, the COD decay, as a function of time, during bulk electrolyses of PW wastewaters (as received from Brazilian petrochemical industry) was not significantly affected by current density and temperature when an electrochemical cell in batch mode was used (see Table 4). On contrary, COD removal was efficiently removed from effluent when an electrochemical flow cell was employed, even when higher concentrations of organic matter was treated. However, when an increase on applied current density and temperature were promoted, using electrochemical flow cell, significant improvements in terms of COD removal and treatment time, were achieved; compared with those obtained at batch mode (see Table 4). Then, based on the scaled-up results, the economic feasibility of electrochemical flow cell system in wastewater treatment should be considered.

Although, the EC and process time could make useless anodic oxidation for complete treatment of petrochemical wastewaters; maybe, it can be a feasible process as a pre-treatment process reducing significantly the cost and time treatment. Moreover, the EC values obtained are lower than reported in our previous work (BEZERRA-ROCHA et al, 2012), during electrochemical treatment of petrochemical wastewaters.

Generally speaking, the mediated electrochemical approach (peroxodisulphates and active chlorine production) can be considered more effective than the direct one, because of the minor problems of electrode fouling and/or corrosion. In contrast with other advanced technologies, the electrochemical approach can be considered more effective than others.

It can be seen that anode flow system is very promising in practical bio-refractory organic wastewater treatment. However, it is worth mentioning that EO is an electrical-dependent process, which could be a negative point to the application of this technique in a sustainable water plant treatment. Nevertheless, the Northeast region of Brazil is irradiated by solar light approximately 10 h every day during 300 days/year, thus, further experiments are in progress in order to improve the operation process from solar light using photovoltaic cells (electric energy production), which could become the electrochemical technique to water decontamination even more sustainable for using in petrochemical platforms.

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5. APPLICATION OF ELECTROCHEMICAL TECHNOLOGIES TO TREAT POLLUTED SOIL BY DIESEL

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This study reports on the effects of electrokinetic remediation to remove organic contaminants and heavy metals from contaminated soil by using different electrolytes. Ti/Ru_{0.3}Ti_{0.7}O₂ electrode with an area of 50 cm² was used as anode, while as cathode a grid of Ti. Different electrokinetic total petroleum hydrocarbon (TPH) removal efficiencies were achieved, depending on the supporting electrolyte used, as follows: Na₂SO₄ (96.46%), citric acid (81.36 %) and NaOH (68.03 %) during the first 15 days of electrochemical treatment. The results described here suggest that the application of electrokinetics can be a promising soil remediation technology; if the soil parameters (electric current and electrolyte) are appropriately controlled based on the understanding of interaction between organic pollutants and soil. The main removal mechanism of diesel from soil was electroosmosis. On the other hand, wastewater collected from the electrokinetic remediation process, which was polluted with TPH, it was successfully oxidized by using electrochemical oxidation treatment. The level of degradation achieved was considerably high (>70%) in all cases, after 10 h of electrolysis.

5.1 INTRODUCTION

The Electrokinetic (EK) process is promising for organic and metals removal from soil. Several research groups have studied on organic movement to and retention near the anode by the EK technique (REDDY, AND SAICHEK, 2004; CHIL-SUNG et al, 2010; ALCÁNTARA et al, 2010; REDDY, 2010; BYUNG-GON et al, 2011; MÉNDEZ et al, 2012; CAMESELLE and REDDY, 2012; PAZOS et al, 2013). Recently, the application of electrokinetic technology to organic is attracting interest from the scientific community to removal pyrene, total petroleum hydrocarbon (TPH), heavy metals, naphthalene (REDDY, 2010; FERRI et al., 2009). The remediation can be

conducted in situ to treat contaminants in low-permeability zones by applying a direct current between electrodes placed in the remediation site, achieving high efficiency on removal. The transport phenomena of contaminants in the soil can be briefly described as follows: electromigration, electroosmosis and electrophoresis. Electromigration is the transport of ions and ion complexes toward the electrode of opposite charge; Electroosmosis is defined as the movement of soil moisture or groundwater, which generally takes place from the anode to the cathode and is due to the existence of a space-charge on the solution side of the particle/solution interface. Its migration toward the cathode causes solution displacement too, thus generating a cathode-directed electroosmotic flow. Electrophoresis, as the movement of charged particles under an electric gradient, contaminants bound to mobile particulate matter can be transported in this manner as well (FERRI et al, 2009; PAZOS et al, 2012; BUSTOS, 2012). These mechanisms facilitate decontamination by initiating physical, chemical or hydrological changes such as desorption, adsorption, oxidation, gas generation, dissolution, precipitation, reduction, ion exchange, pH gradient formation, destruction of soil particle active sites (PAZOS et al, 2012; BUSTOS, 2012).

Several studies have also been assessed the effect electrolytes such as NaCl, KCl, NH_4 , CH_3COONa , Na_2SO_4 , Na_3PO_4 , MnO_4^- , H_2O_2 , CaCl_2 and citric acid on the electrokinetic and rheological behaviours of soil obtaining different removal organic matter efficiencies (FERRI et al, 2009; PAZOS et al, 2012; BUSTOS, 2012). It has been demonstrated to be successful and cost-effective in removing wide variety of pollutants such as heavy metals and organic contaminants in many bench- and field-scale studies. EK remediation has also been proposed as an innovative technology for remediation of saturated or unsaturated soils, Few studies have investigated the removal of diesel from contaminated soil by electrokinetically enhanced oxidation with the presence of both H_2O_2 and Fe_3O_4 (iron electrode corrosion), achieving higher TPH-D removal efficiency (97%) compared to the efficiencies observed from EK (55%) or Fenton oxidation (27%) alone. To improve of individual remediation techniques and to achieve better organic compounds removal efficiencies have been proposed; various combinations of physical, chemical and biological, as a physical-chemical treatment, physical-biological treatment, biological-chemical, physical-chemical-biological treatments to treat diesel contaminants in soil (FERRI et al, 2009; REDDY, 2010; PAZOS et al, 2012; BUSTOS, 2012).

The objective of this work is to test a combined process of electrokinetic remediation for diesel remediation from soil contaminated followed by electrochemical oxidation to remove organic pollutants from wastewater produced. The influence of operating parameters that play an important role in the electrokinetic process, such as effect of the electrolyte and applied current density were investigated.

5.2 MATERIALS AND METHODS

5.2.1 Preparation of soil samples

Sample of soil was collected from Northeast Brazilian gas & oil station. The soil was spiked with commercial diesel fuel by introducing a pollutant solution of diesel fuel (10 mL) in n-hexane (20 mL) into soil samples (1 Kg) to obtain a representative contaminant concentration for soil. About 950 g of soil material were treated in each test. The mixture was easily stirred and blended homogeneously. The mixture was kept at room temperature (25°). All physical parameters of soil were determined according to the ASTM standard methods and are listed in Table 1. The soil pH and electrical conductivity were determined by a pH meter and a conductivity-meter respectively, with a ratio of 1:2.5 soil to water. The organic carbon and cation exchange capacity (CEC) were analysed by dichromate oxidation method and ammonium acetate extraction method, respectively. Afterwards, a representative sample (approx. 50 g) of the mixture was taken for initial analysis of diesel concentration. X-ray diffraction analysis was performed. Table 1 shows the characteristic of the soil used.

5.2.2 Analysis of organic matter removal from soil and Diesel removal

During EK process, organic matter removal from soil was monitored in terms of TOC removal in three soil sections (near to cathodic, central and near to anodic section). Also, Diesel concentration was measured as total petroleum hydrocarbons (TPH) using 10 g of sample treated in order to evaluate the elimination of TPH in the treated soil. The sample was mixed with n-hexane in a Soxhlet extractor for 6 h and 10 g of soil were mixed with 100 mL of n-hexane in a separate funnel. The superior phase was mixed with internal standard and analysed by gas chromatography. The HP-5 capillary column was used with helium carrier gas at a flow rate of 1 mL min⁻¹ and air at 400 mL

min⁻¹. The temperature program used was of 50 °C min⁻¹, after 8 °C min⁻¹, and 320 °C for 10 min⁻¹. The removal efficiency was calculated according to Eq.(1):

$$\text{Removal(\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i is the initial concentration of TPH in the soil and C_f is the final concentration of TPH in the treated soil.

5.3 ELECTROKINETIC CELL

The experiments were performed in a rectangular acrylic cell showed in Fig.1. The sample soil was introduced in the central compartment, in a rectangular system of 30 cm of length \times 10 cm of width \times 10 cm of height. Two electrode chambers, with a working volume of 0.5 L, were placed at the lateral positions of the electrokinetic cell and it was isolated from the test soil by means of filter paper. Ti/Ru_{0.3}Ti_{0.7}O₂ electrodes were used as cathode and anode, with an area of 50 cm², each one of them. The electrode chambers were filled with a solution of Na₂SO₄ 0.1 M, NaOH 0.1 M and citric acid 0.1 M for each one of the experiments. A current density of 2 mA cm⁻² was applied for 15 days in all experiments. Electrical potential and pH (in the electrode compartments) were periodically monitored, during the experimental tests. Table 2 shows a summary of the experiments carried out.

5.4 ELECTROCHEMICAL OXIDATION EXPERIMENTS

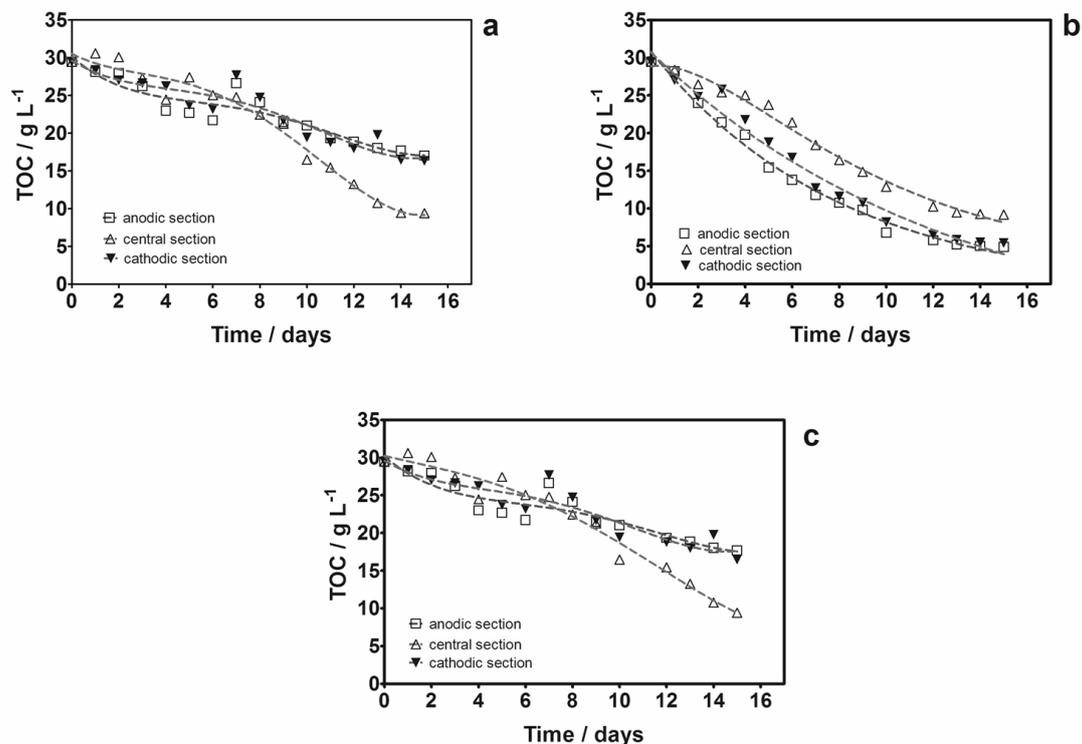
Bulk oxidations were performed in undivided electrochemical cell, the reaction compartment having a capacity of 1 L, and the solution was stirred by a magnetic stirrer. The electrolytic solution (effluent formed after electrokinetic treatment of soil) was stored in the electrochemical batch cell for treating 0.5 L. The oxidation experiments of solution were performed under galvanostatic conditions using a power supply MINIPA-3305M at 25 °C. The cell contained a Ti/Ru_{0.3}Ti_{0.7}O₂ electrode as anode with 50 cm² of area. A current density of 20 mA cm⁻² was applied during 10 h in all experiments.

5.5 RESULTS AND DISCUSSION

5.5.1 Efficiency carbon organic total removal and electrical power consumption

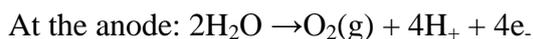
EK experiments were performed using Ti/Ru_{0.3}Ti_{0.7}O₂ and Ti as anode and cathode, respectively, by applying 2 mA cm⁻². During EK process, pH, conductivity and TOC removal were monitored in three soil sections (near to cathodic, central and near to anodic section). After EKR process, hydrocarbon content was also evaluated in the same three soil sections. Results in Fig. 1a clearly show that the initial TOC decreases as a function of time, obtaining different efficiencies depending on the electrokinetic cell sections: 48.11%; 48.51% and 73.14% on anodic, central and cathodic section for NaOH 0.1 M. The organic matter was easily transported via electroosmotic flow. This behaviour confirms the migration of organic pollutants (Ferri et al, 2009; Reddy, 2010; Pazos et al, 2012; Bustos, 2012) from different sections of soil to solutions reservoirs (anodic and cathodic solutions). In the case of Na₂SO₄, TOC decreases as a function of time in all electrokinetic cell sections removing 83.35%, 71.49% and 80.83%, at cathodic, central and anodic section, respectively (Fig. 1b). On the other hand, when citric acid was employed, TOC decay was around 43.35%, 73.49% and 42.83%, at cathodic, central and anodic section, respectively (Fig. 1c). These figures indicate that the Na₂SO₄ favours the elimination of organic matter from all sections in the polluted soil.

Figure 5.1- TOC removal during EK process in three soil sections using as supporting electrolyte (a) NaOH, Na₂SO₄ and (c) citric acid by applying 2.0 mA cm⁻² for 15 days. Anode was Ti/Ru_{0.3}Ti_{0.7}O₂ and as cathode, titanium (Ti).



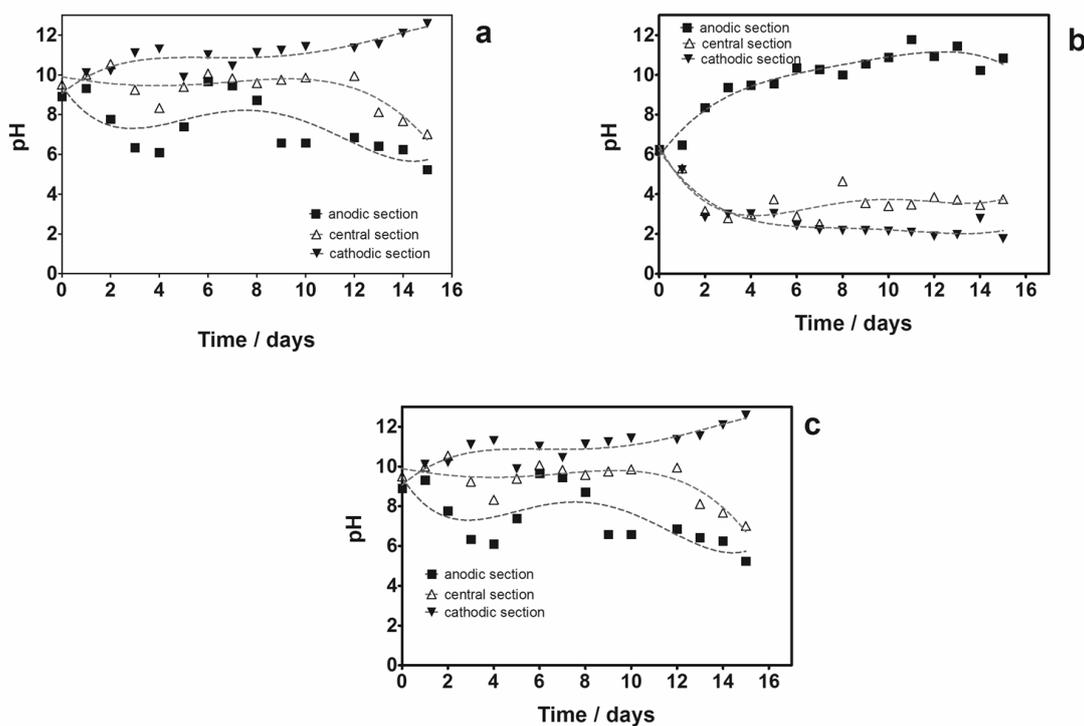
On the other hand, considering the electrical potential measured during the EK experiments, energy consumption was estimated. A total consumption of 121.21 kWh m⁻³ was spent after 15 days of EK treatment when NaOH was used as supporting electrolyte. Whereas, 111.16 kWh m⁻³ was necessary to obtain modest TOC decays when citric acid was employed. Conversely, lower energy consumption was employed when Na₂SO₄ was employed about 44.83 kWh m⁻³. Fig. 2 shows the variation of pH, as a function of time, in the proximity of anode compartment, cathode reservoir and middle section using NaOH, Na₂SO₄ and citric acid as supporting electrolytes, for removing organics. When the electric potential is applied, the electrolysis reactions occur in the electrodes, producing H⁺ and OH⁻ ions at the anode and cathode reservoirs, respectively. The initial pH of the soil-Na₂SO₄ (middle section) was around 6.1 and it decreases to 4.1 during EKR tests, at anodic and middle sections; while at cathodic reservoir, pH increased considerably to around 10.5. Using NaOH 0.1 M, initial pH was around 8.90, after that, it decreases up to 6.1, at anodic and middle sections; while pH around 12 was attained after 15 days of treatment at cathodic section. Similar behaviour was observed at all sections when citric acid was used (Fig. 2c). A key

feature of electrokinetic experiments is the electrolysis of water at the electrodes, resulting in the generation of acid and base at the anode and cathode respectively (FERRI et al, 2009; REDDY, 2010; PAZOS et al, 2012; BUSTOS, 2012). The electrolytic reduction of water at the cathode causes H_2 evolution and oxidation at the anode causes O_2 evolution. An alkaline zone surrounds the cathode and an acidic zone is created at the anode:

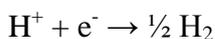


The pH is reduced not only the high concentration of H^+ , but also in a secondary manner by the release of Al^{3+} due to kaolinite dissolution (composition of soil) (FERRI et al, 2009; REDDY, 2010; PAZOS et al, 2012; BUSTOS, 2012). The reduction of water molecules at the cathode leads H^2 generation and increasing pH. Therefore, these reactions cause an acidic solution to be generated at the anode and an alkaline solution to be generated at the cathode. The electrolysis of water affects the remediation process because the ionic products may electromigrate and be transported by electro-osmosis towards the opposite charged electrode location.

Figure 5.2. pH variation, as a function of time, during electrokinetic tests at different supporting electrolytes: (a) NaOH (b) Na_2SO_4 and (c) citric acid.



Thus, an acidic front of solution may move from the anode towards the cathode and an alkaline front of solution may move from the cathode towards the anode. However, the pH will not increase directly to 12 owing to interaction of OH⁻ with residual H⁺ on the cathode surface (FERRI et al, 2009; REDDY, 2010; PAZOS et al, 2012; BUSTOS, 2012).



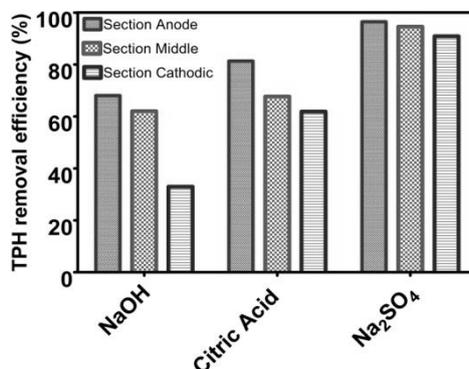
During the electrokinetic remediation, operating acidic and alkaline fronts migrate toward the opposing electrodes and interact approximately with a ¼ of the distance from the cathode to form a zone of abrupt pH change. The movement of these fronts is irregular, and the advection H⁺ front depends on electromigration, electroosmosis, and diffusion mechanisms. Progress is hindered by high soil buffering capacity as a result of substitution with adsorbed cations (PAZOS et al, 2012; BUSTOS, 2012). At the cathode zone OH⁻ front advection is affected by upstream electromigration and the progress of OH⁻ ions is hindered by electroosmosis. As shown Fig. 2a, the outlet catholyte pH increased continuously due to the basic front reaching the cathode and neutralizing the high pH. When NaOH was used, the soil pH may reduce the electroosmotic flow rate by causing the soil minerals to process a more positive surface charge and zeta potential, the flow velocity towards the cathode should have decreased over time (PAZOS et al, 2012; BUSTOS, 2012). Fig 2b shown citric acid the soil pH tended to increase near cathode little in the treatments and decreased little anode, this effect can be attributed to the impact of the electro-osmotic flow. This flow has an acidic pH below 4, and can react with the soil to release ions and increase the electrical conductivity (BUSTOS, 2012).

5.5.2- Concentration of TPH in soil

The initial concentration of TPH in the soil was found to be 9094.06 mg/Kg. Fig. 3 shows the TPH removal efficiency, in terms of percentage, as a function of supporting electrolyte used (NaOH, citric acid and Na₂SO₄). There was a pattern of slight increase in the removal efficiency of TPH from cathodic to anodic section, indicating that the oil was removed mainly by electroosmosis flow. Analysing the figures reported, Na₂SO₄ is the most efficient supporting electrolyte because higher TPH elimination was achieved, more than 90%. The order of TPH removal efficiency is Na₂SO₄ (96.46%) > citric acid (81.36 %) and NaOH (68.03 %) during 15 of EK treatment. The registered electro-

osmotic flow, approximately 42 mL d^{-1} ; 56 mL d^{-1} and 64 mL d^{-1} for NaOH, citric acid and Na_2SO_4 confirm the results obtained for %TPH elimination.

Figure 5.3- TPH removal efficiency using different supporting electrolytes in EK treatment.

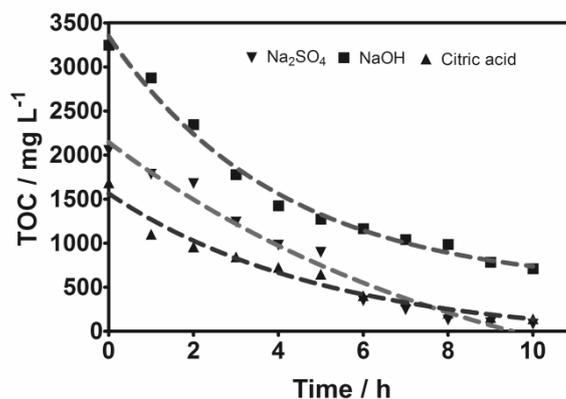


Fonte: autor, 2014.

5.5.3 Electrochemical oxidation

Bulk oxidations were performed in undivided electrochemical cell, the reaction compartment having a capacity of 1 L, and the solution was stirred by a magnetic stirrer. The experiments were conducted at 25°C by applying 20 mA cm^{-2} using $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ electrode. Fig. 4 shows the TOC decays, as a function of time, for the wastewater generated after EK treatment. TOC measurements confirm the elimination of organic matter accumulated in the reservoirs solutions after EK treatment. As can be observed from Fig. 4, more than 90% of organic matter dissolved was removed after 10 h of electrolysis. This results clearly demonstrated that the wastewater produced after EK treatment could be treated by using electrochemical oxidation process. In this context, two electrochemical technologies could be integrated in order to decrease the time of treatment, and consequently, decreasing the energy costs. The elimination of dissolved organic pollutants is due to the fact that OH radicals are produced at anode surface, favoring the electrochemical oxidation of them. However, this electrode is considered an active anode, limiting the efficiency on the removal. This limitation could be avoided when a non-active anode is used, for this reason, it is a new objective of our research. Also, the formation of superior metal oxide at this electrode material decreases the efficiency of the electrochemical oxidation process at solution of NaOH.

Figure 5.4- Electrochemical degradation of wastewater produced after EK treatment. Anode was $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ by applying 20 mA cm^{-2} .



Fonte: autor, 2014.

5.6 CONCLUSIONS

The organic matter was eliminated from polluted soil due to the electromigration and electroosmotic flows, removing more than 80% of organic compounds using Na_2SO_4 0.1 M and 68% employing NaOH 0.1 M after 15 days. The soil pH variation is observed due to the buffering capacity of soil as well as the production of H^+ and OH^- at the electrocatalytic materials used. On the other hand, the liquid collected from the electrokinetic remediation process; it was successfully oxidized by using the electrochemical treatment (electrooxidation), verifying the applicability of combination of two electrochemical technologies.

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6. THE ROLE OF PARTICLE SIZE ON THE CONDUCTIVE DIAMOND ELECTROCHEMICAL OXIDATION OF SOIL-WASHING EFFLUENT POLLUTED WITH ATRAZINE

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Abstract

Soil washing using surfactant solutions is a very effective and widely used technique for the remediation of polluted soil. However, it is not a finalistic technology and once the pollutant is transferred to the washing-solution, the resulting aqueous waste has to be treated. In this work, it is studied the feasibility of Conductive - Diamond Electrochemical – Oxidation (CDEO) to treat the effluent of a surfactant-aided soil washing process and it is pointed out some important mechanistic aspects. Atrazine was selected as the model pesticide and sodium dodecyl sulphate (anionic surfactant) was used as washing agent. Besides COD, TOC, and pollutants concentration, the changes of z-potential and particle size were monitored during electrolysis in order to clarify the degradation mechanisms involved in the electrochemical treatment of emulsions. The results show that CDEO enables a complete reduction in the organic load of the waste. However, the process efficiency seems to be influenced by the size of particles present in the reaction media, which decreases continuously during the treatment. Steric hindrance of the large micelles (mean size 1100 μm) prevents direct oxidation of micelles on the anodic surface and hence only mediated processes can explain the results obtained, being peroxocarbonate and peroxosulphate ions (formed from the oxidation of sulphate ions released from SDS molecule) the main species expected according to the washing fluid composition.

Keywords

Conductive diamond, electrolysis, particle size, surfactant, soil washing

6.1 INTRODUCTION

Pesticides may cause serious pollution problems in soils due to its mutagenic and carcinogenic characteristics (RODRIGO, 2014; LIN, et al, 2014). Among them, atrazine has been the focus of several researches (DOMBEK et al, 2004; MALPASS et al, 2006; MALPASS et al, 2012; MALPASS et al, 2013; MAMIÁN et al, 2009; OTURAN et al, 2012; RIBEIRO et al, 2005) because of its low biodegradability, long half-life and low solubility in water (33 mg dm^{-3} at 22°C). Surfactant-aided soil washing (SASW) has become relevant treatment for this type of polluted soil. This process remediates the soil and thus converts the problem of soil remediation into a potentially easier wastewater treatment problem (LOPEZ-VIZCAINO et al, 2012; SAEZ et al, 2010; VILLA et al, 2012; LOPEZ-VIZCAINO et al, 2011). However, this type of effluent is difficult to treat by conventional wastewater treatment methods because of the complexity of the matrix: an emulsified effluent containing pesticide, surfactant (large molecules with complex organic groups) and particles of soil dragged in the washing process(LOPEZ-VIZCAINO et al, 2012).

Many works have been published during the recent years about the elimination of atrazine from wastewater (OTURAN et al, 2012; ZHANG et al, 2011; MASCIA 2007; BALCI et al, 2009; MALPASS et al, 2007; CHU et al, 2006; PINEDA et al, 2013). In this work, CDEO was selected for the treatment of soil washing effluents from remediated soil polluted with atrazine. This technique has been widely studied in literature to treat numerous types of synthetic and actual wastes (PANIZZA et al, 2005; PANIZZA et al, 2009; MARTÍNEZ-HUITLE 2011; MARTÍNEZ-HUITLE 2009; POLCARO et al, 2005) and it is known for its high efficiency, typically associated to the combination of direct oxidation of the pollutants on the surface of the conductive-diamond with the action of large amounts of $\bullet\text{OH}$ and other oxidants electrogenerated from the oxidation of electrolyte salts (CANIZARES et al, 2009) .

Electrochemical studies about atrazine removal (ZAVISKA et al, 2011; BARANDA et al, 2014) are mainly focussed on the treatability of synthetic solutions, paying attention to the changes of the typical parameters used for monitoring the oxidation and mineralization rates, but not on the break-up of the emulsion neither the changes in the particle size, what becomes in a real novelty in this work. No attempts have been published regarding on the removal of micelles by CDEO, relating the treatment with the emulsified pollutant and the interaction of these micro-drops of

pollutant with the different oxidation mechanisms. Therefore, the objective and main novelty of this work was to investigate the treatment of effluents generated by soil-washing polluted with atrazine by CDEO, focusing on the effect of the size particle and the oxidation mechanisms of atrazine/surfactant micelles.

6.2 MATERIALS AND METHODS

6.2.1 Chemicals

Kaolinite was selected as a model clay soil in this work. This material is not reactive and it has low hydraulic conductivity, low cation exchange capacity and no organic content. Atrazine (Fluka) was selected as model of organic compound. Sodium dodecyl sulphate (SDS) (supplied by Panreac) was used as model of solubilizing agent and NaHCO_3 (96 %, Panreac) as supporting electrolyte. Deionized water Millipore Milli-Q system was used to prepare all solutions.

6.2.2 Analytic techniques

All samples extracted from electrolyzed solution were filtered with 0.45 μm nylon filters (Whatman) before analysis. The atrazine concentration in the liquid phase was determined using an L–L extraction process. This process was carried out in separator flasks of 100 dm^3 using ethyl acetate/hexane as extraction solvent (ratio atrazine solution/solvent = 0.33 v/v). The concentrations of the compounds were quantified by HPLC (Agilent 1100 series) using analytical column Phenomenex Gemini 5 μm C18 at 223 nm and 25°C. 20 μL aliquots were injected, using as mobile phase, a mixture of acetonitrile/water (45:55 v/v) at 0.3 $\text{cm}^3 \text{min}^{-1}$. The total organic carbon (TOC) concentration was monitored using a Multi N/C 3100 Analytik Jena analyser. Atrazine and surfactant removal was monitored through the COD during electrolysis using a HACH DR2000 analyzer. Zeta potential was also measured for the clarified liquid using a Zetasizer Nano ZS (Malvern, UK). Measurements of pH were carried out with an InoLab WTW pH-meter. The particle size was monitored during CDEO using a Mastersizer Hydro 2000SM (Malvern, UK). A colorimetric method was used to determine the concentration of the SDS surfactant (JURADO et al, 2006).

6.2.3 Preparation of spiked soil

The polluted soil sample was made by dissolving atrazine in hexane and then mixing this atrazine/hexane solution with the kaolinite. The spiked clay was aerated during one day to promote evaporation of the hexane. In this way the atrazine was homogeneously distributed on the clay surface. The resulting atrazine concentration in the soil was around 100 mg kg^{-1} of soil.

6.2.4 Surfactant-aided soil washing procedure

Surfactant-aided soil washing tests were carried out in a stirred bench-scale tank operated in discontinuous mode. The tank volume was 1000 cm^3 . Low-permeability soil (1000 g) polluted with $100 \text{ mg atrazine kg}^{-1}$ of soil and 800 cm^3 of washing solution (containing deionised water, 500 mg dm^{-3} of NaHCO_3 and 100 mg dm^{-3} of surfactant) were mixed in the tank for 6 h at a stirring rate of 120 rpm. Then, the same tank acts as a settler (during 24 h) to separate the soil from the effluent generated during the soil-washing process.

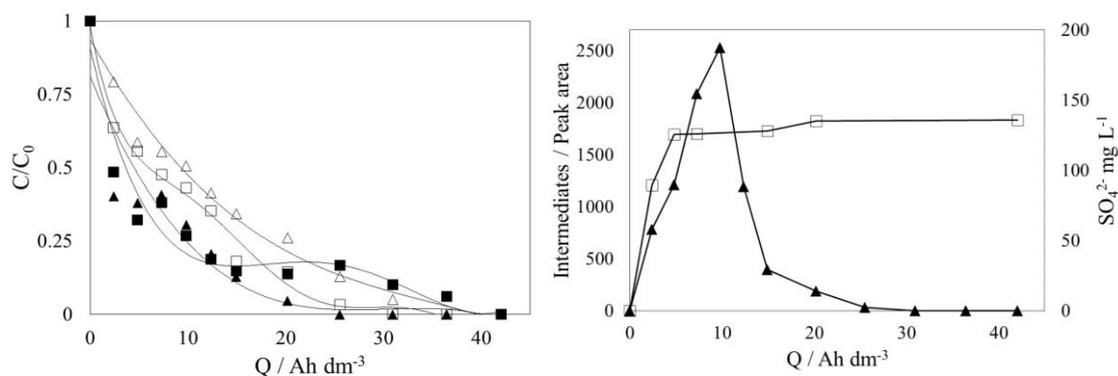
6.2.5 CDEO procedure

Electrochemical experiments were carried out in a bench-scale plant with a single-compartment in the electrochemical flow with inter-electrode gap was about 9 mm. BDD and steel circular (100 mm diameter) electrodes were used as anode and cathode, respectively, with a geometric area of 78 cm^2 . For the electrochemical flow cell, inlet and outlet were provided for effluent circulation through the reactor; the simulated effluent (0.7 dm^3) was stored in a thermos-regulated glass tank (1000 cm^3) and circulated through the cell using a peristaltic pump at a flow rate of $200 \text{ dm}^3 \text{ h}^{-1}$. The electrical current density (30 mA cm^{-2}) was applied using a DC Power Supply (FA-376 PROMAX) and thermostated (Digiterm 100, JP Selecta, Barcelona, Spain) by means of a water bath (25°C).

6.3 RESULTS AND DISCUSSION

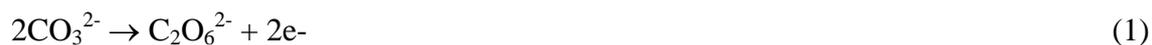
A synthetic soil-washing solution obtained according to the procedure described in the experimental section was separated from the tank and filtered prior to electrochemical experiments to remove particles of soil dragged in during the washing process. It consists of an emulsion of atrazine in water stabilized by the surfactant with specific particle size distribution (lower than 100 μm =0.09%; 500 μm =6.3%; 1000 μm =47.7%; 1500 μm =77.5; 1750 μm =90.1% and 2000 μm =100%) and main characteristic (COD=276 mg dm⁻³; TOC=40.9 mg dm⁻³; Conductivity=0.272 mS cm⁻¹; pH=8.48; z- potential=-22.7 mV and mean particle size=1121 μm). As it can be observed, the washing fluid is a strongly polluted waste with two main organic pollutants (the pesticide and the surfactant) and several species from the viewpoint of reactivity, because the dissolved pesticide, dissolved surfactant and the micro-drops are expected to behave in a different way during the treatment. Regarding particle size distribution it can be observed that mean size is around 1100 μm and that most of the particles (80%) are within the range 500-1750 μm . The extremely high mean size of micelles does not promote but even prevent by steric hindrance the direct oxidation of micelles on the electrode surface. The changes in COD, TOC, atrazine and surfactant concentrations with the electrical charge passed during the galvanostatic CDEO of the soil washing effluent are shown in Figure 1a.

Figure 6.1- Changes during the CDEO of surfactant-soil-washing effluent (a) (▲) TOC: (■) COD (Δ) Atrazine: (□) SDS concentration. (b) total amount of intermediates (▲) quantified as total chromatographic area and (■) concentration of SO_4^{2-} .



As it can be observed, organic load of the washing fluid is completely depleted during the electrolysis, pointing out the effectiveness of the CDEO in the treatment of

complex wastewater. Total removal of pollution is attained for electric charge under 40 Ah dm^{-3} . Considering a typical cell voltage of 5.0 volts, this means than energy consumption below 200 kWh m^{-3} can be sufficient to deplete pollution, which is a very interesting value from the viewpoint of the economic feasibility of the technology. In this point, it is worth to remind that pollution of this effluent lies outside the recommended target for the applicability of CDEO, which was set in the COD range in between $1500\text{-}20000 \text{ mg dm}^{-3}$ (RODRIGO et al, 2010), because within this range the coulombic efficiency of the CDEO technology is nearly 100%. However, it is still efficient enough as to be competitive with other advanced oxidation technologies. Trends observed in the decay of the four parameters are slightly different, being this fact indicative of the complexity of the system. In comparing the changes in the globalized pollution parameters (TOC and COD) with those of the surfactant and pesticide, it can be observed a plateau zone for applied electric charges in the range $5\text{-}10 \text{ Ah dm}^{-3}$, which is not consistent with the exponential decay of the two raw pollutants. This type of change was previously observed in the treatment of other species with low water solubility such as chlorophenols (RODRIGO et al, 2001; CANIZARES et al, 2003; CANIZAREZ et al, 2004) and it was explained in terms of the formation of reaction intermediates with high oxidizability, which consumes more efficiently the oxidants electrogenerated on the anode surface during the electrolysis (mediated electrolysis) and also may react faster on the anode surface (direct electrolysis). Differences observed between TOC and COD pointed out the uncertainty of the globalized parameters in the monitoring of the treatment of complex effluents consisting in heterogeneous mixtures, like the soil washing fluid studied in this work. The comparison of the changes in the raw pollutant concentrations and COD indicates that TOC measurement is failing in giving a proper result, because it reports about total mineralization while raw pollutants and COD still remain in the reaction media. Likewise, significant COD values still remained when surfactant and pesticide are completely depleted from solution. Hence, for complex systems like the one studied in this work, several techniques have to be used in order to have a clear view of the main processes happening in the remediation technology, taking into account the limitations of each analytical technique. Another important point to be considered is the formation of oxidant species in the reaction media. In electrolytes with carbonates/bicarbonates is known to be produced peroxocarbonates (VELAZQUEZ-PENA et al, 2013) according to equations 1 -3.



Likewise, during the degradation of SDS, the release of sulphate ions contained in the surfactant molecule takes place. This release can be clearly observed in Figure 1b, where the concentration of sulphate is shown during the electrolysis. It is well-known (CANIZARES et al, 2009; SERRANO et al, 2002) that peroxodisulphates can be produced by direct (eqs. 2) or hydroxyl-radical mediated (eqs. 3 and 4) oxidation during CDEO. Hence, production of peroxodisulphate is a very important process happening during the electrolysis of SDS-washing-soil effluents and its effect is very significant and should be taken into account in order to explain the oxidation of organics.

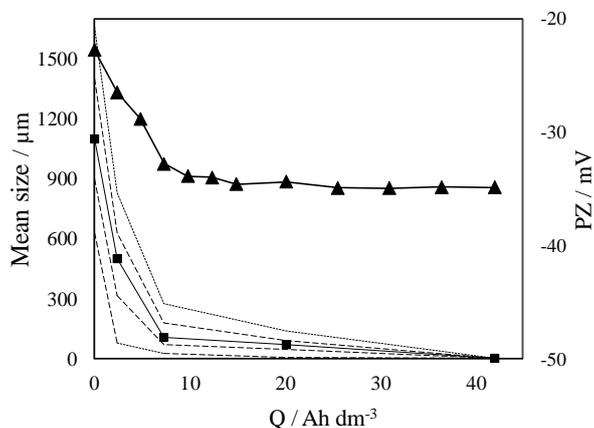


Decomposition of peroxocarbonates and peroxosulphates yields hydrogen peroxide which in addition to contribute to the complex mixture of oxidants produced in the electrolysis, may affect the value of COD measured. Due to the high size of the micelles, their direct oxidation on the surface of the diamond is not alike to happen. This fact means that mediated oxidation is playing an important role in this treatment. Regarding mechanisms, Figure 1b also informs about intermediates produced in the reaction media because it shows the total chromatographic area of the three intermediates detected by HPLC. As it can be observed total concentration is low and complete removal is obtained for electric charges as low as 25 Ah dm⁻³.

In this point, it is important to check the behaviour of the emulsion of atrazine/surfactant during the electrolysis, because the break-up of the emulsion is not expected to be instantaneous and no previous information is found in the literature about the way in which micelles are depleted in an electrochemical oxidation process. To

assess this point, particle size and zeta potential were also monitored during the electrolysis and results are shown in Figure 2.

Figure 6.2- Changes in z-potential (▲) and mean particle size (■) during the CDEO of surfactant/soil-washing effluent. Size limits including (---) 50% of the particles; size limits including 80% of the particles (·····).



Fonte: autor, 2015.

As it can be observed, the particle size decreases rapidly during the initial stages of the electrolysis from 1100 down to 100 μm (for electric applied charges around 7 Ah dm^{-3}) as well as the range of particle sizes. This trend is consistent with the changes obtained in the z-potential, which decreases rapidly until attaining a constant value around -35 mV for similar electrical charge passed. This indicates that the atrazine/surfactant micelles are drastically attacked during the first stages to form smaller particles with more negative surface charge. In this point, it is important to take in mind that it is used an anionic surfactant and thus, the expected superficial charge of micelles is negative. The smaller the particles, the higher the surface of micro-drops which has to be covered with surfactants and hence the more negative is the resulting zeta potential. After this initial rapid reduction in size of the micro-drops, size continues decreasing till the end of the test although at a lower rate, while the z-potential value kept almost constant (in fact a small trend towards more negative values is observed).

Regarding oxidation performance, in reducing the size of the particles, the readily available surface of surfactant and pesticide to be attacked in the micelles becomes higher. Hence, oxidation rate may become promoted, either by the attack of oxidants or even by the direct oxidation on the surface of the electrode once the micelles are reduced to a very low size (as the steric hindrance of micelles is minimized). This can help to explain the increase observed in the oxidation rate of pollutant for electrical

charges higher than 10 Ah dm^{-3} (Figures 1a and 1b) and in particular the plateau observed in the COD and TOC decay. In comparing the decay of surfactant and pesticide, it is observed a faster depletion of the surfactant with is consistent with the attack to the surface of the micro-drops in which this SDS is protecting the pesticide. Likewise, the continuous decrease in the TOC, COD, surfactants and pesticide indicates that these species are mineralized from the beginning of the experiment and that micelles reduction is accompanied by mineralization of the organic species.

6.4 CONCLUSIONS

Surfactant aided soil washing fluid can be efficiently treated by CDEO. This oxidation is very complex from the mechanistic point of view and involves the reduction in size of the micro-drops of pesticide-surfactant formed during the soil washing treatment and the simultaneous mineralization of the organic content. Large size of the micelles prevents their direct oxidation on the diamond surface, indicating that electrolytic process should be controlled by mediated oxidation, being peroxocarbonates the main species expected according to the composition of the soil washing fluid. Release of sulphate during the oxidation of the surfactant and production of persulphates helps to keep a significant organic degradation rate during the process. In comparing the degradation of the two raw organic species, surfactant is depleted faster because it is more easily accessible to oxidants in the surface of the microdrops.

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7. COMBINED SOIL WASHING AND CDEO FOR THE REMOVAL OF ATRAZINE FROM SOILS

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Abstract

In this work, it is studied the removal of atrazine from spiked soils by soil washing using surfactant fluids, followed by the treatment of the resulting washing waste by electrolysis with boron doped diamond (BDD) anode. Results confirm that combination of both technologies is efficient for the removal and total mineralization of atrazine. Ratio surfactant/soil is a key parameter for the removal of atrazine from soil and influences significantly in the characteristic of the wastewater produced, affecting not only to the total organic load but also to the mean size of micelles. The higher the ratio surfactant soil, the lower is the size of the particles. Electrolyses of this type of waste attain the complete mineralization. TOC and COD are removed from the start of the treatment but the key of the treatment is the reduction in size of the micelles, which lead to a higher negative charge in the surface and to the faster depletion of the surfactant as compared with the pesticide.

Keywords: Pesticide, soil remediation, surfactant, soil washing, conductive diamond, electrolysis

7.1 INTRODUCTION

Nowadays, soil remediation has become an environmental matter of the major importance [1-3]. In addition to the negative impact on the ecosystems, transport of pollutant to water reservoirs may decrease the quality and even prevent its use for human supply. For this reason, it is very important the rapid actuation against accidental discharges of hazardous species with efficient technologies that remediate the soil rapidly and avoids diffuse pollution. One of these technologies is soil washing [4-6]. It consists on the extraction of pollutants contained in the soil with a solution that helps to obtain an efficient transfer of the pollution from the soil to a liquid phase. It is an off-site technology, which requires digging and processing of soil in special extractor units. In fact, it can be considered as a soil-liquid extraction operation unit, in which the pollutant is transferred from the solid soil to the liquid washing fluid. In the case of organics, the use of surfactant solutions is the most extended application. Using this operation, soil can be completely remediated from the chemical point of view. However, a highly polluted waste is obtained with a high organic load and complex mixture of pollutants consisting of dissolved organic pollutant, surfactant and micelles (with both species), in addition to the inorganic salts dissolved and exchanged from the soil during the extraction process.

In order to treat this waste, efficient technologies have to be used. Electrolysis with boron doped diamond (BDD) electrodes has become a reference in the recent years [7-10], because of its great robustness and efficiency. It may attain the total removal of pollution by mineralization and to the knowledge of the authors of this manuscript, and based on the huge amounts of results presented in the literature, there are no refractory species to this treatment. Its high efficiency is associated to the production of many types of oxidant species from hydroxyl radicals formed by water electrolysis to peroxocompounds formed directly and by mediated oxidation of sulphate, phosphate, carbonates and even carboxylic acids on the surface of the diamond electrode or by attack of hydroxyl radicals.

Decomposition of these oxidants, forming hydrogen peroxide and other paths that promote the formation of ozone completes the cocktail of oxidants. This mixture is responsible for extending the oxidation from the nearness of the anode surface to the bulk of the waste, promoting the oxidation of pollutants by different mechanisms. The

target wastewater for this treatment is medium-to-highly polluted waste with COD within the range 1500-20000 mg dm⁻³ [7], for which efficiency in the use of electricity of 100% is typically obtained. For lower concentration of COD, mass transport limitations control the oxidation rate and efficiency is drastically reduced. The combination of electrolysis with other technologies, such as the Fenton oxidation [11-19] or the irradiation of ultrasound (US) [20] or UV light [21,22] that promotes the activation of oxidants produced electrochemically by producing more efficient radicals, is the best way to keep efficiency of this treatment in high values.

Pollution of soils with pesticides is a problem of the major importance. Pollution may come from accidental discharge or from the excessive use of pesticide and the environmental impact is usually very high [1]. The capacity of the soil to filter, buffer, degrade, immobilize, and detoxify pesticides is a function of quality of the soil. Pesticide adsorption to soil depends on both the chemical properties of the pesticide (i.e., water solubility, polarity) and properties of the soil (i.e., organic matter and clay contents, pH, surface charge characteristics, permeability) [23-29]. Pesticides can move off-site contaminating surface and groundwater and causing adverse impacts on aquatic ecosystems. Pesticide degradation in soil generally results in a reduction in toxicity; however, some pesticides are persistent organic pollutants or these have breakdown products (metabolites) that are more toxic than the parent compound [23-26]. In this context, several analytical methods for monitoring/degrading pesticides have great attention in the last years [27-29].

Atrazine is one of the most applied pesticides and it has been the focus of several researches [12, 30-35] because of its low biodegradability, long half-life and low solubility in water (33 mg dm⁻³ at 22°C). This work aims to evaluate the effectiveness of a complete treatment of a soil spiked with atrazine, consisting of the soil washing with a sodium dodecyl sulphate solution followed by the electrolysis with BDD anodes of the resulting wastewater. Effect of the ratio surfactant/soil is going to be assessed trying to determine its influence on the soil washing efficiency and on the characteristics of the washing waste.

7.2 MATERIALS AND METHODS

In this work, kaolinite was selected as model soil. This material is not reactive and it has a low hydraulic conductivity, low cation exchange capacity and zero organic content [36-38]. The atrazine was selected as a model organic compound and it was obtained from Fluka. Sodium dodecyl sulphate (SDS) was used as a solubilizing agent (supply by Panreac). NaHCO_3 (96%) was also obtained from Panreac.

7.2.1 Preparation of spiked soil

Samples of polluted soil were prepared by dissolving atrazine in hexane and then mixing this atrazine/hexane solution with kaolinite. The spiked clay was aerated during 1 day to favour evaporation of the hexane and, in this way, the atrazine was homogeneously distributed on the clay surface. This method has been described in the literature by different authors [4, 37, 38]. The resulting atrazine concentration in the soil was around 100 mg kg^{-1} of soil.

7.2.2 Soil washing procedure

Soil washing with surfactant fluid solution was carried out in a stirred tank operated in discontinuous mode. The tank volume was 1000 cm^3 . Low-permeability soil (1000 g) polluted with $100 \text{ mg atrazine kg}^{-1}$ of soil and 800 cm^3 of solubilizing agent (containing deionized water, 500 mg dm^{-3} of NaHCO_3 , and concentrations of sodium dodecyl sulphate (SDS) surfactant ranging from 100 to 5000 mg dm^{-3}) were mixed in the reactor for 6 h at a stirring rate of 120 rpm. The same tank then acted as a settler (during 24 h) to separate the soil from the effluent. These effluents consisted of aqueous mixtures of atrazine and surfactants, which become the influent of the electrolytic treatment.

7.2.3 Electrochemical oxidation of the soil washing effluents

Electrochemical oxidation experiments were carried out in a bench-scale plant with a single-compartment electrochemical flow. Bulk oxidations were performed in a single-compartment cell, as described in previous works [5]. BDD and steel electrodes were used as anode and cathode, respectively. Characteristic of BDD are as follows: sp^3/sp^2 ratio: 225; boron content: 500 ppm; width of the diamond layer: 2.68 μm . For the electrochemical flow cell, inlet and outlet were provided for effluent circulation through the reactor; the simulated effluent was stored in a thermo-regulated glass tank (1000 cm^3) and circulated through the cell using a peristaltic pump at a flow rate of 200 $\text{dm}^3 \text{h}^{-1}$. The electrical current was applied using a DC Power Supply (FA-376 PROMAX). Temperature was kept constant by means of a water bath.

7.2.3 Analyses

The atrazine concentration in the liquid phase was determined using an L–L extraction process. This process was carried out in separator flasks of 100 cm^3 using ethyl acetate/hexane (7 mL/5 mL) as extraction solvent (ratio atrazine solution/solvent = 0.33 v/v). All samples extracted from electrolyzed solution were filtered with 0.25 μm nylon Whatman filters before analysis. The concentrations of the compounds were quantified by HPLC (Agilent 1100 series) using a Phenomenex Gemini 5 μm C18 analytical column. The detection wavelength of 223 nm was used and the oven temperature was maintained at 25°C. 20 μL aliquots were injected, using a mixture of acetonitrile/water (45:55, v/v) at 0.3 $\text{cm}^3 \text{min}^{-1}$ as mobile phase. The total organic carbon (TOC) concentration was monitored using a Multi N/C 3100 Analytik Jena analyser. The atrazine and surfactant removal were also monitored through the COD content during electrolysis using a HACH DR2000 analyzer. Zeta potential was also measured for the clarified liquid using a Zetasizer Nano ZS (Malvern, UK). Measurements of pH were carried out with an InoLab WTW pH-meter. The particle size was monitored during electrochemical oxidation with a Mastersizerhydro 2000SM (Malvern). The colorimetric method used to determine the concentration of the SDS surfactant has been reported by Jurado et al. [39].

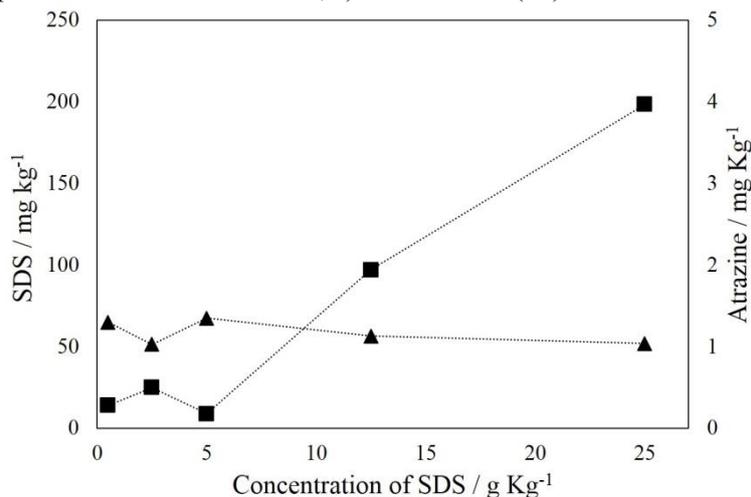
7.3 RESULTS AND DISCUSSIONS

7.3.1 Soil washing

From the viewpoint of a chemical engineer, soil washing is a solid-liquid extraction operation unit, for which it is known that temperature and ratio between extracting agent and solid are the two key parameters in order to obtain an efficient treatment. In a full-scale soil washing application, regulation of temperature is not going to be a suitable choice, because of the expected high cost (due to the expected high amounts of soil to be processed). Hence, temperature will be kept at ambient conditions and the key parameter in the remediation of a soil by washing with a surfactant solution is the ratio surfactant/soil. Taking into account this fact, Fig. 1 shows the concentration of SDS and atrazine in the soil after applying the washing treatment with different surfactant/soil ratios. As it can be observed, both the pollutant and the surfactant are removed efficiently from the soil with this treatment and no significant differences are seen in the concentration of SDS and atrazine with increasing the ratio surfactant/soil.

These results demonstrate that even low concentrations of SDS can be sufficient to extract efficiently all the pollution contained in the soil. Maximum removals of atrazine can be attained with ratios as low as 0.5 g surfactant/kg soil and no significant differences are obtained within the range 0.5-25.0 in the treated soil quality. However, the resulting waste coming from the washing fluid is expected to have different characteristics and hence its later treatment by electrolysis may be strongly influenced by them.

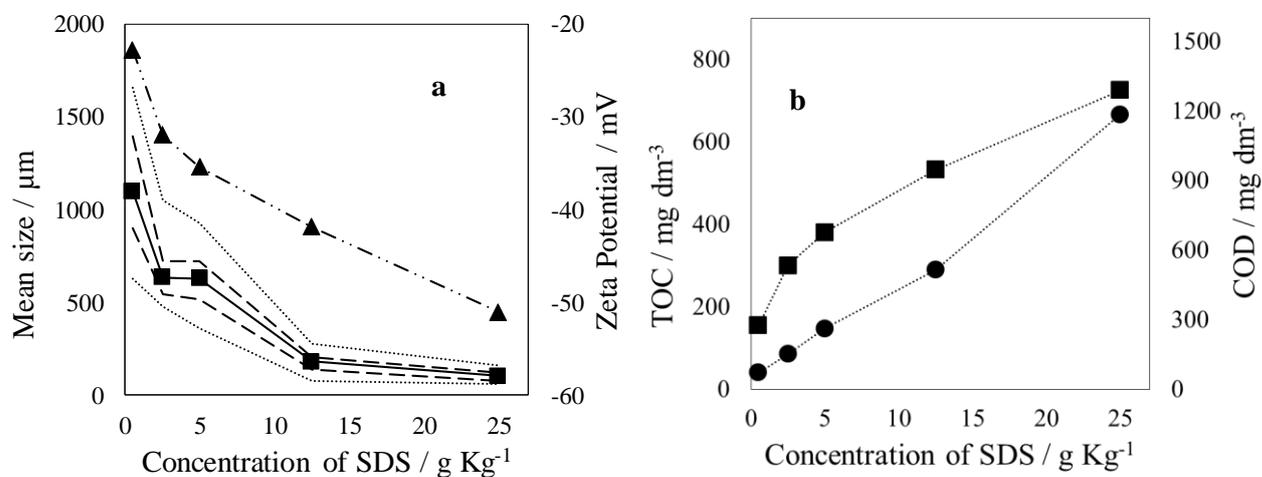
Figure 7.1- Surplus concentration of SDS (■) and atrazine (▲) after the soil washing treatment.



Fonte: autor, 2015.

Fig. 2 shows the main characteristic of the effluents produced in this treatment. As can be observed in Figure 2a, low concentrations of surfactant (>5 g of SDS per Kg of soil) lead to the formation of big micelle (ranging from 1000 to 2000 μm) particles (pesticide micro-drops covered by a layer of surfactant) with a low negative charge (ranging from -25 to -38 mV of zeta potential) and a high dispersion in the size of particles. In increasing the amount of surfactant (> 10 g of SDS per Kg of soil), the size of the particles decreases (< 250 μm) and the superficial charge becomes more negative (-60 mV), meanwhile the dispersion in the size range decreases (see, Fig. 2). Meanwhile, the higher the ratio surfactant/soil, the higher is the pollution of the effluent (in terms of COD and TOC (see, Fig. 2b)), because of the higher content in surfactant of the washing fluid. In addition, the nature of the wastewater produced differs completely.

Figure 7.2- Soil-washing effluent polluted with atrazine. (a) z-potential (\blacktriangle), mean particle size (\blacksquare), size limits including 50% of the particles (---), size limits including 80% of the particles (.....). (b) TOC (\bullet) and COD (\blacksquare) profiles at different ratios SDS/soil.



Fonte: autor, 2015.

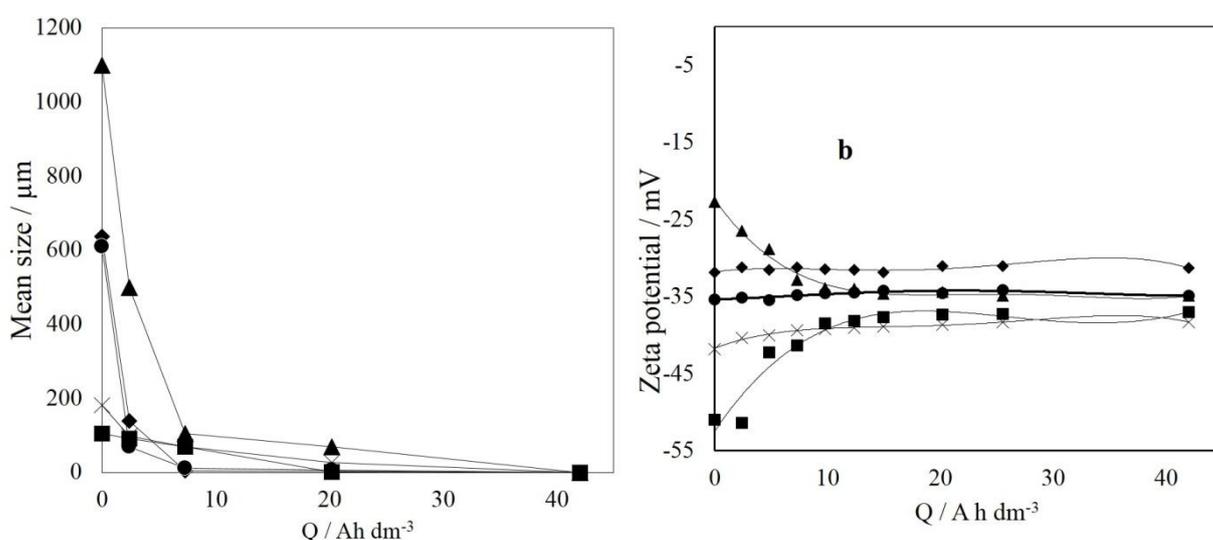
7.3.2. Electrolysis of the soil washing effluent

Fig. 3 shows the changes in the mean particle size and z-potential during the galvanostatic electrolysis of the five soil washing effluents using BDD anodes and applying 30 mA cm^{-2} at 25°C . In applying electric charge, the size of the micelles decreases down to the detection limits of the equipment, following an exponential trend. This is a very interesting process that to the authors' knowledge has not been studied before and it may have a great significance in the design of full size electrolytic processes. Due to steric effects by micelles, the elimination of pollutants is not expected by direct electrolysis but rather, mediated oxidation from oxidants produced on the anode surface is feasible.

As expected, the higher the amount of surfactant, the higher is the resulting electric charge required for the removal of the particulate pollutant, although there is not a direct relationship between both parameters and rate seems to be increased for larger particles. Regarding the superficial charge of the micelles, the initial situation is very different in the five effluents studied but z-potential allows us to observe that during the treatment, the charge of the particles tends to a value around $-30 \pm 5 \text{ mV}$ as the size of the particles decrease. This trend is indicative of the highly complex regrouping processes

of surfactant in the micelles during the electrolysis because the initial z-potential of the five wastes was higher (in absolute value) for the wastes containing smaller particles and lower for the wastes containing bigger micelles. Superficial charge of the smaller micelles formed during electrolysis does not seem to be related only to the size of the micelles as in the soil washing process but to much more complex processes, which may suggest the influence of oxidants electrogenerated on these surfaces.

Figure 7.3- Changes in the mean particle size (a) and z-potential (b) during the electrolysis at j : 30 mA cm^{-2} of the effluents produced during soil washing with the following [SDS]/soil ratios: 0.5 (\blacktriangle), 2.5 (\blacklozenge), 5.0 (\bullet), 12.5 (\times) and 25.0 (\blacksquare).

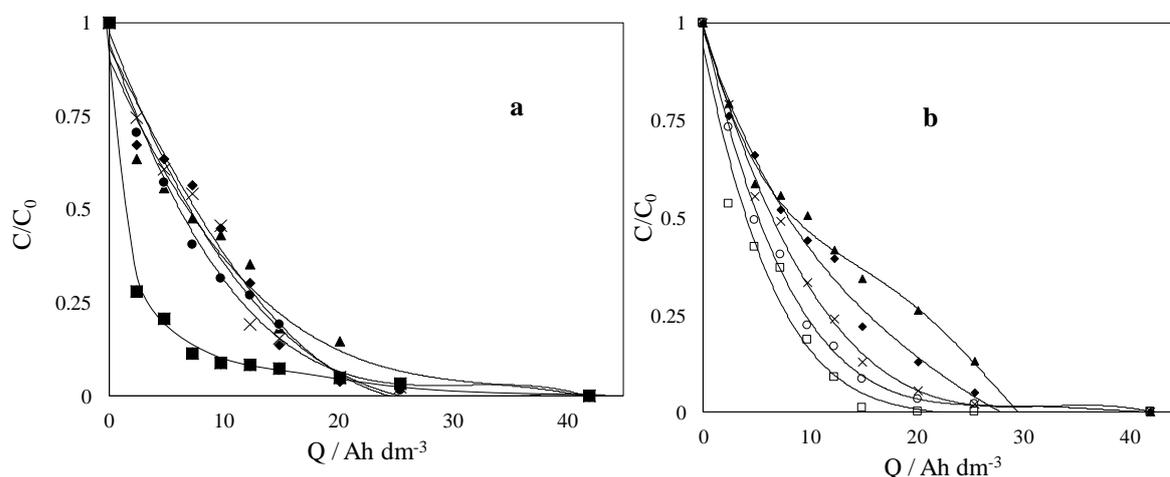


Fonte: autor, 2015.

Fig. 4 shows the changes in the concentration of surfactant and pesticide during the electrolysis of soil washing effluents. In comparing profiles, it can be clearly seen that surfactant is removed faster than pesticide. This behavior is in agreement with the progressive reduction in the size of the micelles during the treatment and it indicates that the removal of pollution precedes though the attack of oxidants to the surface of the micelles where SDS is protecting the pesticide. However, the simultaneous oxidation of pesticide (most probably when dissolved from the micelles) and mineralization clearly indicates that pesticide and reaction intermediates are also attacked and are completely oxidized up to carbon dioxide. Dissolution of pesticide in water is a key factor in explaining the results and it has to be taken into account that atrazine is no completely

insoluble in water but a significant solubility is expected (solubility in water is 33 mg dm^{-3}).

Figure 7.4- SDS (a) and atrazine (b) removal profiles during the electrolysis at $j: 30 \text{ mA cm}^{-2}$ of the effluents produced during soil washing with the following [SDS]/soil ratios: 0.5 (\blacktriangle), 2.5 (\blacklozenge), 5.0 (\bullet), 12.5 (x) and 25.0 (\blacksquare).



Fonte: autor, 2015.

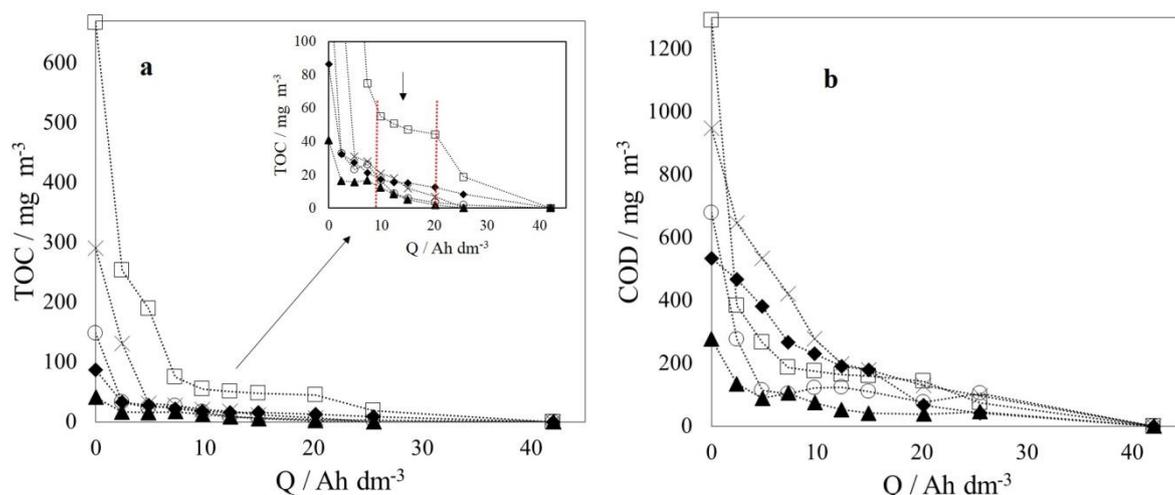
Regarding intermediates produced, Table 1 shows the maximum area of the three intermediates detected according to the HPLC. They are completely depleted during the electrolysis and as it can be observed, the lower the SDS concentration, the higher is the maximum concentration of intermediates detected. This fact indicates that degradation of the larger micelles lead to the formation of higher concentration of intermediates, although it does not influence on the oxidation mechanism.

Table 7-1. Maximum concentration of intermediates measured during the electrolysis of the soil washing effluents.

SDS / g Kg^{-1}	Intermediate 1 (2.41 min)	Intermediate 2 (4.01 min)	Intermediate 3 (5.12 min)
0.5	2531	956	854
2.5	1745	1012	508
5	1898	853	612
12.5	893	645	573
25	965	698	386

Fig. 5 shows the changes of TOC and COD during the five electrolysis. The complete oxidation (COD removal) and mineralization (TOC removal) of the waste is obtained regardless of the initial concentration of surfactant. The electrical charge required for depletion does not differ significantly from one effluent to the other, because the removal of the effluents with the higher organic content (coming from the application of a higher surfactant/soil ratio in the soil washing) is very efficient. Another important point is the plateau zone observed in the TOC vs. Q plots (zoomed in the onset). This plateau was previously observed in the treatment of other pollutants with low solubility [40-42] and could be explained by competing oxidation reactions between the raw pollutant and the intermediates caused by the great differences in their oxidizability.

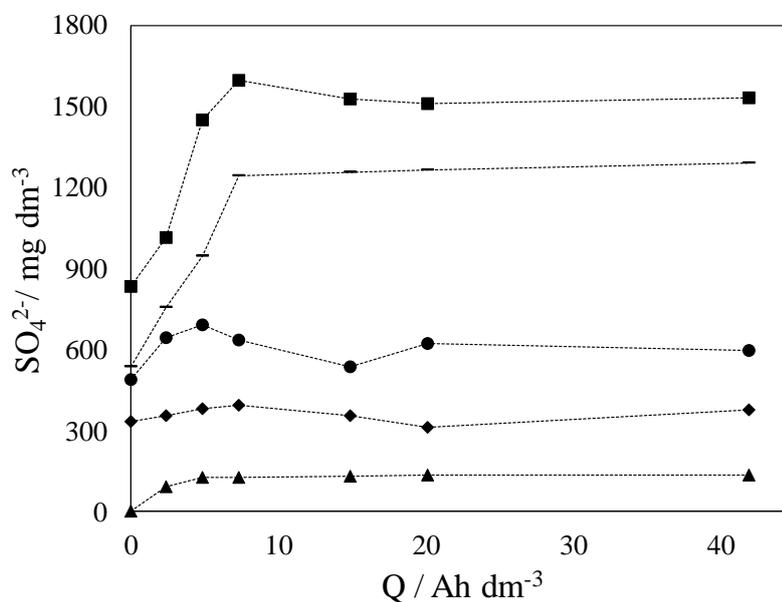
Figure 7-5. TOC and COD removal profiles during electrolysis at j : 30 mA cm^{-2} of the effluents produced during soil washing with the following [SDS]/soil ratios: 0.5 (\blacktriangle), 2.5 (\blacklozenge), 5.0 (\bullet), 12.5 (\times) and 25.0 (\blacksquare).



Taking into account the composition of the soil washing fluid (only carbonates and bicarbonates are present as ionic species), initially only peroxocarbonates and products coming from the decomposition of these species (mainly hydrogen peroxide) are expected to be produced in the reaction media. However, the degradation of SDS may also be related to the production of a very efficient oxidant: the peroxosulphate. Thus, there is a significant release of sulphate when the surfactant is oxidized. This release can explain the further expected oxidation of this anion to peroxosulphate, which could be playing a very important role in the overall oxidation process [44, 45].

Fig. 6 shows the concentration of sulphate ions measured during the electrolysis, which points out the importance of this plausible oxidation mechanism. The higher the concentration of SDS used for washing the soil, the higher is the amount of sulphate contained in the washing fluid and hence the higher is the effect expected of the mediated oxidation. This higher concentration explains the higher degradation rate observed in washing wastes with high ratio SDS/soil and that in spite of being much more contaminated, total depletion of pollutants is attained for a comparable electric charge passed.

Figure 7-6. Sulphate ions produced during the electrolysis at $j: 30 \text{ mA cm}^{-2}$ of the effluents produced during soil washing with the following [SDS]/soil ratios: 0.5 (\blacktriangle), 2.5 (\blacklozenge), 5.0 (\bullet), 12.5 (-) and 25.0 (\blacksquare).



7.4 CONCLUSIONS

From this work, the following conclusions can be drawn:

- Combination of soil washing and electrolysis with diamond electrodes is a very efficient method for the depletion of atrazine from polluted soils,
- Characteristics of the effluent produced in soil washing treatments are strongly influenced by the ratio surfactant/soil used.
- The higher the ratio, the lower the mean particle size, the more negative is the z-potential and the higher is the resulting waste COD and TOC. Maximum removals of atrazine can be attained with ratios as low as 0.5 g surfactant/kg soil

and no significant differences are obtained within the range 0.5-25.0 in the treated soil quality.

- Electrolysis with diamond electrodes of the waste produced in the soil washing is very efficient and attains the total depletion of pollutants by mineralization.
- Mean particle size decreases during the treatment down to zero and the surfactant is removed faster than the pesticide, indicating that oxidation mechanisms involves the attack of oxidants to the surface of micelles.
- Peroxosulphate produced by oxidation of the sulphate release during the oxidation of SDS plays an important role in the oxidation mechanisms of this type of pollutant.

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8 CONSIDERAÇÕES FINAIS

Avaliando os resultados, pode-se concluir que o uso dos métodos eletroquímicos são promissores tornando viável o tratamento de efluentes e solos através da degradação da matéria orgânica. Portanto:

Os resultados obtidos da aplicabilidade da oxidação eletroquímica como tecnologia alternativa para remoção da matéria orgânica em efluentes derivados da indústria do petróleo mostraram-se eficazes sob as condições operacionais estudadas e os materiais eletrocatalíticos empregados Ti/Pt e DDB, obtendo a melhor performance com eletrodo de DDB e menos consumo energético 56.2 kWh m^{-3} reduzindo a Demanda Química de Oxigênio (DQO) 2,746 para 200 mg L^{-1} em 5 h, demonstrando que o sistema em fluxo mostra-se promissor para a prática de tratamento de composto orgânicos persistentes.

O estudo eletroquímico visando à remoção de diesel em solo por meio da remediação eletrocinética e integração da oxidação eletroquímica mostra atrativa devido aos seus mecanismos de aplicabilidade. Neste trabalho foi obtido resultados satisfatórios de remediação de solo com eletrodos ADS ($\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$). Foi possível monitorar o COT (Carbono Orgânico Total) assim como a concentração de Hidrocarbonetos Totais de Petróleo (HTP), obtendo resultados de remoção superiores 60% em 15 dias de tratamento. O comportamento dos eletrólitos influenciou no processo de descontaminação de HTP favorecendo a diminuição da resistência ôhmica do solo, porém apresentaram comportamentos distintos nas seguintes ordens de remoção, NaOH (68.03 %), ácido cítrico (81.36 %) e Na_2SO_4 (96.46%).

O processo de lavagem de solo mostrou-se eficiente para remoção da atrazina em solo, porém ao final do processo a matéria orgânica é transferida do solo para solvente extrator, resultando em efluente não tratado com elevada carga da matéria orgânica. Neste trabalho, foi possível empregar a oxidação eletroquímica como alternativa para remoção da atrazina e surfactante no efluente gerado, além de investigar que formaram micelas após o processo de extração do solo. Em virtude disto, observou-se o comportamento das micelas durante a oxidação eletroquímica, observando diminuição do tamanho médio de partículas. A remoção do surfactante foi mais rápida quando comparada a atrazina, devido o rompimento das micelas, onde a atrazina está rodeada de surfactante. Além disso, pode considerar que são formados peroxocarbonatos e perosulfatos (sendo as principais espécies presentes no efluente o

SO_4^{2-} e CO_3^{2-} de lavagem de solo) obtendo a remoção total em 8h de tratamento da atrazina e surfactante.

Em virtude do comportamento de efluente de lavagem de solo contaminado com pesticida, foi avaliado em distintas concentrações de surfactante empregado para extração da atrazina. Os resultados demonstraram claramente que em maiores concentrações de surfactante há formação de partículas menores e baixas concentrações ocorre a geração de maiores partículas. Aplicando a oxidação eletroquímica foi possível evidenciar o comportamento do tamanho médio das partículas ocorrendo à diminuição mais rápida em menores tamanho de partículas. Neste processo foi possível observar que em maiores concentrações de surfactante a taxa de remoção da atrazina e surfactante são mais favorecidos em virtude da possível formação dos $\text{S}_2\text{O}_8^{2-}$.

Finalmente, é importante ressaltar que este trabalho teve como foco a sua aplicabilidade. Em virtude disto, os objetivos desta tese foram avaliar o comportamento das diferentes tecnologias para propor um tratamento alternativo de efluentes derivados da indústria petrolífera e de agrotóxicos visando minimizar os gastos econômicos. Em virtude disso, selecionamos como perspectivas futuras:

- Emprego de painéis solares com objetivo de evitar sua dependência total da energia elétrica;
- Aplicação em maior escala das tecnologias eletroquímica.

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