



**IARA DO ROSÁRIO GUIMARÃES**

**OXIDAÇÃO DE COMPOSTOS ORGÂNICOS  
CONTENDO NITROGÊNIO E ENXOFRE  
EMPREGANDO ÓXIDOS DE FERRO  
MODIFICADOS**

**LAVRAS - MG**

**2011**

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Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Agroquímica, área de concentração em Agroquímica, para a obtenção do título de Doutor.

Orientador

Dr. Luiz Carlos Alves de Oliveira

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APROVADA em 16 de dezembro de 2010.

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Orientador

**LAVRAS - MG**

**2010**

*À “dona Niva”, que à flor dos seus 58 anos, se fez menina, emocionada,  
passando no vestibular,  
se fez guerreira ao ser mãe, mulher, trabalhadora, dona de casa e estudante.  
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por acreditar nos seus sonhos e por sempre fazer valer a pena, todas as flores  
são para você,  
porque ter 28 anos e concluir o doutorado é uma batalha muito menor que a  
sua.  
Com muito orgulho e admiração.*

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“Bom mesmo é ir a luta com determinação, abraçar a vida e viver com paixão. Perder com classe e vencer com ousadia, pois o triunfo pertence a quem mais se atreve e a vida é muito para ser insignificante. Eu faço e abuso da felicidade e não desisto dos meus sonhos. O mundo está nas mãos daqueles que tem coragem de sonhar e correr o risco de viver seus sonhos.”

Charles Chaplin



## RESUMO

Contaminantes nitrogenados e sulfurados presentes nos combustíveis fósseis são conhecidos pelo impacto negativo no ambiente devido as emissões de  $\text{NO}_x$  e  $\text{SO}_x$ . Como consequência, a remoção dessas espécies está se tornando um desafio de caráter mundial, reforçado por regulamentações sempre mais rigorosas. Dentro desse contexto, nesse trabalho buscou-se o desenvolvimento de novos materiais baseados em óxidos de ferro, de baixo custo e ampla disponibilidade, que atuassem de forma efetiva como catalisadores em processos de oxidação com enfoque especial àqueles compostos que apresentassem enxofre ou nitrogênio na estrutura. Assim, o primeiro estudo, utilizando-se uma limonita reduzida termicamente em atmosfera de  $\text{H}_2$ , pode-se comprovar que o enriquecimento da superfície do material com sítios ativos de  $\text{Fe}^{2+}$  melhoraram significativamente sua atividade em reações de oxidação de quinolina, azul de metileno e dibenzotiofeno. Ainda nesse contexto, no segundo trabalho avaliou-se a reatividade de um sistema Fenton heterogêneo baseado apenas na utilização da fração magnética da limonita natural após um processo simplificado de separação, com foco, essencialmente, no efeito da fração magnética na degradação de quinolina, composto nitrogenado modelo de contaminante do petróleo. O terceiro artigo descreveu-se a síntese, caracterização e testes catalíticos de uma goethita parcialmente substituída por cobre (dopada) e reduzida termicamente na oxidação de quinolina enquanto o quarto aborda a utilização de goethita dopada por  $\text{Ni}^{2+}$  e avaliou-se o efeito dessa substituição isomórfica na degradação do mesmo composto modelo. Dessa forma, esse trabalho visou colaborar, de maneira geral, para compreensão dos efeitos que regem a química dos óxidos de ferro assim como sua contribuição para o desenvolvimento de processos alternativos para remoção de contaminantes da cadeia produtiva do petróleo.

Palavras-chave: Óxidos de ferro. Substituição isomórfica. Oxidação. Contaminantes nitrogenados e sulfurados.

## ABSTRACT

Nitrogen and sulfur contaminants present in fossil fuels are known for negative environmental impact due to emissions of  $\text{NO}_x$  and  $\text{SO}_x$ . As a consequence, the removal of these species is becoming a challenge of global concern, enhanced by ever more stringent regulations. In this context, the aim of this study is to develop new materials based on iron oxides, low cost and wide availability, which effectively acted as catalysts in oxidation processes for removal of unwanted compounds, with particular focus on those compounds that present sulfur and nitrogen as a constituent or heteroatoms. Thus, the first study, using a thermally reduced limonite in  $\text{H}_2$  atmosphere, it is shown that the enrichment of the material surface with active sites of  $\text{Fe}^{2+}$  significantly improve their activity in the oxidation of quinoline, methylene blue and dibenzothiophene. Also in this context, the second study underscored the reactivity of a heterogeneous Fenton system based solely on the use of magnetic fraction of natural limonite after a simplified procedure for separation, focusing primarily on the effect of the magnetic fraction in the degradation of quinoline, nitrogen compound model contaminant oil. The third article describes the synthesis, characterization and catalytic testing of a sample of goethite partially replaced by copper and thermal reduced in the oxidation of quinoline, while the fourth discusses the use of doped goethite by  $\text{Ni}^{2+}$  and evaluates the effect of substitution isomorphous the degradation of the same compound model. Thus, this work aimed at supporting, in general, to understand the effects that govern the chemistry of iron oxides and their contribution to the development of alternative processes for removing contaminants from the oil production chain.

**Keywords:** Iron oxides. Isomorphous substitution. Oxidation. Sulfur and nitrogen contaminants.

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## PRIMEIRA PARTE

### 1 INTRODUÇÃO GERAL

Contaminantes nitrogenados e sulfurados presentes nos combustíveis fósseis são conhecidos pelo impacto negativo no ambiente devido as emissões de  $\text{NO}_x$  e  $\text{SO}_x$ . Como consequência, a remoção desses contaminantes está se tornando um desafio de caráter mundial, reforçado por regulamentações sempre mais rigorosas e restritivas.

Dentre os processos de remoção dos contaminantes nitrogenados e sulfurados o processo de oxidessulfurização (ODS) tem recebido muita atenção para o tratamento de destilados médios de petróleo por duas principais vantagens em relação ao processo clássico de hidrodessulfurização (HDS). Primeiro, a maior vantagem do processo de ODS é que esse pode ser realizado na fase líquida e sob condições brandas de temperatura e pressão. Em segundo lugar, os compostos de enxofre mais refratários para o processo de HDS (dibenzotiofeno e seus derivados alquilados) são facilmente oxidados pelo método ODS.

Um importante fator no processo de dessulfurização oxidativa é avaliar o efeito da presença de outros compostos na fração combustível. Além disso, tem sido constatado que compostos contendo N e S coexistem na grande maioria dos óleos *in natura*. O processo de desnitração é consideravelmente mais difícil que a dessulfurização porque os compostos organonitrogenados são menos reativos que os sulfurados (JIA, 2009; ZEUTHEN; KNUDSEN; WHITEHURST, 2001).

Nesse contexto, esse trabalho busca o desenvolvimento de novos materiais baseados em óxidos de ferro, de baixo custo e ampla disponibilidade, que atuem de forma efetiva como catalisadores em processos de oxidação com

ênfoque especial àqueles compostos que apresentem enxofre ou nitrogênio como constituinte heteroatômico.

Três classes de óxidos de ferro serão abordadas ao longo do trabalho. Nos dois primeiros artigos será descrita a utilização de um óxido de ferro natural (limonita) termicamente modificada com objetivo de aumentar sua atividade catalítica. A limonita é um óxido que apresenta em sua estrutura apenas fases oxidadas de  $\text{Fe}^{3+}$ , conhecidas por sua cinética desfavorecida em reações que envolvam peróxido de hidrogênio. Assim, o primeiro artigo<sup>1</sup> aborda a redução térmica em atmosfera de  $\text{H}_2$  da limonita natural para o enriquecimento da superfície do material com sítios ativos de  $\text{Fe}^{2+}$  (o ferro (II) é mais ativo e mais rápido na formação de radicais hidroxila a partir de peróxido de hidrogênio). O material foi testado em reações de oxidação de quinolina, azul de metileno e dibenzotiofeno.

O segundo artigo<sup>2</sup> trata da reatividade de um sistema Fenton heterogêneo baseado na utilização da fração magnética da limonita natural após um processo simplificado de separação. Com o foco, essencialmente, no efeito da fração magnética na degradação de quinolina, composto nitrogenado modelo de contaminante do petróleo.

Na tentativa de se obter materiais sintéticos com propriedades semelhantes ao material natural, uma outra parte da tese descreve a síntese, caracterização e atividade catalítica de goethitas dopadas com  $\text{Cu}^{2+}$  e  $\text{Ni}^{2+}$ . Nessa parte do trabalho avaliou-se o efeito da incorporação de diferentes cátions na estrutura da goethita ( $\alpha\text{-FeOOH}$ ), com ênfase principal nas alterações químicas, estruturais e propriedades físicas do óxido de ferro na presença do

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<sup>1</sup> Catalytic oxidation of sulfur and nitrogen compounds from diesel fuel.

<sup>2</sup> Brazilian limonite for the oxidation of quinoline: high activity after a simple magnetic separation.



elemento dopante. Dessa forma, o terceiro artigo<sup>3</sup> descreve a síntese, caracterização e testes catalíticos de uma amostra de goethita parcialmente substituída por cobre (goethita dopada com cobre) e reduzida termicamente em atmosfera de H<sub>2</sub> e posterior teste catalítico na oxidação de quinolina. Já o quarto artigo<sup>4</sup> abordou-se a utilização de goethita dopada com Ni<sup>2+</sup> e posterior avaliação do efeito dessa substituição isomórfica na degradação do mesmo composto modelo.

Dessa forma, esse trabalho visa colaborar para a compreensão dos efeitos que regem a química dos óxidos de ferro empregados como catalisadores redoxes, assim como a contribuição para o desenvolvimento de processos alternativos para remoção de contaminantes da cadeia produtiva do petróleo baseadas em óxidos de ferro modificados.

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<sup>3</sup> Synthesis and thermal treatment of Cu-doped goethite: oxidation of quinoline through heterogeneous Fenton process.

<sup>4</sup> Effect of Ni incorporation into goethite in the catalytic activity for oxidation of nitrogen compounds in petroleum.

## 2 REFERENCIAL TEÓRICO

### 2.1 Óxidos de ferro naturais

Limonita não é um mineral verdadeiro e é composta por uma mistura de óxidos de ferro hidratados, em sua maioria goethita ( $\alpha$ -FeOOH) contendo lepidocrocita ( $\gamma$ -FeOOH) e jarosita ( $K_2Fe_6(OH)_{12}(SO_4)_4$ )<sup>5</sup>, além de outros óxidos. Formam uma mistura complexa que em climas tropicais e subtropicais constitui-se de uma mistura com proporção variável de diferentes minerais (PIRSSON; SCHUCHERT, 1924). A limonita pode se apresentar em concentrações anormalmente altas quando associada a alguns tipos de depósitos minerais, sendo também muito encontrada na forma de capas lateríticas ferruginosas<sup>6</sup>, típicas de ambientes tropicais, mesmo sem relação com depósitos minerais. Entre as jazidas minerais que contem óxidos - hidróxidos de ferro estão minerações relacionadas aos depósitos de metais como cobre, cromo, zinco e, especialmente, níquel (BÜYÜKAKINCI; TOPKAYA, 2009; LANDERS; GILKES; WELLS, 2009).

Com relação ao níquel, esse apresenta uma combinação de propriedades de metais ferrosos e não-ferrosos, possuindo afinidade química em fases metálicas e sulfetadas. A maior fonte de níquel lavrado no mundo provém, principalmente, de dois depósitos minerais:

- a) depósitos lateríticos, em que os principais “minérios” são a limonita níquelífera [(Fe-Ni)OOH] e um silicato de níquel hidratado;

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<sup>5</sup> A jarosita é um sulfato hidratado de ferro e potássio formado pela oxidação de sulfetos de ferro.

<sup>6</sup> A laterita é uma formação de superfície muito alterada, característica de áreas tropicais quentes e úmidas, com grande concentração de hidróxidos de ferro e alumínio.

- b) depósitos magmáticos sulfetados, cujo minério é a pentlandita  $[\text{Ni-Fe})_9\text{S}_8]$ .

Os recursos mundiais desses dois tipos de minérios são estimados em 220 milhões de toneladas de níquel com teor médio de 1%. Desses depósitos, cerca de 65% são de depósitos lateríticos - limonitas. As reservas medidas brasileiras de níquel aprovadas pelo DNPM<sup>7</sup> totalizam 301 016 980 milhões de toneladas de minério, com teor médio de 1,61% e com 4.631.842 milhões de toneladas de níquel contido, concentradas nos Estados de Goiás (75,9%), Pará (14,5%), Piauí (6,7%) e Minas Gerais (3,0%) (SILVA, 2010). Com a aquisição da canadense Inco, maior produtora mundial de níquel, pela Companhia Vale do Rio Doce (CVRD), em novembro de 2006, o Brasil passou a ter acesso ainda mais facilitado ao metal (INSTITUTO BRASILEIRO DE MINERAÇÃO - IBRAM, 2010). Após a extração do Ni, o óxi-hidróxido remanescente (FeOOH) era empregado apenas como substrato para áreas de reflorestamento.

Estudos recentes identificaram que determinados tipos de limonita natural são ativos em diversos tipos de reações, como no hidrocraqueamento de resíduo de vácuo de petróleo bruto (LI; MORISHITA; TAKARADA, 2007; MATSUMURA et al., 2005b) e também em diferentes reações de oxidação com intermediários radicalares (FERRAZ et al., 2007; SOUZA et al., 2007). Dentro desse contexto, a limonita natural pode ser considerada como um potencial catalisador dado o seu baixo custo e disponibilidade. A possibilidade do uso da limonita como um catalisador seria mais viável que a utilização de catalisadores comerciais tradicionais. Outra vantagem está relacionada à menor desativação desse catalisador por envenenamento por deposição de coque e, combinado a isso, caso ocorra perda de atividade catalítica, o resíduo pode ser tratado como minério de ferro e pode ser transformado diretamente em um alto forno

siderúrgico. Portanto, a atividade da limonita natural justifica um estudo mais aprofundado visando aplicações industriais desse material.

## **2.2 O processo de substituição isomórfica em óxidos de ferro naturais e sintéticos**

A existência de compostos isoestruturais na natureza sugere que substituições isomórficas possam ser formadas entre dois membros *via* substituição do  $\text{Fe}^{3+}$  (no caso da goethita) por outro cátion. Essa alteração não modifica a estrutura, apenas afeta o tamanho da célula unitária. A probabilidade de substituição depende de similaridades dos raios iônicos e das valências dos cátions. Para um óxido contendo  $\text{Fe}^{3+}$ ,  $\text{M}^{3+}$  é a espécie catiônica mais adequada e um raio cerca de 18 % maior ou menor que o  $\text{Fe}^{3+8}$  (SHANNON; PREWITT, 1969 citados por CORNELL; SCHWERTMANN, 2003) em coordenação seis pode ser tolerável. Substituições isomórficas do ferro em óxidos por um grande número de cátions têm sido observadas na natureza e, mais frequentemente, nos laboratórios.

Um método simples de sintetizar um óxido metálico substituído, particularmente goethita ou hematita, consiste em precipitar a mistura M-Fe a partir da solução dos íons metálicos por adição de base. A ferridrita-M obtida por esse caminho pode ser considerada como um M-Fe hidróxido com substituições tanto na superfície quanto na estrutura interna do óxido (SCHWERTMANN; CORNELL, 2000). A incorporação do elemento dopante é precedida pela adsorção da espécie solúvel no núcleo em crescimento da goethita. Após adsorção, os íons são dessolvatados e incorporados na estrutura da goethita (CORNELL; SCHWERTMANN, 2003).

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<sup>7</sup> DNPM – Departamento Nacional de Produção Mineral.

<sup>8</sup> Raio iônico  $\text{Fe}^{3+}$ : 0,0645 nm.

Estudos referentes à incorporação de íons metálicos em óxidos de ferro é de interesse em diversas áreas. Contudo, grande parte dos trabalhos publicados são essencialmente descritivos, relatando alterações estruturais do óxido puro. O maior ganho proveniente da inserção de íons metálicos consiste em alterações nas propriedades químicas do óxido dopado quando comparado ao material puro, de maneira que vantagens catalíticas ou ganhos relacionados à processos de adsorção sejam perceptíveis.

Dentre os vários tipos de óxidos de ferro, a goethita ( $\alpha$ -FeOOH) é a espécie mais comum e abundante em solos, responsável por suas características físicas e propriedades químicas. Uma característica importante da fase goethita é sua elevada reatividade química. Formada como resultado de reações de hidrólise de óxidos de ferro, a goethita é um sólido pobremente cristalino, com um sistema de cristalização imperfeito, o que gera materiais com elevadas áreas superficiais. Essa característica associada a uma estrutura pouco compacta e com canais abertos resulta em um material com alta capacidade de integração, adsorção e fixação de íons em soluções. A compreensão de como as espécies metálicas são incorporadas na estrutura cristalina da goethita tem muito interesse devido às diversas aplicações ambientais e, fundamentalmente, aplicações em catálise.

A associação da goethita com diferentes metais tem sido estudada em análogos sintéticos (MOHAPATRA; ROUT; ANAND, 2009; MUSTAFA; KHAN; ZAMAN, 2010; STENGL et al., 2010). Campo et al. (2008) avaliaram o efeito da incorporação de Co e Mn em goethitas e a aplicação dos materiais dopados como suporte catalítico para ouro. De acordo com os autores, os óxidos substituído mostraram melhor desempenho como suporte quando comparado à goethita natural uma vez que apresentavam melhor estabilidade térmica, redutibilidade, além de maior área superficial específica.

Krehula, Music e Popovic (2005) estudaram a influência da incorporação de Ni nas propriedades da goethita sintética. Segundo esses autores, a presença do níquel afeta de maneira significativa o tamanho médio das partículas, sendo maiores proporções Ni/Fe responsáveis pela minimização do diâmetro dos materiais. Além disso, teores de Ni<sup>2+</sup> superiores a 10% provocavam o deslocamento de bandas na análise por espectroscopia vibracional na região do infravermelho e diminuição dos parâmetros Mössbauer, como campo hiperfino. Mustafa, Khan e Zaman (2010) sintetizaram uma goethita contendo 0,25 mol% de Fe substituídos por Ni. Nesse trabalho, a área superficial específica do material aumentou de 34 para 125 m<sup>2</sup> g<sup>-1</sup>. Contudo, a estrutura básica da goethita não foi significativamente afetada, uma vez que alterações por XRD, FTIR e TEM não mostraram diferenças significativas.

### **2.3 O problema da indústria do petróleo**

A indústria do petróleo é bastante complexa, composta por mais de um segmento envolvendo atividades específicas diferenciadas. Esta segmentação pode ser feita da seguinte forma: Exploração e Produção de Petróleo; Refino e Petroquímica; e Distribuição de Petróleo e Derivados. Essa indústria requer o desenvolvimento de tecnologias específicas e necessita de contínuo investimento no aprimoramento das tecnologias existentes, em todos os seus segmentos.

Com relação ao segmento do refino e petroquímica, talvez o maior gargalo do setor petrolífero no Brasil esteja relacionado à qualidade do combustível que é repassado à sociedade. Essa preocupação tange principalmente o teor de contaminantes presentes nos produtos combustíveis finais e se alicerça sobre legislações cada vez mais severas e restritivas. Se os atuais 50 mg L<sup>-1</sup> de enxofre permitidos pela legislação brasileira em 2010 já

provoca um certo desconforto na cadeia produtiva, o nível de  $10 \text{ mg L}^{-1}$  previsto para 2013 têm sido considerados como o ponto chave da indústria petroleira, uma vez que os processos de HDT (Hidrotratamento)<sup>9</sup> (mais empregados nas refinarias) apresentam grande restrições técnicas na remoção de certas classes de compostos como os aril-sulfurados e os nitrogenados básicos (CEDENO-CAERO et al., 2008).

Óxidos de ferro modificados (reduzidos e suportados ou simplesmente reduzidos) têm recebido considerável atenção como catalisadores para indústria petroleira, sendo amplamente utilizados reações na remoção de compostos nitrogenados e sulfurados presentes no petróleo (GUIMARÃES et al., 2008; SOUZA et al., 2007, 2009). Minérios de ferro naturais podem ser usados satisfatoriamente como catalisadores devido, além de seu baixo custo, a possibilidade de recuperação de reativação do material (LI; MORISHITA; TAKARADA, 2007).

Como catalisadores de reações redoxes, os óxidos de ferro são frequentemente associados a um agente oxidante forte, como o peróxido de hidrogênio,  $\text{H}_2\text{O}_2$ /ácido fórmico,  $\text{H}_2\text{O}_2$ /ácido acético. Assim, para oxidação de contaminantes do petróleo, a maioria dos sistemas envolve o uso de oxidantes insolúveis em óleo, que conduz a um sistema bifásico óleo-suspensão aquosa. Esse sistema limita a transferência de massa através da interface bifásica do processo de oxidação. Além disso, por suas características, catalisadores a base de óxidos de ferro tendem a permanecer na fase aquosa formada, o que culmina na diminuição da taxa de oxidação (MA; ZHOU; SONG, 2007).

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<sup>9</sup> Conjunto de processos atualmente empregado pelas refinarias para remoção de contaminantes sulfurados e nitrogenados.

## 2.4 O petróleo

O petróleo é classificado basicamente por 3 características: composição básica, densidade e teor de enxofre.

A determinação da composição básica é a classificação dos óleos em função dos tipos de hidrocarbonetos predominantes, por exemplo, em óleos de base parafínica predominam os hidrocarbonetos saturados enquanto óleos de base naftênica têm hidrocarbonetos cíclicos saturados, como o resíduo asfáltico, e óleos com base aromática, hidrocarbonetos cíclicos não-saturados, como o benzeno e tolueno são propícios para a produção destes derivados, utilizados na petroquímica.

A classificação dos óleos pela sua densidade utiliza o grau API (American Petroleum Institute). Os petróleos são classificados como leves (acima de 30° API), médios (entre 21° e 30° API) e pesados (abaixo de 21° API). Os óleos leves são mais valorizados porque permitem produção maior de derivados leves, como a gasolina e o gás liquefeito de petróleo. Finalmente, os óleos são considerados como sweet quando apresentam baixo teor de enxofre (menos de 0,5% de sua massa, óleos leves) ou sour (ácidos), quando apresentam teor mais elevado, denominados de cargas pesadas (SIMÕES, 2008).

O dilema básico no refino de petróleo brasileiro é a utilização de óleos pesados, que são os mais baratos no mercado e disponíveis em maior proporção nas bacias brasileiras. Esse tipo de petróleo, contudo, necessita de altos investimentos em tecnologias de refino, principalmente relacionadas à remoção de constituintes heteroatômicos nitrogenados e sulfurados.



## **2.5 Contaminantes do petróleo**

A preocupação mundial com questões ambientais torna as legislações de emissões cada vez mais restritivas, fazendo com que veículos poluam cada vez menos, fruto do aperfeiçoamento contínuo das tecnologias de combustíveis. A remoção de contaminantes contendo enxofre e nitrogênio é importante porque, além de serem venenos para catalisadores dos processos de tratamento que virão depois do HDT, como o processo de reforma e craqueamento, a presença desses contaminantes prejudicam as propriedades dos produtos finais além de provocarem a emissão de poluentes. Nesse contexto, razões econômicas e ambientais tornam cada vez maior a necessidade de remoção desses compostos em cargas de petróleo.

### **2.5.1 Contaminantes sulfurados**

O enxofre é um elemento naturalmente presente no petróleo e seu percentual varia de acordo com a origem do mesmo. De uma forma geral, nos combustíveis, apresenta-se nas formas de mercaptanas, sulfetos, dissulfetos, tiofenos e gás sulfídrico (Figura 1). Um óleo diesel bruto, que não passou ainda pelo processo de HDT, apresenta tipicamente 1 % (m/m) de enxofre e pode causar corrosão em equipamentos e tubulações, desativação de outros catalisadores do processo de refino e controle de emissões das refinarias, implicando em prejuízos ao setor industrial.

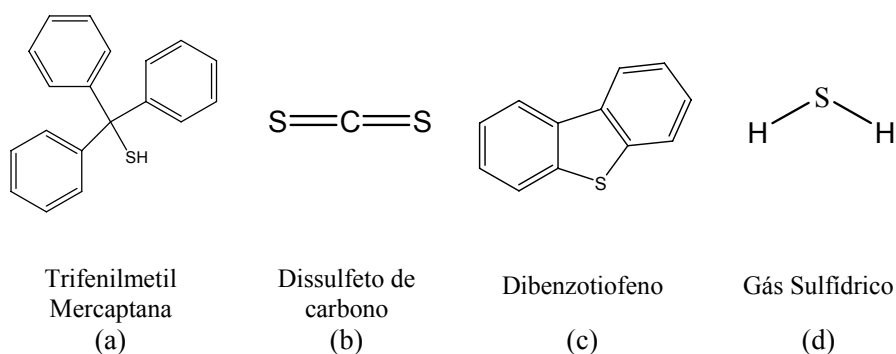


Figura 1 Representação das estruturas das principais classes de contaminantes sulfurados presentes no petróleo

A tendência mundial de processamento de frações de óleo cada vez mais pesadas tem direcionado as pesquisas para a redução nas emissões de óxidos de enxofre na corrente de efluentes gasosos. A situação é particularmente preocupante para as refinarias brasileiras, que processam cargas derivadas de óleos pesados, caracterizados por serem ricos em sulfurados, nitrogenados e impurezas (MATSUMURA et al., 2005a, 2005b).

As consequências se estendem, contudo, para além das fronteiras das refinarias. Um alto teor de enxofre no combustível implica na liberação de compostos como dissulfeto de carbono, dimetilsulfeto e  $\text{SO}_2$  na atmosfera durante sua queima. O  $\text{SO}_2$  tem uma vida média de dois a quatro dias e reage fotoquimicamente para produzir a chuva ácida, alvo de intensos debates ambientalistas. Além disso, se presente nas camadas mais baixas da atmosfera, o dióxido de enxofre pode sofrer um processo de deposição úmida nas vias respiratórias, causando desde irritação até danos pulmonares severos.

### 2.5.2 Contaminantes nitrogenados

Onde quer que um combustível fóssil seja queimado, óxidos de nitrogênio serão formados. Tal fato se dá pela oxidação do nitrogênio que está naturalmente presente no combustível, assim como os sulfurados. Os compostos nitrogenados presentes no petróleo são, predominantemente, constituídos por famílias de alquilpiridinas, quinolinas, alquil e hidroxiquinolinas. Podem ser classificados em dois tipos principais: compostos neutros (indol, carbazol, pirróis) e compostos básicos (piridina, quinolina e acridina). Estruturalmente são compostos heterocíclicos aromáticos que se acumulam nas frações mais pesadas dos destilados do petróleo (Figura 2).

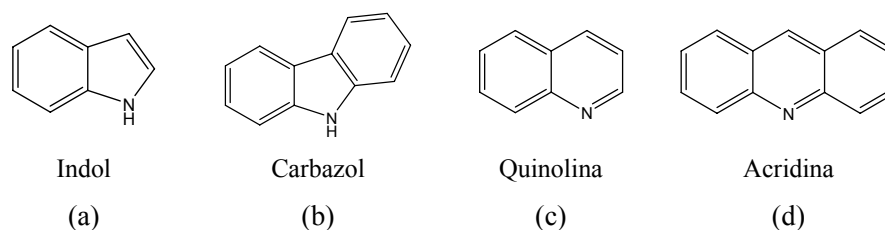


Figura 2 Representação das estruturas das principais classes de contaminantes nitrogenados presentes no petróleo. (a) e (b) compostos neutros e (c) e (d) compostos básicos

Ainda que a quantidade de compostos nitrogenados seja bastante inferior à de compostos sulfurados, os nitrogenados e amônia produzidos, principalmente durante o processo de reforma catalítica, constituem potenciais inibidores dos principais processos de tratamento dos óleos combustíveis, são responsáveis por problemas de desativação de catalisadores de craqueamento, formação de gomas, depósitos e alteração de cor em frações do petróleo.

Esses compostos também são considerados perigosos venenos para catalisadores automotivos, além da potencial liberação de óxidos de nitrogênio, os quais são tóxicos, após a combustão nos motores automotivos (TOMINAGA;

NAGAI, 2010). Além da conhecida chuva ácida, as espécies de NO<sub>x</sub> são os principais componentes requeridos para formação do *smog* fotoquímico em regiões contaminadas e, em sinergia com SO<sub>x</sub>, mesmo em baixas concentrações, podem causar alterações na vegetação, sendo este fato frequentemente observado em regiões industrializadas (KORIAKIN; PONVEL; LEE, 2010).

## **2.6 Processos de tratamento para remoção de sulfurados e nitrogenados do petróleo**

### **2.6.1 Hidrotratamento (HDT)**

O hidrotratamento consiste no processamento de frações do petróleo através da adição de hidrogênio, na presença de um catalisador, sob determinadas condições de temperatura (320 – 380 °C) e pressão (3 – 7 MPa). Trata-se de uma tecnologia consagrada na indústria do refino do petróleo, cujo início de aplicação remete ao período anterior à segunda guerra mundial (POLCK, 2010).

No cenário nacional, a importância do HDT torna-se mais crítica, com participação fundamental na estratégia de aumentar o processamento de petróleos nacionais: óleos com elevados teores de contaminantes (enxofre e nitrogênio) (MATSUMURA et al., 2005a). Dessa forma, as refinarias se vêem obrigadas a realizar consideráveis investimentos em seus parques de refino para adequá-los à demanda atual e futura dos principais agentes do refino do petróleo que estabeleceram, para 2009, o fornecimento de óleo diesel contendo 50 ppm de S e, previsto para o janeiro de 2013, uma redução para 10 ppm (CASTELO-BRANCO; SZKLO; SCHAEFFER, 2010).

O HDT tem como principal objetivo melhorar as propriedades da carga a ser processada, de maneira a enquadrá-la em especificações definidas para os produtos comerciais. Outra aplicação é proteger catalisadores de processos de refino subsequentes que possuam valores elevados e sejam sensíveis aos contaminantes focados nesse trabalho (nitrogenados para catalisadores que possuam sítios ácidos e enxofre para catalisadores de reforma). Para o processo de hidrodessulfurização, catalisadores de Co-Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> são altamente eficientes na remoção de tióis, contudo menos efetivos para derivados benzotiofênicos. Formado essencialmente por alquil-benzotiofenos substituídos e dibenzotiofenos, esses contaminantes são resistentes ao processo de HDT pela natureza do átomo de enxofre rodeado por anéis carbônicos, os quais dificultam a aproximação adequada até a superfície do catalisador, gerando então impedimentos espaciais no heteroátomo que tornam essa classe de compostos refratária ao HDS. Por essa razão, esse processo requer sempre condições reacionais severas de temperatura e pressão, catalisadores sempre mais ativos ou maiores tempos de residência, fatores que acarretam altos custos para as unidades das refinarias e tornariam o processo inviável para atingir os índices exigidos pela nova legislação (CASTELO-BRANCO; SZKLO; SCHAEFFER, 2010).

### **2.6.2 Oxitratamento (ODS)**

Uma alternativa interessante para se alcançar as novas especificações determinadas pela legislação é a dessulfurização oxidativa, oxidessulfurização ou processo de oxitratamento (ODS). Esse processo é tomado como o mais promissor e economicamente viável para se alcançar os índices de contaminantes futuramente exigidos pelas regulamentações ambientais.

Como alternativa complementar ao processo convencional de hidrodesulfurização, a oxidessulfurização leva a compostos oxidados que podem ser separados da fração oleosa. Nesse processo, compostos organossulfurados, particularmente aqueles refratários ao processo de HDS, são oxidados, levando a formação dos sulfóxidos e sulfonas correspondentes e esses produtos podem ser removidos por extração líquido-líquido (Figura 3).

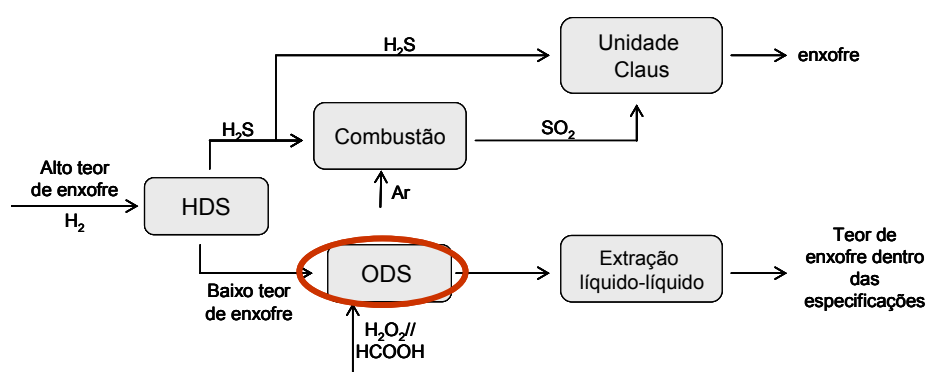


Figura 3 Representação esquemática do processo combinado HDT-ODS para redução dos níveis de enxofre para atingir as especificações desejáveis

Compostos de enxofre são conhecidos por serem fracamente mais polares que hidrocarbonetos de estrutura carbônica similar. Nesse contexto, os compostos oxidados, como as sulfonas ou sulfóxidos, são substancialmente mais polares que suas moléculas iniciais (Figura 4).

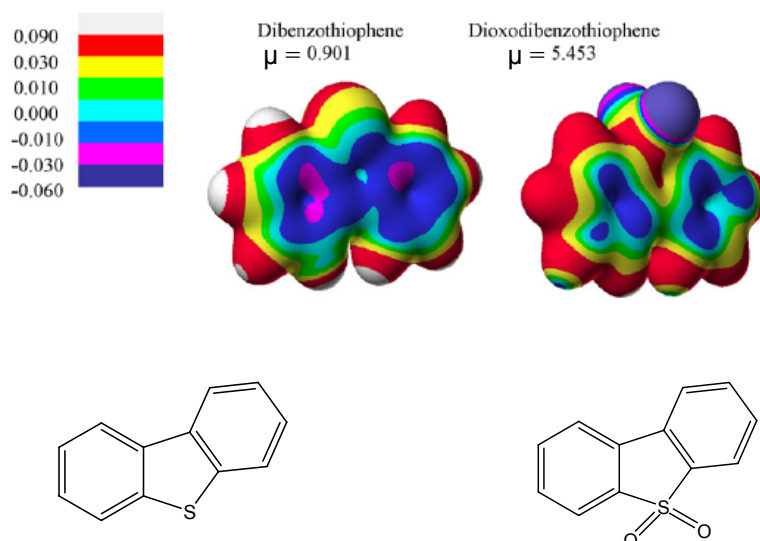


Figura 4 Potencial eletrostático das regiões com densidades de elétrons para o composto dibenzotiofeno e sua sulfona correspondente. O valor abaixo do nome refere-se a magnitude do momento de dipolo, em Debye  
Fonte: Ma, Zhou e Song (2007)

Isso permite a remoção seletiva dos S-compostos do meio hidrocarbônico por um processo combinado de oxidação seletiva e extração com solvente, como mostrado na Figura 5. Nesse processo, os radicais hidroxilas gerados pela decomposição do peróxido de hidrogênio reagem com ácido orgânico para formar os perácidos e oxidam os S-compostos aos produtos correspondentes.

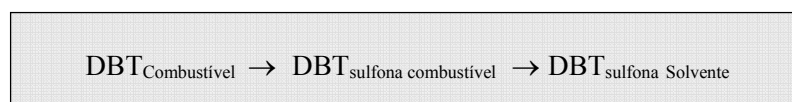


Figura 5 Esquema do processo de ODS para remoção dos contaminantes contendo enxofre em cargas de diesel

Usualmente o processo de ODS utiliza peróxido de hidrogênio como agente oxidante, uma vez que é não poluente e não corrosivo às unidades da refinaria, além de ter um custo acessível e ser comercialmente disponível. Vários estudos, entretanto, têm empregado o oxitratamento utilizando-se diferentes sistemas, incluindo a combinação de peróxido de hidrogênio com ácidos orgânicos, hidroperóxidos, ozônio e  $O_2$ . O ácido orgânico, como fórmico ou acético, atua como um co-catalisador que propicia o meio ácido favorável à formação de perácidos, os quais estabilizam a molécula de  $H_2O_2$ , minimizando sua decomposição a subprodutos como oxigênio e água (HAW et al., 2010; SHAHRANI et al., 2007). O processo de ODS pode ser reforçado com a presença de um agente de transferência de fase, que facilita a transferência dos reagentes e produtos entre as interfaces polar-apolar do meio reacional (CAMPOS-MARTIN; CAPEL-SANCHEZ; FIERRO, 2004).

Esses oxidantes, contudo, são mensuravelmente lentos na ausência de catalisadores. Assim, muitos autores citam a utilização de ácidos e sais em solução como promotores na ativação dos oxidantes (MONDAL et al., 2006). A reutilização dessas espécies fica limitada, devido à dificuldade de separação e recuperação de catalisadores presentes em fase homogênea.

Assim, a preparação de catalisadores para ativação das moléculas oxidantes, como  $H_2O_2$ , constitui o avanço mais desejável na tecnologia de ODS. Esse tipo de catalisador é de particular interesse sob o ponto de vista ambiental porque pode reduzir a lixiviação do metal além de favorecer a recuperação e reutilização do catalisador por períodos sucessivos de reações.

Diferentes compostos baseados em ferro têm sido mencionados como bons catalisadores para muitas reações de oxidação, dentre elas a própria sulfoxidação. Catalisadores baseados em óxidos de ferro de baixo custo, como goethitas, magnetitas e outras fases de ferro, foram empregados em processos de ODS com elevada capacidade de oxidação (CORNELL; SCHWERTMANN,



2003; DAIA et al., 2008; ZHOU et al., 2009). Estes catalisadores são eficientes e seletivos aos contaminantes do petróleo em diesel simulado, além da possibilidade de manter sua estabilidade para os experimentos de reciclagens sucessivas e reativação do catalisador.

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**SEGUNDA PARTE - ARTIGOS****ARTIGO 1****CATALYTIC OXIDATION OF SULFUR AND NITROGEN  
COMPOUNDS FROM DIESEL FUEL**

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## ABSTRACT

The oxidation of nitrogen or sulfur pollutants, using organic substrates as model compounds, was monitored with electrospray ionization mass spectrometry. Quinoline, dibenzothiophene and methylene blue were found to be oxidized through a successive hydroxylation mechanism. These results strongly suggest that highly reactive hydroxyl radicals, generated during the reaction of  $H_2O_2$  on the catalyst surface, are responsible for this oxidation, and confirm that the material is an efficient heterogeneous Fenton-like catalyst, which is able to eliminate around 90% of the sulfur molecules. This is, therefore, an important and useful tool for the elimination of refractory sulfur in the hydrotreatment process with potential application to meet future environmental legislation indexes. It is important to remember that only the heteroatom fraction is degraded, preserving the hydrocarbons of interest in the diesel flows. The catalyst showed activity in successive oxidation cycles presenting a high regeneration capacity.

Keywords: Pollutant. Oxidation process. Natural iron oxide. Electrospray ionization

## 1 Introduction

Nowadays the production of transportation fuels free from polluting compounds is required. It is well known that sulfur and nitrogen containing impurities are important sources of air pollution, besides being potential agents in the formation of acid rain. In this context there is a search for new technologies that can meet the indexes required by increasingly severe legislation. Europe imposed, in 2005, a reduction of sulfur levels from 350 to 50 mg L<sup>-1</sup> and a level lower than 10 mg L<sup>-1</sup> is expected for 2009. In the United States in 2006, the sulfur level was lowered from 500 to the current 15 mg L<sup>-1</sup>. In Brazil there is a strong trend for the reduction from the currently permitted 500–50 mg L<sup>-1</sup>, which is expected for 2009 [1].

The need for removal of these compounds transcends the environmental implications, particularly nitrogen containing compounds, which are present in petroleum derivatives. These compounds poison the hydrorefining catalysts. Sulfur containing compounds also promote corrosion in internal combustion engines due to sulfur oxiacid formation [2]. Hydro desulfurization (HDS) is the conventional hydrorefining process used to reduce the organosulfur compounds in the petroleum products. Depending on the refractory character of the organosulfur compounds, as well as on the nitrogen content, this technique requires severe operational conditions such as high H<sub>2</sub> pressure, elevated temperatures, severe space velocities, high maintenance investment and results in the reduction of the catalyst life-span. Moreover, substantial hydrogen consumption is required due to the hydrogenation of olefins and aromatics in order to reach the specifications of the fuel products. This hydrorefining process is efficient in the removal of thiols and aliphatic disulfides. However its efficiency is compromised due to the presence of aromatic thiophene, especially alkylated dibenzothiophenes, which present a sterical barrier to the sulfur, thus



making these compounds refractory for HDS. Therefore, substances like dibenzothiophene, 4-metildibenzothiophene and 4,6-dimetildibenzothiophene become challenge molecules for the removal of sulfur pollutants. An interesting alternative technology to reach the specifications which refer to fuel sulfur levels is the oxidative desulfurization process (ODS), also called oxidesulfurization [3–5]. Sulfur compounds, essentially those HDS-refractory, such as dibenzothiophenes (Fig. 1a), are oxidized to the corresponding sulfones (Fig. 1b) which can be removed by solvent extraction. The sulfur compounds are slightly polar than the hydrocarbons with similar structure. Therefore the oxidized sulfur compounds, such as sulfones or sulfoxides, allow their selective removal from the hydrocarbons by a combined process of selective oxidation and extraction with solvent or solid phase adsorption [6–16].

This study proposes to evaluate the oxidation of methylene blue, quinoline and dibenzothiophene as representative model compounds of heteroatom molecules present in diesel, aiming at a possible elucidation of the reaction mechanisms involved. The intermediates of the oxi-treatment process were identified by ESIMS and gas chromatography using a FID detector.

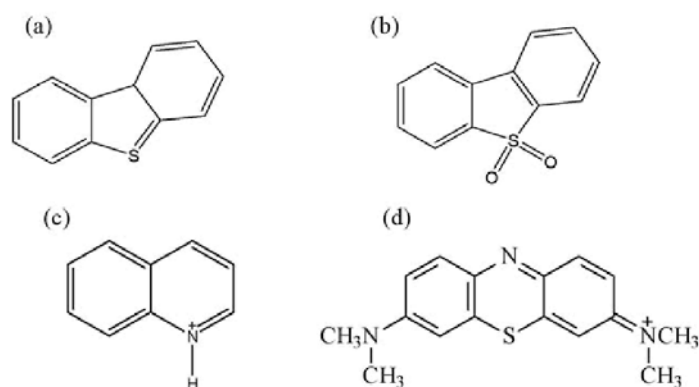


Figura 1 Structure of dibenzothiophene (a) and the corresponding sulfone (b) protonated quinoline (c) and methylene blue (d)

## 2 Materials and methods

### 2.1 Catalyst preparation and characterization

Limonite ore samples (45–46 wt% of Fe), from mines located in Goiás State (Central Brazil), were ground and sieved below 100 mesh (Tyler series), dried for 1 h at 120 °C and then submitted to thermal treatment under H<sub>2</sub> flow (100 mL min<sup>-1</sup>) at 350 °C for 120 min (called sr120), aiming to form Fe<sup>2+</sup> reduced sites from goethite phase (Fe<sup>3+</sup>). Natural and reduced limonite samples were analysed by room temperature Mössbauer spectroscopy (<sup>57</sup>Co/Rh source; isomer shifts are quoted relative to the  $\alpha$ -Fe) and TPR experiments were performed in a CHEMBET 3000 equipment with 20 mg sample under 25 mL min<sup>-1</sup> H<sub>2</sub> (5%)/N<sub>2</sub> with heating rate of 10 °C min<sup>-1</sup>.

### 2.2 Oxidative reactions

The catalytic activity of the materials was tested for their effectiveness on the oxidation of methylene blue (10 mL of 50 mg L<sup>-1</sup> stock solution), quinoline (10 mL of 10 mg L<sup>-1</sup> stock solution) or dibenzothiophene (10 mL of 50 mg L<sup>-1</sup> stock solution) in an oxidant solution comprised of equimolar amounts of H<sub>2</sub>O<sub>2</sub> (30%, v/v) and HCOOH (97 mmol). In the case of the dibenzothiophene (DBT) the solution was prepared utilizing hexane as solvent. The oxidant solution was prepared 10 min before mixing with the dye and limonite. The catalytic tests at pH 6.0 (natural pH of the H<sub>2</sub>O<sub>2</sub> solution) was carried out with a total volume of 10 mL (9.9 mL of the pollutant solution and 0.1 mL of the H<sub>2</sub>O<sub>2</sub>/HCOOH equimolar solution) and 10 mg of the oxide catalyst. The reactions were monitored by GC-FID (in the case of DBT) and ESI-MS (in the case of quinoline or methylene blue dye) measurements. All the reactions were

carried out in triplicate under magnetic stirring in a recirculating temperature controlled bath kept at  $25 \pm 1$  °C.

### 2.3 GC-FID study

The products of the DBT oxidation were analyzed by gas chromatography (Shimadzu, model 2010 equipped with a FID detector). The analyses were made in a DB-5 column (30 m X 0.25 mm X 0.25  $\mu$ m). Helium was used as carrier gas at a flow of 0.57 mL min<sup>-1</sup>. The heating ramp used was: 100 °C for 3 min, heating rate of 6 °C min<sup>-1</sup> to 275 °C and remaining there for 10 min [9]. The analyses were also monitored by total organic carbon (TOC, Shimadzu-TOC-VCPH).

### 2.4 ESI-MS study

In an attempt to identify the intermediates formed, the methylene blue dye and quinoline decomposition were monitored using an electrospray ion source an Agilent ion trap mass spectrometer (ESI-MS). The reaction samples were analyzed by introducing aliquots into the ESI source with a syringe pump at a flow rate of 5  $\mu$ L min<sup>-1</sup>. The spectrum obtained were an average of 50 scans of 0.2 s. Typical ESI-MS conditions were as follows: heated capillary temperature, 150 °C; dry gas (N<sub>2</sub>) at a flow rate of 5 L min<sup>-1</sup>; spray voltage 4 kV; capillary voltage 25 V; tube lens offset voltage, 25 V. For ESI-MS/MS, the parent ion of interest was first isolated by applying an appropriate waveform across the end cap electrodes of the ion trap to resonantly eject all trapped ions, except those ions with m/z ratio of interest. The isolated ions were then subjected to a supplementary AC signal, to resonantly excite them to cause collision-induced dissociation (CID) using helium as a reagent gas. The collision energy was set to a value in which ions were produced in measurable abundance.

### 3 Results and discussion

#### 3.1 Characterization

##### 3.1.1 Temperature programmed reduction (TPR) and Mössbauer Spectroscopy

The TPR analysis is an important tool for elucidation of the content of reduced phase in the catalyst. Fig. 2a shows the TPR profile for natural limonite and the sR120 catalyst. The TPR clearly shows the surface enrichment with  $\text{Fe}^{2+}$  by decreased  $\text{H}_2$  consumption indicated by the first peak, centered near  $300^\circ\text{C}$  and related to limonite reduction to magnetite, as given by Scheme (1):

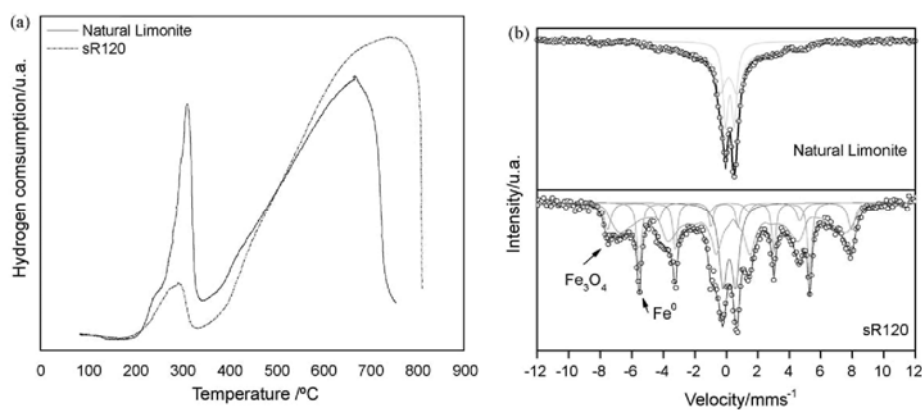
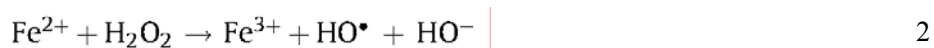


Figure 2 TPR profile for natural limonite and sR120 submitted to thermal treatment (a) and the Mössbauer spectra for natural limonite and sR120 (b)

The second peak at a higher temperature and centered around 800 °C is related to the formation of metallic iron ( $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}^0$ ) [11]. The TPR profile still shows a small quantity of oxidized phase from the remaining thermal treatment, possibly related to the maintenance of the internal structure of the material as  $\text{Fe}^{3+}$  from goethite. It is important to mention that the natural limonite treatment temperature (350 °C) was determined after obtaining the TPR profile, which suggests the optimal temperature for partial reduction of limonite and gives the best catalyst for the production of hydroxyl radicals.

Mössbauer spectroscopy is a fundamental technique for studying iron oxides because it provides information on the nature of phases and on the neighboring atoms. The iron phases present in natural limonite and in the sR120 material after the treatment with  $\text{H}_2$  were identified by Mössbauer spectroscopy at room temperature. The spectra are shown in Fig. 2b. The natural limonite spectrum shows a central accentuated doublet typical for a lower particle size [17,18]. The activity of this material can be related to small goethite crystals present in the limonite. On the other hand, the sR120 material shows the characteristic iron oxide sextet with magnetic ordering. The Mössbauer parameters for the thermally treated material show the presence of different iron phases, with the appearance of sites A and B showing the magnetite ( $\text{Fe}_3\text{O}_4$ ) formation. This formation is desirable because this phase has part of its iron as  $\text{Fe}^{2+}$ , which catalyzes the  $\text{H}_2\text{O}_2$  decomposition improving the material's catalytic activity when compared to natural limonite (Scheme (2)). Moreover, the Mössbauer spectrum shows the presence of metallic iron as indicated in Fig. 2b. This result shows that the thermal treatment based on the TPR analyses can produce a material with reduced phases of the iron oxides and according to other authors the presence of  $\text{Fe}^0$  improves the catalytic activity in these reaction systems by the regeneration of  $\text{Fe}^{2+}$  site after the reaction with  $\text{H}_2\text{O}_2$  to produce hydroxyl radical.



## 3.2 Catalytic activity

### 3.2.1 Quinoline oxidation

The efficiency of the catalyst in the oxidation of organic nitrogen compounds was evaluated by the oxidation of quinoline used as a model compound. The products were monitored by ESIMS. Fig. 3 shows the standard quinoline mass spectrum with the  $m/z = 130$  ratio ( $\text{MM} = 129 + \text{H}^+ = 130$ ) and the same compound after the reaction with the oxidizing agent hydrogen peroxide/ formic acid in the presence of the catalyst.

The quinoline oxidation by catalyst sR120 with the oxidant formed intermediate species with  $m/z = 146, 162$  and  $178$  ratio (Fig. 3), which suggests partial oxidation of the quinoline, as shown by the molecular structures proposed. These signals refer to the first hydroxylated ring, which confirms hydroxyl radical formation and shows the potential catalytic action of the materials in a Fenton-like system [12]. The presence of the hydroxyl groups favors the separation process by liquid–liquid extraction from the apolar matrix (diesel), since the properties of the new compounds formed by diesel flow oxidation differ substantially from the original compound. The mass spectra obtained showed a quinoline removal capacity ( $m/z = 130$ ) close to 90% of the original content after 360 min of reaction. The oxidation does not compromise the hydrocarbons of interest which comprise the diesel.

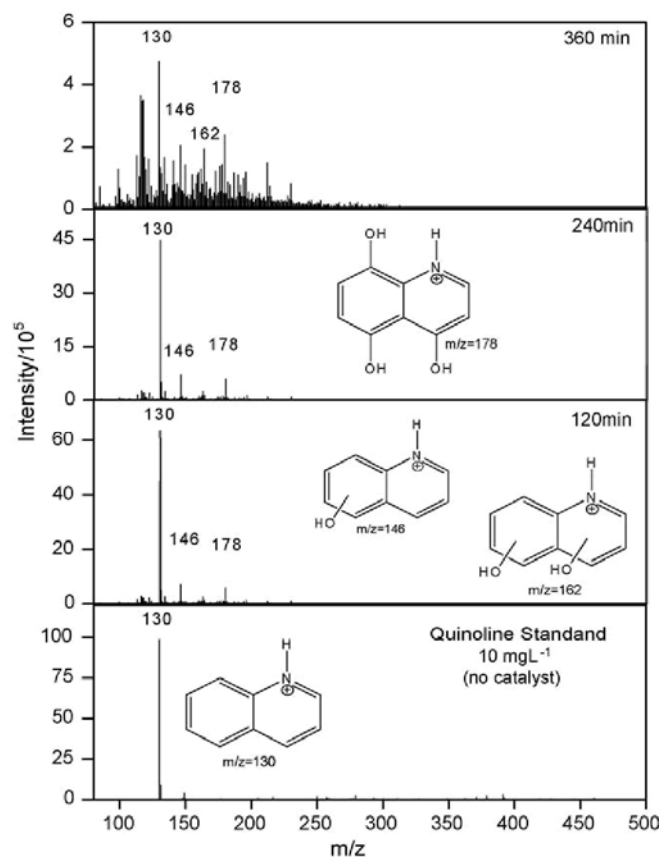


Figure 3 Kinetics of quinoline oxidation monitored by mass spectrometry in the presence of sR120 and  $\text{H}_2\text{O}_2/\text{HCOOH}$

### 3.2.2 Dibenzothiophene oxidation

The sulfur compounds present in petroleum, especially alkylated dibenzothiophenes, present one of the major problems for the petroleum sector. Given the necessity of removal of these compounds, the sR120 catalyst efficiency was evaluated in the dibenzothiophene oxidation, employed as the pollutant sulfur model compound, with  $\text{H}_2\text{O}_2/\text{HCOOH}$ . The oxidation was monitored by GC-FID. The oxidation results are shown in Fig. 4a.

The model mixture for the synthetic diesel showed one peak related to DBT, with a retention time of approximately 6.7 min. After the start of the oxidation treatment, it can be observed that this compound is removed, with progressive sulfone formation during the reaction time. After 240 min, approximately 96% of the DBT was oxidized and sulfone being the principal product formed. Fig. 4b shows the conversion percentages calculated from the chromatographic peaks. These results show clearly that it is possible to get an elevated removal of sulfur compounds, such as dibenzothiophene, using thermally treated limonite and  $\text{H}_2\text{O}_2/\text{HCOOH}$ . In the absence of the catalyst under the same conditions, no significant conversion is observed. To determine the total oxidation (mineralization) of the components of the DBT mixture, a total organic carbon analysis was done. The results are plotted in Fig. 4b.

The data show that virtually all sulfur content was converted to the correspondent sulfone and (Fig. 4b) that there was no significant alteration in the quantity of organic material present, given by TOC variation. According to this evaluation, after the 240 min necessary for sulfur compound degradation, only approximately 24% of the initial organic content was removed. These results suggest that only the heteroatom fraction is attacked by radicals maintaining the hydrocarbon of interest and therefore conserving the energy potential of the diesel. In general the physical and chemical properties of sulfones are significantly different from those of petroleum. Therefore, the sulfones can be easily removed by conventional separation methods.



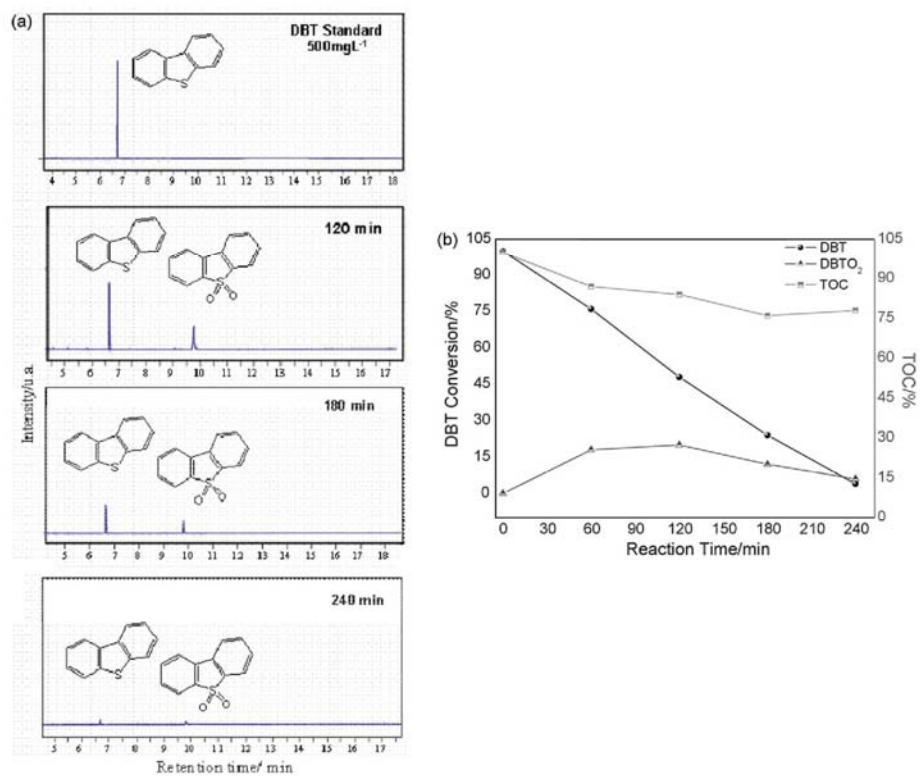


Figure 4 Dibenzothiophene oxidation kinetics monitored by GC-FID (a) and the sR120 catalyst efficiency in DBT conversion and monitored by the total organic carbon (b). Reaction at 298 K and atmospheric pressure. Data: DBT: dibenzothiophene, DBTO<sub>2</sub>: dibenzothiophene sulfone, TOC: total organic carbon

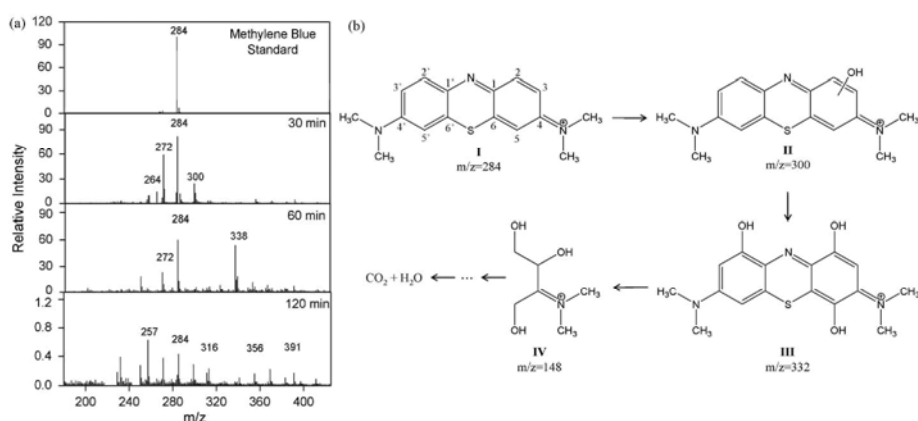


Figure 5 Mass spectra by electrospray ionization applied to methylene blue oxidation using the sR120 catalyst (a) and an illustrating diagram of the possible intermediates formed by methylene blue oxidation (b)

### 3.2.3. Methylene blue oxidation

The presence of the catalyst in the oxidation of methylene blue was investigated, considering that it is a model molecule for nitrogen and sulfur contamination. The methylene blue discoloration was monitored by coupled electrospray mass spectrometric analysis and shows that various reaction intermediates are formed (Fig. 5a) which strongly support the participation of the hydroxyl radical in this reaction.

In the methylene blue discoloration by sR120 limonite using the H<sub>2</sub>O<sub>2</sub>/HCOOH system, many organic intermediates can be observed after 30 min of reaction (Fig. 5a). The results confirm again the hydroxyl radical formation and a degradation via a Fenton-like mechanism due to the signal at m/z = 300, referring to the first hydroxylation ring. After 120 min, almost 100% discoloration is observed, with appearance of signals related to the methylene blue structure, as shown by m/z = 356. The successive hydroxylation leads to ring tension followed by ring-opening reactions as shown by the appearance of

intermediates with  $m/z$  ratios lower than 284. Fig. 5b presents the possible structures responsible for the signals observed in the reaction with the sR120 catalyst. The sR120 activity in terms of methylene blue decomposition can be related to reduce iron sites, available for electron transfer, as well as the metallic iron on the surface, because this phase can act as an efficient electron donor, which is able to regenerate the oxidized sites of the active phase ( $\text{Fe}^{2+}$ ). Theoretical calculations recently published [9] show the hydroxyl position in the methylene blue structure and the structure of the degradation products with lower mass that are formed soon after oxidation. So it can be found that the hydroxyls enter in the 2',2 and 5 ring positions. These results are very important because they help to understand the mechanism involved in the oxidation of a diesel flow.

The iron leaching during all reactions was evaluated by atomic absorption analysis, using a Varian AA 110 equipment. We found 0.055 and 0.067  $\text{mg L}^{-1}$  of iron leaching from the samples of natural limonite and sr120, respectively. We observed that this iron concentration does not lead to a significant homogeneous Fenton reaction.

#### 4 Conclusions

The chemical activity of  $\text{Fe}^{3+}$  on the surface of synthetic goethite can be strongly modified by treating it with  $\text{H}_2$ , to form other chemically reduced iron oxides. The resulting material shows a remarkable effect on the oxidation of quinoline in aqueous medium, with 90% degradation after 360 min reaction. The intermediates evaluated by ESI-MS studies and calculations of the Gibbs free energy of the quinoline oxidation showed successive hydroxylations. The degradation ability is enhanced by the formation of  $\text{Fe}^{2+}$  sites on the iron oxide surface after the thermal treatment under a  $\text{H}_2$  atmosphere, indicating that it

reacts with  $\text{H}_2\text{O}_2/\text{HCOOH}$  via a Fenton-like mechanism, involving  $\cdot\text{OH}$  radicals.

The sR120 catalyst shows an excellent capacity to convert dibenzothiophene to its sulfone, being efficient at room temperature and atmospheric pressure. The catalyst is able to remove most of the sulfur and would be a useful tool to eliminate the HDS refractory sulfur molecules with potential application to satisfy required environmental legislation indexes. This might be a real possibility for an increase of scale and a university-industry technology transfer.

### **Acknowledgment**

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**ARTIGO 2****BRAZILIAN LIMONITE FOR THE OXIDATION OF QUINOLINE:  
HIGH ACTIVITY AFTER A SIMPLE MAGNETIC SEPARATION**

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### ABSTRACT

Natural limonite, after a simple magnetic separation, was investigated as a low-cost catalyst in a Fentonlike system. The materials were characterized with temperature-programmed reduction (TPR), infrared spectroscopy, N<sub>2</sub> adsorption/desorption, and <sup>57</sup>Fe Mossbauer spectroscopy. Results showed that the main iron oxide phases in the materials were goethite ( $\alpha$ -FeOOH) and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) before and after the magnetic separation, respectively. The catalytic tests were carried out using quinoline as a model compound because it simulates the behavior of an important class of pollutants present in the fuel, i.e., nitrogen-containing compounds from contaminated petroleum. Quinoline was found to be oxidized through a successive hydroxylation mechanism. These results strongly suggest that highly reactive hydroxyl radicals, generated during the reaction involving H<sub>2</sub>O<sub>2</sub> on the catalyst surface, are responsible for this oxidation and confirm that the material is an efficient heterogeneous Fenton-like catalyst.

## 1 Introduction

The Fenton process, involving hydrogen peroxide and  $\text{Fe}^{2+}$  in solution, is one of the most active systems for the oxidation of organics in water. This reactivity is due to the in situ generation of a highly oxidant species, i.e., the hydroxyl radical.<sup>1</sup>

To minimize the amount of the forming ferric hydroxide sludge in the homogeneous reaction,<sup>2</sup> the active heterogeneous redox processes are increasingly replacing the homogeneous systems in the catalysis research and in some technological applications because they offer some advantages, such as no sludge formation, operation at near neutral pH, and the possibility to recycle the iron promoter.<sup>3-6</sup> Thus, some iron oxides, such as magnetite (ideal formula,  $\text{Fe}_3\text{O}_4$ ), hematite ( $\alpha\text{Fe}_2\text{O}_3$ ), and goethite ( $\alpha\text{FeOOH}$ ) or natural iron oxides, such as limonite ore, have been used instead of  $\text{Fe}^{2+}$  solutions.<sup>7-10</sup>

Limonite is a natural ore comprised of hydrated iron (III) oxides, mostly made up of goethite ( $\alpha\text{FeOOH}$ ). Recently, a Fenton-like system that combines  $\text{H}_2\text{O}_2$  with an organic acid (e.g.,  $\text{HCOOH}$ ) using limonite ore as the catalyst was

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<sup>1</sup> Souza, W. F.; Guimarães, I. R.; Oliveira, L. C. A.; Guerreiro, M. C.; Guarieiro, A. L. N.; Carvalho, K. T. G. J. *Mol. Catal. A: Chem.* 2007, 278, 145–151.

<sup>2</sup> Chou, S.; Huang, C. *Chemosphere* 1999, 38, 2719–2731.

<sup>3</sup> Kwan, W. P.; Voelker, B. M. *Environ. Sci. Technol.* 2002, 36, 1467–1476.

<sup>4</sup> Souza, W. F.; Guimarães, I. R.; Guerreiro, M. G.; Oliveira, L. C. A. *Appl. Catal., A* 2009, 360, 205–209.

<sup>5</sup> Silva, A. C.; Oliveira, D. Q. L.; Oliveira, L. C. A.; Anastacio, A. S.; Lopes, J. H.; Carvalho, W. P. C. *Appl. Catal., A* 2009, 357, 79–84.

<sup>6</sup> Arends, I. W. C. E.; Sheldon, R. *Appl. Catal., A* 2001, 212, 175–187.

<sup>7</sup> Menini, L.; Silva, M. J.; Lelis, M. F. F.; Fabris, J. D.; Lago, R. M.; Gusevskaya, E. V. *Appl. Catal., A* 2004, 269, 117–121.

<sup>8</sup> Ferraz, W.; Oliveira, L. C. A.; Dallago, R.; Conceição, L. *Catal. Commun.* 2007, 8, 131–134.

<sup>9</sup> Kaneko, T.; Sugita, S.; Shimasaki, K.; Makino, E.; Silalahi, L. H. *Fuel* 2002, 81, 1541–1549.

<sup>10</sup> Li, L.; Morishita, K.; Takarada, T. *Fuel* 2007, 86, 1570–1576.



developed.<sup>8-11</sup> This combined aqueous slurry system is able to perform oil-phase oxidation and simultaneous removal of unstable hydrocarbons and heteroatom compounds from hydrocarbon streams, such as petroleum distillates.<sup>12</sup> However, the mechanism of Fenton oxidant formation was not fully understood. In this paper, kinetic studies and online reaction monitoring with electrospray ionization-mass spectrometry (ESI-MS) allow for the tracing of intermediate formation and may model the main chemical mechanism involved. The reactivity of a heterogeneous Fenton system based on limonite after a magnetic separation process was studied, particularly focusing on the effect of the magnetic part to degrade quinoline in aqueous medium. This would address some interesting applications, such as the removal of nitrogen-containing compounds from petroleum-contaminated water, from industrial effluents.

## 2 Experimental Section

### 2.1 Catalyst Preparation and Characterization

Brazilian natural limonite ore, provided by Petrobrás SA, was employed as a catalyst. Table 1 shows the elemental analysis of the limonite ore, indicating an iron content of about 46 wt %. The limonite ore is a fine orange powder, in which the predominant component is goethite ( $\alpha\text{FeOOH}$ ). It is extremely soft and easily pulverized. Table 1 summarizes the properties of the limonite.

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<sup>11</sup> Guimarães, I. R.; Oliveira, L. C. A.; Queiroz, P. F.; Ramalho, T. C.; Pereira, M.; Fabris, J. D.; Ardisson, J. D. *Appl. Catal.*, A 2008, 347, 89–93.

<sup>12</sup> Souza, W. F. Process for the extractive oxidation of contaminants from raw fuel streams catalyzed by iron oxides. U.S. Patent 0108252.

Table 1 Properties of the Brazilian Limonite

	Brazilian natural limonite
total Fe (wt %)	45.5
Si (wt %)	1.33
Al (wt %)	4.29
Ca (wt %)	0.02
Mg (wt %)	1.32
Cr (wt %)	4.87
Ni (wt %)	0.63
surface area ( $\text{m}^2 \text{g}^{-1}$ )	57.0

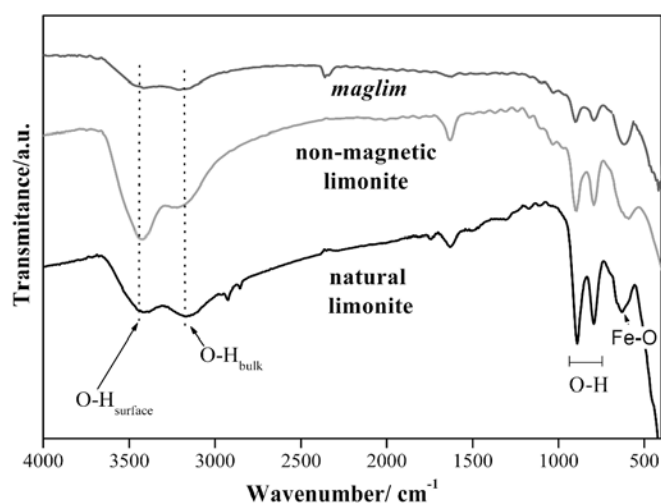


Figure 1 Infrared spectra of the limonite samples

During the sample preparation, the limonite powder (100-mesh under, Tyler series) was mixed with distilled water (1:10, wt/wt) and separated by the magnetic flocculation process. The magnetic material separated (called maglim) corresponding to approximately 67% of the material was dried at 80 °C for 12 h.

The materials were characterized by physical  $\text{N}_2$  adsorption/desorption at 77 K (using an AUTOSORB-1 instrument from Quantachrome). The specific surfaces were derived from  $\text{N}_2$  adsorption isotherms by means of the Brunauer - Emmett - Teller (BET) equation. The pore size distributions were determined

using the density functional theory (DFT). Mossbauer spectroscopy experiments were carried out at room temperature in a spectrometer model MA250 with a  $^{57}\text{Co/Rh}$  source, using an  $\alpha\text{Fe}$  foil as a reference. Data were stored in a 512 channel-MCS memory unit, with the Doppler velocity ranging between about  $\pm 10\text{mms}^{-1}$ . Temperature-programmed reduction (TPR) experiments were performed in a CHEMBET 3000 equipment with  $40\text{ mg}_{\text{sample}}$  under  $80\text{ mL min}^{-1}$   $\text{H}_2$  (5%)/ $\text{N}_2$  with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$ . The natural limonite, nonmagnetic limonite, and maglim (magnetic part) samples were analyzed by Fourier transform infrared spectroscopy (FTIR) using an Excalibur FTS3000 from Bio Rad at  $4\text{ cm}^{-1}$  resolution with an average of 18 scans, from  $400$  to  $4000\text{ cm}^{-1}$ . The samples were pressed into small discs using a pure KBr matrix. Total organic carbon (TOC) measurements were carried out in TOC 500A Shimadzu.

## 2.2 Catalytic Tests

The catalytic properties of the maglim were tested via hydrogen peroxide decomposition and oxidation of quinoline. The hydrogen peroxide (VETEC, 50%) decomposition was carried out with  $7.0\text{ mL}$  solution at  $[\text{H}_2\text{O}_2]=2.7\text{ mol L}^{-1}$  (natural pH of the  $\text{H}_2\text{O}_2$  solution), with  $30.0\text{ mg}$  of catalyst. The activity was measured by the formation of gaseous  $\text{O}_2$  in a simple volumetric glass system based on a buret connected to the reaction system. This system was magnetically stirred at room temperature ( $25 \pm 1\text{ }^\circ\text{C}$ ).

The quinoline oxidation tests were carried out using  $9.9\text{ mL}$  of a standard solution ( $10\text{ mg L}^{-1}$ ) in water at pH 6.0. A total of  $10\text{ mg}$  of the catalyst was used as well as  $\text{H}_2\text{O}_2$  ( $0.1\text{ mL}$ ) as the oxidant. Quinoline solution ( $10.0\text{ mL}$  from a  $100.0\text{ mg L}^{-1}$  stock solution) oxidation was monitored using ESI-MS, in an attempt to identify the intermediately formed chemical species. The reaction samples were analyzed by introducing aliquots into the ESI source with a

syringe pump at a flow rate of  $5 \mu\text{L min}^{-1}$ . The spectral data thus obtained were averaged from 50 scans of 0.2 s each. Typical ESI-MS conditions were as follows: heated capillary temperature,  $150 \text{ }^\circ\text{C}$ ; dry gas ( $\text{N}_2$ ) at a flow rate of  $5 \text{ L min}^{-1}$ ; spray voltage, 4 kV; capillary voltage, 25 V; and tube lens offset voltage, 25 V. For ESI-MS/MS, the parent ion of interest was first isolated by applying an appropriate waveform across the end-cap electrodes of the ion trap to resonantly eject all trapped ions, except those ions with a  $m/z$  ratio of interest. The isolated ions were then subjected to a supplementary AC signal, to resonantly excite them to cause collision-induced dissociation (CID) using helium as a reagent gas.

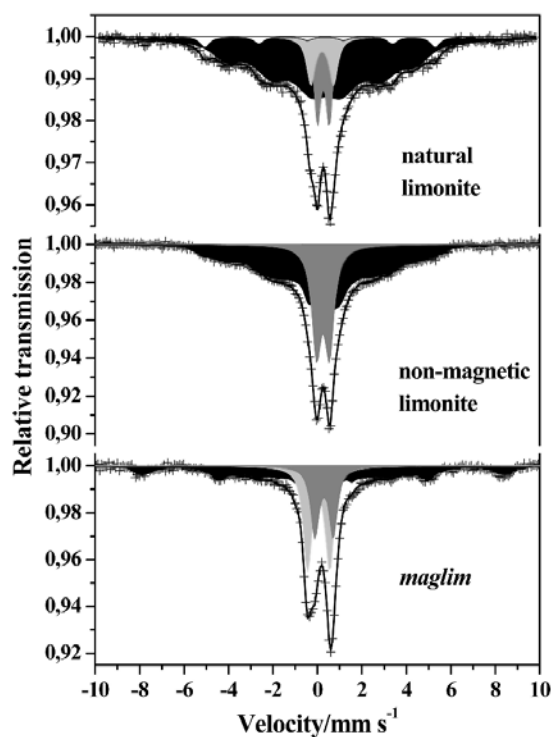


Figure 2 Mössbauer spectra for natural limonite, maglim, and nonmagnetic limonite

Table 2 Room-Temperature ( $\sim 298$  K) Mossbauer Parameters for Natural Limonite before and after Magnetic Separation<sup>a</sup>

sample	<sup>57</sup> Fe site	$\delta$ (mm s <sup>-1</sup> )	$\epsilon, \Delta$ (mm s <sup>-1</sup> )	$B_{\text{hf}}$ (T)	RA (%)
natural limonite	Gt	0.29(2)	-0.25(4)	32.1(2)	71(3)
	Gt	0.24(3)	-0.25(5)	26.4(4)	5(2)
	Fe <sup>3+</sup>	0.273(5)	0.53(1)		14(1)
	Fe <sup>3+</sup>	0.217(9)	1.03(3)		10(2)
nonmagnetic limonite	Gt	0.33(1)	-0.25**	25.7(2)	68(2)
	Fe <sup>3+</sup>	0.368(3)	0.576(7)		32(1)
maglim	Mh	0.31(2)	0**	50.76(3)	41(2)
	Fe <sup>3+</sup>	0.169(4)	1.00(7)		35(1)
	Fe <sup>3+</sup>	0.416(6)	0.83(1)		24(1)

<sup>a</sup>  $\delta$ , isomer shift relative to  $\alpha\text{Fe}$ ;  $\epsilon$ , quadrupole shifting;  $\Delta$ , quadrupole splitting;  $B_{\text{hf}}$ , magnetic hyperfine field; RA, relative sub-spectral area; Gt, goethite; Mh, maghemite

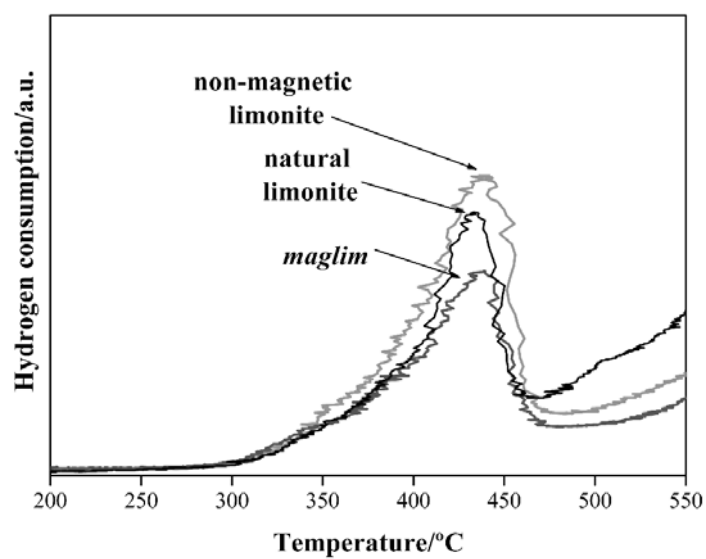


Figure 3 TPR profile of the limonites

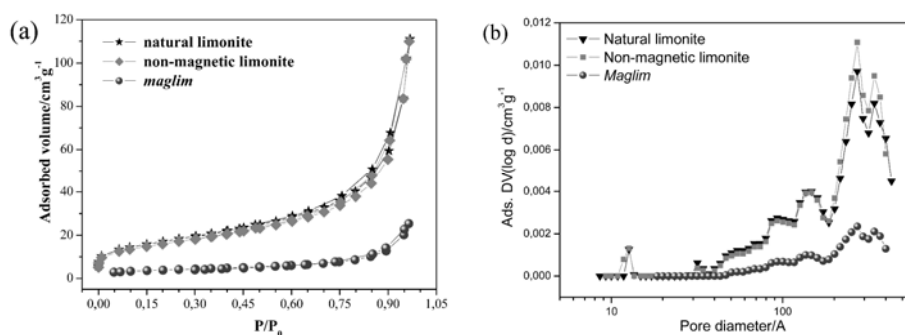


Figure 4 (a) Isotherms of N<sub>2</sub> adsorption/desorption and (b) pore size distribution for the natural limonite before and after magnetic separation

### 3 Results and Discussion

#### 3.1 Characterization of Limonites

Figure 1 shows the infrared spectra of limonite samples. The characteristic bands of  $\alpha$ -FeOOH are quite visible for all materials. For natural limonite, an intense band was observed at 3163 cm<sup>-1</sup> because of the bulk O-H stretching vibrations. The band at approximately 3425 cm<sup>-1</sup> can be attributed to the surface hydroxyl groups and adsorbed water. The typical signals for the goethite phase are intense bands at 805 and 893 cm<sup>-1</sup>, which vibrate in and out of the plane, respectively, and are important diagnostic bands, characteristic of goethite. The band at about 625 cm<sup>-1</sup> is due to Fe-O symmetric stretch vibration in the plane.<sup>13</sup>

Mossbauer spectra for these materials are presented in Figure 2. At 298 K, Mossbauer spectra for natural limonite samples are characterized by two intense doublets and two sextets, with one of these sextets being much more

<sup>13</sup> Oliveira, L. C. A.; Ramalho, T. C.; Souza, E. F.; Gonc-alves, M.; Oliveira, D. Q. L.; Pereira, M. C.; Fabris, J. D. *Appl. Catal., B* 2008, 83, 169–176.

intense and broad. These doublets are characteristic of samples likely formed by iron hydroxide grains with small particle size because of the superparamagnetism phenomena. The superparamagnetic behavior of goethite has been attributed to both a reduced magnetic coupling between the crystallites and a relatively high concentration of vacancy defects.<sup>14</sup> The most intensive and broad sextet presented a hyperfine field of 32.1(2) T, indicating the presence of a poorly crystallized goethite phase.

Mossbauer parameter analysis (Table 2) suggests that the nonmagnetic limonite is composed of poorly crystallized goethite too, as well as in the natural limonite, and mainly a dispersed  $\text{Fe}^{3+}$  phase, evidenced by one intense doublet. On the other hand, the maglim sample is composed of maghemite, which is the magnetic phase, and also two different dispersed  $\text{Fe}^{3+}$  phases.

The TPR profile of the limonites (Figure 3) presented a peak centered at 440 °C. This peak is a typical signal related to the formation of the magnetite phase ( $\text{Fe}_3\text{O}_4$ ), which is a typical iron oxide with structural  $\text{Fe}^{2+}$ , from oxidized phases. The material obtained after magnetic separation, the maglim sample, shows a decrease in the oxidized iron oxide phase according to Mossbauer data.

Figure 4 presents the isotherms of  $\text{N}_2$  adsorption/desorption (Figure 4a) and pore size distribution (Figure 4b) for the limonites.

All of the isotherms present a low adsorption at all relative pressures, characteristic of nonporous materials, where the adsorption branch resembles that of a type II isotherm in the International Union of Pure and Applied Chemistry (IUPAC) classification. This result shows that the magnetic part presents the lowest specific surface area compared to natural limonite and the nonmagnetic part suggests the presence of more compacted material. In fact, the materials showed specific surface areas of 14, 53, and 57  $\text{m}^2 \text{g}^{-1}$  for maglim,

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<sup>14</sup> Cornell, R. M.; Schwertmann, R. M. *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*; Wiley-VCH: Weinheim, Germany, 2003; p 664.

nonmagnetic limonite, and natural limonite, respectively. Figure 4b presents the pore size distributions for the limonites, showing a poor porous structure of these materials.

### 3.2 Catalytic Tests

The catalytic activity of the limonite samples was studied using two reactions: (i) the H<sub>2</sub>O<sub>2</sub> decomposition (Figure 5) and (ii) the oxidation of quinoline with H<sub>2</sub>O<sub>2</sub> in aqueous medium.

It is observed that maglim favored the H<sub>2</sub>O<sub>2</sub> decomposition, probably because of the presence of the maghemite phase on the surface, as observed by Mossbauer spectroscopy. In fact, the maghemite is an iron oxide phase widely used in the hydrogen peroxide decomposition to produce the hydroxyl radical in the heterogeneous Fenton reaction because the redox reaction involving the Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub> is facilitated.<sup>5</sup> The hydroxyl radical generation depends upon the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup> on the iron oxide surface, as shown in eqs 1 and 2 and illustrated in Figure 6.<sup>5</sup>



The ESI-MS spectrum obtained for the quinoline solution ( $m/z_{\text{quinoline}} = 129 + \text{H}^+ = 130$ ) shows only a strong signal at  $m/z$  130, which is related to the protonated quinoline (Figure 7a). After 120 min of reaction with maglim and hydrogen peroxide, some new  $m/z$  signals appear, specifically at 146, 162, and 178, which may indicate hydroxylation steps (Figure 7b). Other  $m/z$  signals appear ( $m/z$  92, 100, and 120) observed at 360 min of reaction, likely related to



quinoline oxidation intermediates,<sup>15</sup> also suggesting that the structural ring was somehow fragmented. These results also indicate that that Fenton oxidation mechanism (\*OH attack) is taking place to a significant extent.<sup>15</sup> It is interesting to observe that, using the natural and nonmagnetic materials, there were no significant catalytic activity, according to the H<sub>2</sub>O<sub>2</sub> decomposition data, confirmed by the presence of a more intense signal m/z 130 at 360 min of reaction related to the quinoline as showed in the ESI-MS analyses in Figure 8.

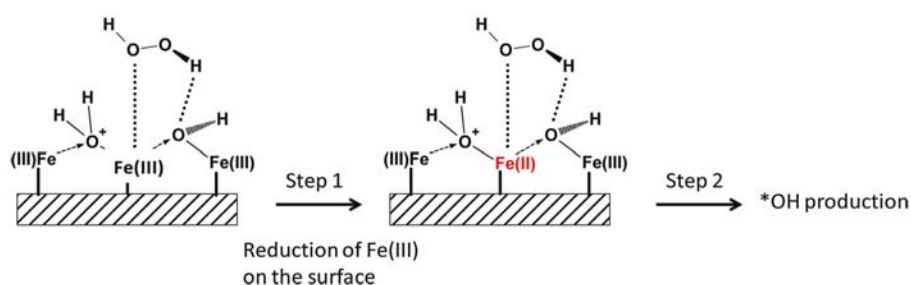


Figure 6 Scheme for hydroxyl radical generation after the iron reduction on the maghemite surface

<sup>15</sup> Lago, R. M.; Moura, F. C. C.; Augusti, R.; Araujo, M. H.; Dalmazio, I.; Santos, L. S.; Eberlin, M. N. *Rapid Commun. Mass Spectrom.* 2006, 20, 1859.

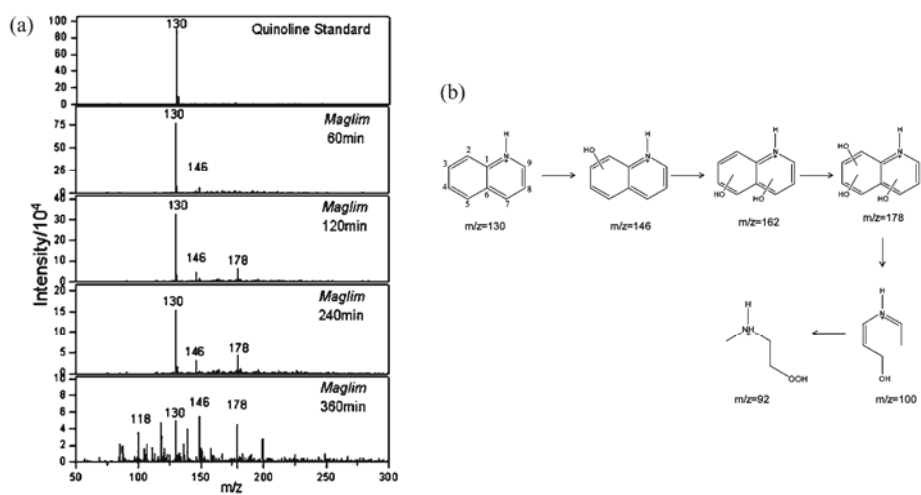


Figure 7 (a) ESI mass spectrum in the positive-ion mode for monitoring the oxidation by the maglim/H<sub>2</sub>O<sub>2</sub> system of quinoline in water and (b) scheme with proposed reaction intermediates

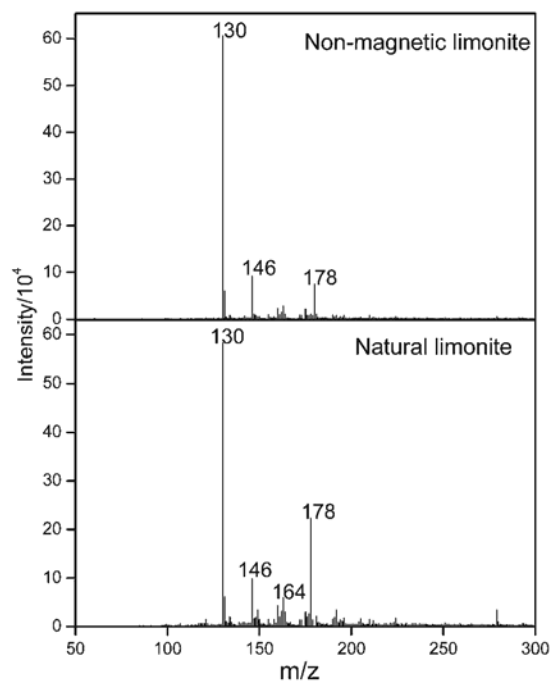


Figure 8 ESI mass spectrum in the positive-ion mode for monitoring the oxidation by the natural/H<sub>2</sub>O<sub>2</sub> and nonmagnetic/H<sub>2</sub>O<sub>2</sub> system of quinoline in water at 360 min of reaction

Total organic carbon was measured during the reaction with quinoline, and the obtained results are shown in Figure 9. It can be observed, however, that the maglim catalyst can oxidize the nitrogen molecule inserting hydroxyl groups; the reaction did not produce a significant TOC reduction, only about 50% after 360 min. Also, it is interesting to observe that the absence of the catalyst showed only a small TOC reduction.

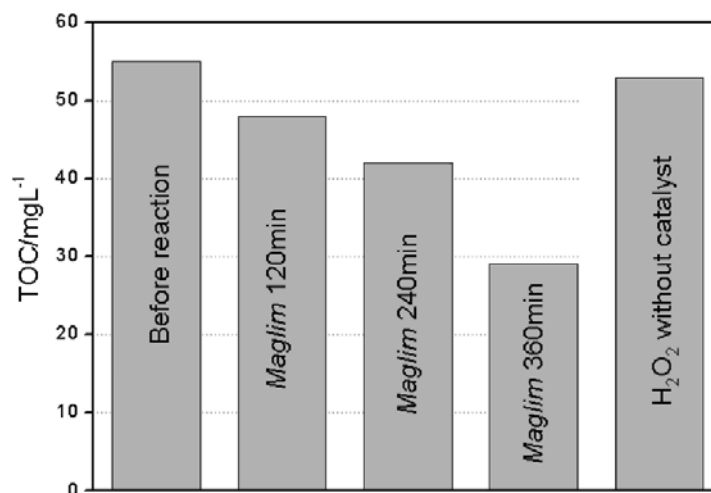


Figure 9 TOC for quinoline oxidation kinetic ( $100.0\text{mgL}^{-1}$ ,  $9.9\text{mL}$ ,  $0.1\text{ mL}$  of  $50\% \text{H}_2\text{O}_2$ ,  $10\text{ mg}$  of catalyst) in the presence of maglim

The iron leaching was monitored by measuring the oxidation of quinoline solution in the batch adsorption experiment with the maglim sample. The iron content in solution, observed in the leaching test, was found to be very low, confirming that this reaction takes place mainly via a heterogeneous process.

#### 4 Conclusions

From our results, we can show that the chemical properties of natural limonite can be modified when a simple magnetic separation is performed. The resulting materials showed a remarkable effect on the oxidation of quinoline in aqueous medium. ESI-MS studies of the quinoline oxidation showed successive hydroxylations, as intermediate reaction steps. These results provide unedited data related to this reaction mechanism by identifying new fragments from

intermediates of the overall chemical pathway involved in the oxidation of quinoline, via a heterogeneous Fenton mechanism.

### **Acknowledgment**

The authors are grateful to CAPQ-DQI (UFLA), Fapemig, CNPq, Finep, and Petrobrás for financial support.

**ARTIGO 3****SYNTHESIS AND THERMAL TREATMENT OF Cu-DOPED  
GOETHITE: OXIDATION OF QUINOLINE THROUGH  
HETEROGENEOUS FENTON PROCESS**

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## ABSTRACT

Samples of Cu-doped goethites were prepared and characterized by Mössbauer spectroscopy, XRD, TPR and BET surface area measurements. Mössbauer data showed the incorporation of  $\text{Cu}^{2+}$  in the goethite structure, and this cation-doping caused a significant decrease of the chemical reduction temperature in the TPR process. The catalytic behavior of these  $\text{Fe}_{1-x}\text{Cu}_x\text{OOH}$  materials was investigated for the  $\text{H}_2\text{O}_2$  decomposition to  $\text{O}_2$  and the Fenton-like reaction to oxidize quinoline. It was observed that  $\text{Cu}^{2+}$  in this goethite and also the thermal treatment with  $\text{H}_2$  produced a strong increase in the catalytic activity during the quinoline oxidation. The successive hydroxylation of quinoline during this oxidation strongly suggests that highly reactive hydroxyl radicals are generated during the reaction involving  $\text{H}_2\text{O}_2$  on the Cu-goethite grain surface, also confirming that these materials are efficient heterogeneous Fenton catalysts.

Keywords: Goethite. Copper. Oxidation. Fenton-like reaction.

## 1 Introduction

Goethite ( $\alpha$ -FeOOH) structurally consists of double bands of edge-sharing  $\text{FeO}_3(\text{OH})_3$  octahedra. The double bands are linked by corner-sharing in such a way as to form 2 x 1 octahedra “tunnels” crossed by hydrogen bridges [1]. The yellow-brown goethite occurs in almost all soils and other iron-containing surface formations. Its relative wide availability and suitable physical and chemical properties have allowed consideration of its use as a heterogeneous catalyst or starting material for catalysis of various industrial processes, including  $\text{NH}_3$  synthesis, high temperature water–gas shift reaction to produce hydrogen, and desulphurization of natural gas [1]. To achieve the desirable catalytic activity the iron oxide should often be modified, dispersed on a supporting material or doped with some cations. Doping-cations are added to principally assist special redox processes, such as the Fenton reaction. The classical Fenton reaction ( $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \cdot\text{OH}$ ), involving hydrogen peroxide and  $\text{Fe}^{2+}$  in solution, is often used to degrade contaminants, such as industrial wastewater textile dyes [2,3]. In order to minimize the amount of the ferric hydroxide sludge forming in the homogeneous reaction, some iron oxides, such as magnetite (ideal formula,  $\text{Fe}_3\text{O}_4$ ), hematite ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ), goethite ( $\alpha$ -FeOOH) or ferrihydrite ( $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ ), are used instead, as heterogeneous catalysts [4]. For this reason, active heterogeneous redox processes are increasingly replacing the homogeneous systems in catalysis research [5–9] and in some technological applications, particularly for environmental remediation. Modifications of the iron oxide structure by doping with isomorphous cations or by thermal treatment have been studied by many authors, in an attempt to improve the catalytic performance of those materials. However, to date, the chemical role of  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  and other ions and their ability to promote the production of the  $\cdot\text{OH}$  radical are not sufficiently clear [10].



It is well known that nitrogen-containing impurities are significant sources of atmospheric pollution, as well as being potential agents of acid rain. In this context there is a search for new technologies that can better satisfy environmental requirements.

In this work, quinoline was used as a model compound present in the diesel fuel, aiming to shed some light on the chemical mechanisms involved in the oxidative reaction. The effect of thermal treatment under a H<sub>2</sub> stream on the surface of goethite and also of copper-doped goethites (Fe<sub>1-x</sub>Cu<sub>x</sub>OOH, x = 0.05) on the Fenton oxidation of quinoline was evaluated.

## 2 Experimental

### 2.1 Catalyst preparation and characterization

All chemicals were high purity grade and were used as purchased. A goethite sample was prepared by co-precipitation, starting from Fe(NO<sub>3</sub>)<sub>3</sub>•6H<sub>2</sub>O (1.7 mol L<sup>-1</sup>) and NaOH (1 mol L<sup>-1</sup>) followed by thermal treatment at 60 °C (72 h). The Cu substituted goethite (GtCu) was prepared from Fe(NO<sub>3</sub>)<sub>3</sub>•6H<sub>2</sub>O (1.7 mol L<sup>-1</sup>) and CuSO<sub>4</sub> (Merck) solution (0.35 mol L<sup>-1</sup>) by precipitation with sodium hydroxide (1.0 mol L<sup>-1</sup>). The precipitates were washed with water until pH 7, dried at 80 °C for 12 h.

The synthetic samples were then ground and sieved to 100 mesh (Tyler series), dried for 1 h at 120 °C. After that, part of the GtCu sample was heated up to 350 °C for 3 h (reduced GtCu) at 20 °C min<sup>-1</sup> under a H<sub>2</sub>, at a flow rate of 50 mL min<sup>-1</sup>, in a tubular furnace. All chemical reactants used were obtained from Aldrich or Merck and used as received. To perform oxidation tests, 0.1 mL of H<sub>2</sub>O<sub>2</sub> 30% (v/v) and 30 mg of these goethite samples were added to the aqueous solutions (prepared with Millipore MilliQ graded water) of quinoline

(3.5 mL at 0.05 g L<sup>-1</sup>) under stirring and nearly constant temperature, at 25 ± 1 °C.

The surface area was determined with the BET method using N<sub>2</sub> adsorption/desorption in an Autosorb 1 Quantachrome instrument. Mössbauer spectroscopy experiments were carried out at room temperature in a spectrometer model MA250 with a <sup>57</sup>Co/Rh source, using an αFe foil as reference. The powder XRD data were obtained in a Rigaku model Geigerflex using Co Kα radiation scanning from 10° to 80° 2θ at a scan rate of 4° min<sup>-1</sup>. TPR experiments were performed in a CHEMBET 3000 equipment with 20 mg<sub>sample</sub> under 80 mL min<sup>-1</sup> H<sub>2</sub> (5%)/N<sub>2</sub> with heating rate of 10 °C min<sup>-1</sup>. Pure, GtCu and reduced GtCu samples were analysed by FTIR using an Excalibur FTS3000 from Bio Rad.

## 2.2 Catalytic tests

The catalytic properties of the material were tested via oxidation of quinoline. The oxidation tests were carried out using 9.9 mL of a quinoline solution (10 mg L<sup>-1</sup>) in water. 10 mg of the catalyst were used and also H<sub>2</sub>O<sub>2</sub> (VETEC, 30%) as oxidant. The reaction progress of quinoline oxidation was monitored with electrospray ESI-MS (Agilent-1100), allowing to identify intermediates formed during this reaction. ESI-MS/MS experiments in the positive ion mode were performed.

Total organic carbon (TOC) measurements were carried out in TOC 500A Shimadzu.

### 2.2.1 ESI-MS study

The quinoline (10 mL from a 50 mg L<sup>-1</sup> stock solution) decomposition was monitored using electrospray ionization mass spectrometry (ESI-MS), in an attempt to identify the intermediately formed chemical species. The reaction samples were analysed by introducing aliquots into the ESI source with a syringe pump at a flow rate of 5 µL min<sup>-1</sup>. The spectral data so obtained were averaged from 50 scans of 0.2 s each. Typical ESI-MS conditions were as follows: heated capillary temperature, 150 °C; dry gas (N<sub>2</sub>) at a flow rate of 5 L min<sup>-1</sup>; spray voltage, 4 kV; capillary voltage, 25 V; tube lens offset voltage, 25 V. For ESI-MS/MS, the parent ion of interest was first isolated by applying an appropriate waveform across the end cap electrodes of the ion trap to resonantly eject all trapped ions, except those ions with m/z ratio of interest. The isolated ions were then subjected to a supplementary AC signal, to resonantly excite them causing collision-induced dissociation (CID) using helium as a reagent gas.

## 3 Results and discussion

### 3.1 Characterization of the goethites

Fig. 1 shows the infrared spectra of prepared goethite and CuGt samples. A typical signal for this goethite is an intense band due to the bulk O–H stretch, which is observed at 3114 cm<sup>-1</sup>. Moreover, O–H bending signals at 799 and 902 cm<sup>-1</sup>, which vibrate in and out of the plane, respectively, are important diagnostic bands, characteristic of goethite. It can be observed that these two bands disappear after thermal treatment. These results and the Fe–O vibration band at ca. 573 cm<sup>-1</sup> suggest that some magnetite may have been formed.

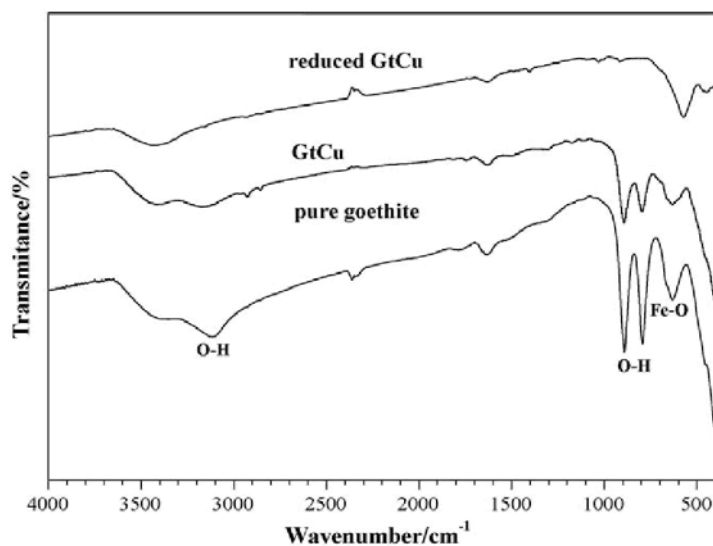


Figura 1 Infrared spectra of the materials after treatments

Corresponding XRD patterns (Fig. 2) suggest the occurrence of poorly crystalline goethite-like phase in the pure and GtCu samples with broad reflections. Values of  $a$ -lattice parameters were determined as being 0.215, 0.215 and 0.136 nm for pure, GtCu and reduced GtCu, respectively. XRD data also indicate that the thermal treatment under  $H_2$  flow causes the reduction of all goethite to magnetite, producing a characteristic cubic structure pattern. Moreover, the presence can also be observed of a small amount of a metallic iron phase.

Mössbauer spectra for these materials are presented in Fig. 3a. In the case of pure goethite, the sample is probably formed by small particle-sized iron hydroxide grains evidenced by a strong (super) paramagnetic central doublet along with a narrow-line-sextet, corresponding to a hyperfine field ( $B_{hf}$ ) of 36.0 T. The superparamagnetic behavior of goethite has been attributed to a relatively high concentration of vacancy defects [11]. The spectrum for the GtCu sample

also presents an intense effect of a putative superparamagnetism; the hyperfine field ( $B_{\text{hf}} = 31.5$  T) for this sextet is much lower in this case than it is for the goethite sample. This result is in line with previously reported data for doped goethite [12]. The room temperature Mössbauer spectrum for the  $\text{H}_2$ -reduced GtCu clearly shows tetrahedral (A) and octahedral (B) sites of magnetite, with  $B_{\text{hf}} = 48.8$  and 46 T, respectively. A magnetic spectral-set corresponding to  $B_{\text{hf}} = 50.43$  T,  $\delta = 0.34\text{mms}^{-1}$  with a relative spectral area of 11% also suggest the occurrence of somemaghemite  $\gamma\text{Fe}_2\text{O}_3$  (Table 1).

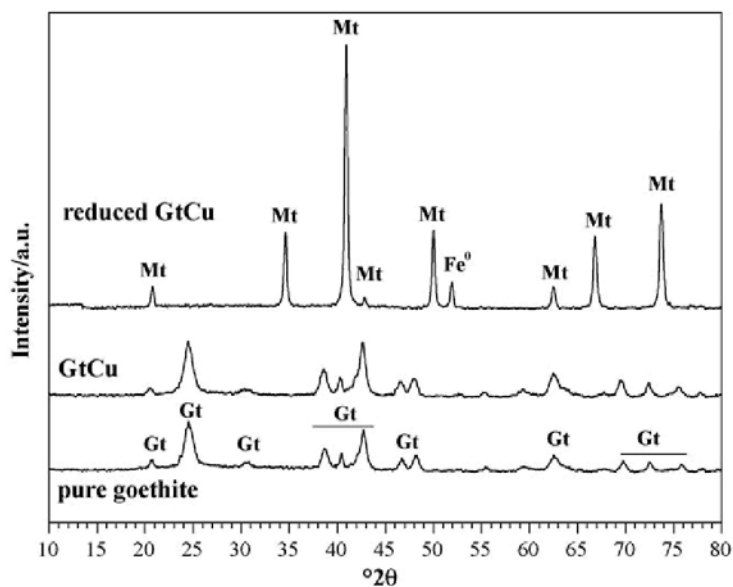


Figura 2 XRD analyses of pure and modified goethites

Table 1 Mössbauer parameters obtained from the fit of the room temperature (~298 K) spectra of pure, doped and doped after reduction goethites.<sup>a</sup>

Sample	<sup>57</sup> Fe site	$\delta$ (mm s <sup>-1</sup> )	$\varepsilon$ (mm s <sup>-1</sup> )	$B_{hf}$ (T)	RA (%)
Pure goethite	Gt	0.34(3)	-0.271(5)	36.0 <sup>b</sup>	100
GtCu	Gt	0.38(3)	-0.224 (9)	31.5 <sup>b</sup>	100
Reduced GtCu	Mt-A	0.30(2)	-0.029(4)	48.8(2)	43
	Mt-B	0.54(2)	0.031(6)	46.0 <sup>b</sup>	40
	Fe <sup>0</sup>	0.0003 <sup>c</sup>	0 <sup>c</sup>	33.0 <sup>c</sup>	6
	Mh	0.34 <sup>c</sup>	0.028 <sup>c</sup>	50.4(5)	11

<sup>a</sup> Gt = goethite; Mt = magnetite; Mh = maghemite; A and B—representations for tetrahedral and octahedral coordination sites in the spinel structure, respectively;  $\delta$  = isomer shift with respect to  $\alpha$ Fe,  $\varepsilon$  = quadrupole shift,  $B_{hf}$  = magnetic hyperfine field, eRA = relative sub-spectral area

<sup>b</sup> Maximum fields of the distribution

<sup>c</sup> Fixed parameters

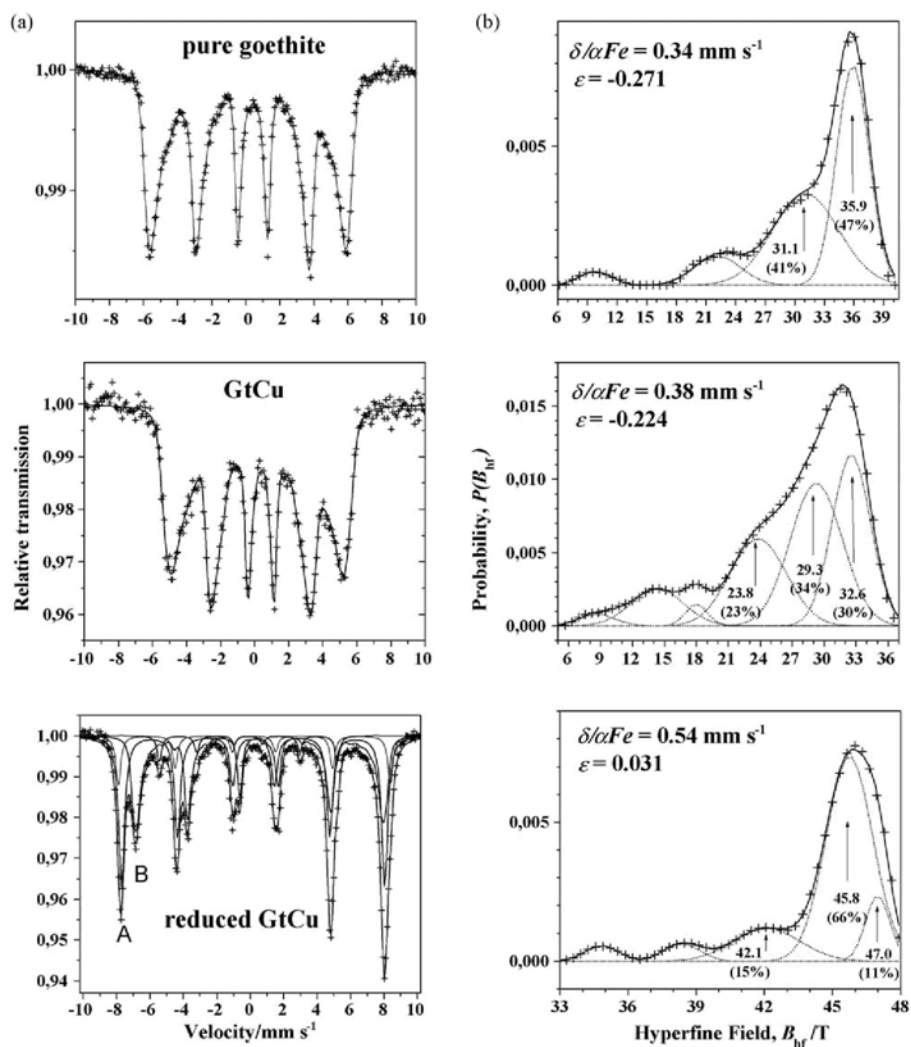


Figure 3 (a) Mössbauer spectra and (b) corresponding hyperfine field distribution for goethite, Cu-goethite and H<sub>2</sub>-reduced Cu-goethite

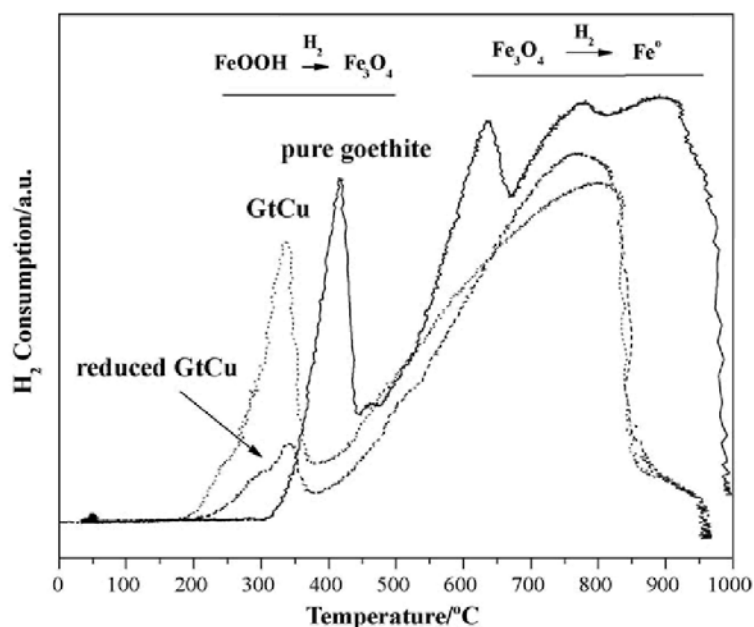


Figure 4 Temperature-programmed reduction profile of the materials

Focusing more attention now on the magnetic spectral sextets, the field distributions (Fig. 3b) lead to at least three main hyperfine fields for each of the two non-reduced samples. However, all values are all approximately similar for both cases. The corresponding  $Fe^{3+/2+}$ -distribution for the  $H_2$ -reduced CuGt, with a relatively sharper probability profile, is also shown.

The temperature-programmed reduction (TPR) in Fig. 4 profile of the pure goethite presented a peak centred at 418 °C with a broad peak from 550 to 800 °C. The first peak is typical for the formation of magnetite, typical iron oxide with structural  $Fe^{2+}$ . The GtCu presented a strong decrease in the temperature (336 °C) of magnetite formation. The TPR profile of the reduced GtCu showed a small peak due to  $Fe^{3+}$ , suggesting the formation of an iron reduced phase after the thermal treatment under  $H_2$  atmosphere.



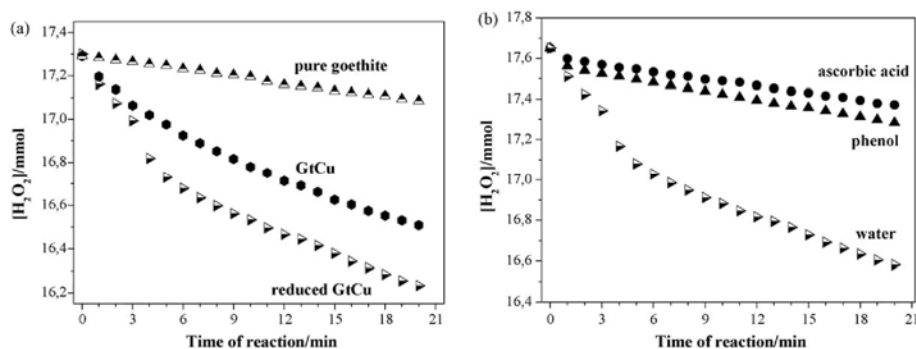


Figure 5 Decomposition of H<sub>2</sub>O<sub>2</sub> in presence of modified goethites in water (a) and in presence of some organic substrates (b)

### 3.2 Catalytic tests

#### 3.2.1 H<sub>2</sub>O<sub>2</sub> decomposition

The catalytic activity of the goethite series was studied using two reactions: (i) the H<sub>2</sub>O<sub>2</sub> decomposition (Eq. (1):



and (ii) the oxidation of quinoline with H<sub>2</sub>O<sub>2</sub> in aqueous medium. The H<sub>2</sub>O<sub>2</sub> decompositions in the presence of different goethites are presented in Fig. 5. It is observed that the GtCu materials and reduced GtCu strongly favored the H<sub>2</sub>O<sub>2</sub> decomposition (Fig. 5a). The decomposition kinetics is a complex reaction, the linear behavior of the decomposition plots, in the first minutes, suggests that the process can be approximate to pseudo-zero order kinetics. The literature shows that the incorporation of metal by isomorphic substitution and/or the conversion of Fe<sup>3+</sup> sites to Fe<sup>2+</sup> enhances H<sub>2</sub>O<sub>2</sub> decomposition rate probably due to textural and/or surface modifications [13]. Accordingly, the present work shows higher

hydrogen peroxide decomposition rate over surface containing copper and iron (doped and reduced sample) when compared to the surface containing only  $\text{Fe}^{3+}$  species.

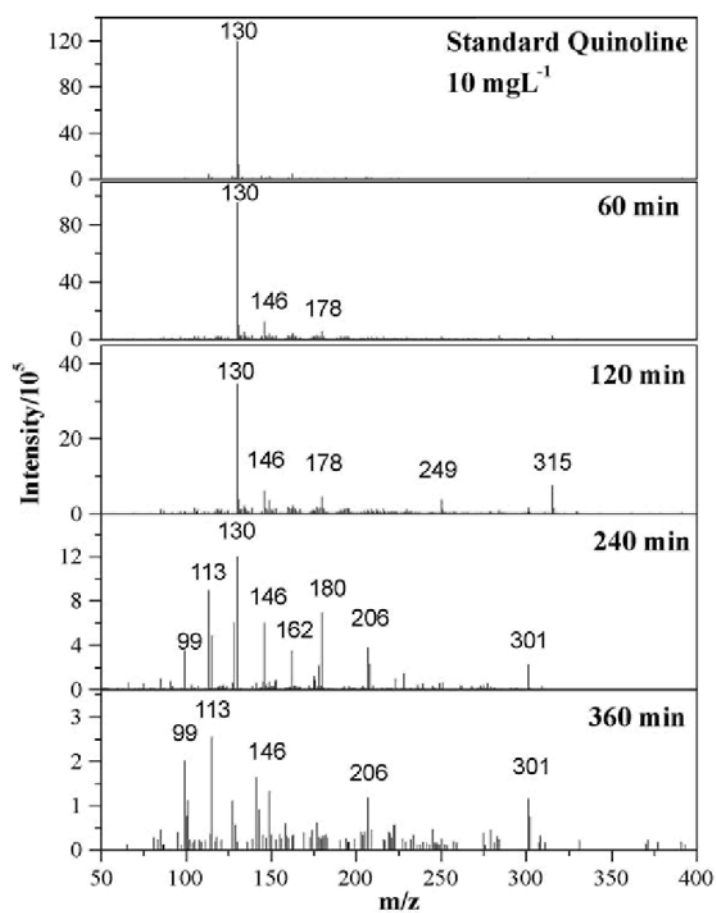


Figure 6 Electropray ionization mass spectrometry (ESI-MS) in the positive ion mode for monitoring the oxidation by the reduced GtCu// $\text{H}_2\text{O}_2$  system of quinoline in water

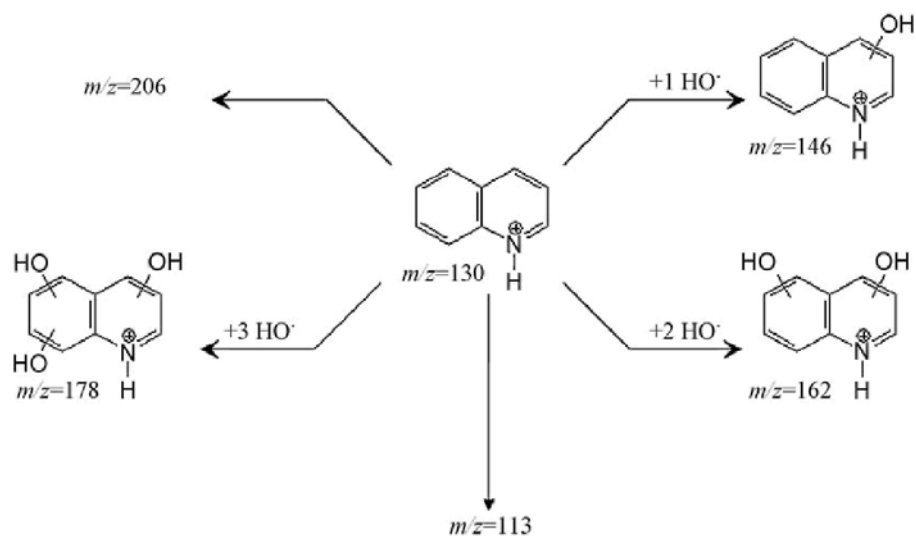


Figure 7 Scheme with proposed intermediates for the oxidation of quinoline (m/z = 130) by the catalyst

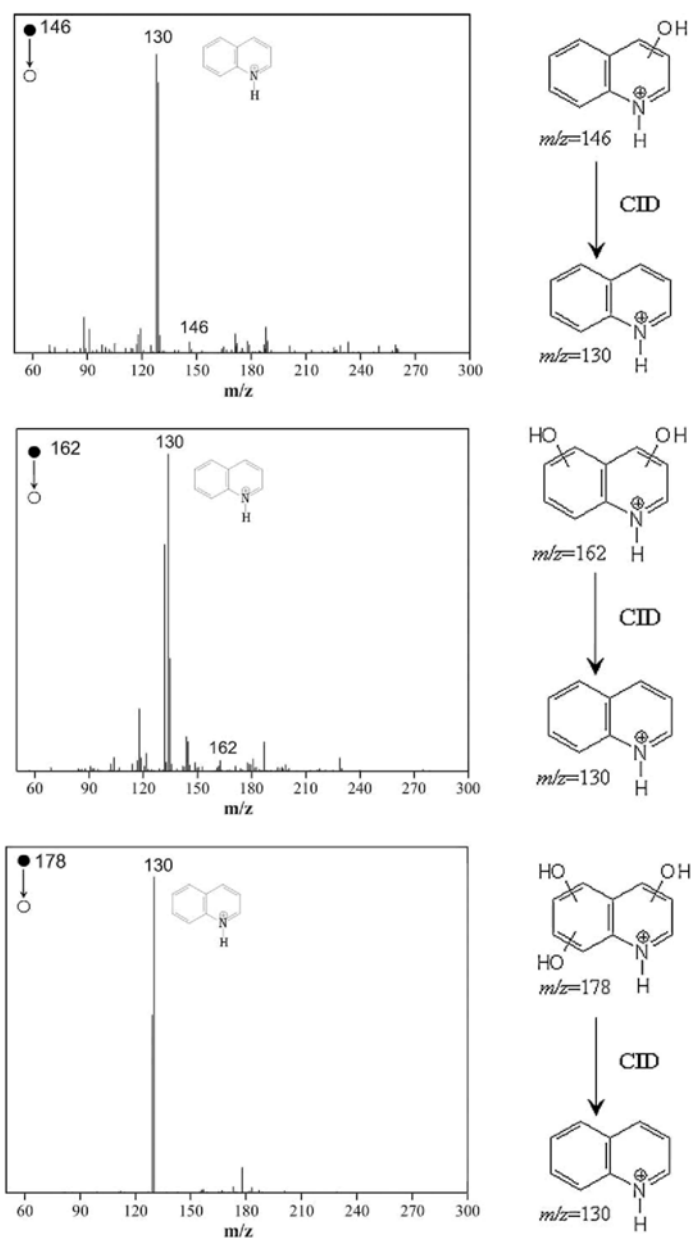


Figure 8 Electrospray ionization mass spectrometry (ESI-MS/MS) spectrum of them/z intercepted during the oxidation of quinoline in water by the reduced GtCu/H<sub>2</sub>O<sub>2</sub> system

\*CID = collision-induced dissociation

Fig. 5b shows the  $\text{H}_2\text{O}_2$  decomposition utilizing the most active catalysts, reduced GtCu, in the presence of two organic compounds (ascorbic acid and phenol). It also can be observed that the  $\text{H}_2\text{O}_2$  decomposition is strongly inhibited by the presence of another organic compound (ascorbic acid or phenol). The reaction inhibition might be due to a competitive process involving the organic substrate and the active surface that could be related to the adsorption of the organic compounds on the active sites of the composite and their reactions with intermediate species in the  $\text{H}_2\text{O}_2$  decomposition reaction. Moreover, a possible mechanism can be based on the activation of  $\text{H}_2\text{O}_2$  via a Haber Weiss mechanism to form a radical  $\text{HO}^\bullet$  [13]. This radical can react by two competitive pathways: the oxidation of an organic molecule or the  $\text{O}_2$  formation via the radical  $\text{HOO}^\bullet$ . Thus, the presence of ascorbic acid and phenol (radical scavengers) can be quenching the radical intermediates decreasing the rate of  $\text{O}_2$  formation.

To investigate the possibility of homogeneous reactions produced by Fe and Cu species leached from the GtCu and reduced GtCu to the aqueous medium, atomic absorption analyses were carried out in the aqueous phases after all the reactions. The obtained concentrations of Fe and Cu were all below the detection limit of the atomic absorption equipment.

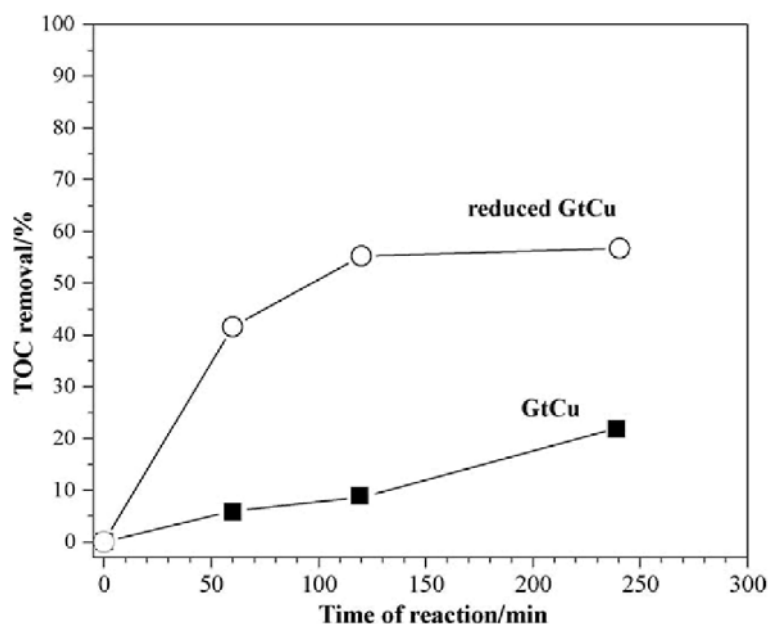


Figura 9 Total organic carbon analyses for the GtCu and reduced GtCu samples

### 3.2.2 Quinoline oxidation in the presence of $H_2O_2$

The quinoline oxidation by the most active catalyst for  $H_2O_2$  decomposition, i.e. the reduced GtCu sample, was studied. The ESIMS spectrum obtained for the quinoline solution only shows a strong signal at  $m/z = 130$ , which is related to the protonated quinoline (Fig. 6). After 240 min of reaction with the reduced GtCu and hydrogen peroxide, some new and strong  $m/z$  signals appear, specifically at 146, 162, 180 and 194, which may indicate hydroxylation steps. At this reaction time, the  $m/z$  signals appearing at  $m/z = 85$ , 99 and 113 are assumed to be related to quinoline oxidation intermediates, from fragmentations of the molecular structural ring.

The results obtained in this work suggest that the Cu in the goethite structure and the thermal treatment under  $H_2$  flow strongly favors the  $H_2O_2$

decomposition with radical as intermediates and consequently the oxidation of quinoline with successive hydroxylations. A work in the literature suggested that  $\text{Cu}^+$  could participate in a Haber Weiss mechanism to generate  $\text{HO}^\bullet$  free radicals [14]. The thermal treatment can be to reduce the  $\text{Fe}^{3+}$  from goethite as well as the  $\text{Cu}^{2+}$ , improving the radical formation as suggested by the following equations:



These results also indicate that the Fenton oxidation mechanism ( $\text{OH}^\bullet$  attack) is taking place to a significant extent. The schematic structures for the hydroxylated intermediates from quinoline oxidation are proposed in Fig. 7.

To test the structural assignments for intermediates showed in Fig. 7, ESI-MS/MS spectra were acquired. Fig. 8 displays the ESI-MS/MS spectra for the structure after many hydroxylations ( $m/z = 146$ ,  $m/z = 162$ , etc.). Those mass values support the structural assignments of Fig. 7 as an  $\text{OH}^\bullet$  attack suggesting that a Fenton reaction takes place in heterogeneous phase [15].

Fig. 9 shows the TOC removal for the most active samples, i.e. GtCu and reduced GtCu, at different reaction times. It can be observed that the treatment with hydrogen flow produced a higher TOC removal (approximately 57% removal) than the material only after impregnation with copper, suggesting that the presence of reduced phases might play a role in the removal process. It is interesting to comment that the TOC removal obtained with these materials was much better than many reaction processes studied from some authors [4,15,16] attesting that the goethite with copper, after thermal treatment with  $\text{H}_2$  flow, is a good catalyst in the oxidation of a important organic pollutant such as quinoline.

## 4 Conclusions

The presence of Cu associated with a thermal treatment under H<sub>2</sub> flow has a significant effect on the catalytic activity of the oxide. In this study, the oxidation of organic compounds with H<sub>2</sub>O<sub>2</sub> has been shown to probably take place via radicals, as suggested by ESI-MS data. An oxidation mechanism was indicated to occur by attack of the free radical \*OH on the molecule, giving rise to hydroxylation products as principal by-products, although compounds resulting from ring cleavage are also detected. The presence of copper increases the activity of the oxide for the H<sub>2</sub>O<sub>2</sub> decomposition, and the reduced species such as Cu<sup>+</sup> and Fe<sup>2+</sup> surface species seem to act directly in the catalytic properties of the catalyst.

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**ARTIGO 4****EFFECT OF Ni INCORPORATION INTO GOETHITE IN THE  
CATALYTIC ACTIVITY FOR OXIDATION OF NITROGEN  
COMPOUNDS IN PETROLEUM**

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## ABSTRACT

Samples of Ni-doped goethites were prepared and characterized by Mössbauer spectroscopy, IV, XRD, TPR and BET surface area measurements. Mössbauer data evidenced the incorporation of  $\text{Ni}^{2+}$  in the goethite structure, and this cation-doping caused a significant decrease of the chemical reduction temperature in the TPR process. The catalytic behavior of these  $\text{Fe}_{1-x}\text{Ni}_x\text{OOH}$  materials was investigated for the  $\text{H}_2\text{O}_2$  decomposition to  $\text{O}_2$  and the oxidation of quinoline. The successive hydroxylation of quinoline during this oxidation strongly suggests that highly reactive hydroxyl radicals are generated during the reaction involving  $\text{H}_2\text{O}_2$  on the Ni-goethite grain surface, also confirming that these materials are efficient heterogeneous Fenton catalysts.

Keywords: Goethite. Nickel. Oxidation. Petroleum.

## 1 Introduction

Many iron oxides play an important role in a variety of disciplines and also serve as a model system of reduction and catalytic reactions [1–3]. Goethite ( $\alpha$ -FeOOH) is commonly used as an adsorbent [4,5], a catalyst precursor and an active component of catalytic material [6–9]. The special importance of goethite ( $\alpha$ -FeOOH) results from the combination of its ubiquitous presence in soils and sediments and its exceptional chemical reactivity. The goethite is a poorly and imperfectly crystallized material having a large surface area. These characteristics and its open channel structure result in an unusual capacity to incorporate, adsorb, and fix ions from migrating solutions [10].

Various metal cations can be incorporated into the  $\alpha$ -FeOOH structure, and many researchers have focused on the influence of the doping of  $\alpha$ -FeOOH on its chemical, microstructural and physical properties [11]. The properties of these iron oxides, such as their saturation magnetization and magnetocrystalline anisotropy constants, strongly depend on the kind and the amount of substituting metal ions [12]. It is well known that the sulfur and nitrogen impurities present in fuels are an important source of air pollution, acid rain and they also affect pollution control devices. In order to decrease pollution, new specifications for sulfur in diesel have been established in many countries; e.g., in the Brazil a sulfur concentration of less than 50ppm has been established for 2010 and for 2013 a sulfur concentration less than 10 ppm. In this context, clean fuels research, including desulfurization and denitrogenation, has become an important subject of environmental catalysis studies worldwide [13]. Conventional hydrotreating (HDT) methods have been effective for the easy-to-remove sulfur and nitrogen compounds, while less competent for removing heterocyclic sulfur or nitrogen compounds (such as dibenzothiophenes and quinolines) which are abundant especially in diesel [14]. Other processes have

been studied in order to remove refractory HDS compounds. Oxidesulfurization (ODS) is a current process and has been discussed recently where the oxidized sulfur compounds can be removed from the hydrocarbon phase by extraction or precipitation. The sulfones are highly polar compounds and are easily separated from the fuel product by extraction during ODS process [15]. Another important factor in the ODS process is to evaluate the effect of other compounds present in the oil fractions. The majority of heteroatom-containing compounds of crude oil, especially nitrogen-containing compounds, still exist in the residual oil and these nitrogen compounds that coexist in distillate oil medium can inhibit the ultra-deep HDS [16]. Meanwhile, the removal of such nitrogen compounds from the middle-distillate oil can improve significantly the ultra-deep HDS performance. In addition, nitrogen compounds in the fuel and  $\text{NH}_3$  produced during hydrocarbon reforming process are also to the catalysts. Besides they are harmful not only to the ODS process, but also to the stability of oil. Therefore it is strongly desired that most nitrogen-containing compounds be removed when processing residual oil, but the reduction of refractory heteroatom-containing compounds is marginal [16].

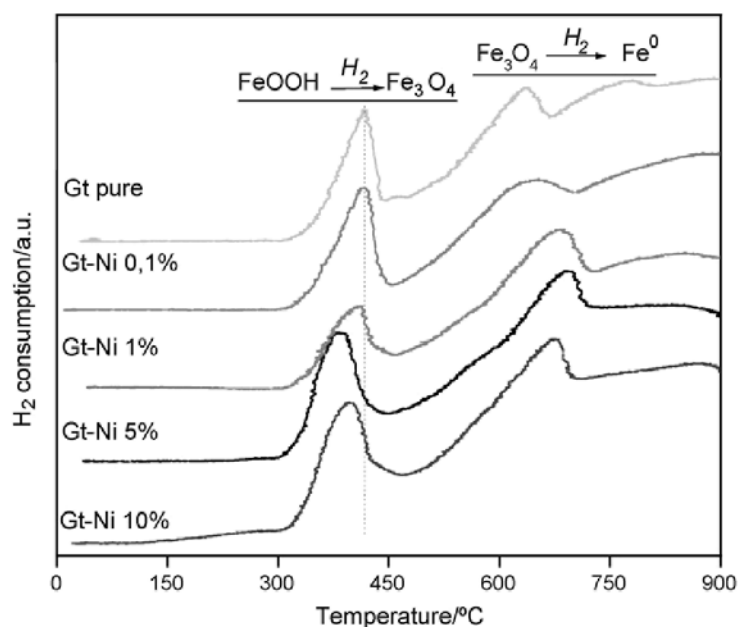


Figura 1 Temperature-programmed reduction profile of the materials

Now it is necessary to develop new approaches to ultra-deep desulfurization and denitrogenation for diesel fuel [14]. Several studies have recently been published involving different iron species for the removal of these contaminants from crude oil [4,5,17]. Recently, a Fenton-like system that combines  $H_2O_2$  and limonite ore as catalyst was developed [17]. This combined aqueous slurry system is able to perform oil phase oxidation and simultaneous removal of unstable hydrocarbons and heteroatom compounds from hydrocarbon streams, such as Petroleum distillates. In the present work, we have focused on the influence of Ni-dopant on the properties of  $\alpha$ -FeOOH particles precipitated in highly alkaline media. This study proposes yet to evaluate the oxidation of quinoline as representative model compound of heteroatom molecule present in diesel, aiming at a possible elucidation of the reaction mechanisms involved.

## 2 Experimental

### 2.1 Catalyst preparation and characterization

All chemicals were high purity grade and were used as purchased. A goethite sample was prepared by co-precipitation, starting from  $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  ( $1.7 \text{ mol L}^{-1}$ ) and  $\text{NaOH}$  ( $1 \text{ mol L}^{-1}$ ) followed by thermal treatment at  $60 \text{ }^\circ\text{C}$  (72 h). The Ni-substituted goethites (GtNi) were prepared from  $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  ( $1.7 \text{ mol L}^{-1}$ ) and  $\text{NiSO}_4$  (Merck) solution by precipitation with sodium hydroxide ( $1.0 \text{ mol L}^{-1}$ ). The concentration of Ni ions in the doped goethite was targeted to be between 0.1 and 10%. The precipitates were washed with water until pH 7, dried at  $80 \text{ }^\circ\text{C}$  for 12 h. The synthetic samples were then ground and sieved to 100 mesh (Tyler series), dried for 1 h at  $120 \text{ }^\circ\text{C}$ . The surface area was determined with the BET method using  $\text{N}_2$  adsorption/desorption in an Autosorb 1 Quantachrome instrument. Mössbauer spectroscopy experiments were carried out at room temperature in a spectrometer model MA250 with a  $^{57}\text{Co}/\text{Rh}$  source, using an  $\alpha\text{Fe}$  foil as reference. The powder XRD data were obtained in a Rigaku model Geigerflex using  $\text{Co K}\alpha$  radiation scanning from  $10^\circ$  to  $80^\circ 2\theta$  at a scan rate of  $48 \text{ min}^{-1}$ . TPR experiments were performed in a CHEMBET 3000 equipment with 40mg sample under  $80 \text{ mL min}^{-1} \text{ H}_2(5\%)/\text{N}_2$  with heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ . Pure and GtNi samples were analysed by FTIR using an Excalibur FTS 3000 from BioRad. The specimens were pressed into small discs using a spectroscopically pure KBr matrix.

### 2.2 Catalytic tests

To perform oxidation tests, 2mL of  $\text{H}_2\text{O}_2$  (VETEC, 50%, v/v) and 30mg of these goethite samples were added to 3.5mL of Millipore MilliQ water under

stirring and nearly constant temperature, at 25 °C. The catalytic properties of the material were tested via oxidation of quinoline. The oxidation tests were carried out using 9.9mL of a quinoline solution ( $10\text{mgL}^{-1}$ ) in water. 10mg of the catalyst were used and also  $\text{H}_2\text{O}_2$  as oxidant.

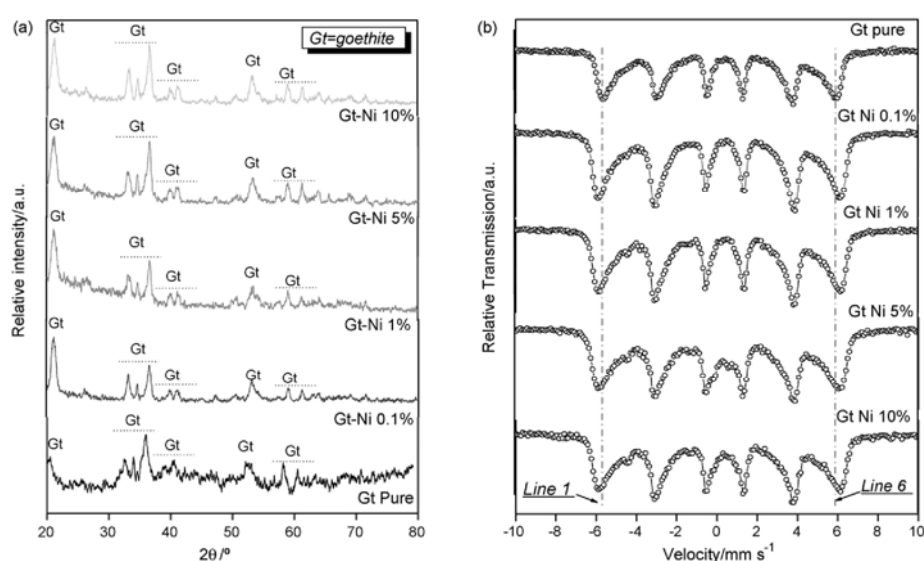


Figure 2 XRD patterns (a) and Mössbauer spectroscopy (b) of samples Gt pure and Ni-doped goethites (Gt = goethite)

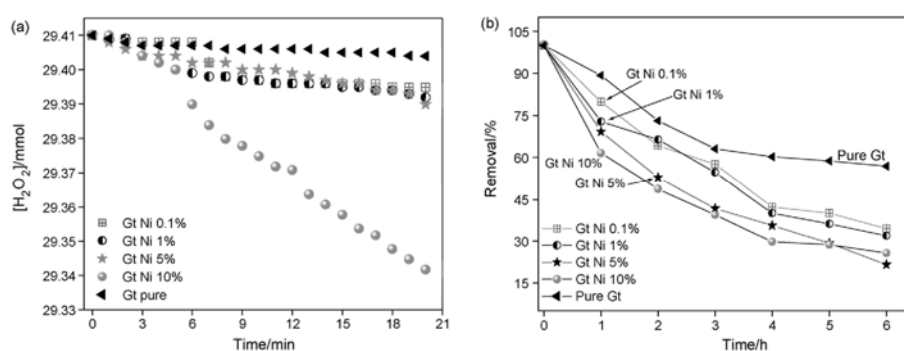


Figure 3  $\text{N}_2$  adsorption–desorption isotherms (a) and BJH pore-size distribution (b) of the pure goethite and the sample Gt–Ni10%



The catalytic activity of the materials was tested for their effectiveness on the oxidation of quinoline (10mL of  $10\text{mgL}^{-1}$  stock solution) in an oxidant solution comprised of  $\text{H}_2\text{O}_2$  (50%, v/v). The catalytic test at pH 6.0 (natural pH of the  $\text{H}_2\text{O}_2$  solution) was carried out with a total volume of 10mL (9.9mL of the contaminant solution and 0.1mL of the  $\text{H}_2\text{O}_2$ ) and 10mg of the oxide catalyst. The monitoring of the quinoline solution remotion was realized by UV(Spectrovision), with scan between 250 and 400 nm.

### 2.3 ESI-MS study

The quinoline oxidation reaction progress was monitored with electrospray ESI-MS (Agilent-1100), allowing to identify intermediates formed during this reaction. ESI-MS/MS experiments in the positive ion mode were performed. The quinoline (10mL from a  $50\text{mgL}^{-1}$  stock solution) decomposition was monitored using electrospray ionization mass spectrometry (ESI-MS), in an attempt to identify the intermediately formed chemical species. The reaction samples were analysed by introducing aliquots into the ESI source with a syringe pump at a flow rate of  $5\text{mLmin}^{-1}$ . The spectral data so obtained were averaged from 50 scans of 0.2 s each. Typical ESI-MS conditions were as follows: heated capillary temperature,  $150\text{ }^\circ\text{C}$ ; dry gas ( $\text{N}_2$ ) at a flow rate of  $5\text{ Lmin}^{-1}$ ; spray voltage, 4 kV; capillary voltage, 25 V; tube lens offset voltage, 25 V. For ESI-MS/MS, the parent ion of interest was first isolated by applying an appropriate waveform across the end cap electrodes of the ion trap to resonantly eject all trapped ions, except those ions with m/z ratio of interest. The isolated ions were then subjected to a supplementary AC signal, to resonantly excite them causing collision-induced dissociation (CID) using helium as a reagent gas.

The iron leaching during all reactions was evaluated by atomic absorption analysis, using a Varian AA 110 equipment. We found 0.065 and

0.078mgL<sup>-1</sup> of iron leaching from the samples of limonite 350 °C/10 min and 350 °C/60 min, respectively. We observed that this concentration of iron does not lead to a homogeneous Fenton reaction.

### 3. Results and discussion

#### 3.1 Characterization of the materials

The reduction properties of the goethites were studied by TPR analyses. Fig. 1 shows the TPR profile for pure and Ni-doped goethites.

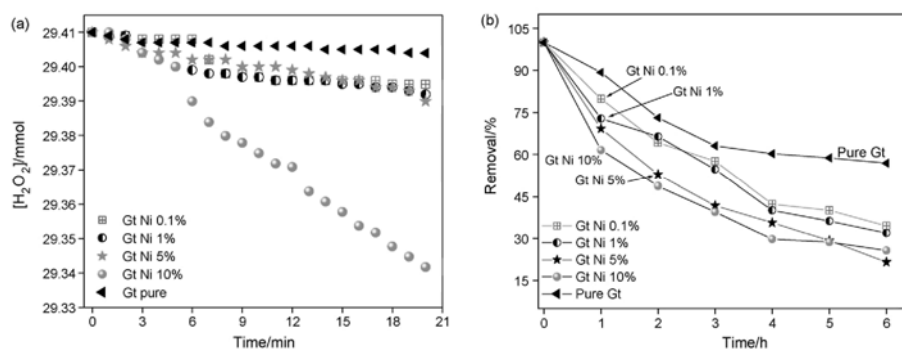


Figure 4 Decomposition of H<sub>2</sub>O<sub>2</sub> in presence of goethites (a) and quinoline oxidation monitored by UV-vis spectroscopy (b). Conditions: 7.0mL solution at [H<sub>2</sub>O<sub>2</sub>] = 2.7 mol L<sup>-1</sup> (natural pH of the H<sub>2</sub>O<sub>2</sub> solution); 30.0mg catalyst.; 25±1 °C

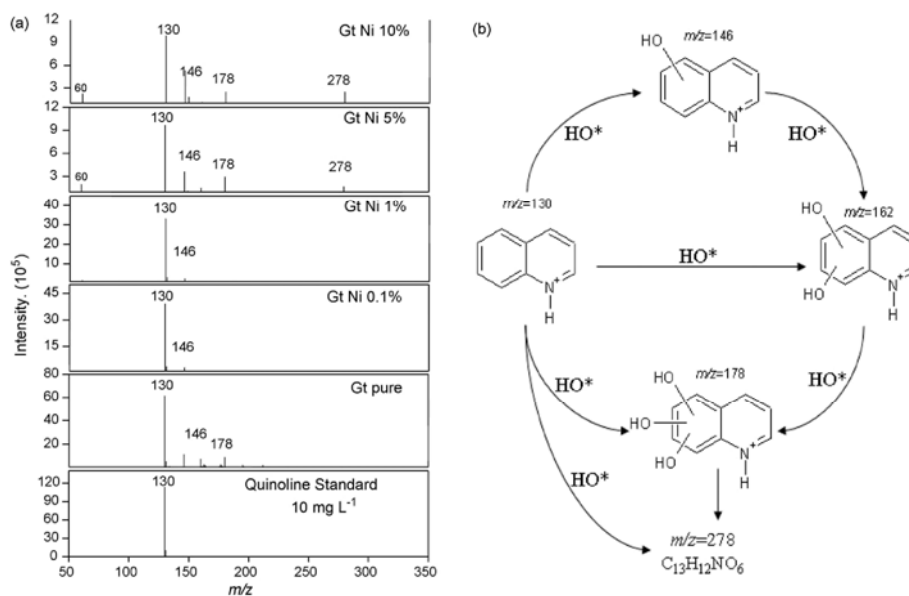


Figure 5 ESI mass spectrum in the positive ion mode for monitoring the oxidation by the goethite/H<sub>2</sub>O<sub>2</sub> system of quinoline in water (a) and scheme with proposed intermediates formation (b)

The TPR clearly shows two regions of H<sub>2</sub> consumption indicated by the first peak, centered at 420 °C and related to goethite reduction to magnetite [5,6]. The second peak centered at 750 °C is related to the formation of metallic iron as shown in Eqs. (1) and (2):



The GtNi 0.1% shows a similar TPR profile compared to Gt pure. On the other hand, the Ni-doped materials with high Ni content presented a different reduction of profile with a decrease in the reduction temperature (400 °C for Gt–Ni1%; 380 °C for Gt–Ni5% and 10%) suggesting that the Ni incorporation into the goethite structure took place.

In order to identify the crystalline phases in the goethites the X-diffraction patterns and also Mössbauer spectroscopy were obtained. Fig. 2 shows characteristic XRD patterns and Mössbauer profiles of samples Gt pure and GtNi.

The powder XRD patterns of the pure goethite and doped samples indicate the presence of a hexagonal crystalline phase ( $d = 0.497, 0.418, 0.336, 0.269, 0.244, 0.225$  and  $0.172$  nm) relative to goethite. The amount of Ni incorporation into goethite does not permit to observe a significant change in the lattice parameter, but it is interesting to observe that no other crystalline phase was formed.

The Mössbauer spectroscopy for the materials was consistent with pure and substituted goethite particles. Pure, well crystallized goethite gives a magnetically ordered Mössbauer spectrum (sextet) at room temperature. According to XRD data the spectra from doped sample are similar, but a shift between the line 1 and line 6 can be observed, which is a typical behavior of materials with isomorphic substitution. Some studies concluded that the main effect of doping with several cations such as Ni, Cr, Mn, and Ga, was an increase in hyperfine field characterized by a distance between line 1 and line 6 [1,4,6,8].

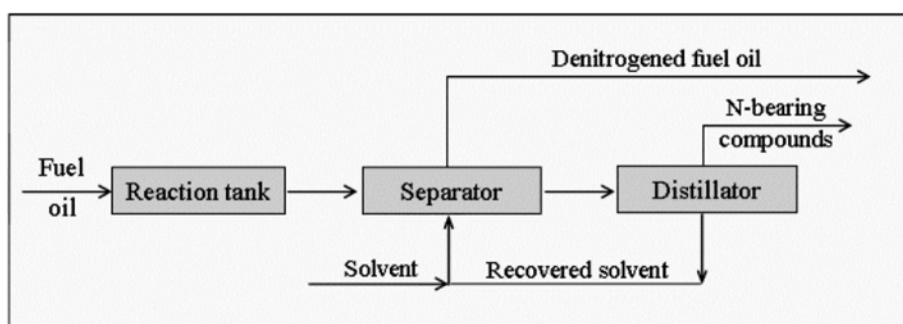


Figura 6 General process flow of extractive denitrogenation

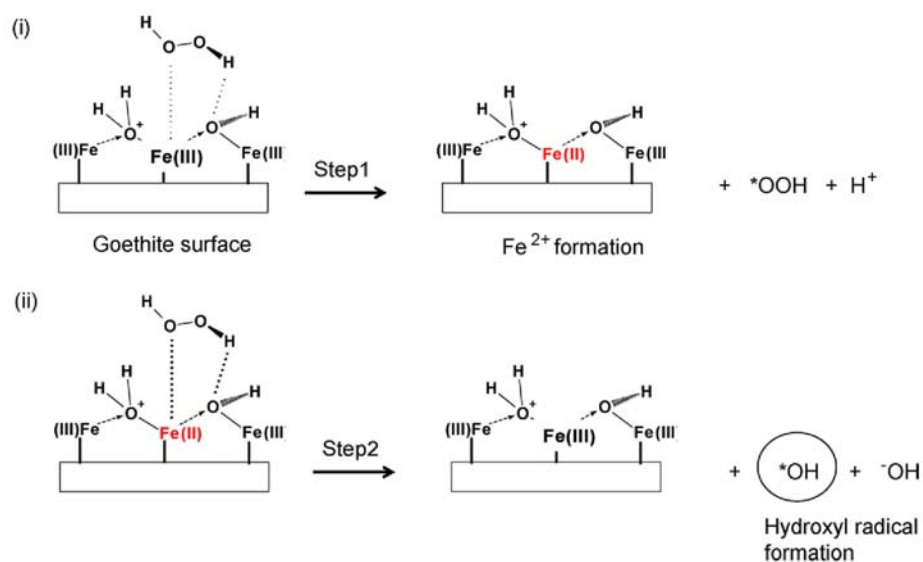


Figure 7 Scheme for hydroxyl radical generation after the in situ iron reduction on the goethite surface

The textural properties of pure goethite and the sample with high amount of Ni (Gt–Ni10%) were studied by  $\text{N}_2$  adsorption–desorption analysis (Fig. 3a). A decrease in the BET specific surface areas can be observed after nickel incorporation (pure Gt =  $95\text{m}^2\text{ g}^{-1}$ , and Gt–Ni10% =  $83\text{m}^2\text{ g}^{-1}$ ). In general, the metal incorporation into goethites causes an increase in the specific surface area [4,19]. In our case it seems that the nickel presence produces a material with large pore diameter like a macroporous material. In fact, the pore-size distributions (Fig. 3b) determined with the Barrett–Joyner–Halenda (BJH) pore-size distribution for these samples, showed that the presence of Ni produced materials with larger pore diameters compared to pure goethite.

### 3.2 Catalytic tests: H<sub>2</sub>O<sub>2</sub> decomposition and quinoline oxidation

The catalytic activity of the goethites was studied using two reactions: H<sub>2</sub>O<sub>2</sub> decomposition to O<sub>2</sub>, and oxidation of the model contaminant quinoline with H<sub>2</sub>O<sub>2</sub> in aqueous medium. The decomposition of H<sub>2</sub>O<sub>2</sub> in the presence of the different goethite samples approximately followed pseudo zero-order kinetics, as indicated by the nearly linear plots obtained between H<sub>2</sub>O<sub>2</sub> concentration and time of reaction (Fig. 4a). This result is according to other studies in the literature [13,20,21]. Ferraz et al. [9] and Oliveira et al. [7] proposed that in the presence of iron phases the decomposition mechanism involves radical formation, such as <sup>\*</sup>OH or <sup>\*</sup>OOH. The oxidation of quinoline by H<sub>2</sub>O<sub>2</sub> in the presence of goethite may be represented by Eq. (3):



and is monitored by ESI-MS. In the control experiment where goethite was absent, no significant removal was observed (Fig. 4b) even after 5 h of reaction. In the presence of pure goethite, a lower activity of quinoline oxidation was observed with only 28% removal after 5 h. On the other hand, in the presence of Ni-substituted goethites, catalytic oxidation of up to 70% was observed after 5 h.

The ESI-MS spectrum obtained for the quinoline solution ( $m/z_{\text{quinoline}} = 129^+ \text{H}^+ = 130$ ) shows only a strong signal at  $m/z = 130$ , which is related to the protonated quinoline (Fig. 5abottom). After 300 min of reaction with goethites and hydrogen peroxide, some new  $m/z$  signals appear, specifically at 146, 162, 178 and 60, which may indicate hydroxylation steps (Fig. 5b) and also other  $m/z$  signals suggesting that the structural ring was somehow fragmented [5,6]. These results also indicate that Fenton oxidation mechanism (<sup>\*</sup>OH attack) is taking place to a significant extent mainly in the presence of substituted goethites. The

hydroxyl groups in the quinoline ring significantly increased the polarity of the molecules. So, the hydroxylation is an important feature because it can facilitate the separation of the nitrogen compounds from petroleum by a simple liquid–liquid extraction [22,23]. As was mentioned before, the oxidation-extraction denitrogenation process is carried out in two steps; first the nitrogen compounds are partially oxidized to their corresponding hydroxylated structures and subsequently are extracted from the diesel phase by a physical extraction, as shown in Fig. 6 [24].

It is interesting to observe that iron leaching was monitored by measuring the oxidation of quinoline solution in the batch adsorption experiment, with the Gt–Ni10% sample. The iron content in solution, observed in the leaching test, was found to be very low, confirming that this reaction takes place mainly via a heterogeneous process.

In fact, the goethite is an iron oxide phase widely used in the hydrogen peroxide decomposition to produce the hydroxyl radical in heterogeneous Fenton reaction because the redox reaction involving the  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$  is facilitated [18,19]. The hydroxyl radical generation depends on the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  on the iron oxide surface as illustrated in Fig. 7 [4]. It is interesting to observe that the catalytic data found suggest that the presence of Ni into the goethite structure facilitated this reduction process, which is according to the TPR data shown in Fig. 2 mainly for the materials with 5% of Ni.

#### **4 Conclusion**

The presence of Ni caused a significant effect on the catalytic activity of the goethites for quinoline oxidation. In this study, the oxidation of organic compounds with  $\text{H}_2\text{O}_2$  has been shown to probably take place via radicals, as suggested by ESI-MS data. An oxidation mechanism was indicated to occur by

attack of the free radical  $^*OH$  on the molecule, giving rise to hydroxylation products as principal by-products, although compounds resulting from ring cleavage are also detected. The presence of Ni increases the activity of the oxide for the  $H_2O_2$  decomposition probably facilitating the reduction of  $Fe^{3+}$  to  $Fe^{2+}$  generating the  $^*OH$  radical.

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## CONSIDERAÇÕES GERAIS

A reatividade química da superfície de goethitas pode ser fortemente modificada pelo tratamento térmico com  $H_2$ , com objetivo de formar fases reduzidas de ferro. O enriquecimento da superfície com  $Fe^{2+}$  está associado a uma reação tipo Fenton, com excelente taxa de conversão de compostos sulfurados e nitrogenados, em temperatura ambiente e pressão atmosférica.

Com relação ao catalisador magnético, tem-se que as propriedades químicas da limonita natural podem ser modificadas quando um simples processo de separação magnética é realizado. O material resultante (maglim) mostra um efeito bastante significativo na oxidação de quinolina em meio aquoso

A presença de  $Cu^{2+}$  associada ao tratamento térmico sob atmosfera redutora ( $H_2$ ) teve um efeito mensurável na atividade do óxido. O aumento na atividade, sobretudo após o tratamento térmico, pode estar relacionado ao fato do  $Cu^+$ , formado pela redução com  $H_2$ , também ser ativo na decomposição de  $H_2O_2$  e formação de radicais.

A incorporação de  $Ni^{2+}$  na estrutura da goethita provoca pequenas alterações na estrutura do cristal, especialmente para materiais com baixa cristalinidade. Essas modificações não são observadas por técnicas de caracterização como XRD e FTIR, comportamento que exige análises mais específicas, como a espectroscopia Mössbauer, para avaliação da substituição isomórfica do ferro pelo níquel. A presença do níquel causa um efeito significativo na atividade catalítica da goethita para oxidação da quinolina. A reação segue um mecanismo de degradação *via* radicalar, como mostrado pelos dados de ESI-MS, em que pode-se observar o ataque dos radicais  $HO^{\bullet}$  à estrutura da molécula, levando a intermediários polihidroxilados como produtos principais e ainda alguns produtos de fragmentação do anel.