Nota Técnica

NEW STRATEGIES FOR TREATMENT AND REUSE OF SPENT SULFIDIC CAUSTIC STREAM FROM PETROLEUM INDUSTRY

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This work examines traditional and new routes for removal of H_2S and other sulfur compounds from spent sufidic caustic (SSC). SH^- (hydrogenosulfide) and S^{2-} (sulfide) ions were quantitatively oxidized at 25 ºC using H_2O_2, NaOCl or a spent sulfochromic mixture. SH^-/S^{2-} ions were also removed via reaction with freshly prepared iron or manganese hydroxides, or after passing the SSC through strong basic anion exchange resins (OH^- form). The treated caustic solution, as well as iron/manganese hydroxides, removed H_2S from diesel samples at 25 ºC. SSC treatment via strong basic anion-exchange resins produced the treated caustic solution with the highest free alkalinity.

Keywords: spent sulfidic caustic; soda reuse; sulfur removal.

INTRODUCTION

The effluents generated in petroleum refineries vary widely in terms of quantity and quality. This is determined by the type of feedstock processed, the existing units in the refinery and operational conditions.[1] Some of these effluents must be treated individually because mixing with other waste streams makes their treatment more difficult.[1,2] One such effluents is derived from the liquid-liquid contact of aqueous sodium hydroxide with a large variety of hydrocarbon streams.[3] The objective is to remove hydrogen sulfide and other sulfur compounds such as thiols from these streams. This treatment is effective and low cost.[4-6] H_2S and other sulfur compounds lead to corrosion of concrete and metallic structures (due to their acidity), which poses difficulties in oil storage, use and handling.[4] These substances also have a negative impacts on wastewater treatment.[4,7,8] Their toxicity and malodorous properties deteriorate finished products,[4,5] and must be treated for environmental protection.[6,9,10] Once most NaOH has reacted with sulfur compounds, the solution is known as spent sulfidic caustic (SSC).[11]

SSC has high pH (usually above 13), dark color, foul odor and is highly toxic. It contains several contaminants such as sulfides, thiosulfates, thiols, phenols, naphtenic acids and emulsified hydrocarbons.[8,12] Its composition is highly dependent on the type of refinery streams that have been treated.[13]

Sodium hydroxide reacts with hydrogen sulfide as follows:[14]

$$H_2S + NaOH \rightarrow NaSH + H_2O \qquad (1)$$
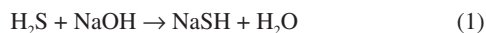
SSC is classified by the RCRA (US Resource Conservation and Recovery Act) as hazardous waste.[15] The odor and reactive (corrosive) nature of SSC does not allow direct biological treatment, even after neutralization and dilution.[16] Direct neutralization of SSC releases H_2S. SSC is also a powerful reducing agent. SH^- (hydrogenosulfide) ions have a high oxygen demand (2 mol O_2 per mol HS^-),[16] resulting in depletion of dissolved oxygen. Therefore, it is necessary to perform pre-treatment in order to reduce its impact on effluent treatment units.[10,17]

The most common methods used to remove sulfur compounds

from SSC are chemical oxidation, air stripping, wet air oxidation and precipitation.[13,18-21] Wet air oxidation is conducted under high temperature and pressure.[13,17] SH^- ions are converted into sulfate (SO_4^{2-}) species. The treated SSC is mixed with a strong acid (usually sulfuric acid) so as to adjust pH close to 7.[13,15] In the chemical oxidation method, the most cited oxidants are hydrogen peroxide, sodium hypochlorite, potassium permanganate, chlorine and ferrate(VI) ions.[22] Considerable safety measures must be taken in these processes.[13] SH^-/S^{2-} ions may be removed via precipitation with transition metals present in wastewaters, particularly under anaerobic conditions.[21] The most employed metal by far is iron.[2] It is cheap and presents low environmental impact.[2,12,22] Iron-sulfur interaction has been the subject of extensive investigation.[12,22,23] Other metals are scarcely cited in these studies. $Fe(II)$ ions are precipitated as FeS and the yield is quantitative provided the pH is above 2-3 (otherwise FeS dissolves, releasing H_2S). $Fe(III)$ ions are reduced by SH^- to $Fe(II)$, this latter being precipitated as FeS together with elemental sulfur.[2,12] Sulfur removal by redox methods is effective but can produce large amounts of chemical sludge.

Biological methods for H_2S (and other sulfur compounds) removal from effluents have received much attention since they may be more efficient and economical than traditional physicochemical methods, provided adequate operational conditions are employed.[11,24] These methods have be performed on-site in many refineries.[13] SH^- ions are preferably oxidized to sulfate species. This conversion is thermodynamically more favorable than the conversion SH^--elemental sulfur or thiosulfate.[9,21,24] However there are situations where destruction of toxic pollutants is only possible by non-biological methods.[2]

Increasingly stringent environmental laws have stimulated research into new waste management strategies. New treatments are focused on the reuse of water and chemicals.[1,13,15] In this regard, SSC can be handled in two ways: by reuse of treated SSC or replacement of the caustic solution by a solid base. Cutting down on water consumption reduces the cost of treatment and generation of final wastes. Other possibilities include the use of activated carbon for H_2S removal from liquid hydrocarbon streams[4] and the use of membrane technology for NaOH recovery.[12]

The objective of this work was to evaluate the effectiveness of conventional and new oxidation routes for processing SSC. In a second step, new procedures for removal of sulfur compounds were

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tested but allowing the reuse of the treated caustic solution. This solution was employed to treat a hydrocarbon stream containing dissolved hydrogen sulfide.

EXPERIMENTAL

Raw materials

SSC from treatment of diesel fractions after desulfurization in a hydrotreater unit of a Brazilian refinery was used in this study. The main properties of the SSC are given in Table 1. The data presented fall within the range of values found in the literature for composition of SSC.[12] Oils and greases were removed prior to the experiments using a phase separator drum. X-ray fluorescence showed the only metal present in detectable amounts was sodium.

Table 1. Characteristics of the SSC employed in this work

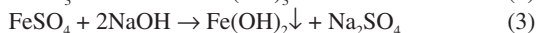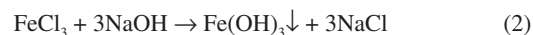| Color	dark brown-yellowish
Free alkalinity	1.7 mol L^{-1}
SH$^-$ concentration	0.7 mol L^{-1} (23 g L^{-1} as S)
Oils and greases	1% vol.
COD	27.8 g L^{-1}

Diesel samples containing 953 mg L^{-1} H$_2$S were also used in this study. These samples were derived from the hydrotreater unit mentioned above.

Treatment of SSC with oxidizing agents

The oxidizing agents employed were: hydrogen peroxide (30 wt%), sodium hypochlorite (5 wt%) and a spent sulfochromic mixture (free acidity 8 mol L^{-1}, [Cr(III)] = 0.8 mol L^{-1}, [Cr(VI)] = 1.7 mol L^{-1}). All experiments were run at 25 ºC under magnetic stirring (200 rpm) in 250 mL beakers. In the case of hydrogen peroxide and sodium hypochlorite, 50 mL of SSC were employed. Addition of the oxidizing solution was performed in 5 mL portions until full consumption of SH$^-$ ions. When the spent sulfochromic mixture was employed, 2-3 mL were added to 50 mL of SSC until disparition of SH$^-$ ions. These treatments were monitored by adding some drops of the treated SSC to 0.1 mol L^{-1} lead acetate in a filter paper. The presence of a black-brown precipitate (PbS) indicates the presence of SH$^-$ ions in the SSC (detection limit 1 mg L^{-1}).[14,25] Reproducibility was found to be in the order of ± 3%, by repeating the experiments in triplicate. After the oxidation procedure, the effluent was neutralized with 3 mol L^{-1} sulfuric acid until pH 7.

Removal of sulfur via precipitating agents

The SSC was treated with freshly prepared iron or manganese hydroxides, prepared via the reaction of 0.2 mol L^{-1} FeCl$_3$, 0.2 mol L^{-1} MnCl$_2$ or 0.2 mol L^{-1} FeSO$_4$ with 6 mol L^{-1} NaOH:

$$FeCl_3 + 3NaOH \rightarrow Fe(OH)_3\downarrow + 3NaCl \qquad (2)$$
$$FeSO_4 + 2NaOH \rightarrow Fe(OH)_2\downarrow + Na_2SO_4 \qquad (3)$$
$$MnCl_2 + 2NaOH \rightarrow Mn(OH)_2\downarrow + 2NaCl \qquad (4)$$

Mn(II) was readily oxidized to Mn(IV) by adding some drops of H$_2$O$_2$ (30 wt%):

$$Mn(OH)_2 + H_2O_2 \rightarrow MnO(OH)_2\downarrow + H_2O \qquad (5)$$

The precipitates were filtered in a filter paper under vacuum. They were not washed. The SSC was passed in 2 mL portions (1.5 mL min^{-1}) through these precipitates (kept in the filter paper) until the lead acetate test produced a positive result. This test is more reliable than using visual control of the color change of the precipitate, from orange-brown (Fe(OH)$_3$) or green (Fe(OH)$_2$) to black (FeS), or from dark-brown (MnO(OH)$_2$) to pink-yellow (MnS + S). Like iron, manganese presents a variable oxidation state (+2 to +4). Reproducibility was found to be in the order of ± 5%, by repeating the experiments in triplicate.

Removal of sulfur via ion-exchange resins

Two strong basic anion exchange resins (type-I) were employed for sulfide adsorption from the SSC: Amberlite IRA 420 (Carlo Erba), Dowex 1 (Dow Chemicals). The main properties of these resins are shown in Table 2. According to the literature, no previous study on the processing of SSC samples by ion-exchange techniques has been published.

Table 2. Anion exchange resins characteristics

Description	Amberlite IRA 420	Dowex 1
Matrix	Styrene-divinylbenzene	Styrene-divinylbenzene
Functional group	Quaternary ammonium	Quaternary ammonium
Structure	Macroporous	Macroporous
Ionic form	Cl$^-$	Cl$^-$
Apparent density	650 g L^{-1}	705 g L^{-1}
Exchange capacity	1.3 eq L^{-1}	1.4 eq L^{-1}
Grain size	0.125-0.177 mm	0.30-1.20 mm
Operating pH range	0-14	0-14
Moisture retention capacity (%)	50-55	43-48

The dynamic method was applied in this study. Glass columns (diameter d = 10 mm) were packed with a slurry of the resin until the settled resin bed attained the established height (L = 100 cm). Therefore, L/d ratio was 100 in all experiments. The resins were previously equilibrated with 1 mol L^{-1} NaOH for 2 h. The SSC was passed through a calibrated rotameter (1.5 mL min^{-1}) before entering the column, at room temperature (~25 ºC). The eluate was collected for sulfur analysis. The capacity of the resins to retain sulfur was estimated from a breakthrough study. For this purpose, the SSC and a standard Na$_2$S solution (1 g L^{-1}, free alkalinity 1.0 mol L^{-1}) were employed. Flow rate was 1.5 mL min^{-1} and the experiments were performed at room temperature (~25 ºC).

Sulfur desorption was tested using freshly prepared H$_2$O$_2$ (1-6 mol L^{-1} in NaOH 1 mol L^{-1}). Flow rate was fixed at 1.0 mL min^{-1} and experiments were run at 25 ºC. The eluate was collected for sulfur analysis. All experiments in this section were run in triplicate and data obtained were within ± 5%.

Removal of H$_2$S from diesel fractions

The SSC treated with iron/manganese hydroxides or via ion-exchange resins was employed to treat diesel samples containing sulfur compounds. Free alkalinity was kept as such.

Liquid-liquid extractions were performed at 25 ºC using an aqueous/organic phase ratio (A/O) equal to 1 (10 mL of caustic solution + 10 mL diesel). The contact time was 3 min. After removal of the treated diesel, 10 mL of a new sample was treated with the

same caustic solution. The presence or absence of H_2S was assessed by placing drops of treated diesel in a filter paper containing lead acetate. Reproducibility was found to be in the order of ± 4%, by repeating the experiments in triplicate.

The possibility of removal of sulfur compounds directly from diesel using $MnO(OH)_2$, $Fe(OH)_3$ or $Fe(OH)_2$, prepared as described earlier, was also investigated. After filtration of the hydroxide, approximately 100 mg were mixed into 100 mL of diesel. This mixture was stirred (200 rpm) at 25 °C for 3 min. Diesel was easily separated from the solid by decantation or centrifuging. The recovered solid was introduced to 100 mL of a new sample. This cycle was stopped when the lead acetate test gave a positive result in the treated diesel. Reproducibility was found to be in the order of ± 5%, by repeating the experiments four times.

### Analytical methods

Chemical oxygen demand (COD) was determined by the method described elsewhere in the literature.[26] Free alkalinity was measured by the potentiometric method using a glass electrode and 0.805 mol L^{-1} HCl.[27] Free acidity was measured in a similar manner with 0.205 mol L^{-1} KOH. pH was measured with a glass electrode.[27] Crystalline phases in the iron/manganese hydroxide samples were identified by X-ray diffraction analysis (Bruker-AXS D5005) and the continuous scanning method at 35 kV and 40 mA, using Co Kα as the radiation source. Sulfide ions were determined by an ion-selective electrode (Orion 9616 BNWP).

## RESULTS AND DISCUSSION

Oxidative treatment

20 mL of H_2O_2 or 125 mL of NaOCl were required to treat 50 mL of SSC. The reactions involving these oxidants are:[14,25]

$$HS^- + 4H_2O_2 \rightarrow 4H_2O + SO_4^{2-} + H^+ \quad (6)$$
$$HS^- + 4NaOCl \rightarrow 4NaCl + SO_4^{2-} + H^+ \quad (7)$$
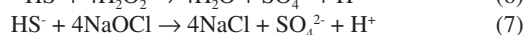
No elemental sulfur was formed in these oxidative treatments.[9,21] COD was reduced by more than 99%. The oxidation of organic matter explains why consumption of H_2O_2 and NaOCl were higher (≈ 20%) than the stoichiometric amount required to oxidize all SH^- ions (reactions 6 and 7).

H_2O_2 must be added slowly under stirring because the reaction is very exothermic. NaOCl does not present this problem, but the volume of treated waste is higher because of its low concentration. After neutralization with sulfuric acid, no turbidity and precipitation were observed.

The use of SSC to treat spent sulfochromic mixture was aimed at employing it as a reactant to treat other wastes. SH^- removal via mixture of appropriate wastes reduces consumption of water and chemicals. These wastes must contain reactive components such as oxidant – reducing and acidic – alkaline species. The reaction between SH^- and Cr(VI) may be expressed as:

$$29\ H^+ + 3\ SH^- + 4\ Cr_2O_7^{2-} \rightarrow 3\ SO_4^{2-} + 8\ Cr^{3+} + 16\ H_2O \quad (8)$$
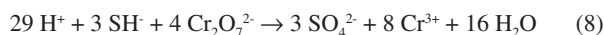
It occurs simultaneously to neutralization of both wastes:

$$H^+ + OH^- \rightarrow H_2O \quad (9)$$

50 mL of spent sulfochromic mixture treated 40 mL of SSC. The amounts of Cr(VI) and SH^- mixed indicate that the amount of

the latter was not sufficient to reduce all Cr(VI) (no elemental sulfur was formed). As in the other oxidative treatments, organic matter was also oxidized by Cr(VI). COD was reduced by more than 99%. This explains the colorless aspect of treated SSC (as seen in Figure 1). Free acidity was drastically reduced from 8 to about 0.5 mol L^{-1} (≈ 6% of the initial value). This is basically due to the oxidation of SH^- ions (reaction 8) and the organic matter. Addition of 6 mol L^{-1} NaOH until pH 7-8 formed a green precipitate, $Cr(OH)_3$, that was subsequently filtered. The original features of the SSC – dark color, foul odor and high toxicity – are no longer observed after treatment (Figure 1) with these oxidants. The final treated effluent meets the requirements for disposal of treated aqueous effluents according to the Directory 357 from the Brazilian National Environmental Council.[28]
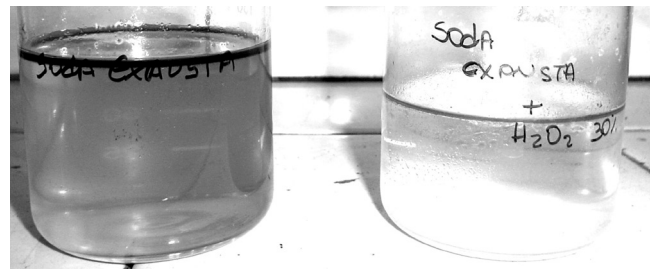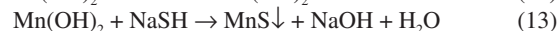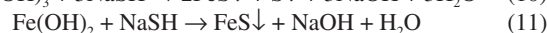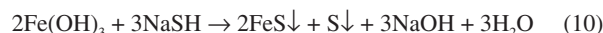

Figure 1. *SSC before (left) and after treatment (right) with H_2O_2*

When two wastes are treated together, the order of addition depends on the relative amounts of reactive species. In the present case, the mixture of both wastes cannot release hydrogen sulfide. If the spent sulfochromic mixture was added to the SSC, the free alkalinity of the latter would be rapidly consumed before oxidation of all SH^- ions, favoring H_2S release.

The disadvantage of treatments with oxidizing agents is the generation of an end waste containing high amounts of Na_2SO_4. Reduction or even suppression of this effluent requires removal of SH^- ions by precipitation.

Sulfur removal via precipitation of insoluble sulfides

This treatment is based on the following reactions:

$$2Fe(OH)_3 + 3NaSH \rightarrow 2FeS\downarrow + S\downarrow + 3NaOH + 3H_2O \quad (10)$$
$$Fe(OH)_2 + NaSH \rightarrow FeS\downarrow + NaOH + H_2O \quad (11)$$
$$MnO(OH)_2 + NaSH \rightarrow Mn(OH)_2\downarrow + S\downarrow + NaOH \quad (12)$$
$$Mn(OH)_2 + NaSH \rightarrow MnS\downarrow + NaOH + H_2O \quad (13)$$

Fe(III) is reduced to Fe(II), precipitating as FeS. In a similar manner, Mn(IV) is reduced to Mn(II). MnS is its final product. According to reactions 10 and 11, Fe(III) can react with 50% more SH^- ions than Fe(II). In fact, experimental data indicate that $Fe(OH)_3$ treated 45% more SSC than $Fe(OH)_2$. However, Mn(IV) was more effective than Fe(III). $MnO(OH)_2$ treated 30% more SSC than $Fe(OH)_3$. This is due to the higher oxidation state of manganese.

Based on reactions 10 to 13, generation of NaOH as one of the products would increase or, at least, keep free alkalinity of the treated SSC. However, although SH^- ions were quantitatively removed, free alkalinity slightly decreased (Table 3), especially when SSC was treated with $Fe(OH)_3$.

It is important to mention that the hydroxides were not washed after precipitation. In separated experiments, after the first washing, water presented pH around 3 and Cl^- (Fe^{3+} ions) or pH 4 and SO_4^{2-} (Fe^{2+} ions). Fe^{3+} ions are more subject to hydrolysis than the Fe^{2+} ions. Perhaps these facts explain the higher decrease in free alkalinity of

**Table 3.** Free alkalinity of SSC before and after treatment with Fe/Mn hydroxides

SSC	Free [OH⁻]
Original	1.7 mol L⁻¹
After treatment with Fe(OH)₂	1.5 mol L⁻¹
After treatment with Fe(OH)₃	1.3 mol L⁻¹
After treatment with MnO(OH)₂	1.6 mol L⁻¹

SSC treated with $Fe(OH)_3$. When iron hydroxides were washed until pH of washing waters = 7 the solids lost virtually all ability to act as a sink for sulfur. X-ray diffraction data of the non-washed and washed solids are shown in Figures 2 and 3, respectively. Crude $Fe(OH)_3$ is essentially an amorphous solid. After washing, some crystalline structures were formed. Almost all peaks represent goethite (α-FeOOH). This result is different from literature data,[22] where washing crude $Fe(OH)_3$ converted it to lepidocrocite (γ-FeOOH), which is much less reactive than the amorphous form for H_2S removal. It appears that crystallization of the initial amorphous solid suppressed its ability to react with NaSH.
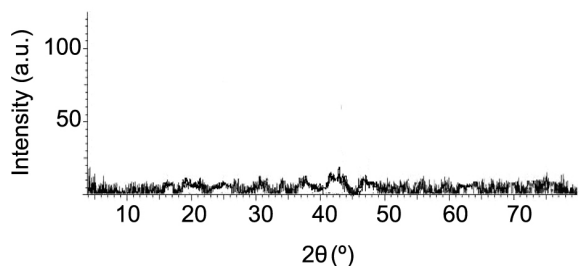
Figure 2. *X-ray diffractogram of non-washed $Fe(OH)_3$. It is essentially an amorphous solid*
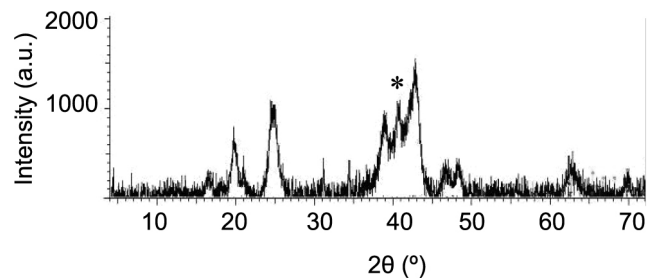
Figure 3. *X-ray diffractogram of the washed $Fe(OH)_3$. The peak represents goethite (α FeOOH). The peak assigned with an * represent iron oxide (Fe_2O_3)*

After the first washing of $MnO(OH)_2$, the pH was around 5. Cl⁻ ions were present in small amounts and no detectable Mn was observed. Washing until pH 7 decreased SH⁻ uptake by 70%. XRD data indicated the solid was amorphous both before and after washing.
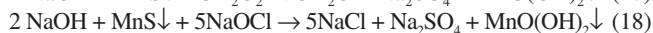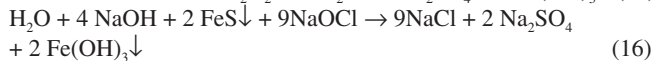
Another possible explanation is the absorption of CO_2 during handling of SSC. According to reaction 14, some free alkalinity is consumed:

$$CO_2 + OH^- \rightarrow HCO_3^- \qquad (14)$$
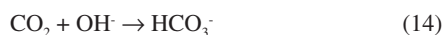
After acidifying a sample of treated SSC with 2 mol L⁻¹ HCl, the gas was passed through 0.2 mol L⁻¹ $Ba(OH)_2$, giving a white precipitate ($BaCO_3$). This result confirms the presence of hydrogenocarbonate ions in the treated SSC.[14,25] However, from the amount of $BaCO_3$ recovered and weighed, the estimated concentration of HCO_3^- is relatively small, 0.05 mol L⁻¹.

Treatments based on precipitation are of interest because they

allow reuse of treated SSC. This strategy reduces waste generation and consumption of water and chemicals.[29] SSC treated in this way presents a yellowish aspect. Although sulfur compounds were removed, 10% COD remained in the treated SSC. The solid produced, FeS or MnS (+ S), may be oxidized by hydrogen peroxide or sodium hypochlorite at 25 ºC in alkaline medium (2 mol L⁻¹ NaOH), thus allowing recovery of iron or manganese hydroxides:

$$4\ NaOH + 2\ FeS\downarrow + 9H_2O_2 \rightarrow 8H_2O + 2Na_2SO_4 + 2\ Fe(OH)_3\downarrow \quad (15)$$
$$H_2O + 4\ NaOH + 2\ FeS\downarrow + 9NaOCl \rightarrow 9NaCl + 2\ Na_2SO_4 + 2\ Fe(OH)_3\downarrow \qquad (16)$$
$$2\ NaOH + MnS\downarrow + 5H_2O_2 \rightarrow 5H_2O + Na_2SO_4 + MnO(OH)_2\downarrow \quad (17)$$
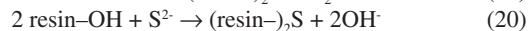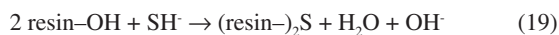$$2\ NaOH + MnS\downarrow + 5NaOCl \rightarrow 5NaCl + Na_2SO_4 + MnO(OH)_2\downarrow \quad (18)$$

Addition of the oxidant must be slow and under stirring (200 rpm) at 25 ºC. The concentration of the oxidant must be low (reactions 15 to 18 are highly exothermic). Filtration was performed under vacuum. No attempt was made to separate $MnO(OH)_2$ or $Fe(OH)_3$ from elemental sulfur. The solids were used to treat diesel samples (see below).

Sulfur removal via ion-exchange resins

Figure 4 shows the breakthrough curves for sulfur present in the SSC (0,7 mol L⁻¹ SH⁻) and 1 mol L⁻¹ Na_2S (in 1 mol L⁻¹ NaOH) on the resins. The behavior of the two resins and reference solution was very similar. From data presented in this figure, the average sulfur uptake was 22.5 g L⁻¹ (Dowex 1) and 21.0 g L⁻¹ (Amberlite IRA 420).
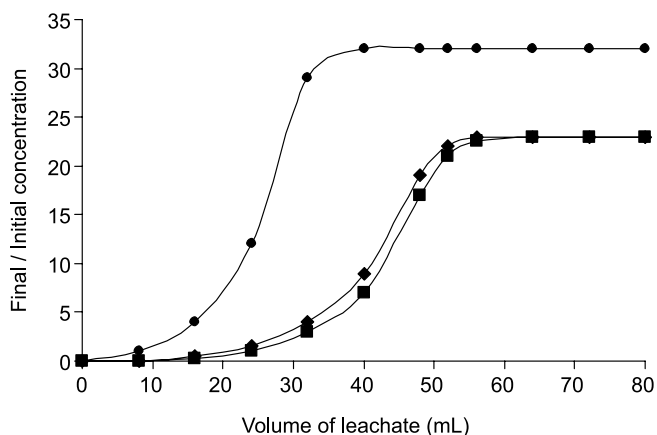
Figure 4. *Breakthrough curves for sulfur (as S^{2-}) present in the SSC (0.7 mol L⁻¹ SH⁻ in 1.7 mol L⁻¹ OH⁻) or 1 mol L⁻¹ Na_2S (in 1 mol L⁻¹ OH⁻) on Amberlite IRA 420 and Dowex 1 resins*

From the exchange capacity of these resins given in Table 2, these results indicate that sulfur is basically adsorbed as S^{2-} ions on both resins since experimental uptake was about half of their exchange capacity shown in Table 2. The resin darkened somewhat and the eluate was almost colorless. Since under the pH of the SSC studied there is a mixture of SH⁻ and S^{2-} ions,[30] the speciation of sulfur inside the resin phases is different from that in the SSC. The free alkalinity of the eluate (treated SSC) was higher (2.0 mol L⁻¹) than the original value (1.7 mol L⁻¹) for the SSC. This result may be explained by the following reactions:

$$2\ resin–OH + SH^- \rightarrow (resin–)_2S + H_2O + OH^- \qquad (19)$$
$$2\ resin–OH + S^{2-} \rightarrow (resin–)_2S + 2OH^- \qquad (20)$$

The great advantage of SSC treatment via ion-exchange resins is the increase in free alkalinity, which reaches about the same level as

the original caustic solution (2 mol L^{-1}). When precipitation methods were employed, the free alkalinity of the treated caustic solutions was reduced as discussed earlier.

As shown in the literature, strong basic anion-exchange resins strongly retain S^{2-} ions, which are not displaced by OH^- ions even in a highly alkaline medium.[30,31] The adjustment of pH to lower values is not a good practice because H_2S is released when pH is below 9.[30] Therefore, the alternative was to oxidize S^{2-} fixed to the resins.[31]

As expected, the increase of H_2O_2 concentration markedly decreased the amount of solution necessary to oxidize sorbed S^{2-} (Figure 5). However, since this oxidation is highly exothermic, the oxidant concentration must be low in order to avoid overheating of the resins. The best results were obtained when H_2O_2 alkaline solution was cold (5-10 °C) and H_2O_2 concentration did not exceed 3 mol L^{-1}. The eluate was colorless thus suggesting that the organic matter sorbed was also oxidized in this procedure. No elemental sulfur was formed under our experimental conditions:
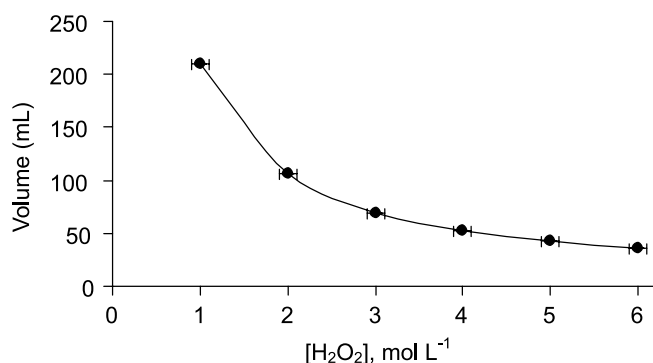
$$S^{2-} \text{ (resin)} + 4H_2O_2 \rightarrow 4H_2O + SO_4^{2-} \tag{21}$$

Figure 5. Influence of H_2O_2 concentration (in 1 mol L^{-1} NaOH) on sulfur desorption via oxidation from Amberlite IRA 420
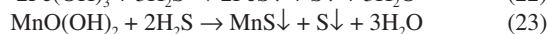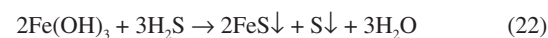
Reuse of treated SSC

Treatment of diesel samples containing 953 mg L^{-1} H_2S with the four treated caustic solutions according to the experimental procedure described previously was performed under the same conditions described earlier. As expected, the amount of diesel treated increased with increasing free alkalinity (Table 4). The presence of residual organic matter and HCO_3^- ions apparently did not influence absorption of sulfur compounds. The amount of diesel treated is about 2% vol. higher than the theoretical amount (according to Equation 1), due to the loss of some H_2S during diesel handling.

Table 4. Volumes of diesel treated with 10 mL of several treated SSC

Free alkalinity (mol L^{-1})	Diesel treated (mL)		Free alkalinity after treatment (mol L^{-1})
	Theoretical	Observed	
2.0	700	715	1.6
1.6	560	575	1.3
1.5	525	535	1.1
1.3	455	465	1.0

Direct removal of H_2S from diesel

The goal was to avoid generation of wastewaters by employing a solid base, $MnO(OH)_2$ or $Fe(OH)_3$, freshly prepared and not washed, in contact with diesel.[4,22,29] The reactions are:

$$2Fe(OH)_3 + 3H_2S \rightarrow 2FeS\downarrow + S\downarrow + 3H_2O \tag{22}$$
$$MnO(OH)_2 + 2H_2S \rightarrow MnS\downarrow + S\downarrow + 3H_2O \tag{23}$$

These reactions were only feasible when the hydroxides were stirred (200 rpm) with diesel. Percolation of the diesel through these solids, as in the case of treatment of SSC was not successful. The permeation rate of the organic liquid was extremely slow (< 0.2 mL min^{-1}).

100 mg $Fe(OH)_3$ treated 52 mL diesel (addition of 5 mL in portions). The theoretical volume was 50 mL. 100 mg $MnO(OH)_2$ treated 70 mL (theoretical volume 67 mL). Once again, some H_2S was lost during handling. The solid was easily centrifuged or decanted (but the mixture must not be passed through a filter paper because filtration is too slow). $MnO(OH)_2$ and $Fe(OH)_3$ obtained after oxidation of MnS (reactions 15 and 16) or FeS (reactions 13 and 14) were ~10% less reactive, probably due to the presence of sulfur as a non-reactive component.

CONCLUSIONS

It was possible to remove sulfur compounds from SSC via chemical oxidation with hydrogen peroxide, sodium hypochlorite or a spent sulfochromic mixture (containing Cr(VI)), at 25 °C under stirring (200 rpm). Besides sulfur compounds, the organic matter was almost fully eliminated, thus producing a colorless treated effluent. Spent acidic and or oxidizing effluents may be mixed with SSC provided addition of these effluents avoids release of toxic substances (such as H_2S). This procedure avoids consumption of chemicals and water. However, SSC is destroyed in this way and must be neutralized before final disposal.

Removal of sulfur compounds from SSC was also performed via treatment with freshly prepared and non-washed manganese/iron hydroxides, at 25 °C, by percolating the SSC through the solid hydroxide. Treatment via percolation in anion-exchange resins was also a successful technique. The free alkalinity of treated SSC decreased in the order: anion-exchange resin > Mn(IV) > Fe(II) > Fe(III). The treated SSC absorbed H_2S from diesel samples. The greater the free alkalinity the higher the volume of diesel treated.

Diesel was successfully directly treated with iron/manganese hydroxides, under stirring at 25 °C, the solid being easily decanted or centrifuged, and reused until full conversion to FeS/MnS (+S). These solids may be treated via oxidation in order to recover $MnO(OH)_2$ or $Fe(OH)_3$, but their reactivity was somewhat lower because of the presence of non-reactive matter (sulfur).

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