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Produção de Carvão Ativado a Partir do Engaço da Uva e Estudo da Regeneração Eletroquímica do Mesmo em um Reator Desenvolvido em Escala Laboratorial

Tese de Doutorado

Odivan Zanella

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PRODUÇÃO DE CARVÃO ATIVADO A PARTIR DO ENGAÇO DA UVA E ESTUDO DA REGENERAÇÃO ELETROQUÍMICA DO MESMO EM UM REATOR DESENVOLVIDO EM ESCALA LABORATORIAL

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RESUMO

Sistemas de tratamento de efluentes, que empregam carvão ativado como sólido adsorvente são amplamente utilizados na indústria. O carvão ativado pode ser produzido a partir de materiais de diferentes origens, sendo os carvões comerciais geralmente obtidos a partir de madeira, casca de coco ou carvão mineral. Buscando aliar alta eficiência de processo e custo acessível de fabricação, a procura de materiais alternativos para fabricação de carvão ativado se apresenta como grande motivação. Outro aspecto importante relacionado com a redução de custos nos processos de adsorção é a reutilização do adsorvente em ciclos de adsorção/regeneração. Neste contexto, o presente trabalho tem por objetivo produzir carvão ativado a partir de engaço de uva e desenvolver um reator eletroquímico de bancada para estudar a regeneração do sólido produzido. Os carvões produzidos foram ativados em atmosfera controlada utilizando dióxido de carbono (CO_2) e também pelo uso de soluções de ácido nítrico (HNO_3) e ácido clorídrico (HCl). Para investigar a eficiência da regeneração de carvão ativado pelo método eletroquímico, construiu-se um reator e o carvão produzido foi saturado com fenol. As condições operacionais do reator eletroquímico (tempo de processamento, modo de operação, a corrente utilizada, a polaridade e o fluido de processamento) foram estudadas, utilizando carvão ativado comercial como referência. O estudo mostrou que o aumento da corrente e do tempo de processo aumentou a eficiência de regeneração. Entre os eletrólitos utilizados, melhores resultados foram atingidos com NaCl. O processo de regeneração eletroquímica desenvolvido neste estudo apresentou capacidades de regeneração de 100%, quando utilizadas as melhores condições de processo, mostrando que esta forma de regeneração para carvão ativado saturado com compostos aromáticos é muito promissora. No que se referem aos carvões ativados produzidos, estes apresentaram área de superficie BET e volume de poros de até $741m^2/g$ e $0,34cm^3/g$ respectivamente. O processo de pirólise mostrou um grande efeito sobre o produto final, e que as condições de carbonização afeta de forma significativa a estrutura porosa dos carvões ativados resultantes. Os carvões produzidos foram aplicados em sucessivos ciclos de adsorção/regeneração eletroquímica. Este estudo mostrou que a regeneração eletroquímica provoca uma redução significativa na área de superfície total e volume de poros, provavelmente devido à destruição parcial dos poros, que promove a perda de massa, resultando em capacidades de adsorção menores. A variação dos grupos de superfície ocasionada pela regeneração eletroquímica influenciou diretamente na adsorção de fenol, com maiores proporções para as interações doador-receptor de elétrons, e para as interações dispersivas de acoplamento de elétrons π-π. A formação de grupos de oxigênio na superfície dos carvões ativados levou ao enfraquecimento das forças de dispersão devido à extração de elétrons da banda π de grupos aromáticos no plano basal dos carvões ativados. Embora o enfraquecimento da interação dispersiva mostre efeito limitante para a adsorção, a adsorção depende fortemente da quantidade de grupos básicos na superfície dos carvões ativados. O processo de regeneração eletroquímica apresentou excelentes características para uma ampliação de escala, sendo possível a realização de aplicações para recuperação de grandes quantidades de carvões ativados saturados. O processo ainda necessita de estudos que apresentem soluções principalmente na preservação da massa de adsorvente e nas características de superfície.

Palavras chaves: regeneração; eletroquímica; carvão ativado; engaço de uva; adsorção.

ABSTRACT

Wastewater treatment systems that use activated carbon as solid adsorbent are widely common in the industry. Activated carbon can be produced from different raw materials. Commercial activated carbon, for example, is usually obtained from wood, coconut shells or mineral coal. Looking for combining high process efficiency and low cost of manufacture, alternative materials for activated carbon production is presented as a great motivation. Another important aspect related to the cost reduction in adsorption processes is the reuse of activated carbon in several cycles of adsorption/regeneration. In this context, this work aims to prepare activated carbon from grape stalks and design an electrochemical reactor in bench scale to regenerate the activated carbon produced, in several cycles of adsorption/regeneration. The activated carbons produced were activated in a controlled atmosphere using carbon dioxide (CO_2) and also by the use of solutions of nitric acid (HNO_3) and hydrochloric acid (HCl). To investigate the effectiveness of regeneration of activated carbon by electrochemical method, was built a reactor and the activated carbon produced was saturated with phenol. Electrochemical reactor operating conditions (the current processing time used, operation mode, the polarity and the processing fluid) were studied, using commercial activated carbon as a reference. The study showed that the increase in electrical current and process time has increased the efficiency of regeneration. Among the electrolytes used, better results were achieved with NaCl. The electrochemical regeneration process developed in this study presented regeneration capacities of the 100%, when used the best process conditions, showing that this form of regeneration for activated carbon saturated with aromatics is very promising. Regarding the characteristics of activated carbons produced, they have BET surface area and pore volume up to 741m m^2/g and 0.34 cm^3/g respectively. The pyrolysis process showed a big effect on the final product, and the carbonization conditions significantly impacts porous structure of activated carbon as a result. The carbons produced were applied in successive adsorption/electrochemical regeneration cycles. This study showed that the electrochemical regeneration causes a significant reduction in total surface area and pore volume, probably due to the partial destruction of the pores, which promotes the loss of mass, resulting in smaller adsorption capabilities. The variation of surface groups caused by electrochemical regeneration influenced directly on adsorption of phenol, with higher proportions to the donor-acceptor interactions of electrons and for dispersive interactions of π-π electrons coupling. The formation of oxygen groups on the surface of activated carbon led to the weakening of the dispersion forces due to the extraction of π band electrons of aromatic groups in the basal plane of activated carbons. Although the weakening of dispersion interaction show limiting effect for adsorption, adsorption depends strongly on the quantity of basic groups on the surface of activated carbons. The electrochemical regeneration process has excellent characteristics for scale-up, making possible the recovery of large amounts of saturated activated coals. The process still requires studies that present solutions particularly in the preservation of the mass of adsorbent and surface characteristics.

Keywords: regeneration; electrochemistry; activated carbon; grape stalk; adsorption.

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CAPÍTULO 1

INTRODUÇÃO

O carvão ativado (CA) é um adsorvente que tem sido amplamente utilizado em um grande número de aplicações, desde usos domésticos, tais como filtro de gases em eletrodomésticos (refrigeradores) e filtros de purificação de águas e usos industriais, tais como no armazenamento de gases, na remoção de poluentes em líquidos e na purificação e separação de gases. Também é utilizado como catalisador ou suporte catalítico e em uma série de aplicações médicas. O CA pode ser produzido a partir de uma variedade de substâncias naturais e sintéticas, onde os materiais lignocelulósicos aparecem como precursores mais utilizados.

A demanda mundial por carvões ativados foi cerca de 4,28 milhões de toneladas em 2012, e espera-se aumentar mais de 10% ao ano até 2018 [1]. Este aumento estimado se deve, principalmente, aos controles de poluição mais rigorosos estabelecidos nos EUA e na China. Por exemplo, na China, o plano já está em vigor, e é chamado de Plano Quinquenal de Reis (2011-2015), que visa melhorar a qualidade da água e do ar através da utilização de processos mais sustentáveis. Assim, a demanda de CA para aplicação na redução das emissões gasosas e no tratamento de efluentes pelo processo de adsorção irá aumentar significativamente [1].

As propriedades químicas e físicas do CA são dependentes do precursor, do método de produção utilizado e também dos métodos e condições de ativação. A composição do material lignocelulósico em relação ao teor de celulose, hemicelulose e lignina, determina de certa forma, o desenvolvimento da porosidade e da área superficial do CA produzido. Os carvões ativados são obtidos seguindo um de dois procedimentos: ativação química ou ativação física. Na ativação química, o precursor é misturado com um agente de ativação, tal como cloreto de zinco, ácido fosfórico ou sais de potássio e a mistura é, em seguida, carbonizada na ausência de oxigênio ou em atmosfera inerte, a uma temperatura não superior a 800°C. A ativação física é a mais utilizada comercialmente, sendo realizada por contato do carvão pré-carbonizado com uma corrente de um gás oxidante em temperaturas de 850-1000°C. O dióxido de carbono e o vapor de água são os agentes oxidantes mais usados para esta aplicação [2].

Apesar do amplo uso de CA em processos de adsorção, o maior obstáculo à sua aplicação pelas indústrias é o alto custo e as dificuldades associadas com a regeneração [3]. Uma vez esgotada a sua capacidade de adsorção, o CA pode ser depositado em aterros controlados, incinerado ou regenerado para reutilização [4-6]. No entanto, a disposição em aterros de resíduos perigosos está se tornando cada vez mais inaceitável devido à crescente preocupação com o efeito dos poluentes no meio ambiente e as mais restritivas normas ambientais. Tal fato motiva o desenvolvimento de sistemas de regeneração, garantindo a sua viabilidade econômica e ambiental [7-9].

Convencionalmente, o CA saturado é regenerado por meio de métodos térmicos, não térmicos e químicos. Os métodos térmicos têm sérias desvantagens, tais como o consumo elevado de energia, a perda de material, a perda de capacidade de adsorção, entre outros. O processo de regeneração térmica mais utilizado envolve a pirólise, em que o CA é exposto a temperaturas até 800°C na ausência de O_2. No entanto, esta técnica tem o inconveniente da perda de carbono, devido ao atrito gerado no processo [10]. Enquanto os métodos não térmicos e químicos, tais como regeneração com solventes e a oxidação química, estão associados ao elevado custo dos reagentes e a perda de capacidade de adsorção devido aos residuais de solventes adsorvidos no CA após a regeneração. Além disso, a eficácia da regeneração destes métodos depende do tipo de poluente [11,12].

A regeneração eletroquímica ganhou maior atenção nos últimos anos devido às suas características únicas, tais como, baixas temperaturas de operação (aproximadamente 25°C), ausência de produtos químicos e possibilidade de decomposição completa dos compostos orgânicos adsorvidos no CA sem danificar as propriedades estruturais e outras características do adsorvente [13].

Tendo em vista a crescente demanda de CA no mercado mundial e a importância do CA no tratamento de efluentes líquidos e emissões gasosas, este trabalho foi desenvolvido com foco em duas premissas principais. A primeira envolve a produção de carvão ativado a partir de resíduos agroindustriais lignocelulósicos, objetivando, além da produção de CA, um destino ambientalmente adequado para estes resíduos. A segunda baseia-se na regeneração eletroquímica do CA saturado, que tem o intuito de diminuir os custos com adsorventes e com a decomposição de poluentes orgânicos aromáticos refratários (por exemplo, o fenol), de modo que os resultados obtidos nesta fase do trabalho possam ser estendidos a diversas espécies de poluentes orgânicos aromáticos refratários.

CAPÍTULO 2

OBJETIVOS

Objetivo geral

O objetivo geral deste trabalho é produzir carvão ativado a partir de engaço de uva, com a finalidade de utilizá-lo na adsorção de poluentes orgânicos e desenvolver um reator eletroquímico para aplicação na regeneração deste carvão ativado carregado com compostos orgânicos.

Os objetivos específicos estão listados a seguir

i. Revisar os métodos de regeneração de carvões ativados;

ii. Desenvolver um reator para regeneração eletroquímica e caracterizar as condições de melhor desempenho deste reator com carvão ativado comercial;

iii. Produzir carvão e realizar ativações em diferentes condições buscando adsorventes com altas capacidades de adsorção para poluentes orgânicos;

iv. Caracterizar as propriedades físico-químicas dos carvões ativados produzidos;

v. Comparar o desempenho dos carvões ativados produzidos a partir do engaço de uva;

vi. Aplicar os carvões ativados produzidos para o processo de adsorção de fenol e posterior regeneração eletroquímica nas condições ótimas do reator desenvolvido.

CAPÍTULO 3

REVISÃO BIBLIOGRÁFICA E FUNDAMENTOS TEÓRICOS

Neste capítulo são abordados os tópicos relevantes aos temas que compõem o presente estudo. Inicialmente é apresentada uma breve descrição sobre o adsorvente utilizado neste trabalho, incluindo a estrutura química do carvão ativado, formas de produção de carvões ativados a partir de matérias lignocelulósicas, formas de obtenção de carvão e procedimentos de ativação. Na sequência apresentam-se as formas de regenerar carvões ativados carregado com diferentes adsorvatos por métodos de dessorção e/ou decomposição. O capítulo é finalizado com as considerações do autor sobre o tema evidenciando onde este estudo se insere e a sua importância.

3.1. Carvões Ativados

O carvão ativado (CA) é um dos sólidos adsorventes mais utilizados nos mais diversos setores. Ao longo das últimas décadas, os sistemas de adsorção que envolve este sólido ganharam importância em processos de separação e purificação em escala industrial. É considerado como uma das melhores tecnologias disponíveis na remoção de contaminantes orgânicos e inorgânicos. Seu uso pode ser aplicado em áreas distintas, como tratamento de efluentes, tratamento de água potável, recuperação de solventes, tratamento de emissões aéreas, descoloração e processamento de minérios. Esta diversidade de aplicações explica a tendência do mercado crescente para o uso de CAs [14,15]. A importância e a crescente demanda se devem à propriedades inerentes a este adsorvente tais como extensa área de superfície e porosidade interna, bem como os grupos funcionais de superfície desenvolvidos. A natureza inerente do precursor, ou um material de partida, bem como os métodos e as condições utilizadas para a síntese de CA, determinam a distribuição do tamanho de poros final e as propriedades de adsorção do CA [16].

O CA pode ser produzido a partir de qualquer precursor carbonáceo ocorrendo sintético ou naturalmente. A economia do processo normalmente indica a seleção de matérias-primas prontamente disponíveis e de baixo custo. Exemplos comuns de matérias-primas de CAs comerciais são materiais de origem vegetal (por exemplo, madeira, cascas de coco, frutas e caroços) e matéria vegetal degradada ou posteriormente como carvão (por exemplo, turfa e todas as categorias de carvão). A distribuição das matérias-primas mais comuns, citadas por Bansal et al. [17], envolvem: madeira 35%, carvão 28%, lignina 14%, cascas de coco 10%, turfa 10% e outros 3%. Precursores de origem na biomassa oferecem uma fonte mais econômica, pois são fontes abundantes, renováveis, com baixo teor mineral, dureza apreciável, e de baixo custo. A literatura referente ao uso de subprodutos agrícolas (lignocelulósicos) é muito extensa. Casca de coco, cascas de amêndoa, caroço de pêssego, caroço de damasco, caroço de ameixa, caroço de cereja e cascas de nozes (como avelãs, noz pecan, noz comun, entre outros) podem ser enumeradas como precursores estudados [18-27].

A estrutura de base de toda a biomassa lignocelulósica é composta por três principais polímeros naturais: celulose ($C_6H_{10}O_5$), hemicelulose ($C_5H_8O_4$) e lignina ($C_9H_{10}O_2$, $C_{10}H_{12}O_3$, $C_{11}H_{14}O_4$) [28]. A lignina é um polímero aromático mononuclear encontrada na parede celular de biomassa, especialmente as espécies de madeira, cuja função é a de estruturação das fibras de celulose em plantas [29]; o mais abundante recurso renovável de carbono na terra depois da celulose, com a produção mundial de 40-50 milhões de toneladas de CA por ano [30]. A lignina é rica em carbono e a sua estrutura molecular é semelhante ao carvão betuminoso, que faz com que seja um precursor adequado para a produção de carvão ativado [29]. A lignina, que consiste de cerca de 27% do teor de biomassa, tem baixa capacidade de adsorção em sua forma natural. Mas, o seu desempenho pode ser altamente melhorado em condições adequadas [28].

As propriedades e características do carvão ativado vão depender do tipo de material utilizado, dos processos químicos e de transformação a que este for sujeito. O processo de produção do CA envolve duas etapas principais: a carbonização ou pirólise da matéria-prima e a ativação do material carbonizado.

A conversão de biomassa lignocelulósica por processo pirolítico gera três fases: carvão, óleos (alcatrão) e gases [31]. A distribuição das fases é uma função dos parâmetros do processo, especialmente a taxa de aquecimento [32,33]. Aquecimento lento promove a conversão sólida, enquanto aquecimento rápido favorece a formação de óleos e gases. Quando o carvão é o produto final desejado, a conversão pirolítica é conduzida por aquecimento lento, que é conhecido como carbonização [33]. *Char* é o resíduo carbonado do processo de carbonização após a remoção de elementos diferentes de carbono, tais como o hidrogênio e o oxigênio a partir do material de partida [34]; ele tem uma estrutura porosa rudimentar, que o torna adequado para a produção de carvão ativado. *Char* tem um alto teor de carbono fixo, que faz com que seja um precursor adequado para tais fins [31].

A carbonização é feita a temperatura elevada (acima de 400°C), em atmosfera inerte (normalmente Nitrogênio ou Argônio) e envolve a decomposição térmica da matéria orgânica com desprendimento dos produtos voláteis (CO, CO_2, H_2 e CH_4). Neste processo o resíduo é composto pelos elementos minerais e por um esqueleto carbonizado, com massa fixa de carbono, e com área superficial específica pequena (algumas dezenas de m^2/g), com estrutura porosa rudimentar [35].

Após a carbonização se processa a ativação. Os métodos de ativação comumente empregados podem ser divididos em dois tipos principais: ativação térmica (ou física) e de ativação química.

Na ativação térmica utilizam-se as propriedades oxidantes de gases como o vapor d’água, CO_2 ou uma mistura destes a temperatura acima de 800°C [17,36]. De modo geral, a ativação física produz uma estrutura de poro tipo fenda, bastante fina, tornando os carvões obtidos, apropriados para o uso em processo de adsorção em fase gasosa, enquanto que a ativação química gera carvões com poros maiores, mais apropriados a aplicações em fase líquida [37]. A vantagem da ativação física sobre a química é que resulta em menor degradação ao meio ambiente, pois os subprodutos da ativação física são gases como CO_2 e CO, em baixos teores.

Na ativação química, utilizam-se compostos como $ZnCl_2$, hidróxidos de metais alcalinos, H_3PO_4, H_2SO_4, entre outros, e aquecimento moderado entre 400°C e 600°C, restringindo a formação de alcatrões. Os grupos químicos incorporados no interior das partículas do precursor reagem com os produtos da decomposição térmica, reduzindo a formação de compostos voláteis e inibe a contração das partículas, ou seja, ocorre ação desidratante do agente ativante sobre o precursor ainda não carbonizado, causando a degradação da celulose, juntamente com outros componentes presentes. Desta forma, a conversão do precursor de carbono é alta, e uma vez que o produto químico é eliminado após o tratamento térmico, uma grande porosidade interna é formada [38]. Carvões ativados com área de superfície muito alta têm sido preparados por ativação química. A estocagem de gás natural é uma aplicação potencial para tais materiais com elevada área de superfície [39]. As vantagens da ativação química sobre a ativação física são: o baixo custo de energia, já que o processo químico requer temperatura mais baixa do que o físico e o alto rendimento do produto final, e a principal desvantagem é a geração de efluentes com potencial poluidor, em alguns casos, não é possível identificar todos os compostos presentes nestes efluentes.

3.1.1. Estrutura Química dos CAs

A estrutura cristalina de um átomo de carbono tem uma influência considerável sobre a sua reatividade química. No entanto, a reatividade química no plano basal é consideravelmente mais baixa que nos sítios de ponta ou nas posições de defeitos. Consequentemente, CA altamente grafitizado com uma superfície homogênea constituída essencialmente de planos basais são menos reativos do que CAs amorfos [40].

Além da estrutura cristalina e porosa, a capacidade de adsorção de carvão ativado é determinada fortemente pela química de superfície. No caso de ocorrerem perturbações na estrutura microcristalina elementar do CA, devido à presença de camadas de grafite imperfeitas, pode resultar em uma variação no arranjo das nuvens de elétrons no esqueleto de carbono e consequentemente na criação de elétrons desemparelhados e valências incompletas, e isso influencia as propriedades de adsorção de carvões ativos, especialmente para compostos polares e polarizáveis. Além disso, os carvões ativos podem ser associados com átomos de enxofre, azoto e halogêneos [41]. Estes heteroátomos podem ser derivados do material de partida e se tornam parte da estrutura química como um resultado da carbonização imperfeita, ou tornam-se quimicamente ligados à superfície durante a ativação ou durante os tratamentos subsequentes. Eles aparecem como grupos funcionais orgânicos tais como: ácidos carboxílicos, lactonas, fenóis, carbonilas, aldeídos, éteres, aminas, nitrocompostos, fosfatos, entre outros [42].

O oxigênio é o heteroátomo mais importante, e a presença de grupos funcionais com oxigênio na superfície do CA influenciam as características de molhabilidade, polaridade e acidez, e as propriedades físico-química tais como reatividade catalítica, elétrica e química. Na verdade, o oxigênio combinado com o carbono confere propriedades que tornam o CA útil e eficaz em certos aspectos na adsorção [43].

Quanto maior o conteúdo de oxigênio, mais ácida é a dispersão aquosa do CA [44]. A presença de grupos ácidos (carboxílicos, lactônicos, fenólicos, anidridos, entre outros) na superfície do CA confere propriedades de trocadores catiônicos, enquanto que carvões ativados que apresentam baixo conteúdo de oxigênio têm propriedades básicas e são trocadores aniônicos [45]. A basicidade da superfície do carvão não é ainda bem entendida. Estruturas correspondentes ao cromeno ou semelhantes à pirona podem agir como sítios básicos. Alguns pesquisadores associaram o caráter básico dos carvões a concentrações de elétrons π dentro do plano base das estruturas do carvão [46]. Na Figura 3.1 são mostrados os grupos responsáveis pelo caráter ácido-base de CAs.

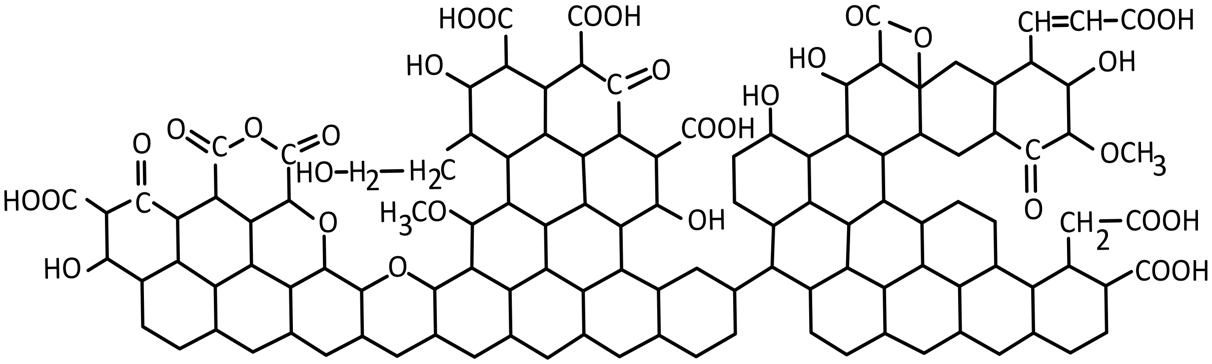

Figura 3.1. Modelo de superfície de carvão ativado oxidado (Adaptado de: Tarkovskya apud [47]).

3.2. Preparação de CAs a partir de biomassa

Neste parte do estudo é apresentado uma revisão da literatura sobre a preparação de CAs a partir da biomassa lignocelulósica. O efeito de vários parâmetros de operação tais como a temperatura de pirólise, a taxa de alimentação do agente de carbonização e tempo de pirólise na carbonização de biomassa lignocelulósica como um precursor de CA foi avaliado. Dados apresentados na literatura revelam que foi possível a produção de CAs com superfície BET de 2200 m^2/g e volume de microporos de 1,0 cm^3/g, em condições adequadas tem sido relatada. Nas Tabelas 3.1 e 3.2 é apresentada uma visão geral sobre a produção de CAs a partir de biomassa lignocelulósica com avaliação das condições de carbonização e tratamento, bem como avaliação de superfície para os CAs produzidos.

Tabela 3.1. Tipo de tratamento químico, tamanho de partícula e condições de carbonização e ativação para várias biomassas lignocelulósicas.

Biomassa	Tamanho da partícula	Condições de carbonização	Condições de ativação	Tratamento químico	Ref.
Semente de uva	–	N_2, 800°C/1h, 30 mL/min, 7°C/min	800°C por 24h	K_2CO_3	[48]
Casca de palmeira	2-2,8 mm	N_2, 200–600°C/2 h, 150 mL/min	500–900°C/2 h, 100 mL/min	CO_2	[49]
Caroço de pêssego	2-2,8 mm	N_2, 850°C/2 h, 80 mL/min, 2°C/min	800°C/3 h, 80 mL/min	50% CO_2/N_2	[50]
Eucalípto	–	N_2, 450°C, 500 mL/min	825°C	N_2/CO_2, 50 mL/min	[51]
Casca de noz de macadâmia	500–700 µm	N_2, 700°C/2 h, 100 mL/min	800°C/0–480 min	CO_2	[52]
Caroço de damasco	1,2–1,7 mm	N_2, 400°C	–	Chemical (H_3PO_4)	[53]
Casca de coco	–	N_2, 850°C/30 min	600°C/30 min	–	[54]
Esparto (grama)	15cm	N_2, 400°C/1 h, 85 mL/min, 10°C/min	800°C, 85mL/min	CO_2	[48]
Casca de coco	–	N_2, 1000°C/2 h, 100 mL/min, 10°C/min	900°C/210 min, 600mL/min	CO_2	[55]
Carvalho (madeira)	0,5-1 mm	N_2, 500°C, 100 mL/min	800°C/120 min	CO_2	[56]
Casca de milho	0,5-1 mm	N_2, 500°C, 100 mL/min	800°C/120 min	CO_2	[56]
Palha de milho	0,5-1 mm	N_2, 500°C, 100 mL/min	800°C/120 min	CO_2	[56]

Nabais e colaboradores [57] concluíram que a produção de carvões ativados utilizando dióxido de carbono como agente de ativação tem um potencial interessante, visto que os CAs resultantes apresentam propriedades microestrutural, o que é de grande importância para processos de adsorção líquida e gasosa. A porosidade dos carbonos produzidos, neste estudo, a partir de esparto, foi de 0,46 cm^3/g, com área de superfície BET aparente de 1122 m^2/g, além disso os CAs apresentaram características básicas com ponto de carga zero entre 9,25 e 10,27. De acordo com os referidos autores, o uso de esparto para a produção de carvão ativado pode criar um excedente econômico valioso para os agricultores, o que é importante em um momento de crise econômica.

Okman e colaboradores [48] usaram semente de uva como matéria-prima para a preparação de CAs através da ativação química com K_2CO_3 durante as temperaturas de carbonização de 600 e 800°C. Os resultados experimentais mostraram que os CAs apresentaram áreas de superfície BET maiores que 1200 m^2/g e volume de microporos de 0,47 cm^3/g. As áreas de superfície dos CAs foram fortemente afetada pela temperatura de carbonização e pela concentração do reagente de ativação. A temperatura ideal de carbonização para as maiores áreas de superfície foi 800°C. A concentração ótima de reagente foi 50% de K_2CO_3 em massa da matéria-prima. Os CAs obtidos apresentaram principalmente características microporosas.

Tabela 3.2. Características físicas dos carvões ativados provindos de diferentes biomassas lignocelulósicas.

Biomassa	*Burn-off* %	S_{BET} (m^2/g)	V_{mic} (cm^3/g)	V_t (cm^3/g)	Ref.
Semente de uva	–	1238	0,47	–	[48]
Casca de palmeira	–	1360	0,47	0,69	[58]
Caroço de pêssego	59	1247	0,44	–	[59]
Eucalípto	83	1491	0,66	0,8	[60]
Casca de noz de macadâmia	34	802	0,3	–	[52]
Caroço de damasco	35	683	0,16	0,747	[61]
Casca de coco	–	1512	0,46	0,618	[62]
Esparto (grama)	60	1122	0,46	–	[57]
Casca de coco	–	2288	1,01	–	[55]
Carvalho (madeira)	51	985	0,38	0,64	[56]
Casca de milho	45	975	0,38	0,68	[56]
Palha de milho	50	616	0,23	0,42	[56]

S_{BET}: área de superfície calculada usando a equação BET; V_{mic}: volume do microporo determinado de acordo com o método de DR, e V_t: volume de poro total calculado através da conversão da quantidade de gás N_2 adsorvido a uma pressão relativa de 0,99 para o volume de líquido de N_2

A casca de coco é o precursor agroindustrial mais popular e industrialmente adotado para a produção de carvão ativado. Yang e colaboradores [55] produziram CA utilizando casca de coco por processo pirolítico com posterior ativação combinando CO_2 e aquecimento por micro-ondas. A carbonização foi realizada a 1000°C sob uma atmosfera de N_2 com aquecimento convencional seguido por ativação a 900°C pelo aquecimento por micro-ondas. A área de superfície BET dos carvões ativados resultou em valores superiores a 2000 m^2/g. Os carvões ativados são constituídos principalmente de microporos com mesoporos contribuindo em 20 % do volume total de poros. A ativação utilizando CO_2 e microondas tem sido considerada uma técnica muito promissora.

Com resíduos de madeira de carvalho, casca de milho e palha de milho, Zhang e colaboradores [56] desenvolveram CAs por processo pirolítico com posterior ativação utilizando CO_2. Os CAs produzidos apresentaram áreas superficiais BET variando de 616 a 985 m^2/g, e volume de microporos variando de 0,23 a 0,38. Tanto a área de superfície como a porosidade são significativamente afetados pelas condições de ativação, pois anteriormente a ativação os CAs apresentavam áreas superficiais BET entre 38 a 90 m^2/g. Em geral , quanto maior for a temperatura de ativação, maiores são as áreas de superfície e volumes de microporos dos CAs resultantes. No entanto, os CAs são afetados de forma diferente pela duração da ativação.

Recentemente, tecnologias de produção de CAs baseadas em biomassa têm atraído considerável atenção devido a qualidade e características dos materiais adsorventes gerados. Até o presente, pouco tem sido publicado sobre a preparação e caracterização de CAs provindos de biomassas (exceto casca de coco) com aplicações em grande escalas para tratamento de efluentes líquidos e gasosos. Mas, o elevado potencial da biomassa lignocelulósica para a produção de CAs foi confirmada por muitos investigadores. Resultados promissores na produção de CA lignocelulósico com grande área de superfície, alta microporosidade e seletividade foram alcançados. Aplicações bem sucedidas de CA baseados em biomassa em sistemas de tratamento de efluentes foram relatados. Contudo, investigações mais detalhadas sobre aplicações destes CAs e otimização de processos, são necessárias para garantir altos investimentos por parte de indústrias.

3.3. Fonte de biomassa – precursor do CA

O engaço da uva é constituído pelo pedúnculo e pelos pedicelos (ramificações mais curtas), e tem como funções básicas suportar e servir de via de alimentação aos grãos. A Figura 3.2 mostra o engaço da uva. O engaço representa 30% do peso de todo residual da indústria da uva e ainda apresenta baixo valor nutritivo e comercial [63].

Figura 3.2. Fotografia do engaço de uva.

O estado do Rio Grande do Sul processou industrialmente 606,1 milhões de quilos de uva no ano de 2014. Deste total, aproximadamente 36,5 milhões de quilos são representados pelo engaço. O principal destino para este resíduo é a disposição nas lavouras. As características estruturais do engaço de uva possibilitam a utilização como matéria prima com boa fonte de carbono para a produção de carvão ativado.

A Tabela 3.3 mostra dados da literatura relativos à composição lignocelulósica do engaço da uva.

Tabela 3.3. Características químicas do engaço de uva.

Elemento	% em massa
Cinzas	5 – 10
Celulose	24 – 38
Lignina	20 – 33
Hemicelulose	14 – 21
Outros	16 – 21

Fonte: [63,64,65]

A composição da biomassa lignocelulósica tem um efeito significativo na estrutura microporosa do produto final (CA). Pesquisadores confirmaram que a lignina é a principal fonte de carbono puro, enquanto que a celulose e hemicelulose são as frações voláteis de biomassa [66].

A decomposição da lignina começa em temperaturas baixas (160-170°C), e este processo continua a uma taxa baixa, até temperaturas elevadas próximas de 900°C. O segundo componente, que começa a decompor é a hemicelulose, seguido pela celulose. A decomposição destes dois polímeros ocorre num intervalo de 200-400°C. Neste intervalo de temperatura ocorre a decomposição principal da biomassa. Portanto, a composição da biomassa lignocelulósica é um parâmetro importante na formação de resíduo carbonado e os resultados mais elevados de conteúdo de lignina indicam maior rendimento de carbono puro [67]. As composições de algumas biomassas lignocelulósicas estão indicadas na Tabela 3.4.

Tabela 3.4. Características químicas de biomassas lignocelulósicas (% em massa seca).

Biomassa	Celulose	Hemicelulose	Lignina	Ref.
Caroço de pêssego	26,6	24,3	47,7	[71]
Caroço de damasco	39,7	34,5	25,7	[71]
Carvalho (madeira)	53,2	24,7	24,6	[72]
Eucalipto (madeira)	57,3	16,8	25,9	[60]
Casca de coco	48,9	19,8	30,1	[73]
Casca de noz	25,6	22,1	52,3	[74]
Casca de palmeira	29,7	16,9	53,4	[69]

Reed e Williams [68] estudaram cinco amostras de biomassa com conteúdo de celulose, hemicelulose e lignina significativamente diferentes. Eles observaram que a temperatura de decomposição térmica em atmosfera de N_2 estava na gama de 325-400, 250-350 e 200-720°C para a celulose, hemicelulose e lignina, respectivamente. Eles também concluíram que a amostra com maior teor de lignina apresentou o maior rendimento de carvão e, consequentemente, maior quantidade de carvão ativado. Em outra investigação conduzida por Daud e Ali [69], a taxa de ativação da casca de palmeira e casca de coco foi comparada. Foi observado que a taxa de ativação do carvão à base de casca de coco foi mais elevada do que a do carvão à base de casca de palmeira, devido ao teor de lignina da casca de palmeira (vide tabela 3.4). Em outro estudo realizado por Daud e colaboradores [70], o efeito da temperatura de carbonização da casca de palmeira foi investigado. Os autores relataram que com o aumento da temperatura de 500 para 900°C, o rendimento de carbono puro diminuiu gradualmente de 33% para 24%. A diminuição na produção de carvão ocorreu devido à liberação de carbono, hidrogênio e oxigênio do carvão como resultado do rearranjo do anel aromático na estrutura de carbono. Eles também concluíram que o volume de microporos aumentou à medida que a temperatura de carbonização foi aumentada gradualmente. Experimentos similares foram realizados com casca de coco por Li e colaboradores [62]. Eles também perceberam que, com o aumento da temperatura de carbonização, o diâmetro da amostra reduziu e o volume de microporos foi desenvolvido. Os autores concluíram que durante a pirólise, as moléculas de celulose, hemicelulose e lignina sofrem desidratação, e com a quebra de ligações ocorre um ordenamento estrutural do carbono residual dando origem as reações de polimerização. Foi identificado que com o aumento da temperatura de carbonização implica em aceleração da reação de polimerização, aumentando o volume de microporos. Foram obtidos CAs com superfície BET de 702 m^2/g a 1000°C.

3.4. Regeneração de CA

O objetivo principal da regeneração consiste em remover os poluentes adsorvidos, a fim de recuperar a capacidade de adsorção original do CA. Este processo pode ser realizado a partir de duas vertentes distintas. A primeira contempla a regeneração baseada apenas na dessorção dos compostos adsorvidos no CA sem a preocupação em destruí-los, onde ocorre apenas o transporte de massa de uma fase (superfície do CA) para outra. Já a segunda vertente, trata da regeneração baseada na decomposição dos poluentes adsorvidos no CA envolvendo reações de decomposição com possibilidade da completa mineralização dos poluentes. A Figura 3.3 apresenta um esquema das principais técnicas de regeneração divididas em dois grupos: dessorção e decomposição. Apartir dessa divisão estabelecida dos processos de regeneração esta seção informa os conceitos gerais e as principais caracteríticas das técnicas de regeneração.

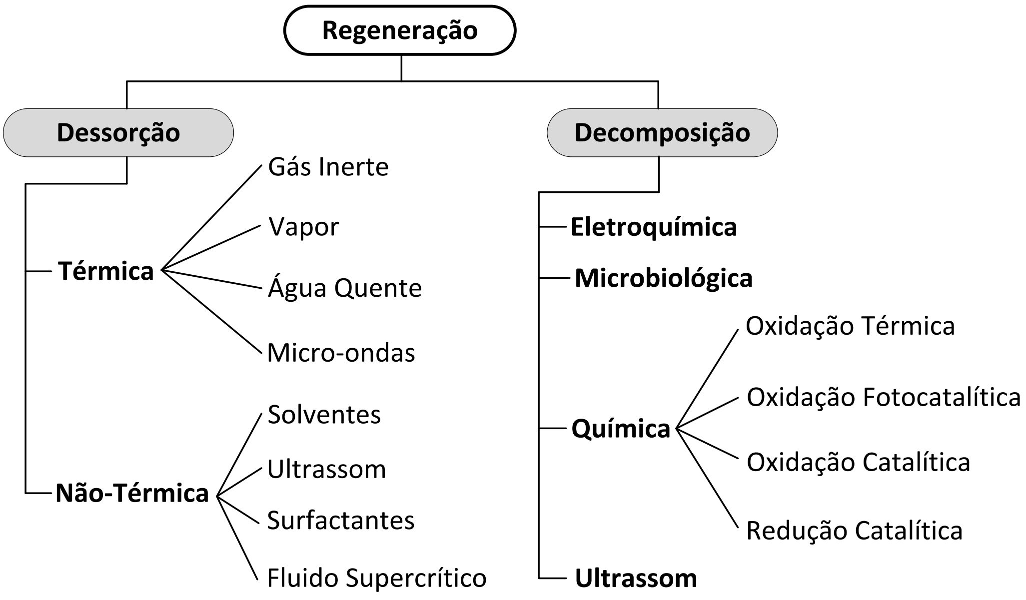

Figura 3.3. Principais técnicas para regeneração de CA utilizados em processos de adsorção.

3.4.1. Métodos de Regeneração de CA por Dessorção

Métodos de regeneração por dessorção podem ser aplicados tanto para CA carregados com compostos orgânicos ou inorgânicos. Nos métodos de regeneração por dessorção, não ocorre decomposição do adsorvato, o que acontece nestes casos é uma transferência do composto adsorvido na fase sólida para outro meio. Assim, em aplicações que envolvam compostos perigosos, esta não é uma tecnologia interessante, visto a geração de um passivo ambiental. O principal objetivo em aplicar processos de regeneração por dessorção em CA está relacionado com a facilidade e com a rapidez no processo, além da eficiência de recuperação da capacidade de adsorção do CA e a recuperação de compostos de interesse. Um exemplo disto foi apresentado por Soleimani e Tahereh [75] onde o cianeto de ouro que adsorvido sobre o CA, é rapidamente recuperado por um processo de duas fases à temperatura ambiente. O primeiro passo compreende o contato do CA carregado com cianeto de ouro com uma solução de hidróxido de sódio. O segundo passo consiste em fazer contatar o CA carregado com cianeto de ouro e molhado com solução de hidróxido de sódio, com uma segunda solução composta de um solvente orgânico, preferencialmente uma solução aquosa de acetona ou acetonitrila 40% (v/v). Este estudo mostrou que esta técnica de regeneração apresenta recuperação de mais de 80% do ouro adsorvido a partir de CA em menos de 2 h.

A regeneração por dessorção de CA saturado está dividida em dois grupos: regeneração térmica e não-térmica.

3.4.2. Métodos de Regeneração de CA por Decomposição

Métodos de regeneração por decomposição são aplicados para CA carregados com compostos orgânicos ou inorgânicos oxidáveis. Um processo de regeneração ideal deve renovar a superfície do CA e destruir os contaminantes adsorvidos, de modo que estas substâncias não sejam transferidas para outro meio, ou, dessorver os contaminantes e destruí-los em solução.

Os objetivos da regeneração por decomposição são transformar os contaminantes adsorvidos em subprodutos menos tóxicos ou mineralizá-los completamente, restabelecer a capacidade de sorção e aumentar a vida útil do CA, reduzindo desta forma os custos no processo de adsorção.

Os métodos de regeneração por decomposição para CA saturado estão divididos em quatro grupos: regeneração eletroquímica, microbiológica, química e por ultrassom. A seguir serão apresentadas as principais características da regeneração eletroquímica escolhida neste estudo para aplicação na regeneração de carvões ativados saturados com compostos orgânicos.

3.4.3. Regeneração Eletroquímica

A técnica de regeneração eletroquímica para CA carregado com compostos orgânicos é considerada como uma das principais, mais eficazes e promissoras técnicas de regeneração [76-80] e vem sendo extensamente estudada [79,81-87]. Os principais motivos para tanto são a capacidade de regeneração do CA com possibilidade de decomposição total dos adsorbatos e facilidades de controle do processo.

De acordo com estudos prévios [76,78,79,82], na tentativa de regenerar eletroquimicamente o CA carregado, e percebendo a baixa condutividade deste adsorvente, foi imprescindível o uso de um eletrólito, que é o reagente principal do processo, objetivando a transferência de elétrons. Além disso, é indispensável controlar o tempo e energia necessários para a regeneração, visto que, estas variáveis apresentam sinergia, quando o controle é realizado corretamente.

A regeneração eletroquímica refere-se à regeneração de um adsorvente carregado, disposto dentro de uma célula eletrolítica contendo uma solução de eletrólito, na qual é aplicado a um dado potencial elétrico [78,81,84,88,89]. O mecanismo de regeneração eletroquímica envolve a eletrodessorção e/ou a destruição dos contaminantes adsorvidos no carvão ativado com objetivo de restaurar a capacidade do adsorvente.

A decomposição orgânica em meio aquoso pode ocorrer por meio de duas vias:

i. conversão eletroquímica - onde compostos não biodegradáveis são transformados em compostos biodegradáveis;

ii. combustão eletroquímica - onde todos os contaminantes orgânicos são totalmente mineralizados.

De acordo com García-Otón [78] o método eletroquímico é mais eficaz para regeneração do carvão ativado, em comparação com regeneração térmica, uma vez que dificilmente modifica a estrutura porosa do material. Portanto, além de regenerar o CA possibilitando o seu reuso, a regeneração eletroquímica pode aumentar a capacidade de adsorção do CA pelas modificações químicas dos grupos de superfície.

A técnica de regeneração eletroquímica é capaz de oxidar ou reduzir íons metálicos, cianetos (CN^-), compostos organoclorados, hidrocarbonetos aromáticos e alifáticos. O uso de eletrodos metálicos revestidos de óxidos de metais nobres propicia a formação do ânion OH^- que pode ser fisicamente adsorvido na superfície anódica durante a eletrólise da água. A geração desse agente oxidante é realizada sem que ocorra a perda ou dissolução do material anódico, sendo por esses motivos denominados como ânodos dimensionalmente estáveis, usualmente conhecidos por sua sigla em inglês DAS - Dimensionally Stable Anodes. Os eletrodos mais utilizados são de titânio metálico, revestidos com óxidos de metais nobres (por exemplo, platina).

Para Comninellis e Pulgarim [90] a eletrooxidação de compostos orgânicos sobre eletrodos de platina pode ocorrer através da formação de uma película de óxido do material do ânodo na superfície do eletrodo. A adsorção do radical hidroxila na superfície do ânodo ocorre como o primeiro passo, de acordo com a reação:

$$PtO_x + H_2O \rightarrow PtO_x(\bullet OH) + H^+ + e^- \qquad (3.1)$$

Num segundo passo, o radical hidroxila pode reagir com o oxigênio presente no óxido anódico, produzindo um superóxido, conforme equação 3.2 a seguir:

$$PtO_x(\bullet OH) \rightarrow PtO_{x+1} + H^+ + e^- \qquad (3.2)$$

Portanto, a coexistência de dois estados de oxigênio ativo na superfície do eletrodo pode ser considerada, onde um dos estados está quimicamente adsorvido, e um radical hidroxila está fisicamente adsorvido. Na falta de material orgânico, ambas as fases do oxigênio ativo podem produzir O_2 de acordo com as reações (3.3) e (3.4).

$$PtO_x(\bullet OH) \rightarrow \frac{1}{2}O + PtO_x + H^+ + e^- \qquad (3.3)$$

$$PtO_x \rightarrow \frac{1}{2}O + PtO_x \qquad (3.4)$$

Na presença de radicais orgânicos (*R*), é possível chegar a completa mineralização desses compostos, pela ação dos produtos da oxidação dos radicais hidroxila, ou radicais seletivos (R_{OX}) podem ser obtidos, através da interação com o oxigênio ativo quimicamente adsorvido, como mostrado nas reações (3.5) e (3.6).

$$R + PtO_x(\bullet OH)_z \rightarrow PtO_x + zH^+ + ze^- + CO_2 \qquad (3.5)$$

$$R + PtO_{x+1} \rightarrow PtO + R_{ox} \qquad (3.6)$$

A regeneração eletroquímica de CA pode ser realizada sobre o eletrodo catiônico ou sobre o eletrodo aniônico. Narbaitz and Cen [76] mostraram que a regeneração catódica é de 5 a 10% mais eficiente do que a regeneração anódica. Por outro lado, na regeneração catódica uma pequena quantidade de fenol permanece no eletrólito, ao passo que o fenol residual na anódica não foi detectado.

Narbaitz e Cen [49], Zhou e Lei [79], e Zhang [77] constataram que o NaCl é o eletrólito de melhor desempenho entre vários outros sais, quando realizado regeneração de CA carregado com fenol, e que concentrações de NaCl (maiores que 3% em massa) não melhoram a eficiência de regeneração.

A Figura 3.4 apresenta uma situação típica de célula eletrolítica para regeneração de carvão ativado carregado com compostos orgânicos. A densidade de corrente aplicada é um dos fatores mais importantes na oxidação de compostos orgânicos. Zhou and Lei [79] mostraram que na ausência de corrente elétrica a eficiência na regeneração do carvão ativado carregado com compostos orgânicos, foi entre 1 e 2%, valores que podem ser desconsiderados pela margem de erro relacionada ao método utilizado pelos pesquisadores.

Assim a capacidade de regeneração utilizando esta técnica, deve ser atribuída à corrente aplicada.

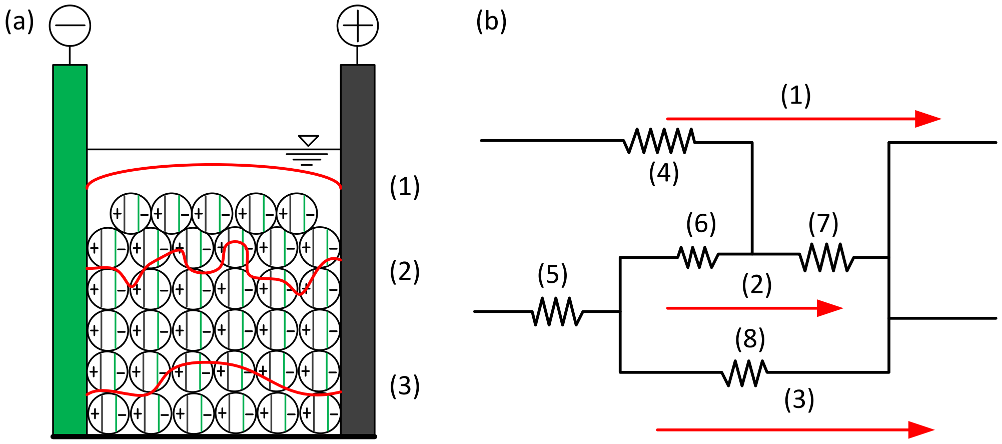

Figura 3.4. Modo de corrente para regeneração eletroquímica de CA (a) e circuito equivalente do sistema (b). (1) By-pass de corrente; (2) Corrente efetiva; (3) Curto circuito de corrente; (4) Resistência de contato; (5) Resistência entre partículas; (6) Resistência de reação; (7) Resistência interna da partícula; (8) by-pass de resistência. Adaptado de: Wang and Balasubramanian [91].

Se o reator está operando em condições galvanostáticas, é possível identificar dois regimes diferentes de funcionamento, que são o controle da corrente e o controle de transferência de massa [92].

Em um estudo recente, Narbaitz e Karimi-Jashni [83] investigaram quatro diferentes reatores eletroquímicos para regenerar CA carregado com fenol. Um reator de vidro simples com operação em batelada composto por eletrodos horizontais; um reator de aço inoxidável do tipo coluna; um reator batelada em vidro com capacidade para recirculação do eletrólito; e um reator dividido em células com separação dos eletrodos por uma membrana trocadora de íons. Os autores encontraram resultados de regenerações na faixa de 74 a 90%; e concluíram que a regeneração eletroquímica de CA está em desenvolvimento e uma configuração ótima de reator ainda deve ser desenvolvida. No entanto, estes consideram que estudos em escala de laboratório são muito promissores [83].

A eletrooxidação de fenol ocorre através da formação do radical fenoxi, que reage com outras espécies presentes na solução, ou reage com outras moléculas de fenol produzindo um radical dímero; esse radical pode ser oxidado formando polímeros ou quinonas, dependendo das condições utilizadas. Para concentrações elevadas de fenol em meio básico, a polimerização é favorecida, enquanto que para baixas concentrações de fenol em meio ácido a formação de quinonas é favorecida. A partir da reação de oxidação da quinona, ácidos carboxílicos (ácido maleico e oxálico) são obtidos. Estes produtos são de difícil oxidação, mas são compostos biodegradáveis e, portanto, o processo de eletrooxidação pode ser associado a um processo biológico [93].

A regeneração eletroquímica de CA carregado com compostos orgânicos apresenta algumas vantagens em relação aos métodos térmicos e não térmicos. Pode ser convenientemente operado *in situ* [88,91,94-96], com um menor consumo de energia e curto tempo de regeneração; o elétron é o único reagente, e requer tratamentos e equipamentos simples. Além disso, o ajuste apropriado da corrente aplicada (ou potencial de eletrodo) e de outras variáveis operacionais (tais como o tempo de eletrólise, a composição do elétrodo, etc) pode permitir a transformação de poluentes orgânicos em compostos menos perigosos, ou até mesmo a sua completa mineralização [95].

Em geral, a regeneração eletroquímica de CA tem ganhado atenção devido às suas características únicas, tais como operação a baixa temperatura, sem adição de produtos químicos e dessorção in situ de compostos orgânicos depositados sobre o CA, além de reduzir os danos às propriedades estruturais e características do CA [96].

3.5. Considerações finais do capítulo

A síntese de carvões ativados é um tema de investigação muito importante devido às características que estes materiais apresentam, relacionadas com a sua estrutura porosa e os grupos funcionais de superfície. A produção de CA a partir de precursores lignocelulósico além de baixos custos e a utilização de fontes renováveis, pode ser útil na utilização de resíduos agroindustriais. Muitas aplicações para os CAs estão relacionadas principalmente com as características físicas e químicas da sua superfície nomeadamente, da distribuição de tamanho de poros, área superficial e volume de poros. Estas propriedades, conjugadas com a crescente preocupação ambiental, resultam na aplicação industrial dos carvões ativados nos mais diversos processos, por exemplo: em processos de adsorção, suporte de catalizadores, entre outros.

No entanto, após a adsorção de compostos tóxicos, o carvão ativado torna-se um resíduo perigoso que devem ser tratado ou disposto corretamente. A incineração de carvões ativados saturados é frequentemente o tratamento final mais utilizado, porém, tem alguns inconvenientes principais: os custos de operação, a destruição do adsorvente, bem como a emissão de compostos possivelmente tóxicos. Estudos têm mostrado que os carvões ativados geralmente não recuperam a sua capacidade de adsorção total por este método devido à perda de massa e por consequência a perda de área superficial.

A viabilidade econômica de processos que utilizam adsorção é, assim, diretamente relacionada com a sua eficiência na regeneração e reciclagem do carvão ativado. Métodos de regeneração eletroquímicos são estratégias alternativas que podem apresentar bons resultados devido a características do processo, por exemplo, operações à temperatura e pressão ambientes, baixo consumo de energia e com requisito de tempos curtos. Além disso, o ajuste apropriado da corrente (ou potencial) aplicada e outras variáveis operacionais (como o tempo de reação) podem permitir a modificação de poluentes orgânicos em compostos menos nocivos ou mesmo a mineralização completa, usando elétrons como o único reagente. Assim, os poluentes adsorvidos podem ser tratados sem oxidantes adicionais.

O presente trabalho está inserido neste contexto pela produção de carvão ativado a partir de engaço de uva e desenvolvimento de um reator eletroquímico aplicado à regeneração do carvão ativado saturado com fenol.

CAPÍTULO 4

INTRODUÇÃO AOS CAPÍTULOS 5 A 8

Os capítulos 5, 6, 7 e 8 estão apresentados em forma de artigos científicos. Em cada artigo são apresentados os seguintes itens: introdução ao assunto abordado, materiais e métodos detalhados, resultados, discussão e referências.

No Capítulo 5 é apresentado o artigo intitulado "Desorption - and Decomposition-Based Techniques for the Regeneration of Activated Carbon". Artigo de revisão sobre métodos de regeneração de carvões ativados saturados, publicado na revista Chemical Engineering & Technology.

No Capítulo 6, é apresentado o estudo e desenvolvimento do reator eletroquímico utilizado na regeneração de carvão ativado saturado com fenol. São avaliados efeitos de corrente, modo de operação do reator, tipo de eletrólito, regeneração catódica ou anódica e tempo de regeneração na configuração e caracterização do reator desenvolvido. Este artigo foi submetido à revista Chemical Engineering Journal.

No Capítulo 7, são apresentados os aspectos da produção de carvão ativado a partir de engaço de uva com avaliação de diferentes condições de ativação. Neste estudo objetivou-se o desenvolvimento de carvão ativado com altas capacidades de adsorção relativa à área de superfície e à porosidade. Um amplo estudo da superfície dos carvões ativados desenvolvido é apresentado neste capítulo. Este artigo foi submetido à revista Chemical Engineering Science.

Por fim no Capítulo 8, são apresentados dados da capacidade de adsorção do carvão ativado produzido para fenol, e dados de regeneração eletroquímica realizada no reator desenvolvido neste trabalho. Também é apresentada uma comparação entre o desempenho do carvão ativado produzido a partir do engaço de uva e o carvão ativado comercial no processo de adsorção/regeneração. Este artigo ainda será submetido à publicação.

CAPÍTULO 5

Artigo: Desorption - and Decomposition-Based Techniques for the Regeneration of Activated Carbon

Neste capítulo, é apresentado o artigo de revisão sobre regeneração de carvões ativados utilizados em processos de adsorção, publicado na revista Chemical Engineering & Technology, volume 37, número 9, páginas 1447 - 1459, em 2014. Neste estudo, são abordados aspectos importantes relacionados às principais técnicas de regeneração de carvão ativado, avaliando-se parâmetros individuais e comparando desenpenho entre diferentes técnicas. É apresentada uma visão geral dos trabalhos de maior relevância e recentemente publicados nesta área.

5.1. Artigo: Desorption - and Decomposition-Based Techniques for the Regeneration of Activated Carbon

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Desorption- and Decomposition-Based Techniques for the Regeneration of Activated Carbon

Activated carbon (AC) is an adsorbent used in most adsorption processes related to micro removal of pollutants from the water phase, but the application is limited due to high costs and environmental issues related to the disposal after saturation. Different regeneration techniques, reducing costs and minimizing environmental impact, are reported for the reuse of saturated AC. These techniques can be performed via two separate strands: regeneration based only on desorption of adsorbed compounds in AC, or based on the decomposition of pollutants adsorbed on AC. Literature on the regeneration of saturated ACs is reviewed and promising techniques are highlighted. One of the most challenging bottlenecks preventing the commercial application of regeneration technologies is the difficulty of scaling-up.

Keywords: Activated carbon, Absorption, Adsorption, Regeneration technology

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1 Introduction

1.1 General Aspects

Activated carbon (AC) has proven to be an effective adsorbent to remove a wide variety of organic and inorganic pollutants dissolved in aqueous solutions or in gas streams. Because AC presents an exceptionally high surface area, it is an adsorbent widely used for wastewater treatment [1–3]. Hence, the well-developed porous structure of AC and a wide range of surface functional groups are responsible for most adsorption mechanisms. Being a porous material, AC is able to distribute chemical compounds on its hydrophobic surface, making it accessible to other reagents.

Despite its widespread use in adsorption processes, the main drawback to its industrial application will principally depend on the nature of the pollutants adsorbed upon it and especially the ease with which they can be desorbed [4]. Once its adsorption capacity has been exhausted, ACs can be deposited in landfills, incinerated or regenerated for reuse [5–7]. However, the disposal of hazardous waste in landfills is becoming increasingly unacceptable due to growing concerns about the effect of pollutants on the environment and more stringent environmental standards. This has motivated the development of regeneration systems to allow broader application of AC adsorption and ensure its economic viability and environmental security [8–10].

The main purpose of regeneration is to remove the adsorbed pollutants in order to recover the original adsorption capacity of the AC. This process can be performed via two distinct process routes. The first involves regeneration based only on desorption of the adsorbed compounds without AC reactions, requiring only the mass transport from one phase, the AC surface, to another. The second addresses regeneration based on decomposition of the pollutants adsorbed on the AC, involving decomposition reactions with the possibility of complete mineralization of the pollutants. Fig. 1 illustrates schematically the routes of the main regeneration techniques divided into two groups: desorption and decomposition.

Much of the research presented in this review reflects development, influential concern about the costs involved in regeneration, as well as environmental issues surrounding the process. On this basis, this article consists of a summary and a literature survey on major regeneration techniques for AC, which may be of scientific value for future work and for future commercial applications. A discussion of the main techniques and studies is included, presenting their advantages and disadvantages in addition to issues relevant to the advance of studies on this subject.

1.2 Activated Carbon in Large-Scale Applications

The worldwide demand for AC was about 4.28 million tons in 2012, and it is expected to increase more than 10 % annually

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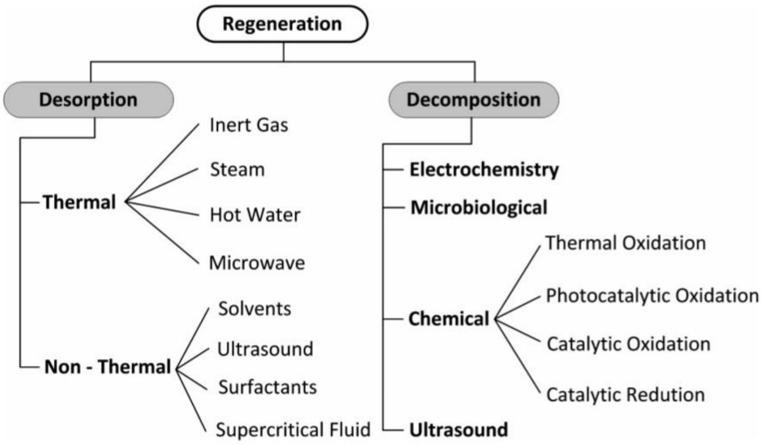

Figure 1. AC regeneration techniques used in adsorption processes.

over the next five years. This increase in AC demand is probably due to the restrictive pollution legislation established in the USA and China. For example, in China, there is a project called the Twelfth Five Year Plan (2011–2015), which aims to improve the quality of water and air through the use of more environmentally friendly processes. In this way, the AC application demand to reduce emissions and for wastewater treatment by adsorption processes will increase significantly [11].

The application of AC in large scale can be observed in various fields such as: (i) purification of different types of liquid food ingredients, including edible oils, extracts, concentrates, additives, and acids; (ii) discoloration, deodorization, and reduction of contaminant liquids, including juice concentrates and spirit beds in beverages production; (iii) discoloration and purification of different kinds of processing liquid phase using fixed-bed columns for a wide variety of chemicals and chemical intermediates; (iv) purification of drinking water and reduction of geosmin and methyl isoborneol, flavor and odor components, total organic carbon (TOC), and herbicides such as atrazine. Other applications include air purification, control of organic vapors, odor control, corrosive acid gas and metal removal.

The treatment of gases, originated from municipal solid waste combustion, is another example of large-scale application. The process is practical and has a good efficiency; however, it generates large amounts of saturated AC intended to controlled landfills.

Aikyo and Suzuki [12] indicated some problems in large-scale application of AC adsorption applied to municipal fuel gas, regarding the disposal of solid containing absorbed dioxins. Most owners or operators of municipal solid waste incineration plants often find that the cost of AC, including the purchase and disposal costs, is expensive compared with other items of operation and management. Minimizing the cost of AC has become an important issue, and from the viewpoint of engineering applications an interesting initiative would be to reduce the cost of operation.

The individual cost of adsorbents, i.e., AC, depends on availability, processing necessary conditions, both local treatment and recycling issues, and lifetime. Cost will vary when the adsorbents are made in and for the developed, developing or underdeveloped countries. The production costs of AC as well as the surface area and costs of raw materials are presented in Tab. 1.

The costs of AC regeneration rarely appear in the literature, which is a suggestion for future work. Huling and colleagues [14] performed cost studies involving the process of regeneration of AC saturated with methyl *tert*-butyl ether using Fenton-drive, and as a result they obtained a cost of 1.32 US $ per kg granular activated carbon (GAC). They concluded that the cost of regeneration could be lower than that of production associated with the cost of adsorbent disposal.

Weng and Hsu [1] studied the cost to regenerate AC saturated from a treatment plant wastewater using an electrochemical technique. Considering the energy demand, the optimum conditions for a 91.1 % regeneration (RE) with an energy cost of 39 US $ per ton were: 0.1 M NaCl, 24 h, and 5 V cm^{-1}. Compared to thermal, ultrasonic, and base washing regenerations, this electrochemical process is effective and economically viable for GAC regeneration.

Horng and Tseng [15] examined an in situ recirculation system, which couples a H_2O_2/UV photoreactor to an adsorber with saturated GAC for regeneration. Acetone and isopropyl alcohol (IPA) were chosen as representative organic adsorbates, since they are water-soluble and commonly used in industrial operations. The regeneration reaction for the intermittent UV mode requires less oxidant to achieve GAC regeneration within a certain time interval. Therefore, it is a more economically advantageous mode than the continuous one. The operating cost was about 0.04 US $ for treating every gram of acetone in the air.

2 Regeneration by Desorption Methods

Methods of regeneration by desorption can be generally applied to AC loaded with both organic and inorganic compounds. Desorption regeneration methods involve the transfer

Table 1. Costs of activated carbon production plant. Adapted from [13].

Raw material	Raw material cost [US $ kg^{-1}]	Average cost of production [US $ kg^{-1}]	N_2 BET surface area, [m^2g^{-1}] (mean values)
Wood	0.808	2.17	800
Pet coke	1.394	1.19	2000
Carbon black	1.459	1.18	500
Charcoal	1.186	1.28	1450
Lignite	0.739	1.95	1500

of the compound adsorbed onto the surface of a solid phase to another phase, but even during low thermal treatment, a fraction of the adsorbate is not desorbed, but undergoes chemical transformations on the carbon surface, e.g., polymerization, cracking, reactions with the secondary products evolved during regeneration, so the process cannot be considered fully reversible. In fact, during desorption, the adsorbate is not the only species evolved, but there are other gases that can be found in the gas. This is not an appropriate technology, because the pollutant issue is just postponed, or the transport requires the wastewater compound to be treated by adsorption with subsequent desorption in another medium. The main purpose of applying desorptive regeneration to AC is related to the ease and speed of the process, the recovery efficiency of the AC adsorption capacity, and the recovery of compounds of interest, but a pure desorption process in which the adsorbate is totally removed is very difficult to achieve. An example was presented by Soleimani and Kaghazchi [16], in which gold cyanide adsorbed on AC is quickly recovered from the AC by a two-step process at ambient temperature. The first step comprises contacting gold cyanide-loaded AC with 1 M sodium hydroxide solution. After a sufficient pre-soak time period, usually about 15 min, the aqueous base solution is removed from the bottle. The second step consists in contacting the AC loaded with gold cyanide with 50 mL of a solution of an organic solvent, most preferably a 40 vol % aqueous solution of acetonitrile, acetone, methanol, ethanol, and isopropanol, which recovered more than 80 % of the adsorbed gold from AC in less than 2 h.

The regeneration by desorption of saturated AC is divided into two types of process, nonthermal and thermal, which are discussed separately below.

2.1 Thermal Regeneration

In this case, regeneration refers to thermal drying processes applying temperatures near 105 °C, as well as thermal desorption and reactive treatment at high temperatures ranging between 700 °C and 1000 °C in the presence of inert gases or oxidizing gases in limited amounts, such as steam or flue gas [17–19]. For the case involving only desorption of compounds from the surface of the adsorbent, only processes with temperatures of approximately 105 °C are considered.

Even in batch scale, San Miguel [6] reported that thermal regeneration is the most commonly used technique in recovering saturated coal. The author explained that high-temperature regeneration is not generally carried out in situ, instead requiring the saturated AC to be sent to special regeneration units, such as multiple hearth furnaces and rotary kilns [17, 20–22], where the discharged pollutants would be released to the air. Consequently, this should not be considered a suitable environmental method [23–25]. This practice has disadvantages, such as the increased energy demand due to the high temperatures employed in the process, as well as the loss of a considerable amount of coal of 5–15 % due to friction and washing during regeneration [6, 22, 24–28]. The adsorption capacity can even drop to zero after a few cycles.

Although thermal regeneration is widely used, the process is not completely understood, so the choice of parameters and operating conditions for regeneration are far from optimal [10, 17, 18, 29]. Therefore, the fundamental steps of regeneration need to be analyzed. From an economic standpoint, the sweep/purge agent is very important because it determines the process conditions like temperature and reaction time and the design parameters [6, 30]. Air, however, is rarely used due to the higher reactivity of oxygen, which can damage the pore structure of the carbon.

Thermogravimetric analysis (TGA) and temperature-programmed desorption (TPD), together with gravimetric analysis or mass spectroscopy have been applied to study the thermal behavior of regenerated AC loaded with compounds [31].

Another method of thermal regeneration is microwave irradiation. This technique has been proposed as potentially viable for regenerating saturated AC and has been extensively studied because of its heating capacity at the molecular level, which leads to rapid and homogeneous thermal reactions [32–37]. Foo and Hameed [38] demonstrated that the microwave regeneration of loaded AC with methylene blue for 2–3 min was sufficient to regenerate the adsorbent, so that after five cycles of adsorption-regeneration, it exhibited removal in the range of 75–77 %, the same as shown in the first adsorption cycle. A 600-W modified domestic microwave oven with a heating frequency of 2.45 GHz was applied for the regeneration step. The reaction was performed in a glass reactor fixed in the chamber of the microwave oven. Nitrogen gas at a pre-set flow rate of 300 cm^3min^{-1} was used to purge air in the reactor before the start of microwave heating and it continued to flow during the regeneration stage.

Microwave regeneration offers advantages over other thermal techniques, such as higher heating rates, the possibility of selective heating, precise temperature control, small space requirements, energy savings, greater efficiency for intermittent use, and waste reduction [36–42]. The technique of microwave regeneration was extensively discussed by Yuen and Hameed [33], who have presented the drawbacks, progress, challenges, and future expectations in the application of microwave regeneration of AC. Microwave regeneration gives rise to a better performance of the ACs in terms of adsorption capacity and rate of adsorption compared to conventional heating.

2.2 Nonthermal Regeneration

Methods of regeneration of AC by nonthermal desorption with solvents have been reported in many studies [22, 43–46] for the great majority of organic adsorbates. One method of nondestructive regeneration using solvents is based on the pH change near the surface of AC. The pH variation promotes imbalance between the surface and the ionized form of the adsorbate, making the adsorption process unfavorable [44]. This process has been applied for desorption of phenol from AC with hydroxide [43]. In this case, the phenol is converted to sodium phenoxide.

Another method based on solvent regeneration involves the exposing/sluicing/dowsing the AC with an organic solvent that has a higher affinity for the surface of the AC than the adsorbed compounds. The adsorbates are transferred from the surface to the solvent. Product recovery from the liquid phase can be accomplished by conventional distillation, with solvent recycling. Most research work reported in the literature is related to desorption of phenols and aromatic compounds [22, 47]. Acetone and methanol are two of the most common solvents for the regeneration of AC loaded with organic compounds. Both are capable of dissolving a wide range of organic compounds and also have other desirable characteristics, such as a low boiling points of 56 °C and 65 °C, respectively, and relatively low cost. Of course, the use of volatile organic solvents in practice requires extra care due to flammability hazards and the need for other processes for recycling, thus avoiding discharge to the environment. Studies applying acetone and methanol in the regeneration of phenol adsorbed on AC show good results: for example, Cooney et al. [22] reported that acetone was able to recover 85.7 % and methanol 70.6 % of the adsorption capacity of the AC; Chinn and King [43] stated that using acetone for ten cycles yielded a loss of 30 % of the initial sorption capacity, while for methanol, after four cycles, the adsorption capacity was maintained equal to the initial capacity.

Cooney et al. [22] reported that the regeneration of saturated AC with solvent is an alternative to thermal regeneration and offers several advantages as follows:

- can be performed relatively quickly in situ, thus minimizing downtime for the adsorbent and completely eliminates unloading, transporting, and repackaging of carbon;
- frictionless, hence loss of AC through attrition is minimized;
- no degradation of the carbon surface or pore structure due to pyrolysis and re-oxidation; only a modest loss of adsorption capacity during the initial cycles, which occurs due to irreversible adsorption;
- recovery of valuable adsorbates is possible, or if none are valuable, they can be easily eliminated by combustion with residual solvent after concentration by distillation.

For Li and Deng [48], one drawback of solvent regeneration lies in the fact that regeneration is not complete because the pores in AC can easily contain air, affecting the recovery rate.

In regeneration processes using a supercritical fluid in the desorption step, CO_2 is the most commonly applied compound. This desorption method proved to be an effective means for desorption of AC loaded with low- and high-molecular-weight organic compounds [49–52]. The advantages of taking supercritical CO_2 as an agent for desorption include lower energy consumption and a lower carbon loss in comparison with thermal regeneration processes [50]. As most organic compounds are soluble in the supercritical fluid, desorption can be performed at the same temperature as adsorption, which makes the operation safer, as does CO_2's inert properties. The adsorption capacity of AC after desorption with supercritical CO_2 is sufficiently close to that of virgin AC, providing cyclical operation [53].

The regeneration of saturated AC with organic compounds involves the usage of concentrated solutions of surfactants to desorb the adsorbates from the surface of the AC and solubilize them in micelles in the regenerant solution.

Organic solutes tend to be solubilized in the hydrophobic core of the micelles. Any pollutant ion that presents an opposite charge to the micelle surface may bind at its outer periphery. Multivalent counter-ions will bind to a greater extent than monovalent ions. The higher the valence state, the stronger is the binding [54, 55]. Based on the nature of the polar head group of the amphiphile, micelles can be categorized as anionic, cationic, nonionic, or zwitterionic. The potential of the aqueous micellar solution in the regeneration of AC lies in its ability to solubilize hydrophobic compounds, which are otherwise insoluble in water. The solubilizing effects of micelles can improve or degrade separation [56].

Fig. 2 illustrates a schematic route of AC regeneration by desorption using a surfactant. In this scheme, the AC is saturated at time zero, and as soon as the surfactant is added at time *t*, micelles are formed. Consequently, the difference in concentration and higher affinity provides desorption on the surface of the AC, making it possible to reuse the adsorbent.

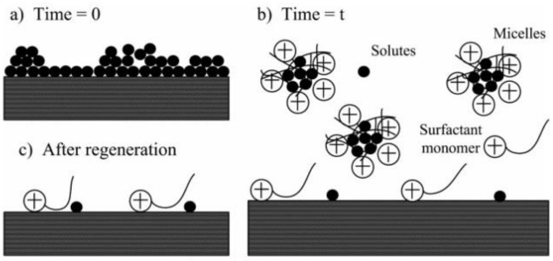

Figure 2. Surfactant-enhanced carbon regeneration steps. Adapted from [54].

In regeneration using saturated AC and micelle formation, certain features are important when choosing the surfactant. Some aspects to consider include the following:

- high solute solubilization capacity;
- formation of large micelles;
- low concentration of monomer, so that a small amount of surfactant is used;
- minimum phase separation, macroemulsion formation, precipitation, gelatinization, etc.

Anionic and cationic surfactants can be considered good reagents for application in the regeneration of AC. Nonionic surfactants are not suitable because they may be adsorbed onto the surface of AC [54]. A process of chemisorption can occur between the nonionic surfactant and the active sites of AC, thus preventing a future adsorption process; i.e., even after regeneration, it would not be possible to reuse the AC.

Techniques employing different hybrid processes have produced good results and synergistic effects, as in a study by Doruiche et al. [57], in which the authors developed a technique for regenerative AC loaded with sulfur ions from a H_2S adsorption process. This study presents a regeneration process that combines electrodialysis with a bipolar membrane and a desorption column. In the bipolar membrane, the main objective was to produce hydroxyl ions, which made it possible to regenerate the saturated exchange column with these ions (OH–), replacing the sulfur ions adsorbed on AC. The desulfurization operation reaches approximately 90 % extraction with a current density of approximately 30 %.

3 Regeneration by Decomposition Methods

The objectives of regeneration by decomposition consist in transforming adsorbed contaminants into less toxic byproducts or mineralizing them completely, restoring the sorption capacity and extending the life of the AC, as well as reducing costs in the adsorption process. Methods for regeneration by decomposition can be applied to AC loaded with oxidizable organic or inorganic compounds. An ideal regeneration process must renew the surface of the AC and destroy the adsorbed contaminants, so that these substances are not transferred to another phase, or it must desorb the contaminants to destroy them in solution. These methods can be divided into four groups: electrochemical, microbiological, chemical, and ultrasound methods. The main characteristics of these methods are given in the following sections.

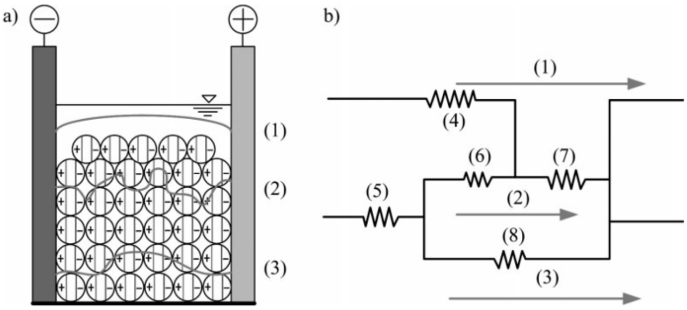

Figure 3. Current mode for spent GAC regeneration in an electrochemical reactor (a) and equivalent circuit of the system (b). (1) Bypass current; (2) effective current; (3) short-circuit current; (4) contact resistance; (5) inter-particle resistance; (6) reaction resistance; (7) inner-particle resistance; (8) bypass resistance. Adapted from [73].

3.1 Electrochemical Regeneration

Electrochemical regeneration of carbon loaded with organic compounds is considered one of the most effective and promising regeneration techniques [58–62] and has been extensively studied [61, 63–69]. In attempts to regenerate AC electrochemically, due to the low electrical conductivity of the adsorbent, it is necessary to use an electrolyte for electron transfer; control of the time and energy required for regeneration also proved to be very important [58, 60, 61, 64].

Electrochemical regeneration refers to the regeneration of a saturated adsorbent placed within an electrolytic cell containing an electrolyte solution to which a given potential current is applied [58, 60, 63, 70, 71]. The mechanism of electrochemical regeneration involves the electrodesorption and/or destruction of organic contaminants adsorbed on the AC to restore the capacity of the adsorbent. According to Garcia-Otón et al. [60], the electrochemical method is more effective for the regeneration of AC compared to thermal regeneration because it hardly modifies the pore structure of the material. Therefore, electrochemical technology can increase the adsorption capacity of the AC and regenerate loaded AC.

Narbaitz and Cen [58] reported that cathodic regeneration is 5–10 % more efficient than anodic regeneration. Moreover, cathodic regeneration leaves a small amount of residual pollutant in the electrolyte, while the anodic residual pollutant was not detectable. Narbaitz and Cen [58], Zhou and Lei [61], and Zhang and Zhong [59] found that NaCl is the electrolyte that presents the best performance among several other salts when attempting regeneration of AC loaded with phenol and that higher concentrations of NaCl did not improve the regeneration efficiency.

A typical situation with an electrolytic cell for the regeneration of AC loaded with organic compounds is presented in Fig. 3. The applied current density is one of the most important factors in the oxidation of organic compounds. Zhou and Lei [61] showed that in the absence of electric current, the regeneration of AC loaded with organic compounds had an efficiency between 1 and 2 %, values that can be disregarded by the margin of error. Thus, the regenerative capacity using this technique should be attributed to the applied current. If the reactor is operating under galvanostatic conditions, it is possible to identify two different regimes of operation, i.e., the current control and the control of mass transport [72].

In a recent study, Narbaitz and Karimi [65] investigated four different reactors to regenerate AC loaded with phenol: a glass reactor with simple batch operation composed of horizontal electrodes, a stainless-steel column reactor, a glass batch reactor with a capacity for recirculation of the electrolyte, and a reactor partitioned into cells with separation of the electrodes by an ion exchange membrane. The study provided satisfactory results with 74–90 % regeneration, although the electrochemical regeneration of AC is still under development and an ideal reactor configuration has yet to be determined. Studies at the laboratory scale are very promising [65].

There are some advantages of this technique over thermal and nonthermal methods: electrochemical regeneration can conveniently be operated in situ [1, 70, 73–75] with a lower power consumption and shorter regeneration time; the electron is the only reagent, and it requires simple equipment and treatments. Furthermore, proper adjustment of the applied current or potential electrode and other operational variables such as electrolysis, composition of the electrode, etc. may allow modification of organic pollutants into less hazardous compounds or even their complete mineralization [74]. Narbaitz and Cen [58] found that electrochemical regeneration reached high efficiencies without apparent loss of carbon mass.

Essentially, electrochemical treatment is considered to be an advanced oxidation process. Electrochemical oxidation can be achieved either directly at the anode or indirectly in solution [76]. Therefore, the electrochemical regeneration of AC has gained increased attention in recent years due to its unique characteristics such as low-temperature operation, no need for added chemicals, and the in situ desorption of organic compounds deposited on carbon without damaging the structural properties and characteristics of the carbon [75].

3.2 Microbiological Regeneration (Bioregeneration)

Bioregeneration can restore the adsorption capacity of AC loaded with organic compounds through the action of microorganisms using organic substrates as their sole source of power and energy. This fact leads to the renewal of potential adsorption, greater system stability, and a prolonged duration of service [77–82].

The processes of removing organic compounds in aqueous solutions include adsorption on the surface of AC, adsorption on a biofilm, and microbial oxidation [83]. A synergistic effect can be observed from a combination of sorption and biodegradation processes [80]. The application of these two processes simultaneously has proven to be successful in removing pollutants [82], even at a concentration above that to which the biomass has been acclimatized [84]. As biodegradation and adsorption can occur simultaneously, the active sites of the adsorbent can be regenerated biologically by several mechanisms [85].

In the literature, the use of biological systems for the biodegradation of pollutants adsorbed onto AC is mostly explained by two different mechanisms. One mechanism involves the degradation of the substance adsorbed on the adsorbent surface due to exoenzymatic reactions. According to the hypothesis of Perrotti and Rodman [86], bacteria cannot only physically migrate through the microporous structure of the AC to remove adsorbed components but also have the ability to excrete enzymes that function outside the cell boundaries. These exoenzymes are produced inside the cells and are believed to act on adsorbed substrates, inducing hydrolytic transformation. The adsorption sites are renewed when products are desorbed by microbial action in solution, due to weakening adsorption. Xiaojian et al. [83], however, reported that some of the micropores and mesopores are inaccessible to exoenzymes due to the size of the exoenzymes. The other mechanism suggests that desorption of sorbed substrate occurs as a result of the concentration gradient between the surface of the substrate of the adsorbent and the liquid phase [81, 85, 87]. As the substrate concentration dissolved in the liquid volume is reduced by biodegradation, desorption is further induced. To promote bioregeneration significantly, a large reduction in the concentration of the liquid phase is necessary, especially for strongly adsorbed compounds. Although both mechanisms suggest bioregeneration by desorption and biodegradation processes in sequence, several kinetic studies of bioregeneration [88–90] assume that microbiological regeneration is a one-step process and is governed by first-order kinetics with respect to the adsorbed substrate. This is obviously an oversimplification.

Fig. 4 illustrates the mechanisms of AC bioregeneration for the two cases discussed: regeneration by action on the surface of AC and regeneration by concentration gradient.

Effective regeneration depends on several factors as follows:

- presence of microbial agents able to utilize the adsorbate as the sole energy source [87];
- presence of mineral components, e.g., nitrogen, phosphorus, sulfur, etc., necessary for the normal metabolism of the microorganism [87];
- creation of ideal conditions for vital activities of microorganisms like temperature, pH, dissolved oxygen concentration, contact time, and spatial distribution of carbon molecules [91];
- optimization of the ratio of the concentrations of microorganisms and the adsorbate, etc. [92].

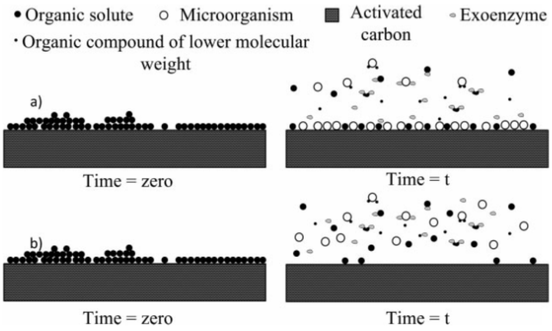

Figure 4. Bioregeneration mechanisms: (a) regeneration by acting on the surface of AC, (b) regeneration by concentration gradient.

For further information regarding this regeneration technique, a review on the subject written by Aktas and Çeçen [78] presents a detailed analysis of several physical-chemical bioregeneration mechanisms and quantification methods.

3.3 Chemical Regeneration

Chemical regeneration methods for saturated AC may involve complete mineralization of the adsorbed species to CO_2 and water or the transformation of complex molecules into simpler compounds that are less dangerous, water-soluble, or more biodegradable; this occurs at mild temperatures of 150–180 °C) and short contact times. Advanced oxidation processes (AOP) are technologies with great potential in the regeneration of saturated AC with a wide variety of organic compounds through the highly selective production of oxidants, such as hydroxyl radicals ($^{\bullet}OH$). Chemical oxidation by chlorine, chlorine dioxide, peroxide, ozone, and potassium permanganate has been thoroughly studied, and part of the adsorption capacity of the AC can be recovered.

Catalytic oxidation processes can occur by desorption followed by oxidation in the liquid phase, or by the direct oxidation of species adsorbed on an adsorbent, i.e., AC, modified by a catalyst. In the first approach, water is not in contact with the catalyst and metal or catalyst dissolution is not a problem, because the AC was not modified with a catalyst. In the second approach, the dissolution of the metal may occur and should be monitored. However, it is possible that the saturated carbon can be regenerated directly by a process called wet oxidative regeneration (WOR) [93, 94]. Regeneration by wet oxidation is performed in a process of wastewater treatment known to decompose organic compounds under mild conditions (150–180 °C) compared to subcritical water [95–97].

In the wet oxidation method, which uses hydrogen peroxide (H_2O_2) (wet peroxide oxidation, WPO), one can increase the rate of decomposition of organic compounds in the process [98] for the decomposition of H_2O_2, which is promoted by AC. This results in the generation of hydroxyl, a strong oxidant [97]. Furthermore, due to the increase in temperature, the dielectric constant is reduced and the water solubility of organic compounds is higher [99]. Regeneration using WPO AC does not burn and not retain solvent on the regenerated AC. Moreover, it is performed with lower energy compared with thermal regeneration with water at an applied pressure ranging between 0.3 and 0.9 MPa.

The advantages of the combination of adsorption and regeneration by catalytic oxidation are the following [100]:

- the process will be accelerated by the presence of high concentrations of pollutants eluted from the adsorbent;
- a large number of cycles of adsorption/regeneration without loss of capacity;
- low-temperature regeneration can be performed in situ, even in small units, thereby improving process economics, which is intended to replace the common method of thermal regeneration.

The use of ozone as an oxidant in the process of regeneration of saturated AC is of increasing interest. Due to its high oxidizing power, it can react with the adsorbed species on AC, removing them from the surface. The reaction can be carried out directly or through free radicals that arise from the decomposition of ozone on the carbon surface [101]. On this basis, the regeneration of AC by direct ozonation would have the following advantages:

- oxidation can be carried out at room temperature;
- can be easily combined with adsorption and performed in situ;
- water treatment plants have many ozonation facilities.

However, interactions between ozone and AC may occur. According to some studies [102–105], ozone can modify the surface properties of AC, such as specific surface area, pore volume, and chemical functional groups. In particular, Valdes et al. [105] showed that absorption of ozone can reduce the AC adsorption properties due to the attachment of surface oxygen groups (SOG), which obstruct the entry of compounds into micropores.

The oxidation potential of an oxidant is related to its redox potential, $E°$. An oxidant with a high value of $E°$ is a strong oxidizing agent. However, kinetic factors are often superior thermodynamic properties in the control of oxidation reactions. Still, a strong oxidant usually displays a faster oxidation reaction.

Photocatalytic oxidation is characterized as an advanced oxidation process and can be used in regenerating AC saturated with organic compounds. The destruction of these compounds occurs simultaneously with the regeneration process [106]. For mineralization of organic compounds, the method employs photocatalysts, e.g., TiO_2, SnO_2, ZrO_2, arranged in layers within the bed or impregnated into AC. In the process, UV light or sunlight is used to generate highly reactive free radicals responsible for the destruction of organic compounds.

Liu and colleagues [107] studied the photooxidation of *p*-dichlorobenzene and trichloroethene on AC impregnated with Pt-TiO_2 in a photoreactor plate. This study demonstrated one very important characteristic of the process: the regeneration is limited by the photocatalytic reaction rate early in the regeneration cycle and then by desorbing the adsorbates from the interior of the AC.

Fenton's reaction which means oxidation of ferrous ion Fe^{2+} by hydrogen peroxide (H_2O_2) to produce hydroxyl radicals, is another way to regenerate AC saturated with organic compounds and has been studied by many researchers, demonstrating its success [14, 108–110]. The Fenton-driven mechanism comprises transforming contaminants on or near the surface of AC. The process involves the reaction of hydrogen peroxide with various forms of iron in solution or attached to the surface of AC for the production of hydroxyl radicals $^{\bullet}OH$ and radical intermediates, i.e., superoxide $O_2^{\bullet}$ and hydroperoxyl $^{\bullet}HO_2$, and transforming radicals dependent on the adsorbed and desorbed contaminants.

For Huling et al. [108], the limiting rates of Fenton's systems are in the production of $^{\bullet}OH$ and Fe(II). With the addition of a reducing agent such as hydroxylamine (NH_2OH) as indicated in Eq. (1), an additional path for the faster reduction of Fe(III) to Fe(II) can be achieved.

$$2\,NH_3OH^+ + 4\,Fe^{3+} \rightarrow N_2O + 4\,Fe^{2+} + H_2O + 6\,H^+ \qquad (1)$$

With additional paths for the reduction of Fe(III) to Fe(II), the system can increase the production of radicals in the Fenton process by improving the conditions for the regeneration of saturated AC.

3.4 Regeneration by Ultrasound

One promising method that is less studied as an alternative to conventional AC regeneration is regeneration by ultrasound. Volatile organic compounds (VOCs) that are chemically or physically adsorbed to AC can be desorbed ultrasonically, followed by the decomposition of the species in the liquid phase directly on AC or its degradation by ultrasound [111, 112]. Since 1990, there has been increasing interest in the use of ultrasound to destroy organic contaminants present in water and/or residual waters [111]. In comparison with other treatment technologies for organic pollutants, such as UV light, high-voltage corona, and incineration of solvent extraction, sonochemical degradation has significant advantages, such as security, cleanness, and energy conservation, without causing secondary pollution [113, 114].

Ultrasound acts through the phenomenon of cavitation. Cavitation can be generally defined as the phenomenon of the formation, growth, and implosive collapse of microbubbles in a liquid, occurring in a short time interval of milliseconds. The collapse of these bubbles creates extreme conditions, such as high temperatures and pressures within the local interface and the bubble collapse. These extreme conditions can break the chemical bonds of H_2O and generate highly reactive species such as oxygen radicals $^{\bullet}O$, hydroxyl $^{\bullet}OH$, hydrogen $^{\bullet}H$, and hydroperoxyl $^{\bullet}HO_2$, which, together with the acoustic vortex, attack organic pollutants present in the medium [115–117].

The primary effects of ultrasound are of thermal, mechanical, i.e., cavitation and micro streaming, and chemical, i.e., sonochemical, nature. Knowledge of the basic effects and drawbacks of ultrasound is essential to develop techniques for the regeneration of AC. However, some conclusions related to the effects of ultrasound on desorption of saturated AC contradict one another. For example, for Hamdaoui et al. [118], high-pressure waves and the shock velocity produced by the acoustic cavitation is the major effect on desorption. Qin et al. [119] concluded that the specific effects of ultrasonic energy causes higher rates of desorption. Breitbach and Bathen [117] indicate that thermal effects involved in this technique are responsible for improving the results of desorption. Yu and co-workers [120] demonstrated that the acoustic microstreaming vortex significantly increases the rate of desorption. Rege et al. [121] found that the mass transport in the desorption process is caused by cavitation and the acoustic microstreaming vortex. One possibility is that these effects are simultaneous, and the studies thus far have not been able to identify with certainty which effect is mainly responsible for the phenomenon of desorption.

4 Applications of the Regeneration Techniques

An analysis of applications of the techniques of regeneration processes involving desorption and decomposition was performed using the results of various studies on regenerating AC. Tabs. 2 and 3 present data evaluated in the form of efficiency comparisons for regenerative processes of desorption and decomposition.

Sabio and colleagues [10] studied the thermal regeneration of AC saturated with *p*-nitrophenol by three different processes: pyrolysis, gasification, and carbonated direct pyrolysis. The results show that only pyrolysis was not able to complete regeneration. The effect of gassing depends largely on the gassing agent used, i.e., CO_2 or air. The study indicates that it is most advantageous to use direct gasification, obtaining values of regeneration up to 100 %, compared to pyrolysis.

In a study carried out by Alvarez et al. [122], the regeneration of AC-saturated phenol was measured by two different techniques: pyrolysis and oxidation (ozone). For pyrolysis followed by gasification with CO_2, the sorption capacity of AC was completely recovered only when the burn-off was 15 %. As for direct AC ozonation, ozone affects the chemical structure of AC, and this decreases the sorption capacity, reaching maximum values of 80 %. The usage of ozone in excess can produce surface oxygen groups (SOG), which consequently reduces the surface area and has a negative effect on the sorption of phenol.

Pastrana-Martinez and colleagues [123] conducted studies on the thermal regeneration of AC saturated with fluroxypyr and recovered up to 89 % of the sorption capacity. An important observation in this study is related to pH changes, because

Table 2. Percentage recovery of AC regenerated by desorption. GAC, granular activated carbon; PAC, powdered activated carbon.

Compound	Time [h]	Temperature [°C]	Activated carbon	Technique	Regeneration [%]	Ref.
Leachate	0.5	100	GAC	Steam	73	[1]
Fluroxipir	1.8	1300	AC-cloth	Thermal	65–89	[123]
p-Nitrophenol	3–5	350–725	GAC	Direct gasification	100–117	[10]
p-Nitrophenol	3–5	300–800	GAC	Pyrolysis	76	[10]
p-Nitrophenol	3–5	300–800	GAC	Gasified pyrolysis	73–99	[10]
Phenol	1	850	GAC	Pyrolysis: 15 % burn-off	90	[122]
Promethazine	2	300–500	PAC	Microwave	40	[125]
Salicylic acid	–	450–850	PAC	Microwave	95	[126]
Phenol	4	1000	GAC	Microwave	70–80	[34]
Coking wastewater	0.33	Room	GAC	Solvents	98	[45]
Benzene	1.33	–	GAC	Supercritical CO_2	85	[53]
Toluene	1.33	–	GAC	Supercritical CO_2	85	[53]
Leachate	48	Room	GAC	Base washing	75	[1]
Toluene	1	42	GAC	Supercritical CO_2	68–100	[124]
Hg(II)	2	25	GAC	Ultrasound	24	[133]
Cr(VI)	2	25	GAC	Ultrasound	35	[133]
Cu(II)	2	25	GAC	Ultrasound	37	[133]
Mn(II)	2	25	GAC	Ultrasound	43	[133]
Chromium(VI)	2	30	PAC	Ultrasound	29	[134]

Table 3. Percentage recovery of AC regenerated by decomposition. GAC, granular activated carbon; PAC, powdered activated carbon; WO, wet oxidation; WPO, wet peroxide oxidation.

Compound	Time [h]	Temperature [°C]	Activated carbon	Technique	Regeneration [%]	Ref.
4-Chlorophenol	72	25	GAC	Bioregeneration	69	[84]
2,4-Dichlorophenol	72	25	GAC	Bioregeneration	68	[84]
2-Nitrophenol	48–72	25	PAC - SA4	Bioregeneration	85	[128]
2-Nitrophenol	48–72	25	PAC - CA1	Bioregeneration	90	[128]
Phenol	72	22–25	PAC - SA4	Bioregeneration	58	[90]
Phenol	72	22–25	PAC - CA1	Bioregeneration	94	[90]
Phenol	48	22–25	GAC - PKDA	Bioregeneration	67	[90]
Phenol	24	22–25	GAC - Cagran	Bioregeneration	85	[90]
Tetrachlorethylene	320	–	GAC	Bioregeneration	40	[92]
Toluene	320	–	GAC	Bioregeneration	46	[92]
Benzene	320	–	GAC	Bioregeneration	38	[92]
Carbon tetrachloride	320	–	GAC	Bioregeneration	29	[92]
Acid Orange 7	312	26 ± 1	GAC	Bioregeneration	15	[135]
Phenol	50	–	PAC	Bioregeneration	77 ± 4	[85]
p-Methylphenol	30	–	PAC	Bioregeneration	69 ± 4	[85]
p-Ethylphenol	52	–	PAC	Bioregeneration	68 ± 4	[85]
p-Isopropylphenol	60	–	PAC	Bioregeneration	58 ± 6	[85]
Leachate	12	Room	GAC	Electrochemistry	91	[1]
Phenol	10	Room	GAC	Electrochemistry	70	[127]
Phenol	5	Room	GAC	Electrochemistry	80	[59]
Phenol	3	30	GAC	Electrochemistry	80	[62]
p-Nitrophenol	1.5	–	AC	Electrochemistry	90	[61]
Toluene	3	–	AC	Electrochemistry	99	[60]
Crystal violet dye	0.17	–	AC	Electrochemistry	100	[71]
Bentazone	1.5	–	AC-cloth	Electrochemistry	80–90	[136]
Phenol	5	Room	GAC	Electrochemistry	85	[70]
Methyl *tert*-butyl ether	2	–	GAC	Fenton-drive	91	[109]
Methyl *tert*-butyl ether	–	21–50	GAC	Fenton-drive	97	[14]
Bisphenol A	8	40	PAC	Photocatalysis	52	[131]
Sulfamethazine	8	40	PAC	Photocatalysis	57	[131]
Clofibric acid	8	40	PAC	Photocatalysis	83	[131]
Phenol	72	50	GAC	Photocatalysis	78	[42]
Methanol	3	25	GAC	Photocatalysis	80	[137]
Phenol	1	Room	GAC	Oxidation: ozone	80	[122]
Brilliant Blue R and Turquoise G	3	150–250	PAC	Chemistry WO	98	[129]
Brilliant Blue R and Turquoise G	3	150–250	GAC	Chemistry WO	98	[129]
Trichloroethylene	14	150–180	GAC	Chemistry WPO	71	[130]
Leachate	2	Room	GAC	Ultrasound	67	[1]
Phenol	20	25	GAC	Ultrasound	70	[132]
Trichloroethylene	1	20	GAC	Ultrasound	64	[138]

pH values near 2 yielded less residues on the carbon surface compared to pH 10.

Guo et al. [45] reported that with solvents in the regeneration of water-saturated AC from residual coke, *n*-pentane can effectively regenerate the surface of AC after repeated saturation with organic compounds. The desirable regenerative effect of *n*-pentane on activated charcoal may be due to desorption of ester incorporated within the internal structure of AC.

Tan and Lee [124] studied desorption of toluene from AC with supercritical CO_2 into a rotating bed. Desorption efficiency was enhanced with increasing rotational speed which was attributed to the presence of centrifugal force. The study also demonstrated that the efficiency is better with larger flows of CO_2, and efficiency decreases with a reduction in particle diameter.

In a study reported by Caliskan and colleagues [125], saturated AC was regenerated with promethazine by the microwave technique, and the data were compared with conventional thermal regeneration. The low rates of regeneration of 40 % found for microwave thermal cracking are related to molecules adsorbed within the pores of AC. Using the same technique, Ania and colleagues [126] studied the regeneration of salicylic acid in AC. After six cycles it was possible to achieve 95 % regeneration in a single extraction step. Salicylic acid is desorbed in a molecular state and then partially decomposed in the gas phase. This reduces the formation of deposits within the pores of the AC, improving the process efficiency, unlike the study by Caliskan [125] described above.

Hsu and Weng [1] used four different techniques for regenerating GAC saturated with organic compounds: steam, water washing, ultrasound, and electrochemistry. The electrochemical process provided the best results with 91 % regeneration. The influence of parameters such as time of regeneration, voltage, and processing fluid were analyzed. By increasing the voltage and time of regeneration, a higher efficiency could be achieved. Using the same technique, Karimi-Jashni and Narbaitz [127] investigated the regeneration of GAC saturated with phenol. Cathodic reactivation was more efficient compared with anodic reactivation; however, when increasing the degree of mixing efficiency in the cathodic electrolyte, reactivation decreased, while no significant change in anode efficiency was observed. Higher degrees of electrolyte in the mixture reduced the local pH at the cathode and consequently lowered the driving force for desorption, thus decreasing the efficiency of regeneration. The results were similar to those found in the work of Zhang and colleagues [59].

Bioregeneration involving the degradation of compounds to renew GAC saturated with 4-chlorophenol and 2,4-dichlorophenol was studied by Oh et al. [84]. These authors found that for higher efficiency, the biomass must be acclimatized to the concentration of chlorophenol. In situations where the concentrations are higher than the acclimatized value, excess adsorbent has to be employed.

In a study by Aktas and Çeçen [128], two types of PAC were employed in the adsorption of 2-nitrophenol with subsequent bioregeneration. AC loaded with 2-nitrophenol can be partially regenerated co-metabolically in the presence of phenol as the growth substrate. However, bioregeneration cometabolic of chemically AC was more in accordance with the highest desorbability. Instead of biodegradation, desorption was the rate-limiting step in the bioregeneration of phenol and 2-nitrophenol.

Shende and Mahajani [129] conducted a study of regeneration by wet oxidation on GAC and PAC saturated with dyes. SEM analysis showed a broadening and loss of pore structure between adjacent pores in the regenerated carbon, compared with the virgin carbon. In the temperature range of 150–250 °C, the process showed no thermal regeneration. When checking the control mechanism of regeneration by wet oxidation, the authors found that for GAC and PAC the regeneration was a surface phenomenon. In a similar study, Okawa and colleagues [130] regenerated GAC saturated with trichlorophenol by wet oxidation using H_2O_2. The results suggested that regeneration at higher temperatures (180 °C) and lower pH (pH 2.5) is more effective. In conducting multiple regeneration cycles, the adsorption capacity gradually decreases. This decrease can be attributed to the oxidation of GAC during regeneration.

Yap and Lim [131] used solar photocatalysis to regenerate AC doped with titanium dioxide and saturated with three different compounds: bisphenol A, sulfamethazine, and clofibric acid. The results obtained demonstrated that the performance of photocatalytic solar regeneration increases with the intensity of light, titanium dioxide load, and temperature. This technique has advantages and environmental benefits because it requires simple installation and maintenance and also does not consume manufactured energy. The AC/titanium dioxide compound remained photostable, allowing several cycles of regeneration.

Huling and colleagues [109] used the Fenton mechanism to regenerate GAC saturated with methyl *tert*-butyl ether and realized that there was no loss of sorption capacity in subsequent cycles. No deterioration of carbon under oxidative conditions occurred. This was attributed to the oxidation of target contaminants relative to the surface carbon. The byproducts of the oxidation reaction from methyl *tert*-butyl ether did not accumulate significantly in the GAC.

Juang et al. [132] studied the regeneration of GAC saturated with phenol using ultrasound. The authors concluded that ultrasound has an effect on the microporosity of carbon, i.e., the BET surface area and total pore volume was reduced by 25 %.

5 Final Considerations

In all cases, the methods for the regeneration of AC based on desorption involve the generation of effluent with high concentrations of desorbed compounds, which may cause serious problems in relation to further treatment. In general, the application of adsorption with subsequent regeneration by desorption implies the transfer of the compound removed from the treated effluent to a solution that concentrates this compound. For oxidizable organic and inorganic compounds, desorption alone is not an interesting application, but applicable decomposition processes are very attractive. However, when dealing with inorganic compounds, the decomposition, i.e., oxidation or reduction, involves greater complexity and in some cases is not possible; the process of regeneration by desorption is well accepted.

A review of the literature on chemical regeneration indicates that, although there have been a number of studies related to this technique, there is no clear understanding of the underlying mechanisms, so there is still much to learn before a commercially viable application can be established. Recent studies show trends in the combined processes for the regeneration of saturated AC; processes using membranes with desorption columns are good examples.

Although relatively less studied, electrochemical regeneration appears to be a very promising alternative that presents some advantages over conventional methods. The mechanism of electrochemical regeneration was investigated by several authors; however, it is still necessary to understand how to extend this method and develop a technique for in situ electrochemical regeneration based on knowledge of the process mechanisms.

On the basis of the effects of the ultrasound technique, the method proved to be promising for improved AC regeneration. However, its effects are not well understood at present, thus it is not possible to say with certainty which effect is mainly responsible for the phenomenon of desorption/decomposition, and whether these phenomena occur on the surface of the AC or in the solution after desorption.

Bioregeneration simultaneously facilitates the degradation of adsorbed organic compounds and the regeneration of saturated AC. However, most studies have raised concerns about its technical feasibility and limitations, such as the low efficiency of regeneration due to the resistance of intra-particle mass transfer, microbial fouling, and deterioration of the quality of the carbon surface. A rigorous economic evaluation is also necessary to check the feasibility of bioregeneration against conventional regeneration processes.

Photocatalytic regeneration is a slow process that is still inappropriate for practical application. One possible way to maximize the efficiency of regeneration by photocatalytic decomposition is to increase the rate of desorption by heating and to combine the photocatalytic oxidation rate with the rate of desorption.

In regeneration by oxidation of AC saturated with organic compounds, two processes can occur, causing a decrease of adsorption capacity. Firstly, the process may induce chemical and physical changes in the AC surface, thereby changing the adsorption capacity. The second process involves the incomplete decomposition of the target compounds, resulting in the accumulation of oxidation byproducts, which occupy adsorption sites that would otherwise be available for the adsorption of target compounds. The second process may be inconsequential, assuming that the byproducts of oxidation are environmentally acceptable when desorbed and eluted from the AC.

It is important to state that the nature of the adsorbate and its ability to interact with the solid adsorbent are key factors that control the application of techniques for the regeneration of AC. Finally, there is much more to investigate before it is possible to achieve efficient regenerative processes and commercial-scale applications. Studies indicate that the path is correct; however, substantial research that examines large-scale applications is still missing.

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References

[1] C. H. Weng, M. C. Hsu, *Sep. Purif. Technol.* **2008**, *64* (*2*), 227–236.

[2] M. Streat, D. J. Horner, *Process Saf. Environ. Prot.* **2000**, *78* (*5*), 363–382.

[3] S. Biniak, M. Pakula, G. S. Szymanski, A. Swiatkowski, *Langmuir* **1999**, *15*, 6117–6122.

[4] H. Lata, V. K. Garg, R. K. Gupta, *Desalination* **2008**, *219*, 250–261.

[5] C. O. Ania, J. B. Parra, J. A. Menéndez, J. J. Pis, *Microporous Mesoporous Mater.* **2005**, *85*, 7–15.

[6] G. San Miguel, S. D. Lambert, N. J. D. Graham, *Water Res.* **2001**, *35* (*11*), 740–748.

[7] G. Z. Qu, J. Li, Y. Wu, G. F. Li, D. Li, *Chem. Eng. J.* **2009**, *146*, 168–173.

[8] I. Dranca, T. Lupascu, K. Vogelsang, L. Monahova, *J. Therm. Anal. Calorim.* **2001**, *64* (*3*), 945–953.

[9] M. G. Plaza, S. García, F. Rubiera, J. J. Pis, C. Pevida, *Chem. Eng. J.* **2010**, *163*, 41–47.

[10] E. Sabio, E. González, J. F. González, C. M. González-García, A. Ramiro, J. Gañan, *Carbon* **2004**, *42* (*11*), 2285–2293.

[11] *World Activated Carbon to 2016*, Freedonia, Cleveland, OH **2012**. http://www.freedoniagroup.com/DocumentDetails.aspx?DocumentId=578390 (accessed January 10, 2013)

[12] H. Aikyo, M. Suzuki, *Petrotech* **1998**, *21*, 1067–1073.

[13] G. G. Stavropoulos, A. A. Zabaniotou, *Fuel Process. Technol.* **2009**, *90* (*7–8*), 952–957.

[14] S. G. Huling, E. Kan, C. Caldwell, S. Park, *J. Hazard. Mater.* **2012**, *205–206*, 55–62.

[15] R. S. Horng, I. C. Tseng, *J. Hazard. Mater.* **2008**, *154* (*1–3*), 366–372.

[16] M. Soleimani, T. Kaghazchi, *J. Chin. Inst. Chem. Eng.* **2008**, *39* (*1*), 9–11.

[17] M. Suzuki, D. M. Misic, O. Koyama, K. Kawazoe, *Chem. Eng. Sci.* **1978**, *33* (*3*), 271–279.

[18] J. S. J. Van Deventer, B. S. Camby, *Thermochim. Acta* **1988**, *136*, 179–189.

[19] P. Harriott, A. T. Y. Cheng, *AIChE J.* **1988**, *34* (*10*), 1656–1662.

[20] M. Sheintuch, Y. I. Matatov-Meytal, *Catal. Today* **1999**, *53* (*1*), 73–80.

[21] C. Kazuyuki, J. M. Smith, M. Suzuki, *AIChE J.* **1981**, *27*, 213–220.

[22] D. O. Cooney, A. Nagerl, A. L. Hines, *Water Res.* **1983**, *17*, 403–410.

[23] W. Minghong, B. Borong, Z. Ruimin, Z. Jinliang, H. Longxin, *Radiat. Phys. Chem.* **1998**, *53* (*4*), 431–435.

[24] F. Salvador, C. S. Jimenez, *Carbon* **1996**, *34* (*4*), 511–516.

[25] R. J. Martin, W. J. Ng, *Water Res.* **1985**, *19* (*12*), 1527–1535.

[26] D. M. Ruthven, *Principles of Adsorption and Adsorption Processes*, John Wiley & Sons, New York **1984**.

[27] E. H. Hwang, Y. S. Ko, J. K. Jeon, *J. Ind. Eng. Chem.* **2007**, *13* (*3*), 387–394.

[28] T. Charinpanitkul, P. Limsuwan, C. Chalotorn, N. Sano, T. Yamamoto, P. Tongpram, P. Wongsarivej, A. Soottitantawat, W. Tanthapanichakoon, *J. Ind. Eng. Chem.* **2010**, *16* (*1*), 91–95.

[29] M. A. Waer, V. L. Snoeyink, K. L. Mallon, *J. AWWA* **1992**, *84* (*3*), 82–91.
[30] G. San Miguel, S. D. Lambert, N. J. D. Graham, *Appl. Catal., B* **2003**, *40* (*3*), 185–94.
[31] C. Moreno-Castilla, J. Rivera-Utrilla, M. V. Lopez-Ramon, F. Carrasco-Marin, *Carbon* **1995**, *33* (*6*), 845–851.
[32] K. Yang, J. Peng, C. Srinivasakannan, L. Zhang, H. Xia, X. Duan, *Bioresource Technol.* **2010**, *101* (*15*), 6163–6169.
[33] F. K. Yuen, B. H. Hameed, *Adv. Colloid Interface Sci.* **2009**, *149* (*1–2*), 19–27.
[34] X. Liu, X. Quan, L. Bo, S. Chen, Y. Zhao, *Carbon* **2004**, *42* (*2*), 415–422.
[35] X. Liu, G. Yu, *Chemosphere* **2006**, *63* (*2*), 228–235.
[36] D. A. Jones, T. P. Lelyveld, S. D. Mavrofidis, S. W. Kingman, N. J. Miles, *Resour. Conserv. Recycl.* **2002**, *34* (*2*), 75–90.
[37] S. C. Ma, J. Yao, X. Ma, L. Gao, M. Guo, *Chem. Eng. Technol.* **2013**, *36* (*7*), 1217–1224.
[38] K. Y. Foo, B. H. Hameed, *J. Anal. Appl. Pyrolysis* **2012**, *98*, 123–128.
[39] A. A. Salema, F. N. Ani, *Bioresour. Technol.* **2011**, *102* (*3*), 3388–3395.
[40] C. Y. Cha, C. T. Carlisle, *J. Air Waste Manage. Assoc.* **2001**, *51* (*12*), 1628–1641.
[41] H. S. Ku, E. Siores, A. Taube, J. A. R. Ball, *Comput. Ind. Eng.* **2002**, *42* (*2–4*), 281–290.
[42] S. X. Liu, C. L. Sun, S. R. Zhang, *Bull. Environ. Contam. Toxicol.* **2004**, *73* (*6*), 1017–1024.
[43] D. Chinn, C. J. King, *Ind. Eng. Chem. Res.* **1999**, *38* (*10*), 3746–3753.
[44] H. S. McLaughlin, *Chem. Eng. Prog.* **1995**, *91* (*7*), 45–53.
[45] D. Guo, Q. Shi, B. He, X. Yuan, *J. Hazard. Mater.* **2011**, *186* (*2–3*), 1788–1793.
[46] T. Sutikno, K. J. Himmelstein, *Ind. Eng. Chem. Fundam.* **1983**, *22* (*4*), 420–425.
[47] J. E. Kilduff, C. J. King, *Ind. Eng. Chem. Res.* **1997**, *36* (*5*), 1603–1613.
[48] H. M. Li, B. J. Deng, *Tech. Dev. Chem. Ind.* **2006**, *35*, 21–24.
[49] F. Recasens, B. J. McCoy, J. M. Smith, *AIChE J.* **1989**, *35* (*6*), 951–958.
[50] A. Heidari, M. N. Lotfollahi, H. Baseri, *Chem. Eng. Technol.* **2013**, *36* (*2*), 315–322.
[51] G. Madras, C. Erkey, A. Akgerman, *Ind. Eng. Chem. Res.* **1993**, *32* (*6*), 1163–1168.
[52] S. J. Macnaughton, N. R. Foster, *Ind. Eng. Chem. Res.* **1995**, *34* (*1*), 275–282.
[53] C. S. Tan, D. C. Liou, *Sep. Sci. Technol.* **1989**, *24* (*1–2*), 111–127.
[54] M. K. Purkait, A. Maiti, S. DasGupta, *J. Hazard. Mater.* **2007**, *145* (*1–2*), 287–295.
[55] C. C. Leng, N. G. Pinto, *Ind. Eng. Chem. Res.* **1996**, *35* (*6*), 2024–2031.
[56] L. J. C. Love, J. G. Dorsey, *Anal. Chem.* **1984**, *56* (*11*), 1132–1148.
[57] N. Drouiche, H. Grib, N. Abdi, H. Lounici, A. Pauss, N. Mameri, *J. Hazard. Mater.* **2009**, *170* (*1*), 197–202.
[58] R. M. Narbaitz, J. Cen, *Water Res.* **1994**, *28* (*8*), 1771–1778.
[59] H. Zhang, L. Ye, H. Zhong, *J. Chem. Technol. Biotechnol.* **2002**, *77* (*11*), 1246–1250.
[60] M. García-Otón, F. Montilla, M. A. Lillo-Ródenas, E. Morallón, J. L. Vázquez, *J. Appl. Electrochem.* **2005**, *35* (*3*), 319–325.
[61] M. H. Zhou, L. C. Lei, *Electrochim. Acta* **2006**, *51* (*21*), 4489–4496.
[62] R. Berenguer, J. P. Marco-Lozar, C. Quijada, D. Cazorla-Amorós, E. Morallón, *Carbon* **2010**, *48* (*10*), 2734–2745.
[63] N. W. Brown, E. P. L. Roberts, A. Chasiotis, T. Cherdron, N. Sanghrajka, *Water Res.* **2004**, *38* (*13*), 3067–3074.
[64] R. M. Narbaitz, A. Karimi-Jashni, *Environ. Technol.* **2009**, *30* (*1*), 27–36.
[65] R. M. Narbaitz, A. Karimi-Jashni, *Chem. Eng. J.* **2012**, *197*, 414–423.
[66] R. M. Narbaitz, J. McEwen, *Water Res.* **2012**, *46* (*15*), 4852–4860.
[67] O. J. Murphy, G. D. Hitchens, L. Kaba, C. E. Verostko, *Water Res.* **1992**, *26* (*4*), 443–451.
[68] D. C. Johnson, J. Feng, L. L. Houk, *Electrochim. Acta* **2000**, *46* (*2–3*), 323–330.
[69] M. Panizza, C. Bocca, G. Cerisola, *Water Res.* **2000**, *34* (*9*), 2601–2605.
[70] H. Zhang, *Chem. Eng. J.* **2002**, *85*, 81–85.
[71] N. W. Brown, E. P. L. Roberts, A. A. Garforth, R. A. W. Dryfe, *Electrochim. Acta* **2004**, *49* (*20*), 3269–3281.
[72] M. Panizza, P. A. Michaud, G. Cerisola, C. H. Comninellis, *J. Electroanal. Chem.* **2001**, *507* (*1–2*), 206–214.
[73] L. Wang, N. Balasubramanian, *Chem. Eng. J.* **2009**, *155* (*3*), 763–768.
[74] R. Berenguer, J. P. Marco-Lozar, C. Quijada, D. Cazorla-Amorós, E. Morallón, *Energy Fuels* **2010**, *24* (*6*), 3366–3372.
[75] Y. Han, X. Quan, S. Chen, H. Zhao, C. Cui, Y. Zhao, *Sep. Purif. Technol.* **2006**, *50* (*3*), 365–372.
[76] T. H. Kim, C. Park, E. B. Shin, S. Kim, *Desalination* **2003**, *155* (*1*), 59–65.
[77] K. Nath, M. S. Bhakhar, *Environ. Sci. Pollut. Res.* **2011**, *18* (*4*), 534–546.
[78] Ö. Aktas, F. Çeçen, *Int. Biodeterior. Biodegrad.* **2007**, *59* (*4*), 257–272.
[79] M. Silva, A. Fernandes, A. Mendes, C. M. Manaia, O. C. Nunes, *Water Res.* **2004**, *38* (*11*), 267–2684.
[80] F. Orshansky, N. Narkis, *Water Res.* **1997**, *31* (*3*), 391–398.
[81] R. J. De Jonge, A. M. Breure, J. G. Van Andel, *Water Res.* **1996**, *30* (*4*), 875–882.
[82] K. L. Sublette, E. H. Snider, N. D. Sylvester, *Water Res.* **1982**, *16*, 1075–1082.
[83] Z. Xiaojian, W. Zhansheng, G. Xiasheng, *Water Res.* **1991**, *25* (*2*), 165–172.
[84] W. Oh, P. Lim, C. Seng, A. N. A. Sujari, *Bioresource Technol.* **2011**, *102* (*20*), 9497–9502.
[85] K. M. Lee, P. E. Lim, *Chemosphere* **2005**, *58* (*4*), 407–416.
[86] A. E. Perrotti, C. A. Rodman, *AIChE Symp. Ser.* **1974**, *144*, 316–325.
[87] N. Klimenko, S. Smolin, S. Grechanyk, V. Kofanov, L. Nevynna. L. Samoylenko, *Colloids Surf., A* **2004**, *230* (*1*), 141–158.
[88] D. Kim, T. Miyahara, T. Noike, *Water Sci. Technol.* **1997**, *36* (*12*), 239–249.
[89] S. Vinitnantharat, A. Baral, Y. Ishibashi, S. R. Ha, *Environ. Technol.* **2001**, *22* (*3*), 339–344.

[90] O. Aktas, F. Çeçen, *J. Chem. Technol. Biotechnol.* **2006**, *81* (*7*), 1081–1092.

[91] N. Klimenko, M. Winther-Nielsen, S. Smolin, L. Nevynna, J. Sydorenko, *Water Res.* **2002**, *36* (*20*), 5132–5140.

[92] A. R. H. Putz, D. E. Losh, G. E. Speitel, *J. Environ. Eng.* **2005**, *131* (*2*), 196–205.

[93] V. S. Mishra, V. V. Mahajani, J. B. Joshi, *Ind. Eng. Chem. Res.* **1995**, *34* (*1*), 42–48.

[94] J. Kálmán, I. Szebényi, *Water Sci. Technol.* **1987**, *19* (*7*), 1237–1238.

[95] A. B. Thomsen, *Water Res.* **1998**, *32* (*1*), 136–146.

[96] K. Naito, K. Huang, A. Endo, M. Nakaiwa, T. Akiya, H. Yanagishita, T. Nakane, *J. Chem. Eng. Japan* **2001**, *34* (*12*), 1545–1548.

[97] F. Jin, J. Cao, Z. Zhou, T. Moriya, H. Enomoto, *Chem. Lett.* **2004**, *33* (*7*), 910–911.

[98] F. J. Rivas, S. T. Kolaczkowski, F. J. Beltrán, D. B. McLurgh, *Chem. Eng. Sci.* **1998**, *53*, 2575–2586.

[99] Y. Yoshii, S. Miura, S. Okazaki, *Chem. Phys. Lett.* **2001**, *345* (*1–2*), 195–200.

[100] Y. I. Matatov-Meytal, M. Sheintuch, G. E. Shter, G. S. Grader, *Carbon* **1997**, *35* (*10–11*), 1527–1531.

[101] U. Jans, J. Hoigne, *Ozone Sci. Eng.* **1998**, *20* (*1*), 67–90.

[102] V. Gómez-Serrano, P. M. Álvarez, J. Jaramillo, F. J. Beltrán, *Carbon* **2002**, *40* (*4*), 513–522.

[103] H. L. Chiang, P. C. Chiang, C. P. Huang, *Chemosphere* **2002**, *47* (*3*), 267–275.

[104] H. L. Chiang, C. P. Huang, P. C. Chiang, *Chemosphere* **2002**, *47* (*3*), 257–265.

[105] H. Valdés, M. Sánchez-Polo, J. Rivera-Utrilla, C. A. Zaror, *Langmuir* **2002**, *18* (*6*), 2111–2116.

[106] S. Notthakun, J. C. Crittenden, D. W. Hand, D. L. Perram, M. E. Mullins, *J. Environ. Eng.* **1993**, *199* (*4*), 695–714.

[107] J. Liu, D. C. Crittenden, D. W. Hand, D. L. Perram, *J. Environ. Eng.* **1996**, *122* (*8*), 707–714.

[108] S. G. Huling, P. K. Jones, W. P. Ela, R. G. Arnold, *J. Environ. Eng.* **2005**, *131* (*2*), 287–297.

[109] S. G. Huling, P. K. Jones, W. P. Ela, R. G. Arnold, *Water Res.* **2005**, *39* (*10*), 2145–2153.

[110] S. Kommineni, W. P. Ela, R. G. Arnold, S. G. Huling, B. J. Hester, E. A. Betterton, *Environ. Eng. Sci.* **2003**, *20* (*4*), 361–373.

[111] L. L. Jae, O. Mitsumasa, *Ultrason. Sonochem.* **2005**, *12* (*4*), 277–282.

[112] T. J. Mason, J. P. Lorimer, *Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry*, Ellis Horwood Ltd, New York **1988**.

[113] H. Hao, M. Wu, Y. Chen, Y. Yin, Z. Lu, *Environ. Toxicol.* **2003**, *18* (*6*), 413–417.

[114] K. C. Teo, Y. Xu, C. Yang, *Ultrason. Sonochem.* **2001**, *8* (*3*), 241–246.

[115] J. G. Wang, P. Q. Guo, X. K. Wang, Z. M. Gu, *Prog. Chem.* **2005**, *17* (*3*), 549–553.

[116] N. H. Ince, G. Tezcanli, R. K. Belen, I. G. Apikyan, *Appl. Catal., B* **2001**, *29* (*3*), 167–176.

[117] M. Breitbach, D. Bathen, *Ultrason. Sonochem.* **2001**, *8* (*3*), 277–283.

[118] O. Hamdaoui, E. Naffrechoux, L. Tifouti, C. Pétrier, *Ultrason. Sonochem.* **2003**, *10* (*2*), 109–114.

[119] W. Qin, Y. Yuan, Y. Dai, *Chin. J. Chem. Eng.* **2001**, *9* (*4*), 427–430.

[120] S. Yu, D. Gao, Z. Qin, *Int. Sugar J.* **2000**, *102*, 202–204.

[121] S. U. Rege, R. T. Yang, C. A. Cain, *AIChE J.* **1998**, *44* (*7*), 1519–1528.

[122] P. M. Álvarez, F. J. Beltrán, V. Gómez-Serrano, J. Jaramillo, E. M. Rodríguez, *Water Res.* **2004**, *38* (*8*), 2155–2165.

[123] L. M. Pastrana-Martínez, M. V. López-Ramón, C. Moreno-Castilla, *J. Colloid Interface Sci.* **2009**, *331* (*1*), 2–7.

[124] C. S. Tan, P. L. Lee, *J. Supercrit. Fluids* **2008**, *46* (*2*), 99–104.

[125] E. Çalıskan, J. M. Bermúdez, J. B. Parra, J. A. Menéndez, M. Mahramanlıoglu, C. O. Ania, *J. Environ. Manage.* **2012**, *102*, 134–140.

[126] C. O. Ania, J. B. Parra, J. A. Menéndez, J. J. Pis, *Water Res.* **2007**, *41* (*15*), 3299–3306.

[127] A. Karimi-Jashni, R. Narbaitz, *J. Environ. Eng.* **2005**, *131* (*3*), 443–449.

[128] O. Aktas, F. Çeçen, *J. Hazard. Mater.* **2010**, *177* (*1–3*), 956–961.

[129] R. V. Shende, V. V. Mahajani, *Waste Manage.* **2002**, *22* (*1*), 73–83.

[130] K. Okawa, K. Suzuki, T. Takeshita, T. Nakano, *Water Res.* **2007**, *41* (*5*), 1045–1051.

[131] P. S. Yap, T. T. Lim, *Water Res.* **2012**, *46* (*9*), 3054–3064.

[132] R. S. Juang, S. H. Lin, C. H. Cheng, *Ultrason. Sonochem.* **2006**, *13* (*3*), 251–260.

[133] O. Hamdaoui, R. Djeribi, E. Naffrechoux, *Ind. Eng. Chem. Res.* **2005**, *44* (*13*), 4737–4744.

[134] G. Jing, Z. Zhou, L. Song, M. Dong, *Desalination* **2011**, *279* (*1–3*), 423–427.

[135] W. A. Al-Amrani, P. E. Lim, C. E. Seng, W. S. Wan Ngah, *Bioresource Technol.* **2012**, *118*, 633–637.

[136] C. O. Ania, F. Beguin, *Environ. Sci. Technol.* **2008**, *42* (*12*), 4500–4506.

[137] Y. Tao, C. Y. Wu, D. W. Mazyck, *Chemosphere* **2006**, *65* (*1*), 35–42.

[138] J. L. Lim, M. Okada, *Ultrason. Sonochem.* **2005**, *12* (*4*), 277–282.

CAPÍTULO 6

Artigo: Electrochemical regeneration of phenol-saturated activated carbon – proposal of a reactor

Neste capítulo, é apresentado o estudo do desenvolvimento de um reator eletroquímico utilizado para regeneração de carvão ativado saturado com fenol. Foram investigadas as condições de funcionamento do reator baseado nos efeitos de tempo de regeneração, corrente utilizada, polaridade, modo de operação e tipo de eletrólito. O desempenho do reator foi avaliado pela readsorção de fenol e o estudo aponta que a técnica eletroquímica é um processo promissor na regeneração de carvão ativado saturado com compostos orgânicos.

6.1. Artigo: Electrochemical regeneration of phenol-saturated activated carbon – proposal of a reactor

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Abstract: An electrochemical process was used to investigate the activated carbon (AC) regeneration efficiency saturated with aromatics. For this purpose it was developed an electrochemical reactor and investigated the operational conditions of this equipment, applied in AC regeneration process. The influence of regeneration parameters such as processing time, the current used, the polarity and the processing fluid (electrolyte) were studied. The performance of electrochemical regeneration was evaluated by adsorption tests using phenol as adsorbate. The increase of current applied and the process time was found to enhance the regeneration efficiency (RE). Another aspect that indicated a better reactor performance was the type of electrolyte used, showing best results for NaCl. The polarity showed the highest influence on the process, when the cathodic regeneration was more efficient. The electrochemical regeneration process developed in this study presented regeneration capacities greater than 100%, when the best process conditions where used, showing that this form of regeneration for AC saturated with aromatics is very promising.

Keywords: regeneration; electrochemistry; activated carbon; phenol; adsorption.

6.1.1. Introduction

Activated carbon (AC) is a widely used adsorbent in a large number of applications. Despite the widespread use of AC in adsorption processes, the biggest obstacle to its application by industry is the high cost and difficulties associated with regeneration [1]. It is observed that, having exhausted its adsorption capacity, the CA can be deposited in controlled landfills, incinerated or regenerated for reuse [2]. However, the provision in hazardous waste landfills is becoming increasingly unacceptable because of growing concern about the effect of pollutants in the environment and more stringent environmental standards. This fact motivates the development of regenerative systems, ensuring their economic and environmental viability [3].

The main purpose of regeneration is to remove the adsorbed pollutants in order to recover the original adsorption capacity of the AC. This process can be performed by two distinct *process routes*. The first involves the regeneration based only on desorption of the adsorbed compounds without AC reactions, requiring only the mass transport from one phase (AC surface) to another. The second route addresses regeneration based on the decomposition of the pollutants adsorbed on the AC, involving decomposition reactions with the possibility of complete mineralization of the pollutants [3].

Conventionally, the saturated AC can be regenerated by thermal and non-thermal chemical methods. Thermal methods have serious disadvantages such as high energy consumption and material loss, loss of adsorption capacity, for example [4]. The non-thermal and chemical methods such as solvents regeneration and chemical oxidation are associated to high cost of reagents and loss of adsorption capacity due to residual solvent adsorbed in the AC after regeneration. In addition, it can be observed that the effectiveness of regeneration of these methods depends on the type of pollutant to be removed [5,6].

The electrochemical regeneration has gained increased attention in recent years due to its unique characteristics, such as low operating temperature (about 25°C) without addition of chemical products and the possibility of complete decomposition of the organic compounds adsorbed on the AC without damaging the structural properties and characteristics of the adsorbent [7].

The electrochemical regeneration refers to the regeneration of a loaded adsorbent disposed within an electrolytic cell containing a electrolyte solution applied to a potential current [8,9]. The electrochemical regeneration mechanism involves electrodesorption and/or destruction of contaminants adsorbed on the activated carbon in order to restore the adsorbent capacity.

The organic decomposition in an aqueous medium can occur via two pathways:

i. Electrochemical conversion - where the non-biodegradable compounds are converted into biodegradable compounds;
ii. Electrochemical combustion - where all the organic contaminants are completely mineralized.

According to Garcia-Otón [8], the electrochemical method is more effective when compared to thermal regeneration, since it hardly changes the pore structure of the material. So, in addition to regenerate the AC enabling its reuse, the electrochemical technology can increase the AC adsorption capacity.

The AC electrochemical regeneration can be performed on the cationic electrode or the anionic electrode [10,11,12]. Narbaitz and Cen [10] showed that the cathode regeneration is 5 to 10% more efficient than the anodic regeneration. On the other hand, in the cathodic regeneration a small amount of residual compound remains in the electrolyte, while the remaining compound in the anodic regeneration was not detected.

In this context, this work aims to study activated carbon regeneration loaded with organic compounds using an electrochemical reactor developed in bench scale. The study also evalutes the best electrochemical regeneration conditions for the activated carbon loaded with phenol.

6.1.2. Materials and methods

6.1.2.1. Materials

The activated carbon (AC) selected for this work was provided by Synth (Synth - Brazil), with a mean particle size between 1 and 2 mm and $pH_{PZC} = 7.8$. These conditions have been previously determined [13]. Before saturation, the AC samples were washed several times with distilled water and dried in an oven at 105°C for 24 h. Phenol, NaOH, HCl and NaCl solutions were prepared by dissolving analytical grade reagents in deionized water. Analytical grade reagents and deionized water was used throughout the study unless otherwise indicated.

6.1.2.2. Phenol saturation of the activated carbon

The adsorption experiments performed in this work step aimed to set up and characterize the electrochemical reactor. Initially it was carried out a factorial design 2^3 with triplicate at the center point. The objective was to evaluate the effects of temperature, pH and adsorption time, as shown in Table 6.1.

Table 6.1. Scale factors for the evaluation of the adsorption conditions.

Factor	Intervals evaluated				
Temperature °C		20 (-1)	40 (0)	60 (1)	
pH		4 (-1)	6 (0)	8 (1)	
Time (hours)	6 (-1.8)	10 (-1)	15 (0)	20 (1)	24 (+1.8)

The adsorption experiments for the AC saturation were performed in batch scale using 250 mL flasks agitated on an orbital shaker with temperature and agitation speed controled. To each flask was placed 1 g of AC in 200 ml of phenol solution with an approximate concentration of 20 g/L and stirring was initiated applying time, temperature and pH in a predetermined schedule. After the equilibrium period, the solids were filtered and the phenol concentration in the residual solution was measured by UV–Vis absorption, at the wavelength of 270 nm. The AC load phenol was washed with 100 ml of distilled water and dried in an oven at 105°C (± 5°C) for 24 h. After this procedure the AC is ready to be regenerated.

The model of the Sips isotherm was used for regeneration percentage evaluation (the Sips model represented well the experimental data).

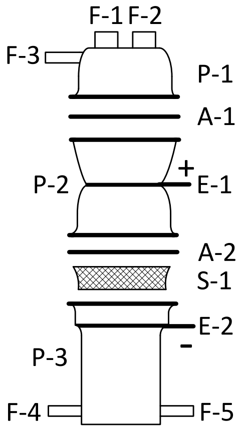
6.1.2.3. Regenerating system

To AC regeneration technique used in this work a reactor was developed based on physical and chemical principles of electrochemical processes. This project was based on the work previously published by Wang and Balasubramanian [14] and Narbaitz and Karimi-Jashni [15], but with some changes in the reactor, according to the problems identified in this study. Also, some details reported by the authors in their work were considered.

The reactor has been designed to regenerate 1 g of activated carbon on every batch. This AC mass was chosen based on the adsorption process carried out in bench scale, where it was used the same amount. The electrochemical reactor was constructed in borosilicate glass, and divided into three compartments (P-1, P-2 and P-3) according to Figure 6.1.

Equipment specification - electrochemical reactor

Schematic design



Description

P-1 → Upper compartment
P-2 → Central compartment
P-3 → Lower compartment
A-1 e A-2 → Gaskets
E-1 e E-2 → Platinized titanium electrode
S-1 → Solid support
F-1, F-2, F-3 e F-4 → Connections

Reactor data

Operating temperature → 10-400°C
Operating pressure → 1 atm
Operating mode → Agitation / Circulation
F-1 e F-2 → Internal opening 18 mm
F-3, F-4 e F-5 → Internal opening 6 mm

Figure 6.1. Technical specifications of the electrochemical reactor developed.

In the upper compartment (P-1) were constructed two openings (F-1 and F-2) of 18 mm exit gases formed in the regeneration process and to collect samples and measurements (pH, electrical conductivity, etc.) and a connection (F-3) 6 mm used for circulation of electrolyte. In the central compartment (P-2) has been fixed a platinized titanium electrode (E-1) which can act as cathode or anode. This electrode has a shank which serves as a connection to a source which, through an opening (stagnant with a rubber bushing) reaches the outside of the reactor enables the application of electric current to the electrodes without electrolyte leakage. In the lower compartment (P-3) of the reactor, it were constructed two 6 mm connections (F-4 and F-5); one serves for circulation of the electrolyte and the other for sampling. There is also in this compartment a platinized titanium electrode (E-2) with the same functions as the electrode of the central part of the reactor. On the lower electrode compartment is where the AC sample is packed for the application of electrochemical regeneration process. To contain the sample, it was developed a support (S-1) made of polyvinyl chloride (PVC) with an aperture of 0.5 mm pores. This support is a kind of cocoon that prevents dispersion of the sample by the reactor.

To join the compartments, brushed glass joints were constructed with 6 mm edge at the reactor assembly receiving rings (A-1 and A-2) rubber ensuring the tightness of the reactor.

The main technical characteristics of the reactor are presented below.

i. Volume: 130 cm³.

ii. Cross-sectional area: 9 cm².

iii. Effective area of the electrodes: 5.43 cm².

iv. Operating voltage: 12 volts.

The reactor was developed to enable different operating configurations: (a) varying the operation mode - agitation or circulation; (b) varying the operating condition - cationic or anionic; (c) varying the direction of the electrolyte flow - up or down; (c) varying the electrolyte - water, sodium chloride (NaCl), sodium hydroxide (NaOH), among others; (d) varying the current or the applied voltage. Figure 6.2 illustrates the possible reactor operation modes in the regeneration process to which it is inserted.

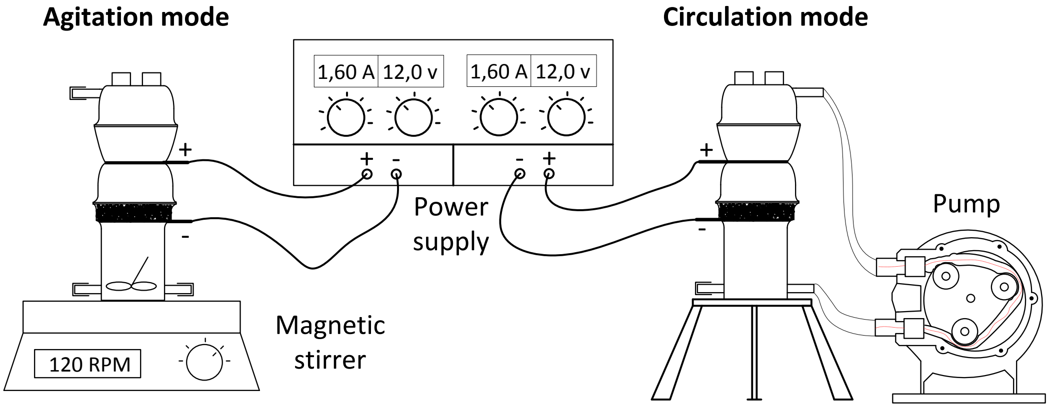


Figure 6.2. Illustration of the settings used in the regeneration process.

6.1.2.4. *Reactor characterization*

In order to characterize the optimal operating conditions of the reactor, the AC was loaded with phenol. Initially it was made up an experimental design, with tests carried out in triplicate, which aimed to evaluate effects of the applied current (0.4/0.8/1.6/2.4 A), type of electrolyte, cathode or anode regeneration, regeneration time and operation mode. The operating voltage was set at 12 v. The experiments were carried out in triplicate and the means were evaluated using analysis of variance by Statistica 7.0 software (StatSoft Inc., Tulsa, OK). Means were considered significantly different at $p<0.05$.

When using the stirring mode of operation, the speed used in the process was approximately 120 rpm (±10 rpm). For the circulation mode, the employed electrolyte flow rate was 40 ml/min. Specifications of electrolytes: distilled water, sodium chloride (NaCl - 3%) and sodium hydroxide (NaOH) 0.5 mol/L.

In the electrochemical regeneration experiments, in each cycle, 1 g of AC charged with phenol, was provided in support of PVC on the lower electrode compartment. For each test condition, we generated a data resorption, i.e. after regeneration samples AC (1 g) were washed with 100 ml of distilled water and dry in an oven at 105°C (± 5°C) for 24 h, then again ready to phenol adsorption process. With the data adsorption and resorption was possible to determine the percentage regeneration for each condition. This percentage was determined by Equation 6.1 which takes into account into account to condition equilibrium of the adsorbent related to the adsorption isotherm (Sips model).

$$\%Yield = \left[\frac{\frac{(C_{02} - C_{e2}).V}{M}}{\frac{q_m.b.C_e^{\gamma}}{1 + b.C_e^{\gamma}}}\right] * 100 \tag{6.1}$$

where C_{02} is the concentration in the initial stage of resorption (mg/L), C_{e2} is the equilibrium concentration of resorption (mg/L), V is the solution volume (L), M is the AC mass (mg), q_m is the maximum adsorption capacity of virgin AC (mg/g), b is the constant of the Sips isotherm (L/mg), C_e equilibrium concentration in the adsorption (mg/L) and γ is the exponent of Sips isotherm.

The surface area of the ACs were determined from the N_2 adsorption isotherms conducted in a volumetric apparatus (Micrometrics Tristar II 3020). Adsorbents were degassed at 300°C for 12 h prior to adsorption experiments. The Brunauer, Emmett and Teller (BET) surface area was determined by applying the BET equation to the adsorption data of N_2 at 77 K [16]. The pore size distribution of mesopores and micropores was calculated using the Barrett-Joyner-Hallenda and Horvath-Kawazoe methods [17, 18]. The total pore volume was evaluated from the amount adsorbed at a relative pressure of approximately 0.99. The elemental composition of samples (C, N, H and S) was analyzed by a PerkinElmer 2400 apparatus.

6.1.3. Results and discussion

6.1.3.1. Determination of the adsorption conditions

Adsorption assays comprise an important step in this study due to the fact that the effectiveness of the electrochemical regeneration (reactor developed in this study) is based on the solid adsorption capacity used. In order to carry out the adsorption study of phenol activated carbon and to determine the adsorption capacity, it was initially evaluated the best process conditions concerning the effects of temperature, pH and time to be used, and the results are shown in Table 6.2.

Table 6.2. Experimental design of phenol adsorption on activated carbon to different temperatures, pH and contact time.

Temperature °C	pH	Time (h)	q_e (mg/g)
-1 (20)	-1 (4)	-1 (10)	292.80
1 (60)	-1 (4)	-1 (10)	214.33
-1 (20)	1 (8)	-1 (10)	292.65
1 (60)	1 (8)	-1 (10)	213.98
-1 (20)	-1 (4)	1 (20)	354.88
1 (60)	-1 (4)	1 (20)	241.00
-1 (20)	1 (8)	1 (20)	381.09
1 (60)	1 (8)	1 (20)	233.00
0 (40)	0 (6)	1.68 (24)	330.28
0 (40)	0 (6)	-1.68 (6)	197.00
0 (40)	0 (6)	0 (15)	306.33
0 (40)	0 (6)	0 (15)	307.57
0 (40)	0 (6)	0 (15)	304.66

The results of these tests were evaluated by analysis of variance by Statistica 7.0 software (StatSoft Inc., Tulsa, OK). For phenol adsorption on AC, according to analysis of variance (Table 6.3), the main effects of temperature and time, and the interaction of two temperature-time factors were significant ($p < 0.05$).

Based on the data variance, which showed significant interaction between two factors studied, it was evaluated the optimal process conditions using the surface contour shown in Figure 6.3, which illustrates the temperature-time interaction for pH level 0 (6.0). It was chosen pH 6.0 due to non-significance of the studied pH range, ie between pH 4.0 and pH 8.0, the phenol adsorption on the AC was not influenced by the variation of pH. As the initial solution of phenol used in the tests has a pH 6.5, there was no need to adjust this in the experiments.

Table 6.3. Analysis of variance for phenol adsorption on activated carbon to variations in temperature, pH and time.

Factor	**Sum of squares**	**Degrees of freedom**	***p-value***
Temperature (L)	**21935.670**	**1**	**0.0004***
Temperature (Q)	680.080	1	0.1229
pH (L)	41.460	1	0.6553
Time (L)	**13104.390**	**1**	**0.0010***
Time (Q)	**2172.110**	**1**	**0,0252***
Temperature x pH	146.310	1	0.4169
Temperature x time	**1378.780**	**1**	**0.0498***
pH x time	41.460	1	0.6553
Error	715.420	4	
Total SS	39917.340	12	

* significant parameters at 95% confidence

Analyzing Figure 6.3, it is possible to identify that considering the optimization of the adsorption conditions, the value of qe (mg/g - phenol accumulation on AC) shows results for temperatures greater than 20°C and 24 h time. In this experiment it was not possible to observe the equilibrium of the process along the time, that is, when it was used a 24 h period, it seems that there is no equilibrium in the process, indicating that the time was not enough. Therefore, a kinetic assay was carried out for phenol adsorption process with AC with 7 days interval, and it was observed that there was no significant change after 24 h. Tancredi *et al*. [19] in phenol AC adsorption studies, these authors found the same conditions as temperature and contact time. It can also be observed from Figure 6.3 that time shows a great significance with respect to temperature.

Analysis of variance showed that the regression model (Equation 6.2) showed a good fit to the experimental data with a coefficient of determination $R^2 = 0.98$.

$$Y = 306.2 - 104.7\,A + 61.5\,B - 30.1\,B^2 + 2.3\,A\,B \qquad (6.2)$$

where Y is the adsorption capacity (mg/g), A is the temperature (°C), B is the contact time (hours).

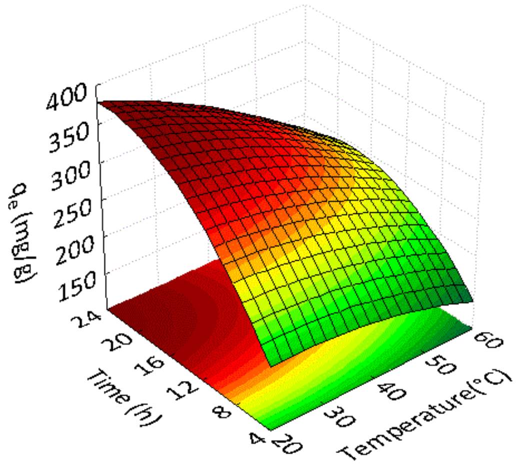


Figure 6.3. Surface Analysis for phenol adsorption onto activated charcoal as a function of temperature and time (pH 6.0).

6.1.3.2. Electrochemical regeneration

In order to determine the maximum efficiency of the electrochemical reactor relative to the AC load phenol the regeneration was evaluated aiming to find the best process conditions considering residence time, current, polarity, electrolyte and mode of operation (agitation or circulation) to be used.

After the regeneration process, the activated carbon used was renewed again for the adsorption process as set out conditions, and from the resorption of data it was possible to determine the regeneration percentage for each trial based on planning. From the middle of these experiments was carried out to study the optimization of reactor operating conditions. The regeneration percentage was determined by Equation 6.1.

Figure 6.4 shows the results for the regeneration process using the mode stirring in the reactor, and Figure 6.5 shows the results for the mode of movement. In each of the modes of operation current changes were made, time, electrode polarity and type of electrolyte.

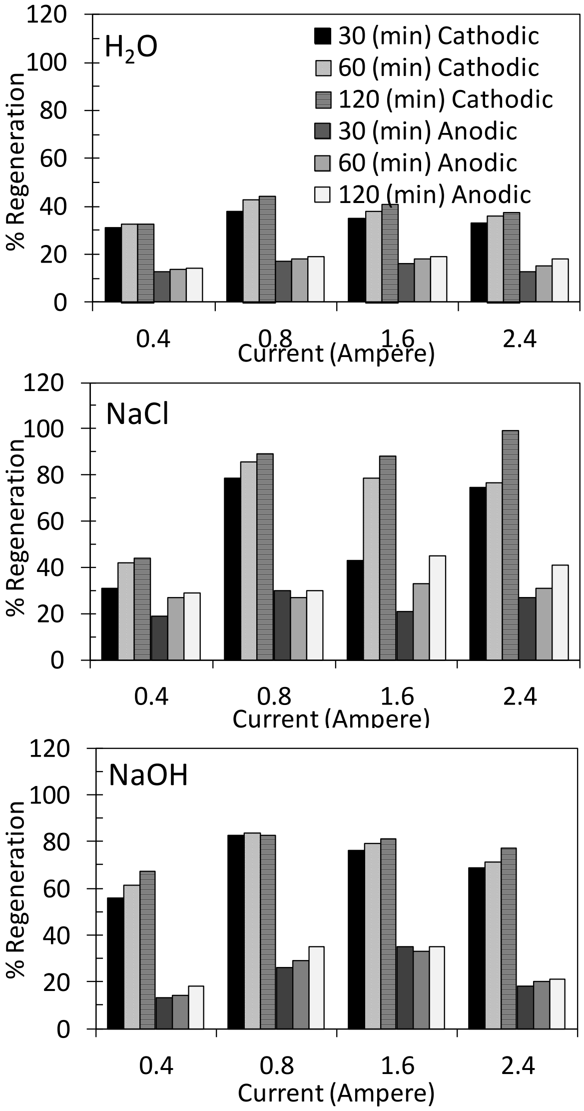


Figure 6.4. Regeneration agitation mode.

The effects of electrode polarity (anodic or cathodic regeneration), regardless reactor operation mode setting, shows that the values obtained RE % by cathodic regeneration are generally higher than the anodic regeneration. This result is similar to results found by other authors who studied the saturated AC electrochemical regeneration with aromatic compounds [8,10,12,20]. Moreover, differences between the cathodic and anodic regeneration is greater for the agitation reactor operating mode. Another important observation is related to the current applied in the polarity. For the anodic regeneration, showed less variation in the current process, that is, has no significance. An exception occurs in the anodic regeneration mode agitation, NaOH electrolyte, wherein the RE % showed differences, showing that for currents between 0.8 and 1.6 A, the process had better yields.

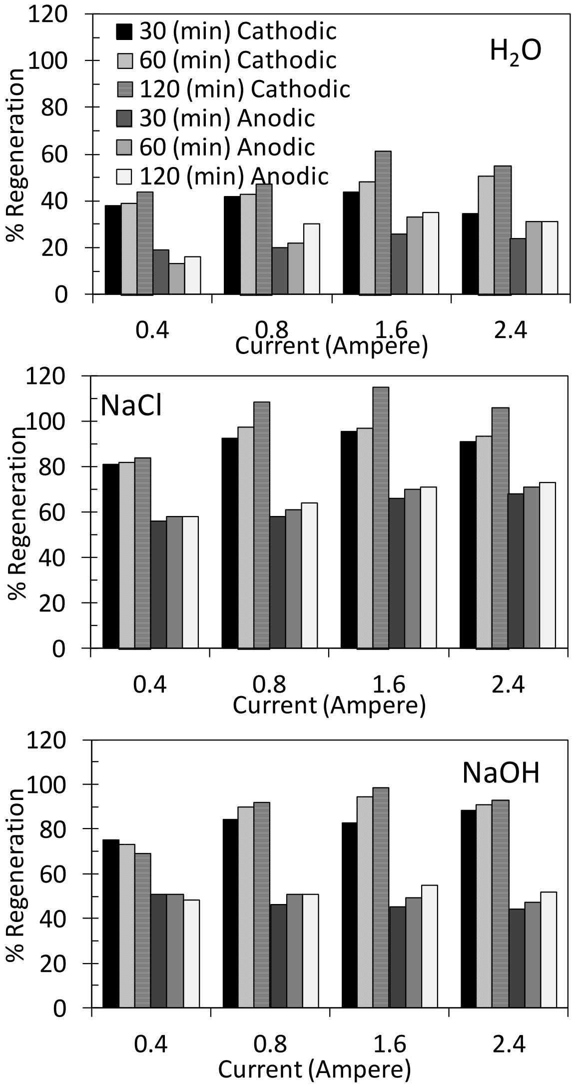


Figure 6.5. Regeneration circulation mode.

The influence of operation mode does not depend directly from any of the effects studied, but it is known that there is a synergy between the factors, and this leads to an optimum operating range. However, the circulation mode showed the most significant effects on the efficiency of the regeneration so that the agitation. The electrolytic current effects on the regeneration efficiency can also be analyzed from Figures 6.4 and 6.5. In most applications, higher values are achieved with regenerative current of 1.6 A. However, evaluating only the cathodic regeneration is observed that the process does not follow the general trend, there have two exceptions related to the type of electrolyte used and the operating mode. These variations can be found in the stirring mode using NaOH as the electrolyte, where the highest yield was 0.8 A current, taking into account the time of 120 minutes and using NaCl as the electrolyte for a current of 2.4 A gave the highest yield.

Several authors report that NaCl is the most efficient electrolyte for electrochemical regeneration [10-12].

The process time (regeneration) also showed significant variations. The efficiency of regeneration shows an increase with prolonged process time. With the exception of one case, circulation mode, 0.4 A and NaOH, all others showed higher yields with time of 120 min. Extra rehearsals with longer times to 120 min were performed, but the results were similar. Thus it was decided to conduct the studies in 120 min.

Based on the results obtained in the experiments and significance analysis, the reactor operating conditions for the regeneration of loaded AC with phenol were set as follows: flow mode; time equal to 120 min; applied current of 1.6 A; Cathodic regeneration; NaCl as the electrolyte. With this configuration, it was possible to obtain regeneration percents greater than 100%, i.e., the adsorption capacity of the AC was increased; This result also demonstrates that the electrochemical reactor can be used as a pretreatment to increase the adsorption capacity of the AC.

The effect of the polarity of the regeneration process can be explained taking into account the electric charge of the AC and the electric charge of the adsorbate (ion). During the anodic regeneration are produced attractive electrostatic interactions between AC species polarized positively and phenolates ($C_6H_5O^-$). The AC has its positive surface charge increased due to the higher concentration of deprotonated species in the double layer region around the anode and the activated carbon particles. If this happens, desorption is complicated and low regeneration percentages are obtained. On the contrary, when regeneration is carried out at the cathode, the AC is subjected to a negative potential, a negative charge that accumulates on it. Thus, phenolate species are more readily desorbed from the AC and repulsive interactions, distanced from the adsorbent surface, thus achieving higher regeneration %. The electrode polarity is a factor of extreme importance in the electrochemical regeneration. It can promote or prevent desorption of phenol (or phenolates) of the surface of AC. Moreover, the current used has a great impact on the process, thus the higher the applied current, the greater the degree of polarization of negative charges accumulated on AC particles by cathodic regenerations or greater positive charge in the anodic regeneration.

The polarity of the electrode on the resulting electric field may also affect the transport phenolates desorbed from the pores of AC, which results in competition or cooperation of two primary mechanisms, ionic migration (electric potential) and diffusion (concentration gradient). While the phenol concentration gradients force the phenolate ions to flow out of the pores, the transport of these species will depend on the direction of the electric field. In both cathodic regeneration concentration gradient of the electric potential as they are in the same direction, so the movement phenolates desorbed out of the pores is combined. In the anodic regeneration, while the concentration gradient assists desorption, the electric potential favors adsorption phenolates. Accordingly, for cathodic regeneration, with the higher applied current greater regeneration efficiency is reached. However, considering the results presented in Figure 6.5, it is observed that in practice not the case in this way, which is a slight variation occurs in the regeneration %, where the current range studied, we obtained similar or greater regeneration % both current 1.6 as to 2.4 A. One hypothesis that could explain this is that the weight of the migration contribution to the overall transport process within the pores should increase with increasing applied current, however, this factor increases the number of anions in the electrolyte solution increases the repulsion between the solution in AC/electrolyte interface thus preventing phenolates exit the pores of the activated carbon.

However, the role of electric current is far more complex since it has an effect on other steps of the electrochemical mechanism of regeneration, such as in the decomposition of the desorbed compounds.

We analyzed the surface area and porosity after the regeneration process to evaluate the changes related to the process. Figure 6.6 and Table 6.4 show the results of these analyzes. Regeneration cathode was used and the electrolyte (H_2O, NaOH and NaCl) in accordance with the best previous results.

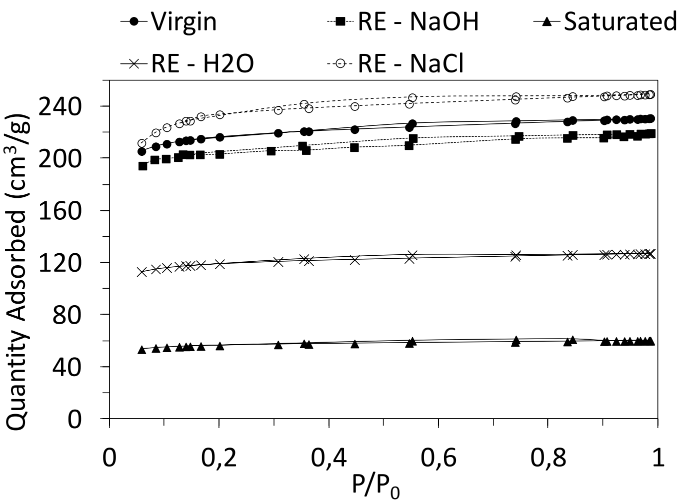


Figure 6.6. Regeneration effect on the N_2 isotherms (recovery porosity).

Table 6.4. Structural characterization of AC samples regenerated.

Sample	BET A_{BET}(m^2/g)	V_{tot} (cm^3/g)	V_{micro} (cm^3/g)
AC	765,3	0,37	0,29
Saturated-AC*	196,3	0,08	0,07
RE-NaCl	819,8	0,40	0,28
RE-NaOH	726,9	0,33	0,26
RE-H_2O	414,7	0,17	0,15

Note: A_{BET} - surface area BET; V_{tot} - total pore volume; V_{micro} - micropore volume
* No pretreatment

Structural characterization reveals that the dependence of the textural properties (recovery area and pore) of AC in relation to electrochemical variables is qualitatively consistent with the regeneration percentage of results. From the results shown in Figure 6.6 and Table 6.4, it is observed that the regeneration process is capable of recovering the structural characteristics of AC or, in the case of using NaCl as the electrolyte; it was possible to increase the surface area, and the total pore volume. This result indicates that the electrochemical reactions occurred phenol and/or the products of electrochemical reactions at the surface of the C. As discussed above, this may be due to a combination of several factors which are responsible for increased phenol/phenolate desorption under favorable conditions ion migration and concentration gradients. However, the low recovery of surface area and porosity observed for samples regenerated using H_2O as an electrolyte (which agrees with the results of regeneration %) suggests that the process does not favor the desorption of phenol/phenolate, or the product of decomposing the phenol may be regenerated being adsorbed on AC blocking the pores, resulting thereby in low efficiencies.

According to several authors [21,22,23], the species generated in the phenol decomposition can be dimers, oligomers, polymers, and other products, and these could result from reactions on the surface of AC during the electrochemical regeneration, or could be produced on the electrodes electrochemically and then adsorbed on AC already regenerated.

6.1.4. Conclusions

It was designed and built an electrochemical reactor for AC regeneration saturated phenol. The effects of electrode polarity of the applied current, type of electrolyte and the regeneration time and recovery efficiency of AC were studied.

The best results in terms of regeneration efficiency and recovery porosity were obtained by cathodic regeneration current of 1.6 A, electrolyte NaCl 3% (w/w), and time 120 min. Under these conditions, the regeneration percentage was higher than 100%. This high efficiency may be due to a combination of several factors that produce greater desorption of phenol/phenolate and phenol resorption lowest decomposition products.

Low regeneration percentage values obtained in the anodic regeneration may be a consequence of the negative influence of more positive potential, which facilitates the adsorption of phenolates ($C_6H_5O^-$) hindering the free migration of ionic compounds desorbed from the pores of the AC.

The electrochemical regeneration process employed in regeneration of AC loaded with phenol technique proved to be a good chance to become applicable in the field (in situ), and that has no reports of large-scale applications. The technique is not fully understood, it is not known for sure if you can transfer conditions for different contaminants. What is known, in this paper it was shown, that the electrochemical process is functional, can be used with good results.

In order to achieve better performance for the process, further studies should be performed. In particular should be studied decomposition of phenol in the reactor and the adsorption of the main compounds of the decomposition of phenol. Thus, knowing the control parameters on the adsorption of certain products, you can create one on the adsorption of this unfavorable environment while maintaining the AC surface completely renovated (regenerated).

References

[1] H. Lata, V.K. Garg, R.K. Gupta, Adsorptive removal of basic dye by chemically activated Parthenium biomass: equilibrium and kinetic modeling, Desalination, 219(1-3), (2008) 250-261.

[2] G. San Miguel, S.D. Lambert, N.J.D. Graham, The regeneration of field spent activated carbons, Water Res., 35(11), (2001) 740-748.

[3] O. Zanella, I.C. Tessaro, L.A. Féris, Desorption and Decomposition - Based Techniques for the Regeneration of Activated Carbon , Chem. Eng. Technol., 37(9), (2014) 1447–1459.

[4] G. San Miguel, S.D. Lambert, N.J. Graham, Thermal regeneration of granular activated carbons using inert atmospheric conditions, Environ. Technol., 23(12), (2002) 1337–1346.

[5] D. Chinn, C.J. King, Adsorption of glycols, sugars, and related multiple–OH compounds onto activated carbons. 2. Solvent regeneration, Ind. Eng. Chem. Res., 38(10), (1999), 3746–3753.

[6] J.F. González, J.M. Encinar, A. Ramiro, E. Sabio, Regeneration by wet oxidation of an activated carbon saturated with p-nitrophenol, Ind. Eng. Chem. Res., 41(5), (2002), 1344–1351.

[7] Y. Han, X. Quan, S. Chen, H. Zhao, C. Cui, Y. Zhao, Electrochemically enhanced adsorption of aniline on activated carbon fibers, Sep. Purif. Technol., 50(3), (2006), 365–372.

[8] M. García-Otón, F. Montilla, M.A. Lillo-ródenas, E. Morallón, J.L. Vázquez, Electrochemical regeneration of activated carbon saturated with toluene, J. Appl. Electrochem., 35(3), (2005) 319-325.

[9] N.W.Brown, E.P.L. Roberts, A. Chasiotis, T. Cherdron, N. Sanghrajka, Atrazine removal using adsorption and electrochemical regeneration, Water Res., 38(13), (2004) 3067-3074.

[10] R.M. Narbaitz, J. Cen, Electrochemical regeneration of granular activated carbon, Water Res., 28(8), (1994) 1771-1778.

[11] M.H. Zhou, L.C. Lei, Electrochemical regeneration of activated carbon loaded with p-nitrophenol in a fluidized electrochemical reactor, Electrochim. Acta, 51(21), (2006) 4489-4496.

[12] H. Zhang, L. Ye, H. Zhong, Regeneration of phenol-saturated activated carbon in an electrochemical reactor, J. Chem. Technol. Biot., 77(11), (2002) 1246-1250.

[13] O.Zanella, I.C.Tessaro, L.A.Féris, Study of $CaCl_2$ as an agent that modifies the surface of activated carbon used in sorption/treatment cycles for nitrate removal. Brazilian J. Chemical Eng., 31, (2013) 205-210.

[14] L. Wang, N. Balasubramanian, Electrochemical regeneration of granular activated carbon saturated with organic compounds, Chem. Eng. J., 155(3) (2009) 763-768.

[15] R.M. Narbaitz, A. Karimi-Jashni, Electrochemical reactivation of granular activated carbon: Impact of reactor configuration, Chem. Eng. J., 197, (2012) 414-423.

[16] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of Gases in Multimolecular Layers, Journal of the American Chemical Society, 60, (1938)309-319.

[17] G. Horváth, K. Kawazoe, Method for the calculation of effective pore size distribution in molecular sieve carbon, Journal of Chemical Engineering of Japan, 16, (1983) 470-475.

[18] E.P. Barrett, L.G. Joyner, P.P. Halenda, The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms, Journal of the American Chemical Society, 73, (1951)373-380.

[19] N. Tancredi, N. Mederoa, F. Möller, J. Píriza, C. Plada, T. Corderob, Phenol adsorption onto powdered and granular activated carbon, prepared from Eucalyptus wood, J. Coll. Interf. Sci., 279, (2004) 357–363.

[20] R. Berenguer, J.P. Marco-Lozar, C. Quijada, D. Cazorla-Amorós, E. Morallón, Electrochemical regeneration and porosity recovery of phenol-saturated granular activated carbon in an alkaline medium, Carbon, 48(10), (2010) 2734-2745.

[21] T.M.Grant, C.J.King, Mechanism of irreversible adsorption of phenilic-compounds by activated carbons, Ind. Eng. Chem. Res., 29(2), (1990) 264-271.

[22] R.Vidic, M.T.Suidan, Role of dissolved oxygen on the adsoptive capacity of activated carbon for synthetic and natural organic matter, Enviro. Sci. Technol., 25(9), (1991) 1612-1608.

[23] A.C.O.Pimenta, J.E.Kilduff, Oxidative coupling and the irreversible adsorption of phenol by grafite, J. Colloid Interface Sci., 293(2), (2006) 278-289.

CAPÍTULO 7

Artigo: Porous structure and characterisation of activated carbons obtained from grape stalks

Neste capítulo, é apresentado o estudo da produção de carvão ativado a partir de engaço de uva, desde avaliação do precursor (engaço de uva), processo de pirólise para a produção do carvão e finalizando com o estudo de diferentes processos de ativação. Foram investigadas as condições de ativação utilizando agentes como dióxido de carbono, ácido nírico e ácido clorídrico. Os resultados são apresentados e discutidos em função das características de superfície dos carvões ativados produzidos.

7.1. Artigo: Porous structure and characterisation of activated carbons obtained from grape stalks

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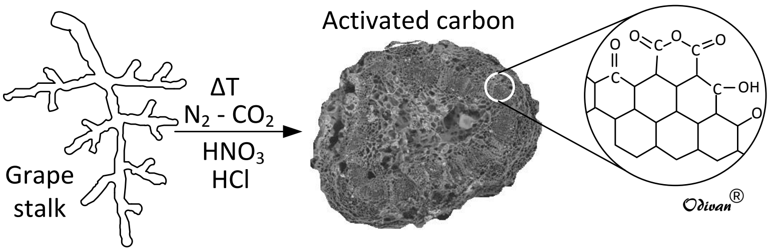

Graphical Abstract

Abstract: This work reports the activated carbon production from grape stalks, with activation in controlled atmosphere using carbon dioxide and also by the use of nitric acid and hydrochloric acid solutions. The results showed that the activated carbons produced have interesting properties, namely, apparent BET surface area and pore volume of up to 741 m^2/g and 0.34 cm^3/g, respectively. Activated carbons can be developed with acidic or basic surface, with a wide range of functional groups of the surface and have a very fascinating structure, as shown in the SEM images.

Keywords: grape stalks; activated carbon; adsorbents.

7.1.1. Introduction

Activated carbon (AC) has proven to be an effective adsorbent to remove a wide variety of organic and inorganic pollutants dissolved in aqueous solutions; including medicinal use, gas storage, pollutant and odor removal, gas separation, and catalysis. AC is an extremely versatile material with large surface area, large internal surface area, pore volume, good chemical stability, and various oxygen-containing functional groups on the surface [1].

The AC can be produced from any carbonaceous precursor to naturally occurring or synthetic. The economic process typically indicates the selection of inexpensive raw materials readily available. However, commercially available AC is very expensive. To reduce the production costs, the utilization of renewable and less expensive precursors for the preparation of AC is attracting the interest of researchers all over the world. Source precursors biomass offer a more economical source; they are abundant, renewable and present low mineral content, good toughness, and low cost. The literature concerning the use of agricultural by-products (lignocellulosic) is very extensive. Coconut shells, almond shells, peach kernel, apricot kernel, plum pits, cherry pits and nut shells (such as hazelnuts, pecans, etc.) can be listed as precursors studied [2-11].

The composition of lignocellulosic biomass precursors has a significant effect on the microporous structure of the AC end. Researchers have confirmed that the lignin is the major source of pure carbon, whereas the cellulose and hemicellulose are the volatile fractions of the biomass [12].

Reed and Williams [13] studied five samples of biomass content of cellulose, hemicellulose and lignin significantly different. They observed that the thermal decomposition temperature under N_2 was in the range 325-400, 250-350 and 200-720°C for cellulose, hemicellulose and lignin, respectively. They also concluded that the sample with higher lignin content had the highest yield of carbon and hence greater amount of AC. In another study conducted by Daud and Ali [14], the palm tree bark activation fee and coconut shell was compared. It was observed that the activation rate of the carbon coconut shell base was higher than that of the palm shell carbon-based, palm shell due to the lignin content. In another study by Daud and colleagues [15], the effect of palm bark carbonization temperature was investigated. The authors reported that with increasing temperature of 500 to 900°C, the yield of pure carbon gradually decreased from 33% to 24%. The decrease in carbon production was due to the release of carbon, hydrogen and oxygen as a result of the aromatic ring of the arrangement of the carbon structure. They also concluded that the volume of micropores increased as the carbonization temperature was gradually increased.

The grape stalks are an industrial waste generated in the wine industry and presents major problems for disposal. On the one hand is a compound with high humidity, therefore has low heat capacity. It remains for extended periods in the soil before complete the whole decomposition process. The stalks consists of the stalk and the pedicels (shorter branches), and its basic function is to support and serve power via the grain of the grape. In this way, this study aims to investigate the production of AC from grape stalks, using three different activation processes. At the end it is desired to obtain AC with large surface area, well developed porosity and heterogeneous surface chemistry, concerning surface functional groups.

7.1.2. Materials and methods

The grape stalks used as a precursor for the production of carbon was provided by a wine and grape juice industry in the state of Rio Grande do Sul - Brazil. The grape stalks were separated just after extracting the grains, and were not treated with any chemical additive. The samples grape stalks (1 kg) were washed with distilled water for several cycles or until the washing water did not exhibit turbidity and/or visible residues. Then the solid was dried in an oven at 105°C (± 5°C) for 24 hours, crushed and sieved in order to obtain a standardized precursor dimension and stored at room temperature until use. The particle size fraction between 0.3 and 1.0 mm was chosen for the preparation of charcoal.

7.1.2.1. Pyrolysis and activation of Carbon

In the carbonization step (pyrolysis), it was weighed 50 g of grape stalks which was loaded into a quartz reactor of 45 cm length and 2.0 cm in inner diameter, disposed within a furnace (muffle furnace) capable of heating to 1600°C. Figure 7.1 illustrates the process. The precursor was carbonized to 400°C at a heating rate of 10°C/min, remaining for 1 h at the final temperature at a constant N_2 flow of 100 cm^3/min. After carbonization reactor was cooled to room temperature under N_2 flow. The carbon produced was stored at room temperature until activation.

The physical carbon activation process was conducted by heating at a rate of 10°C/min in a CO_2 atmosphere at a constant flow of 100 cm^3/min at different temperatures and different times in order to obtain ACs with different characteristics, allowing optimization process. After activation, the samples were cooled to room temperature and CO_2 flow sequence washed with 0.5 L of distilled water for 24 hours.

The chemical activation process was performed by oxidation in different ways, depending on the oxidizing agent. Oxidation with 33% HNO_3 was carried out by boiling under reflux for 20 min. Oxidation with 1 M HCl was performed at 20°C for 24 h under stirring. After oxidation, the samples were washed with distilled water until neutrality was achieved and dried in a muffle at 105°C. This process was conducted in cycles.

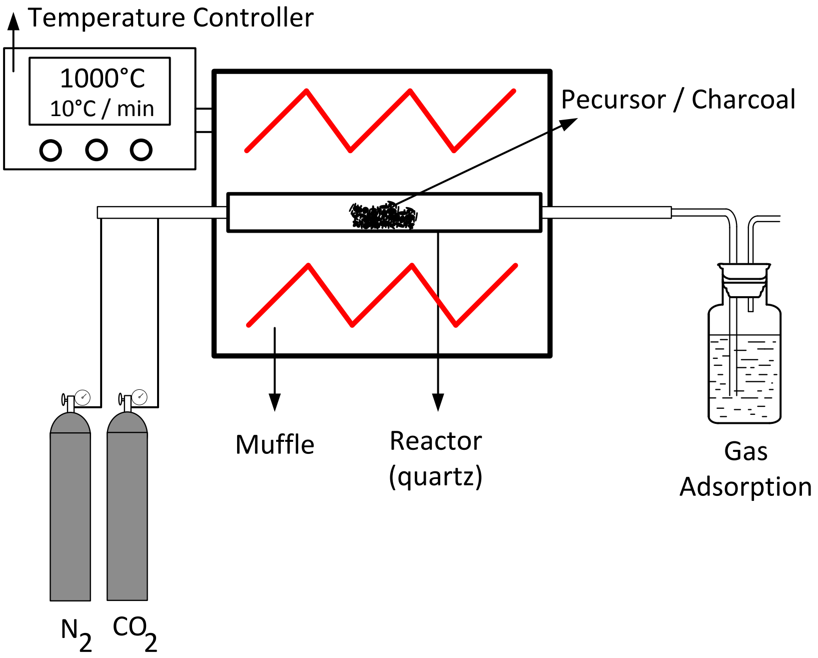

Figure 7.1. Illustration of the process of pyrolysis and activation of carbon.

The heat treatment was performed after oxidation at 700°C for 90 min, using a flow rate of 100 cm^3/min of nitrogen and a heating rate of 10°C/min. These conditions were based preliminary tests. After each activation cycle the reactor was cooled under nitrogen flow, the AC was collected and was washed with 0.5 L of distilled water for 24 hours and dried in a muffle at 105°C, and the yield and textural properties were determined before starting a new cycle.

The activated carbons were assigned by activating agent, the temperature and the number of application cycles, for example, CO_2/500/60/1, the activation was carried out with CO_2 at 500°C for 60 minutes and one cycle of activation was completed. Each process is identified by a letter.

The yield in the production of AC was determined based on the initial mass of the precursor and the final mass of AC on a dry basis as follows Equation 7.1:

$$\%Yield = \frac{w_f}{w_i} * 100 \tag{7.1}$$

where w_i represents the initial sample weight in grams before carbonization and w_f represents the weight in grams of the sample at the end of the activation process.

7.1.2.2. Characterisation

Thermogravimetric (TGA) and differential thermal (DTA) analysis were performed in a thermobalance (TA Instruments Q600 STD). These analyzes were designed primarily to identify the temperature values where the grape stalks reacts in an inert atmosphere. The samples were analyzed in a platinum crucible containing 20 mg of sample. The heating rate was 10°C/min starting at 25°C and heating to 900°C in an atmosphere of N_2 (99.9%) with a constant flow of 30 ml/min.

Structural properties of grape stalks samples were determined according to the standard methods given in literature (lignin, cellulose and hemicelluloses) [16, 17]. The ash mass fraction of the raw material was determined by calcinations at 800°C in a crucible for 2 h.

The surface areas of the ACs were determined from the N_2 adsorption isotherms conducted in a volumetric apparatus (Micrometrics Tristar II 3020). Adsorbents were degassed at 300°C for 12 h prior to adsorption experiments. The Brunauer, Emmett and Teller (BET) surface area was determined by applying the BET equation to the adsorption data of N_2 at 77 K [18]. The pore size distribution of mesopores and micropores was calculated using the Barrett-Joyner-Hallenda and Horvath-Kawazoe methods [19, 20]. The total pore volume was evaluated from the amount adsorbed at a relative pressure of approximately 0.99. The elemental composition of samples (C, N, H and S) was analyzed by a PerkinElmer 2400 apparatus.

Fourier transform infrared spectroscopy (FTIR) was used to qualitatively evaluate the chemical structure of carbon materials. The IR spectra were collected using a Varian 640 FTIR spectrometer. The GAC samples were grounded into fine powder and mixed with KBr at a weight ratio of 700:1. About 200 mg of the mixture was used for the preparation of KBr pellets. The IR spectrum was obtained over a frequency between 500 and 4000/cm.

The types and amounts of surface functional groups that present in the AC samples were determined by the Boehm analysis [21]. The amounts of carboxylic, lactonic and phenolic groups were determined by neutralizing them with basic solutions having different base strengths such as, $NaHCO_3$, Na_2CO_3, NaOH, and C_2H_5ONa. The basic group content was determined by the method of titration with HCl. The point of zero charge (pH_{PZC}), defined as the pH at which the surface of the sorbent has a neutral charge, was determined using the methodology proposed by Herczynska (the "experiment of the 11 points") [22]. The morphology of the ACs was evaluated by Scanning Electron Microscopy (SEM) with a Hitachi TM3000 apparatus.

7.1.3. Results and discussion

Thermogravimetric analysis (TG-DTG) provides important information related to weight loss in the temperature range chosen for the production of ACs. TG and DTG curves of grape stalks were obtained at a heating rate of 10°C/min, and are presented in Figure 7.2.

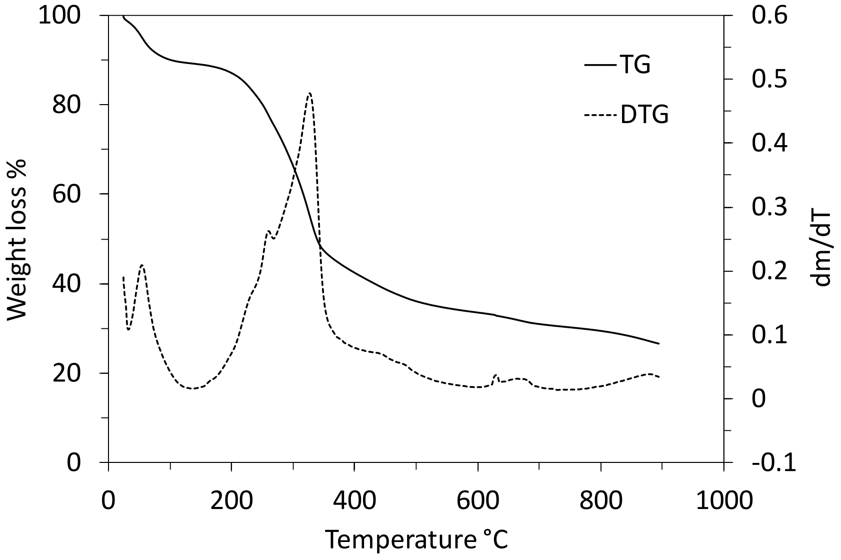

Figure 7.2. Diagram of the TG-DTG grape stalks (heating rate 10°C/min).

The TG curve, Figure 7.2, shows that the effective thermal decomposition starts around 200°C. A higher weight loss occurred in the temperature range between 240-340°C and 340-560°C (48%); mass loss rate was maximal interval between the first and the second bit lower range, respectively. The results show that, after 560°C, a slow loss of weight was identified, added to the final temperature. It is also observed that the grape stalks had three stages of carbonization of greater significance: the weight loss effect shown by the DTG curve below 130°C is attributed to the removal of water; The peak in the 35-130°C range can be attributed to the dehydration of grape stalks [23], where the weight loss was 10%; As the temperature was increased to the range of 130-360°C, decomposition of grape stalks DTG showed two peaks.

In the 130-260°C temperature range, the peak appears can be attributed to the pyrolysis of hemicellulose, with the weight loss of approximately 12%, whereas in the range 260-360°C, the peak may be attributed to the pyrolysis cellulose and lignin, where a weight loss of about 32% was found. The precursor’s higher content in cellulose in comparison to lignin, indicated by the thermogravimetric curve, is confirmed by the results obtained from the laboratory analysis of the precursor, which indicated cellulose and lignin contents of 34.30 and 18.61 wt%, respectively, as can be seen in Table 7.1.

Table 7.1. Characterisation of the precursors

Elemental analysis (wt%)	C	39.64
	H	5.74
	N	1.65
	S	<ld
	O[1]	46.63
Humidity (wt%)		13.25
Ash (wt%)		6.31
Lignin (wt%)		18.61
Cellulose (wt%)		34.30
Hemicellulose (wt%)[2]		47.09

<ld, below detection limit

[1] by difference 100 - (39.64 + 5.74 + 1.65 + 6.31)

[2] by difference 100 - (18.61 + 34.30)

These results are agreed with lignocellulosic materials characteristics reported by Zeriouh and Belbirl [24] (≈200°C for hemicellulose, ≈280°C for cellulose and ≈350°C for lignin). TG and DTG curves lines tend to form due to decomposition of lignin with increasing temperature. It is known that the decomposition of lignin is spread out over a wide temperature range and its peak decomposition cannot be determined [25]. However, it is believed that the long, flat tail is observed at elevated temperatures caused by the decomposition of lignin.

The yield on carbonization of grape stalks and subsequent activation carbon are shown in Figure 7.3.

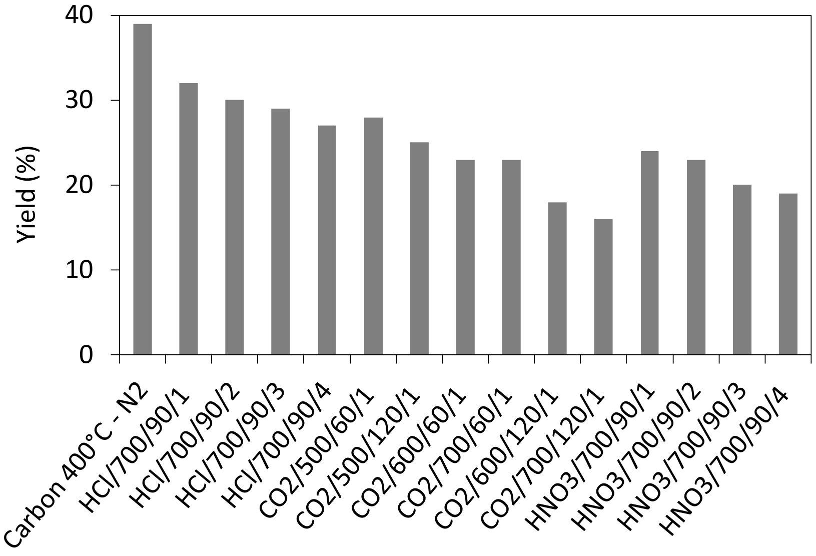

Figure 7.3. Percentage yield in pyrolysis and carbon activation.

It was observed that the AC yield depends on the temperature, time and activating agent. With increasing temperature, the chemical components of the volatile carbon are released, causing lower yields of AC. These results support the general idea that the increase in carbonization temperature decreases the amount of volatiles in the carbon unstable samples. The results are in agreement with the TG curve shown in Figure 7.2. Observing the different activating agents, it can be seen that CO_2 causes the greatest losses of AC compounds, followed by HNO_3 and then by HCl. The treatment with HNO_3 was generally used for oxidizing the porous surface of the carbon; which removed the mineral elements in each cycle, with a yield of 19% in the fourth cycle. Moreover HCl bit reacted with carbon surface, with yields above 26%, however, AC low surface area. The CO_2 to be a great power oxidant gas reaction with the carbon surface, AC presented with a yield of 15%.

The results of surface area BET analysis of the total pore volume, the volume of micropores and mesopores and elemental composition of AC are given in Table 7.2.

Results show that the carbon content does not increase with increasing BET area, or does not follow a pattern; however, for cases that show BET larger areas, the amount of carbon was greater than 80%. The hydrogen content was lower than the one of carbon in all cases, it was an expected trend. For nitrogen were obtained in most cases below the initial values, but for the third and fourth activation cycle of the AC HNO_3 introduced amount of nitrogen greater than the initial one. The AC of the elemental composition does not present a logical, because the material is quite heterogeneous and trigger different reactions to different production processes. Similar results were reported by other authors [26; 27].

Table 7.2. Textural and chemical characterisation of the activated carbons prepared with different activation agent.

Sample	BET A_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	Elemental composition (wt%) C	H	N
Precursor	0.22				39.64	5.74	1.65
Carbon 400°C - N_2	18				63.21	3.19	1.31
HCl/700/90/1	123	0.07	0.07	0.00	69.08	0.93	1.11
HCl/700/90/2	139	0.07	0.06	0.01	65.45	0.98	1.09
HCl/700/90/3	269	0.11	0.10	0.01	71.23	0.85	1.27
HCl/700/90/4	296	0.13	0.12	0.01	67.43	0.63	1.22
CO_2/500/60/1	311	0.14	0.14	0.00	73.12	1.45	1.51
CO_2/500/120/1	325	0.16	0.14	0.02	69.55	1.29	1.21
CO_2/600/60/1	360	0.17	0.16	0.01	69.43	0.64	0.84
CO_2/700/60/1	439	0.20	0.19	0.01	73.12	0.98	0.65
CO_2/600/120/1	472	0.22	0.21	0.01	81.05	0.93	0.78
CO_2/700/120/1	606	0.29	0.27	0.02	87.51	1.33	0.44
HNO_3/700/90/1	376	0.19	0.15	0.04	75.32	1.45	1.35
HNO_3/700/90/2	593	0.30	0.24	0.06	81.22	1.66	1.55
HNO_3/700/90/3	627	0.32	0.24	0.08	81.94	1.21	2.39
HNO_3/700/90/4	741	0.34	0.25	0.09	82.74	0.73	1.86

Note: Sample (activation agent/temperature/time/cycle)

Table 7.2 shows that the BET surface area and the pore volume increase with the number of cycles for HCl and HNO_3. It also grows with the increase of temperature and activation time for CO_2. The magnitude of increase of porosity is directly proportional to the magnitude of the increase of the BET area, possibly indicating that for higher number of cycles in the case of using HNO_3 and longer times for the use of CO_2 can be achieved result area BET greater. The improvement in porous structure with a decrease in the yield of AC (Figure 7.3) indicates an increase of the extent of reaction between the activation agent and carbon; the increased extension reaction allows for the creation of new pores in the carbon resulting in a higher surface area and pore volume.

Figure 7.4a shows the nitrogen adsorption isotherms for the activated carbons for CO_2/700/120/1, HNO_3/700/90/3 and HNO_3/700/90/4 whose BET area was 606, 627 and

741 m²/g respectively. According to the classification of the IUPAC, the isotherms have been type I-characterizing microporous activated carbon.

It is observed in Figure 7.4a that the activation HNO_3 has a greater slope of the adsorption curve, indicating that is a well-developed mesopore structure, compared to that of activated carbon with CO_2 curve. This corroborates with the results shown in Table 7.2, where the volume of larger mesopores HNO_3 for activation than for CO_2. From the micropore and mesopore volumes provided in Table 7.2, it can be inferred that the mesopores account for about 7% of the total pore volume for the AC CO_2/700/120/1 and 25 to 26% ACs HNO_3/700/90/3 and HNO_3/700/90/4.

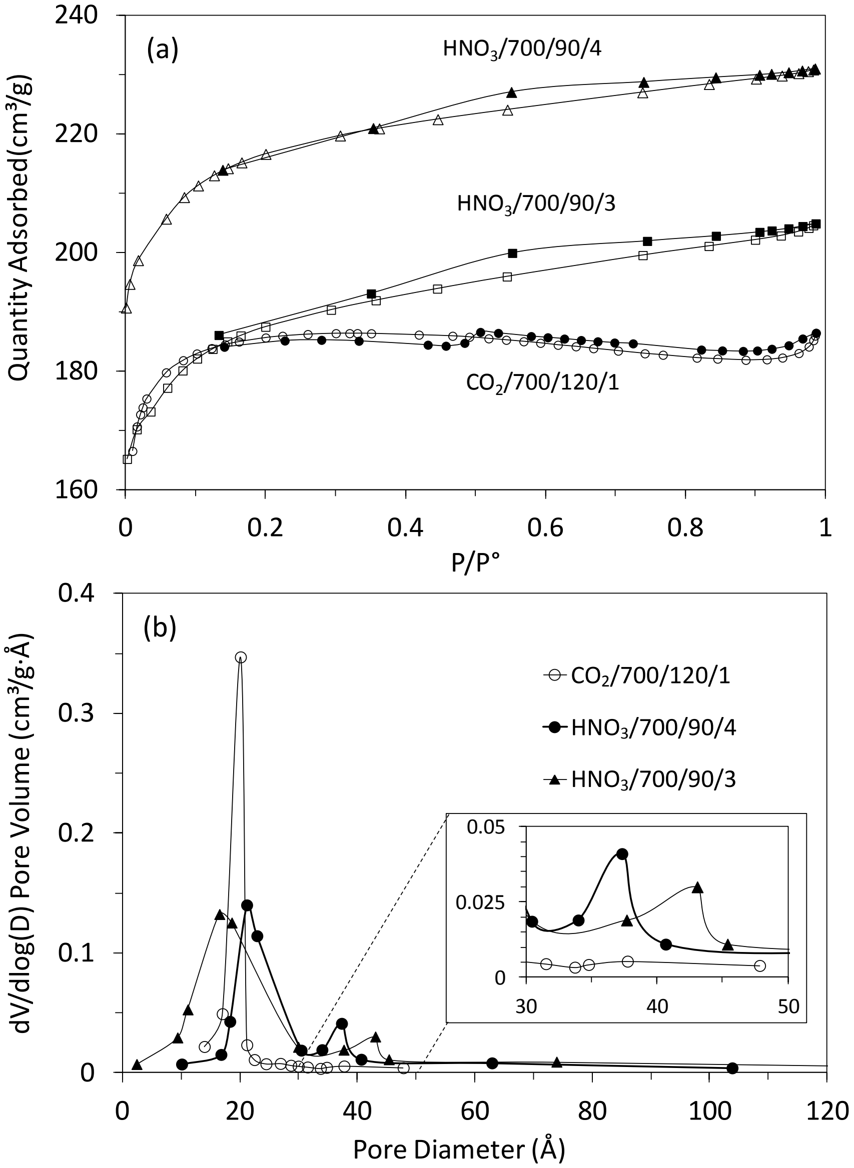

Figure 7.4. N_2 adsorption isotherms at 77K (a) and pore size distribution (b).

Figure 7.4b shows the distribution of AC of pore sizes prepared by activation with CO_2/700/120/1, HNO_3/700/90/3 and HNO_3/700/90/4. It is observed that the ACs have produced developed microporous structure, however, the expansion of Figure 7.4b between 30 and 50 Å, it is possible to see the presence of mesopores for ACs with HNO_3.

By activation performed with CO_2 the development of pores is mainly micropores (15-20 Å), this finding is confirmed by the volume of pores results shown in Table 7.2. When activation is accomplished with CO_2 the micropore volume is greater than 93% in all cases; Furthermore, when comparing the three cases shown in Figure 7.4b, the micropore volume for activation with CO_2 is higher. The expansion of Figure 7.4b (30-50 Å) can be seen that for activations using HNO_3 appear the development of mesopores, although in small amounts. This difference in the development in the pores of the carbon activation process can be explained by differences between the reactants; CO_2 in gas form and in the form of HNO_3 aqueous solution react differently on the surface of carbon because of its different molecular configuration. Thus, the resulting pattern of pore structures can be influenced.

There are usually four stages in the pore development during the activation process: (i) opening of previously inaccessibly pores; (ii) creation of new pores by selective activation; (iii) widening of the existing pores and (iv) merger of the existing pores due to pore wall breakage [28].

A comparison of AC isotherms (Figure 7.4a) shows that activation using HNO_3 produces a higher nitrogen adsorption capacity in relation to the activation using CO_2. It should however be noted that with a higher CO_2 microporosity is produced. The increased microporosity using CO_2 could be due to the higher reactivity of the gas expands and generates micropores at a faster pace due to the facilitated diffusion of CO_2 into the inner parts of the carbon contributing to the further development of micropores. On the other hand, the CO_2 more aggressively attacks the surface of the carbon causing a lower yield of the final AC.

Although the identification of all the chemical species on the surface of an AC is not an easy task; However, the information about the chemical nature of the carbon surface can be obtained using infrared spectroscopy Fourier transform (FTIR). FTIR analysis of the AC results are shown in Figure 7.5. The spectra for the three runs were very similar, showing essentially the same major peaks, though to different extents, indicating that the quantitative amounts of functional groups on the surface of activated carbons are different.

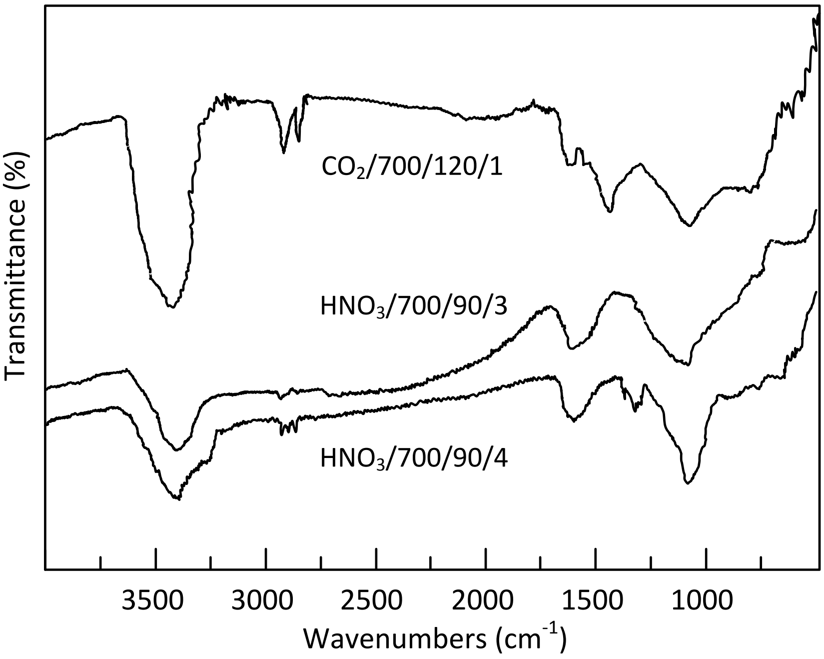

Figure 7.5. Representative FTIR spectra for samples CO_2/700/120/1, HNO_3/700/90/3 e HNO_3/700/90/4.

The broad band extended between 900 and 1300 cm^{-1} is assigned to both –C–O stretching and –O–H bending modes of alcoholic, phenolic and carboxylic groups. Likewise, bands in the vicinity of 1350 cm^{-1} are ascribable to O—H and C=O vibrations [29]. Around 1420 cm^{-1} appears a band ascribable to aromatic C=C stretching mode. The band in the 1620 and 1750 cm^{-1} region is associated with C=O stretching mode in carbonyls and lactones [30]. The band at around 3430 cm^{-1} can be assigned to the O - H stretching vibration mode of hydroxyl functional groups, while the band at around 2920 cm^{-1} can be assigned to the C–H symmetric and asymmetric vibration mode of methyl and methylene groups [31].

Therefore, it can be concluded that the kinds of surface functional groups are indifferent to the activation method and also to the activation conditions in this work.

The pH_{PZC} and the types and amounts of surface functional groups that present in the activated carbon samples were determined by the Boehm analysis and the results were given in Table 7.3.

Table 7.3. The Boehm analysis results of activated carbons (meq/g).

Samples	Acidic surface functional groups			Total acid	Basic surface functional groups	pH_{PZC}
	Carboxyl	Lactonic	Phenolic			
Carbon 400°C - N_2	0.05	0.13	0.10	0.28	0.05	7.6
CO_2/700/120/1	0.35	0.15	0.17	0.67	0.50	7.8
HNO_3/700/90/3	0.64	0.09	0.24	0.97	0.32	5.5
HNO_3/700/90/4	0.81	0.11	0.19	1.11	0.28	5.2

The activation promoted by HNO_3 and CO_2 was generally used to react with the porous carbon surface; it enhanced the number of property removed the mineral elements and improved the surface hydrophilic. Nitric acid activation produced ACs with $ph_{PZC} < 7.6$ (pH_{PZC} Carbon) and treatment with CO_2 this value was higher than the pH_{PZC} carbon. The treatment with nitric acid caused the introduction of a significant number of oxygenated acidic surface groups onto the carbon surface, while the CO_2 treatment increases the basicity of carbon. Similar results were found by Shim *et al.*, Liu *et al.* e Wibowo *et al.* [32, 33, 34]. Usually the Surface chemistry of carbon materials is determined by the acidity and basicity of their surface.

The microstructure of the ACs produced from grape stalks is very interesting, as can be seen in Figure 6. The SEM images of sample HNO_3/700/90/4, used as example, show the preservation of the precursor shape after the activation. The final carbon sample is, at macroscopic scale, comparable with a small rod or cylinder with external surface shown in Figure 7.6.

The ACs outer surface exhibits smooth and homogenous texture resulting from the carbonization of the tissue of the coat of the grape stalks, with no relevant presence of cracks and large macropores, showing that the structure of the outer surface was preserved in the carbon after pyrolysis. Depending on the applications of the carbon, the outer layer can be an undesirable resistance for the diffusion of molecules, or can be potentially a barrier for separation. On the contrary, the inner layers exposed by the opening of the outer layers of the coat showed a well-developed network of channels and macropores that can provide favorable conditions for diffusion.

In conclusion, not only the macroscopic aspect is maintained but also the interior part of the precursor is directly transformed from the grape stalks to the AC. The fibrous structure of the final material gives more flexibility as it can be confined and used in various forms, such as tows, fabrics and felts, which can be very useful in a number of industrial and environmental applications.

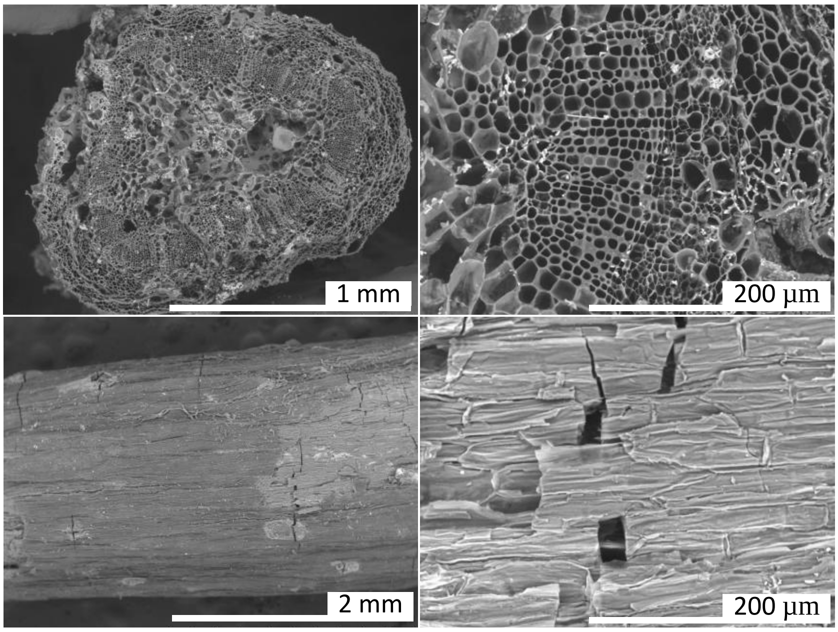

Figure 7.6. Representative SEM micrographs of sample HNO_3/700/90/4.

7.1.4. Conclusions

The results revealed that the grape stalks are an attractive source for synthesis of activated carbon. The results obtained allow us to conclude that grape stalks have an interesting potential for the production of activated carbons using carbon dioxide and nitric acid as activation agent.

The pyrolysis process showed a great effect on the final product, and careful selection of carbonization conditions significantly affect to the porous structure of the resulting carbons.

It was clearly observed from the SEM images that the granular structure was maintained along the activation process independently of the oxidizing agent used. Also, SEM images have shown the presence of nanofibers on the interior structure of the carbons, which have origin on the precursor structure. The ACs produced in the work now reported have interesting microstructural, chemical and textural properties with the advantage of being produced in the fibrous form, which opens the door to a wide range of possibilities for their application.

The porosity of the produced ACs is mainly composed of micropores with BET apparent surface area and pore volume up to 741 m^2/g and 0.34 cm^3/g, respectively. The activated carbons have basic characteristics to CO_2 activation ($pH_{PZC} = 7.6$); and acid characteristics to HNO_3 activation (pH_{PZC} between 5.2-5.5).

References

[1] O. Zanella, I.C. Tessaro, L.A. Féris, Desorption and Decomposition - Based Techniques for the Regeneration of Activated Carbon , Chem. Eng. Technol., 37(9), (2014) 1447–1459.

[2] R. Arriagada, R. Garcia, M. Molina-Sabio, F. Rodriguez-Reinoso, Effect of steam activation on the porosity and chemical nature of activated carbons from Eucalyptus globules and peach stones, Microp. Mat., 8, (1997) 123-130.

[3] A.F. Martins, A.L. Cardoso, J.A. Stahl, J. Diniz, Low temperature conversion of rice husks, eucalyptus sawdust and peach stones for the production of carbon-like adsorbent, Biores. Technol., 98, (2007) 1095-1100.

[4] T. Zhang, W. Walawender, L.T. Fan, M. Fan, D. Daugaard, R.C. Brown, Preparation of activated carbon from forest and agricultural residues through CO_2 activation, Chem. Eng. J., 105, (2004) 105 53-59.

[5] M.L. Martinez, M.M. Torres, C.A. Guzman, D.M. Maestri, Preparation and characteristics of activated carbon from olive stones and walnut shells, Ind, Crops Prod., 23, (2006) 23-28.

[6] M. Molina-Sabio, F. Rodriguez-Reinoso, Role of chemical activation in the development of carbon porosity, Coll. Surf. A: Physicoch. Eng. Aspects, 241 (2004) 15-25.

[7] N. Spahis, A. Addoun, H. Mahmoudi, N. Ghaffour, Purification of water by activated carbon prepared from olive stones, Desalination, 222, (2008) 519-527.

[8] A.A. Attia, B.S. Girgis, N.A. Fathy, Removal of methylene blue by carbons derived from peach stones by H3PO4 activation: Batch and column studies, Dyes and Pigments, 76, (2008) 282-289.

[9] P. Galiatsatou, M. Metaxas, V. Kasselouri-Rigopoulou, Adsorption of zinc by activated carbons prepared from solvent extracted olive pulp, J. Hazar. Mat., 91, (2002) 187-203.

[10] P. Vazquez, L. Pizzion, M. Blanco, C. Caceres, H. Thomas, R. Arraigada, S. Bendezu, R. Cid, R. Garcia, NDMO(W)-based hydrotreatment catalysts supported on peach stones activated carbon, App. Catal. A: General, 184, (1999) 303-313.

[11] V. Boonamnuayvitaya, S. Sae-ung, W. Tanthepanichakoon, Preparation of activated carbons from coffee residue for adsorption of formaldhyde Sep. Purif. Technol., 42, (2005) 159-168.

[12] J. González, J. Encinar, J. Canito, E. Sabio, M. Chacón, Pyrolysis of cherry stones: energy uses of the different fractions and kinetic study, J. Anal. Appl. Pyrol., 67, (2003) 165–190

[13] A.R. Reed, P.T. Williams, Thermal processing of biomass natural fiber wastes by pyrolysis, Int. J. Energy Res., 28, (2004) 131–145.

[14] W. Daud, W. Ali, Comparison on pore development of activated carbon produced from palm shell and coconut shell, Bioresour. Technol., 93, (2004) 63–69.

[15] W. Daud, W. Ali, M. Sulaiman, Effect of carbonization temperature on the yield and porosity of char produced from palm shell, J. Chem. Technol. Biotechnol., 76, (2001) 1281–1285.

[16] V.P.J. Soest, Use of detergents in the analysis of fibrous feeds. 2. A rapid method for the determination of fiber and lignin, Journal of A.O.A.C, 46(5), (1963) 829-835.

[17] V.P.J. Soest, R.H. Wine, Use of detergents in the analysis of fibrous feeds. 4. Determination of plant cell wall constituents, Journal of A.O.A.C, 50, (1967) 50-55.

[18] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of Gases in Multimolecular Layers, Journal of the American Chemical Society, 60, (1938)309-319.

[19] G. HorvÁTh, K. Kawazoe, Method for the calculation of effective pore size distribution in molecular sieve carbon, Journal of Chemical Engineering of Japan, 16, (1983) 470-475.

[20] E.P. Barrett, L.G. Joyner, P.P. Halenda, The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms, Journal of the American Chemical Society, 73, (1951)373-380.

[21] H.P. Boehm, Chemical identification of surface groups, Adv. Catal., 1, (1966) 179–274.

[22] E. Herczynska, Adsorption isotherms of potential determining ions, Journal of Inorganic and Nuclear Chemistry, 26, (1964) 2127-2133.

[23] O. Paris, C. Zollfrank, G.A. Zickler, Decomposition and carbonization of wood biopolymers—a microstructure study of softwood pyrolysis, Carbon, 43, (2005) 53–66.

[24] A. Zeriouh, L. Belbirl, Thermal decomposition of a Moroccan wood under a nitrogen atmosphere, Thermochim. Acta, 258, (1995) 243–248.

[25] M. Müller-Hagedorn, H. Bockhorn, L. Krebs, U. Müller, A comparative kinetic study on the pyrolysis of three different wood species, J. Anal. Appl. Pyrol., 68–69, (2003) 231–249.

[26] D. Jimenez-Cordero, F. Heras, N. Alonso-Morales, M.A. Gilarranz, J.J. Rodrigue, Porous structure and morphology of granular chars from flash and conventional pyrolysis of grape seeds, Biomass and bioenergy, 54, (2013) 123 – 132.

[27] J.M.V. Nabais, C. Laginhas, M.M.L.R. Carrott, P.J.M. Carrott, J.E.C. Amorós, A.V.N. Gisbert, Surface and porous characterisation of activated carbons made from a novel biomass precursor the esparto grass, Applied Surface Science, 265, (2013) 919–924.

[28] F. Rodríguez-Reinoso, In: Fundamental Issues in Control of Carbon Gasification Reactivity, Kluwer Academic, Netherlands, (1991) 533–571.

[29] P.M. Álvarez, J.F. García-Araya, F.J. Beltrán, F.J. Masa, F. Medina, Ozonation of activated carbons: effect on the adsorption of selected phenolic compounds from aqueous solutions, Journal of Colloid and Interface Science, 283, (2005) 503–512.

[30] D. Monah, K.P. Sinqh, V.K. Sinqh, Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth, Ind Eng Chem Res, 44, (2005) 1027–1042.

[31] K. Nakanishi, Infra-red Absorption Spectroscopy-Practical, Holden-Day, San Francisco CA (1962) 17–57.

[32] J.W. Shim, S.J. Park, S.K. Ryu, Effect of modification with hno3 and naoh on metal adsorption by pitch-based activated carbon fibers, Carbon, 39, (2001) 1635-1642.

[33] S.X. Liu, X. Chen, X.Y. Chen, Z.F. Liu, H.L. Wang, Activated carbon with excellent Chromium (VI) adsorption performance prepared by acid-base surface modification, J. Hazard. Mater., 141, (2007) 315-319.

[34] N. Wibowo, L. Setyadhi, D. Wibowo, J. Setiawan, S. Ismadji, Adsorption of benzene and toluene from aqueous solutions onto activated carbon and its acid and heat treated forms: influence of surface chemistry on adsorption, J. Hazard. Mater., 146,(2007) 237-242.

CAPÍTULO 8

Artigo: Electrochemical regeneration of activated carbons obtained from grape stalks and saturated with phenol

Neste capítulo, é apresentado o estudo da capacidade de adsorção para fenol relativo aos carvões ativados desenvolvidos a partir de engaço de uva e a aplicação destes carvões carregados na regeneração eletroquímica em sucessivos ciclos adsorção/regeneração. Foram investigadas as capacidades de adsorção e readsorção para os carvões desenvolvidos em comparação com carvão ativado comercial. Os resultados são apresentados e discutidos em função da capacidade de adsorção (eficiência de regeneração) e das características de superfície dos cavões ativados produzidos, para análises de área de superfície BET, grupos funcionais de superfície e estrutura porosa.

8.1. Artigo: Electrochemical regeneration of activated carbons obtained from grape stalks and saturated with phenol

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Abstract: An electrochemical reactor was used to investigate the effectiveness of regeneration of activated carbon saturated with phenol, and made from grape stalks. In the study we also used a commercial activated carbon for comparison of results. The electrochemical reactor operated under optimum operating conditions, voltage 12 v, cathodic regeneration, NaCl as electrolyte, 1.6 A current and 120 minutes was the regeneration time. The regeneration process modifies the surface functional group of activated carbons and provides significant variation in phenol resorption, especially in the range of carboxyl groups and basic groups that directly affect the adsorption capacity for phenol. These variations involve weakening the dispersion forces, which reduces adsorption. On the other hand, involves increasing the electrostatic force and this leads to an increase in adsorption. For the adsorption of phenol, it is suggested that the absence of basic functional groups of the surface and the presence of carboxyl groups are predominant factors which prevent adsorption. The electrochemical regeneration process provided an increase of basic groups and reduction of carboxyl groups for 3 activated carbons, resulting in increased adsorption capacity, but the regeneration causes the loss of mass of the activated carbon causing the reduction of adsorption.

Keywords: regeneration; electrochemical; grape stalks; activated carbon.

8.1.1. Introduction

Activated carbon (AC) has an extraordinarily large surface area and pore volume, making it suitable for a wide range of applications. Are widely used as adsorbents in wastewater treatment, can be used as a decolorizing agent, a taste and odor removing agent or as a purification agent in food processing, in the industrial area, the most common applications of activated carbon are for process off-gases, tank vent emissions, work area air purification, and odor control, either within the plant or related to plant exhausts. Additionally, activated carbon is used in the hazardous waste remediation area to treat off-gases from air strippers and from soil vapor extraction remediation projects. The hundreds of other uses include its utilization as an adsorbent in gas mask filters and as pollution control material in a range of filters [1].

Commercially available activated carbons remain limited due to the high cost resulting from the use of non-renewable and expensive starting materials, such as coal. However, researchers are attempting to produce cheaper, more effective and environmentally friendly activated carbons. Recently, low-cost precursors have become the focus of researchers worldwide (for example, precursors from wastes and agricultural by-products, such as olive fruit stones [2], orange peels [3], rice husks [4], and many others).

Moreover, the possibility of using an AC in successive adsorption–regeneration cycles is essential from the economic point of view. In general, the most attractive option is given by a compromise situation considering both the regeneration efficiency and the number of uses for which the degree of porosity recovery is considered acceptable.

There are several established methods for the regeneration of activated carbon (RE) saturated with different adsorbent. Shende and Mahajani [5] studied the wet oxidative regeneration of activated carbon loaded with dyes, Weng and Hsu [6] investigated an electrochemical process applied to the regeneration of activated carbon saturated from a sewage wastewater while Tan and Lee [7] evaluated the efficiency of supercritical CO_2 desorption in fixed bed of activated carbon saturated with toluene. Similarly, Sabio and colleagues [8] used three techniques of thermal regeneration: pyrolysis, gasification pyrolysis and gasification directly, using activated carbon saturated with *p*-nitrophenol. Cooney and colleagues [9] evaluated nineteen solvents in batch process that involves desorption of organic adsorbate (phenol) from activated carbon. Liu, Yu and Han [10] studied the regeneration by microwave irradiation of activated carbon saturated with 2,4,5-triclorobiphenyl (PCB29). Coelho and colleagues [11] studied the effect of chemical and structural properties of the surface of activated carbon in sorption process of molinate in aqueous solutions with subsequent bioregeneration using bacterial cultures. Drouiche and colleagues [12] also developed a treatment method for regenerating activated carbon saturated with H_2S using electrodialysis equipped with cationic, anionic and a bipolar membrane.

Each of the regeneration techniques has its respective characteristics and application area. However, cost is the limiting factor for the application of these methods.

Most recently, an alternative, electrochemical (EC), method was shown to be an effective approach to regenerate AC, by which the RE could achieve as high as 70–100%. This method can be operated in situ and has not only the advantage of oxidize organic contaminants in the anode, but it also allows recovering activated adsorbing site of exhausted AC [1].

Electrochemical regeneration refers to the regeneration of a saturated adsorbent placed within an electrolytic cell containing an electrolyte solution to which a given potential current is applied. The mechanism of electrochemical regeneration involves the electrodesorption and/or destruction of organic contaminants adsorbed on the activated carbon to restore the capacity of the adsorbent. According to Garcia-Otón [60], the electrochemical method is more effective for the regeneration of activated carbon compared to thermal regeneration because it hardly modifies the pore structure of the material. Therefore, electrochemical technology can increase the adsorption capacity of the activated carbon and regenerate loaded activated carbon [1].

In this study, experiments were conducted to examine the effectiveness of using an electrochemical regeneration in the recovery process based on the adsorption capacity of four different activated carbons.

This study, regeneration factors were applied in parallel studies developed, namely, the reactor was operated according to results obtained in other studies of this research group in which it was concluded that these factors maximize the regenerative capacity of the reactor. The main objective was to evaluate the regeneration capacity for different activated carbons related to the electrochemical reactor in standard operation, analyzing the behavior and the adsorption capacity of activated carbons in successive cycles of adsorption / electrochemical regeneration. It is expected that the results of this study can provide useful information for the development of electrochemical regeneration applied on a large scale.

8.1.2. Materials and methods

8.1.2.1. Specifications of the reagents and adsorbents

For this work we used four different activated carbons: a commercial activated carbon (D), and three activated carbons developed in previous work carried out by the same research group. The carbons were made from grape stalks pyrolysis at 400°C in inert atmosphere and activated in different ways. Activated carbon by oxidation with CO_2 at 700°C for 120 min (C); activated carbon with HNO_3 at 700°C for 90 min, held for 3 cycles (B); and activated carbon with HNO_3 at 700°C for 90 min was carried out in four cycles (A). The cycle comprises oxidation with HNO_3 performed by boiling under reflux, for 20 min and subsequent pyrolysis in an inert atmosphere (N_2) for 90 min at 700°C. Phenol was used as adsorbate and for regeneration it was used an electrochemical reactor developed and characterized in previous studies by the same research group. Table 8.1 shows the main characteristics of coals used in this study. These data are part of the research group database.

Table 8.1. Characteristics of activated carbons in the early studies (taken data from earlier studies carried out in this research group).

Sample	A	B	C	D
BET - A_{BET}(m^2/g)	741	627	606	765
V_{tot} - (cm^3/g)	0.34	0.32	0.29	0.37
V_{micro} - (cm^3/g)	0.25	0.24	0.27	0.29
Carbon	82.74	81.94	87.51	89.84
Hidrogen	0.73	1.21	1.33	0.68
Nitrogen	1.86	2.39	0.44	1.28
pH_{PZC}	5.2	5.5	7.8	7.6
Acidic groups (meq/g)				
Carboxyl	0.81	0.64	0.35	0.10
Lactonic	0.11	0.09	0.15	0.38
Phenolic	0.19	0.24	0.17	0.43
Total acid	1.11	0.97	0.67	0.91
Basic groups (meq/g)	0.28	0.32	0.50	0.05

Note: A_{BET} - surface area BET; V_{tot} - total pore volume; V_{micro} - micropore volume

8.1.2.2. Tests for adsorption and regeneration

Phenol solutions were used with a concentration of 20 to 2500 mg/L, 1 g of activated carbon for 200 ml of solution, adsorption time of 24 hours, 20°C and pH 6.5 (adsorption these conditions showed the best results in previous studies). The phenol solution at the required concentration was packed in 200 ml bottles and placed in a shaker device staying at a specified time. At the end of the process, the suspension is filtered, and thus separated aliquots which were subjected to determination of the concentration. With the initial concentration and final concentration of phenol in the process it was possible to calculate the phenol concentration on the surface of the adsorbent by Equation 8.1.

$$q_e = \frac{(C_i - C_e)}{M_s}.V \tag{8.1}$$

where q_e represents the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g), C_i is the initial sorbate concentration (mg/L), C_e is the equilibrium concentration (mg/L), V is the volume of the solution (L), and M_s is the mass of sorbent (g).

After the adsorption step, carbon was washed with 25 mL of distilled water and subjected to the regeneration process. Saturated with activated carbon was carried out the electrochemical regeneration step where it was used to regenerate a reactor designed 1 g solid. The electrochemical reactor, characterized in previous studies, was performed by the group, where the best regeneration results for recovery efficiency and porosity were obtained by cathodic regeneration current of 1.6 A, electrolyte NaCl 3% (w/w), and time 120 min. The voltage used in the study was 12 v. Under these conditions, the regeneration percentage was above 100%. Based on these results we carried out the regeneration process in all cases these conditions. Figure 8.1 illustrates the regeneration process specifying the key of the regeneration process.

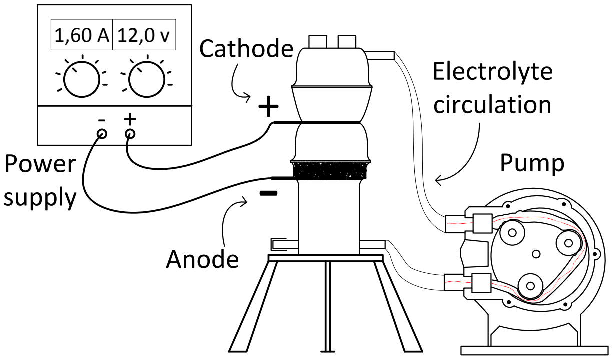

Figure 8.1. Illustration of the electrochemical regeneration process.

With the regenerated activated carbon, started another adsorption step in which the end there was obtained the accumulation of the first cycle. Thus, it was possible to determine the percentage efficiency of the regeneration process according to Equation 8.2. This process was performed by consecutive cycles.

$$Efficiency\ (\%) = \frac{q_e\ in\ the\ test}{\left(q_e\ initial\!\!\left/_{100}\right.\right)} \tag{8.2}$$

The model of Langmuir isotherm [13] was used to calculate the maximum adsorption capacity for each regeneration cycle. The Langmuir mathematical model is shown in Equation 8.3.

$$q_e = \frac{q_{max}\,.\,K_L.\,C_e}{1 + K_L.\,C_e} \tag{8.3}$$

where q_e is the equilibrium amount adsorbed (mg/g), q_{max} is the maximum adsorption capacity (mg/g), K_L is the constant of adsorption (L/mg), and C_e is the solute concentration in equilibrium (mg/L).

8.1.2.3. Characterisation

The surface areas of the ACs were determined from the N_2 adsorption isotherms conducted in a volumetric apparatus (Micrometrics Tristar II 3020). Adsorbents were degassed at 300°C for 12 h prior to adsorption experiments. The Brunauer, Emmett and Teller (BET) surface area was determined by applying the BET equation to the adsorption data of N_2 at 77 K [14]. The pore size distribution of mesopores and micropores was calculated using the Barrett-Joyner-Hallenda and Horvath-Kawazoe methods [15, 16]. The total pore volume was evaluated from the amount adsorbed at a relative pressure of approximately 0.99. The elemental composition of samples (C, N and H) was analyzed by a PerkinElmer 2400 apparatus.

The types and amounts of surface functional groups that present in the AC samples were determined by the Boehm analysis [17]. The amounts of carboxylic, lactonic and phenolic groups were determined by neutralizing them with basic solutions having different base strengths such as, $NaHCO_3$, Na_2CO_3, NaOH, and C_2H_5ONa. The basic group content was determined by the method of titration with HCl.

8.1.3. Results

The results of this study show a evaluation of phenol adsorption on activated carbon, regenerated in an electrochemical reactor, developed and characterized in previous studies by the same research group. The assessment in the adsorption process enables understanding of the regeneration step regarding factors that directly affect the adsorption capacity. Accordingly, Figure 8.2 shows the experimental adsorption isotherms and in Table 8.2 it can be seen the maximum adsorption capacity and determination coefficients obtained by applying the Langmuir isotherm model.

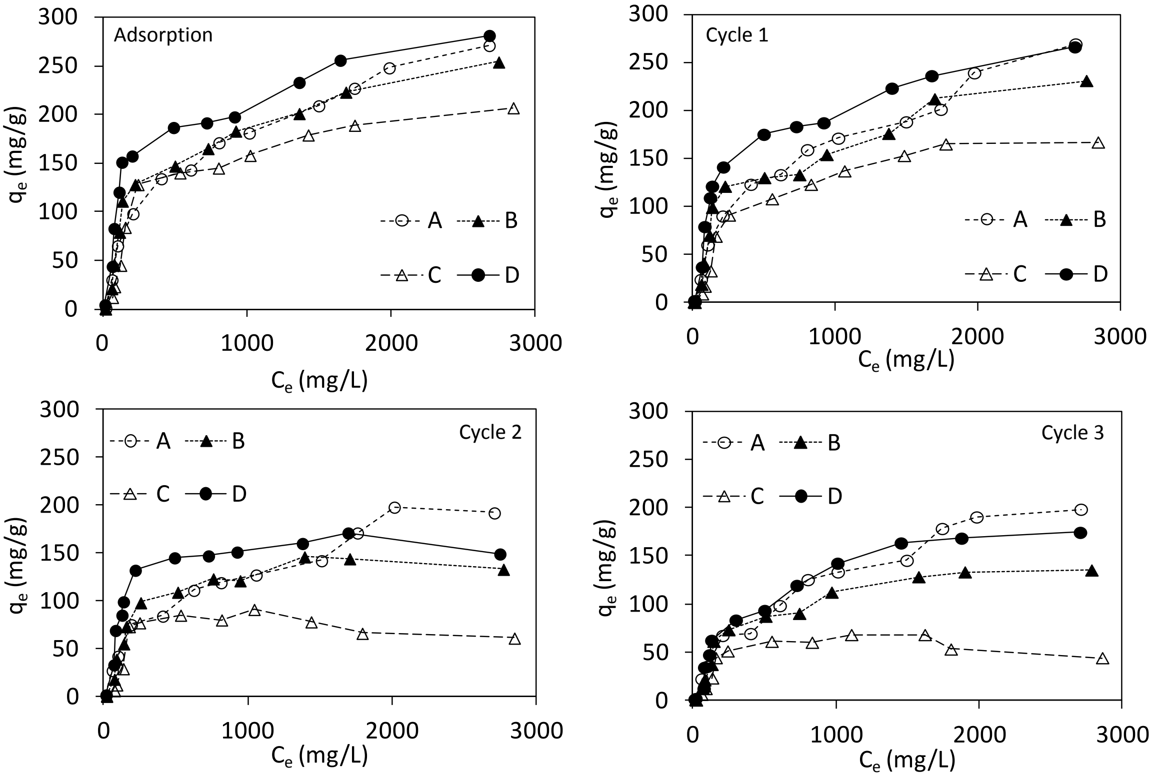

Figure 8.2. Isotherms of adsorption and resorption for electrochemical regeneration cycles.

Figure 8.2 shows the effects of electrochemical regeneration of the phenol adsorption performance (experimental isotherms) the different types of activated carbon for the initial and subsequent adsorption cycles. The electrochemical regeneration considerably influences the adsorption capacity recovery for the four types of coal. It is observed that carbon that was activated with CO_2 (C) was reduced by approximately 65% of its initial adsorption capacity over the cycles. The commercial activated carbon (D) initially had the highest adsorption capacity for the study range of experimental isotherms. However, analyzing the results of the Langmuir model for maximum adsorption capacity, seen in Table 8.2, we find that, even with lower adsorption capacity in the concentration range studied in Figure 2, the activated carbon A, showed higher maximum capacity of in all adsorption cycles. For the four types of activated carbon, the cycle 2 showed the lowest adsorption rates, which in the next cycle were recovered except for the activated carbon C. The reduction of the adsorption capacity along the isotherm cycle 2 (Figure 8.2), lead to non-convergence of the model thus in Table 8.2, the maximum adsorption capacity was represented by the experimental capacity. It is observed in Table 8.2 that the coefficient of determination was higher than 0.90, for cases that the converged model, demonstrating a good fit and reliable results.

Table 8.2. Maximum capacity of absorption and coefficient of determination obtained from the Langmuir isotherm model.

Sample	Adsorption		Cycle 1		Cycle 2		Cycle 3	
	$q_{e.max}$ (mg/g)	R^2	$q_{e.max}$ (mg/g)	R^2	q_e (mg/g)	R^2	$q_{e.max}$ (mg/g)	R^2
A	329	0.99	328	0.98	198*	x	304	0.98
B	294	0.95	303	0.92	146*	x	149	0.96
C	190	0.95	173	0.96	91*	x	68*	x
D	298	0.92	283	0.95	171*	x	218	0.97

* q_e experimentally determined (the isotherm model did not converge)

$q_{e.max}$ maximum adsorption capacity: Langmuir isotherm

Eleven investigated successive cycles of adsorption/regeneration electrochemical phenol concentration of 2000 mg/L in the adsorption step. This concentration was chosen because it has greater stability in the adsorption, i.e., it was possible to perform various tests on adsorption accuracy above 97%. Another reason for choosing this concentration was that the reactor used to regenerate the carbon was characterized and optimized at this concentration.

Figure 8.3 presents the data for the electrochemical regeneration efficiency percentage based on the initial adsorption capacity of activated carbon, and the adsorption capacity after each regeneration step, thereby covering all cycles. The percentage calculations were determined by Equation 8.2.

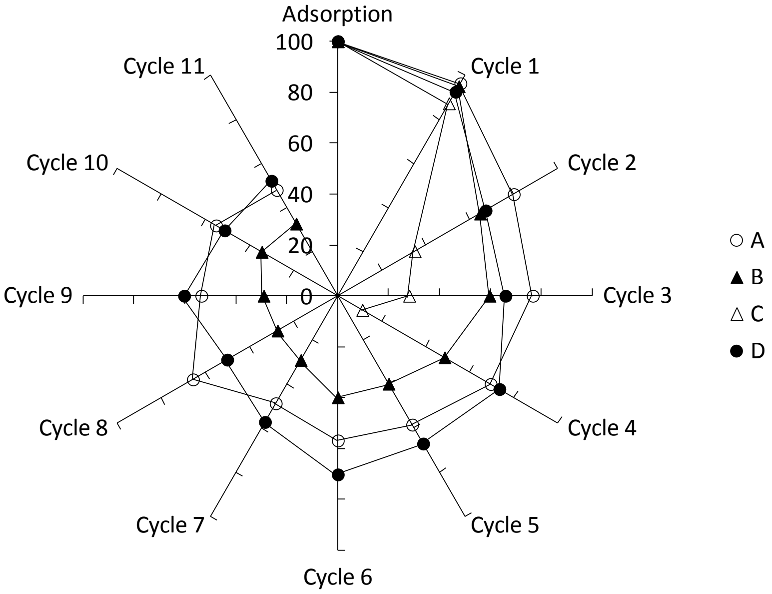

Figure 8.3. Regeneration percentage efficiency for 11 cycles of adsorption/electrochemical regeneration. Whereas the initial adsorption at 100% efficiency.

Considering the adsorption percentage of 100%; adsorption to the first, i.e., before the first regeneration cycle, can be seen from Figure 8.3 that for the four carbons studied the efficiency decreases over cycles. For activated carbon C 4 cycles were performed only after the fourth cycle efficiency was less than 10%, while that from the second cycle efficiency was below 40%. Carbon B from the cycle 4 showed less than 50% efficiency, and cycle 11, its efficiency was less than 30%. The A and D carbons performed better compared to carbon B and C, therefore, still needs improvement in the recovery process because it is believed that the reduction in adsorption capacity is the result of low turnover rate. Even operating the electrochemical reactor at its optimum capacity, with the controlling factors in synergy, the results shown not performed well.

Table 8.3 shows the characteristics of activated carbons (A, B, C and D) after 11 cycles of adsorption/regeneration. These results are compared with those presented in Table 8.1. It can be seen from this table that the area BET values as well as the total pore volume and micropore volume percent and the carbon to four carbons studied decreased. Hydrogen percentage increased to four carbons and nitrogen percentage decreased to carbon A and increased to B, C and D. The carbon C decreased the basic groups and the acidic groups increased, while the carbons A, B and D increased the basic groups and decreased the acid groups.

Table 8.3. Characteristics of the activated carbons after 11 regeneration cycles.

Sample	A	B	C	D
BET - $A_{BET}(m^2/g)$	544	417	109	524
V_{tot} - (cm^3/g)	0.26	0.18	0.11	0.24
V_{micro} - (cm^3/g)	0.13	0.09	0.05	0.16
Carbon	77.23	69.12	61.19	73.21
Hidrogen	2.61	2.15	1.97	2.23
Nitrogen	1.11	2.76	3.66	2.61
Acidic groups (meq/g)				
Carboxyl	0.21	0.39	0.29	0.14
Lactonic	0.09	0.11	0.17	0.21
Phenolic	0.13	0.11	0.23	0.29
Total acid	0.43	0.61	0.69	0.64
Basic groups (meq/g)	0.44	0.38	0.13	0.17

Note: A_{BET} - surface area BET; V_{tot} - total pore volume; V_{micro} - micropore volume

8.1.4. Discussion

Despite many studies on phenol adsorption on activated carbon, still there is a lot to investigate, for this reason, there is a longstanding debate and conflicting results in the literature. Despite this, three adsorption routes are widely accepted and investigated in several studies: the electron donor–acceptor interaction, dispersive interaction of π-π electron coupling and competing adsorption of solvent molecules [18].

Two different ways of electron donor–acceptor interaction were occurred. One involves the interaction of carbonyl groups (electron donor) of AC with aromatic ring (electron acceptor) of phenol while the other one involves the interaction between basic sites of AC (electron donor) and aromatic ring (electron acceptor) of phenol [18, 19]. The strength of donor–acceptor interaction depends mainly the dipole moment of the oxygen groups on basal plane. Carbonyl groups on the carbon surface are known as strong donors because of their high dipole moments. Taking into account of suggested electron donor–

acceptor interactions, it is acceptable that increase in the carbonyl and basic functional groups shows promoting effect of phenol adsorption.

The results show that an increase in the basic groups indicating increased absorption, but experimentally one observes a decrease in the adsorption capacity, seen in Figure 8.3. This reduction is related to the performance of the regeneration process, which was not effective in recovering the adsorption capacity, or even caused the loss of surface area and pore volume of the activated carbon.

The electron acceptor capacity of carbon surface would reduce upon oxidation of carbonyl groups to carboxyl groups, possibly related to the electrochemical regeneration process. Increased amount of carboxylic groups supports transformation of carbonyls to carboxylics [20]. From the Boehm titration results (activated carbon C), the decreased total basic groups cause less phenol adsorption. As mentioned earlier, dispersion interaction is related with the π electron of aromatic ring of phenol and delocalised π electron of basal plane of the AC. Chemisorbed oxygen removes electrons from π band of the AC and lead to weakening of the dispersion forces between phenol and AC. The decrease of basic groups indicates increased oxygen content of the AC that is responsible for the weaker dispersion correspondingly lower phenol adsorption interaction.

The adsorption of water molecules to active sites of the AC is regarded as a major factor which hinders the adsorption of phenol. Competitive adsorption between water and phenol molecules occurs in overall adsorption process due to the affinity of water molecules to the surface oxygen complexes; particularly the carboxylic groups. Molecular diameter of water is smaller than phenol molecule so water molecules could easily diffuse into the pores. According to Boehm titration results (Table 8.1 and 8.3), the AC surface features minor amounts of carboxyl groups after eleven regeneration cycles that worsens in terms of hydrophilic character. Thus, carboxyl groups are responsible for adsorption of water molecules through hydrogen bonding, decreasing the carboxylic groups, increases the phenol adsorption capacity.

Considering the hypotheses related to the adsorption of phenol discussed above, the causes for the decrease in adsorption capacity add to the effects of the electrochemical regeneration process. The loss of surface area (BET area) is caused by secondary reactions of the electrochemical process, it was observed by the color of increase in electrolyte solution early in the process, in addition to the initial mass of activated carbon *A* before the first cycle was 1.023 g, and at the end of the eleventh cycle was 0.905 g. Variations in surface chemical groups are caused by the interaction of reaction products of the electrochemical regeneration. The increase of basic groups (Table 8.1 and 8.3) for the activated carbons A, B and D gave a reduction in the adsorption capacity at a slower rate when compared to activated carbon C which because of the rapid decrease of basic groups lost 85% of the adsorption capacity in the fourth cycle.

The adsorption of water molecules is also a factor that must be considered, since, while the activated carbon regenerates the electrochemical reactor, the released sites can be filled with water, and remains so for the new adsorption process.

The maximum adsorption capacities of the samples were determined using the Langmuir model. The values in Table 8.2 indicate that the carbons A and B showed the maximum adsorption capacity of greater than carbon D (commercial), but that this has not been experimentally observed. However, the mathematical model considers the tendency of the isotherm compared to the experimental curve, which for A and B had a higher slope carbon providing a greater maximum adsorption capacity calculated.

8.1.5. Conclusions

From the results of the study it can be concluded that the electrochemical regeneration causes a significant reduction in the total surface area and pore volume due to partial destruction of the pores promoting weight loss resulting in lower adsorption capacities. The variation of surface groups, caused by the electrochemical regeneration directly influences the three adsorption routes, with higher rates for interactions donor-acceptor of electrons, and dispersive interaction of π-π electron coupling. Formation of oxygen groups on the surface of activated carbons can lead to weakening of the dispersion forces due to the extraction of electrons from the π band of aromatic groups on the basal plane of activated carbon. While the weakening of the dispersion shows interaction constraining effect on adsorption, the adsorption is strongly dependent on the amount of basic groups on the surface of activated carbon. The electrochemical regeneration process presented excellent characteristics for a scaling-up, being it possible to perform recovery applications for large amounts of saturated activated carbon. The process still requires studies mainly present in the preservation solutions of the adsorbent mass and surface characteristics.

References

[1] O. Zanella, I.C. Tessaro, L.A. Féris, Desorption and Decomposition - Based Techniques for the Regeneration of Activated Carbon , Chem. Eng. Technol., 37(9), (2014) 1447–1459.

[2] D.O. Valencia, M.R. Sun-Kou, Corrigendum to Comparative cadmium adsorption study on activated carbon prepared from aguaje (Mauritia flexuosa) and olive fruit stones (Olea europaea L.), J. Environ. Chem. Eng., 2(4), (2014) 2280-2288.

[3] M.E. Fernandez, G.V. Nunell, P.R. Bonelli, A.L. Cukierman, Activated carbon developed from orange peels: Batch and dynamic competitive adsorption of basic dyes, Ind. Crops Prod., 62, (2014) 437-445.

[4] J. Alvarez, G. Lopez, M. Amutio, J. Bilbao, M. Olazar, Upgrading the rice husk char obtained by flash pyrolysis for the production of amorphous silica and high quality activated carbon, Bior. Technol., 170, (2014) 132-137.

[5] R.V. Shende, V.V. Mahajani, Wet oxidative regeneration of activated carbon loaded with reactive dye, Waste Manag., 22, (2002) 73-83.

[6] C.H. Weng, M.C. Hsu, Regeneration of granular activated carbon by an electrochemical process. Sep. Purific. Technol., 64, (2008) 227-236.

[7] C.S. Tan, P.L. Lee, Supercritical CO_2 desorption of toluene from activated carbon in rotating packed bed, J. Superc. Fluids, 46, (2008) 99-104.

[8] E. Sabio, E. González, J.F. González, C.M. García, A. Ramiro, J. Gañan, Thermal regeneration of activated carbon saturated with p-nitrophenol, Carbon, 42, (2004) 2285-

2293.

[9] D.O. Cooney, A. Nagerl, A.L. Hines, Solvent regeneration of activated carbon, Water Res., 17, (1983) 403-410.

[10] X. Liu, G. Yu, W. Han, Granular activated carbon adsorption and microwave regeneration for treatment of 2,4,5-trichlorobiphenyl in simulated soil-washing solution, J. Hazard. Mater., 147, (2007) 746-751.

[11] C. Coelho, A.S. Oliveira, M.F.R. Pereira, O.C. Nunes, The influence of activated carbon surface properties on the adsorption of the herbicide molinate and the bio-regeneration of the adsorbent, J. Hazard. Mater., 138, (2006) 343-349.

[12] N. Drouiche, H. Grib, N. Abdi, H. Lounici, A. Pauss, N. Mameri, Electrodialysis with bipolar membrane for regeneration of a spent activated carbon, J. Hazard. Mater., 170, (2009) 197-202.

[13] I. Langmuir, "The adsorption of gases on plane surfaces of glass, mica and platinum," Journal of the American Chemical Society, 40(9) (1918), 1361–1403.

[14] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of Gases in Multimolecular Layers, Journal of the American Chemical Society, 60, (1938)309-319.

[15] G. HorvÁTh, K. Kawazoe, Method for the calculation of effective pore size distribution in molecular sieve carbon, Journal of Chemical Engineering of Japan, 16, (1983) 470-475.

[16] E.P. Barrett, L.G. Joyner, P.P. Halenda, The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms, Journal of the American Chemical Society, 73, (1951)373-380.

[17] H.P. Boehm, Chemical identification of surface groups, Adv. Catal., 1, (1966) 179–274.

[18] A.P. Terzyk, Further insights into the role of carbon surface functionalities in themechanism of phenol adsorption, J. Colloid Interface Sci., 268 (2003) 301–329.

[19] L.R. Radovic, I.F. Silva, J.I. Ume, J.A. Menéndez, C.A.L.Y. Leon, A.W. Scaroni, An experimental and theoretical study of the adsorption of aromatics possessing electron-

withdrawing and electron-donating functional groups by chemically modified activated carbons, Carbon, 35 (1997) 1339‑1348.

[20] D.M. Nevskaia, A. Santianes, V. Muñoz, A. Guerrero-Ruíz, Interaction of aqueous solutions of phenol with commercial activated carbons: an adsorption and kinetic study, Carbon, 37 (1999) 1065‑1074

CAPÍTULO 9

CONSIDERAÇÕES FINAIS

O presente trabalho apresentou estudos para a produção de carvão ativado a partir de precursor lignolulósico (engaço de uva) com amplo estudo de ativação, e aplicação destes adsorventes desenvolvidos em processos de adsorção/regeneração. Também foi desenvolvido um reator eletroquímico e foram realizados estudos de otimização deste reator aplicado ao processo de regeneração de carvão ativado saturado com fenol.

As técnicas de regeneração disponíveis para renovar a capacidade de adsorção de carvão ativado carregado vêm sendo estudadas, porém, muitos efeitos ainda não são conhecidos, sendo esta a preocupação de muitos autores. A regeneração traz como aspecto positivo a reutilização do CA, e para compostos orgânicos e inorgânicos oxidáveis a destruição destes em compostos menos perigosos ou a mineralização completa. A necessidade de se conhecer todos os fatores físico-químicos da técnica aplicada, bem como as alterações que possam prejudicar a capacidade de adsorção, ou ainda, modificar a superfície do CA, é um desafio para estudos futuros. Sabe-se que muitas técnicas regenerativas têm grande efetividade, embora não se conheça os fenômenos que antecedem o resultado final, é funcional, mas não se sabe como.

Pelo desenvolvimento do reator eletroquímico aplicado na regeneração de CAs carregados com fenol, notamos que a técnica realmente tem grandes possibilidades de se tornar aplicável no campo (*in-situ*) em aplicações regenerativas, sendo que, não se tem relatos de aplicações em grande escala. A técnica não esta totalmente compreendida, ainda não se sabe ao certo se é possível transferir condições para diferentes contaminantes. O que se sabe, e neste trabalho foi mostrado, é que o processo eletroquímico é funcional, pode ser utilizado com bons resultados.

Ainda não se pode concluir que nas condições estabelecidas no estudo de regeneração eletroquímica, efetivamente se tem as condições ótimas de processo, visto que, o objetivo não é apenas recuperar a capacidade de adsorção do CA, e sim, também, avaliar as condições de decomposição para o fenol, e se isto poderá ser estendido a outros compostos orgânicos.

A produção de carvão ativado a partir de precursores lignocelulósico, além de baixos custos, é possível desenvolver adsorventes com grandes capacidade e especificidades adsortivas. É uma forma de produzir carvão ativado a partir de precursores renováveis e com características semelhantes aos carvões ativados minerais.

O processo de pirólise mostrou um grande efeito sobre o produto final, e uma cuidadosa seleção das condições de carbonização afeta de forma significativa a estrutura porosa dos carvões ativados resultantes.

Foi claramente observado a partir das imagens de MEV que a estrutura granular foi mantida ao longo do processo de ativação, independentemente, do agente de oxidação utilizado. Além disso, as imagens de MEV mostraram a presença de nanofibras sobre a estrutura interior dos carvões ativados, que têm origem na estrutura precursora. Os carvões ativados produzidos neste trabalho apresentaram grupos funcionais de superfície e propriedades texturais bastante interessantes, do ponto de vista da adsorção de compostos orgânicos, com a vantagem de ser produzido na forma fibrosa, o que possibilita uma vasta gama de aplicação.

Os carvões ativados desenvolvidos a partir do engaço de uva demonstraram eficiência adsortiva para fenol. A capacidade de adsorção de fenol, nas mesmas condições de processo, foi maior comparada ao carvão ativado comercial, levando em consideração a máxima capacidade de adsorção pelo modelo de isoterma de Langmuir.

Na aplicação dos carvões ativados e do reator eletroquímico em sucessivos ciclos de adsorção/regeneração, percebeu-se que ainda são necessários muitos estudos principalmente no que diz respeito à conservação das características texturais dos carvões ativados, buscando a regeneração completa e a conservação de suas propriedades.

Neste estudo houve uma preocupação com a reutilização de resíduos agroindustriais com o objetivo de proporcionar agregação de valores a estes materiais, mas também se buscou a aplicação e o desenvolvimento de técnicas promissoras na área de tratamento de efluentes líquidos e emissões gasosas, uma vez que os resultados desta pesquisa podem ser ampliados a todos os processos de tratamento e purificação que envolve técnicas de adsorção.

SUGESTÕES PARA TRABALHOS FUTUROS

Os resultados do presente trabalho indicam que novos estudos devem ser realizados nas áreas abordadas a fim de promover a melhoria voltada à especificidade dos carvões ativados feitos a partir de engaço de uva e estudo da técnica de regeneração eletroquímica para aplicações em grande escala e relacionados aos custos do processo. Entre os possíveis tópicos a serem pesquisados futuramente, destacam-se os listados a seguir.

- Utilizar diferentes técnicas de ativação dos carvões ativados feitos a partir de engaço de uva e aplicar em estudos comparativos aos desenvolvidos nesta tese.
- Aplicar os carvões ativados em processo de adsorção para diferentes compostos orgânicos.
- Estudar a decomposição dos compostos orgânicos no reator eletroquímico, provenientes da dessorção envolvida no processo de regeneração.
- Utilizar o reator eletroquímico na regeneração e decomposição de diferentes compostos orgânicos.
- Ampliar a escala de regeneração eletroquímica e estudar os custos envolvidos no processo.

REFERÊNCIAS

[1] Freedonia Report, Activated carbon: world demand to rise 8.1% annually through 2018. <http://www.freedoniagroup.com/DocumentDetails.aspx?DocumentId=578390> (acessado 10.01.13).

[2] S. Guo, J. Peng, W. Li, K. Yang, L. Zhang, S. Zhang, H. Xia, Effects of CO_2 activation on porous structures of coconut shell-based activated carbons, App. Surf. Sci., 255(20), (2009) 8443–8449.

[3] H. Lata, V.K. Garg, R.K. Gupta, Adsorptive removal of basic dye by chemically activated Parthenium biomass: equilibrium and kinetic modeling, Desalination, 219(1-3), (2008) 250-261.

[4] C.O. Ania, J.B. Parra, J.A. Menéndez, J.J. Pis, Effect of microwave and conventional regeneration on the microporous and mesoporous network and on the adsorptive capacity of activated carbons, Micropor. Mesopor. Mater., 85(1-2), (2005) 7-15.

[5] G. San Miguel, S.D. Lambert, N.J.D. Graham, The regeneration of field spent activated carbons, Water Res., 35(11), (2001) 740-748.

[6] G.Z. Qu, J. Li, Y. Wu, G.F. Li, D. Li, Regeneration of acid orange 7-exhausted granular activated carbon with dielectric barrier discharge plasma, Chem. Eng. J., 146(2), (2009) 168-173.

[7] I. Dranca, T. Lupascu, K. Vogelsang, L. Monahova, Utilization of Thermal Analysis to Establish the Optimal Conditions for Regeneration of Activated Carbons, J. Therm. Anal. Calorim., 64(3), (2001) 945-953.

[8] M.G. Plaza, S. García, F. Rubiera, J.J. Pis, C. Pevida, Post-combustion CO_2 capture with a commercial activated carbon: comparison of different regeneration strategies, Chem. Eng. J., 163(1-2), (2010) 41–47.

[9] E. Sabio, E. González, J.F. González, C.M. González-García, A. Ramiro, J. Gañan, Thermal regeneration of activated carbon saturated with p-nitrophenol, Carbon, 42(11), (2004) 2285–2293.

[10] G. San Miguel, S.D. Lambert, N.J. Graham, Thermal regeneration of granular activated carbons using inert atmospheric conditions, Environ. Technol., 23(12), (2002) 1337–1346.

[11] D. Chinn, C.J. King, Adsorption of glycols, sugars, and related multiple–OH compounds onto activated carbons. 2. Solvent regeneration, Ind. Eng. Chem. Res., 38(10), (1999), 3746–3753.

[12] J.F. González, J.M. Encinar, A. Ramiro, E. Sabio, Regeneration by wet oxidation of an activated carbon saturated with p-nitrophenol, Ind. Eng. Chem. Res., 41(5), (2002), 1344–1351.

[13] Y. Han, X. Quan, S. Chen, H. Zhao, C. Cui, Y. Zhao, Electrochemically enhanced adsorption of aniline on activated carbon fibers, Sep. Purif. Technol., 50(3), (2006), 365–372.

[14] F. Rodriguez-Reinoso, M. Molina-Sabio, Textural and chemical characterization of microporous carbons, Adv Coll. Interf. Sci., 76, (1998) 271-294.

[15] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Orfao, Modification of the surface chemistry of activated carbons, Carbon, 37, (1999) 1379-1389.

[16] S. Biniak, G. Szymanski, J. Siedlewski, A. Swiatkowski, The characterization of activated carbons with oxygen and nitrogen surface groups, Carbon, 35, (1997) 1799-1810.

[17] R.C. Bansal, J.B. Donnet, F. Stoeckli, Active Carbon, New York: Marcel Dekker, 1988.

[18] R. Arriagada, R. Garcia, M. Molina-Sabio, F. Rodriguez-Reinoso, Effect of steam activation on the porosity and chemical nature of activated carbons from Eucalyptus globules and peach stones, Microp. Mat., 8, (1997) 123-130.

[19] A.F. Martins, A.L. Cardoso, J.A. Stahl, J. Diniz, Low temperature conversion of rice husks, eucalyptus sawdust and peach stones for the production of carbon-like adsorbent, Biores. Technol., 98, (2007) 1095-1100.

[20] T. Zhang, W. Walawender, L.T. Fan, M. Fan, D. Daugaard, R.C. Brown, Preparation of activated carbon from forest and agricultural residues through CO_2 activation, Chem. Eng. J., 105, (2004) 105 53-59.

[21] M.L. Martinez, M.M. Torres, C.A. Guzman, D.M. Maestri, Preparation and characteristics of activated carbon from olive stones and walnut shells, Ind, Crops Prod., 23, (2006) 23-28.

[22] M. Molina-Sabio, F. Rodriguez-Reinoso, Role of chemical activation in the development of carbon porosity, Coll. Surf. A: Physicoch. Eng. Aspects, 241 (2004) 15-25.

[23] N. Spahis, A. Addoun, H. Mahmoudi, N. Ghaffour, Purification of water by activated carbon prepared from olive stones, Desalination, 222, (2008) 519-527.

[24] A.A. Attia, B.S. Girgis, N.A. Fathy, Removal of methylene blue by carbons derived from peach stones by H_3PO_4 activation: Batch and column studies, Dyes and Pigments, 76, (2008) 282-289.

[25] P. Galiatsatou, M. Metaxas, V. Kasselouri-Rigopoulou, Adsorption of zinc by activated carbons prepared from solvent extracted olive pulp, J. Hazar. Mat., 91, (2002) 187-203.

[26] P. Vazquez, L. Pizzion, M. Blanco, C. Caceres, H. Thomas, R. Arraigada, S. Bendezu, R. Cid, R. Garcia, NDMO(W)-based hydrotreatment catalysts supported on peach stones activated carbon, App. Catal. A: General, 184, (1999) 303-313.

[27] V. Boonamnuayvitaya, S. Sae-ung, W. Tanthepanichakoon, Preparation of activated carbons from coffee residue for adsorption of formaldhyde Sep. Purif. Technol., 42, (2005) 159-168.

[28] M. Balat, H. Balat, C. Öz, Progress in bioethanol processing, Prog Energy Combust Sci., 34, (2008) 551–573.

[29] P. Suhas, M. Carrott, C. Ribeiro, Lignin—from natural adsorbent to activated carbon: a review, Biores. Technol., 98, (2007) 2301–2312.

[30] Ili, 2014. The International Lignin Institute. http://www.ili-lignin.com, Acessado em 27/01/2014.

[31] E. Schröder, K. Thomauske, C. Weber, A. Hornung, V. Tumiatti, Experiments on the generation of activated carbon from biomass, J. Anal. Appl. Pyrol., 79, (2007) 106–111

[32] J. González, S. Román, J. Encinar, G. Martínez, Pyrolysis of various biomass residues and char utilization for the production of activated carbons, J. Anal. Appl. Pyrol., 85, (2009) 134–141

[33] V. Strezov, M. Patterson, V. Zymla, K. Fisher, T. Evans, P. Nelson, Fundamental aspects of biomass carbonization, J. Anal Appl. Pyrol., 79, (2007) 91–100

[34] F. Rodriguez-Reinoso, A. Sepulveda-Escribano, H.S. Nalwa, Porous carbons in adsorption and catalysis, 5th ed., San Diego: Academic Press, 2001.

[35] A.H. Ei-Sheikh, A.P. Newman, H.K. Al-Daffaee, S. Phull, N. Cresswell, Characterization of activated carbon prepared from a single cultivar of Jordanian olive stones by chemical and physicochemical techniques, J. Anal. Appl. Pyrol., 71(1), (2004) 151-164.

[36] B.S. Girgis, A.A. El-Hendawy, Porosity development in activated carbons obtained from date pits under chemical activation with phosphoric acid, Microp. Mesop. Mat., 52(2), (2002) 105-117.

[37] P.M.S.Sai, K. Krishnaiah, Development of the pore-size distribution in activated carbon produced from coconut shell char in a fluidized-bed reactor, Ind. Eng. Chem. Res., 44(1), (2005) 51-60.

[38] F. Rodríguez-Reinoso, M. Molina-Sabio, Activated carbons from lignocellulosic materials by chemical and/or physical activation: an overview, Carbon, 30(7), (1992) 1111–1118.

[39] Y. Guo, D.A. Rockstraw, Activated carbons prepared from rice hull by one-step phosphoric acid activation, Microp. Mesop. Mat., 100(1-3), (2007) 12-19.

[40] T.J. Bandosz, Activated Carbon Surfaces in Environmental Remediation. 7th ed., New York: Academic Press, 2006.

[41] K. László, Adsorption from aqueous phenol and aniline solutions on activated carbons with different surface chemistry, Colloids Surf. A: Physicochem. Eng. Aspects, 265, (2005) 32-39.

[42] A.A. El-Hendawy, Variation in the FTIR of a biomass under impregnation, carbonization and oxidation conditions, J. Anal. Appl. Pyrol., 75(1), (2007) 59-66.

[43] V.V.S. Guilarduci, J.P. Mesquita, P.B. Martelli, H.F. Gorgulho, Adsorção de fenol sobre carvão ativado em meio alcalino, Química Nova, 29(6), (2006) 1226-1232.

[44] T. Budinova E. Ekinci, F. Yardim, A. Grimm, E. Bjornbnm, V. Minkova, M. Goranova, Characterization and application of activated carbon produced by H3PO4 and water vapor activation, Fuel Proces. Technol., 87(10), (2006) 899-905.

[45] D.J. Kim, H.I. Lee, J.E. Yei, S.J. Kim, J.M. Kim, Ordered mesoporous carbons: implication of surface chemistry, pore structure and adsorption of methyl mercaptan, Carbon, 43(9), (2005) 1868-1873.

[46] Y. El-Sayed, T.J. Bandosz, Adsorption of valeric acid from aqueous solution onto activated carbons: role of surface basic sites, J. Colloid Interface Sci., 273(1), (2004) 64-72.

[47] R.C. Bansal, M. Goyal, Activated carbon adsorption, USA: CRC Press, 2005.

[40] I. Okman, S. Karagöz, T. Tay, M. Erdem, Activated Carbons From Grape Seeds By Chemical Activation With Potassium Carbonate And Potassium Hydroxide. App. Surf. Sci., 293(28), (2014) 138-142.

[49] J. Guo, A. Lua, Textural and chemical properties of adsorbent prepared from palm shell by phosphoric acid activation, Mat. Chem. Phys., 80 (2003), pp. 114–119.

[50] C. Gomez-de-Salazar, A. Sepulveda-Escribano, F. Rodriguez-Reinoso, Preparation of carbon molecular sieves by controlled oxidation treatments, Carbon, 38, (2000) 1889–1892.

[51] A. Amaya, J. Píriz, N. Tancredi, T. Cordero, Activated carbon pellets from eucalyptus char and tar TG studies, J. Therm. Anal. Calorim., 89, (2007) 987–991.

[52] C. Nguyen, D. Do, Preparation of carbon molecular sieves from macadamia nut shells, Carbon, 33, (1995) 1717–1725.

[53] M. Soleimani, T. Kaghazchi, Activated hard shell of apricot stones: a promising adsorbent in gold recovery, Chin. J. Chem. Eng., 16, (2008) 112–118.

[54] S. Vijaya Lakshmi, S.R. Patwardhan, Carbon molecular sieves from acidified coconut shell char, Proceeding of biennial conference, (1997) 302–303.

[55] K. Yang, J. Peng, C. Srinivasakannan, L. Zhang, H. Xia, X. Duan, Preparation of high surface area activated carbon from coconut shells using microwave heating, Biores. Technol., 101(15), (2010) 6163–6169.

[56] T. Zhang, W.P. Walawender, L.T. Fan, M. Fan, D. Daugaard, R.C. Brown, Preparation of activated carbon from forest and agricultural residues through CO_2 activation, Chem. Eng. J., 105(1-2), (2004) 53–59.

[57] J.M. Valente Nabais. C. Laginhas, M.M.L. Ribeiro Carrott. P.J.M. Carrott. J.E. Crespo Amorós. A.V. Nadal Gisbert, Surface and porous characterisation of activated carbons made from a novel biomass precursor, the esparto grass, Appl. Surf. Sci.,265, (2013) 919–924.

[58] J. Guo, A. Lua, Characterization of adsorbent prepared from oil-palm shell by CO_2 activation for removal of gaseous pollutants, Mat. Lett., 55, (2002) 334–339.

[59] R. Arriagada, R. Garcia, M. Molina-Sabio, F. Rodriguez-Reinoso, Effect of steam activation on the porosity and chemical nature of activated carbons from Eucalyptus globulus and peach stones, Micropor. Mat., 8, (1997) 123–130.

[60] Y. Ngernyen, C. Tangsathitkulchai, M. Tangsathitkulchai, Porous properties of activated carbon produced from Eucalyptus and Wattle wood by carbon dioxide activation, Korean J. Chem. Eng., 23, (2006) 1046–1054.

[61] A. Youssef, N. Radwan, I. Abdel-Gawad, G. Singer, Textural properties of activated carbons from apricot stones, Coll. Surf. A, 252, (2005) 143–151.

[62] W. Li, K. Yang, J. Peng, L. Zhang, S. Guo, H. Xia, Effects of carbonization temperatures on characteristics of porosity in coconut shell chars and activated carbons derived from carbonized coconut shell chars, Ind. Crops. Prod., 28, (2008) 190–198.

[63] S.O. Prozil, Caracterização Química do Engaço da Uva e Possíveis Aplicações, Departamento de Química, Universidade de Aveiro, Aveiro, 2008, (Dissertação de Mestrado).

[64] G. Spigno, T. Pizzorno, D.M. De Faveri, Cellulose and hemicelluloses recovery from grape stalks. Biores. Technol., 99(10), (2008) 4329-4337.

[65] J.M. Cruz, H. Dominguez, J.C. Parajo, Assessment of the production of antioxidants from winemaking waste solids, J. Agricult. Food Chem., 52(18), (2004) 5612-5620.

[66] J. González, J. Encinar, J. Canito, E. Sabio, M. Chacón, Pyrolysis of cherry stones: energy uses of the different fractions and kinetic study, J. Anal. Appl. Pyrol., 67, (2003) 165–190.

[67] V. Strezov, M. Patterson, V. Zymla, K. Fisher, T. Evans, P. Nelson, Fundamental aspects of biomass carbonization, J. Anal. Appl. Pyrol., 79, (2007) 91–100.

[68] A.R. Reed, P.T. Williams, Thermal processing of biomass natural fiber wastes by pyrolysis, Int. J. Energy Res., 28, (2004) 131–145.

[69] W. Daud, W. Ali, Comparison on pore development of activated carbon produced from palm shell and coconut shell, Bioresour. Technol., 93, (2004) 63–69.

[70] W. Daud, W. Ali, M. Sulaiman, Effect of carbonization temperature on the yield and porosity of char produced from palm shell, J. Chem. Technol. Biotechnol., 76, (2001) 1281–1285.

[71] B. Kaynak, H. Topal, A. Atimtay, Peach and apricot stone combustion in a bubbling fluidized bed, Fuel Process Technol., 86, (2005) 1175–1193.

[72] M. Jagtoyen, F. Derbyshire, Activated carbons from yellow poplar and white oak by H_3PO_4 activation, Carbon, 36, (1998) 1085–1097.

[73] A. Tsamba, W. Yang, W. Blasiak, Pyrolysis characteristics and global kinetics of coconut and cashew nut shells, Fuel Process Technol., 87, (2006) 523–530.

[74] A. Demirba. Relationships between lignin contents and fixed carbon contents of biomass samples, Energy Convers Manage., 44, (2003) 1481–1486.

[75] M. Soleimani, T. Kaghazchi, Gold recovery from loaded activated carbon using different solvents, J. Chin. Inst. Chem. Eng., 39(1), (2008), 9–11.

[76] R.M. Narbaitz, J. Cen, Electrochemical regeneration of granular activated carbon, Water Res., 28(8), (1994) 1771-1778.

[77] H. Zhang, L. Ye, H. Zhong, Regeneration of phenol-saturated activated carbon in an electrochemical reactor, J. Chem. Technol. Biot., 77(11), (2002) 1246-1250.

[78] M. García-Otón, F. Montilla, M.A. Lillo-ródenas, E. Morallón, J.L. Vázquez, Electrochemical regeneration of activated carbon saturated with toluene, J. Appl. Electrochem., 35(3), (2005) 319-325.

[79] M.H. Zhou, L.C. Lei, Electrochemical regeneration of activated carbon loaded with p-nitrophenol in a fluidized electrochemical reactor, Electrochim. Acta, 51(21), (2006) 4489-4496.

[80] R. Berenguer, J.P. Marco-Lozar, C. Quijada, D. Cazorla-Amorós, E., Electrochemical regeneration and porosity recovery of phenol-saturated granular activated carbon in an alkaline medium, , 48(10), (2010) 2734-2745.

[81] N.W.Brown, E.P.L. Roberts, A. Chasiotis, T. Cherdron, N. Sanghrajka, Atrazine removal using adsorption and electrochemical regeneration, Water Res., 38(13), (2004) 3067-3074.

[82] R.M. Narbaitz, A. Karimi-Jashni, Electrochemical regeneration of granular activated carbons loaded with phenol and natural-organic matter, Environ. Technol., 30(1), (2009) 27-36.

[83] R.M. Narbaitz, A. Karimi-Jashni, Electrochemical reactivation of granular activated carbon: Impact of reactor configuration, Chem. Eng. J., 197, (2012) 414-423.

[84] R.M. Narbaitz, J. McEwen, Electrochemical regeneration of field spent GAC from two water treatment plants, Water Res., 46(15), (2012) 4852-4860.

[85] O.J. Murphy, G.D. Hitchens, L. Kaba, C.E. Verostko, Direct electrochemical oxidation of organics for waste-water treatment, Water Res., 26(4), (1992) 443–451.

[86] D.C. Johnson, J. Feng, L.L. Houk, Direct electrochemical degradation of organic wastes in aqueous media, Electrochim. Acta, 46(2–3), (2000) 323–330.

[87] M. Panizza, C. Bocca, G. Cerisola, Electrochemical treatment of wastewater containing polyaromatic organic pollutants, Water Res., 34(9), (2000) 2601–2605.

[88] H. Zhang, Regeneration of exhausted activated carbon by electrochemical method, Chem. Eng. J., 85, (2002) 81-85.

[89] N.W. Brown, E.P.L. Roberts, A.A. Garforth, R.A.W. Dryfe, Electrochemical regeneration of a carbon-based adsorbent loaded with crystal violet dye, Electrochim. Acta, 49(20), (2004) 3269–3281.

[90] C.H. Comninellis, C. Pulgarin, “Anodic oxidation of phenol for waste water treatment”, J. Appl. Electroch., 21, 703-708, 1991.

[91] L. Wang, N. Balasubramanian, Electrochemical regeneration of granular activated carbon saturated with organic compounds, Chem. Eng. J., 155(3) (2009) 763-768.

[92] M. Panizza, P.A. Michaud, G. Cerisola, C.H. Comninellis, Anodic oxidation of 2-naphthol at boron-doped diamond electrodes, J. Electroanal. Chem., 507(1-2), (2001) 206-214.

[93] G. Busca, S. Berardinelli, C. Resini, L. Arrighi, Technologies for the removal of phenol from fluid streams: a short review of recent developments, J. Hazard.Mat., 160 (2008) 265–288.

[94] R. Berenguer, J.P. Marco-Lozar, C. Quijada, D. Cazorla-Amorós, E. Morallón, Comparison among chemical, thermal, and electrochemical regeneration of phenol-saturated activated carbon, Energ. Fuel., 24(6), (2010) 3366-3372.

[95] C.H. Weng, M.C. Hsu, Regeneration of granular activated carbon by an electrochemical process, Sep. Purif. Technol., 64(2), (2008) 227-236.

[96] Y. Han, X. Quan, S. Chen, H. Zhao, C. Cui, Y. Zhao, Electrochemically enhanced adsorption of aniline on activated carbon fibers, Sep. Purif. Technol., 50(3), (2006) 365-372.