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Tecnologia eletroquímica como tratamento alternativo de efluentes derivados da indústria textil e petroquímica

Jéssica Horacina Bezerra Rocha

Tese de Doutorado
Natal/RN, outubro de 2014

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TECNOLOGIA ELETROQUÍMICA COMO TRATAMENTO ALTERNATIVO DE EFLUENTES DERIVADOS DA INDÚSTRIA TEXTIL E PETROQUÍMICA.

Tese submetida ao Programa de Pós-graduação em Química da Universidade Federal do Rio Grande do Norte, como requisito para obtenção do título de doutor em Química.

Orientador: Dr. Carlos Alberto Martinez-Huitle
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Tese apresentada ao Programa de Pós-graduação em Química da Universidade Federal do Rio Grande do Norte, em cumprimento às exigências para obtenção do título de Doutora em Química.

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RESUMO

Neste trabalho, o tratamento de efluentes da indústria têxtil, contendo corantes como Amarelo de Novacron (YN), Vermelho de Remazol BR (RRB) e Azul de Novacron CD (NB), e o tratamento de efluentes da indústria do petróleo (água produzida), foram investigadas por oxidação anódica (AO) com ânodos de Platina suportada em titânio (Ti/Pt) e Diamante Dopado com Boro (DDB). Certamente, um dos principais parâmetros neste tipo de tratamento é o tipo de material eletrocatalítico utilizado, uma vez que os mecanismos e os produtos de algumas reações anódicas dependem dele. A eletrólise galvanostática dos efluentes sintéticos RRB, NB e YN foi investigada a fim de encontrar as melhores condições para a remoção da cor e da carga orgânica do corante. De acordo com os resultados experimentais obtidos, o processo de OA é adequado para descoloração de águas residuais contendo esses corantes têxteis, devido às propriedades eletrocatalíticas de DDB e Pt. A remoção da carga orgânica foi mais eficiente com DDB, em todos os casos, e os corantes foram degradados à ácidos carboxílicos alifáticos no final da eletrólise. Consumo de energia para a remoção de cor durante OA das soluções sintéticas de RRB, NB e YN depende principalmente das condições de funcionamento, por exemplo, RRB, passa de 3,30 kWh m^{-3} em 20 mA cm^{-2} para 4,28 kWh m^{-3} em 60 mA cm^{-2} (pH = 1); 15,23 kWh m^{-3} em 20 mA cm^{-2} para 24,75 kWh m^{-3} em 60 mA cm^{-2} (pH = 4,5); 10,80 kWh m^{-3} em 20 mA cm^{-2} para 31,5 kWh m^{-3} em 60 mA cm^{-2} (pH = 8) (dados estimados por volume de efluente tratado). No estudo da OA da água produzida de petróleo, as eletrólises galvanostáticas no ânodo de DDB levaram à completa remoção de DQO (98%), devido às grandes quantidades de radicais hidroxila e peroxodissulfatos gerados a partir da oxidação da água e sulfatos em solução, respectivamente. A taxa de remoção da DQO aumenta com o incremento da corrente aplicada (15-60 mA cm^{-2}). Por outro lado, no eletrodo de Pt, aproximadamente 50% de remoção da carga orgânica foi alcançada através da aplicação de 15 a 30 mA cm^{-2} e 80% de remoção de DQO a 60 $mAcm^{-2}$. Dessa forma, os resultados obtidos na aplicação desta tecnologia foram satisfatórios dependendo do material eletrocatalítico e das condições operacionais utilizadas, tanto para remoção de carga orgânica em efluentes têxteis e petroquimicos quanto para remoção de cor, no caso dos efluentes têxteis. Portanto, a aplicação do tratamento eletroquímico pode ser considerada como uma alternativa viável no pré-tratamento ou tratamento de efluentes derivados da indústria têxtil e petroquímica.

Palavras Chaves: Oxidação eletroquímica. Materiais eletrocatalíticos. Tratamento de efluentes. Corantes. Água produzida.

ABSTRACT

In this work, the treatment of wastewater from the textile industry, containing dyes as Yellow Novacron (YN), Red Remazol BR (RRB) and Blue Novacron CD (NB), and also, the treatment of wastewater from petrochemical industry (produced water) were investigated by anodic oxidation (OA) with platinum anodes supported on titanium (Ti/Pt) and boron-doped diamond (DDB). Definitely, one of the main parameters of this kind of treatment is the type of electrocatalytic material used, since the mechanisms and products of some anodic reactions depend on it. The OA of synthetic effluents containing with RRB, NB and YN were investigated in order to find the best conditions for the removal of color and organic content of the dye. According to the experimental results, the process of OA is suitable for decolorization of wastewaters containing these textile dyes due to electrocatalytic properties of DDB and Pt anodes. Removal of the organic load was more efficient at DDB, in all cases; where the dyes were degraded to aliphatic carboxylic acids at the end of the electrolysis. Energy requirements for the removal of color during OA of solutions of RRB, NB and YN depends mainly on the operating conditions, for example, RRB passes of 3.30 kWh m^{-3} at 20 mA cm^{-2} for 4.28 kWh m^{-3} at 60 mA cm^{-2} (pH = 1); 15.23 kWh m^{-3} at 20 mA cm^{-2} to 24.75 kWh m^{-3} at 60 mA cm^{-2} (pH 4.5); 10.80 kWh m^{-3} at 20 mA cm^{-2} to 31.5 kWh m^{-3} at 60 mA cm^{-2} (pH = 8) (estimated data for volume of treated effluent). On the other hand, in the study of OA of produced water effluent generated by petrochemical industry, galvanostatic electrolysis using DDB led to the complete removal of COD (98%), due to large amounts of hydroxyl radicals and peroxodisulphates generated from the oxidation of water and sulfates in solution, respectively. Thus, the rate of COD removal increases with increasing applied current density (15-60 mAcm^{-2}). Moreover, at Pt electrode, approximately 50% removal of the organic load was achieved by applying from 15 to 30 mAcm^{-2} while 80% of COD removal was achieved for 60 mAcm^{-2}. Thus, the results obtained in the application of this technology were satisfactory depending on the electrocatalytic materials and operating conditions used for removal of organic load (petrochemical and textile effluents) as well as for the removal of color (in the case of textile effluents). Therefore, the applicability of electrochemical treatment can be considered as a new alternative like pretreatment or treatment of effluents derived from textiles and petrochemical industries.

Keywords: Electrochemical oxidation. Electrocatalytic materials. Wastewater treatment. Dyes. Water produced.

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LISTA DE ABREVIATURAS E SIGLAS

Abs - Absorbance
BDD - Boron-Doped Diamond Boro
BTEX - Benzene, toluene, ethylbenzene and xylenes
COD - Chemical Oxygen Demand
EC - Electrocoagulation
EO - Electrochemical Oxidation or electro-oxidation
EPH - Eletrodo Padrão de Hidrogênio
ERRO - Espécies reativas de Oxigênio
HU - Hansen Units
IDEMA - Instituto de Desenvolvimento sustentável e Meio Ambiente
IEO - Indirect Electro-oxidation
NB - Novacron Blue CD
NY - Novacron Yellow
PAHs - Polyaromatic Hydrocarbons
PEF - Photoelectro-Fenton
POA’s - Processos Oxidativos Avançados
PW - Produced Water
RDO - Reação de Desprendimento de Oxigênio
RRB - Remazol Red BR
TOC - Total Orgânic Carbon

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1 INTRODUÇÃO

Muitos problemas no mundo relacionados com a falta de água limpa e fresca são bem conhecidas: muitas pessoas não têm acesso à água potável, saneamento e milhões de pessoas morrem por ano de doenças transmitidas por água contaminada. Inúmeras pessoas adoecem por infecção e contaminação. Infecções diarreicas e parasitoses intestinais causadas por bactérias e vírus entéricos transmitidos pela água têm se tornado uma das principais causas de desnutrição, devido à má digestão do alimento consumido por pessoas infectadas pela água (LIMA, et al. 2000; BEHRMAN et al. 2004; SHANNON et al. 2008).

Um número crescente de contaminantes, nos países em desenvolvimento e industrializados, estão entrando no abastecimento de água através da atividade humana a partir de compostos tradicionais, tais como metais pesados e nitrosaminas. Cada vez mais, a saúde pública e as preocupações ambientais se esforçam para descontaminar águas antes consideradas limpas. Métodos mais eficazes e de baixo custo para a desinfecção e descontaminação de águas são necessários, sem forçar ainda mais o ambiente ou colocar em perigo a saúde humana pelo próprio tratamento. A água também afeta fortemente a energia elétrica e produção de alimentos, a produção industrial, bem como a qualidade do nosso meio ambiente, afetando as economias de ambos os países em desenvolvimento e industrializados (SHANNON et al. 2008).

Nas próximas décadas, a escassez de água pode ser uma palavra de ordem que pede ação variando de indiscriminada migração da população para a guerra, a menos que novas formas de abastecimento de água potável sejam encontrados. Felizmente, as recentes abundâncias de atividades em pesquisas de tratamentos de águas oferecem esperança na mitigação do impacto das águas com deficiência em todo o mundo. Os métodos convencionais de desinfecção da água, saneamento e dessalinização pode resolver muitos desses problemas com qualidade e oferta (SHANNON et al. 2008). No entanto, os tratamentos químicos intensivos (tais como os que envolvem amônia, os compostos de cloro, ácido clorídrico, hidróxido de sódio, ozônio, permanganato, alúmen e sais férricos, coagulação e auxiliares de filtração, anti-incrustantes, produtos químicos para controle de corrosão, e resinas de troca de iônicas e regenerantes) e resíduos resultantes do tratamento (lodo, salmouras, resíduos tóxicos) podem aumentar os problemas de contaminação e salgar fontes de água doce. Felizmente, há muito mais que a ciência e a tecnologia podem fazer para reduzir as consequências do impacto ambiental e aumentar a eficiência, pois os métodos de tratamento atuais ainda estão longe de limites da lei natural em sua capacidade de separar os compostos, desativar ou remover patógenos nocivos e agentes químicos, moléculas de água de transporte, e os íons que se movem contra gradientes de concentração (SHANNON et al. 2008).

Neste contexto, este trabalho propõe uso da tecnologia eletroquímica como alternativa para remover a matéria orgânica proveniente de efluentes da indústria têxtil e petrolífera. Com o intuito de minimizar o impacto ambiental causado aos ambientes aquáticos. Portanto, o objetivo principal deste estudo é investigar a influência de vários parâmetros do processo, como a natureza do material de eletrodo, densidade de corrente aplicada, eletrólito suporte, variação da temperatura e pH, na remoção de matéria orgânica destes efluentes, a fim de identificar as melhores condições experimentais que resultem em uma alta eficiência de corrente e baixo custo de energia.

Dessa forma, esta tese foi dividida em capítulos, sendo este 1º Capitulo uma breve justificativa do tema abordado. No 2º Capítulo são apresentados os objetivos propostos para este trabalho. Um referencial teórico do tema faz parte do terceiro capítulo. Os capítulos 4, 5, 6, 7, e 8 são artigos que foram publicados em periódicos internacionais.

No Capítulo 4 é descrito o processo eletroquímico de remoção da cor do corante têxtil (Amarelo Novacron C-RG) dissolvido em efluentes sintéticos, analisando a influência do NaCl, utilizando eletrodos de diamante dopado com boro (DDB). Esse tipo de eletrodo têm uma adsortividade superficial, portanto sua grande estabilidade frente à oxidação permite que a reação ocorra com reagentes e intermediários em um estado não-adsorvido. O processo é significativamente aceleradado pela presença do NaCl em solução; Curiosamente, o processo de mediação não depende da densidade de corrente aplicada, mas depende de concentração de NaCl. Com base nos resultados, o Cl- foi selecionado como um mediador apropriado durante a oxidação YN em DDB; que mostra melhorias superiores na taxa de remoção de cor. Os parâmetros de eficiência de remoção e consumo de energia mostrou a viabilidade de usar este processo como uma alternativa para a remoção de cor de efluentes têxteis, este trabalho resultou em um artigo o qual foi publicado na revista *Sustainable Environment Research.*

Com a realização do trabalho descrito no Capítulo 4, resolveu-se comparar, no Capítulo 5, a eficiência de remoção deste corante via oxidação direta e indireta utilizando ânodos de diamante dopado com boro (DDB) e platina suportada em titânio (Pt/Ti) na ausência e presença de NaCl em solução. Neste processo, observou-se que os processos eletroquímicos (direta/indireta) favorecem vias de oxidação específicas dependendo do material eletrocatalítico utilizado. Enquanto o ânodo de Pt/Ti favorece a remoção da cor por oxidação direta e indireta, devido à fragmentação do grupo azo corante; o eletrodo DDB favorece a remoção da cor e da carga orgânica, em ambos os processos (95% e até 87%, respectivamente), devido à ruptura do corante em diferentes partes da sua estrutura química. Este estudo originou mais um artigo e seus resultados foram publicados em *Electrochimica Acta.*

O Capítulo 6 desta tese também gerou um artigo, o qual foi publicado em *Electrocatalysis.* Nele, é descrito o tratamento de soluções contendo corante Vermelho de Remazol BR (RRB) e Azul de Novacron CD (NB) por oxidação anódica, utilizando ânodos de DDB. Os corantes aqui usados foram obtidos de uma indústria textile da região, a fim de propor a tecnologia eletroquímica como um método alternativo para eliminação dos corantes residuais que contaminam as aguas. Eletrólises galvanostáticas das soluções de RRB e NB levaram à remoção completa da cor e demanda química de oxigênio (DQO) em diferentes condições de funcionamento (densidade de corrente, temperatura e pH), evidenciando a aplicabilidade do tratamento eletroquímico.

O Capítulo 07 é resultado de um estudo literário sobre as tecnologias eletroquímicas para remoção de hidrocarbonetos de petróleo a partir da água produzida, gerando o quarto artigo desta tese que foi publicado em *Exploration and Production: Oil and Gas Review*.

No Capítulo 08 é descrito a aplicação da oxidação eletroquímica como alternativa no tratamento da água produzida proveniente da indústria petroquímica brasileira. Neste trabalho utilizou-se platina suportada em Ti (Ti/Pt) e diamante dopado com boro (DDB) como ânodos. A influência de diversos parâmetros operacionais, como corrente, eletrólito suporte, velocidade de agitação e temperatura sobre o desempenho foi estudada e o consumo de energia foi avaliado. Os resultados deste trabalho foram pulicados em *Fuel Processing Technolog*y, mostrando que eletrólises galvanostáticas no ânodo de DDB levaram à completa remoção da DQO (98%), devido às grandes quantidades de radicais hidroxila e peroxodissulfatos gerados a partir da oxidação da água, e o percentual de remoção de DQO aumenta com o aumento das correntes aplicadas (15-60 mA cm^{-2}). Por outro lado, no ânodo de Pt, aproximadamente 50% de remoção de DQO foi alcançada através da aplicação de 15 a 30 mA cm^{-2} de densidade de corrente e 80% de remoção da DQO a 60 mA cm^{-2}. Embora, o consumo de energia e processo de tempo tornem a oxidação anódica insuficinete para o tratamento completo de efluentes petroquímicos; talvez, possa ser um processo viável como de pré-tratamento, pois reduz significativamente o custo e tempo de tratamento.

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CAPÍTULO 02

2 OBJETIVOS

2.1 OBJETIVOS GERAIS

Desenvolver, caracterizar, testar e aplicar métodos de eletroxidação para a remoção de resíduos orgânicos em águas residuais sintéticas de indústria têxteis e indústria do petróleo.

2.2 OBJETIVOS ESPECÍFICOS

Desenvolver uma célula eletroquímica com ânodo plano para realizar os experimentos.

Investigar o efeito do material anódico (DDB e Ti/Pt) e avalir o efeito das variáveis experimentais: densidade de corrente elétrica, temperatura, pH e concentração inicial do composto orgânico (no caso de águas residuais sintéticas).

Avaliar o processo eletroquímico em termos de sua eficiência de corrente e consumo energético

Estudar a eliminação da matéria orgânica mediante a Espectroscopia de absorção molecular (UV-Vis), carbono orgânico total (COT), demanda química de oxigênio (DQO) e, em alguns casos, determinar os subprodutos da oxidação por cromatografia gasosa acoplada a espectrometria de massa (CG-MS).

CAPÍTULO 03

3 REVISÃO BIBLIOGRÁFICA

3.1 ÁGUA

A água é um bem comum a todos os seres humanos e de fundamental importância para existência e sobrevivência de todos os seres vivos no planeta. Esta, por sua vez, vem se tornando cada vez mais escassa devido ao seu uso irracional e sua extração excessiva.

No Brasil a disponibilidade hídrica per capita, determinada a partir de valores totalizados para o País, indica uma situação satisfatória, quando comparada aos valores dos demais países informados pela Organização das Nações Unidas (ONU). Todavia, existe uma distribuição espacial desigual dos recursos hídricos no território brasileiro. Cerca de 80% de sua disponibilidade hídrica estão concentrados na região hidrográfica Amazônica, onde se encontra o menor contingente populacional e valores reduzidos de demandas consuntivas (ANA, 2013).

Devido à modernidade tecnológica, o esforço para o desenvolvimento econômico, durante muito tempo, subestimou o impacto das atividades industriais na natureza e na qualidade de vida das gerações futuras. Espaços próximos aos rios eram escolhidos para a implantação de fábricas e indústrias, com o objetivo de facilitar o uso da sua água em seus processos físicos e químicos, além de propiciar o descarte dos resíduos sem interesse econômico. Esse processo entrou logo em colapso com a percepção de que a água é, na verdade, um bem finito e esgotável (DUARTE, 2014). Deste modo, nos últimos anos, nosso país vem sofrendo com a escassez de água potável, haja vista que boa parte dos nossos recursos hídricos encontram-se poluídos por contaminantes orgânicos (por exemplo: Rio Tietê como mostrado na Figura 1) e além do mais, a estiagem das chuvas e seca, em boa parte do território brasileiro, principalmente, o sertão, são castigados pela falta de água. Dessa forma, novos métodos de tratamento de efluentes vem sendo discutidos por diversos autores.

Figura 1 - Rio Tietê

Fonte: http://info.abril.com.br/

3.1.1 Purificação e Tratamento de Água

As atividades humanas do dia-a-dia têm influenciado o fluxo e armazenamento de água e a qualidade da água doce disponível. O estudo de tratamento de efluentes, sejam domésticos ou industriais, tem ganhado bastante força nos últimos anos e um dos principais fatores que mais impulsionam este tipo de estudo reside na escassez crescente de água potável existente no globo terrestre bem como a alta estabilidade dos poluentes orgânicos que são extremamente resistentes à luz e a agentes oxidantes moderados. Estes fatores têm motivado o surgimento de novas leis ambientais, contendo padrões para a emissão de poluentes, cada vez mais rigorosos e o desenvolvimento de tecnologias adequadas para o tratamento de efluentes.

A oxidação biológica é, certamente, o processo mais econômico, porém uma das suas desvantagens é requerer uma grande área para construção de tanques de armazenamento de efluentes onde o volume a ser tratado permanece dias até completar o tratamento através das bactérias facultativas que são as responsáveis pela degradação da matéria orgânica. Os Métodos físico-químicos (filtração, coagulação, adsorção e floculação), a oxidação química (uso de cloro, ozônio, peróxido de hidrogênio, a oxidação do ar úmido) e os processos oxidativos avançados, mais comumente conhecidos como POAs (reação de Fenton, ozônio + radiação UV, fotoquímica) são usados atualmente para tratamento de agua potável e efluentes industriais. Por causa das características extremamente diversas desses efluentes, que normalmente contém uma mistura de compostos orgânicos e inorgânicos, assim como, micro-organismos, nenhuma estratégia universal de recuperação é viável. Por isso, a purificação e tratamento de efluentes constituem um dos maiores objetivos do tratamento de efluentes. Para atingir este objetivo, existem vários processos de tratamento, baseados em fenômenos ou princípios físicos, químicos ou biológicos, ou ainda, em suas combinações.

Os processos físicos são caracterizados por operações que removem substâncias ou micro-organismos fisicamente separáveis dos líquidos ou que não se encontram em dissolução. São exemplos de processos físicos: remoção de sólidos grosseiros; remoção de sólidos decantáveis; remoção de sólidos flutuantes; remoção da umidade do lodo; filtração dos efluentes; incineração do lodo; diluição dos efluentes; homogeneização dos efluentes e floculação. Diferentes métodos físicos são também amplamente usados para a remoção de cor, tais como processos de filtração com membrana, troca iônica e técnicas de adsorção por carvão ativado (LORENC-GRABOWSKA; GRYGLEWICZ, 2007). De acordo com informações na literatura, adsorção em fase líquida é também um dos métodos mais populares e eficientes para remoção de poluentes de efluentes (micro-organismos ou matéria orgânica). O processo de adsorção sólido-líquido explora a habilidade que certos sólidos têm de concentrar na sua superfície substâncias específicas presentes em soluções aquosas. Dessa forma, os componentes das soluções aquosas podem ser separados.

Os processos químicos são processos nos quais ocorre adição de produtos químicos e são utilizados de forma auxiliar aos processos físicos e biológicos, ou até mesmo complementando-os. Alguns métodos químicos de tratamentos incluem coagulação ou floculação, combinados com flotação e filtração, ozonização, processos eletroquímicos, oxidação química, cloração, neutralização ou correção do pH e métodos de oxidações convencionais por agentes oxidantes. O processo químico de oxidação para remoção de orgânicos é frequentemente o mais usado devido ao seu manejo simples. Pode-se citar como exemplo ozônio ou o processo de decomposição oxidativa utilizando processo Fenton. Entretanto, o tratamento eletroquímico é considerado um processo moderno e poderoso de controle de poluição, oferecendo boa eficiência de descontaminação. Em alguns casos, este processo não requer nenhum tipo de produto químico adicional. Os equipamentos necessários e a operação são geralmente simples. Porém, são processos que podem promover a formação de subprodutos indesejáveis que podem ser mais nocivos do que as espécies iniciais do processo. Processo Oxidativos Avançados (POA) têm a mesma característica química: a produção de radicais hidroxilas (•OH). Os radicais •OH são espécies extraordinariamente reativas que atacam a maioria das moléculas orgânicas. Estes processos também são caracterizados pela baixa seletividade do ataque, o que é uma característica muito importante para um oxidante utilizado no tratamento de agua. A versatilidade dos POA é realçada pelo fato de existirem diversas possibilidades para a produção dos radicais hidroxilas, o que permite a escolha do método mais adequado de acordo com o tratamento necessário (ANDREOZZI et al. 1999).

Como os regulamentos ambientais se tornam cada vez mais rigorosos, são necessários novos e promissores processos para o tratamento eficiente de vários tipos de águas com custos de operação relativamente baixos. Neste contexto, os pesquisadores estão tentando vários processos alternativos, como a técnica eletroquímica, oxidação úmida, ozonização, método fotocatalítico para a degradação de compostos orgânicos e eliminação de micro-organismos.

3.2 TRATAMENTO E DESINFECÇÃO DA ÁGUA E EFLUENTES VIA OXIDAÇÃO ELETROQUÍMICA

3.2.1 Desinfecção Eletroquímica da Água

As alternativas mais interessantes para incluir cloro na purificação de águas são: (SHANNON et al. 2008): (i) sistemas químicos, tais como o ozônio, a prata, o cobre, o ferrato, iodo, bromo, peróxido de hidrogênio e permanganato de potássio, (FACILE et al. 2000; XU et al., 2002) (ii) sistemas de propriedades físico-químicas, tais como desinfecção fotodinâmica (MILLS et al. 1997; BLAKE et al. 1999; BLAKE, 1999), (iii) a desinfecção eletroquímica, e (iv) sistemas físicos, como a radiação ultravioleta, ultrassom, campos elétricos pulsados, irradiação, elevada desinfecção magnética e sistemas de micro-ondas (WATTS et al. 1995; SHANNON et al. 2008). Embora o ozônio e a radiação ultravioleta tenham ganhado aceitação dentro do processo de tratamento de água, a maioria das outras alternativas, atualmente não preenchem os requisitos para a desinfecção de água potável e residual primária (KERWICK et al. 2005; SHANNON et al. 2008). Sistemas de desinfecção sequenciais tais como UV/cloro combinado e ozônio/cloro combinado estão sendo considerados por muitos utilitários de água potável, enquanto componente de inativação de suas estações de tratamento de multi-barreira pois, em comparação com o cloro livre, tanto UV e ozônio são muito eficazes. Além disso, o cloro combinado pode fornecer um valor residual em sistemas de distribuição, sem formação de altos níveis de subprodutos da desinfecção (SHANNON et al. 2008). No entanto, as mudanças tecnológicas da desinfecção levantaram novas preocupações porque os vírus, embora efetivamente controlados por ozônio, são resistentes a desinfecção por UV e por cloro combinado. Por outro lado, o ozônio pode formar o íon bromato como subproduto cancerígeno na água contendo íons de brometo, cloro combinado e pode formar outros subprodutos da desinfecção não regulamentados, por exemplo, ácido iodo-acético e halo-acetonitrilas (KRASNER et al. 2006; MUELLNER et al. 2007), que podem ser mais tóxicos e cancerígenos do que aqueles associados com cloro livre. Em contraste, a desinfecção eletroquímica surgiu como uma das alternativas mais promissoras ao cloro fornecendo desinfecção primária e residual (KERWICK et al. 2005).

O maior objetivo para fornecimento de água potável e acessível é desinfetar a água de patógenos tradicionais e emergentes, sem criar mais problemas devido ao processo de desinfecção em si. Agentes patogênicos possuem um efeito devastador na saúde pública, especialmente nos países em desenvolvimento. Agentes infecciosos de veiculação hídrica responsáveis por estas doenças incluem uma variedade de helmintos, protozoários, fungos, bactérias, vírus e priões (WORLD HEALTH ORGANIZATION, 2003). Enquanto alguns agentes infecciosos foram erradicados ou diminuídos, novos continuam a surgir, então a desinfecção da água tem se tornado cada vez mais desafiadora.

Inúmeros sistemas eletroquímicos e materiais eletrocatalíticos foram testados contra uma variedade de microrganismos e sua eficiência para a redução da carga orgânica é em grande parte dependente das condições do reator eletroquímico, material do ânodo, a composição de eletrólitos e eletrólise.

O método mais popular de desinfecção eletroquímica é eletrocloração. Sua principal vantagem é a geração local de desinfectantes, evitando assim os problemas de cloração comum, tais como transporte e armazenamento de cloro (RAJESHWAR et al. 1997). Existem dois tipos de processos que envolvem cloração de eletrossíntese ou de cloro livre a partir de um gerador de salmoura em eletrolítico ou a produção direta de oxidantes a partir da água a ser tratada por meio do eletrolisador.

Espécies de cloro ativo, como Cl_2, HOCl, ClO_2 e OCl^- têm sido amplamente reconhecidos como principais oxidantes responsáveis pela inativação de células em eletrocloração. Estas espécies podem ser produzidas no ânodo por meio das seguintes reações (MARTINEZ-HUITLE; BRILLAS, 2008):

$$H_2O + Cl^- \rightarrow ClOH^\bullet + H^+ + 2\,e^- \tag{1}$$

$$H_2O + ClOH^\bullet + Cl^- \rightarrow Cl_2 + O_2 + 3\,H^+ + 4\,e^- \tag{2}$$

$Cl_2 + 2\,OH^- \rightarrow H_2O + OCl^- + Cl^-$ (3)

$ClOH^\bullet + Cl_2 \rightarrow ClO_2 + 3\,H^+ + 2\,Cl^- + e^-$ (4)

Estudos recentes têm atribuído o poder de desinfecção maior da eletrocloração ao papel oxidante de espécies reativas de oxigênio (ERO), tais como radical hidroxila (• OH), o oxigênio atômico (• O), peróxido de hidrogênio e ozônio, que pode ser gerada a partir da descarga de água no ânodo como segue (PANIZZA; CERISOLA, 2005; POLCARO et al. 2007; SANTANA, 2005):

$H_2O \rightarrow {}^\bullet OH + H^+ + e^-$ (5)

${}^\bullet OH \rightarrow {}^\bullet O + H^+ + e^-$ (6)

$2\,{}^\bullet O \rightarrow O_2$ (7)

$2\,{}^\bullet OH \rightarrow H_2O_2$ (8)

$O_2 + {}^\bullet O \rightarrow O_3$ (9)

• OH é a segunda espécie mais oxidante conhecida depois do flúor, com um alto potencial padrão ($E^o = 2{,}8$ V) que garante a sua reação rápida com a maioria dos produtos orgânicos. No entanto, o curto tempo de vida • OH e as outras ERO em solução, tornam apenas possível salientar o seu papel na desinfecção usando corrente contínua.

A cinética das diferentes fases paralelas / série envolvidos nas reações (1) - (9) depende do material do ânodo; e isso determina as espécies oxidantes predominantes produzidas. Com base nesta afirmação, Kraft et al. (2007), mostraram que a produção eletroquímica de cloro livre em eletrodos de IrO_2 e IrO_2/RuO_2 é superior a ânodos de DDB e Pt, em condições comparáveis. Uma conclusão semelhante foi relatada recentemente por Scialdone et al. (2009). Em seguida, os óxidos de metal mistos de Ir e/ou Ru são preferíveis como ânodos para eletrocloração para melhorar a geração de espécies de cloro ativos como os principais desinfectantes (MARTINEZ-HUITLE; BRILLAS, 2008).

Novos materiais foram desenvolvidos de modo a evitar a produção de subprodutos e perigosos agentes da desinfecção. Eles podem ser projetados em reatores de fluxo através de sistemas de alto rendimento. A configuração e os custos associados de tais sistemas poderiam torná-los economicamente viável para aplicações que vão desde grandes estações de tratamento de água potável e não potável para sistemas dedicados ao consumo humano e higiene.

Recentemente, eletrodos de filmes de DDB foram considerados particularmente atraente como ânodos, devido às suas excelentes propriedades, incluindo a grande faixa de potencial, baixa adsorção de espécies, estabilidade à corrosão em meios muito agressivos, alta eficiência em processos de oxidação, que são significativamente diferentes dos outros ânodos convencionais, tais como Pt, PbO_2, dopado e não dopado SnO_2, IrO_2, RuO_2, etc (FURUTA et al. 2005; PANIZZA; CERISOLA, 2005). Filmes de diamante são materiais adequados para algumas aplicações industriais, tais como a síntese química, eletroanálise e sensores e biossensores, embora tenham sido aplicadas principalmente na oxidação anódica para destruir poluentes orgânicos refratários ou substâncias tóxicas para o tratamento de águas residuais (TRÖSTER et al. 2004; KRAFT, 2007; MATTHÉE et al. 2006; MARTINEZ HUITLE; FERRO, 2006; SCIALDONE et al. 2009). Ânodos de DDB também são capazes de produzir quantidades muito mais sensíveis de ERO e outras espécies oxidantes, tais como peroxodissulfato, peroxodicarbonato e peroxodifosfato proveniente da oxidação de íons presentes na solução, permitindo também uma desinfecção rápida e permanente (reações (10) para (12)) (MICHAUD et al. 2000; SAHA et al. 2003; CAÑIZARES et al. 2005; SIRÉS et al. 2006; MARTINEZ-HUITLE; BRILLAS, 2008).

$$2\,HSO_4^{-} \rightarrow S_2O_8^{2-} + 2\,H^{+} + 2\,e^{-} \qquad (10)$$

$$2\,HCO_3^{-} \rightarrow C_2O_6^{2-} + 2\,H^{+} + 2\,e^{-} \qquad (11)$$

$$2\,PO_4^{3-} \rightarrow P_2O_8^{4} + 2\,e^{-} \qquad (12)$$

Ao contrário de PbO_2, SnO_2 e TiO_2, filmes de DDB depositados sobre Silício (Si), Tântalo (Ta), Nióbio (Nb) e Tungstênio (W) por deposição química a vapor têm mostrado excelente estabilidade eletroquímica (MATTHÉE et al. 2006; KRAFT, 2007; SCIALDONE et al. 2009). A aplicação de eletrodos de DDB para o tratamento de águas residuais tem sido quase sempre estudado com meio suportado em silício (Si), apesar das dificuldades relacionadas à fragilidade e condutividade relativamente baixa do substrato de Si. Embora películas DDB sintetizados em Nb, Ta e W sejam promissoras, a sua preparação em larga escala é impossível, devido aos custos inaceitavelmente elevados destes substratos metálicos. O uso industrial de filmes de diamante para o tratamento de águas residuais vem sendo usado até que um suporte de alta qualidade seja obtido para escala industrial. Uma alternativa possível é o titânio, o qual possui todos os recursos necessários para ser um bom material de substrato, e ânodo de Ti/BDD já foi utilizado para a destruição de alguns poluentes. No entanto, a deposição de diamante em Ti deve ser fortemente melhorada, pois surgem fendas e provocam o desprendimento do filme de diamante durante a eletrólise a longo prazo (PANIZZA; CERISOLA, 2005; MARTINEZ-HUITLE; FERRO, 2006). Por estas razões, os eletrodos de Si/BDD têm sido propostos nos últimos anos, como material de desinfecção de água potável, onde menores dimensões do ânodo são requeridas em comparação com uma instalação de tratamento de águas residuais.

3.2.2 Tratamento de Efluentes Têxteis e Petroquímicos

A contaminação de solos e lençóis freáticos por compostos orgânicos pouco ou não biodegradáveis tem sido assunto de grande atenção no mundo acadêmico e industrial, e a legislação ambiental torna-se cada vez mais rigorosa ao descarte de efluentes gerados pelas indústrias e a desinfecção de água potável.

Águas residuárias contendo compostos provenientes das indústrias têxtil e petroquímica constituem uma séria ameaça à saúde humana e também são bastante tóxicas à maioria da vida aquática. O alto grau de toxidade destes compostos fenólicos faz com que os limites de concentração para emissão em mananciais e redes de esgoto, estabelecidos pela CETESB (Brasil, Leis, decretos, etc), sejam de 0,5 ppm e 10,0 ppm, respectivamente. Existem vários métodos de tratamento de efluentes industriais contendo poluentes orgânicos, incluindo a incineração, adsorção, tratamento biológico e oxidação química e eletroquímica. A escolha do tipo de tratamento dependerá não só dos custos relacionados ao processo, mas também da facilidade de controle, confiabilidade e eficiência do tratamento.

Dentre os métodos de tratamento utilizados para decompor compostos orgânicos, destacam-se os Processos Oxidativos Avançados (POA's). Estes processos baseiam-se na utilização de agentes bastante reativos, como os radicais $^{\bullet}OH$, os quais são responsáveis por um forte processo oxidativo. Em alguns casos, a ação de agentes intermediários, como o hipoclorito ou $^{\bullet}OH$, representa a única maneira de se degradar o poluente orgânico e mineralizá-lo. Dependendo da composição química, níveis de concentração e força iônica da água residuária, POA's, como a oxidação Fenton, oxidação fotoquímica ou eletroxidação indireta, através de $^{\bullet}OH$ produzido pela decomposição da água (PANIZZA; CERISOLA, 2001, MARTÍNEZ-HUITLE; FERRO, 2006; MARTÍNEZ-HUITLE; BRILLAS, 2009), podem ser usados com sucesso para a remoção de poluentes orgânicos (POLCARO et al. 2000). A Eletrorredução (ER), Eletrocoagulação (EC), Oxidação eletroquímica ou eletro-oxidação (EO) com diferentes ânodos e Eletro-oxidação Indireta (EOI) com cloro ativo são os principais métodos para a remoção de poluentes derivados da indústria do petróleo.

O tratamento empregando processos biológicos ou químicos é frequentemente eficiente no que tange ao cumprimento da legislação pertinente. Porém, atualmente, este requisito não é mais suficiente, uma vez que considerações ambientais estão permanentemente na pauta. Por um lado, a tecnologia convencional para o tratamento químico de águas residuais e potável demanda transporte, estocagem e manuseio de produtos químicos perigosos, além de proporcionar a geração de lamas tóxicas. De outro lado, os processos biológicos são lentos e demandam grandes áreas físicas, além de gerar produtos biodegradáveis solúveis e resíduos celulares. Adicionalmente, compostos orgânicos com alto peso molecular ou microrganismos, presentes em alguns tipos de efluentes industriais aquosos, tendem a ser resistentes à biodegradação. Diante deste quadro, a pesquisa e desenvolvimento de novas tecnologias de tratamento de efluentes que sejam ambientalmente orientadas são cada vez mais estimulados. Neste campo, a Tecnologia Eletroquímica, por ser considerada uma “tecnologia limpa” por fazer uso somente do elétron como reagente, pode se constituir numa alternativa atrativa para o tratamento de efluentes contendo compostos orgânicos via eletroxidação na superfície do ânodo (PELEGRINO et al. 2002; MARTÍNEZ-HUITLE; FERRO, 2006; MARTÍNEZ-HUITLE; BRILLAS, 2009).

Nos últimos anos, a Oxidação Eletroquímica (OE) de efluentes refratários tem recebido uma considerável atenção, graças às suas características atraentes já citadas anteriormente. Por estes motivos, tem sido proposta como uma alternativa promissora para o tratamento de águas residuais (MARTÍNEZ-HUITLE; BRILLAS, 2009). Recebe outras denominações como oxidação anódica direta ou eletro-oxidação anódica pelo fato de não haver geração de cloro em solução (SIRÉS; BRILLAS, 2011). Dois mecanismos diferentes são responsáveis pela degradação eletroquímica de moléculas orgânicas envolvendo a oxidação de poluentes numa célula eletrolítica: oxidação direta e indireta (MARTÍNEZ-HUITLE et al. 2006 e 2009). A oxidação anódica se dá pela transferência direta de elétrons para o ânodo, no qual os poluentes são adsorvidos sobre a superfície do ânodo e destruídos pela reação anódica de transferência de elétrons. Comninellis (1994) classificou os ânodos como ativos e não ativos por apresentarem comportamentos diferentes. Na oxidação direta, eletrodos não ativos devem ser utilizados. Como exemplo, pode-se destacar os ânodos PbO_2, SnO_2 e DDB. Já os considerados ativos incluem-se aço, Pt, IrO_2 o RuO_2. Segundo Martínez-Huitle e Ferro (2006), a viabilidade do processo de eletroxidação anódica é dependente de três parâmetros: a geração de radicais hidroxila física ou quimicamente adsorvidos na superfície do eletrodo, atividade eletrocatalítica dos materiais anódicos e a produção de O_2. Além disso, a difusão de poluentes e a densidade de corrente também são determinantes no processo.

Pode-se destacar ainda que no tratamento de águas residuárias, é aplicada alta tensão para alcançar oxidação de poluentes e manter a atividade do ânodo, que possui forte influência (como descrito anteriormente) na seletividade e eficiência do processo de conversão ou combustão eletroquímica.

Por outro lado, a oxidação indireta ocorre através de mediadores presentes na solução capazes de gerar eletroquimicamente espécies fortemente oxidantes cujas quais permanecem aderidas ao ânodo, onde são geradas continuamente. Cloro, hipoclorito, radicais hidroxila, ozônio e peróxido de hidrogênio são exemplos de algumas dessas espécies (SIRÉS e BRILLAS, 2011; MARTÍNEZ-HUITLE; BRILLAS, 2009; KLAVARIOTI et al. 2009). A existência da oxidação indireta ou reação química com espécies geradas eletroquimicamente no ânodo como fisissorção do "oxigênio ativo" (radical hidroxila adsorvido fisicamente) ou quimissorção do “oxigênio ativo" (oxigênio na rede de um ânodo de óxido metálico (MO)) permitiu a proposta de duas abordagens principais para a redução da poluição em águas residuárias por eletro-oxidação: (i) conversão eletroquímica, por meio da qual os compostos orgânicos refratários são seletivamente transformados em compostos biodegradáveis como ácidos carboxílicos por quimissorção do "oxigênio ativo" e (ii) combustão eletroquímica, na qual os produtos orgânicos são mineralizados por adsorção física do •OH. O método de combustão eletroquímica (ou incineração eletroquímica) ocorre quando os compostos orgânicos são completamente mineralizados, isto é, oxidados à CO_2 e H_2O, com •OH adsorvido fisicamente. Esse radical possui um alto potencial padrão (E^0 = 2,80 V) o que assegura sua rápida reação com a maioria dos compostos orgânicos e gera derivados halogenados ou hidroxilados para conversão em CO_2 (SIRÉS e BRILLAS, 2011; MARTÍNEZ-HUITLE; BRILLAS, 2009). Os parâmetros operacionais que afetam o desempenho do processo de OE são: o material dos eletrodos, o tipo do eletrólito suporte, a corrente aplicada, a carga orgânica e o pH da solução (KLAVARIOTI et al. 2009). Ainda, de acordo com a interação entre os radicais •OH e o material do ânodo durante a eletro-oxidação em solução ácida, Kapalka et al. (2008) classificaram os materiais eletródicos de alto a baixo poder oxidante. Como regra geral estabelecida, quanto menor a interação entre o radical •OH e o material do ânodo, mais favorável será a reação de oxidação dos compostos orgânicos em detrimento da reação de desprendimento de oxigênio (RDO), como é o caso do ânodo de DDB (alto poder oxidante). Por outro lado, quanto maior a interação entre o radical •OH e o material anódico, a RDO será favorecida, como é o caso do ânodo de RuO_2 (baixo poder oxidante). A relação estabelecida por Kapalka et al. (2008) pode ser explicada pelo sobre-potencial da evolução de O_2 durante a oxidação eletroquímica, ou seja, quanto maior for esse sobre-potencial, menor será a concentração de O_2 em solução (característica dos eletrodos não ativos) levando a combustão da matéria orgânica e que resulta numa maior eficiência de corrente. Entretanto, vale salientar que, a RDO é uma reação parasita e, como seu próprio nome já diz, acontecerá inevitavelmente. Além da influência que o material eletródico pode exercer no processo de OE eles também devem apresentar grande resistência ao calor, aos eletrólitos presentes e à passagem da corrente elétrica. Se um eletrodo não sofre alterações na sua estrutura, mesmo sujeito a tais condições, é chamado de eletrodo inerte e sua função é a simples troca de elétrons com a solução. Os eletrodos inertes mais comuns são o grafite e a platina. Já o eletrodo ativo, além de transferir elétrons, participa do processo eletroquímico, sendo também modificado pela ação da corrente elétrica, formando ou recebendo íons metálicos (RODRIGUES et al. 2001). Nos últimos anos, o uso de ânodos de DDB cresceu e ganhou atenção, pois mostraram possuir estabilidade química e eletroquímica, boa condutividade, bem como alcançaram melhores taxas de mineralização (KLAVARIOTI et al. 2009). Ao utilizar eletrodos estáveis ou inertes, que não se dissolvem em solução, ao invés de eletrodos de sacrifício como na eletrocoagulação, não ocorre o processo de coagulação, apenas eletroflotação e eletro-oxidação.

Além da classificação em bons ou ruins eletro-catalisadores da reação de oxigênio proposta por Comninellis (1994), de maneira geral, os ânodos ainda podem ser divididos em duas categorias: ativos e não ativos. Em ambos os tipos de ânodos o primeiro passo consiste na eletrolise da água, levando a formação de radicais hidroxila (•OH) adsorvido sobre a superfície do eletrodo. No caso de ânodos ativos, esse radical interage fortemente com a superfície do ânodo que é transformado em "oxigênio ativo" quimissorvido. Os radicais hidroxila também reagem para formar o superóxido MO_{x+1} nos locais ativos do óxido MO_X. Os superóxidos fissisorvidos oxidam as moléculas orgânicas. Por outro lado, a superfície de ânodos não ativos interage fracamente com os radicais hidroxila, que reagem diretamente com radicais orgânicos até alcançar a total mineralização (COMNINELLIS, 1994).

As espécies MO_{x+1} também serão responsáveis pela formação de oxigênio (reação parasita, RDO), um processo competitivo. Alem disso, também deve ser considerado outro caminho para a reação, em que o composto orgânico é completamente mineralizado em CO_2 e agua. Na superfície do ânodo, o "oxigênio ativo" pode-se apresentar de duas formas: fisissorvido, adsorção dos radicais hidroxila (•OH) e/ou quimissorvido (oxigênio na rede, MO_{x+1}). Na ausência de qualquer composto orgânico oxidável, o "oxigênio ativo" produz O_2. A reação de combustão é mais provável que ocorra sob condições de elevados sobrepotenciais para evolução da reação de oxigênio na superfície de DDB, PbO_2, SnO_2 e Sb_2O_5. Por conseguinte, durante a eletro-oxidação de moléculas orgânicas, é provável que todas as reações exerçam influência sobre o processo global.

3.3 LEGISLAÇÃO BRASILEIRA

A legislação brasileira é regida pela Constituição da República Federativa (1988), a qual em seu Art. 200, estabelece que: ao sistema único de saúde compete, além de outras atribuições, nos termos da lei: VI - fiscalizar e inspecionar alimentos, compreendido o controle de seu teor nutricional, bem como bebidas e águas para consumo humano; VII - participar do controle e fiscalização da produção, transporte, guarda e utilização de substâncias e produtos psicoativos, tóxicos e radioativos; VIII - colaborar na proteção do meio ambiente, nele compreendido o do trabalho. Além desta constituição temos a Política Nacional de Recursos Hídricos, fruto de uma série de acontecimentos históricos, nacionais e internacionais, que trouxeram significativas contribuições para a implementação desta Política no Brasil, que tem como objetivo promover a atenção para o tema e para a importância da água, principalmente, na saúde.

Os procedimentos de controle e de vigilância da qualidade da água para consumo humano são regidos pela portaria 2914 de 12 de Dezembro de 2011, a qual estabelece, também, a quantidade de substâncias químicas que causam sérios riscos a saúde. Na Tabela 1 é possível observar algumas destas substâncias e seus valores máximos permissíveis para água destinada ao consumo humano.

Tabela 1 - Padrão de potabilidade para substâncias químicas que representam risco à saúde.

PARÂMETRO	UNIDADE	VMP(1)
	INORGÂNICAS	
Antimônio	mg/L	0,005
Arsênio	mg/L	0,01
Bário	mg/L	0,7
Cádmio	mg/L	0,005
Cianeto	mg/L	0,07
Chumbo	mg/L	0,01
Cobre	mg/L	2
Cromo	mg/L	0,05
Fluoreto(2)	mg/L	1,5
Mercúrio	mg/L	0,001
Nitrato (como N)	mg/L	10
Nitrito (como N)	mg/L	1
Selênio	mg/L	0,01
	ORGÂNICAS	
Acrilamida	µg/L	0,5
Benzeno	µg/L	5
Benzo[a]pireno	µg/L	0,7
Cloreto de Vinila	µg/L	5

1,2 Dicloroetano	μg/L	10
1,1 Dicloroeteno	μg/L	30
Diclorometano	μg/L	20
Estireno	μg/L	20
Tetracloreto de Carbono	μg/L	2
Tetracloroeteno	μg/L	40
Triclorobenzenos	μg/L	20
Tricloroeteno	μg/L	70
DESINFETANTES E PRODUTOS SECUNDÁRIOS DA DESINFECÇÃO		
Bromato	mg/L	0,025
Clorito	mg/L	0,2
Cloro livre	mg/L	5
Monocloramina	mg/L	3
2,4,6 Triclorofenol	mg/L	0,2
Trihalometanos Total	mg/L	0,1

Fonte: Portaria 2**914/2011 do Ministério da Saúde**

O reuso de água não potável é regido pela Resolução Nº 54 de 28 de Novembro de 2005 do Conselho Nacional de Recursos Hídricos (CNRH), a qual estabelece modalidades, diretrizes e critérios gerais que regulamentem e estimulem a prática de reuso direto não potável de água em todo o território nacional.

O descarte de efluentes deve obedecer às legislações específicas. No Brasil, este descarte deve seguir a resolução CONAMA 357/05 e 430/11, e, especificamente, os efluentes derivados das industrias petrolíferas devem obedecer a Resolução do CONAMA 393/08, que complementa a resolução CONAMA 357/05. Estas resoluções possuem como principais parâmetros analisados o Teor de Óleos e Graxas (TOG), Carbono Orgânico Total (COT), Demanda Química de Oxigênio (DQO), Sólidos em Suspenção Total, entre outros, os quais estão diretamente relacionados com a quantidade de poluentes que serão descartados em ambientes aquáticos, ocasionando a mortandade das espécies, bem como a proliferação de doenças, por se tratar de compostos carcinogênicos.

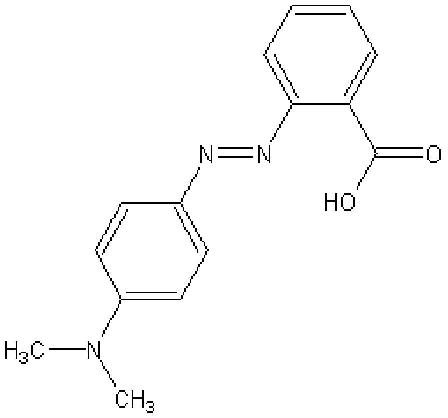
3.4 CORANTES TÊXTEIS

A origem dos corantes têxteis é incerta, mas existem indícios de seu uso desde os primórdios da civilização. Sua presença foi observada em amostras de tecidos de tumbas egípcias datadas de 2500 a. C. Até o século 19, só existiam pigmentos naturais cujas fórmulas eram guardadas secretamente. A grande revolução na história ocorreu quando o químico inglês Willian H. Pequim descobriu, em 1856, o primeiro corante sintético. A partir daí, muitos corantes orgânicos começaram a ser sintetizados em grande escala. Cerca de 10.000 são produzidos em escala industrial. Estima-se que atualmente 2.000 tipos de corantes estão disponíveis para a indústria têxtil. Essa diversidade pode ser justificada pelo fato de que cada tipo de fibra a ser colorida requer corantes com características próprias e bem definidas.

Existem vários tipos de corantes sintéticos, dentre eles estão, os corantes azos, dispersos, reativos, ácidos, pré-metalizados, etc., sendo classificado de acordo com sua estrutura química ou pelo método que se fixa à fibra.

Corantes azos (Figura 2) formam o maior grupo entre os corantes sintéticos (60-70%). Seu sistema de cromóforos consiste em grupos azo (-N = N-) em associação com sistemas aromáticos e auxocromos (-OH,-SO_3, etc.). Estima-se que cerca de 50.000 toneladas de corantes são descarregadas a partir de indústrias de tingimento e coloração a cada ano. Atualmente, a indústria têxtil de tingimento está sob considerável pressão para reduzir a cor de efluentes gerados (FERNANDES et. al., 2004).

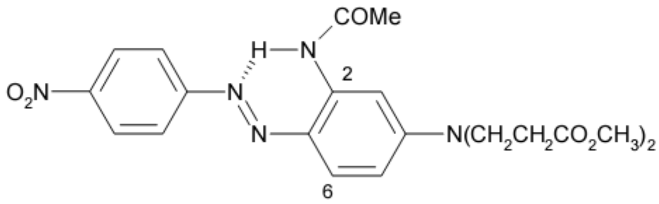
Figura 2- Estrutura química típica do corante azo Vermelho de Metila



Fonte (autor, 2014)

Os corantes dispersos (Figura 3) são compostos aromáticos não iônicos, na maioria contêm grupos azo como cromóforo, são pouco solúveis em água e altamente utilizados na tintura de fibras sintéticas, tais como poliéster, triacetato de celulose e poliamidas. A adição de agentes dispersantes durante a etapa de tintura sob alta temperatura (80 ºC) é uma das responsáveis pelo transporte do corante à fibra hidrofóbica, cuja etapa tem mudado a concepção desses corantes como prováveis poluentes de águas superficiais. Esses corantes formam sistemas de micelas estáveis nestas soluções, que são facilmente transportadas em meio aquoso, contribuindo para sua presença em águas superficiais, para sua acumulação em sedimentos, solos e conseqüente contaminação da água potável oriunda de estações de tratamento de água. A preocupação com rejeitos contendo essa classe de corantes tem crescido nos anos mais recentes, devido a suas comprovadas propriedades mutagênicas (GUARATINI e ZANONI, 2000).

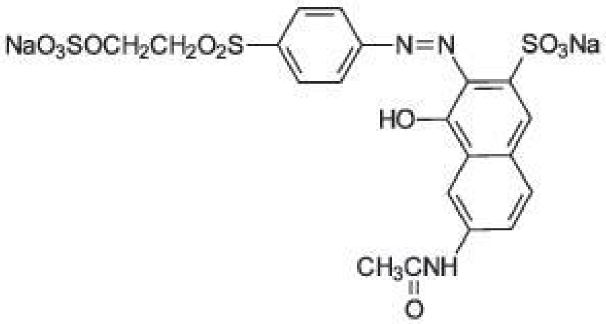
Figura 3- Estrutura química típica do corante disperso Vermelho 278



Fonte (autor, 2014)

Os corantes reativos contêm um grupo eletrofílico (reativo) capaz de formar ligação covalente com grupos hidroxila das fibras celulósicas, com grupos amino, hidroxila e tióis das fibras protéicas e também com grupos amino das poliamidas. Existem numerosos tipos de corantes reativos, porém os principais contêm a função azo e antraquinona como grupos cromóforos e os grupos clorotriazinila e sulfato-etil-sulfonila como grupos reativos. Neste tipo de corante, a reação química se processa diretamente através da substituição do grupo nucleofílico pelo grupo hidroxila da celulose (Figura 4). Como exemplo podemos citar o tingimento usando compostos contendo sulfato-etil-sulfona, cuja adição do corante à fibra requer apenas a prévia eliminação do grupo sulfato em meio alcalino gerando o composto vinilsulfona (GUARATINI e ZANONI, 2000).

Figura 4- Estrutura química típica do corante reativo Alaranjado de Remazol 3R



Fonte (autor, 2014)

3.5 ÁGUA PRODUZIDA

A água produzida é a água aprisionada nas formações subterrâneas que é trazida à superfície juntamente com petróleo e gás durante as atividades de produção desses fluidos. É considerada um dos maiores fluxos de resíduos na indústria do petróleo, óleo e gás. As operações de perfuração e extração que visam maximizar a produção de óleo pode ser contrabalanceada pela grande produção de água contaminada com poluentes, como metais pesados (Cd, Cr, Cu, Pb, Hg, Ag, Ni, Zn), compostos orgânicos dissolvidos e / sólidos em suspensão. Benzeno, tolueno, xileno, fenol, compostos aromáticos halogenados, clorofórmio e tricloroetileno são os principais poluentes orgânicos presentes na água produzida (AHMADUNA et al. 2009, USEPA).

O impacto ambiental devido à eliminação da água produzida é determinado pela toxicidade e a quantidade dos seus constituintes. Alguns deles permanecem dissolvidos, enquanto outros tendem a desaparecer devido a decomposição, a evaporação, a transformação em um outro composto menos tóxico, a deposição no fundo do mar, etc. O efeito mais prejudicial está relacionado com os compostos que permanecem solúveis em água, como eles interagem diretamente com a vida (AHMADUNA et al. 2009). Seu tratamento tem sido um desafio em função de sua complexidade e da quantidade do resíduo gerado. Dessa forma, devido às restrições impostas pela legislação ambiental vigente, faz-se necessário um tratamento com o objetivo de reduzir o teor dos contaminantes a níveis permitidos, antes de ser descartada no meio ambiente.

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CAPÍTULO 4

4 ELECTROCHEMICAL DECOLOURIZATION PROCESS OF TEXTILE DYE IN THE PRESENCE OF NaCl AT BORON DOPED DIAMOND ELECTRODE

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4.1 ABSTRACT

Aim of this work is to discuss the electrochemical colour removal process of a textile dye (Yellow Novacron (YN)) dissolved in synthetic wastewaters, analyzing the influence of NaCl. Experiments were carried out at boron-doped diamond (BDD) electrodes, in alkaline media in presence and absence of NaCl in solution. BDD electrodes have a poor superficial adsorptivity so their great stability toward oxidation allows the reaction to take place with reactants and intermediates in a non-adsorbed state. The process is significantly accelerated by the presence of a halogen salt in solution; interestingly, the mediated process does not depend on applied current density; but it depends on NaCl concentration. Based on the results, Cl^- was selected as a suitable mediator during YN oxidation at BDD; showing higher improvements in the colour removal rate. The parameters of removal efficiency and energy consumption showed the feasibility to use this process as an alternative for removing colour from textile effluents.

Keywords: Indirect oxidation. Mediators. Dye. Active chlorine. Boron doped diamond.

4.2 INTRODUCTION

Electrochemical treatment is one of the methods used for the removal of organic and inorganic impurities from water and wastewater. Consequently, several research groups are attempting to use electrochemical methods as an effective method for detoxification of wastewaters containing biorefractory pollutants and drinking water disinfection (COMNINELLIS; PULGARIN, 1993, COMNINELLIS, 1994; RAJESHWAR et al. 1994; STEWARD, 1998; RODERS et al. 1999; JÜTTNER et al. 2000; GALLA et al. 2000; NELSON, 2002; MARTINEZ-HUITLE et al. 2005; PANIZZA; CERISOLA, 2009; BRILLAS et al. 2009)

Electrochemical oxidation can be subdivided in two main categories: "Direct” and "Indirect" oxidation. Whereas the electron transfer takes place between electrodes and decomposable species in direct electrochemical oxidation; indirect oxidation mainly uses electrochemically oxidized species as mediators for the destruction of organic compounds (DHOOGE et al. 1982; FARMER et al. 1992; CHIANG et al., 1995; BRINGMANN et al. 1995; CHUNG et al. 2000; VARELA et al. 2001).

For indirect electrooxidation, destruction of organic compounds by anodically generated chlorine and hypochlorite is well known. A particularly interesting case is that of active-chlorine mediation, which has been reported in several papers (MIELUCH et al. 1975; BOSCOLETTO et al. 1994; COMNINELLIS; NERINI, 1995; BONFATTI et al. 2000a; BONFATTI et al. 2000b; PANIZZA; CERISOLA, 2003; NIKOLAEVSKY et al. 1998; DJEIRANISHVILI et al. 1998). The interest for this path to electrochemical oxidation is due to two reasons: (i) the ubiquitous presence of chloride ions in a number of effluents and also of natural waters, which makes the involvement of active chlorine in anodic processes in these media, inevitable; (ii) the chemistry and electrochemistry of chlorine higher oxidation states at pH not far from neutrality, makes its use as oxidant mediator of some practical interest (MARTINEZ-HUITLE et al. 2005).

Bonfatti et al. reported that at different pH values in the alkaline region, a complex substrate like glucose can be incinerated within a wide anodic current density range (BONFATTI et al. 2000a). These experimental data were accounted by the assumption that the main part of the oxidation process is a surface reaction, based on adsorbed oxy-chloro radicals. The role played by the anodic shift of the oxygen evolution, caused by Cl^- ions in solution, has been considered. In fact, this aspect has been discussed in a few papers

(HICKLING; WILSON, 1949; PASEKA et al. 1973; MARTINEZ-HUITLE et al. 2005), mainly in relation with the electrosynthesis of strong oxidants.

It is clear from the literature, that most of the works attempted to degrade complex substrates at high concentration using anodic materials and then conducted experiments at alkaline or acidic conditions. As a result, if the electrochemical technology has to become practically applied, low concentration halogen salts must be considered to increase the elimination rate.

As an innovative alternative, the electrochemical processes for treating wastewater containing dyes have been recently proposed (MARTINEZ-HUITLE et al. 2004; MARTINEZ-HUITLE; FERRO, 2006; MARTINEZ-HUITLE; BRILLAS, 2009). This technique has been used for decolourization and degrading dyes from aqueous solutions by several scientific groups, as recently reviewed in detail by Martínez-Huitle and Brillas, 2009; in particular, using diamond anodes. However, few attempts to degrade or to eliminate dyes from aqueous solutions by electrogenerated active chlorine species using BDD anodes have been published. Therefore, as a further development of the research carried out in the previous studies (MARTINEZ-HUITLE et al. 2005; BONFATTI el al. 2000a; BONFATTI et al. 2000b), in the present work it has been considered opportune to extend the research to the anodic oxidation of dyes, in the presence of NaCl on the BDD anode.

In this frame, we propose the use of electrochemical technology as alternative to remove synthetic dyes from water in order to eliminate their strong colour and their ecotoxicological consequences on aquatic environment. Then, the principal objective of this study is to investigate the indirect oxidation process using BDD anode on the colour removal of a synthetic solution containing YN (dye widely used in the Northeast Brazilian Textile industries, affecting aquatic ecosystems due to their colouration persistence, and also due to their carcinogenic and mutagenic properties (INSTRUÇÃO NORMATIVA Nº 1 of 03/11/2004), in order to understand the influence of the active chlorine which gives high current efficiency and needs low energy requirements.

4.3 MATERIALS AND METHODS

4.3.1 Materials

Ultrapure water was obtained by Simplicity water purification system. Chemicals were of the highest quality commercially available, and were used without further purification.

Na_2SO_4, NaCl and NaOH were purchased from Fluka. YN dye was purchased by Brazilian Textile Industry and no data about structure or chemical formula were obtained because it is a dye protected by patent restriction. Dyestuff solution was prepared dissolving textile dye in distilled wastewater containing 0.5 M Na_2SO_4 + 0.25 M NaOH. The textile dyeing industrial effluent generally contains with 100-150 mg L^{-1} of dissolved salts and pH ranging from 8 to 10. Therefore, synthetic dye solutions contained 200 mg L^{-1} of YN dye, as initial concentration, were adjusted at pH 10 using NaOH. On the other hand, Na_2SO4 was also used in order to imitate the salt content in real textile effluent. Different NaCl concentrations were also tested in order to understand the influence of strong oxidant species formed from this salts, during colour removal.

4.3.2 Procedures and Equipments

As a first step, we have characterized typical BDD surface topologies by atomic force microscopy (AFM); a Nanoscope IIIa Scanning Probe microscope controller connected with a nanoscope multimode SPM, both from Digital Instruments were adopted for AFM analysis.

Cyclic voltammetries (CV) were performed at room temperature in solutions stirred by bubbling nitrogen and at a scan rate of 100 mV s^{-1}; the chosen range potential was cycled using a step potential of 2 mV and repeating the measurement at least five times or until these were reproducible signals; in every case, the last cycle was recorded. The nominal BDD area of the electrode was 0.78 cm^2 (a disk with a diameter of 1 cm) and a small Pt wire was used as cathode, with the same real surface area. Potential values were referred to a saturated calomel electrode (SCE).

Bulk electrolyses were carried out in a single-body, thermostated Pyrex glass cell of 400 mL; the anode was a BDD plate, with a geometrical area of 15 cm^2, and the test solution volume was 350 mL. A Ti plate was used as cathode when the BDD anode was investigated. Thin, highly boron-doped diamond electrodes (BDD) films were synthesized by Adamant Technologies (Neuchatel, Switzerland). The diamond films have a thickness of 1 µm (±10%) and a resistivity of 15 mΩ·cm (±30%), consistent with a boron concentration between 3500 and 5000 ppm. Experiments were performed at room temperature (~25 °C), investigating the role of applied current density (j_{appl}) and mediator; the j_{appl} range was established at 10, 30 and 50 mA cm^{-2}. Solutions were vigorously stirred, using a magnetic stirrer. The stirring rate was kept almost constant (350±10 rpm). In this condition, the estimate mass transfer coefficient in the cell, determined using the ferri/ferrocyanide couple, was 2×10^{-5} m s^{-1}. The current density for the electrolysis was kept at the desired level using a VERSTAT3 potentiostat-galvanostat (Princeton Applied Research).

4.3.3 Analytical Methods

Experimentally, decolourisation efficiency or percentage of colour removal is determined by the expression [10]:

$$Colour\ removal\ (\%) = \left(\frac{\left[ABS_0^M - ABS_t^M \right]}{ABS_0^M} \right) \times 100 \tag{1}$$

where ABS_0^M and ABS_t^M are the average absorbances before electrolysis and after an electrolysis time *t*, respectively, at the maximum visible wavelength (λ_{max} = 410 nm YN) of the synthetic wastewater. Colour removal was monitored by measuring absorbance decrease; using a UV 1800 Shimadzu spectrophotometer. The energy consumption per volume of treated effluent was estimated and expressed in kWh m^{-3}. The average cell voltage, during the electrolysis, is taken for calculating the energy consumption, as follows (MARTINEZ-HUITLE; BRILLAS, 2009):

$$Energy\ consumption = \left(\frac{V \times A \times t}{V_s} \right) \tag{2}$$

where *t* is the time of electrolysis (h); *V* and *A* are the average cell voltage and the electrolysis current, respectively; and *Vs* is the sample volume (m^3).

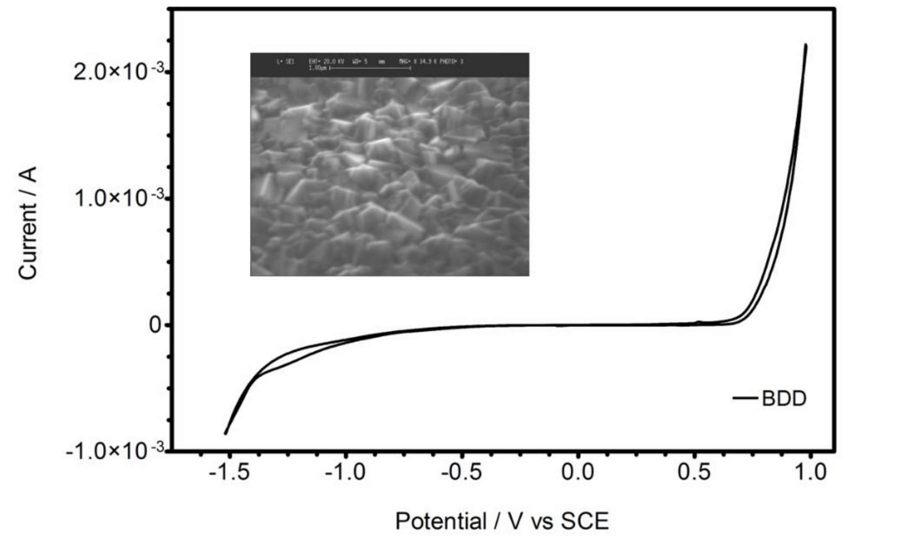
Final samples were analyzed by gas chromatography (GC), using a serial detector CG-PID/FID, column OV624 (gas flow: 3.0 ml/min), initial temperature of 40.15 ºC/1.0 min, after 10 ºC/min to 150 ºC, with a total analysis time of 32 min. Split-less injector temperature was of 250 ºC, lamp temperature (PID) was of 280 ºC and detector FID was of 300 ºC. Before the GC/MS analysis, the samples were treated by solid phase micro-extraction (SPME) with an 85 µm film of poly-(dimethylsiloxane) fiber. Once the extraction was completed (10 min), the fiber was withdrawn back inside the fiber holder, removed from the reaction sample, and then injected by a 1:25 split method. The temperature of transfer line was 240°C, the ions trap was 170°C and desorption time in the splitless mode at 260°C was 3 min.

4.4 RESULTS AND DISCUSSION

4.4.1 Morphological and Electrochemical Characterization of the Diamond Films

Inset in Figure 1 shows AFM image of polycrystalline films deposited on *p*-Si. This figure shows that the boron doped diamond layer is continuous and consists of microcrystals randomly arranged and it is similar to those already reported in the literature (GOETING et al. 1998; FERREIRA et al. 2002; FERRO, 2002). Figure 1 shows the cyclic voltammograms for alkaline media on diamond electrodes. The cyclic voltammetric curves for the diamond electrode obtained after purging with nitrogen gas is featureless, and the background current is very low (less than 1<µA). In the alkaline media the curve exhibited a slight oxidation peak at ca. +0.9V vs. SCE. Thus, it can be assumed that this peak is due to the water decomposition. These results are in agreement with Yano et al., 1998.

Figure 1. CV curves for the BDD electrode, in alkaline media (0.25 mol dm^{-3} NaOH + 0.5 mol dm^{-3} Na_2SO_4). BDD area of the electrode was 0.78 cm^2. Scan rate: 100 mV s^{-1}. Inset: BDD images carried out by the AFM technique.



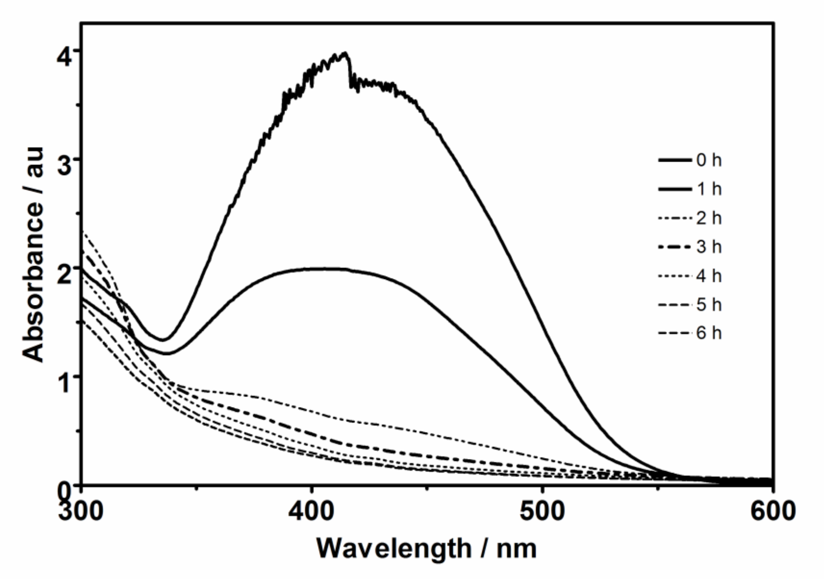
4.4.2 Direct Anodic Oxidation

4.4.2.1 Colour Removal

The visible spectrum of YN is reported in the Figures 2, it shows maximum absorption peak in the range of visible light which are in accordance with the colour of YN solutions.

Thus, the measurement of the colour removal was obtained using a UV/vis spectrophotometer at 410 nm for YN. These figures show the decrease with time of the absorbance band at 410 nm during galvanostatic electrolysis of YN synthetic wastewaters containing 190 mg L^{-1} by applying 30 mA cm^{-2} of current density under alkaline conditions. As can be observed, absorbance was satisfactorily reduced during the treatment. The intensity of the visible band decreases continuously until its disappearance after about 180 min of electrolysis leading to complete solution decolourization. Furthermore, the decay of the absorbance is indicating that during the first stages of the treatment, there are mechanisms that involve the oxidation of the dye to other more simple organics. The oxidation of these complex molecules can lead to the formation of many intermediates by elimination of chromophore groups prior to the formation of aliphatic carboxylic acids and carbon dioxide, as observed by other authors (SANROMAN et al. 2004; LOPEZ-GRIMAU; GUTIERREZ, 2006; PANIZZA; CERISOLA; 2007).

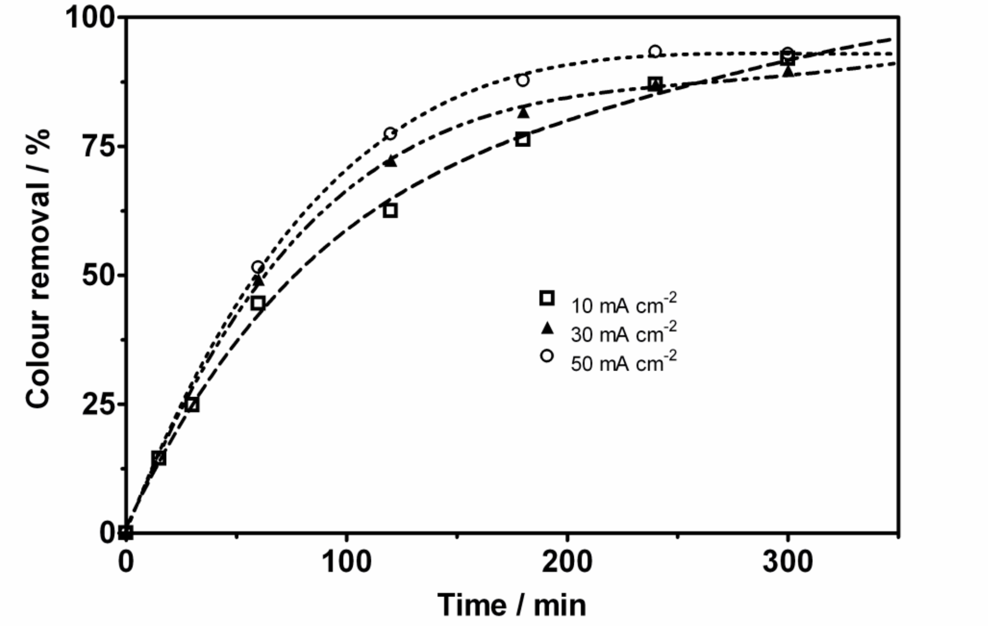
Figure 2. Colour removals as a function of time during direct anodic oxidation of YN at the BDD electrode under alkaline (0.25 M NaOH + 0.5 M Na_2SO_4) conditions. j_{appl} = 30 mA cm^{-2}.



4.4.2.2 Influence of Applied Current Density

Figure 3 presents the influence of the applied current density on the decay of colour during electrochemical oxidation of synthetic waste of YN containing 190 mg L^{-1}. As can be observed, the nearly complete removal of colour, in all cases, was achieved; independently of the applied current density. Although the elimination rate increase when the applied current density values were modestly increased, as can be observed in the Figures 3. It indicates the complete dye attack by means of its reaction with electrogenerated $^{\bullet}OH$ radicals on BDD surface (MARSELLI et al. 2003; BENSALAH et al. 2009). On the contrary, it seems that the decolourization time depends mainly on the applied current density. In fact, colour removal times decrease when an increase in the applied current density was attained (Figures 3). This behaviour suggests that the oxidation of dye could be carried out by both direct electro-oxidation and mediated oxidation (hydroxyl radicals and other strong oxidants electro-generated from the oxidation of the supporting electrolyte). It appears that the oxidation by the electro-generated reagents from the anodic oxidation of supporting electrolyte plays important role in the efficiency of the electrochemical process.

Figure 3. Influence of applied current density on the evolution with time of the percentage colour removal during BDD-anodic oxidation of YN. Operating conditions: $[YN]_0$=200 mg L^{-1}, Electrolyte: 0.25 M NaOH + 0.5 M Na_2SO_4, Temperature T=25 °C, agitation rate: 350 rpm.



It is important to remark that, Comninellis explained the different behaviour of electrodes in electrochemical oxidation process, considering two limiting cases: the so-called ‘‘active’’ and ‘‘non-active’’ anodes (COMNINELLIS, 1994). Typical examples are Pt, IrO_2 and RuO_2 for the former and PbO_2, SnO_2 and BDD for the latter. The proposed model assumes that the initial reaction in both kind of anodes (generically denoted as M) corresponds to the oxidation of water molecules leading to the formation of physisorbed hydroxyl radical ($M(^{\bullet}OH)$). Both, electrochemical and chemical reactivity of heterogeneous $M(^{\bullet}OH)$ are dependent on the nature of the electrode material. The surface of active anodes interacts strongly with $^{\bullet}OH$ and then, a so-called higher oxide or superoxide (MO) may be formed. This may occur when higher oxidation states are available for a metal oxide anode, above the standard potential for oxygen evolution (E^{o} = 1.23 V vs. SHE). The redox couple MO/M acts as a mediator in the oxidation of organics, which competes with the side reaction of oxygen evolution via chemical decomposition of the higher oxide species. In contrast, the surface of a non-active anode interacts so weakly with $^{\bullet}OH$ that allows the direct reaction of organics. Then, at BDD electrodes (our case), the $^{\bullet}OH$ radicals formed by water electrolysis (equation 3) can be either electrochemically oxidized to dioxygen (equation 4) or contribute to the complete oxidation of the organic compounds, in this case, dyes (equation 5) (GOETING et al. 1998. FERRO, 2002):

$$H_2O \rightarrow {}^{\bullet}OH + H^+ + e \tag{3}$$

$$^{\bullet}OH \rightarrow \frac{1}{2}O_2 + H^+ + e \tag{4}$$

$$\text{dyes} \xrightarrow{^{\bullet}OH} CO_2 + H_2O \tag{5}$$

It is important to consider that, other oxidants can be produced at the diamond surface ($H_2S_2O_8$, O_3) (CAÑIZARES et al., 2006) and participate in the oxidation of the dye, in the proximity of the electrode surface and/or in the bulk of the electrolyte. Peroxodisulphates have been already demonstrated to be formed in solutions containing sulphates, especially under lower pH conditions (from 1 to 3) and high temperatures (60°C), during electrolysis with BDD electrodes (equation 6). However, in minor amount these can be produced underalkaline conditions under 25°C (PANIZZA et al. 2007; BENSALAH et al. 2009).

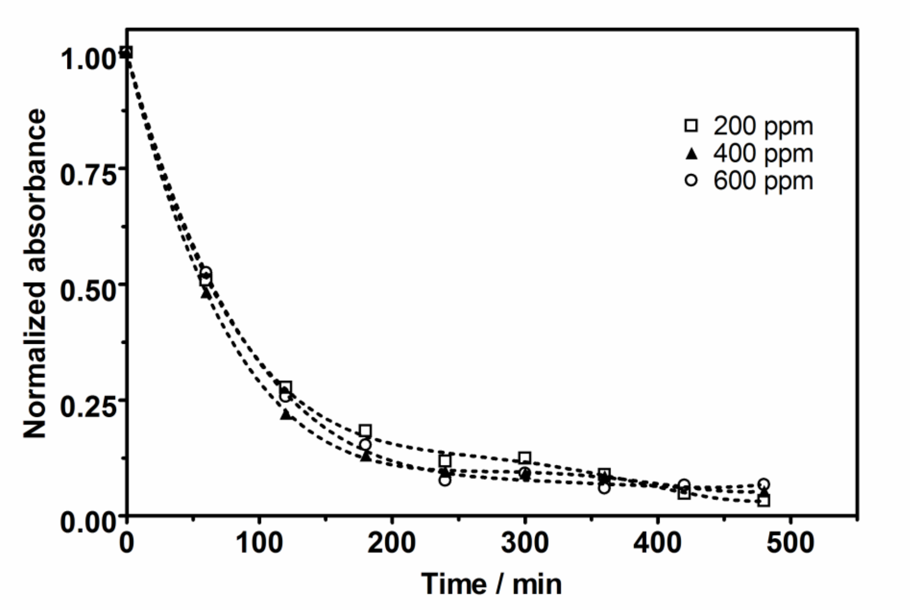
$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \tag{6}$$

These reagents are known to be very powerful oxidants and can oxidize organic matter leading to a slight increase in colour removal rates (PANIZZA et al. 2007). Therefore, the elimination colour rate can be rather favoured under experimental conditions chosen in this work (Figure 3). This outcome is in agreement with the data reported by other authors during the anodic oxidation of dyes using BDD electrodes (CAÑIZARES et al. 2006; PANIZZA; CERISOLA, 2007; PANIZZA et al. 2007; BENSALAH et al. 2009; MARTINEZ-HUITLE; BRILLAS, 2009).

4.4.2.3 Influence of Dye Concentration

Figure 4 shows the influence of initial dye concentration (in mg L^{-1}) as a function of the time during galvanostatic electrolyses of YN synthetic wastewaters under 30 mA cm^{-2} of applied current density. As can be observed, the trends of normalized absorbance (ABS_t/ABS_0) are moderately overlapped and same electrolysis-times are required to achieve complete colour abatement. This indicates that the decolourization rate and process efficiency not depend on organic matter concentration. This outcome is in agreement with the data reported by Bensalah et al., 2009. This is usually explained in terms of mass transfer mechanisms, assuming that both direct oxidation and mediated oxidation on the BDD surface by hydroxyl radicals and other electrogenerated oxidants from the supporting electrolyte (peroxodisulphates) contribute in the total electrochemical process (PANIZZA; CERISOLA, 2007; BENSALAH et al. 2009; MARTINEZ-HUITLE; BRILLAS, 2009).

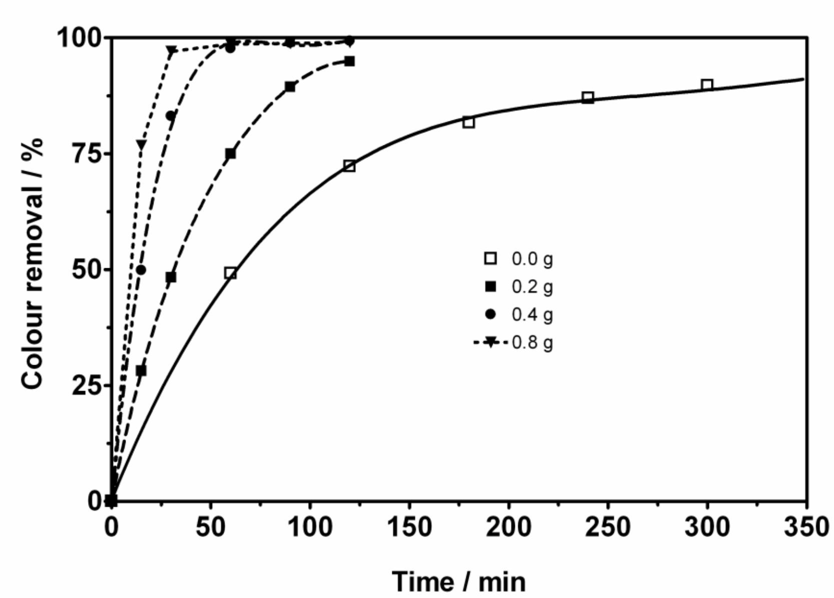
Figure 4. Influence of initial YN concentration on the evolution with time of normalized absorbance during BDD-anodic oxidation. Operating conditions: Electrolyte: 0.25 M NaOH + 0.5 M Na_2SO_4, Current density *j*=30 mA cm^{-2}, Temperature T=25 °C, agitation rate: 350 rpm.



4.4.2.4 Indirect Anodic Oxidation

In this case, the kinetics of mediated YN decolourization removal was studied at by applying 30 mA cm^{-2} of current density, in the presence of 0.2, 0.4 and 0.8 g NaCl in 350 mL of solution. As shown in Fig. 5, the electrochemical decolourization of YN on BDD anode was accelerated significantly by the presence of the halide salt in solution; interestingly, the mediated process did not depend on applied current density, but it depends on NaCl concentration in solution. The role of the NaCl, during the oxidation of other dyes, has been discussed by other authors (MARTINEZ-HUITLE; FERRO, 2006; MARTINEZ-HUITLE; BRILLAS, 2009) employing different electrocatalytic materials; such as Pt, IrO_2, RuO_2 and so on (active anodes (COMNINELLIS, 1994)). Nevertheless, no attempts have been published using BDD anodes for removing dyes in presence of NaCl. Therefore it is important to understand the role of the active chlorine formed on BDD surface (considered a non active electrode) during decolourisation process.

Figure 5. Effects of NaCl at different concentration values during colour removal of YN on BDD anode as a function of time. Operating conditions: Electrolyte: 0.25 M NaOH + 0.5 M Na_2SO_4, Current density *j*=30 mA cm^{-2}, Temperature T=25 °C, agitation rate: 350 rpm.



It is well-known that electrolysis of chloride aqueous solutions in an undivided cell involves the direct oxidation of chloride ion at the anode to yield soluble chlorine (MARTINEZ-HUITLE; BRILLAS, 2008; MARTINEZ-HUITLE; BRILLAS, 2009):

$$2\ Cl^- \rightarrow Cl_{2(aq)} + 2\ e^- \qquad (7)$$

and the reduction of water at the cathode (it is pH dependent) giving hydroxide ion and hydrogen gas from reaction. If the local concentration of dissolved chlorine exceeds its solubility, then supersaturation drives the formation of bubbles of chlorine gas. As electrogenerated chlorine diffuses away from the anode, it can react with chloride ion to form trichloride ion:

$$Cl_{2(aq)} + Cl^{-} \rightarrow Cl_3^{-} \qquad (8)$$

or is rapidly hydrolyzed to be disproportionated to hypochlorous acid and chloride ion:

$$Cl_{2(aq)} + 2H_2O + HClO \rightarrow 3Cl^{-} + 2H^{+} + 3OH^{-} \qquad (9)$$

In the bulk solution this acid is in equilibrium with hypochlorite ion ($pK_a = 7.55$ as follows:

$$HClO \rightarrow ClO^{-} + H^{+} \qquad (10)$$

Cl_3^{-} is formed in very low concentration up to pH ca. 4, while the predominant species is $Cl_{2(aq)}$ until pH near 3, HClO in the pH range 3-8 and ClO^{-} for pH > 8. The mediated oxidation of dyes with these species is then expected to be faster in acidic than in alkaline media because of the higher standard potential of $Cl_{2(aq)}$ (E^{o} = 1.36 V vs. SHE) and HClO (E^{o} = 1.49 V vs. SHE) than ClO^{-} (E^{o} = 0.89 V vs. SHE). However, tthese rates of electrode reactions are a function of the electrocatalytic activity of the anode, chloride concentration and current density (GALLA et al. 1998; NELSON, 2002; MARTINEZ-HUITLE et al. 2005; MARTINEZ-HUITLE; BRILLAS, 2008; MARTINEZ-HUITLE; BRILLAS, 2009).

Many results have been reported in the literature using active electrodes; while few comparative investigations were performed employing BDD anodes. Förster et al., 2002 investigated about hypochlorite formation on platinum and diamond electrodes; the hypochlorite formation yield on diamond film electrodes was found higher than on Pt electrodes. In this way, it is also important that the equilibrium between the different forms of active chlorine in the electrolysis solution depends on the pH, temperature and concentration (FERRO et al. 2000; FÖRSTER et al. 2002). As reported by them, the pH range where a high concentration of hypochlorite was observed range from 8 to 11.5. Therefore, during the YN oxidation at alkaline media (pH≈8-10) the production and participation of hypochlorite can be considered. However, the evidence obtained by Ferro *et al.* clearly shows that diamond electrodes are more efficient in the production of “active chlorine” (chlorine, hypochlorous acid and hypochlorite) at lower pH values (FERRO et al. 2000). For this reason, in the alkaline media case, the “active chlorine production” can be considered in competition with an important parasitic reaction such as oxygen evolution, where it limits the electrogeneration of strong oxidants at BDD surface. Therefore, YN oxidation in presence of NaCl is faster in the beginning of the process (high active chlorine species production) and limited in the final stages by oxygen evolution reaction.

In a previous paper (MARTINEZ-HUITLE et al. 2008), the electrochemical incineration of oxalic acid (OA) was studied, in acidic and alkaline media using BDD anode materials in order to investigate the role of halides. OA anodic oxidation experiments were carried out in the presence of 5 g dm^{-3} of halides in the solution and performed under galvanostatic conditions at 300 and 600 A m^{-2}. The electrochemical oxidation of OA at the BDD electrode is significantly accelerated by the presence of a halogen salt in solution; interestingly, the mediated process does not depend on applied current density. According to measurements reported previously (MARTINEZ-HUITLE et al. 2005) and results obtained by other authors (HICKLING et al. 1949; BONFATTI et al. 2000a; BONFATTI et al. 2000b), the electrochemical mediation seems to be the consequence of some specific roles played by the considered halogen salt. In the case of Cl^-, its effect can be a hybrid process, with the possible electro-generation of strong oxidants (BONFATTI et al. 2000a), and hydroxyl radicals by water decomposition. And, as previously mentioned, these observations support our assertions reported in this paper (Figure 5). Based on Environmental Protection Agency (EPA) standard method 8021 (METHOD EPA 8021, 1996), GC analysis were performed with the final samples after electrochemical treatment and the results did not reveal traces of organochlorinated compounds, formed during the electrochemical oxidation in presence of NaCl in solution. This result indicates that the mediated electrochemical oxidation can be considered a suitable alternative to accelerate the treatment process of the industrial effluents.

It is worth noting though that large amounts of NaCl could lead to an increase in wastewater toxicity due to the formation of organochlorinated substances. Moreover, as already has been discussed the mechanisms taking place in the presence of chlorine are highly pH dependent. Therefore, the addition of NaCl in electrochemical wastewater treatment should be carefully considered.

4.4.2.5 Energy Consumption and Cost Estimation

Table 1 presents the energy consumption required to remove 95% of the dye colour at different conditions. As can be observed, during the electrolyses of synthetic wastewaters containing 200 mg L^{-1} of dye (YN); the energy consumption seems to be proportional to the applied current density. For example, it increases from 5.22 to 44.65 kWh per volume of treated effluent (m^3) when the current density passes from 10 to 50 mA cm^{-2}. Table 1 also compares the energy consumption (kWh m^{-3} of colour removed) during anodic oxidation at different NaCl concentrations in solution. Finally, taking into consideration an electrical energy cost of about R$ 0.3 (R$ = Brazilian currency (reais); Brazilian price taxes excluded) per kW h (Agência Nacional de Energia Elétrica, Brazil), the process expenditure was estimated and reported in Table 1 in order to show the viability of this process as an alternative decolourization treatment of textile effluents (equation 11).

$$\text{Cost (R\$ m}^{-3}\text{)} = [\text{Energy consumption (kWh m}^{-3}\text{)} \times 0.3 \text{ (R\$/kWh)}] \qquad (11)$$

Also, the price obtained under different experimental conditions was converted to US Dollars.

Table 1. Parameters of efficiency for the electrochemical decolourization process using BDD anode. Energy consumption (kWh/m^3 of effluent treated), calculated for a 95% elimination of the colour in the solution.

		Current density[a]	
	10 mA cm^{-2}	30 mA cm^{-2}	50 mA cm^{-2}
Energy consumption[c]	5.22	22.62	44.65
Cost[d]	0.87 (1.56)	3.81 (6.78)	7.54 (13.4)
		Concentration of NaCl in solution[b]	
	0.2 g	0.4 g	0.8 g
Energy consumption[c]	7.37	3.17	1.80
Cost[d]	1.24 (2.21)	0.53 (0.95)	0.31 (0.54)

[a] *Temp=25°C, agitation rate = 350 rpm, [NaCl] = 0,0 g/L.*

[b] *Temp=25°C, agitation rate = 350 rpm, current density = 30 mA cm^{-2}, Volume = 350 mL.*

[c] *kW h m^{-3}* [d] *US Dollars (Brazilian currency)*

4.5 CONCLUSIONS

In this work, the electrochemical oxidation of YN at BDD electrode has been investigated under different experimental conditions. Bulk electrolyses have shown that in the absence of NaCl, only a slow YN decolourization depletion was obtained; and that, decolourization rate depends on current density applied. On contrary, in the presence of NaCl, effluent colour was completely eliminated by mediation of the electrogenerated active chlorine species. It was also found that YN depletion was independent of the applied current density, but the process depends on NaCl concentration in solution. This effect, which is well-documented in the literature (COMNINELLIS; NERINI, 1995; BONFATTI et al. 2000a; PANIZZA; CERISOLA, 2003; MARTINEZ-HUITLE et al. 2005; MARTINEZ-HUITLE; FERRO, 2008), and is pH dependent, is associated with the formation of chlorohydroxyl radicals (METHOD EPA 8021, 1996) or oxyhalo compounds (COMNINELLIS; NERINI, 1995; MARTINEZ-HUITLE et al. 2005; MARTINEZ-HUITLE; FERRO, 2008) that can also oxidize the organic matter. Nevertheless, the specific role of the oxyhalo compounds formed during electrochemical oxidation of dyes should be investigated. For this reason, the next step in our investigations will be determinate a detailed analysis of oxychloro-compounds evolution during the oxidation of dyes at BDD electrode.

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CAPÍTULO 5

5 ELECTROCHEMICAL DEGRADATION OF NOVACRON YELLOW C-RG USING BORON-DOPED DIAMOND AND PLATINUM ANODES: DIRECT AND INDIRECT OXIDATION

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5.1 ABSTRACT

The present study discusses the electrochemical degradation process of a textile dye, Novacron Yellow C-RG (NY), dissolved in synthetic wastewaters, via direct and indirect oxidation. Experiments were conducted using boron-doped diamond (BDD) and platinum supported on Ti (Pt/Ti) electrodes in the absence and presence of NaCl in the solution. The direct process for removing color is relatively similar for both anodes, while the electrochemical degradation is significantly accelerated by the presence of halogen salt in the solution. Interestingly, it does not depend on applied current density, but rather on NaCl concentration. Therefore, the electrochemical processes (direct/indirect) favor specific oxidation pathways depending on electrocatalytic material. Whereas, the Pt/Ti anode favors preferentially color removal by direct and indirect oxidation (100% of color removal) due to the fragmentation of the azo dye group; BDD electrode favors color and organic load removals in both processes (95% and up to 87%, respectively), due to the rupture of dye in different parts of its chemical structure. Parameters of removal efficiency and energy consumption for the electrochemical process were estimated. Finally, an explanation has been attempted for the role of halide, in relation with the oxygen evolution reaction, concomitant with the electrochemical incineration as well as electrocatalytic mechanisms, for each one of the electrodes used.

Keywords: Direct/indirect oxidation. Dye. Boron-doped diamond. Titanium-coated with platinum. Electrocatalytic pathways.

5.2 INTRODUCTION

Textile dyes can be classified according to how they attach to textile fibers (for example, direct, acid, reactive) or by their chemical structure (azo, anthraquinone, indigoide) (FORGACS et al. 2004). The most used, in the textile industry, are azo dyes, where the N=N-group is attached to an aromatic ring, due to their relatively easy application and stability during use. As a result of the use of substantial amount of dyes and water during the washing and drying process, these industries produce large volumes of wastewater, which contains a large number of dyes that are not attached to the fiber surface (FORGACS et al. 2004; MARTINEZ-HUITLE; BRILLAS, 2009).

In this context, efficient treatments must be used for removing organic matter from textile effluents. Biological treatment is the most widely used technique. However, when applied to textile industry waste, biological processes are slow and require large areas of land, in addition to generating soluble biodegradable products and cellular waste (MARTINEZ-HUITLE; BRILLAS, 2009). Furthermore, organic compounds with high molecular weight, present in some types of aqueous industrial effluents, tend to be resistant to biodegradation.

Therefore, the research and development of new environmentally-friendly technologies for treating organic textile industrial wastes are constantly encouraged. Among them, electrochemical technology is considered a “clean process” in that it uses only electrons as reagents, and it is an attractive alternative for treating effluents containing organic compounds through direct or indirect electrochemical oxidation (MARTINEZ-HUITLE; FERRO, 2006; PANIZZA; CERISOLA, 2009).

The electrochemical treatment of industrial wastewater, by direct or indirect approaches, is based on the elimination of pollutants directly on the anode surface or/and production of •OH (MARSELLI et al. 2003; COMINELLIS, 1994) and other oxidants, such as chlorine, (per)bromate, persulfate, ozone, hydrogen peroxide, percarbonate, and others, directly on-site using only water, salt, and energy (SIRÉS et al. 2014). In the case of active chlorine, the interest in this oxidant is based on the ubiquitous presence of chloride ions in a certain number of effluents and natural waters, making possible the involvement of active chlorine during electrochemical treatment; and the chemistry and electrochemistry of higher oxidation states for chlorine close to neutral pH (MARTINEZ-HUITLE; FERRO, 2006).

In this context, relevant results for the degradation of dyes using active clorine have been published (MARTINEZ-HUITLE; BRILLAS, 2009; LÓPEZ-GRIMAU; GUTIÉRREZ, 2006; AQUINO, et al. 2013; AQUINO et al. 2011; SALES SOLANO et al. 2013; AQUINO et al. 2012; BEZERRA ROCHA et al. 2012). For example, López-Grimau and Gutierrez (2006), investigated the electrochemical oxidation of 1 dm^3 of 100 mg dm^{-3} of Reactive Orange 4, using an electrochemical cell with a flow rate of 25 dm^3 h^{-1} and an anode of Pt/Ti with an area of 486 cm^2, demonstrating the effect of the supporting electrolyte (20 g dm^{-3} NaCl or 25 g dm^{-3} Na_2SO_4), pH and current density on color removal and energy consumption. For 40 mA cm^{-2} and pH 9.0, total discoloration was achieved with NaCl after 5 min, while employing Na_2SO_4 as supporting electrolyte, 91% of color removal was achieved under similar experimental conditions. This means that oxidation by $^\bullet OH$ was efficient in Na_2SO_4 at high current density; while this efficiency increases due to the active chlorine species produced when NaCl was used. This implies significant savings in energy consumption for discoloration of the NaCl-rich effluent (12.4 kWh m^{-3}) in comparison with Na_2SO_4 (44.1 kWh m^{-3}). Color removal efficiency for NaCl was independent on pH and current density, as expected when greater concentrations of strong oxidants (mainly ClO^- and $\bullet OH$) were produced.

On the other hand, Aquino and co-workers studied the electrochemical degradation of the Reactive Red 141 azo dye using a one-compartment filter-press flow cell with a boron-doped diamond anode (AQUINO et al. 2013). The effect of current density (10-50 mA cm^{-2}), pH (3-11), NaCl concentration ([NaCl]=0-2.34 g L^{-1}) and temperature (15-55°C) on the system's performance were investigated, obtaining that the charge required for 90% decolorization at pH<4 was dependent on the higher values of [NaCl] (>1.5 g L^{-1}), due to the electrogeneration of active chlorine (mainly as HClO). Higher temperatures (>40°C) led to a decrease in COD, as a consequence of side reactions. Conversely, higher values of TOC removal, which can be reached only with strong oxidants (such as $^\bullet OH$ and $Cl^\bullet$), were efficiently attained at low [NaCl] values (<0.7 g L^{-1}) in acidic solutions that inhibit the formation of ClO_3^- and ClO_4^-.

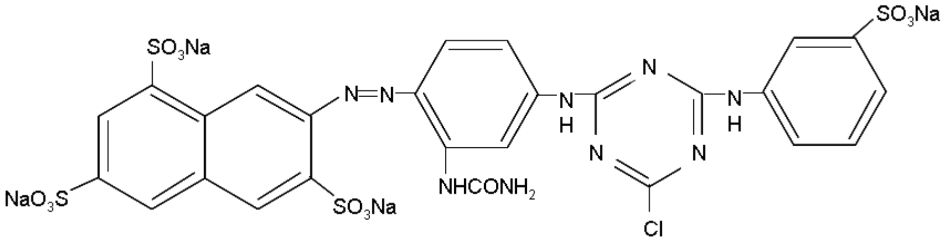
Afterwards, Aquino et al. (2011), also studied the degradation of the real textile effluent in a filter-press reactor using a boron-doped diamond (Nb/BDD) or a Ti-Pt/β-PbO_2 anode, investigating the effect of adding NaCl (1.5 g L^{-1}). These results indicated that the addition of chloride ions significantly increases the decolorization rate and almost total abatement of the effluent COD was attained using Nb/BDD as anode with an energy consumption of about $30 kWhm^{-3}$. However, the recent study by Sales Solano et al. (2013), clearly demonstrated that the effect of active chlorine can favor the formation of the organochloride compounds (chloroform) when chloride is used to improve the color and COD removal. At this point, the action of electrogenerated strong oxidant species should be further studied in order to elucidate the different oxidation mechanisms attained to the Cl-mediated system.

In several reports (LÓPEZ-GRIMAU; GUTIERREZ, 2006, MIELUCH et al. 1975; COMNINELLIS; PULGARIN, 1993; DJEIRANISHVILI et al. 1998; FERRO et al. 1998), the experimental data were accounted for by the assumption that the main part of the incineration process is a surface reaction, based on adsorbed oxychloro-radicals. However, the possibility that some role could be played by the anodic shift of the oxygen evolution as well as the participation of active chlorine species, caused by Cl^- ions in solution, has only been taken into consideration in recent studies (BONFATTI et al. 2000A; BONFATTI et al. 2000b; De BATTISTI et al. 2000; MARTINEZ-HUITLE et al. 2005). Alternatively, experimental evidences have showed that, in the case of chloride mediation, incineration reactions should be mainly a set of volume rather than surface reactions, reducing its dependence on the nature of the electrocatalytic material (PANIZZA; CERISOLA, 2003; MARTINEZ-HUITLE et al. 2005; MARTINEZ-HUITLE et al. 2008; SILVA, et al. 2013; SALES SOLANO et al. 2013). However, it should be taken into account that the efficiency of a mixture of electrogenerated oxidants depends mainly on the particular concentration of each species and pH of the effluent (MAESELLI et al. 2003, MARTINEZ-HUITLE; BRILLAS, 2008; CAÑIZARES et al. 2009; KAPALKA et al. 2010; BEZERRA-ROCHA et al. 2011; SANCHEZ-CARRETERO et al. 2011; SALES SOLANO et al. 2013; INDERMUHLE et al. 2013).

Taking into consideration the above information, as a further development of the investigation carried out on the role of chlorides (MARTINEZ-HUITLE et al. 2005; Martinez-Huitle et al., 2008), we opted to extend this study, in the absence and presence of Cl^- using BDD and Pt/Ti anodes, to better focus on volume and surface effects during direct and indirect electrochemical incineration. The use of the BDD electrode can also contribute to explain the high efficiencies reached by non-active anodes in the removal of organic pollutants by Cl-mediated oxidation process (CAÑIZARES et al. 2009; KAPALKA et al. 2010; INDERMUHLE et al. 2013) since it is not clear, if the pathway followed during the degradation has a similar sequence by using active and non-active anodes.

Novacron Yellow C-RG (NY) has been considered an interesting substrate (Figure 1) because it is a widely used dye in textile industries in northeastern Brazil that affects aquatic ecosystems due to its persistent color, carcinogenic and mutagenic properties, in accordance with local environmental legislation (Instrução Normativa nº 1 03/11/2014), and Federal Brazilian Resolution CONAMA 357/2005.

Figure 1. Chemical structure of NY.



Fonte (autor, 2014)

5.3 EXPERIMENTAL

5.3.1 Reagents

Ultrapure water was obtained using a water purification system (MilliQ). The chemical reagents used were of the highest quality available on the market, without additional purification. Na_2SO_4 was obtained from Fluka and Novacron Yellow C-RG (NY), a reactive azo dye, was supplied by a Brazilian textile company (Figure 1). Dye solutions were prepared by dissolving dye (200 mg L^{-1}) in ultrapure water containing 0.25 mol L^{-1} of Na_2SO_4 since this salt is present in many textile wastewaters and it displays good electrical conductivity.

5.3.2 Electrochemical Measurements

Electrochemical analyses were performed with an Autolab model PGSTAT320N (Metrohm). Quasi-steady polarization curves were carried out at a scan rate of 5 mV s^{-1} and with a 0.45 mV step potential, in solutions of NaCl at different concentrations, using Na_2SO_4 to further increase the electrolyte conductivity. Experiments were carried out in a conventional three-electrode system, and measurements were performed between 0 and 3.3 V. Pt/Ti and BDD, with an exposed geometric area of ca. 0.75 cm^2, were used as the working electrode, while a platinum wire and an Ag/AgCl (KCl 3 mol L^{-1}) electrode were employed as the auxiliary and reference electrodes, respectively.

5.3.3 Electrochemical Oxidation

Bulk oxidation experiments were performed under galvanostatic conditions, with a MINIPA-3305M power supply, in an electrochemical cell with a 350 mL reaction compartment, using BDD or Pt/Ti anodes. The BDD was supplied by Adamant Technologies (Neuchatel, Switzerland); while the Pt/Ti electrode was purchased by Industrie De Nora S.p.A (Milan, Italy). Both electrodes were used as anodes while a titanium plate was used as a cathode, with an area of 10 cm^2 in all cases. Direct oxidation experiments were conducted at 25°C to study the effect of the applied current density (J = 10, 30 and 50 mA cm^{-2}). Additionally, the effect of initial dye concentration (200, 400 and 600 mg L^{-1}) was investigated by applying a current density of 30 mA cm^{-2}. For mediated oxidation, experiments were performed varying concentrations of NaCl in the solution (0.2, 0.4 and 0.8 g in 350 mL (corresponding to 0.01, 0.02 and 0.04 mol L^{-1}) of solution containing NY dye), by applying 10 mA cm^{-2}. Also, total organic carbon (TOC) was measured to determine whether the organic load was reduced after electrochemical treatment.

Few samples of anolyte were extracted into non-aqueous medium and were subjected to GC-MS analysis using GC-MS-QP Shimadzu Mass Spectrometer to identify the intermediates (SALES SOLANO et al. 2013), at specific electrolysis times, during the course of the reaction in order to understate the fragmentation of the chemical structure of the dye.

5.3.4 Color Removal Analysis

Color removal was analyzed in a Shimadzu UV1800 spectrophotometer and monitored by decreasing absorbance measurement. Experimentally, discoloration efficiency or color removal percentage was calculated by Equation 1 (MARTINEZ-HUITLE; BRILLAS, 2009):

$$\text{Color removal} = [(ABS_0 - ABS_t)/ABS_0] \times 100 \qquad (1)$$

where, ABS_0 and ABS_t represent absorbance before and after electrolysis in time t, at the maximum visible wavelength (λ_{max}=422 nm for NY) for the solution under study. Relative absorbance was obtained in accordance with Equation 2:

$$\text{relative absorbance} = \frac{\left[ABS_t\right]}{ABS_0} \qquad (2)$$

Energy consumption per volume of treated wastewater was estimated in kWh m^{-3}. Average cell potential during electrolysis was used to calculate energy consumption, as seen in Equation 3:

$$\text{Energy consumption} = (V \times I \times t) / V_s \qquad (3)$$

where t is the electrolysis time (h), V and I depict the average potential and current of the cell during electrolysis, respectively, and V_s is the volume of the sample (m^3).

5.3.5 Analysis of Total Organic Carbon (TOC)

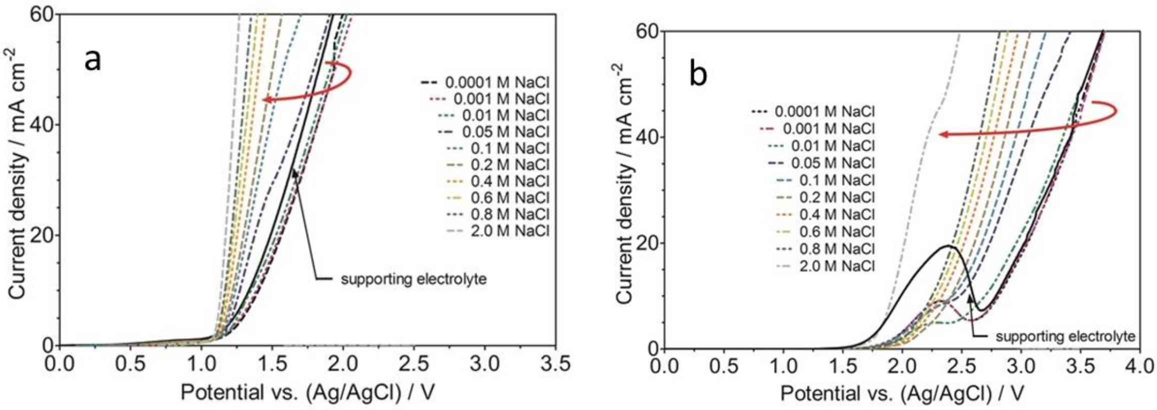
Total organic carbon (TOC) content is an indicator of environmental pollution and recent environmental laws (CONAMA N° 357/2005) require that it be measured. It is important for environmental control of water and wastewater. The TOC analyzer used in the present study was the Analytik Jena Multi N/C 3100. The equipment measures the amount of Total Carbon (TC) and Inorganic Carbon (IC) in the sample. TOC was estimated by difference between TC and IC.

5.4 RESULTS AND DISCUSSION

5.4.1 Polarization Curves in the Presence of Halide Ion

Prior to direct and indirect electrochemical oxidations, and on the basis of the introductory considerations on the possible effect of halide on the oxygen evolution reaction (o.e.r.) depended on the electrode material used; quasi-steady polarization curves were recorded in background solutions containing 0.25 mol L^{-1} Na_2SO_4, in the absence and in the presence of different concentrations of Cl^-. The results obtained in the presence of chloride ions (1×10^{-4} to 2.0 mol L^{-1}), at both anode materials, are shown in Fig. 2. In the case of the Pt/Ti anode, the whole polarization curve is shifted to more positive potentials (Fig. 2a), while increasing the chloride concentration, up to 0.001 mol L^{-1}; above this value, a reversal of the trend is observed. As a direct consequence of this occurrence, the anode potential in the region of J values applied for electrochemical incineration of organics reaches values of the order of 2.0 V (vs Ag/AgCl). At these polarization levels, the number and reactivity of hydroxyl radicals, adsorbed at the electrode surface and/or confined in a reaction cage around the electrode itself, may lead to fast incineration of a number of organic substrates (FERRO et al. 1998; BONFATTI et al. 2000a; MARTINEZ-HUITLE et al. 2005). The coexistence of oxychloro-radicals, often assumed as intermediates also in the chlorine evolution reaction, can further ease the electrochemical mineralization processes. The inversion of the trend upon increasing chloride concentration above 2.0 mol L^{-1} is due to the increase of the importance of the Cl_2/H_2O system as a potentiostatic buffer, as already indicated in a previous work (MARTINEZ-HUITLE et al. 2005).

Figure 2. Current-potential curves for the Pt electrode in the presence of different amounts of NaCl on (a) Pt/Ti and (b) BDD anodes. Supporting electrolyte (dashed line): 0.25 M Na_2SO_4; scan rate: 5 mV s^{-1}.



Analogous experiments were carried out using BDD anode in the presence of NaCl, as shown in Fig. 2b, employing the same range of Cl^- concentrations. In that case, at very small NaCl concentrations (0.001 mol L^{-1}), a shift of J/E curves in the positive direction is observed; although the effect is much less evident than observed with the Pt/Ti electrode, see Fig. 2a. Above 0.01 M NaCl, the anode potential becomes increasingly buffered by the halide electroactivity. The formation of $Cl^{\bullet}$ species could be considered, alongside with other active chlorine species generated at the anode surface (MARSELLI et al. 2003, SANCHEZ-CARRETERO et al. 2011).

Another feature that should be mentioned in the case of BDD is the fact that the polarization behaviors are also completely different in the absence of Cl^- and in the presence of Cl^- at very lower concentrations (Fig. 2b); where it is only observed the direct oxidation of the salt ions (anodic peak around 2.36 V). It can also be perceived that, at higher concentrations of sulfates (0.25 mol L^{-1}), a slight shift of the oxygen evolution toward lower anodic potential is favored. This suggests that, direct oxidation of species, H_2O and SO_4^{2-} (higher concentration of salt ions in the solution), is attained on the anode surface to produce stable oxidants ($^{\bullet}OH$ and $S_2O_8^{2-}$) (SANCHEZ-CARRETERO et al. 2011). This assumption is supported by the fact that the previously marked oxidation potentials appear around those expected from the standard values reported in the literature (SANCHEZ-CARRETERO et al. 2011). These figures are in accordance with the results reported by Rodrigo and co-workers, (2009) and De Freitas Araújo (2013).

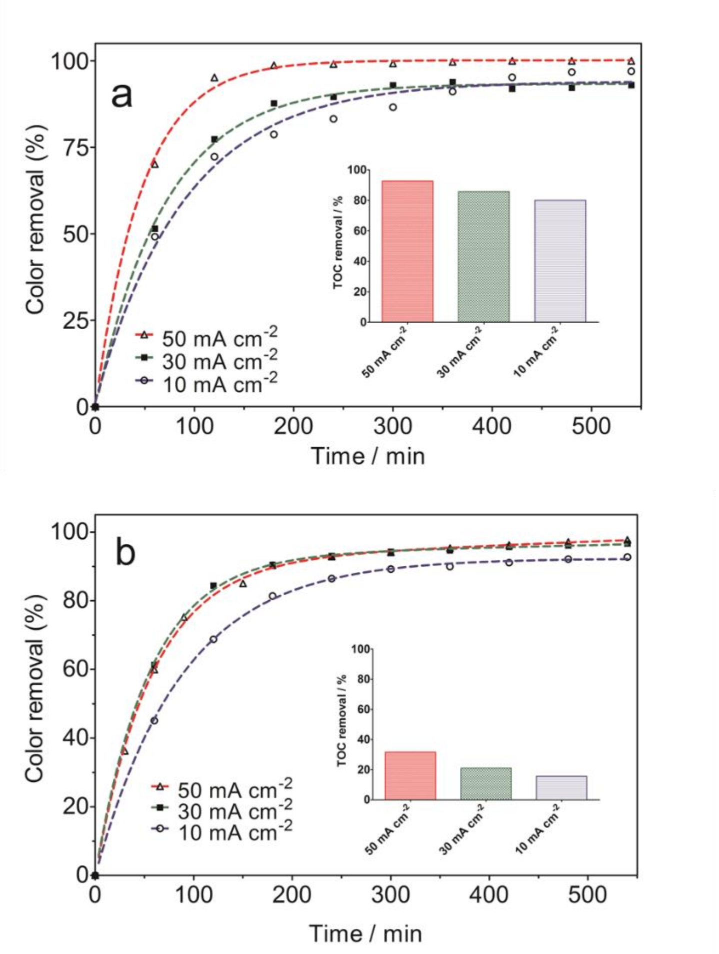
Regarding the peak observed at 2.36 V (see Fig. 2b), it decreases when an increase in Cl^- concentration is attained (up to 0.1 mol L^{-1} of NaCl). This behavior can be attributed to an interaction between hydroxyl radicals and Cl^- to form active chlorine species (e.g.: $Cl^- + {}^{\bullet}OH \rightarrow ClO^- + H^+ + e^-$) on BDD surface (MARSELLI et al. 2003; CAÑIZARES et al. 2009; SANCHEZ-CARRETERO et al. 2011). This justifies the formation of many new types of oxidants (desirable and undesirable, such as $Cl^{\bullet}$, Cl_2, ClO_2^- and ClO_3^-, ClO_4^-, respectively) with this non-active material, and this also explains the higher concentration produced by some of them. After that, the whole polarization curve is shifted to less positive potentials (Fig. 2b), while increasing the chloride concentration due to the increase of the importance of Cl_2/oxy-chloro radicals system at BDD surface.

The conclusion for this part of our study is that the concentration of halide in solution and the electrocatalytic material play an important role in relation with the oxygen evolution reaction (MARTINEZ-HUITLE et al. 2005), in concomitance with the production of active chlorine species. However, we can deduce that the type and extension of the production of oxidants depend on the nature of anode material (MARTINEZ-HUITLE et al. 2005; MARTINEZ-HUITLE et al. 2008) and it influences on the efficiency of electrochemical approach adopted because the oxidation of pollutants could take place from the vicinity of the electrode surface to the bulk of the electrolyte (PANIZZA; CERISOLA, 2003; KAPALKA et al. 2010; INDERMUHLE et al. 2013). Nevertheless, despite the fact that these assumptions are very well known for active anodes (BONFATTI et al. 2000a), it is not completely clear for non-active anodes yet.

5.4.2 Direct Electrochemical Oxidation

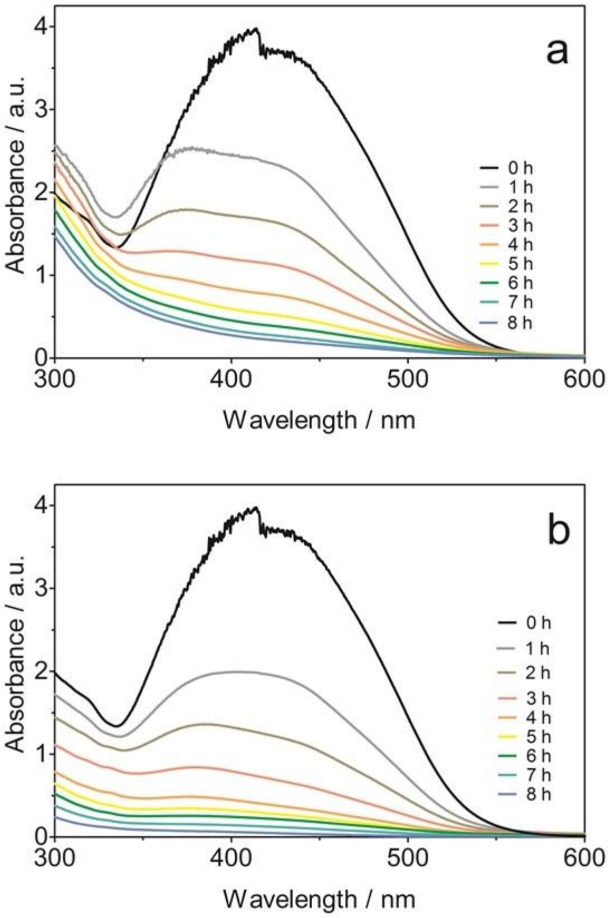
Figures 3a and 3b show the effect of the applied current density on color decay during electrochemical oxidation of the synthetic dye solution, containing 200 mg L^{-1} of NY in 0.25 M Na_2SO_4 at 25°C, using BDD and Pt/Ti electrodes, respectively. In all cases, color removal was completely achieved independent of the applied current density.

Figure 3. Influence of applied current density, as a function of time, in color removal during anodic oxidation of NY at (a) BDD and (b) Pt/Ti. Experimental conditions: $[NY]_0$=200 mg L^{-1}, Electrolyte: 0.25 M Na_2SO_4, T=25 °C, Rate of agitation: 400 rpm. Insets: % of TOC removal, as a function of applied current density, after 540 min.



This behavior is observed from the visible spectra of NY (Figures 4a and 4b), that indicate how the bands of absorbance decrease with time during galvanostatic electrolysis of a solution with 200 mg L^{-1} of NY, by applying 30 mA cm^{-2}. The intensity of the bands continuously decays, resulting in more than 90% of color removal after 420 min using BDD or Pt/Ti anodes. These findings suggest that initial treatment stages exhibit mechanisms involving dye oxidation to more simple organic compounds, by breaking chromophore group or dye chemical structure, prior to the formation of aliphatic carboxylic acids and carbon dioxide (AQUINO et al. 2011, AQUINO et al. 2012; BEZERRA-ROCHA et al. 2012; DE FREITAS ARAÚJO, 2013).

Figure 4. Color removal, as a function of time, during anodic oxidation of NY in 0.25 M Na_2SO_4 at J = 30 mA cm^{-2}: (a) BDD and (b) Pt/Ti.



Although the color removal rate increased moderately when the applied current density was raised (Figures 3a and 3b); discolorization times are different, indicating that color removal occurs by both direct and mediated electrooxidation via strong oxidants produced by oxidation of the supporting electrolyte on the BDD or Pt/Ti surfaces (AQUINO et al. 2012; SILVA, et al. 2013, INDERMUHLE et al. 2013). On the other hand, it should be noted that, Pt/Ti (active anode) is moderately more efficient for removing color than the BDD (non-active anode) (Figures 3a and 3b). That behavior seems to be related to the effectiveness of •OH produced on the surface at both anodes to oxidize organics or other species such as anions contained in solution (MARSELLI et al. 2003). Then, we can assume that the degradation of NY depends predominantly on the nature of electrocatalytic material as well as on the attack of oxidants toward the chemical structure of the dye.

In order to verify the assumptions above, the percentage of elimination of organic matter was determined by Total Organic Carbon (TOC), after complete color removal using BDD and Pt/Ti by applying different current densities at 25°C (see insets on Figures 3a and 3b). It was found that the BDD electrode exhibited a higher TOC removal, by applying 10, 30 and 50 mA cm^{-2}, after 540 min of electrolysis. TOC removal increased when an increase on applied current density was attained (Figure 3a). Using Pt/Ti, lower TOC removals were achieved, after 540 min of electrochemical treatment, when different values of current density were applied (Figure 3b). Approximately 17, 20 and 32% of TOC removals were achieved by applying 10, 30 and 50 mA cm^{-2}, respectively. In fact, as shown by the potentiodynamic measurements (Fig. 2a), Pt/Ti displayed low oxygen evolution overpotential and consequently it favored the secondary reaction of oxygen evolution (PANNIZA; CERISOLA, 2007) in comparison with NY oxidation. At the same time, this behavior occurs because for the Pt/Ti electrode, adsorption of the dye could be considered a pre-requisite during electrochemical degradation, breaking of the chromophore group (as a first stage during the process). This leads to molecule rupture and the formation of different intermediates, which can be more difficult to degrade or can accumulate on the surface of the electrode; decreasing its efficiency.

Conversely, BDD anode is more efficient for organic matter removal. In fact, more than 80% of TOC removal was achieved at all values of applied current density (Fig. 3a). NY is oxidized not only by direct electron transfer at the anode surface, but mainly by reaction with $^{\bullet}OH$ and $S_2O_8^{2-}$ (in agreement with the potentiodynamic measurements (Fig. 2b)) (CAÑIZARES et al. 2009; SALES SOLANO et al. 2013). These oxidants, during a very short time, are available to attack the chemical structure of the dye without preference for a particular functional group, leading to the formation of intermediates that are rapidly oxidized into CO_2 and water.

Anyway, differences between the BDD and Pt/Ti anodes, in respect to the color removal, are not very evident to indicate that the degradation pathway as well as the attack of oxidants to chemical structure of dye may also be playing a significant role in this case. For this reason, the study of intermediates formed during electrochemical treatment of NY becomes a topic of great importance in this research, which would give relevant information to address these questions.

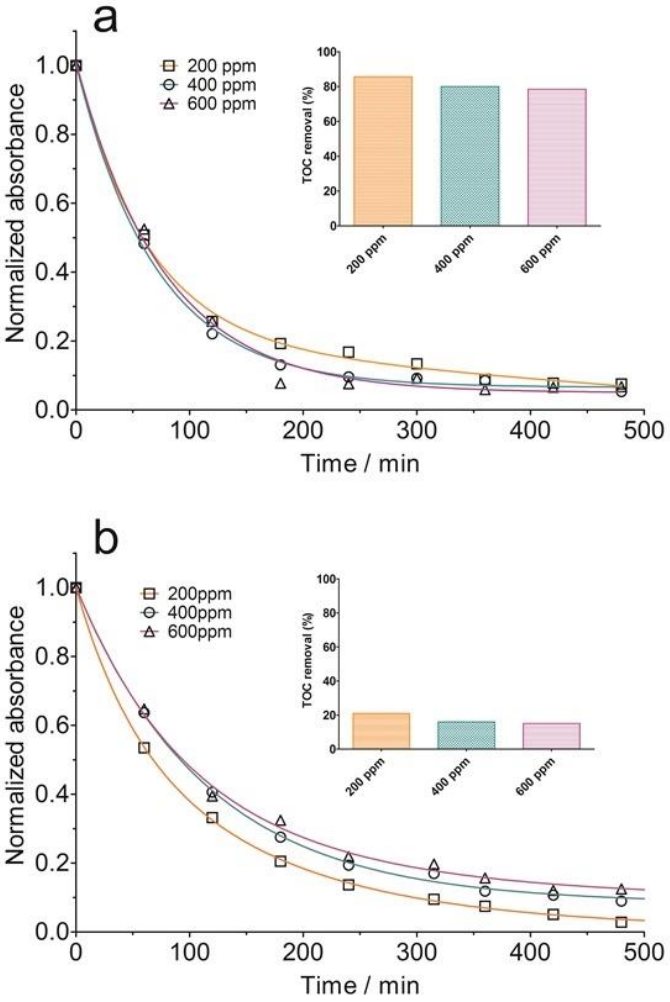
Then, during the anodic oxidations of NY by applying 10, 30 and 50 mA cm^{-2} at 25°C using BDD and Pt/Ti, few samples were collected and analyzed by GC/MS technique. Using a BDD anode, it was possible to determine that, higher concentrations of aniline (m/z 91) and 2-chloro-1,2,3 triazine (m/z 116) were formed during the first 2 h of electrolysis. Whereas, after 4 h of treatment, different by-products were identified, such as 1-naphthol (m/z 144), 2-2-naphthylamine (m/z 143), aniline (m/z 91) and 2-chloro-1,2,3 triazine (m/z 116). At the completion of the electrolysis, higher concentrations of oxalic acid (m/z 90) were detected.

In the case of Pt/Ti electrode, the mass spectra obtained after 2 h, the m/z 275, m/z 129 and m/z 91 ions corresponded to the main phenolic by-products; 2-[(3-diazenylphenyl) sulfonyl] ethanesulfonate, 4-choloro-1,2,3-triazine-2-amine and aniline, respectively. After 4 h of electrolysis, 1-naphthol (m/z 144), aniline (m/z 91) and 2-chloro-1,2,3 triazine (m/z 116) and 2-[(3-diazenylphenyl) sulfonyl] ethanesulfonate, were identified.

Considering the by-products formed after 2 h of electrolysis (aniline and 2-chloro-1,2,3 triazine), it could be assumed that using BDD anode, no attack to azo dye group is attained as the first step of the degradation. Conversely, using a Pt/Ti electrode, the chromophore group (−N=N−) is fragmented producing 2-[(3-diazenylphenyl) sulfonyl] ethanesulfonate. After that, the chemical structure of the dye was completely fragmented after 4 h of electrolysis; in both cases. Results clearly confirm that the lower rate of the color removal of NY in the beginning of the process using BDD anode is attributed to the conversion of NY to more simple molecules, enhancing the TOC decay. On the contrary, an efficient elimination of color was achieved with a Pt/Ti electrode, but with a limited decrease of TOC, due to the by-products formed. Assuming that, aniline is formed during oxidation of NY at Pt/Ti; it could be adsorbed on the surface or forming a polymeric film passivating the electrode (as already indicated by BIALLOZOR; KUPNIEWSKA, 2005; TALLMAN et al. 2002), justifying lower TOC removals.

In order to further examine the activity of the BDD and Pt/Ti electrodes, the role of dye concentration for complete color elimination, was examined. Figures 5a and 5b show the effect of the initial dye concentration (mg L^{-1}) on relative absorbance decay as well as TOC elimination, as a function of time, during galvanostatic electrolysis of the synthetic dye solution by applying 30 mA cm^{-2}.

Figure 5. Influence of the initial concentration of NY in color removal, as a function of electrolysis time, during the electrochemical oxidation process at (a) BDD and (b) Pt/Ti anodes. Operational conditions: Electrolyte: 0.25 M Na_2SO_4, T=25 °C, Agitation speed: 400 rpm. Insets: % of TOC removal, after 480 min.



For the BDD anode (Figure 5a), color removal rates are identical in the initial stages (overlapping curves). This behavior is related to the participation of electrogenerated hydroxyl radicals and persulfates produced from supporting electrolyte on BDD surface (in accordance with the results obtained at potentiodynamic measurements), favoring higher TOC removals (ranging from 75 to 85% (insets in Figure 5a)). However, in the final stages of electrolysis, lower NY removal rate was observed due to mass transfer limitations (INDERMUHLE et al. 2013).

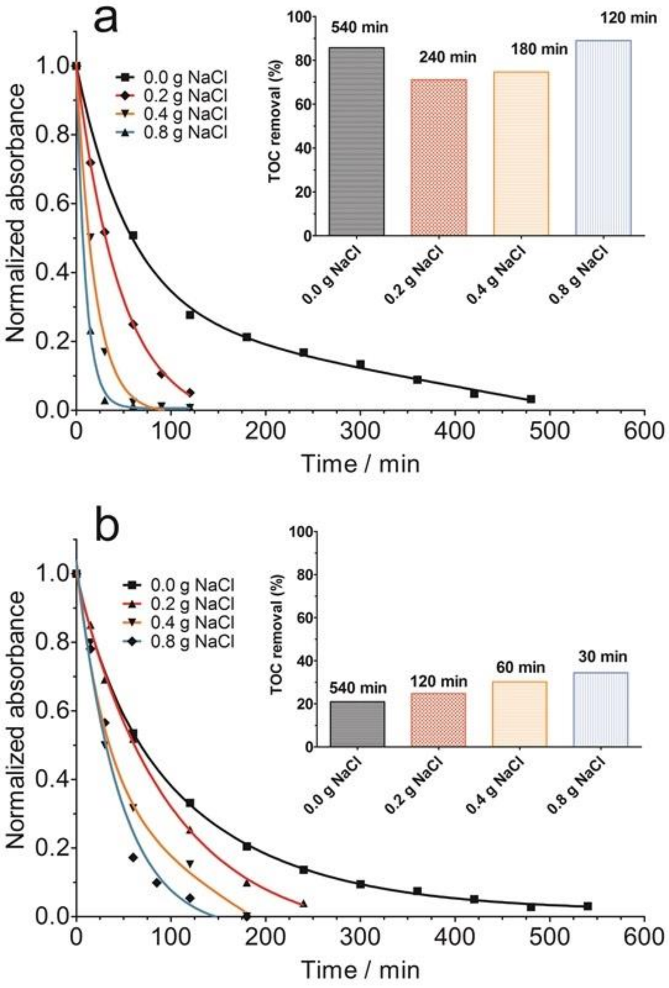
The behavior was different when a Pt/Ti electrode was used (Figure 5b), where the rate decreases when the dye concentration increased. This behavior is due to mass transfer limitations and the stages of adsorption/desorption performed in this type of electrode (MARTINEZ-HUITLE et al. 2005). Also, we can infer that at higher concentrations of dye, higher concentrations of aniline are produced, provoking a significant decrease in the electrode efficiency due to the passivation phenomenon. In fact, lower TOC removals were achieved when electrolysis of NY using a Pt/Ti anode were performed (inset Fig. 5b).

5.4.3 Indirect Electrochemical Oxidation: Active Chlorine

The kinetics of color removal for NY were studied using mediated oxidation by applying 10 mA cm^{-2}, in the presence of 0.2, 0.4 and 0.8 g of NaCl in 350 mL of synthetic dye solution, using Pt/Ti and BDD anodes. Figures 6a and 6b show that color removal rate for both electrodes rose significantly in the presence of NaCl in solution. Interestingly, the process does not depend on the current density applied, but rather on NaCl content in the solution. Similar results have been recorded by other authors, including: Bonfatti et al. (2000a) and (2000b), when analyzing electrooxidation of glucose mediated by Cl^{-}; Panizza and Cerisola (2003) studying oxidation of 2-naphthol mediated by Cl^{-} using a Ti-Ru-Sn ternary oxide electrode; Martínez-Huitle et al. (2008) during oxalic acid oxidation using a BDD electrode and different halide concentrations in solution, and Sales Solano et al. (2013) treating a real textile industrial effluent by strong oxidant species.

TOC decay was also monitored when quasi-complete elimination of color was achieved, in all cases (Insets in Fig 6a and 6b). Clearly, in comparison to the oxidation of NY in the absence of NaCl in solution (TOC decay of 86% and 21% for BDD and Pt anodes, respectively), higher TOC removal efficiencies were accomplished when 95% of color removal was attained using BDD anode by adding Cl^{-} to NY solution (71.1%, 74.7% and 88.9% when 0.2, 0.4 and 0.8 g of NaCl were added in 350 mL of synthetic dye solution). Conversely, with the Pt/Ti electrode, a modest enhancement on TOC removal was achieved when 0.2, 0.4 and 0.8 g of NaCl were added in solution; obtaining 24.7%, 30.2% and 34.4% of organic load elimination (see Fig. 6b).

Figure 6. Effects of NaCl at different concentrations, as a function of time, during mediated oxidation of NY by using (a) BDD and (b) Pt/Ti anodes. Operational conditions: $[NY]_0$=200 mg L^{-1}, Electrolyte: 0.25 M Na_2SO_4, T=25 °C, rate of agitation: 400 rpm. Insets: % of TOC removal, as a function of NaCl concentration.



In consideration of the fact that, in the case of chloride mediation, incineration reactions should be mainly a set of volume rather than surface reactions and it depends mainly on oxidant species produced, the change from Pt to BDD should not involve dramatic changes in the incineration mechanism (SALES SOLANO, et al. 2013). However, restricting now our results to the potentiodynamic measurements and the figures related to the indirect oxidation of NY, the process seems to be the consequence of some specific roles played by the halogen salt on the anode surface to generate active chlorine species ($Cl^{\bullet}$, Cl_2, ClO^-, HClO, ClO_2^- and so on) (MARSELLI, et al. 2003; KAPALKA et al. 2010; SANCHEZ-CARRETERO et al. 2011); accelerating the organic degradation.

We can hypothesize that the mechanisms behind their effects and oxidants produced are likely to be different, depending on the electrocatalytic material used. For Pt/Ti, the effect of chlorides may be a hybrid of two mechanisms where the anion may partially change the stoichiometry and microstructure of the oxide film that grows on the Pt electrode surface at strongly positive potentials (MARTINEZ-HUITLE et al. 2005); as a consequence, the o.e.r. becomes inhibited (or less favored) and the electrochemical incineration is consequently privileged. In fact, the quasi-state polarization curves indicate that, between 0.01 and 0.05 mol L^{-1} of Cl^{-} concentrations (range correspondent to the NaCl concentrations used during indirect oxidation of NY), the o.e.r. is inhibited but the production of strong oxidants is modest. Then, if the electrogeneration of strong oxidants is partially attained, the oxidation occurs principally in the vicinity of the anode surface where the mixture of oxidants reacts with the organic pollutant. At the same time, a part of active chlorine species reacts through bulk reactions; but it is dependent on the Cl^{-} concentration. In fact, these assumptions confirm the results reported in Fig. 6b, concerning to the modest enhancement in the TOC removal in chloride media.

Conversely, for the BDD anode, the main factor seems to be the electrogeneration of strong oxidants, active chlorine species, reacting in solution (Cañizares et al., 2009). On the basis of results on potentiodynamic measurements, the effective role played by the electrochemically Cl^{-} ions may support the idea that a strong oxidant, or mixture of oxidants, is generated in a first stage, and consumed in a solution region strictly confined around the electrode surface. The generated oxidants may be simply $^{\bullet}OH$, $S_2O_8^{2-}$ and ClO^{-}, in the case of lower Cl^{-} concentrations. But, for Cl^{-} concentrations above 0.01 mol L^{-1} (0.2 g in 350 mL), a more complex situation can be attained, where a very active oxidation mixture is formed with the electrode potentials attained at 10−60 mA cm^{-2} (FERRO et al. 2000), increasing the concentration of oxidants in solution compared with those generated at Pt/Ti, which primarily act on anode surface and after that, in the volume of the solution. Consequently, it favors an effective organic matter oxidation (KAPALKA et al. 2010; AQUINO et al. 2011; BEZERRA ROCHA et al. 2011; AQUINO et al. 2012; BEZERRA-ROCHA et al. 2012; SALES SOLANO et al. 2013; INDERMUHLE et al. 2013). These assumptions are in accordance with the performances obtained during color and TOC removal, at different Cl^{-} concentrations.

During the sample analysis by GC/MS technique, for the electrolysis using BDD and Pt/Ti anodes in the presence of chlorides by applying 10 mA cm^{-2}, a minor number of intermediates was detected, such as phenol (m/z 94), 1-naphthol (m/z 144), aniline (m/z 91), 2-chloro-1,2,3 triazine (m/z 116), traces of acetic acid (m/z 61) and oxalic acid (m/z 90). Although, the analysis of the fists stages of Cl-mediated oxidation at BDD anode indicates that the attack of chloro-oxidant species is performed at the site of the azo bond, the formation of other intermediates indicates that no preferential pathway is followed by this process. On the contrary, with a Pt/Ti electrode, the formation of similar intermediates, not only to direct anodic oxidation but also at indirect process, suggests that the attack of the azo dye group is the principal step.

5.4.4 Energy Consumption and Cost

Table 1 depicts the energy consumption needed to remove 95% of the color in different conditions using BDD and Pt/Ti anodes, respectively. During electrolysis of the synthetic dye solution containing 200 mg L^{-1} of dye (NY), energy consumption is directly proportional to the current density applied and electrolysis time. For example, in the BDD electrode (Table 1) consumption increases from 5.22 for 44.65 kWh per volume of treated wastewater (m^3) when current density rises from 10 to 50 mA cm^{-2}. With the Pt/Ti electrode, initial energy consumption is slightly higher than the BDD electrode; when current density increases from 10 to 50 mA cm^{-2}, energy consumption rises from 8.96 to 34.65 kWh m^{-3}. Table 1 also compares energy consumption (kWh m^{-3} of color removed) during mediated oxidation at different concentrations of NaCl in solution.

Finally, the cost of the process was estimated considering an electrical energy cost of about R$ 0.3 (R$ = Brazilian currency (reais), excluding tax) per kWh (National Electrical Energy Agency, Brazil), as shown in Table 1, to demonstrate the viability of this process as an alternative for treating textile industry wastewater (Equation 12).

$$Cost\ (R\$\ m^{-3}) = [Energy\ consumption\ (kWh\ m^{-3}) \times 0.3 (R\$/kWh)] \tag{12}$$

Table 1 – Energy Consumption (kWh/m^3 of treated wastewater), calculated for 95% of color elimination in the solution during electrochemical oxidation of NY at BDD and Pt/Ti electrodes, for direct and mediated oxidation processes.

	BDD			**Pt/Ti**		
	Current Density (mA cm^{-2})[a]					
	10	30	50	10	30	50
Energy Consumption[c]	5.22	22.62	44.65	8.96	21.84	34.65
Cost[d]	1.56	6.78	13.4	2.69	6.55	10.39
	Concentration of NaCl in solution (g/ 350 mL)[b]					
	0.2	0.4	0.8	0.2	0.4	0.8
Energy Consumption[c]	7.37	3.17	1.80	12.48	5.41	5.69
Cost[d]	2.21	0.95	0.54	3.74	1.62	1.71

[a] Temp=25°C, agitation = 400 rpm, [NaCl] = 0.0 g/L.

[b] Temp=25°C, agitation = 400 rpm, current density = 10 mA cm^{-2}, Volume = 350 mL.

[c] kW h m^{-3}.

[d] Brazilian currency.

5.5 CONCLUSIONS

In the present study, oxidation of NY using BDD and Pt/Ti electrodes was investigated under different experimental conditions. Electrolyses demonstrated that, in the absence of NaCl, only a slow TOC reduction using Pt anode was obtained while a greater efficiency was recorded for the BDD electrode (more than 85%). It is important to remark that; color removal was slightly more efficient using Pt/Ti than BDD. This way, the above approaches (color removal/organic load removal) can be considered as two different oxidation pathways for each one of the electrocatalytic materials due to the differences on the by-products identified (graphical abstract).

On the other hand, in the presence of NaCl using BDD and Pt/Ti electrodes, NY was oxidized by the mediation of active chlorine electrochemically generated during the process. However, it was independent on applied current density, although the Cl^{-} concentration in the solution is a determining parameter. The effect of chloride on the electrooxidation of organics with BDD depends on the reaction between electrogenerated $^{\bullet}OH$ and Cl^{-} ions or the conversion of chloride ion to chlorine which is further hydrolysed to other active species (MARSELLI et al. 2003; KAPALKA et al. 2010). This behavior seems to be related to different experimental conditions, but it is principally dependent on the concentration of free $^{\bullet}OH$ radicals that cannot combine with the components of their non-active surface and then, during a very short time, they are available to produce oxidants or oxidize organics.

On the basis of the results obtained for anodic oxidation of NY, the production of active chlorine species at the anode surface plays a decisive role, and their reactivity to oxidize organic pollutants depends on the incineration reactions that can be attained in a reaction zone close to the electrode (reaction cage) or in the bulk of solution. However, these incineration reactions can be affected by the nature of the metal oxide electrode, in the case of non-active anodes; and being a non-determining parameter for non-active anodes, such as BDD which mainly favors bulk reactions.

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CAPÍTULO 6

6 ELECTROCHEMICAL DEGRADATION OF REMAZOL RED BR AND NOVACRON BLUE C-D DYES USING DIAMOND ELECTRODE

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6.1 ABSTRACT

In this paper, the treatment of dye solutions containing Remazol Red BR (RRB) and Novacron Blue C-D (NB) by anodic oxidation using boron doped diamond anodes (BDD) has been investigated. Galvanostatic electrolyses of RRB and NB solutions have led to the complete decolourisation and chemical oxygen demand (COD) removal at different operating conditions (current density, pH and temperature). Energy requirements for removing colour during galvanostatic electrolyses of RRB and NB synthetic solutions depend mainly on operating conditions; for example for RRB, it passes from 3.30 kWh m^{-3} at 20 mA cm^{-2} to 4.28 kWh m^{-3} at 60 mA cm^{-2} (pH = 1); 17.25 kWh m^{-3} at 20 mA cm^{-2} to 28.87 kWh m^{-3} at 60 mA cm^{-2} (pH = 4.5); 13.50 kWh m^{-3} at 20 mA cm^{-2} to 37.80 kWh m^{-3} at 60 mA cm^{-2} (pH = 8). Additionally, colour and COD removal rates were favoured when an increase on the temperature was attained, decreasing the energy consumption requirements. According to the experimental results obtained, the electrochemical oxidation process is suitable for depuration wastewaters containing these textile dyes, due to the electrocatalytic properties of BDD anode.

Keywords: Diamond electrode. Dyes. Decolourization. Hydroxyl radicals. Wastewater treatment.

6.2 INTRODUCTION

Dyes are used in many technological fields, such as in various branches of the textile industry, leather tanning industry, paper production, food technology, agricultural research, light-harvesting arrays, photo-electrochemical cells and in hair colourings. Due to large-scale production and extensive application, dyes can cause considerable environmental pollution and are serious health-risk factors (FORGACS et al. 2004).

Textile dyes can be classified by the way they are fixed to the textile fibber (e.g. direct, reactive, acid, etc) or by their chemical structure (e.g. azo, anthraquinone, indigoide). In the textile industry, 60% of the dyes used are azo dyes, in which the –N=N– group is connected to an aromatic ring. Reactive dyes are widely used due to their relatively easy application in the dyeing process and stability during wear.

The textile industry produces large quantities of wastewater during the washing and dyeing process, which contain large quantities of dye, and are disposed together with the textile effluent. It should be mentioned that coloration in water courses affects water transparency, gas solubility and, additionally, these compounds can present carcinogenic and mutagenic properties (FORGACS et al. 2004; MARTINEZ-HUITLE; BRILLAS, 2009).

For the removal of dyes from wastewater a wide range of techniques, such as chemical precipitation, chemical oxidation and/or adsorption with subsequent biological treatment have been developed (SHAUL et al. 1991; GUPTA et al. 1992; SHUKLA et al. 1992; IVANOV et al. 1996; SOKOLOWSKA-GADJA et al. 1996; TUNAY et al. 1999; KADABASIL et al. 1999; HAO et al. 2000; ROBINSON et. al. 2001; FORGACS et al. 2004; MARTINEZ-HUITLE; BRILLAS, 2009). As an innovative alternative, the electrochemical technologies (electrochemical oxidation (EO), electrochemical reduction, electrocoagulation, indirect electro-oxidation with strong oxidants and emerging photoassisted electrochemical treatments) for treating wastewaters containing organic pollutants have been proposed (CHEN et al. 2004; MARTINEZ-HUITLE; FERRO, 2006; PANIZZA; CERISOLA, 2009; BRILLAS et al. 2009). The application of these electrochemical technologies for wastewater treatment is benefiting from advantages such as versatility, environmental compatibility and potential cost effectiveness (COMNINELLIS, 1994; CHEN et al. 2004; MARTINEZ-HUITLE; FERRO, 2006; PANIZZA; CERISOLA, 2009; BRILLAS et al. 2009). In recent years, these techniques have been investigated for decolourising and degrading dyes from aqueous solutions (dyes solutions, synthetic and actual wastewaters) by several scientific groups and a wide variety of electrode materials have been suggested, such as dimensionally stable anodes, noble metals, carbon-based anodes, PbO_2 and diamond electrodes (MARTINEZ-HUITLE; BRILLAS, 2009).

Boron doped diamond (BDD) electrodes are relatively new electrode materials that have received great attention, because they possess several technologically important characteristics. Thanks to these properties, they are excellent materials for EO process. In fact, it has been demonstrated that many biorefractory compounds and industrial wastes, including dyes, are completely mineralized with high current efficiencies (MARTINEZ-HUITLE; FERRO, 2006; PANIZZA; CERISOLA, 2009; BRILLAS et al. 2009). For example: Panizza and Cerisola (2008) considered the influence of several experimental variables on the EO efficiency by exploring the mineralization of wastewaters containing Acid Blue 22 in a flow cell equipped with a Si/BDD anode. A significant rise in current efficiency was obtained with increasing dye concentration from 0.1 to 0.3 mM and flow rate from 100 to 300 dm^3 h^{-1} because the process was controlled by the mass transport of pollutants towards the anode. Ammar et al. (2006) also investigated the effect of current, dye concentration and pH on the EO of Indigo Carmine solutions at 35 °C in a stirred undivided cell with a Si/BDD anode, obtaining total mineralization from 600 to 300 min due to the higher production of BDD($^{\bullet}OH$) radicals that accelerates the oxidation of organics. Canizares et al. (2006) and Faouzi et al. (2006) explored the influence of applied current density and initial dye concentration on the mineralization of azo dyes such as Eriochrome Black T, Methyl Orange and Congo Red. They employed an undivided flow cell with a Si/BDD anode, obtaining that the current efficiency was similar for all dyes and mainly depended on their concentration, being bigger for highly loaded than diluted wastes. This behaviour was attributed to mediated oxidation by $^{\bullet}OH$ and $S_2O_8^{2-}$ in the solution. These authors have reported that after 4 h of electrolysis at 30 $mAcm^{-2}$, all solutions were completely decolorized and mineralized. On the other hand, Bensalah et al. (2009) have studied the treatment of wastewaters containing Alphazurine A by anodic oxidation using BDD anodes. The authors reported that the energy required for removing 95% of initial COD depends mainly on the applied current density, temperature and agitation rate. In fact, it was observed that it passes from 57 kWh at 30 $mAcm^{-2}$ to 138 kWh at 90 $mAcm^{-2}$ per kg COD removed; from 102 kWh at 25 °C to 89 kWh at 60 °C and from 141 kWh at 100 rpm to 29 kWh at 400 rpm.

In this context, this research aims to test the performance of EO process using BDD anodes as an alternative to remove dyes from water in order to eliminate their strong colour and their ecotoxicological consequences on the aquatic environment. The principal objective of this study was to investigate the influence of the main operating parameters, such as current density, pH, textile dye concentration and temperature, on the colour and COD removal of solutions containing Remazol Red BR (RRB) and Novacron Blue C-D (NB) (dyes widely used in the Northeast Brazilian Textile industries), in order to identify the electrochemical conditions which give high current efficiency with low energy requirements and for attaining Brazilian legal requirements (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, ISO 2211:1973).

6.3 MATERIALS AND METHODS

6.3.1 Chemicals and Dye Solution

Ultrapure water (16-18 MΩ cm) was obtained by Simplicity water purification system. Chemicals were of the highest quality commercially available, and were used without further purification. H_2SO_4, Na_2SO_4 and NaOH were purchased from Fluka. RRB ($C_{37}H_{28}N_4Na_2O_{10}S_3$) and NB ($C_{16}H_{10}N_2O_2$) dyes were purchased by Brazilian Textile Industry. Synthetic dye solutions were prepared dissolving dyes in water containing 0.5 M Na_2SO_4 and/or 0.5 M Na_2SO_4 + 0.25 M NaOH, adjusting pH value to 1, 4.5 and 8 using 0.5 M H_2SO_4 or 0.1 M NaOH. Dye solutions were prepared containing 190 mg L^{-1} of each dye.

6.3.2 Electro-Oxidation Experiments

Bulk oxidations were performed in an undivided electrochemical cell, the reaction compartment having a capacity of 0.40 L. The anodic oxidation experiments of NB and RRB were performed under galvanostatic conditions using a VERSTAT3 potentiostat-galvanostat (Princeton Applied Research). BDD anode was supplied by Adamant Technologies (Neuchatel, Switzerland). BDD was used as the anode, and titanium as the cathode. Both electrodes were square, each with 10 cm^2 geometrical area. The temperature of the electrolyte was controlled using a water thermostat. Experiments were performed at 25 °C for studying the role of applied current density ($j = 20$, 40 and 60 mA cm^{-2}) and pH (1, 4.5 and 8), while the temperature effect (25, 40 and 60°C) was studied under a current density of 40 mA cm^{-2}.

6.3.3 Analytical methods

Experimentally, decolourization efficiency or percentage of colour removal is determined by the expression (MARTINEZ-HUITLE; BRILLAS, 2009):

$$Colour\ removal\,(\%) = \left(\frac{\left[ABS_0^M - ABS_t^M \right]}{ABS_0^M} \right) \times 100 \tag{1}$$

where ABS_0^M and ABS_t^M are the average absorbances before electrolysis and after an electrolysis time *t*, respectively, at the maximum visible wavelength (λ_{max} = 600 nm and 510 nm for NB and RRB, respectively) of the wastewater (MARTINEZ-HUITLE; BRILLAS, 2009). Relative absorbance parameter was also employed:

$$\text{relative absorbance} = \frac{\left[ABS_t \right]}{ABS_0} \tag{2}$$

where ABS_t corresponds to the absorbance of each dye at time t and ABS_0 is its initial absorbance. Colour removal was monitored by measuring absorbance decrease using a UV 1800 Shimadzu spectrophotometer.

Units (UH) were determined using a Hach Model DR/2500 spectrophotometer calibrated with a method 8025 (Pt-Co units) (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, ISO 2211:1973). pH variation was measured using a Methrom pH meter. Decontamination of dye solutions was monitored from the abatement of their COD. Values of COD were obtained using a HANNA HI 83099 spectrophotometer after digestion of samples in a HANNA thermo-reactor.

The energy consumption per volume of treated effluent was estimated and expressed in kWh m^{-3}. The average cell voltage during the electrolysis (cell voltage is reasonably constant with just some minor oscillations, for this reason is calculated the average cell voltage), is taken for calculating the energy consumption, as follows (MARTINEZ-HUITLE; BRILLAS, 2009):

$$Energy\ consumption = \left(\frac{V \times A \times t}{1000 \times V_s} \right) \tag{3}$$

where *t* is the time of electrolysis (h); *V* and *A* are the average cell voltage (volts) and the electrolysis current (amperes), respectively; and V_S is the sample volume (m^3).

During each electrolysis, some samples of anolyte were extracted into non-aqueous medium and were subjected to GC-MS analysis using GC-MS-QP Shimadzu Mass Spectrometer to identify the by-products during the course of the reaction.

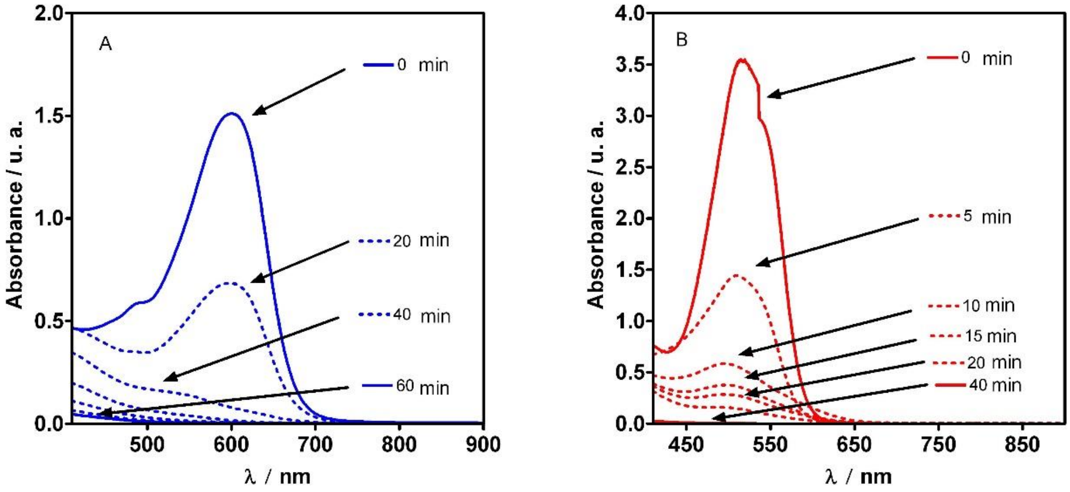
6.4 RESULTS AND DISCUSSION

6.4.1 Colour Removal

The visible spectrum of NB and RRB are reported in the Figures 1a and 1b, respectively. These figures show maximum absorption peaks in the range of visible light, which are in accordance with the colour of RRB and NB solutions. Thus, the measurement of the colour removal was obtained using a UV/vis spectrophotometer at 600 nm and 510 nm for NB and RRB, respectively. Figures 1a and 1b show a decrease of the absorbance band, as a function of time, at 600 and 510 nm during galvanostatic electrolysis of NB and RRB (190 mg L^{-1} and 40 mA cm^{-2} of current density under acidic conditions), respectively.

As it can be observed in Figure 1a and 1b, the absorbance was drastically reduced during the treatment. The intensity of the visible band decreases continuously until its disappearance after about 60 and 40 min of electrolysis for NB and RRB, respectively; leading to a complete solution decolourization. Furthermore, it should be noted that rapid changes in absorbance are achieved, thus indicating that the oxidation of these dyes to other more simple organic compounds occurs by chemical structure fragmentation of dyes (chromophore group breaking), as previously observed by other authors (SANROMAN et al. 2004; LOPEZ-GRIMAU; GUTIERREZ, 2006; PANIZZA; CERISOLA, 2007).

Figure 1. Evolution with time of absorbance band for A) NB and B) RBB during BDD-anodic oxidation. Operating conditions: Electrolyte: 0.5 M Na_2SO_4 (pH = 1), Current density j=40 mA cm^{-2}, Temperature T=25 °C, agitation rate: 400 rpm.



6.4.2 Influence on Applied Current Density

Figures 2, 3 and 4 show the influence of applied current density on the decay of colour during electrochemical treatment of solutions containing with 190 mg L^{-1} of NB and RRB under different pH conditions (1, 4.5 and 8.0, respectively). As it can be observed in Figures 2, 3 and 4, the complete removal of colour, in all cases, was achieved. However, the elimination colour rate increases when the current density was increased (Figures 2, 3 and 4). This behaviour indicates dye degradation through its reaction with electrogenerated $^{\bullet}OH$ radicals on BDD surface (HATTORI et al. 2003; CAÑIZARES et al. 2006; FAOUZI et al. 2006; LAN et al. 2006). By contrast to the complete solutions decolourization, it seems that the decolourisation time mainly depends on the applied current density and pH conditions. The colour removal time for RRB and NB solutions decreases when the applied current density is increased (Figures 2, 3 and 4). However, at higher pH values (4.5 and 8), the decolourization time increases by about a factor of two (see Figures 3 and 4) compared to the time employed under lower pH values (pH 1) as showed in Figure 2a and 2b. This behaviour suggests that the elimination of dyes (NB and RRB) could be carried out by both direct electro-oxidation and mediated oxidation (hydroxyl radicals and other strong oxidants electro-generated from the oxidation of the supporting electrolyte) (CAÑIZARES et al. 2006; FAOUZI et al. 2006). Thus, it appears that the oxidation by the electro-generated reagents from the anodic oxidation plays an important role in the efficiency of the electrochemical process.

Figure 2. Influence of applied current density on the colour removal as a function of the time under acidic conditions (pH 1) during BDD-anodic oxidation of textile dyes: a) NB (pH 1) and b) RRB (pH 1). Operating conditions: dye concentration= 190 mg L^{-1}, Temperature T=25 °C, agitation rate: 400 rpm. Inset: Colour removal photographs during electrochemical processes at different current densities values.

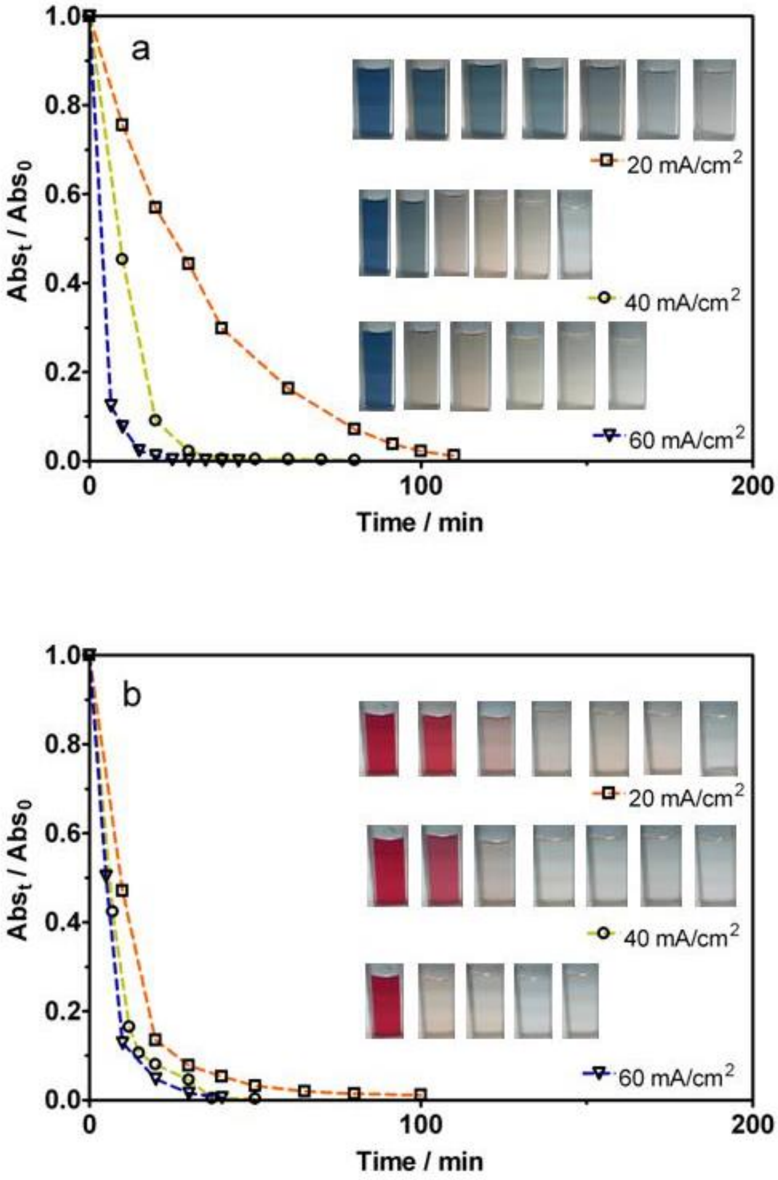
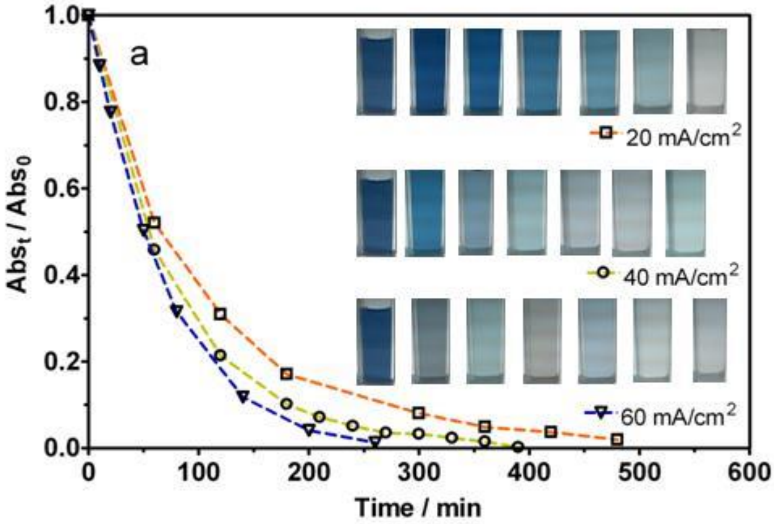


Figure 3. Influence of applied current density on the colour removal as a function of the time under acidic conditions (pH 4.5) during BDD-anodic oxidation of textile dyes: a) NB (pH 4.5) and b) RRB (pH 4.5). Operating conditions: dye concentration= 190 mg L^{-1}, Temperature T=25 °C, agitation rate: 400 rpm. Inset: Colour removal photographs during electrochemical processes at different current densities values.



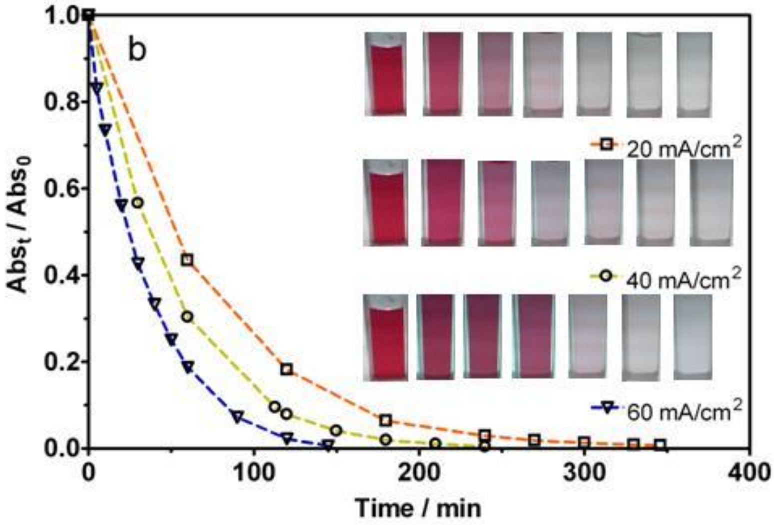
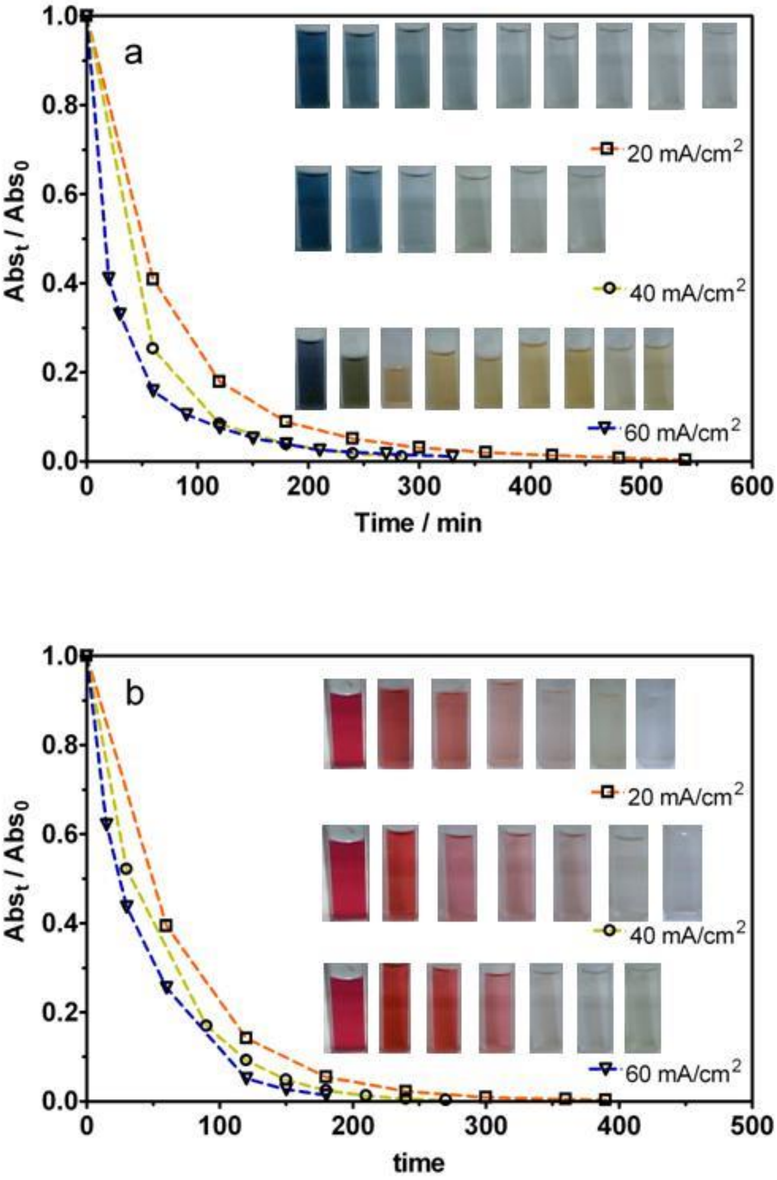


Figure 4. Influence of applied current density on the colour removal as a function of the time under alkaline conditions (pH 8.0) during BDD-anodic oxidation of textile dyes: a) NB (pH 8) and b) RRB (pH 8). Operating conditions: dye concentration= 190 mg L^{-1}, Temperature T=25 °C, agitation rate: 400 rpm. Inset: Colour removal photographs during electrochemical processes at different current densities values.



In the case of BDD anodes, $^{\bullet}OH$ radicals formed by water oxidation (equation 4) can be either electrochemically oxidized to dioxygen (equation 5) or contribute to the complete oxidation of the organic compounds, in this case, dyes (equation 6) (MARSELLI et al .2003; MARTINEZ-HUITLE et al. 2004; PANIZZA; CERISOLA, 2008; BENSALAH et al. 2009):

$$H_2O \rightarrow {}^{\bullet}OH + H^+ + 2e \qquad (4)$$

$$^{\bullet}\mathrm{OH} \rightarrow \frac{1}{2}\mathrm{O_2} + \mathrm{H^+} + e \quad (5)$$

$$\mathrm{dyes} \xrightarrow{^{\bullet}\mathrm{OH}} \mathrm{CO_2} + \mathrm{H_2O} \quad (6)$$

Other oxidants can be also formed at the diamond surface ($H_2S_2O_8$, O_3) (PANIZZA; CERISOLA, 2008; BENSALAH et al. 2009) and participate in the oxidation of the dye, in the proximity of the electrode surface and/or in the bulk of the electrolyte. Peroxodisulphates have been already demonstrated to be formed in solutions containing sulphates, during electrolysis using BDD electrodes (equation 7):

$$2\mathrm{SO_4}^{2-} \rightarrow \mathrm{S_2O_8}^{2-} + 2\mathrm{e}^- \quad (7)$$

These reagents are known to be very powerful oxidants and can oxidize organic matter leading to an increase in colour and COD removal rates (PANIZZA; CERISOLA, 2008). Therefore, in the NB and RRB electrochemical decolourisation, the decolourisation rate was higher at pH 1 than pH 4.5 and 8 (Figure 2a and 2b). This outcome is in agreement with the data reported by other authors during the anodic oxidation of dyes using BDD electrodes (FOUZI et al. 2006; PANIZZA; CERISOLA, 2008; BENSALAH et al. 2009).

6.4.3 Influence of pH and Dye Structure

As can be observed in Figure 2a and 2b (pH = 1), the influence of the chemical structure of the dye is evident. The electrochemical decolourisation of RRB seems independent on applied current density, whereas in the case of NB, the decolourisation rate was strongly dependent on applied current density, in which a faster colour removal was obtained at higher j values (40 and 60 mA cm^{-2}). In fact, the influence of the chemical structure of the dye and pH on the electrochemical decolourisation process has been confirmed by other authors. For example, Ammar et al. (2006) investigated the effects of current, dye concentration and pH on the electrochemical oxidation of 100 cm^3 of Indigo Carmine solutions with 0.05 M Na_2SO_4 at 35°C in a stirred undivided cell with a 3 cm^2 Si/BDD anode and a 3 cm^2 stainless steel cathode. A faster colour decay of the dye at pH 3.0 was observed with increasing current from 100 and 300 mA. However, the 220 mg dm^{-3} Indigo Carmine solution at 100 mA becomes colourless more quickly at pH 10.0 (120 min) than at pH 3.0 (270 min), because the electroactive species in alkaline medium (the unprotonated form) was more easily oxidized than that of acid medium (the diprotonated form). According to these results, the behaviour showed by anodic oxidation of NB and RRB dyes using BDD under acidic (Figures 2a and 2b) and alkaline (Figures 3 and 4) conditions can be explained by the dyes electroactive species present in solution because the electroactive species in more acidic medium are more easily oxidized than that of alkaline medium. Furthermore, this behaviour was confirmed by COD removal results under similar conditions, as explained below.

6.4.4 Hazen Colour

Textile industries employ specific methods for removing colour from wastewater (biological or physical chemical treatments) and, after that, decolourisation is followed by determining the Hazen colour (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, ISO 2211:1973). According to the Brazilian laws (INSTRUÇÃO NORMATIVA nº1 de 03/11/2004-IDEMA), the colour in the residual effluents from textile industry must be lower than 300 HU. Therefore, HU values were measured after electrochemical decolourisations treatment. As it can be observed from the results reported in Table 1, the total colour removal for each dyestuff solutions was achieved, attaining the Brazilian legal requirements (INSTRUÇÃO NORMATIVA nº1 de 03/11/2004-IDEMA). In fact, the 300 HU limit established by Brazilian regulations was achieved after short times (see, Table 1) or 50-60% of electrochemical treatment, as showed in photographs in Figures 2, 3 and 4. These findings suggest that the electrochemical treatment could be employed as an alternative for removing colour from industrial dye wastewaters.

Table 1. Hazen colour (HU; Pt-Co units' method) values into Brazilian laws for treated effluent, during anodic oxidation of RRB and NB at different applied current densities and pH values. Experimental conditions: Initial values of HU for NB and RRB were about 4000 and 26110, respectively; [dye concentration]$_0$=190 mg L^{-1}; Temp = 25°C, Electrolyte: 0.25 M Na_2SO_4.

Remazol Red BR (RRB)

Current density (mA cm^{-2})	**pH**	**Hazen Units**[a] **(Pt-Co units' method)**	**Decolourisation time (min)**[b]	**Decolourisation efficiency (%)**
20	1	330	40	90
40		320	15	94
60		325	15	95
20	4.5	310	160	85
40		305	100	90
60		295	75	95
20	8	315	180	89
40		290	140	94
60		289	92	96

Novacron Blue C-D (NB)

Current density (mA cm^{-2})	**pH**	**Hazen Units**[a] **(Pt-Co units' method)**	**Decolourisation time (min)**[b]	**Decolourisation efficiency**
20	1	285	60	90
40		300	20	95
60		298	12	98
20	4.5	321	240	89
40		311	150	93
60		304	120	97
20	8	309	240	90
40		290	150	92
60		298	135	95

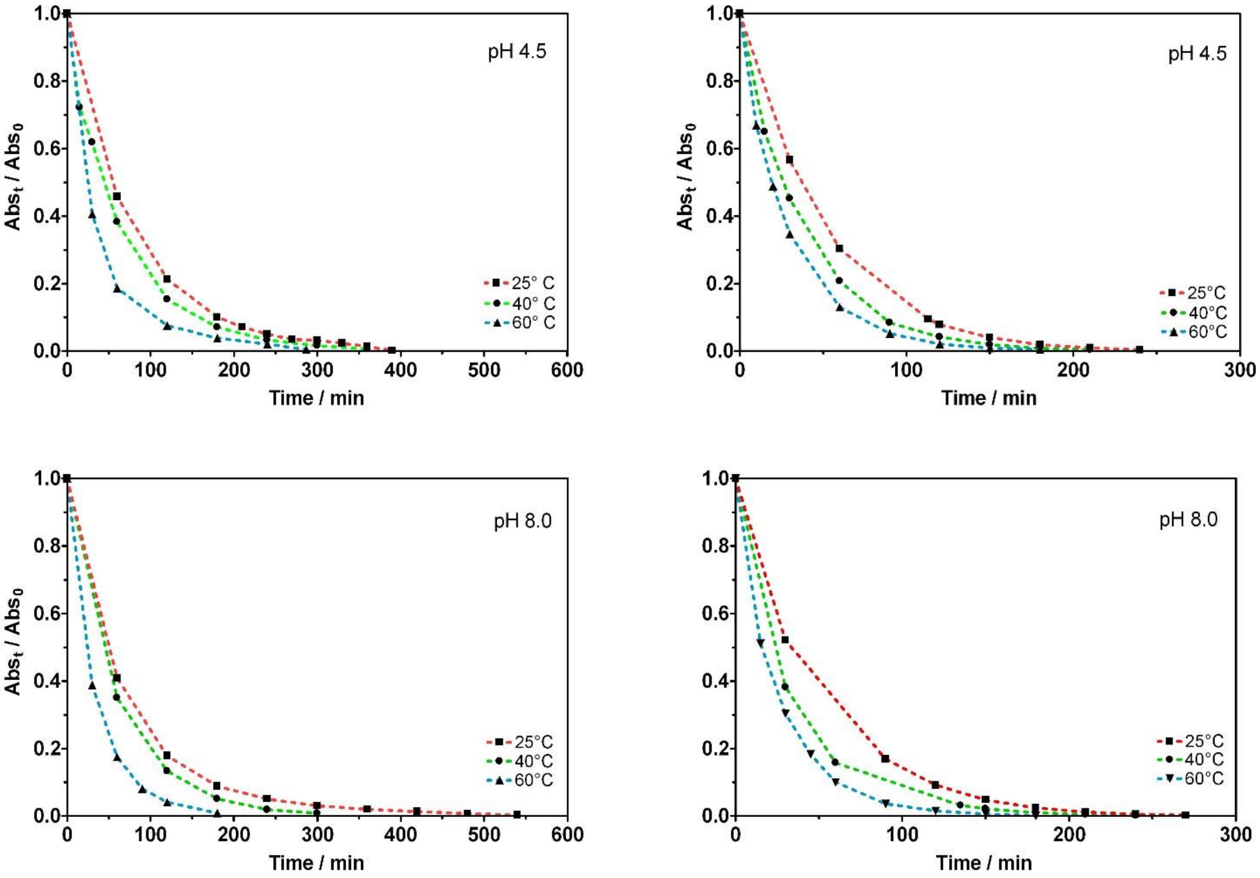
[a] HU values obtained after 60% of the total time used for decolourising the effluent.

[b] Decolourisation time necessary for diminishing from initial HU value to Brazilian limit.

6.4.5 Effect of Temperature

Figure 5 shows the influence of temperature on the colour decay, as a function of time, by applying 40 mA cm^{-2} of current density for removing NB and RRB under different pH conditions (pH 1 was not considered because the colour elimination was rapidly achieved at 25°C). As it can be seen, total colour removal was achieved in all cases. It seems that the temperature has a significant impact on the kinetics of the electrochemical oxidation of NB and RRB because the colour removal rate was considerably increased by increasing the temperature (from 25 to 40 or 60°C). The increase of temperature from 25 to 60°C decreases the electrolysis-time required for the total colour removal.

Figure 5. Influence of temperature on the evolution with time of colour removal during anodic oxidation of NB and RRB under acidic and alkaline conditions. Operating conditions: [dye concentration]$_0$=190 mg L^{-1}, Electrolyte: 0.5 M Na_2SO_4, j=40 mA cm^{-2}, Temperatures=25, 40 and 60 °C, agitation rate: 400 rpm.



6.4.6 Removal of the Chemical Oxygen Demand

Figures 6 and 7 show the variation of COD as a function of time for the experiments using BDD at different experimental conditions (current density, pH and temperature). In all cases, an almost complete COD removal was accomplished. Nevertheless, similarly to the decolourisation, the best conditions for COD removal were the higher current density (60 mA cm^{-2}) and higher temperature (60 ºC). Results clearly indicate that, an increase in the applied current density favours the oxidation rate and the eletrolysis-time increases when the pH is increased. This behaviour confirms that dye degradation is via its reaction with electrogenerated $^{\bullet}OH$ radicals on BDD surface (HATTORI et al. 2003; CAÑIZARES et al. 2006; FOUZI et al. 2006; FAN et al. 2006). On the other hand, as shown in Figure 7, the increase on the temperature from 25 to 60°C decreases the electrolysis-time required for the COD removal. These results are in agreement with the decolourisation ones.

Furthermore, the influence of dye structure was confirmed by COD decay at different applied current densities and pH conditions. As it can be observed from Figure 6, for anodic oxidation of NB at pH 1, the COD removal is dependent on applied current density. The COD removal rate increases when the current density is increased, while for the electrolysis of NB at pH 4.5 and 8, comparable behaviour of COD removal were observed. The lack of improvement of the COD removal rate is probably due to the lower concentration of electroactive species in more alkaline medium (less easily oxidized) than that of acidic medium.

Figure 6. Influence of applied current density (20, 40 and 60 mA cm^{-2}) on the COD removal, as a function of the time, during BDD-anodic oxidation of textile dyes: (a) pH 1 (b) pH 4.5 and (c) pH 8 for NB solution and (d) pH 1 (e) pH 4.5 and (f) pH 8 for RRB solution. Operating conditions: dye concentration= 190 mg L^{-1}, Temperature T=25 °C, agitation rate: 400 rpm.

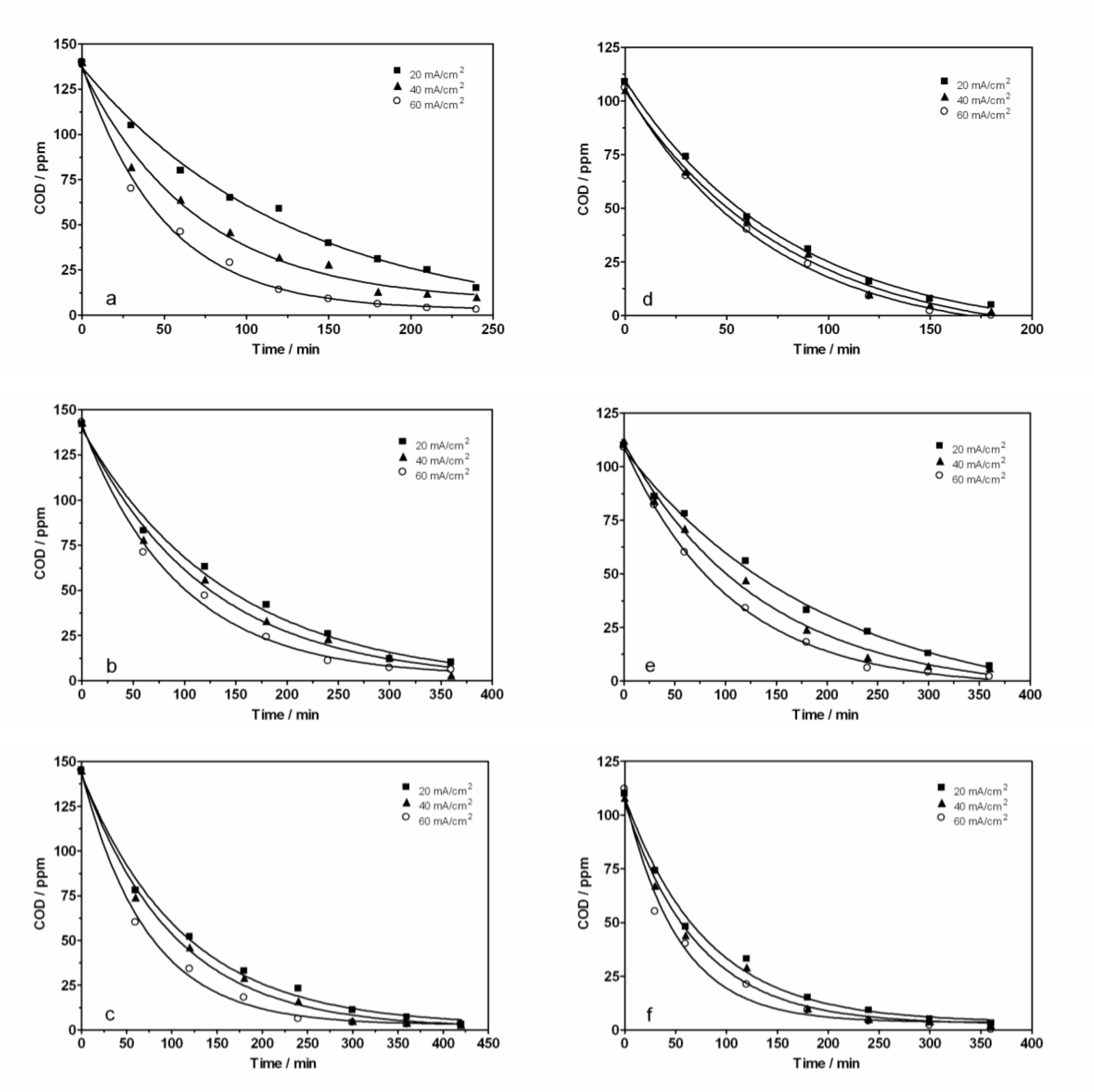
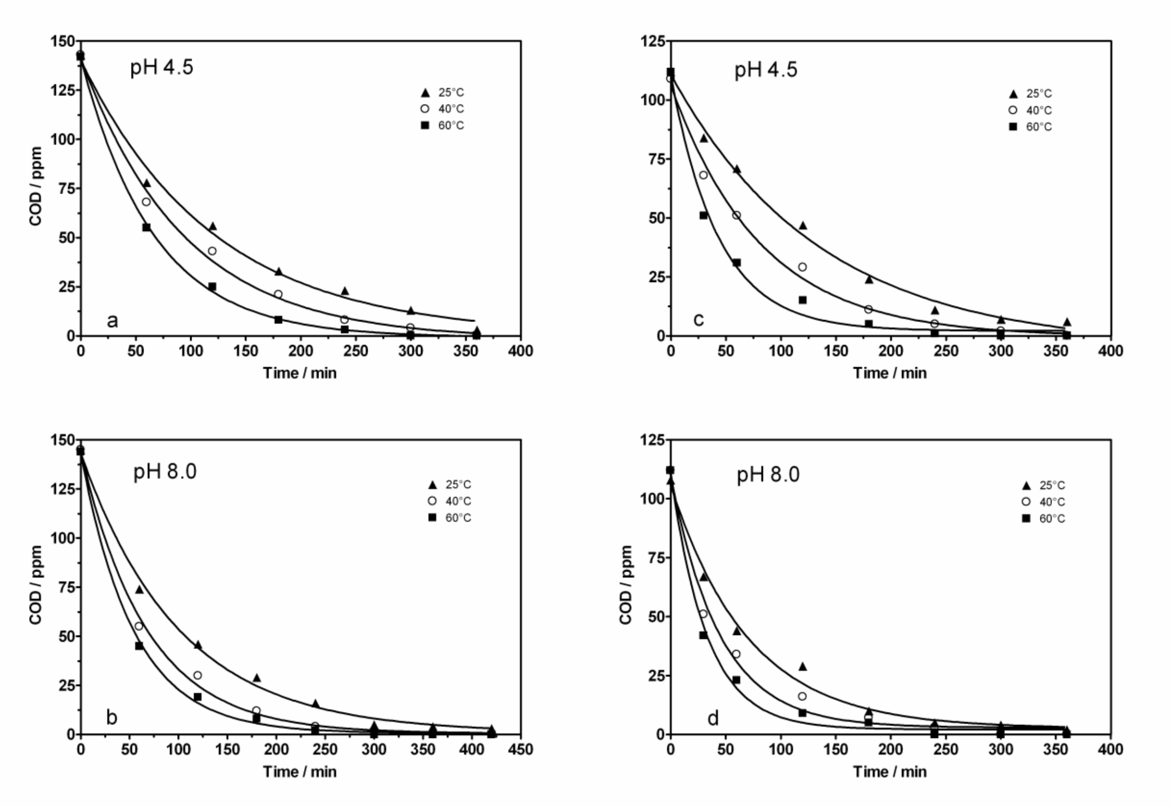


Figure 7. Influence of temperature on the evolution with time of COD removal during anodic oxidation of NB (a and b) and RRB (c and d) under acidic and alkaline conditions. Operating conditions: [dye concentration]$_0$=190 mg L^{-1}, Electrolyte: 0.5 M Na_2SO_4, j=40 mA cm^{-2}, Temperatures=25, 40 and 60 °C, agitation rate: 400 rpm.



6.4.7 By-Products Formation

The mass spectra recorded during electrochemical oxidation of NB dye at BDD anode material (50% of electrolysis time), showed m/z peaks at 136, 93 and 122 attributed to the formation of 4,4-N,N-dimethyl aniline, aniline and benzoic acid. The formation of these by-products confirms the chromophore group breaking, as indicated by UV spectrophotometric analysis. The solution after 150 min of electrolysis showed an additional m/z peak at 108 corresponding to the formation of hydroquinone. In the end of the process, mass spectrum showed m/z peaks at 46, 90 and 76 is due to the formation of simple aliphatic carboxylic acids like acetic, formic and oxalic acids.

In the case of electrochemical oxidation of RRB, a minor number of intermediates was detected, the sample solutions at 50% of decolourisation showed two m/z peaks at 138, 136 and 110 corresponding to the formation of 2-hydroxy benzoic acid, dimethyl aniline and 1,4-dihydroxy benzene, respectively. The attack of $^{\bullet}$OH radicals at the site of the azo bond results in the formation of above intermediates. In addition, the absence of the quasi-molecular ion of RRB is typical for sulphonic acid esters with an –O–SO_3H group, indicating a very strong fragmentation. After that, the spectra showed two m/z peaks at 94 and 122 corresponding to the formation of phenol and benzoic acid. The mass spectrum recorded at the end of the electrolysis showed m/z peaks at 46, 90 and 76 is due to the formation of simple aliphatic carboxylic acids like acetic, formic and oxalic acids.

The information obtained about by-products formed during NB and RRB degradation confirm the assumptions about the low COD depletion, in the final stages of electrolysis, that is due to the formation of several by-products, mainly aliphatic acids, decreasing the removal efficiency. Moreover, these data have shown the applicability of this electrochemical technology for the treatment of NB and RRB dyes solutions without formation (at the end of the electrochemical process) of more dangerous compounds, with release of SO_4^{2-}, NH_4^+, and NO_3^- ions.

6.4.8 Energy Consumption and Cost Estimation

Key points for the development of clean methodologies are the energetic and economic aspects: to make predictions, even if only indicative, about these aspects, allows indications about the feasibility of the process. Table 2 presented the energy consumption required to remove 99% of the dye colour under different experimental conditions. As it can be observed, during the electrolyses of solutions containing NB and RRB, the energy consumption has an increase relatively proportional to the applied current density. For example, for RRB at pH 1, it increases from 3.30 to 4.28 kWh per volume of treated effluent (m^3) when the current density increases from 20 to 60 mA cm^{-2}. Table 2 also compares the energy consumption during anodic oxidation under different pH conditions for NB and RRB dyes, showing that electrochemical decolourisation depends on the pH conditions. For example for RRB:

- at pH 1 it increases from 3.30 kWh m^{-3} at 20 mA cm^{-2} to 4.28 kWh m^{-3} at 60 mA cm^{-2};
- at pH 4.5 it increases from 17.25 kWh m^{-3} at 20 mA cm^{-2} to 28.87 kWh m^{-3} at 60 mA cm^{-2};
- at pH 8 it increases from 13.50 kWh m^{-3} at 20 mA cm^{-2} to 37.80 kWh m^{-3} at 60 mA cm^{-2}.

Table 2. Energy consumption calculated from Eq. 3, per volume of treated effluent (m^3) during decolourisation of RRB and NB for different applied current densities and pH values. [dye concentration]$_0$=190 mg L^{-1}, Electrolyte: 0.25 M Na_2SO_4. Temp = 25°C.

Remazol Red BR (RRB)				
Current density ($mA\ cm^{-2}$)	**pH**	**Energy consumption ($kW\ h\ m^{-3}$)**	**Decolourisation time (min)[a]**	**Cost (Dollar(real)[b])**
20	1	3.30	80	0.8 (1.3)[a]
40		3.98	37	0.9 (1.6)[a]
60		4.28	30	1.0 (1.8)[a]
20	4.5	17.25	300	4.1 (7.2)[a]
40		26.25	210	6.2 (11.0)[a]
60		28.87	140	6.8 (12.1)[a]
20	8	13.50	300	3.2 (5.6)[a]
40		34.20	240	8.0 (14.3)[a]
60		37.80	180	8.9 (15.9)[a]

Novacron Blue C-D (NB)				
Current density ($mA\ cm^{-2}$)	**pH**	**Energy consumption ($kW\ h\ m^{-3}$)**	**Decolourisation time (min)[a]**	**Cost (Dollar(real)[b])**
20	1	4.95	110	1.2 (2.0)[a]
40		4.40	40	1.0 (1.8)[a]
60		4,13	25	0.9 (1.7)[a]
20	4.5	18.90	420	4.4 (7.9)[a]
40		45.00	360	10.6 (18.9)[a]
60		57.52	260	13.5 (24.2)[a]
20	8	21.93	450	5.1 (9.2)[a]
40		36.75	300	8.6 (15.4)[a]
60		52.65	260	12.4 (22.1)[a]

- [a] *99% of decolourisation*
- [b] *Brazilian currency (reais – R$)*

It is important to remark that, opposite effects were observed only for decolourisation of NB under acidic conditions (pH=1); energy consumption decreased when applied current density increased. It suggests that the process is probably affected by an influence of the chemical structure, since the electrical potential considerably increased, while the treatment time decreased. This is the reason, for the clear increase in energy consumption to the decolourisation process for NB at pH 4.5 and 8 (Table 2) respect to RRB. Similar energy estimations were also reported in Table 3 for the effect on temperature under different pH conditions, showing that while the temperature increases, energy consumption decreases substantially.

On the contrary, energy consumptions and costs process for COD removal are higher than decolourisation treatment, as showed in Table 4, due to the increase in the time and incomplete COD elimination in some cases. These results indicate that EO is unfeasible for practical applications as the only treatment process of textile dye solutions. However, these performances on COD removal efficiencies (Figures 6 and 7) suggest the possibility to use the EO as refining technology in an integrated process and/or coupled with other advanced oxidation processes.

Finally, taking into consideration an electrical energy cost of about R$ 0.42 (R$ = Brazilian currency (Real); Brazilian price taxes excluded) per kWh (Agência Nacional de Energia Elétrica, Brazil), the process expenditure was estimated and reported in Tables 2, 3 and 4 in order to show the viability of this process as an alternative for treatment of dyestuffs. This price was also converted to dollar and reported in Tables 2, 3 and 4.

Table 3. Energy consumption calculated from Eq. 3, per volume of treated effluent (m^3) during decolourisation of RRB and NB for different temperatures and pH values. Experimental conditions: [dye concentration]$_0$=190 mg L^{-1}, current density = 40 $mAcm^{-2}$; Electrolyte: 0.25 M Na_2SO_4.

Remazol Red BR (RRB)

pH	**Temperature (°C)**	**Energy consumption (kW h m^{-3})**	**Decolourisation time (min)**	**Cost (Dollar(real)[a])**
4.5	25	26.25	210	6.2 (11.0)[a]
	40	18.00	180	4.2 (7.5)[a]
	60	12.30	120	2.9 (5.1)[a]
8.0	25	34.20	240	8.0 (14.3)[a]
	40	17.25	150	4.0 (7.2)[a]
	60	11.91	120	2.8 (5.0)[a]

Novacron Blue C-D (NB)

pH	**Temperature (°C)**	**Energy consumption (kW h m^{-3})**	**Decolourisation time (min)**	**Cost (Dollar(real)[a])**
4.5	25	45.00	360	10.6 (18.9)[a]
	40	31.50	300	7.4 (13.2)[a]
	60	26.40	240	6.2 (11.1)[a]
8.0	25	36.75	300	8.6 (15.4)[a]
	40	31.88	250	7.5 (13.3)[a]
	60	17.25	150	4.1 (7.24)[a]

[a] *Brazilian currency (reais – R$)*

Table 4. Energy consumption and cost, as a function of COD removal, during anodic oxidation of NB and RRB solutions for different applied current densities and pH conditions. [dye concentration]$_0$=190 mg L^{-1}, Electrolyte: 0.25 M Na_2SO_4.

Novacron Blue C-D (NB)

pH	**Time (min)[a]**	**Energy consumption (kW h m^{-3})**	**Cost (Dollar (real)[b])**	**% COD removal**
1[c]	240	10.8	4.5 (4.5)[b]	89.28
1[d]	240	20.4	10.2 (11.1)[b]	92.85
1[e]	240	39.1	16.2 (14.7)[b]	97.85
4.5[c]	360	16.2	3.8 (6.8)[b]	92.95
4.5[d]	360	45.0	10.6 (18.9)[b]	97.88
4.5[e]	360	79.6	18.7 (33.5)[b]	98.59
8[c]	420	20.4	4.8 (8.6)[b]	97.93
8[d]	420	51.4	12.1 (21.6)[b]	98.62
8[e]	420	85.0	20.1 (35.7)[b]	98.62

Remazol Red BR (RRB)

pH	**Time (min)[a]**	**Energy consumption (kW h m^{-3})**	**Cost (Dollar (real)[b])**	**% COD removal**
1[c]	180	7.4	1.7 (3.1)[b]	95.41
1[d]	180	19.3	4.5 (8.1)[b]	98.16
1[e]	180	25.6	6.0 (10.8)[b]	100.00
4.5[c]	360	20.7	4.8 (8.7)[b]	93.63
4.5[d]	360	45.0	10.6 (18.9)[b]	94.54
4.5[e]	360	74.2	17.5 (31.2)[b]	98.18
8[c]	360	16.2	3.8 (6.8)[b]	97.27
8[d]	360	51.3	12.1 (21.5)[b]	98.18
8[e]	360	75.6	17.8 (31.7)[b]	100.00

[a] *Electrolysis times obtained from Figure 6.*

[b] *Brazilian currency (reais – R$).*

[c] *20 mA cm^{-2}.*

[d] *40 mA cm^{-2}.*

[e] *60 mA cm^{-2}.*

6.5 CONCLUDING REMARKS

The main conclusions of this work can be summarized in the following points:

(i) BDD-anodic oxidation can be used successfully to remove completely all colour and COD from wastewaters polluted with textile dyes, considering the specific operating conditions (current density, pH and temperature).

(ii) The influence of current density, temperature and pH as functions of time, during galvanostatic electrolyses of dye wastewaters, showed that oxidation by the electro-generated reagents from the anodic oxidation of supporting electrolyte (e. g.: $^{\bullet}OH$ and peroxodisulphates) plays an important role in the efficiency of the electrochemical process.

(iii) Energy consumption measured during galvanostatic electrolyses of dye solutions depends largely on the applied current density but is only modestly influence by temperature. Perhaps, the energy consumption makes anodic oxidation uncompetitive for complete elimination of wastewaters polluted with dyes (complete COD removal, see Table 4), but it could still be feasible as a pre-treatment process for decolorizing wastewaters (see, Tables 2 and 3).

Further experiments are in progress in order to demonstrate the applicability of electrochemical technologies for removing dyes contamination from real effluents using diamond electrodes and these figures will be reported in the near future.

6.6 ACKNOWLEDGEMENTS

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CAPÍTULO 7

7 ELECTROCHEMICAL TECHNOLOGY FOR REMOVING PETROLEUM HYDROCARBONS FROM PRODUCED WATER

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7.1 ABSTRACT

Produced water is the largest waste stream generated in oil and gas industries. It is a mixture of different organic and inorganic compounds. Due to the increasing volume of waste all over the world in the current decade, the outcome and effect of discharging produced water on the environment has lately become a significant issue of environmental concern. Produced water 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, current technologies cannot remove small suspended oil particles and dissolved elements. For these reasons, major research efforts in the future could focus on the optimization of current technologies for treating produced water in order to comply with reuse and discharge limits. Recently, electrochemical technologies are a promising alternative for the treatment of this kind of wastewaters containing inorganic/organic pollutants. Thus, this paper presents a review of efficient electrochemical technologies developed to remove petroleum hydrocarbons from produced water generated by petrochemical industry.

7.2 INTRODUCTION

7.2.1 Petrochemical Industry

The significance of oil and natural gas in modern civilization is well known. Nevertheless, like most production activities, oil and gas production processes generate large volumes of liquid waste. Oilfield wastewater or produced water contains various organic and inorganic components. Discharging produced water can pollute surface and underground water and soil (AHMADUNA et al. 2009).

The permitted oil and grease (O&G) limits for treated produced water discharge offshore in some countries are around 30mg/L (milligram per liter) daily average and 50 mg/L instantaneous (USEPA). As regards the significant matter of environmental concern, many countries have implemented more stringent regulatory standards for discharging produced water. On the other hand, because large volumes of produced water 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.

7.2.2 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 “produced water” when saline water mixed with hydrocarbons comes to the surface (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 produced water (EKINS et al. 2007). Then, produced water is considered to be one of the largest waste streams in the petroleum, oil and gas industry.

7.2.2.1 Characteristics of Produced Water

Some factors such as geological location of the field, its geological formation, lifetime of its reservoirs, and type of hydrocarbon product being produced affect the physical and chemical properties of produced water (VEIL et al. 2004; AHMADUNA et al. 2009). Produced waters 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 produced water from different sources can vary by order of magnitude. However, produced water composition is qualitatively similar to oil and/or gas production (FILLO et al. 1992). The major compounds of produced water include: (i) Dissolved and dispersed oil compounds (a mixture of hydrocarbons including benzene, toluene, ethylbenzene, and xylenes (BTEX), naphthalene, phenantherene, 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 (HANSEN et al. 1994).

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 produced water (prior to treatment) depend on several factors (HANSEN et al. 1994; AHMADUNA et al. 2009).

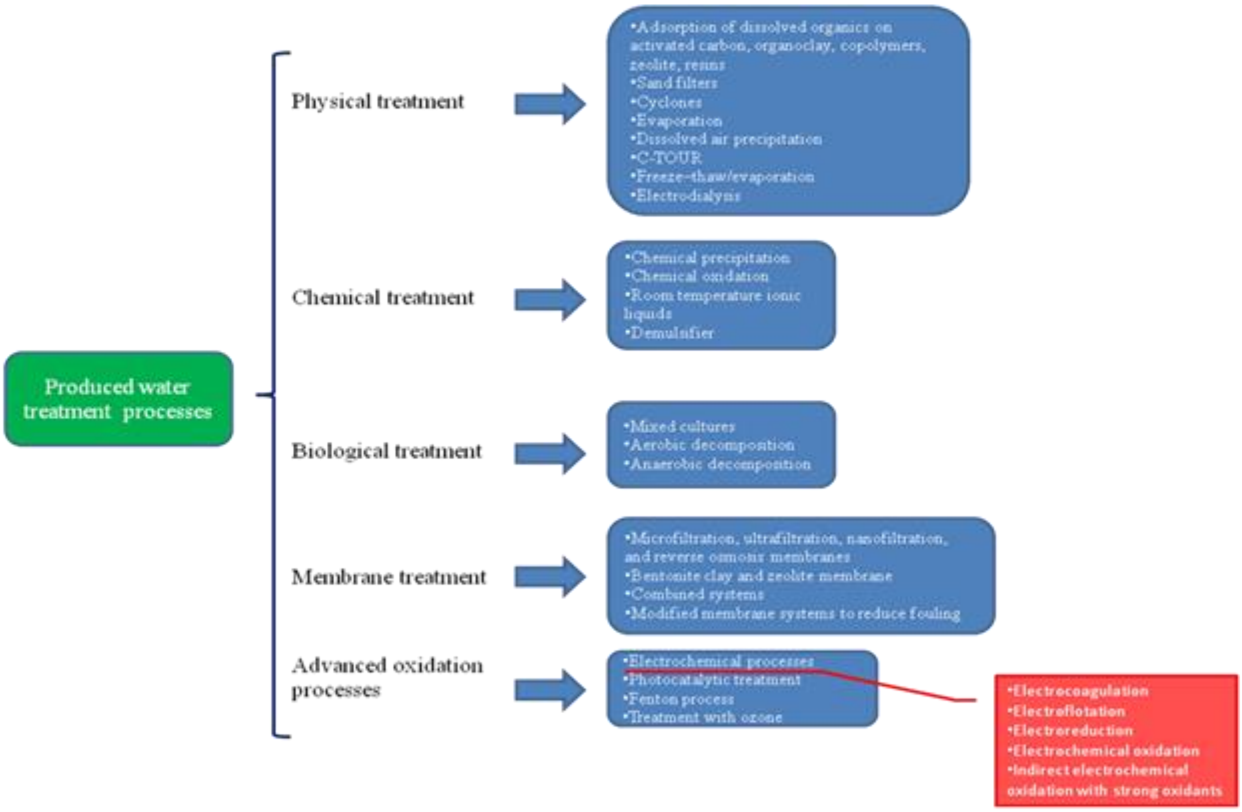
7.2.2.2 Impact of Produced Water Discharge

Produced water from oil and gas industries often is permitted to be discharged to the environment. Water’s toxicity and organic loading can generally characterize the impact of discharging produced water into the sea. Effects of produced water components on the environment are [1]: (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.

7.2.3 Treatment of Produced Water

In order to meet environmental regulations as well as reuse and recycling of produced water, many researchers have focused on treating oily saline produced water. Oil content and salinity of produced water from offshore and onshore activities can be reduced through various physical, chemical, and biological methods. 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. On the other hand, biological treatment is a cost-effective method for removing dissolved and suspended compounds from oilfield wastewater in onshore extraction facilities. Therefore, considerable studies have been conducted to investigate new treatment technologies in order to remove the pollutants from produced water. Fig. 1 summarizes the main technologies utilized for the removal of these pollutants. An extensive literature reporting the characteristics and applications of most important conventional technologies developed for this purpose including physico-chemical and chemical methods, advanced oxidation processes (AOPs), microbiological treatments and biological decomposition, has been collected in an authoritative review (AHMADUNA et al. 2009).

Figure 1. Main methods used for the removal of organic dyes from produced waters.



In contrast, only little information on the interest of electrochemical technologies for destroying petrochemical pollutants from water has been shown in some segregate scientific studies in the last years (RAJKUMAR et al. 2004; LI et al. 2006; SANTOS et al. 2006; MA et al. 2006; LIMA et al. 2009; ABDELWAHAB et al. 2009; TRAN et al. 2009a; TRAN et al. 2009b), without considering the recent advances of these promising methods, mainly developed in this year (TRAN et al. 2010; KÖRBAHTi et al. 2010; YAVUS et al. 2010; ZANBOTTO RAMALHO et al. 2010). Therefore, a general overview of lab and pilot plant experiments related to the most relevant applications of all these electrochemical methods for removing petroleum hydrocarbons from produced waters will be presented.

7.2.4 Electrochemistry for Environment

Electrochemistry, as a branch of physical chemistry plays an important role in most areas of science and technology. Electrochemistry offers promising approaches for the prevention of pollution problems in the process industry. The inherent advantage is its environmental compatibility, due to the fact that it uses a clean reagent, the electron

(RAJESHWAR et al. 1994; MARTINEZ-HUITLE; FERRO, 2006). The advantages of electrochemistry such as versatility, energy efficiency, amenability to automation, environmental compatibility and cost effectiveness have reached a promising stage of development and can now be effectively used for the destruction of toxic or biorefractory organics (MARTINEZ-HUITLE; FERRO, 2006; MARTINEZ-HUITLE; BRILLAS, 2009).

For the above reasons, 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.

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 the removal of petroleum pollutants from wastewaters (Fig. 1). 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 produced water.

7.2.4.1 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. 2009a). 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, as will be detailed below. An example is the elimination of polycyclic aromatic hydrocarbons (PAHs) (TRAN et al. 2009a; TRAN et al. 2009b; 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.

7.2.4.2 Electrocoagulation

A traditional physico-chemical treatment of phase separation for the decontamination of petroleum hydrocarbons wastewaters before discharge to the environment is coagulation. It consists in the addition of coagulating agents such as Fe^{3+} or Al^{3+} ions, usually in the form of chlorides, for organic pollutants precipitation. The electrochemical technology can produce similar effects by means of the EC method. This technique uses 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. These species act as coagulants or destabilization agents that bring about charge neutralization for organic pollutants separation from the wastewater. The coagulated particles can also be separated by electroflotation when they are attached to the bubbles of H_2 gas evolved at the cathode and transported to the top of the solution where they can be separated. In general, the following main processes take place during an EC treatment (MARTINEZ-HUITLE; BRILLAS, 2009):

(i) Electrode reactions to produce metal ions from Fe or Al anodes and H_2 gas at the cathode,
(ii) formation of coagulants in the wastewater,
(iii) removal of pollutants with coagulants by sedimentation or by electroflotation with evolved H_2,
(iv) other electrochemical and chemical reactions involving reduction of organic impurities and metal ions at the cathode and coagulation of colloidal particles.

Many advantages for EC have been reported (MARTINEZ-HUITLE; BRILLAS, 2009):
(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.

However, this method presents as major 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 aluminium ions in the effluent that have to be removed.

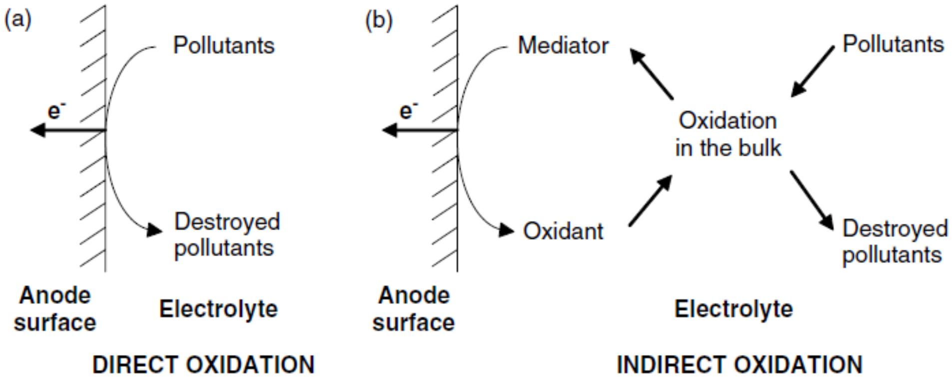
Apart from the electrolytic system and anode material used, petrochemical hydrocarbons removal mainly depends on solution pH, retention time (tr), stirring or flow rate and applied current density (or cell voltage) (MA et al. 2006; ABDELWAHAD et al. 2009; YAVUZ et al. 2010). For example, EC process of 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 met the discharged standards after 2 h EC time with energy consumption of 1.8 kWh g^{-1} phenol and electrode consumption 0.091 gAl g^{-1} phenol. On the other hand, Ma et al. (2006) and Yavuz et al. (2010), studied combinated EC and EO processes. In the first case, oil field produced water by separated with crude oil were treated by an electrochemical process in laboratory pilot-scale plant, using double anodes with active metal (M) and graphite (C) and iron as cathode and a noble metal content catalyst with big surface. Due to the strong oxidizing potential of the chemicals produced and coagulants produced, when the wastewater pass through the laboratory pilot-scale plant the organic pollutants including bacteria 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%, Ca^{2+} 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 (YAVUZ et al., 2010), 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.

7.2.4.3 Electrochemical Oxidation

EO is the most popular electrochemical technology for removing organic pollutants from wastewaters (RAJESHWAR et al. 1994; MARTINEZ-HUITLE; FERRO, 2006; MARTINEZ-HUITLE; BRILLAS, 2009). This technique has been recently used for decolorizing and degrading dyes from aqueous solutions. It consists in the oxidation of pollutants in an electrolytic cell by (Figure 2):

(i) Direct anodic oxidation (or direct electron transfer to the anode), which yields very poor decontamination.
(ii) Chemical reaction with electrogenerated species from water discharge at the anode such as physically adsorbed “active oxygen” (physisorbed hydroxyl radical ($^{\bullet}OH$)) 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.

Figure 2. Schemes for (a) EO and (b) IEO treatment of pollutants..



Fonte: Adapted from Zanbotto Ramalho et al., 2010

The existence of indirect or mediated oxidation with different heterogeneous species formed from water discharge has allowed the proposal of two main approaches for the pollution abatement in wastewaters by EO (MARTINEZ-HUITLE; FERRO, 2006):

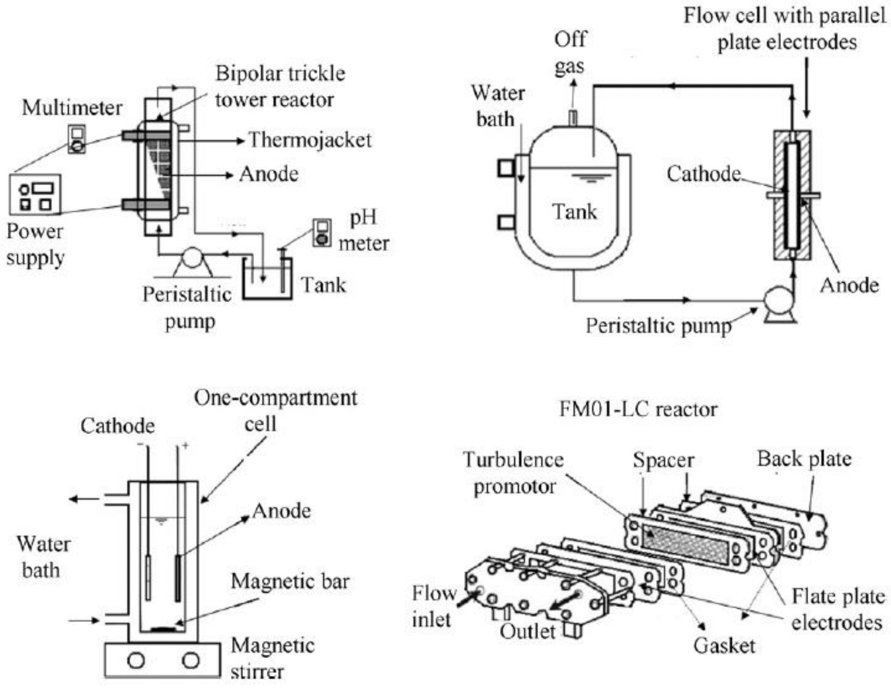
(i) The electrochemical conversion method, in which refractory organics are selectively transformed into biodegradable compounds, usually carboxylic acids, with chemisorbed “active oxygen”.

(ii) The electrochemical combustion (or electrochemical incineration) method, where organics are completely mineralized, i.e., oxidized to CO_2 and inorganic ions, with physisorbed $^{\bullet}OH$. This radical is the second strongest oxidant known after fluorine, with a high standard potential (E^o = 2.80 V vs. SHE) that ensures its fast reaction with most organics giving dehydrogenated or hydroxylated derivatives up to conversion into CO_2.

In both cases significant cell voltages are applied to the electrochemical cell for the simultaneous oxidation of pollutants and water, thus maintaining the anode activity. The use of low cell voltages avoiding O_2 evolution frequently causes the loss of anode activity because some by-products formed from direct anodic oxidation can be adsorbed on its surface. However, the nature of the anode material influences strongly both the selectivity and efficiency of the EO process.

Figure 3 illustrates some electrochemical plants and cells designed for this technique operating in batch mode up to attain the maximum solution decontamination. A good design of these reactors allows optimizing the mass transport coefficient for reaching the maximum current efficiency. The most important experimental parameters measured in EO are the abatement of COD and/or TOC accounts for by the percentage of degradation or mineralization achieved. The latter data are also used to obtain simple current and energetic efficiency parameters that characterize the EO process.

Figure 3. Sketches of electrochemical plants and cells used in electro-oxidation for removing dyes in batch operation mode: bipolar trickle tower reactor, one-compartment cell with parallel plate electrodes, stirred two-electrode one-compartment tank reactor with a jacket for external thermostatization and filterpress flow cell (FM01-LC reactor).



It is important to nothing that, high dissolved concentrations of NaCl are found in produced waters; then, 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 (IEO).

7.2.4.4 Indirect Electro-oxidation with Strong Oxidants

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).

(ii) The EF process in which organics can be mineralized with homogeneous $^{\bullet}OH$ 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 $^{\bullet}$OH and other reactive oxygen species and weaker oxidants produced from anodic oxidation of water and anions of the wastewater (MARTINEZ-HUITLE; FERRO, 2006; MARTINEZ-HUITLE; BRILLAS, 2009; YAVUZ et al. 2010; ZANBOTTO RAMALHO et al. 2010). 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. Analogous electrochemical systems (Figure 3) to those reported above for EO are utilized in the IEO treatment of petrochemical hydrocarbons effluents with active chlorine.

7.2.4.5 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 et al. 2004; SANTOS, et al. 2006; LIMA et al. 2009; TRAN et al. 2009a; TRAN et al. 2009b; TRAN et al. 2010; KÖRBAHTI et al. 2010; YAVUZ et al. 2010). Table 1 summarizes the most relevant results obtained for the degradation of petroleum hydrocarbons by EF, direct and indirect EO process. An inspection of Table 1 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 $Ti/Ru_{0.34}Ti_{0.66}O_2$ 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 O_2, Cl_2 and H_2 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 (COD_0=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%.

Table 1. Percentage petroleum pollutants removals and energy consumption determined for the EO, IEO and EF with different anodes of selected petrochemical wastewaters.

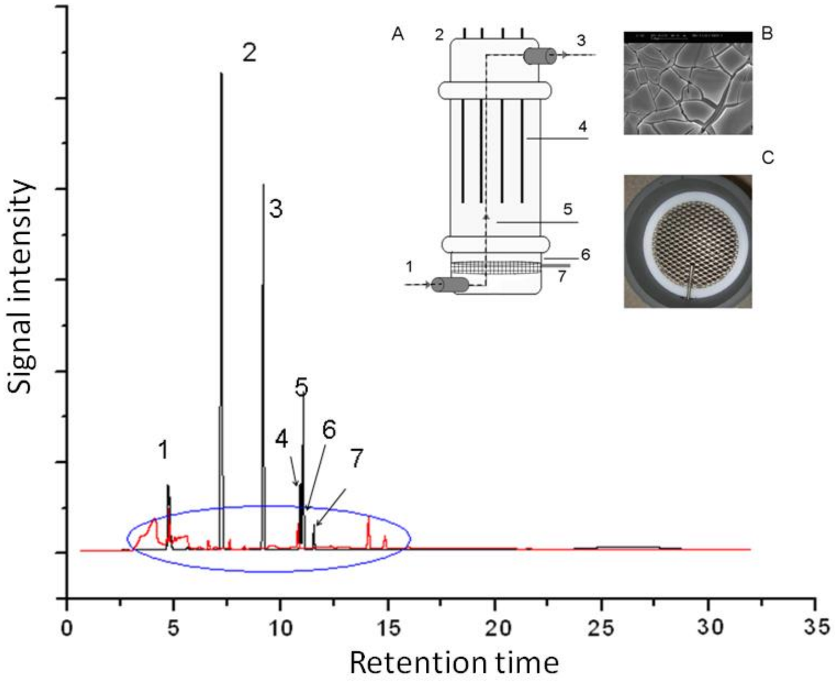
Anode used* wastewater	**C_0 / mg dm^{-3}**	**j^d / mA cm^{-2}**	**Electrolysis time / h**	**Current efficiency/ %**	**COD decay / %**	**Energy consumption/ Cost**	**Ref.**
Ti/TiO$_2$-RuO$_2$-IrO$_2$ Oil refinery	602^a 141^b 112^c	54	20^d	7.5	92	105.8 kWh m^{-3}	Rajkumar, et al., 2004
Ti/Ru$_{0.34}$Ti$_{0.66}$O$_2$ Oil extraction industry	315a 887c	100	70	5	57	$-^f$	Santos et al., 2006
Ti/RuO$_2$-TiO$_2$ Produced water	103^g 1.8^b	8.6-17.8	2	65	99^h	$-^f$	Lima et al., 2009
Ti/RuO$_2$ Creosote oil solution containing PAHs	2102^a 237^i	9.23	1.5	70	61 26^j	42 kWh m^{-3}	Tran et a., 2009a
Industry waste containing PAHs	18440-7709^k	9.23	1.5 6.5	67 100	65-95^l	1680-735 kWh t^{-1}	Tran et al., 2009b
Amphoteric surfactant solution containing PAHs	418^k	4-13	1.5	45	80-82^l	5.11 US$ m^{-3}	Tran et al., 2010
Pt/Ir Bilge water (seawater + petroleum pollutants)	3080a 23916b	12.8	4	79	85-100	13.9-50.9 kWh kg^{-1}	Körbahti and Artut, 2010
Nb/BDD Petroleum refinery (EO process)	590a 193c	5	1	90 100	96 99^m	4 kWh g^{-1}	Yavuz et al., 2010
							Yavuz et

	590a	3	1	90	95	2 kWh g^{-1}	al., 2010
Petroleum refinery	193b				98^{m}		
(IEO process)	1775c						
							Yavuz et
Iron	590a	1	0.25	70	98	0.15 kWh g^{-1}	al., 2010
Petroleum refinery	193b				75^{m}		
(EF process)							Yavuz et
	590b	20	3.5	76	70	7 kWh g^{-1}	al., 2010
Ru mixed metal oxide	193c				94^{m}		
Petroleum refinery							

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

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/cm^2 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/cm^2. However, an only application of EO for removing petroleum hydrocarbons from produced water has been reported. Zanbotto Ramalho et al. (2010) studied the anodic oxidation of organic pollutants from produced water generated by petroleum exploration of the Petrobras plant-Brazil using an electrochemical reactor with a $Ti/RuO_2–TiO_2–SnO_2$ electrode (Inset Figure 4). Under galvanostatic conditions ($j = 89$ 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), as observed from Figure 4. Importantly, 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 (kWh m^{-3}) ranging from 4.84 to 0.97 and removal prices from 1.41 to 0.28 (Brazil currency: R$ (real)).

Figure 4. Organic pollutants removal from produced water by controlled current density electrolysis (89 mA cm^{-2}): initial sample (black line) and after EO process (red line). Experimental conditions: T = 25 °C; electrode area 19 cm^2, NaCl: 15,000 g dm^{-3}, pH: 6.86, flow rate: (A) 0.25 dm^3/h. Symbols: (1) phenol; (2) benzene; (3) toluene; (4) ethyl benzene; (5) *o*-xylene; (6) *m*-xylene and (7) *p*-xylene. Produced water samples contain approximately 20–30 mg dm^{-3} of benzene, toluene, ethyl benzene, xylenes, and 5 mg dm^{-3} of phenol. Inset: (A) electrochemical reactor: (1) electrolyte inlet; (2) cathodic electric contacts; (3) electrolyte outlet; (4) stainless steel AISI 304 bars as cathodes; (5) flow direction; (6) anode and (7) electric anode contact. (B) MeV image of Ti/RuO_2–TiO_2–SnO_2 anode. (C) Image of mesh anode.



7.2.4.6 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) (YAVUZ et al., 2010; LI et al., 2006; LI et al., 2007). Li et al. (2006) found that the COD removal efficiency of produced water by PEC process was much higher than that of by photocatalytic or EO. Li et al. (2007) also compared treatment of produced water 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).

7.3 CONCLUDING REMARKS

Electrochemical technologies to remove organic pollutants from produced waters 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 produced waters 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 electrochemical technologies could be applied to reduce the environmental disaster as occurred in Mexico Gulf with the oil massive spill.

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CAPÍTULO 8

8 APPLICATION OF ELECTROCHEMICAL OXIDATION AS ALTERNATIVE TREATMENT OF PRODUCED WATER GENERATED BY BRAZILIAN PETROCHEMICAL INDUSTRY

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8.1 ABSTRACT

This paper presents the anodic oxidation of real produced water, generated by petroleum exploration of the Petrobras plant-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 has been studied and the energy consumption has been also evaluated. Galvanostatic electrolyses at BDD lead to complete COD removal (98%) due to the high amounts of effective hydroxyl radicals and peroxodisulphates generated from water oxidation and the COD removal rate increases with rising applied current (from 15 to 60 $mAcm^{-2}$). Conversely, at Pt electrode, about 50% of COD removals were achieved by applying 15 and 30 $mAcm^{-2}$ of current density, and 80% of COD removal at 60 $mAcm^{-2}$. Although, the energy consumption and process time 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.

Keywords: Produced water. Water treatment. Electrochemical oxidation. Petrochemical pollution.

8.2 INTRODUCTION

Produced water (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. 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 (AHMADUNA et al. 2009; USEPA). 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 produced water 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).

The amount of PW generated varies during oil production: a new field produces 5–15 vol. %, while at the end of its lifetime; it reaches 75–90 vol. % (veil et al.,2004). PW is a serious environmental problem, and in offshore areas the discharge is made directly into the sea, being the most harmful effect associated to the compounds that remain soluble in water. Therefore, considerable studies have been conducted to investigate new techniques in order to remove these compounds from contaminated environments.

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) (MARTINEZ-HUITLE; FERRO, 2006; SÄRKKÄ et al. 2008; MARTINEZ-HUITLE; BRILLAS, 2009; PANIZZA; CERISOLA, 2009; BRILLAS et al. 2009; ZHOU et al. 2011). In this context electrochemical methods can be a promising alternative to traditional processes for the treatment of petrochemical wastewaters. So far, many papers reported that electrochemical treatment has been applied successfully for the complete oxidation of various organic pollutants, including surfactants, oils, grease, gasoline residues (MARTINEZ-

HUITLE; FERRO, 2006; PANIZZA; CERISOLA, 2009). 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 (MARTINEZ-HUITLE; FERRO, 2006; MARTINEZ-HUITLE; BRILLAS, 2009; PANIZZA; CERISOLA, 2009); obtaining different removal organic matter efficiencies.

In the case of applicability of electrochemical technology for treating petrochemical wastewaters (synthetic or real wastewaters), a limited number of reports have published (RAJKUMAR et al. 2004; SANTOS et al. 2006; MA et al. 2006; LIMA et al. 2009; ABDELWAHAD et al. 2009; TRAN et al. 2009a; TRAN et al. 2009b; TRAN et al. 2010; KÖRBAHTI et al. 2010; YAVUZ et al. 2010; ZANBOTTO RAMALHO et al. 2010). For example, Santos et al. (2006) investigated the electrochemical remediation of oil extraction industry wastewater using $Ti/Ru_{0.34}Ti_{0.66}O_2$ 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 O_2, Cl_2 and H_2 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 (COD_0=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%.

However, an only application of EO for removing petroleum hydrocarbons from real samples of produced water has been reported until now. 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 $Ti/RuO_2–TiO_2–SnO_2$ electrode. Under galvanostatic conditions ($j = 89\ mAcm^{-2}$), 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). Importantly, 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 ($kWh\ m^{-3}$) ranging from 4.84 to 0.97 and removal prices from 1.41 to 0.28 (Brazil currency: R$ (real)).

Based on the results reported by other authors (RAJKUMAR et al. 2004; SANTOS et al. 2006; MA et al. 2006; LIMA et al. 2009; ABDELWAHAD et al. 2009; TRAN et al. 2009a; TRAN et al. 2009b; TRAN et al. 2010; KÖRBAHTI et al. 2010; YAVUZ et al. 2010; ZANBOTTO RAMALHO et al. 2010), this research aims to test the performance of Ti/Pt and BDD anodes for the EO of a real sample of PW of a petrochemical industry in the Northeast Brazilian region. The influence of several process parameters such as nature of electrode material, applied current density, agitation rate, supporting electrolyte and temperature on organic matter removal have been evaluated.

8.3 EXPERIMENTAL

8.3.1 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 7.5 and electric conductivity around 4.64 μS cm^{-1}. It contains 4.38 g L^{-1} of total dissolved solids, 2.7 mg L^{-1} of phenol and 15 mg L^{-1} of oils and greases. Chemical oxygen demand (COD) was about 1588 ppm. Table 1 reports the average composition of the produced water as received in the terminal, concerning to inorganic species.

Table 1. Average concentration of inorganic species in the produced water samples

Ion	mg L^{-1}
Cl^{-}	22,470
Na^{+}	18,876
Ca^{2+}	987
Mg^{2+}	678
K^{+}	236
Sr^{2+}	139
NH^{4+}	98
S^{2-}	120
Ba^{2+}	112
Cr^{3+}	9.8
SO$_4^{2-}$	6.2

Fe^{3+}	7.9
Cd^{2+}	3.3
Mn^{2+}	2.2
Li^{+}	2.0
Zn^{2+}	0.7
Cu^{2+}	0.35
Ni^{2+}	0.14
Pb^{2+}	0.08
Ag^{+}	<0.5
Al^{3+}	<0.1
Sn^{4+}	<0.1
F^{-}	<0.1
Co^{2+}	<0.1
CN^{-}	<0.1

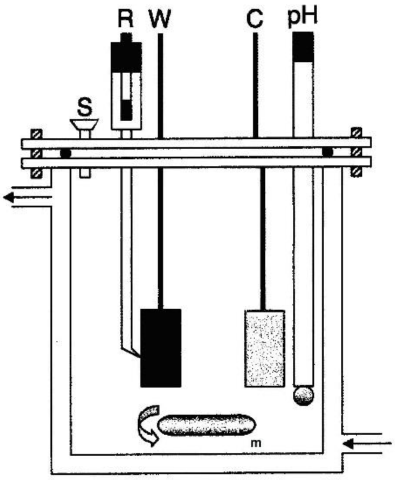
8.3.2 Chemicals

Chemicals were of the highest quality commercially available, and were used without further purification. Na_2SO_4 was purchased from Fluka.

8.3.3 Electrolytic Systems

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 (Figure 1). The PW was stored in the electrochemical batch cell for treating 0.5 L. The oxidation experiments of PW were performed under galvanostatic conditions using a VERSTAT3 (Princeton Applied Research). The cell contained a Ti/Pt or BDD electrode as anode and a 15 cm^2 Ti grid as cathode. Pt anode was a Ti plate coated with Pt with total dimensions of 10 cm^2 operating on both sides, whereas the BDD anode was a plate with an area of 10 cm^2 and with one side only exposed to the solution. In both systems the inter-electrode distance was 1.5 cm. 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 ⟨1 0 0⟩ wafers (1–3 mΩ 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 mΩ cm. In order to stabilize its surface and to obtain reproducible results, the BDD electrode was pre-treated at 25 °C by anodic polarization in 1 M $HClO_4$ at 10 mA cm^{-2} for 30 min using stainless steel plate as counter electrode. This treatment confers to the electrode surface its hydrophilic nature, as already indicated by Panizza and Cerisolla (2010).

Figure 1. Diagram of the one-compartment electrochemical cell used for studying anodic oxidation of petrochemical wastewater: C, counter, R, reference, and W, working electrodes, respectively; pH electrode; S, sample holder; and m, magnetic stirrer.



8.3.4 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:

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

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, as indicated by Panizza and Cerisola, 2010.

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

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 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 consumption, as follows:

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

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 3) was measured using a Varian AA 340 Atomic Absorption Spectrometer. On the other hand, during each some electrolysis, some 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.

8.4 RESULTS AND DISCUSSIONS

8.4.1 Electrochemical Treatment of PW using the Ti/Pt and BDD Anodes

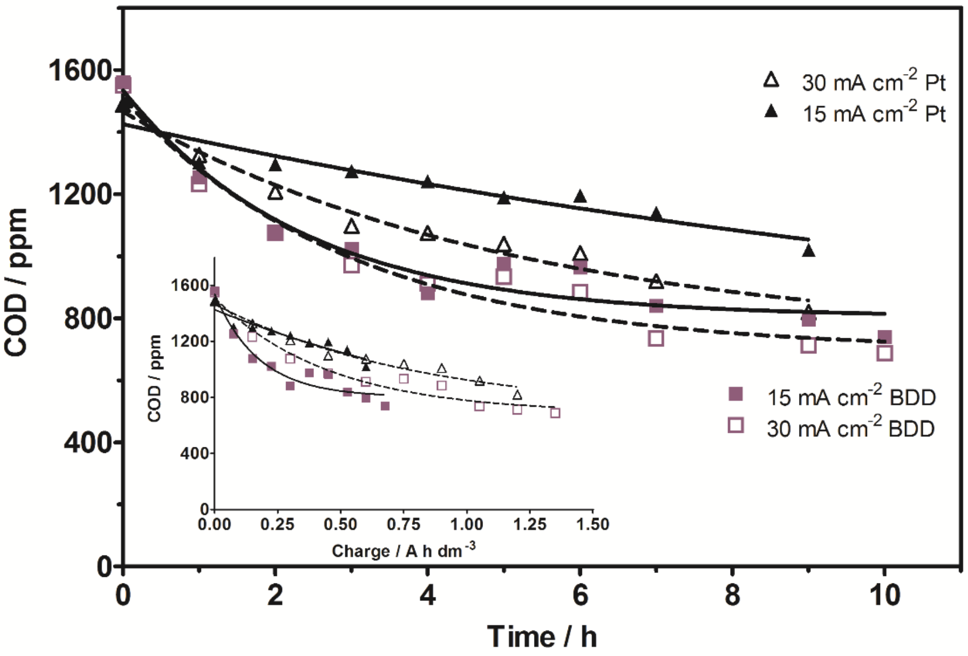
In order to find the best condition for the anodic treatment of the petrochemical wastewater (employing the PW samples as received from petrochemical industry), preliminary experiments were performed at 25°C for studying the role of anode material (Ti/Pt and BDD anodes) and applied current density (j=15 and 30 mAcm^{-2}). Fig. 2 shows the trend of the COD as a function of time and specific charge (inset) during the anodic treatment by applying 15 and 30 mAcm^{-2} of current density. Results clearly indicate that a modest COD removal rate was achieved at different applied current densities, using Ti/Pt and BDD anodes. At 15 and 30 mAcm^{-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 in 10 h of treatment. However, more efficient COD removal rate was attained by applying 30 mAcm^{-2} using BDD anode because of there is a greater charge passing into the cell that favors the electrogeneration of more hydroxyl radicals, according to Eq. (4).

$$H_2O \rightarrow {}^{\bullet}OH + H^+ + e \qquad (4)$$

After that, organic pollutants are oxidized by hydroxyl radicals, according to Eq. (5).

$$\text{organic pollutants} \xrightarrow{{}^{\bullet}OH} CO_2 + H_2O \qquad (5)$$

Figure 2. Influence of applied current density on the COD removal as a function of time and specific charge (inset) during PW anodic oxidation using Ti/Pt and BDD anodes. Operating conditions: PW sample, as obtained from Brazilian platform, *j* = 15 mA cm^{-2} and 30 mA cm^{-2}, Temperature T=25 °C, agitation rate: 400 rpm.



As shown in Figure 2, inset, increasing current density results in a higher charge consumed for complete mineralization due to a relative greater amount of $^{\bullet}$OH wasted in parasite non-oxidizing reactions such as oxygen evolution.

To understand the efficacy of current used for EO, from COD values (Figure 2), different TCE values were estimated, depending on anode material and current density. For Pt anode at 15 and 30 mAcm^{-2}, 42% and 58% were achieved respectively, whereas at BDD anode, 90% and 48% were obtained, respectively. These values confirm that a significant 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 all the applied current densities using Pt and BDD anodes where COD decreases at the beginning of electrolysis; after that, it remains almost stable forming a plateau (ranging from 45 to 60% of COD removal), increasing the treatment time. This behaviour is frequently characteristic of electrolyses under mass transport control when the electrolyses is performed applying a current higher than the limiting one, as already indicated by other authors (SANTOS et al. 2006; PANIZZA; CERISOLA, 2010). For a cell configuration used in this study, the mass transfer coefficient was 5.9 × 10^{-6} m s^{-1} and the limiting current results in a value of 0.11 A, according Eq. 2. This current is relatively low than all the currents applied in this work (0.15–0.35A), suggesting that the oxidation in these conditions could be occurring under mass transport control. These assumptions, treating a real effluent, are in agreement with the studies recently published by Panizza and Cerisola (2010), during the anodic oxidation of a real carwash wastewater.

Although the low COD depletion is probably also due to two additional factors: (i) the presence of surfactants and corrosion inhibitors in the petrochemical wastewaters and the (ii) poor conductivity of this real effluent. In the first case, these surfactants and corrosion inhibitors produced foam in the reservoir during the treatment. This foam is adsorbed in the anode surface avoiding an efficient elimination of organic matter dissolved in the real wastewater. In fact, after electrochemical treatment a film was clearly observed at BDD surface. This consideration partially explains the lower COD removals obtained at Pt and BDD anodes, in comparison with the different behaviors observed in other studies on the degradation of several organic pollutants (MARTINEZ HUITLE; FERRO, 2006; PANIZZA; CERILOSA, 2009). For example, in the same experimental set-up, we observed that the time for complete mineralization of 200 mg dm^{-3} of alphazurine was obtained after 10 h, obtaining higher efficiencies at BDD anode (BENSALAH et al. 2009). On the second case, the poor conductivity for this real effluent avoids the efficient production of $^{\bullet}OH$ on anode surfaces (Eq. 4), limiting the oxidation of organic pollutants (Eq. 5).

On the other hand, as well-know from literature (MICHAUD et al., 2000; CAÑIZARES et al. 2005; MARTINEZ HUITLE; BRILLAS, 2009), changes in temperature have an important influence on oxidation rate. For this reason, an increase on the temperature of petrochemical wastewater, during anodic oxidation treatment at Pt and BDD anodes, was performed. However, it was observed that changes in temperature have only a slightly influence on oxidation rate by applying 15, 30 and 60 mAcm^{-2} (data not shown), since the COD removal after 10 h of treatment at 40 °C was very similar to obtained to 25 °C (ranging from 40 to 60% of COD removal) using Pt and BDD anodes.

Nevertheless, other studies on the oxidation of other organic pollutants on Pt and BDD anodes (CHEN et al., 2006; PANIZZA et al. 2007; PANIZZA et al. 2008; MARTINEZ HUITLE; BRILLAS, 2009; PANIZZA; CERISOLA 2010) reported that an increase of temperature favors organic oxidation, but 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 (Eq. (5)), peroxodisulfate (Eq. (6)) and hydrogen peroxide (Eq. (7)).

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (5)$$

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \qquad (6)$$

$$2^{\bullet}OH \rightarrow H_2O_2 \qquad (7)$$

These powerful oxidizing agents can oxidize organic materials by a chemical reaction whose rate increases with temperature.

Generally, under high concentrations of NaCl in solution (such as observed in our PW samples), EO via $^{\bullet}OH$ radicals is 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 (ZANBOTTO RAMALHO et al. 2010):

$$H_2O + M + Cl^- \rightarrow M[^{\bullet}ClOH] + H^+ + 2e^- \qquad (8)$$

$$R + M[^{\bullet}ClOH] \rightarrow M + RO + H^+ + Cl^- \qquad (9)$$

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

$$H_2O + M[^{\bullet}OH] \rightarrow M + O_2 + 3H^+ + 3e^- \qquad (10)$$

$$H_2O + M[^{\bullet}ClOH] + Cl^- \rightarrow M + O_2 + Cl_2 + 3H^+ + 4e^- \qquad (11)$$

$$H_2O + M[^{\bullet}OH] \rightarrow M + H_2O_2 + H^+ + e^- \qquad (12)$$

Furthermore, hypochlorite can be formed as follows:

$$H_2O + Cl^- \rightarrow HOCl + H^+ + 2e^- \qquad (13)$$

Therefore, direct anodic oxidation, through the reaction (9), 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:

$$H_2O + M[^{\bullet}ClOH] + Cl_2 \rightarrow M + ClO_2 + 3H^+ + 2Cl^- + e^- \quad (14)$$

$$O_2 + M[^{\bullet}OH] \rightarrow M + O_3 + H^+ + e^- \quad (15)$$

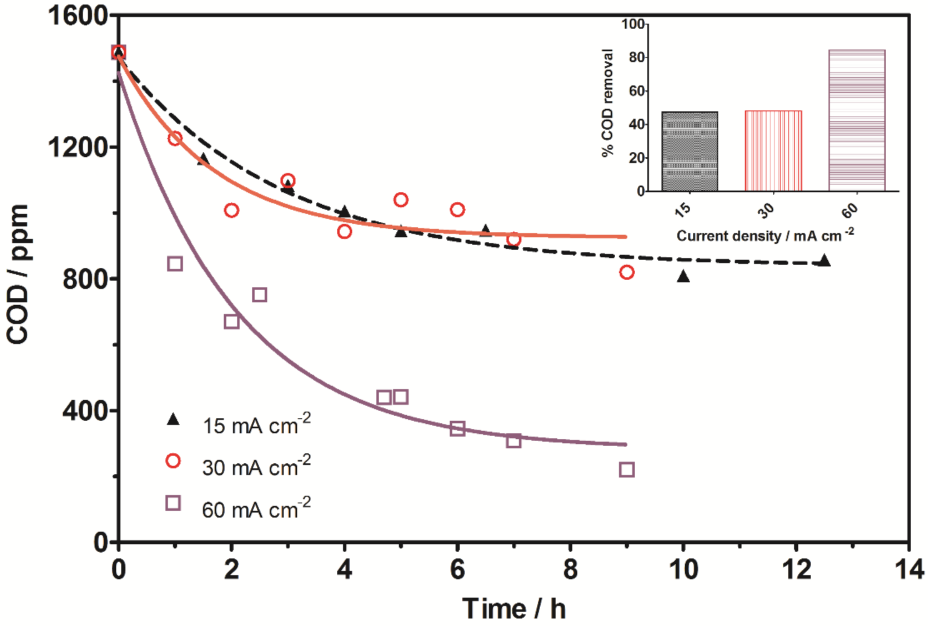
Primary and secondary oxidants are quite stable and migrate in the solution bulk, which indirectly oxidize the effluent. The efficiency of indirect oxidation depends on the diffusion rate of oxidants in the solution, concentration produced and pH value (ZANBOTTO RAMALHO, 2010). In acidic conditions, 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 chloride strong oxidants.

However, in our case, the electrochemical treatment of petrochemical wastewaters (containing with higher concentrations of chlorides ions (Table 1)) did not show an increase in the COD removal. Perhaps, no appreciable amount of oxidizing species was generated during the electrolyses under these experimental conditions (40°C), even though the concentration of Cl^- was diminished (see Table 3) after electrochemical treatment. It could be due to the presence of surfactants and corrosion inhibitors that avoid the production of chloride strong oxidants on the anode surfaces (Pt or BDD).

Therefore, a new set of experiments were performed by applying 15, 30 and 60 $mAcm^{-2}$ of current density at 60°C, but dissolving an know-amount of Na_2SO_4 in 0.5 L of PW sample. As mentioned above, peroxodisulphates can be electrochemically formed in solutions containing sulphates (Eq. (6)), especially at higher temperatures (60°C) (MICHAUD et al. 2000). For this reason, petrochemical wastewaters were treated electrochemically using Pt and BDD employing these experimental conditions.

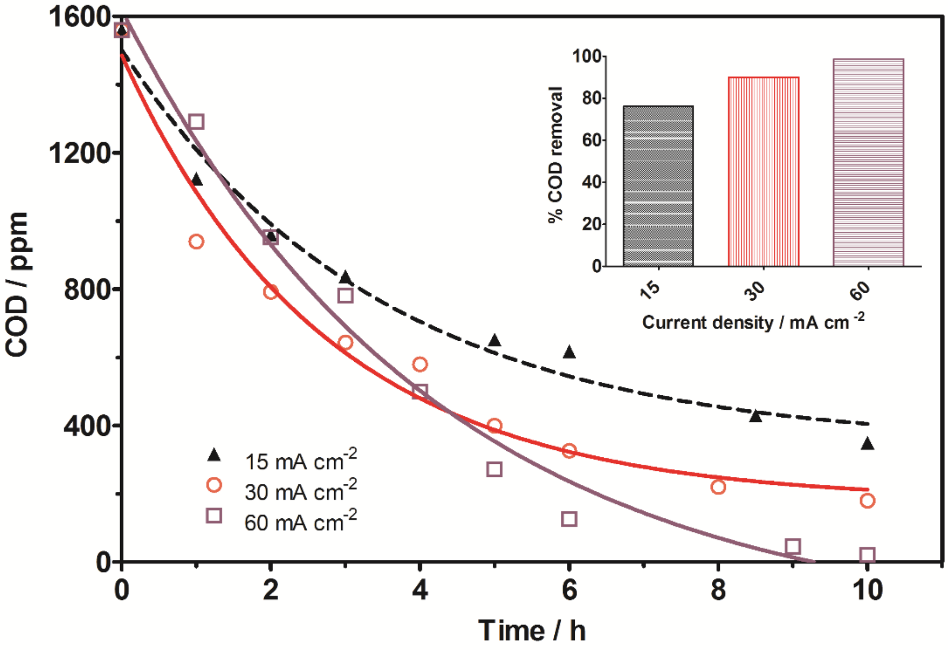
The influence of the current density on the COD decay during the EO of the petrochemical wastewater at 60°C using Pt and BDD anodes is shown in Figures 3 and 4. These results clearly indicate that the COD elimination rate and %COD removal are strongly influenced by the anode material and applied current density. At Pt electrode (Figure 3), a good performance of elimination was only achieved by applying 60 $mAcm^{-2}$ of current density at 60°C. Whereas that, lower % of COD removals were obtained at 15 and 30 $mAcm^{-2}$, as showed in the inset of Figure 3. The low COD depletion, the rapid decrease of the reaction rate, and the consequent low value of current efficiency could be explained by the growth of an adherent passivating film on the anode surface that poisoned on the electrode by dissolved corrosion inhibitors in PW or the accumulation of oxidation intermediates, as already reported by other authors (PANIZZA et al. 2007; PANIZZA et al. 2008; PANIZZA; CERISOLA, 2010). Despite the fact that the results obtained under these experimental conditions (15, 30 and 60 mAcm^{-2}, 5 g of Na_2SO_4, 60°C) showed significant efficiencies, these figures were not satisfactory for industrial applications.

Figure 3. Influence of applied current on the evolution of COD, as a function of time, during electrochemical treatment of actual petrochemical wastewater on Pt anode at different current densities (15, 30 and 60 mA cm^{-2}). Inset: % COD removal as a function of current density. Conditions: T = 60 °C, 5 g of Na_2SO_4, agitation rate: 400 rpm.



Conversely, using BDD anodes (Figure 4), the COD decreased efficiently, meaning the complete oxidation of organic pollutants contained in PW and all its metabolites by means of the electrogenerated oxidant species (Eq. (4) and (6)). In fact, increasing the current 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 15 and 30 mAcm^{-2} (inset, Figure 4), probably because the oxidation was faster due to the higher amount of oxidant species, principally peroxodisulphates electrogenerated on BDD surface. In fact, no passivating film was observed on BDD surface after all electrolysis treatments under these conditions, as observed in the first experiments set. This result indicated that the peroxodisulphates electrochemically generated contributes in the oxidation of organic pollutants and avoid the 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 $^{\bullet}$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 (GANDINI et al. 2000; MARTINEZ-HUITLE et al. 2004).

Figure 4. Influence of applied current on the evolution of COD, as a function of time, during electrochemical treatment of actual petrochemical wastewater on BDD anode at different current densities (15, 30 and 60 mA cm^{-2}). Inset: % COD removal as a function of current density. Conditions: T = 60 °C, 5 g of Na_2SO_4, agitation rate: 400 rpm.



Furthermore, results reported in Figures 3 and 4 were used to estimate the TCE values, these estimations showed that BDD achieved higher current efficiencies than Pt, as indicated in Table 2. This behavior can be explained by the different electrocatalytic properties of each anode material. As reported by other authors (MARTINEZ-HUITLE; FERRO, 2006; PANIZZA; CERISOLA, 2007; MARTINEZ-HUITLE; BRILLAS, 2009; PANIZZA; CERISOLA, 2009; PANIZZA; CERISOLA, 2010), at BDD anode, which is well known to have weak adsorption properties at higher temperatures due to its inert surface, hydroxyl radicals and peroxodisulphates are very weakly adsorbed and consequently they are very reactive toward organics oxidation. 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 (MARTINEZ-HUITLE and FERRO, 2006; PANIZZA; CERISOLA, 2009; OLIVEIRA et al. 2011).

Table 2. Total current efficiencies and energy requirements for electrochemical treatment of petrochemical wastewater at different applied current densities.[a]

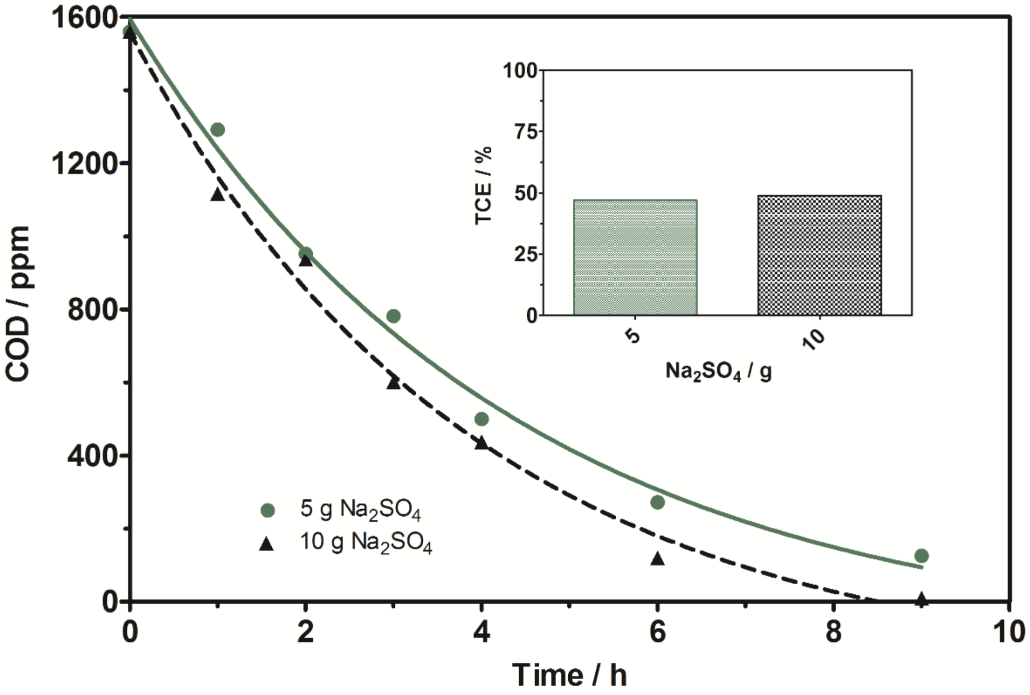
	Total current efficiencies (%)		Energy consumption (kW h dm^{-3})	
Current density (mAcm^{-2})	Pt	BDD	Pt	BDD
15	56.29	100.00	18.75	15.81
30	41.44	93.54	42.12	36.48
60	39.34	46.97	139.52	109.80

[a] *Temperature=60 °C, agitation rate of 400 rpm and 5 g of Na_2SO_4 dissolved in PW sample.*

8.4.2 Influence of Na_2SO_4 Concentration

Figure 5 shows the influence of initial Na_2SO_4 concentration (in g L^{-1}) as a function of the time and TCE (inset) values during galvanostatic electrolyses of petrochemical wastewater under 60 mAcm^{-2} of applied current density at 60°C. 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 Na_2SO_4 in solution. This indicates that the oxidation rate and process efficiency depend modestly on Na_2SO_4 dissolved in the effluent. This is usually explained in terms of mass transfer limitations that are avoided in bulk reactor, assuming that both direct oxidation and mediated oxidation (by hydroxyl radicals and other electrogenerated oxidants from the supporting electrolyte (peroxodisulphates)) contributes in the electrochemical process. In fact, treatment time, in the presence of Na_2SO_4, was reduced respect to the time employed to eliminate COD completely at real discharged conditions. On the other hand, an increase on current efficiency was observed (inset on Figure 5) because the electrogeneration of peroxodisulphates avoid mass transport limitations and also the secondary reaction of oxygen evolution. These results are in agreement with the studies reported by other authors (BENSALAH et al. 2009; PANIZZA et al. 2007) on the oxidation of organic compounds at boron-doped diamond electrode.

Figure 5. 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 on BDD anode, applying 60 mA cm^{-2} at 60°C.

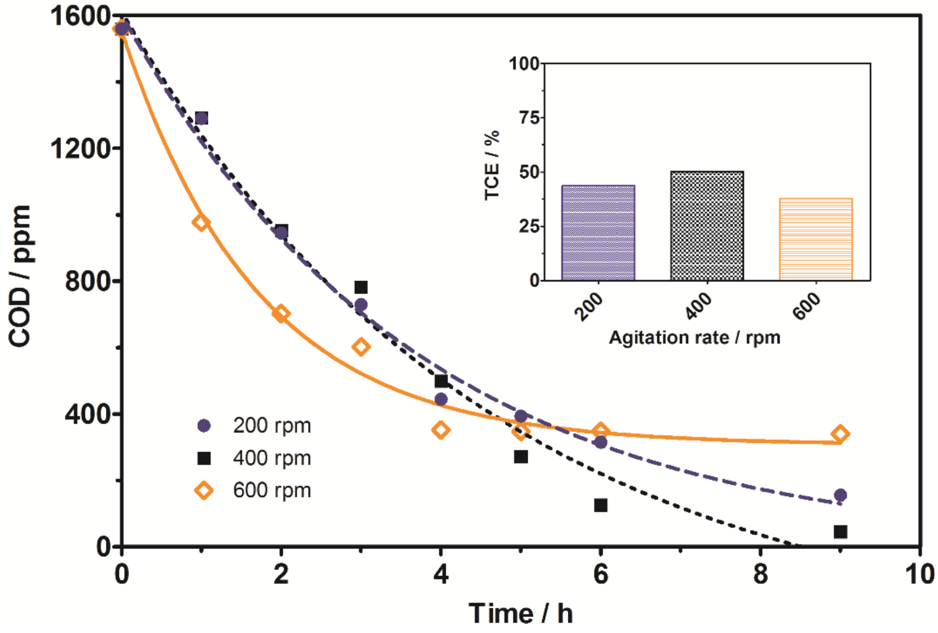


8.4.3 Effect of the Agitation Rate

In order to verify the important role of mass transfer on the electrochemical treatment of PW, the influence of agitation rate during BDD-anodic oxidation was studied varying the magnetic stirrer rate. Experiments were performed at three rates, in the range of 200–600 rpm. Figure 6 shows the agitation rate effect on the COD removal as a function of the time, during galvanostatic electrolyses of petrochemical wastewaters containing 5g L^{-1} of Na_2SO_4 by applying 60 mA cm^{-2} of current density at 60°C. As can be seen, the almost total COD removal was obtained under 200 and 400 rpm of agitation rate. It appears that the hydrodynamic conditions strongly affect the rate of COD removal. Less than 200 rpm of agitation rate, mass transport limitations were observed in the final stages of the electrolysis process (with 43% of TCE); while at 400 rpm, complete COD removal was achieved (50% TCE). On the other hand, high magnetic stirrer rates led to slow and lower efficient (37% TCE) electrochemical process (600 rpm) which confirms the suggestion previously mentioned concerning the mass transfer limitations due to the direct (the oxidation is controlled by the rate at which organic molecules are carried from the bulk liquid to the electrode surface (in the initial stages), rather than by the rate at which electrons are delivered to the anode

(MARTINEZ-HUITLE; FERRO, 2006; PANIZZA; CERISOLA, 2009)) and indirect electrochemical processes under the current density conditions.

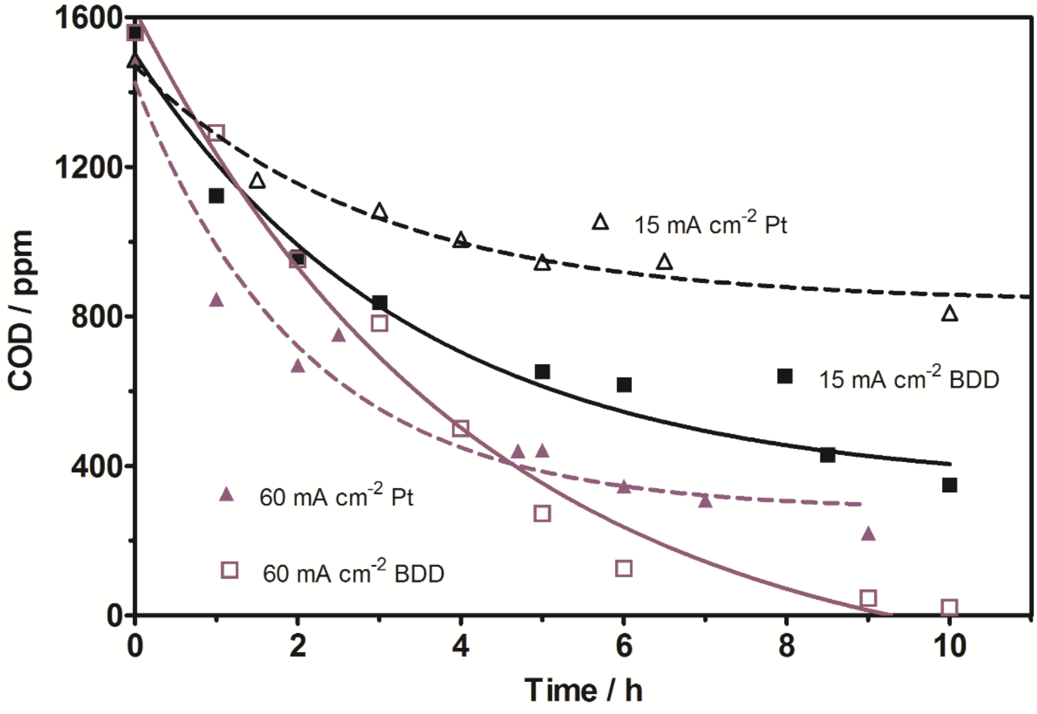
Figure 6. Influence of agitation rate on the COD decay, as a function of time and total current efficiency (inset) during oxidation of real petrochemical effluent on BDD anode, applying 60 mA cm^{-2} at 60°C under different agitation rates.



8.4.4 Comparison of the Electrode Materials

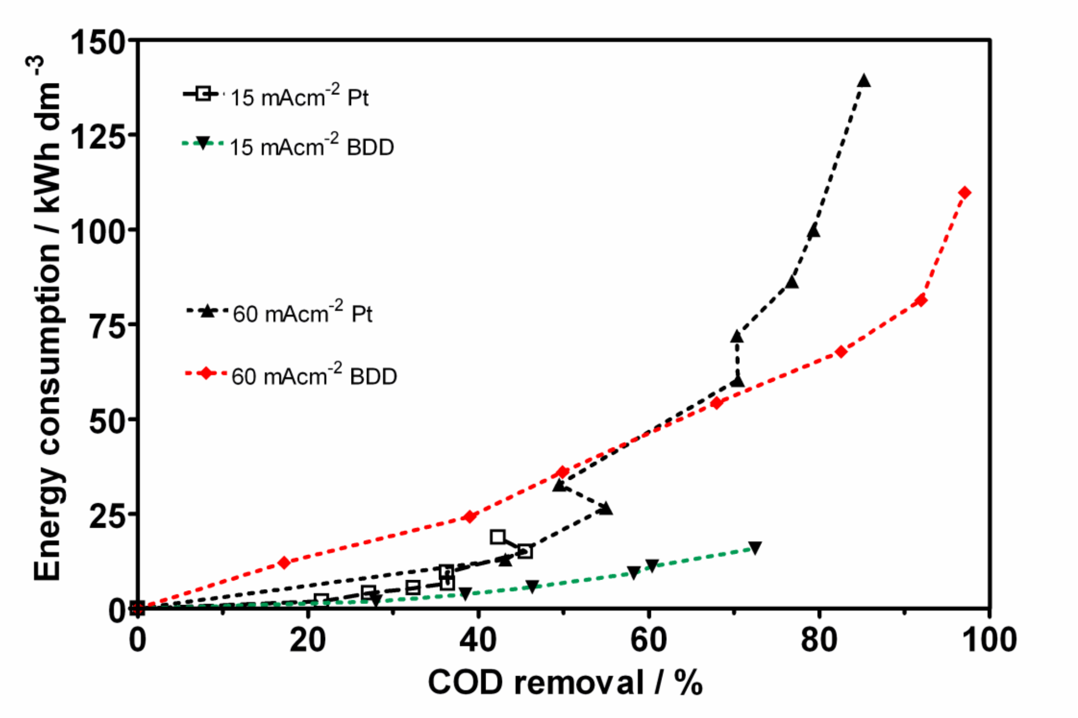
Comparison between the trend of COD removal, as a function of time, for Pt and BDD anodes by applying 15 and 60 mAcm^{-2} of current density is presented in Fig. 7. This graph clearly evidences that BDD anode allows significantly faster COD removal than Pt, at different current densities. As already detailed and described by authoritative reviews (MARTINEZ-HUITLE; FERRO; 2006; MARTINEZ-HUITLE; BRILLAS, 2009, PANIZZA; CERISOLA, 2009; BRILLAS et al. 2009), the greater oxidation ability of BDD can be explained by the high reactivity of the strong oxidant species (hydroxyl radicals and peroxodisulphates) electrogenerated on this electrode. In fact, during electrolysis of PW in absence of Na_2SO_4 in solution, a lower COD removal was achieved for both anode materials (Figure 2). Conversely, when a small amount of Na_2SO_4 was dissolved in the petrochemical wastewater, an enhancement was achieved on the COD decay, being more evident at BDD anode (Figure 7). On the other hand, lower removal efficiencies achieved in the final stages of electrochemical process take place as a result of the mass transfer limitations due to 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 7).

Figure 7. 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 $mAcm^{-2}$ of current density at 60°C.



For large scale application, it is very important to estimate the treatment costs, and thus Fig. 8 reports the energy consumption (kWh dm^{-3}) at 15 and 60 $mAcm^{-2}$, as a function of COD removal (values for all applied current densities used, are reported in Table 2). As can be observed, BDD consumed less energy than Pt anode, achieving higher COD removal than Pt. For example, 109 kWh dm^{-3} and 140 kWh dm^{-3} are consumed for BDD and Pt anode, respectively; but a 98% of COD removal was achieved at BDD while only 85% using Pt electrode. These results point out the high performance BDD-anodic oxidation for treating petrochemical wastewaters. Although BDD oxidation is very effective, its energy consumption could be too high for practical application as the only treatment process, but it can be a feasible process for produced waters generated by petrochemical industry as a pre-treatment process as a previous step to biological depuration or it could be coupled with other wastewater treatments (e. g.: UV irradiation, Fenton, adsorption) reducing significantly the cost and time treatment (OLIVEIRA et al. 2011)

Figure 8. 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.



Finally, 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 60 mAcm^{-2} (60°C and 5 g of Na_2SO_4), is present in Table 3. 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 forming a salts deposit, as observed at this electrode after electrolysis treatment; and confirmed by the decrease of heavy metals dissolved (Table 3). 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 energy consumption.

Table 3. 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^-	5268	Cl^-	7483
Na^+	9755	Na^+	8963
Ca^{2+}	425	Ca^{2+}	365
Mg^{2+}	120	Mg^{2+}	50
K^+	56	K^+	45
NH^{4+}	>0.1	NH^{4+}	>0.1
Ba^{2+}	72	Ba^{2+}	55
Cr^{3+}	>0.1	Cr^{3+}	-
Fe^{3+}	>1	Fe^{3+}	>0.5
Cd^{2+}	-	Cd^{2+}	-
Mn^{2+}	1.8	Mn^{2+}	1.8
Zn^{2+}	-	Zn^{2+}	-
Cu^{2+}	-	Cu^{2+}	-
Ni^{2+}	-	Ni^{2+}	0.5
Pb^{2+}	-	Pb^{2+}	-
Al^{3+}	-	Al^{3+}	-

Pollutant (µg L^{-1})	**Initial concentration**	**E1**	**E2**	**E3**	**E4**
Benzene	670.01	48.96	1.45	15.53	0.71
Toluene	339.79	127.65	59.74	7.06	-
Ethylbenzene	673.33	35.98	15.66	25.97	0.15
Xylene	1706.49	45.60	41.00	2.06	-
Benzo(a)pyrene	1398.00	289.36	163.89	-	-
Benzo(a)perylene	870.00	193.41	56.32	9.58	0.25
Chrysene	-	-	-	-	-
Fluoranthene	954.00	750.71	357.12	-	-
Indeno(1,2,3-cd)pyrene	549.00	120.34	79.60	-	-
Anthracene	9380.00	304.2	13.5	146.20	0.96
Benz(a)anthracene	145.60	89.74	46.27	-	15.62
Dibenz(a,h)anthracene	48.74	21.60	-	12.60	-
Phenanthrene	484.00	259.00	8.50	-	-
Naphthalene	329.00	216.94	-	1.80	-

E1: Electrochemical treatment under real discharged conditions by applying 30 mA cm^{-2} and 25 °C at Ti/Pt

E2: Electrochemical treatment under real discharged conditions by applying 30 mA cm^{-2} and 25 °C at BDD

E3: Electrochemical treatment adding 5 g de Na_2SO_4 in the effluent by applying 30 mA cm^{-2} and 60 °C at Ti/Pt
E4: Electrochemical treatment adding 5 g de Na_2SO_4 in the effluent by applying 30 mA cm^{-2} and 60 °C at BDD

8.5 CONCLUSIONS

This study showed that anodic oxidation can be used successfully to remove completely organic pollutants from petrochemical wastewaters. 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. 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. On contrary, COD removal depends on the strong oxidant species electrochemically generated on BDD surface (peroxodisulphates, due to the addition of Na_2SO_4 in PW sample) under specific temperature conditions. In fact, when GC-MS analysis were performed to determine the concentration of the principal petroleum hydrocarbons; 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, Na_2SO_4 dissolved in the effluent and temperature) was done and presented in Table 4. The results clearly indicate that the electrochemical treatment of PW in the presence of Na_2SO_4 and 60 °C allowed an efficient degradation of these organic compounds respect to the electrolysis performed under real PW discharged conditions at 25 °C. It is important to remark that concentration of Na_2SO_4 dissolved did not affected noticeably the oxidation rate, but total COD removal was influenced by the agitation rate. Although, the energy consumption and process time 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 energy consumption values obtained are lower than reported by other authors during electrochemical treatment of petrochemical wastewaters (synthetic or real effluents) (RAJKUMAR et al. 2004; SANTOS et al. 2006; MA et al. 2006; LIMA et al. 2009; ABDELWAHAD et al. 2009; TRAN et al. 2009a; TRAN et al. 2009b; TRAN et al. 2010; KÖRBAHTI et al. 2010; YAVUZ et al. 2010; ZANBOTTO RAMALHO et al. 2010).

Generally speaking, the mediated electrochemical approach (peroxodisulphates 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 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. However, due to the proximity to equatorial line, the Northeast region of Brazil is irradiated by solar light approximately 10 h every day, 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.

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CAPÍTULO 9

9. CONSIDERAÇÕES FINAIS

Este trabalho levou as seguintes Conclusões:

- Na eletroxidação do corante Amarelo de Novacron no eletrodo DDB e Pt, observou- se que as eletrólises mostraram que, na ausência de NaCl, apenas uma lenta diminuição na concentração de YN foi obtida. Por outro lado, na presença de NaCl, o YN foi completamente oxidado pela mediação do cloro ativo gerado eletroquimicamente no início do processo. Demonstrou-se ainda que o decaimento da cor do YN foi independente da densidade de corrente aplicada, mas o processo depende da concentração de NaCl na solução. Após isso, HClO e compostos cloro-oxigenados no estado de maior oxidação são formados em potenciais que o eletrodo atinge em 30-50 mA cm^{-2}. Assim, a oxidação do YN é mediada pelos oxidantes de cloro ativo formados, a partir da reação entre os •OH e espécies de cloro em solução. Por outro lado, a eliminação do COT foi satisfatória apenas no eletrodo de diamante, pois a superfície de um ânodo não ativo interage tão fracamente com •OH que permite a reação direta com os produtos orgânicos e ao mesmo tempo, favorece a produção de novos oxidantes a partir do cloreto, que por sua vez vão participar, oxidando a matéria orgânica em solução.
- O tratamento eletroquímico depende fortemente do material eletrocatalítico usado, como confirmado pelos valores do COT durante a degradação do Amarelo de Novacron; porém, este tratamento alternativo poderia ser aplicado como um pré-tratamento ou tratamento completo do efluente.
- Na Oxidação Eletroquímica realizada em efluentes têxteis sintéticos contendo soluções de Vermelho de Remazol e Azul de novacron, a completa remoção da cor foi obtida em todos os casos devido à eletrogeração de radicais hidroxilas a partir da eletrólise da água. Sendo assim, oxidação anódica utilizando DDB, pode ser usada com sucesso para eliminar completamente toda a cor de efluentes sintéticos contaminados com corantes têxteis, considerando as condições específicas (densidade de corrente, pH e temperatura).
- Em todos os casos observou-se que, a influência da densidade de corrente, temperatura e pH em função do tempo, durante a eletrólise galvanostática, mostraram que os reagentes eletrogerados a partir da oxidação anódica do eletrólito suporte (por exemplo: OH e

peroxodisulfatos) desempenham um papel importante na eficiência do processo eletroquímico.

- O consumo de energia elétrica permitiu avaliar a aplicabilidade do processo eletroquímico, apresentando valores bastante aceitáveis, os quais permitiram estimar o custo do tratamento eletroquímico. Assim, segundo estes resultados, o processo eletroquímico poderia ser aplicado como um método de pré-tratamento antes do tratamento biológico reduzindo o tempo total de tratamento do efluente.
- O estudo realizado com a oxidação eletroquímica da água produzida de petróleo mostrou que este método pode ser utilizado com sucesso para remover os poluentes orgânicos de efluentes petroquímicos. Neste caso, a eficiência de descontaminação e o tempo depende das condições de operação, tais como densidade de corrente, o eletrólito, temperatura e natureza do material. O decaimento da DQO não foi significativamente afetado pela densidade de corrente e temperatura, dependendo, portanto, das espécies oxidantes eletrogerados na superfície do DDB superfície (peroxodissulfatos, devido à adição de Na_2SO_4), sob condições específicas de temperatura. A análise por GC-MS foi realizada para determinar a concentração dos principais hidrocarbonetos de petróleo e os resultados indicaram claramente que o tratamento eletroquímico da água produzida, na presença de Na_2SO_4 e de 60 ° C permitiu uma eficiente degradação destes compostos orgânicos em relação à eletrólise realizada sob condições reais a 25 ° C. É importante ressaltar que a concentração de Na_2SO_4 dissolvido não afetou sensivelmente a taxa de oxidação, mas a remoção de DQO total foi influenciado pela velocidade de agitação.
- De maneira geral, o tratamento de efluentes via eletrooxidação pode ser considerado mais eficaz do que outros métodos de tratamento. Vale ressaltar que esta tecnologia é um processo elétrico-dependente, o que poderia ser um ponto negativo para a aplicação desta técnica em uma Estação de Tratamento de água sustentável. No entanto, devido à proximidade com a linha equatorial, a região Nordeste do Brasil é irradiada pela luz solar de aproximadamente 10 h todos os dias, assim, novos experimentos estão em andamento, no grupo de Eletroquímica Ambiental e Aplicada desta instituição de ensino, a fim de melhorar o processo de funcionamento da luz solar utilizando células fotovoltaicas (produção de energia elétrica), o que poderia tornar a técnica eletroquímica para descontaminação da água ainda mais sustentável.