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Red Mud waste from the Bayer process as a catalyst for the desulfurization of hydrocarbon fuels†

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The management of Red Mud generated as a waste by-product of bauxite processing in the aluminum industry is key to the long-term sustainability of alumina production. At the same time, the desulfurization of fuel oil to low-level sulfur is an ongoing challenge to the petroleum industry. In an attempt to address both these issue in an integrated fashion, Red Mud waste was studied as a catalyst in a desulfurization process using a simulated Diesel containing dibenzothiophene (DBT) as a model heterocyclic organic sulfur compound. The new process combines an oxidative-adsorptive desulfurization in which a combination of H_2O_2//H_3CCOOH and Red Mud was able to catalytically oxidize the sulfur compound to the corresponding sulfoxide (DBTO) and sulfone ($DBTO_2$) which are then reversibly adsorbed onto the Red Mud. Regenerative tests of Red Mud were performed, maintaining a high activity in recycles suggesting that the Red Mud could be reused after a simple thermal treatment releasing DBTO and $DBTO_2$. The approach synergistically addresses both problems: removal of sulfur compounds while at the same time offering a potential useful application of Red Mud. Red Mud was characterized by Mössbauer Spectroscopy, Infrared Spectroscopy, X-ray Diffraction (XRD), Scanning Electron Microscopy with dispersive energy (SEM-EDS), BET Surface area (BET), and release of volatile compounds from Red Mud by Gas chromatography-Mass Spectrometry (GC-MS) using a solvent-free solid injector (SFSI). The kinetics of the desulfurization reactions were monitored by GC-MS.

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Introduction and motivation

Red Mud is a solid waste generated by the aluminum industry in the processing of bauxite ores following the Bayer process.[1,2] The disposal of Red Mud is and has been a considerable challenge to the aluminium industry and the management of this waste is considered to be a key sustainability issue for the alumina refining industry.[2] The petroleum industry also faces ongoing challenges throughout the supply chain, notably maintaining a consistent quality of the fuel with respect to performance and environmental regulations.[3,4] Sulfur compounds represent one of the most undesirable contaminants in petroleum products and fuels. They occur in various forms in the crude oil feed and can been classified into four main groups: mercaptans, sulfides, disulfides and thiophenes.[5,6] The commonly used industrial process for desulfurization is not fully efficient for the removal of compounds such as dibenzothiophene and its derivatives.[7] Therefore, new environmentally friendly and energy saving processes that could be applied to desulfurization are continuously being explored.[8]

Red Mud

The main constituents of Red Mud waste are the oxides Fe_2O_3, Al_2O_3, SiO_2, TiO_2 as well as smaller amounts of CaO and Na_2O that impart a high alkalinity on the material.[9–11] Currently there are an estimated 3 billion tons of Red Mud stockpiled around the world and an additional estimated 120 million tons are generated by the aluminum industry per year.[12–14] The most important barriers to remediation and disposal of bauxite residue are its high alkalinity ($pH > 12$) and the large amounts generated. Several interesting initiatives to design an application and alternative use for Red Mud have been explored, however, despite the numerous conceivable ways to utilise Red Mud, current applications have not yet shown technical efficiency or economic viability for the full reuse or remediation of this waste.[9,12,15–17]

In this context, the development of technologies allowing a full and preferably value-added reuse of Red Mud is of great interest. Motivated by the recognition that some of the metal oxides typically present in Red Mud, are known to have catalytic activity, there have been several initiatives in the scientific community to use this waste as a catalyst.[1,10,18] Any alternative

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use of Red Mud as a catalyst could contribute to the reduction of environmental impact and at the same time add value to this material.[1,9,19]

Desulfurization

Sulfur, in both, its volatile SO_x oxide or reduced H_2S forms, constitutes a considerable environmental and technical problem. The sulfur compounds are highly undesirable in refining processes as they can lead to the deactivation of some catalysts used in crude oil processing and cause corrosion problems in pipelines, pumping and refining equipments, resulting in substantial financial losses to the industry.[6] The consequences extend, however, beyond the limit of refineries. Specifically, the presence of elevated levels of sulfur in fuels results in the release of compounds, such as carbon disulfide (CS_2), dimethyl sulfide ($(CH_3)_2S$) and sulfur oxides (SO_x). These compounds affect directly the air quality and the environment, causing several problems: smog above cities, acid rain and respiratory problems for human beings. They also inhibit the functioning of catalytic converters that are fitted to car exhausts further compounding this problem.[6]

Globally multiple avenues are being pursued to reduce the negative impacts to the environment caused by the emission of sulfur compounds and other pollutants.[20–23] Among these is hydrodesulphurization (HDS), the conventional method for removal of sulfur from fuels, which employs a high temperature and high pressure reductive catalytic process. HDS is an efficient method, however, it is not or only partially effective for removing heterocyclic sulfur compounds such as dibenzothiophene (DBT) and its derivatives. The development of new technologies and materials applied in a complementary manner to the existing conventional sulfur removing industrial process has been highlighted as a possible approach to meet government regulations worldwide[4,21,22] and academia as well as refinery operators are expending substantial research efforts to find a viable and feasible solution to achieve deep desulfurization of fuels.[6,20,24]

Recently studies have therefore focused on the oxidative desulfurization (ODS) as one of the new strategies with which it may be economically feasible to achieve the low levels of contaminants required by present and future environmental regulations, in particular for Diesel oil.[5,20,21] Several ODS systems have been studied, such as *tert*-butyl hydroperoxide or H_2O_2/V_2O_5 catalysts supported on different metallic oxides,[3] cyclohexanone peroxide/tungsten supported on resin D152,[4] H_2O_2 and H_3CCOOH/sol–gel Fe–TiO_2,[22] H_2O_2 and H_3CCOOH/ionic liquids,[23] H_2O_2/nano-magnetic silica with phosphotungstic acid,[25] and others.[21]

Souza *et al.* have applied the limonite/H_2O_2//HCOOH system as a oxidant. Their results showed an almost complete removal of sulfur compounds, with approximately 96% of the dibenzothiophene being oxidized after 240 min. Sulfone was the principal product formed and was identified by GC/GC-MS.[24]

Oliveira and co-workers developed an amphiphilic niobium oxyhydroxide which was applied as a hybrid catalyst in oxidative desulphurization, specifically with this material being active for DBT oxidation. They highlight that the oxidized molecules with higher polarity migrate to the polar phase after reaction with the peroxo species on the catalyst.[26] Among different chemical oxidants, which have been studied in oxidative desulfurization, the best option is hydrogen peroxide, as it is considered an environmentally friendly yet powerful oxidant, either by itself or when combined with organic acids.[6,20]

On the basis of present knowledge, the ODS process is therefore in principle able to effect the oxidation of sulfur containing compounds such as benzothiophene compounds, into the corresponding sulfoxides and sulfones. The process consist of the two distinct consecutive steps: (1) oxidation of organosulfur compounds and (2) separation of the oxidation products by extraction into a polar solvent or onto an absorbent, with no current technology integrating both steps established on a commercial scale.[21,22] While the two-step process is in principle promising, it has significant disadvantages inherent in the use of organic solvents and adsorbents for extracting the oxidation products, representing a technical and economical barrier to large scale application.

Red Mud as a desulfurization catalyst

A possible and desirable strategy for the realization of an economically and ecologically viable ODS process would be to use a material able to selectively remove sulfur compounds from fuels by a combined process of oxidation and adsorption of the oxidized products formed, thus eliminating the need for solvents.

Given the large amount of Red Mud available, its low or effectively negative value and the known potential catalytic activity of the metal oxides present, we here report the use of this material as a catalyst for the oxidative desulfurization of a simulated diesel (representing heavy oil fractions) and at the same time as an adsorbent for the resulting sulfoxide/sulfone reaction products.

Results and discussion

Characterization of Red Mud waste

The powder X-ray diffraction pattern of the actual Red Mud used in this study is given in Fig. 1. The XRD analysis of Red Mud showed a typical pattern with the presence of poorly crystalline phases, with low intensity broad diffraction lines. As expected, a multi-component pattern was produced. With such complex patterns, it is possible to fit a number of different combinations of phases. Accordingly, we have associated these peaks to phases which are known to be major components of Red Mud. The pattern shows peaks assignable to the phases quartz ($Qz = SiO_2$), gibbsite ($Gb = \gamma\text{-}Al(OH)_3$), goethite ($Gt = \alpha\text{-}FeOOH$) and hematite ($Hm = Fe_2O_3$), with the iron oxides peaks giving the highest intensity. The gibbsite phase represents the fraction of aluminum hydroxides, which were not completely extracted in the Bayer process.[27] According to the literature, Red Mud typically also contains other amorphous phases such as AlO(OH), TiO_2, $CaCO_3$, not identifiable by XRD.[11,27,28]

The Mössbauer spectrum of the Red Mud (acquired at ambient temperature, ~298 K) is shown in Fig. 2.

The spectrum shows two sextets related to hematite (δ 0.36 mm s^{-1}, Δ -0.22 mm s^{-1}, B_{hf} 50.8 T, relative area 58%) and goethite (δ 0.74 mm s^{-1}, Δ -0.031 mm s^{-1}, B_{hf} 48.6 T, relative area 2%). Two central accentuated doublets were also observed (δ 0.36 mm s^{-1}, Δ 0.58 mm s^{-1}, relative area 35%) and (δ -0.38 mm s^{-1}, Δ 4.11 mm s^{-1}, relative area 5%). They are typical of iron oxides with small particle sizes, congruent with the previous analysis performed by Rio Tinto ALCAN, which showed that the majority of particles (>70%) are less than 10 μm. The Mössbauer spectrum is consistent with the XRD results as the goethite and hematite phases were also identified. Small variations of the value of B_{hf} parameter of Mössbauer analysis have been observed for materials with low crystallinity or when they have isomorphic substitution (Si, Al).[29–31]

According to literature reports, the point of zero charge (PZC) of Red Mud is strongly dependent of the origin and composition of the bauxite, variability in the Bayer process parameters, the addition of different types of flocculants and the composition of the background electrolyte.[11] Fig. 3 shows the curve of electrophoretic mobility of material studied. The electrokinetic potential was determined by plotting the zeta potential *vs.* pH, which allows the determination of the pH at which the surface charges are in equilibrium (point of zero charge, PZC). The PZC found for this particular Red Mud was 6.10, very similar to the values reported in other studies with ranges of 8.3 to 5.3 having been observed previously.[11,32]

As illustrated by the SEM-EDX images shown in Fig. 4, on the microscopic scale (≤20 μm) the morphology of the catalyst

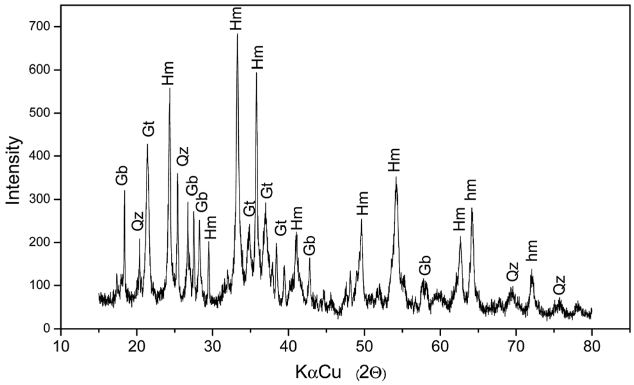


Fig. 1 Powder XRD pattern of Red Mud.

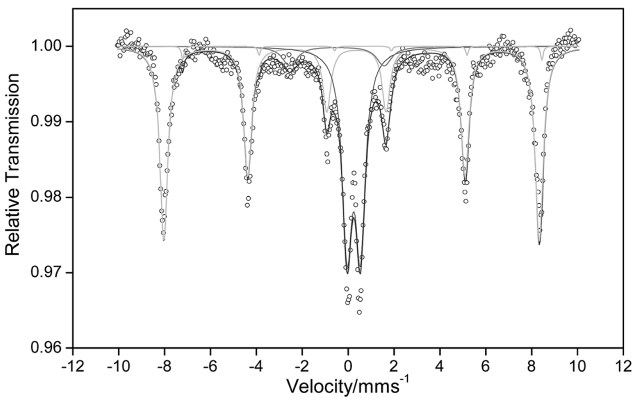


Fig. 2 Mössbauer spectrum of Red Mud.

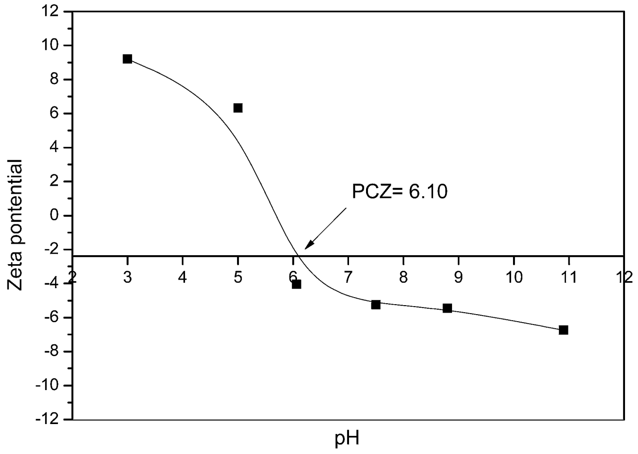


Fig. 3 PCZ of Red Mud.

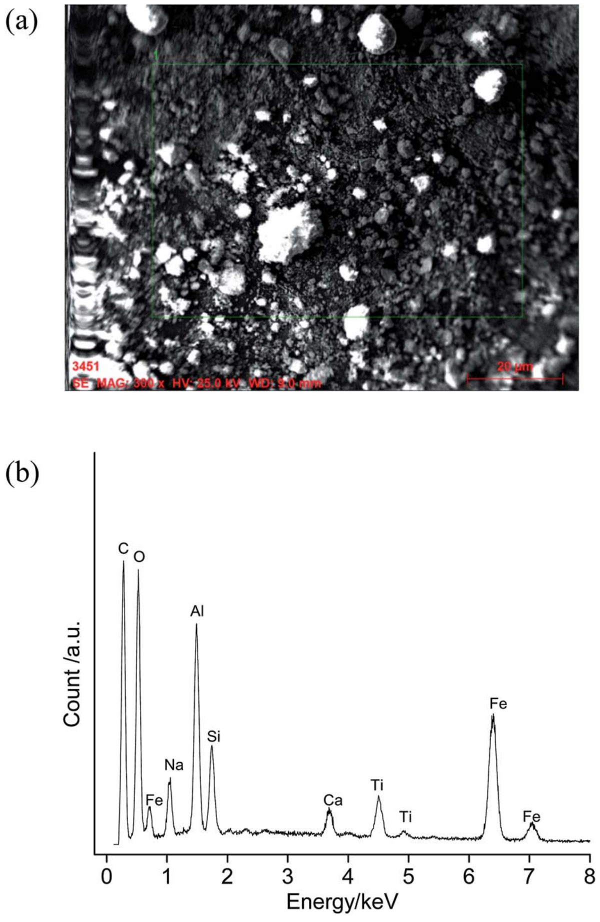


Fig. 4 Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) of Red Mud.

Table 1 Semi-quantitative elemental analysis by EDX

Element	% Mass	% Atomic
Oxygen	37	55
Sodium	9	10
Aluminum	17	16
Silicon	6	5
Calcium	2	1
Titanium	5	2
Iron	24	11

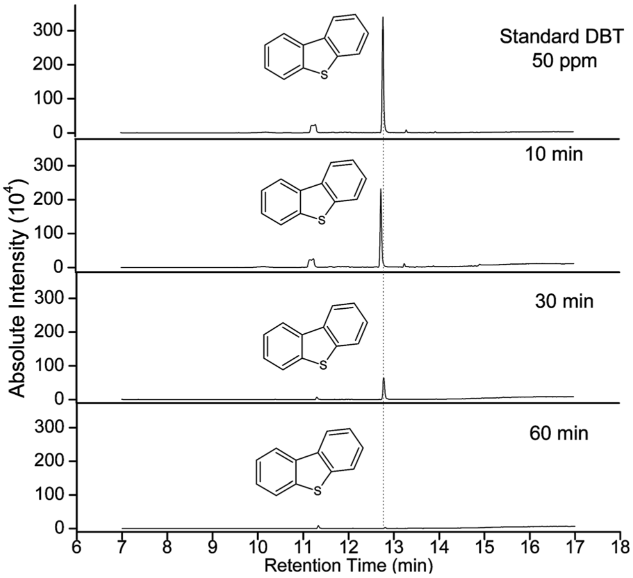


Fig. 5 Oxidation of DBT as a function of time followed by quantitative GC-MS. Reaction conditions: [DBT] = 50 mgL^{-1}; [H_2O_2/H_3CCOOH] = 3.5 mmol L^{-1}; $m_{\text{catalyst}} = 10$ mg; $T = 25 \pm 1$ °C.

shows as an agglomerate of particles with rounded shapes and irregular size distribution, *i.e.*, the aggregate particles are of poorly-crystallized/amorphous forms.[33] This variety of sizes and shapes may reflect the diverse composition of the material, formed by the junction of different minerals.

The EDX analyses provides a semi-quantitative elemental analysis of the Red Mud surface as listed in Table 1.[33]

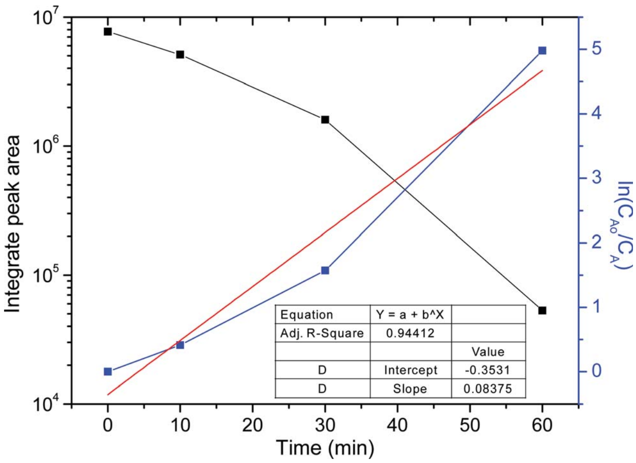


Fig. 6 Integrated peak area and approximate reaction order.

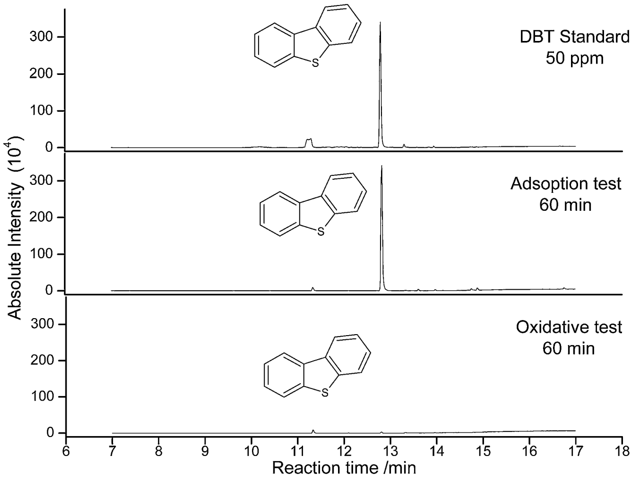


Fig. 7 Comparison of DBT removal from adsorptive and oxidative tests.

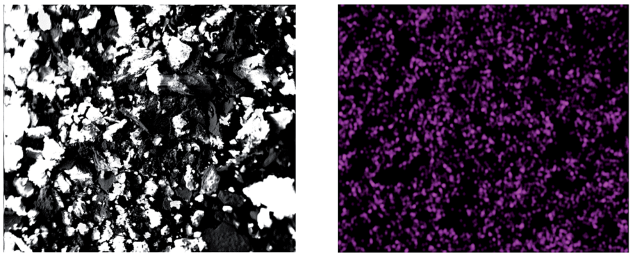


Fig. 8 (a) SEM image and (b) EDS mapping of sulfur on Red Mud after use as a catalyst and adsorbent.

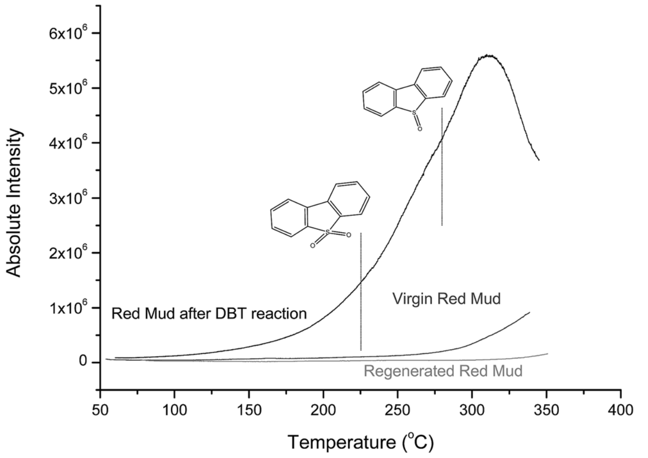


Fig. 9 Release profile of volatile compounds monitored by GC-MS.

The Red Mud was also characterized by adsorption and desorption of nitrogen. The specific surface area (SSA) found to this material was $S_{\text{BET}} = 14\ \text{m}^2\ \text{g}^{-1}$, consistent with the values reported for Red Mud by literature and previous analysis.[11,15,34,35]

Catalytic removal of DBT

Red Mud (10 mg) was tested for its principal effectiveness for the oxidation of dibenzothiophene (DBT) using 10 mL of a solution of DBT (50 mg L^{-1} in toluene, used as the hydrocarbon medium) and 0.1 μL of an equimolar mixture of $[H_2O_2//H_3CCOOH] = 3.5$ mmol L^{-1} as the oxidant. The acetic acid was applied as an activity promoter, as in the presence of hydrogen peroxide under acidic condition, the more active peroxyacetic acid is formed.[22]

The oxidation of DBT was monitored by the variation in initial concentration by gas chromatography with mass spectrometric detection (GC-MS). The total ion count chromatograms are shown in Fig. 5.

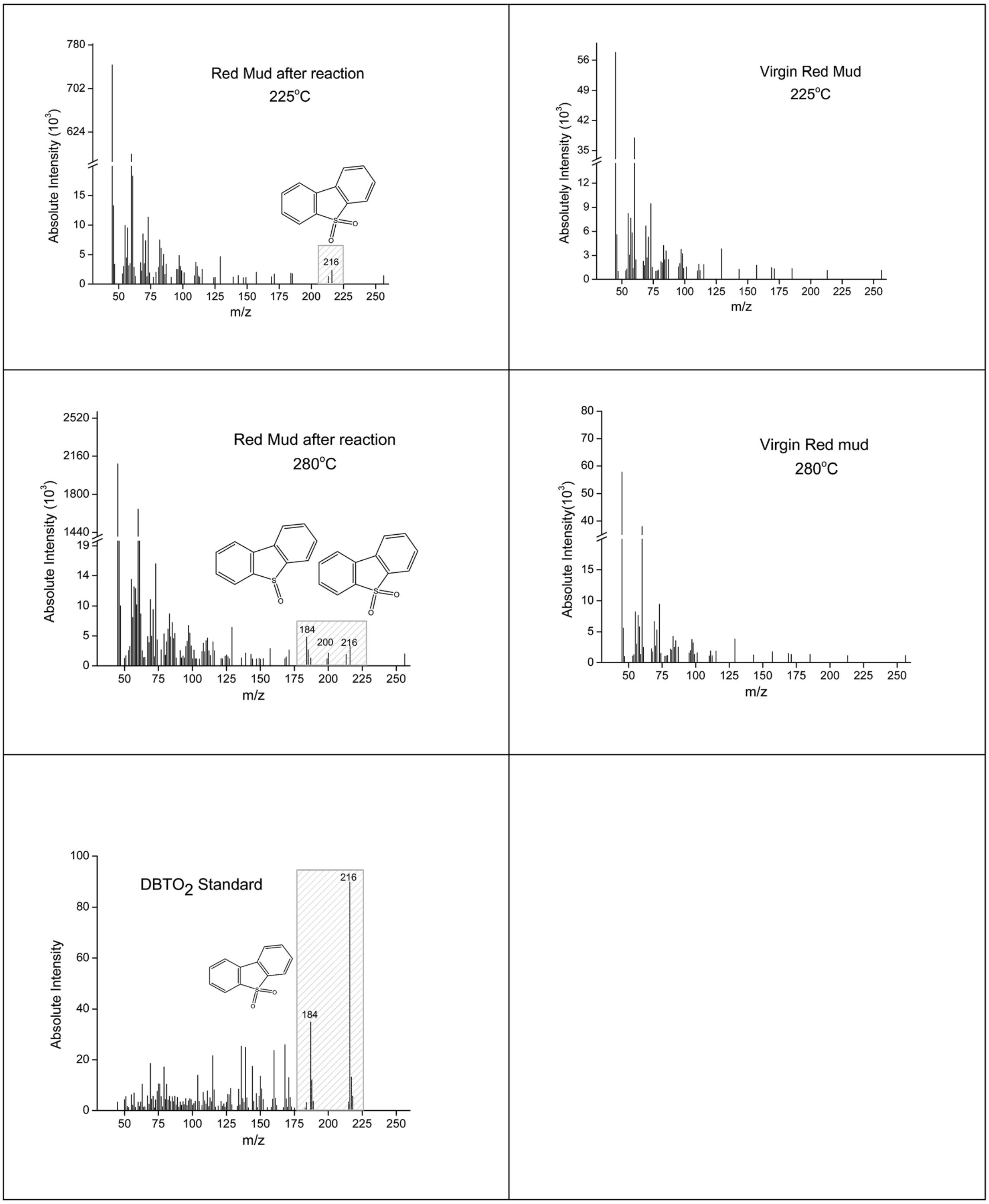


Fig. 10 Mass spectra of ions volatilized from Red Mud after catalytic DBT oxidation and virgin Red Mud obtained at 225 °C and 280 °C.

According to the chromatogram, the combination of Red Mud with the oxidants results in an efficient removal of DBT from the solution: after 10 min of reaction time a significant decrease, about 35%, in the intensity of the signal related to sulfur compound is observed and after 60 min. the remaining signal approaches the detection limit. No other peaks for oxidized products were detected by GC-MS analysis suggesting the existence of a removal mechanism by an adsorption process, *i.e.*, the reagent combination Red Mud/active oxygen is able to oxidize DBT and at the same time adsorb the oxidation products.

A plot of the integrated peak areas from the total ion count chromatograms as a function of reaction time is shown in Fig. 6.

Using the limited number of data points obtained we attempted an approximate kinetic analysis. Both a direct plot of $\ln(C_{A0}/C_{A})$ *vs.* time and a van't Hoff analysis expressing k as a function of time and reaction order gave the best fit for a first order process, for which the rate constant for the apparent consumption of DBT was calculated to be $k \approx 0.08375\ \text{min}^{-1}$.[36] The pH of the solution was monitored throughout the reaction using an indicator paper and remained constant at pH ~6. A test of active phase leaching was performed, by leaving the Red Mud in contact with DBT solution for 60 min. After that the Red Mud was removed by filtration and the oxidants (H_2O_2//H_3CCOOH) added without any activity being observed confirming the catalyst is truly heterogeneous.

The hypothesis that Red Mud acts as an oxidation catalyst and adsorbent at the same time is supported by the following control reactions:

- In the absence of Red Mud, H_2O_2 by itself as well as the combination of H_2O_2//H_3CCOOH by itself are inactive as an oxidant and the concentration of DBT remained constant in both experiments. This is congruent with earlier observations.[22]

- *Vice versa* in the absence of oxidants but presence of Red Mud no decrease of the DBT concentration was observed, *i.e.*, the Red Mud does not act as an adsorbent for DBT by itself.

- The GC-MS traces of the oxidation and adsorption control reaction solution tests after 60 minutes are shown in Fig. 7.

Fig. 8 shows the EDS-SEM mapping of Red Mud after its use as an oxidation catalyst and adsorbents.

The mapping EDS shows elevated dispersion of the sulfur on the Red Mud surface after the reaction. The pink points are associated with the presence of oxidized DBT on active sites on surface of the material with a fairly homogeneous distribution being observed. (EDS mapping of Red Mud before the reaction did not show the presence of any sulfur).

The presence of oxidized DBT on the surface of the Red Mud was also probed by gas chromatography-mass spectrometry (GC-MS) using a solvent-free solid injector (SFSI). The difference of the GC-MS trace of gas samples volatilized from virgin and Red Mud after a DBT oxidation reaction after 60 min are shown in Fig. 9.

The release profile of volatile compounds from Red Mud shows a substantially higher intensity peaking at $T \approx 325$ °C, which is close to the boiling points of dibenzothiophene sulfoxide (DBTO) at 285 °C and dibenzothiophene sulfone ($DBTO_2$) at 307 °C. Mass spectra obtained at various temperatures covered by the large peak in Fig. 9 are shown in Fig. 10 and compared to controls using virgin Red Mud.

The mass spectrum at 225 °C of the Red Mud after its use as a catalyst shows a peak at $m/z = 216$, assignable to the sulfone species. At 280 °C, an additional signal at $m/z = 200$, associated with the release of the intermediate sulfoxide is seen. The peak at $m/z = 184$ is assigned to a fragment in dibenzothiophene sulfone $DBTO_2$ spectrum, which also can be seen at MS spectra of authentic $DBTO_2$ shown in Fig. 10. These fragments were not observed in the mass spectra of the virgin Red Mud. The differences between the MS spectra are further direct evidence for the removal of DBT from the hydrocarbon medium.

The composition of the Red Mud before and after the oxidation reaction was also studied by infrared spectroscopy. Fig. 11 compares the two spectra, which show the typical band of the oxides constituting Red Mud along with peaks for bound water present in the material (~10% w/w). The spectra interpretation is complicated because of the complex composition of Red Mud due to the presence of several mineralogical phases containing numerous adsorption and oxidative sites. The positions of the absorption bands are similar in both spectra. The bands 535 and 465 cm^{-1} are attributed to the Fe–O bond in goethite and hematite, however, the bending vibration of Si–O and Al–O, are also in the 465 cm^{-1} region.[27,33] The overlapping bands in the 1000 cm^{-1} region are assigned to angular deformation of Al–O and Si–O.[37] The Red Mud after DBT shows additional bands at 1418 and 1465 cm^{-1}, attributed to C=C bonds from aromatic compounds and at 1160 cm^{-1} there is a soft shoulder peak characteristic of angular deformation to C–H bond from aromatic compounds. These bands are present only in the spectrum of Red Mud after the oxidation reaction. The S=O bands from sulfone also occur in this region, but are obscured by the overall broad peak shape.[31] Also present in both spectra are stretching vibrations between 3100–3500 cm^{-1} and 1644 cm^{-1} from O–H and H–O–H bonds from the surface of goethite and hematite, as well as from bound water present in

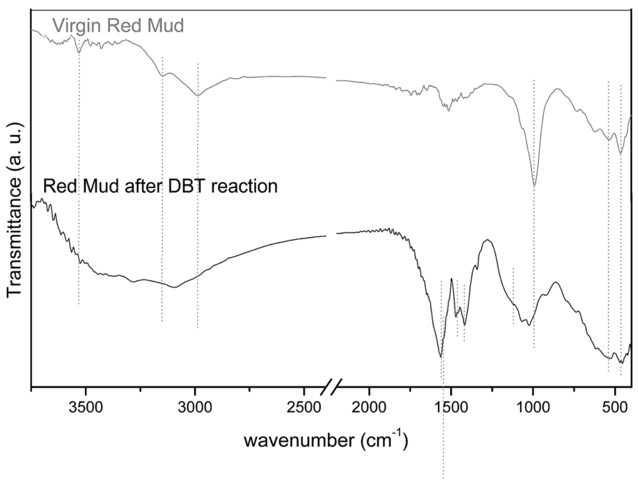


Fig. 11 Infrared spectra of Virgin Red Mud and Red Mud after use as a catalyst.

some of the mineral phases of Red Mud. The distinct band at 3100 cm^{-1} is due to the bulk hydroxyl stretch and two less intense bands at 3300 and 3660 cm^{-1} can be attributed to the surface hydroxyl groups in goethite.[31]

Recycling and regeneration of the catalyst

The deactivation of catalysts is generally a consequence of processes that result in the loss of the active phase or by poisoning or occupation and blocking of the active sites by adsorption. In this work deactivation would logically occur by adsorption of the oxidized sulfur compounds. Since chemisorption was identified as reversible process in our work and on the basis of the GC-MS results discussed above (Fig. 9 and 10), we postulated that any surface adsorbed species in Red Mud could be removed allowing regeneration and subsequent recycling of the oxidation catalyst, an important feature for a potential industrial application. Several tests were conducted to evaluate the regeneration of the Red Mud after the DBT oxidation reaction by a thermal desorption process. The catalyst was subjected to a heat treatment (10 °C min^{-1} from 25 °C to 300 °C, kept at the final temperature for one hour under an oxidizing atmosphere of air at a 10 mL min^{-1} flow). The material recovered from this regenerative treatment was highly active in a new oxidation cycle giving ~97% removal of DBT under the same reaction conditions specified earlier, *i.e.*, within the estimated analytical error range the material can be fully regenerated and reused for sulfur compound removal.

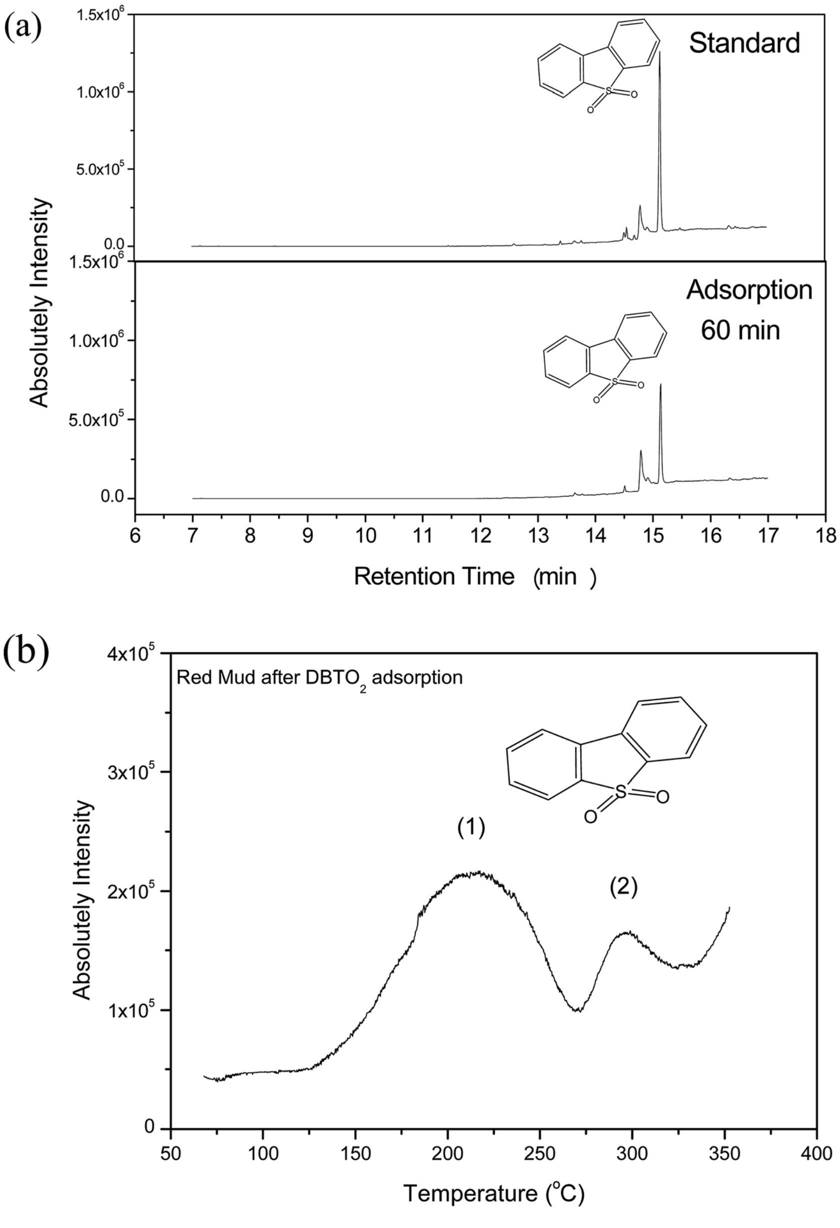


Fig. 12 (a) Adsorption of DBTO$_2$ standard after 60 min. Experimental condition: [DBTO$_2$] = 50 mg L^{-1}; $m_{\text{adsorbent}} = 10$ mg; $T = 25 \pm 1$ °C. (b) Release profile of dibenzothiophene sulfone monitored by GC-MS.

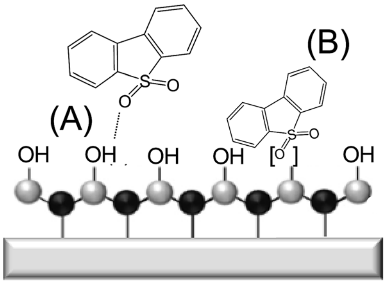


Fig. 13 Proposal adsorption modes of $DBTO_2$ on the Red Mud surface (gray spheres are Fe, Al, Si or Ti; black spheres are O).

The Red Mud obtained from the thermal regeneration process, was also analyzed by solvent-free solid injector (SFSI) coupled with gas chromatography-mass spectrometry (GC-MS). The GC-MS traces are part of Fig. 9 and verify a complete removal of adsorbed compounds from the material after its use in the DBT oxidation reaction. This result asserts that the material was regenerated and can be reused in successive reaction cycles.

The regenerative system described here is promising. Since during the heating of Red Mud, the oxidized sulfur compounds ($DBTO_2$ and DBTO) are released in sequence, these compounds could be recovered in a small volume with high concentrations possibly allowing a specific separate treatment and transformation to value-added products, which allows the treatment of the effluent be made by HDS process, already established in the industry, thus leading to a complete use of the carbon value chain.

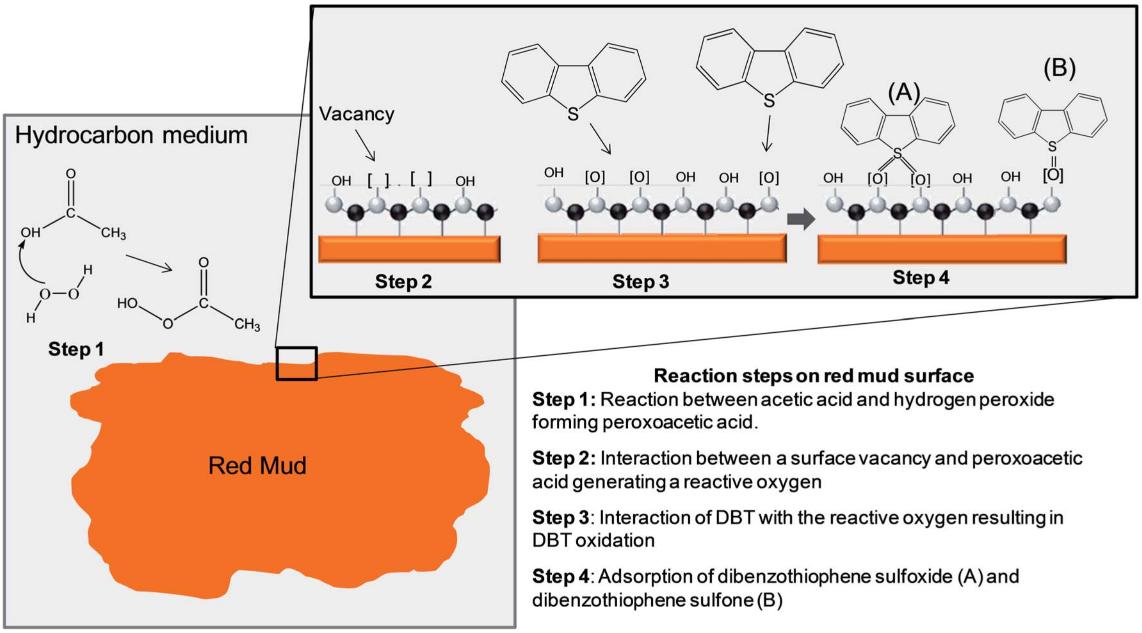
Adsorption of authentic dibenzothiophene sulfone standards

In order to probe the mechanism of DBT oxidation, the adsorption of an authentic dibenzothiophene sulfone standard ($[DBTO_2] = 50$ mg L^{-1}) onto Red Mud (10 mg) was evaluated. As with the test with DBT (see above), the adsorption over time was monitored by GC-MS and the desorption from the Red Mud after impregnation with $DBTO_2$ using solvent-free solid injector (SFSI). The results of both tests are shown in Fig. 12.

Fig. 12a shows that after 60 minutes the Red Mud had adsorbed ~50% of $DBTO_2$ present, while the reversibility of the process was confirmed by the corresponding release profile, which identified two distinct sites and stages of ad- and desorption. Since the release of the $DBTO_2$ occurred at two distinctly different temperatures, this suggests the presence of two different interactions between the surface and the substrate, as proposed in Fig. 13.

At site (A) the sulfone interacts with a hydroxyl group on the surface through a single hydrogen bond, which is would explain the release of $DBTO_2$ at the lower temperatures (beginning at ~130 °C). On the other hand, for site (B) we propose a stronger interaction, assuming that the oxygen of $DBTO_2$ molecule can fill vacancies on the Red Mud surface. In this case, the release of $DBTO_2$ molecule occurs at a higher temperature, starting near 270 °C. Evidence for the presence of vacancies on the Red Mud surface was provided by a H_2O_2 decomposition test, in which the O_2 liberation in presence of organic compounds and water is similar.[38]

On the basis of these results, we propose that the DBT removal is in fact a process that occurs on the surface of Red Mud. That hypothesis is further supported by the comparison of the profiles of the release compounds from Red Mud after the DBT oxidation test (Fig. 9) and from the Red Mud after $DBTO_2$



Reaction steps on red mud surface

Step 1: Reaction between acetic acid and hydrogen peroxide forming peroxoacetic acid.

Step 2: Interaction between a surface vacancy and peroxoacetic acid generating a reactive oxygen

Step 3: Interaction of DBT with the reactive oxygen resulting in DBT oxidation

Step 4: Adsorption of dibenzothiophene sulfoxide (A) and dibenzothiophene sulfone (B)

Fig. 14 Possible mechanism of an oxidative adsorptive process of DBT on the surface of Red Mud (gray spheres are Fe, Al, Si or Ti; black spheres are O).

adsorption (Fig. 12b), both of which show a different temperature region for release of compounds by heating the solids. A possible pathway and mechanism of DBT oxidation on the Red Mud surface is presented in Fig. 14.

We propose that the first step is the formation of peroxoacetic from the reaction H_2O_2 with H_3CCOOH.[21,22] The peroxoacetic formed is able to insert an oxygen into a vacancy present on the Red Mud surface. The oxidation of DBT then occurs by interaction with this oxygen, resulting in a formation of dibenzothiophene sulfoxide and dibenzothiophene sulfone. Two types of interactions could occur. In the first the DBT would interact with two neighboring oxygens, resulting in the formation of $DBTO_2$. This is substantiated by the mass spectrum from solvent-free solid injector (SFSI) (Fig. 10), in which the release of this compound is seen at 225 °C. In the second the DBT interacts with just with one oxygen, resulting in formation DBTO. This is substantiated by the release of this compound at 280 °C from mass spectrum of solvent-free solid injector (SFSI).

Experimental

Source of sample

Red Mud samples (∼41% of Fe) were obtained from Rio Tinto Alcan's Jonquiére, Quebec operation, Canada. Before use the material was dried to constant weight at 60 °C (±1 °C) and sieved in 35 mesh sieve, to <0.5 mm grain size. Further details of the Red Mud composition as previously determined by the supplier are given previous publications.[39]

Catalyst characterization

The transmission Mössbauer spectroscopy experiments were carried out in a CMTE model MA250 spectrometer with a $^{57}Co/Rh$ source at room temperature, using α-Fe as a reference. The zeta potential determination was performed by measuring electrophoretic mobility using an apparatus Zeta-Meter System 3.0. The average of 10 readings electrophoretic mobility in pH 3, 5, 6, 7, 9 and 11 were taken to determine the PZC. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Digilab Excalibur spectrometer with a spectral range from 400 to 4000 cm^{-1}. Samples were ground to a powder and pressed into KBr pellets. The FT-IR spectra were collected with a resolution of 4 cm^{-1} over an average of 32 scans. The powder XRD data were obtained with a Phillips model PW1830/40 equipment using CuKα radiation ($\lambda = 1{,}54$ Å), current of 30 mA, voltage of 30 kV and scanning from 10 to 80° (2θ) at a scan rate of 1° min^{-1}. The morphology were analysed by scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS), using a FEI Inspect 50S apparatus with a 15 kV of tension. The release profiles of volatile compounds monitored before and after the DBT oxidation were analyzed by Gas chromatography-mass spectrometry (GC-MS) using a solvent-free solid injector (SFSI), 1 mg of Red Mud was inserted into a glass capillary vial (1 mm i.d. × 5 mm in length). The vial was placed in a solvent-free solid injector, which are connected to the GC-MS, the rate heating used was 10 °C min^{-1} from 25 °C to 350 °C.

Catalytic reactions

The catalytic reactions were carried out with a total volume of 10 mL (9.9 mL of the DBT solution at 50 mg L^{-1} concentration and 0.1 mL of the $H_2O_2//H_3COOH$) also 10 mg of Red Mud as a catalyst. The oxidant mixture of H_2O_2 (50% v/v) and H_3COOH was prepared 2 hours before mixing with the DBT. The adsorption of DBT was also performed using 10 mL of DBT solution and 10 mg of the Red Mud. The DBT removal was monitored by gas chromatography coupled to mass spectroscopy (GC-MS) using a Shimadzu, model 2010. The analyses were made using a RTX-5MS column (30 m × 0.25 mm × 0.25 mm). The heating ramp was 60 °C for 1 min, heating rate of 15 °C min^{-1} to 270 °C and remaining there for 2 min.

Conclusion

Red Mud is an effective catalyst for the oxidation of dibenzothiophene (DBT) to dibenzothiophene sulfoxide (DBTO) and dibenzothiophene sulfone ($DBTO_2$). The process is a promising alternative with potential for application on an industrial scale, at it is in principle easily implemented, efficient and low cost, as it employs a waste material of negative value and can be carried out at room temperature and atmospheric pressure.

The removal DBT occurs by combined oxidative adsorption processes on the Red Mud surface which presents two different types of interaction resulting in the formation of dibenzothiophene sulfoxide and dibenzothiophene sulfone. Additional experiments not reported here in detail suggest that a variation in chemical constitution of Red Mud does not significantly affect its activity.[40] In addition, the Red Mud could be regenerated by a thermal treatment in air resulting in a recovered catalyst activity of 97% compared to virgin, *i.e.*, unused Red Mud.

What differentiates the system described here is the ability to effect DBT removal in one-step, using a solvent free system, in which the polar products (sulfoxides and sulfones) do not have to be extracted by solvents or adsorbed in a separate step. In this process, both an environmentally friendly oxidation system (H_2O_2 and CH_3COOH) and catalyst (Red Mud waste) are employed.

The possibility to recover the sulfur compounds during the regeneration process from the Red Mud also shows potential prospect for industrial applications, since the Sulfoxides and Sulfone at higher concentration could be amenable to conventional HDS processes potentially yielding comparatively valuable biphenyls. The application of Red Mud as a catalyst for sulfur compound removal from heavy fuel oils may thus make a contribution to solve two pressing problems in the aluminum and petrochemical industries in Brazil and elsewhere.

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