Characterization of the Tunisian petroleum refineries caustic effluent

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Abstract

A heterogeneous spent soda effluent generated from Tunisian petroleum refineries has been filtrated and separated in four solid fractions with a particle diameter of 160 to 100, 100 to 40, 40 to 16 and 16 to 10 μm and the fifth one with diameters $< 10 \mu\text{m}$ obtained after total evaporation of the remained filtrate. Spectroscopic characterizations of the condensed phases by means of X-ray induced photoelectron and IR absorption, as well as pH-metry, potentiometry and stationary voltammetry at $\text{Ag}_2\text{S}/\text{Ag}$ electrode studies of the filtrate, show that the whole of the separated fractions contain Na_2S , NaHS , $\text{C}_2\text{H}_5\text{SNa}$, $\text{Na}_2\text{S}_2\text{O}_3$, Na_2SO_3 and methyl, ethyl and propyl mercaptans.

Keywords NaOH · Mercaptans · Caustic effluent · Sulfur · Petroleum refinery

Introduction

To comply with the standards, gasoline and LPG (liquefied petroleum gas) fraction resulting from the distillation of petroleum must be free of sulfur compounds, such as H_2S , mercaptans R-SH (R : CH_3- , C_2H_5- ...) and disulfides. To eliminate them, the action of NaOCl or by Cl_2 is an essential step [1], leading to the generation of organochlorine compounds, environmentally harmful. The use of H_2O_2 as a washing solution entails additional costs due to the decomposition of the hydrogen peroxide caused by the transition metals [2]. Although the caustic soda washing of these fractions in Fig. 1 is a well-adapted and economical method, it is highly polluting [3, 4]. The waste solution is very far from the standards of rejection; consequently, its storage constitutes a crucial and important problem, especially if its composition is not well known. Our aim in this work consists to determine the chemical composition of soda waste solution generated from the contact of aqueous sodium hydroxide with hydrocarbon streams in Tunisian petroleum refineries.

Materials and methods

Samples of soda ash were supplied from one of the underground storage basins of the Tunisian refinery station. HCl (37%), AgNO_3 (99.5%), Na_2S (60%) and K_2SO_4 (99.9%) were purchased from PROLABO. $\text{C}_2\text{H}_5\text{SH}$ (99%) and NH_4OH (25%) were purchased from ACROS. FTIR-ATR characterizations were performed using a Perkin-Elmer Spectrum 100 FT-IR Spectrophotometer. XPS spectra were recorded using an electron spectrometer with a nonmonochromatized $\text{Al-K}\alpha$ radiation source of 200 W (15 kV) and a hemispheric electron analyzer equipped with nine Channeltron electron multipliers. After the survey, spectra were obtained, and higher resolution scans were performed at pass energy of 1.12 eV. The intensities of the different contributions were obtained by integrating each peak after eliminating the S-shaped baselines and adjusting the experimental curves to a combination of Lorentz (30%) and Gaussian (70%) lines. All the binding energies were compared to that of the line of the C_{1s} of 284.4 eV, obtaining values with a precision of ± 0.2 eV. The elemental analysis was performed using a Carlo Erba EA1108 device equipped with an autosampler.

Cyclic voltammetry experiments were carried out in a conventional three-electrode cell under N_2 atmosphere. The working electrode was $\text{Ag}_2\text{S}/\text{Ag}$ sphere (Radiometer), and a platinum wire was used as the counter electrode as well as sulphate electrode (se). Potentials were measured against Saturated Calomel Electrode (SCE) immersed in the same

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Fig. 1 Diagram of a gasoline and LPG washing installation with soda

Table 1 S_1 , S_2 , S_3 , S_4 and S_5 masses and porosities

Solids	S_1	S_2	S_3	S_4	S_5
Particle diameters/ μm	160 to 100	100 to 40	40 to 16	16 to 10	< 10 μm
Mass/g	0.085	0.147	0.140	0.137	1022.491
%	0.0083	0.0144	0.0137	0.0134	99.9502

electrolyte through a Luggin capillary. Cyclic voltammograms were recorded at a constant sweep rate. A Metrohm Millivoltmeter Mettler Toledo-MP 220 was used for the pH-metric measurement, the constant sweep rate is 0.2 mL/min. Gran's method allows us to accurately determine the equivalence points of the obtained curves [5].

Results and discussion

Samples of approximately 1023 g of soda ash were vacuum filtrated using 4 glass frits with porosities comprised between 160 and 10 μm , leading to four solide samples, namely S_1 , S_2 , S_3 and S_4 and a homogeneous filtrate. From this filtrate, a volume of 10 mL leads to solid (S_5), after total evaporation. Table 1 illustrates the solid mass and porosities. IR characterisations were undertaken for S_1 , S_2 , S_3 , S_4 and S_5 . For technical reasons, solid S_4 has been excluded from XPS analysis. While the remained filtrate was titrated using the pH-metric and potentiometric techniques and studied by means of the voltamperometric approach.

Characterisation of the solid phases

The solid phases were examined by XPS to analyze their surface compositions. Calibration of C1s from adventitious contamination set at 284.8 eV. Figure 2 shows the photoelectronic spectra of S_1 , S_2 , S_3 , and S_5 , revealing O_{1s} , C_{1s} and S_{2p} signals. The latter one corresponds to unresolved doublets, indicating the presence of the sulfur element in an oxidized state. With Table 2 we can see those surface compositions and binding energies of S_1 , S_2 , S_3 , and S_5 ; that S_1 , S_2 , S_3 , and S_5 are majority constituted by carbon, sodium, oxygen and sulfur elements, which are the basic elements of the removed impurities from gasoline fractions and LPG during their washing by the caustic solution, while silicon, calcium, iron and boron are present as traces.

Figure 3 shows the deconvoluted S_{2p} signals of S_1 , S_2 , S_3 and S_5 leading to A, B, C, D and E bands that the possible attributions are reported in Table 3.

From this table, sulfur in the form of $\text{Na}_2\text{S}_2\text{O}_3$, Na_2SO_3 , $\text{RS}_2\text{O}_2\text{R}$, RSOR , RSO_3^- , SO_4^{2-} and $\text{S}_4\text{O}_6^{2-}$ could be suggested. FTIR characterization was performed to confirm the XPS results. As expected, Fig. 4 that the major of the absorption bands are illustrated in Table 4 shows in addition to the hydroxyl band, from 3700 to 2700 cm^{-1} , H-S band appearing from 2600 to 2400 cm^{-1} . Moreover, a carbonate band is observed at around 1650 cm^{-1} and could be assigned to the presence of Na_2CO_3 . Besides, a C-S band is observed in the region from 1440 to 1410 cm^{-1} .

Besides, for S_1 , S_2 , S_3 , S_4 , and S_5 the characteristic band's vibration of the $\text{CH}_2\text{-S-}$ group C-S bonds observed

Fig. 2 XPS spectra of S₁, S₂, S₃ et S₅ XPS spectra of S₁, S₂, S₃ et S₅**Table 2** Surface compositions and binding energies of S₁, S₂, S₃, and S₅

Element	Binding energy	%			
		S ₁	S ₂	S ₃	S ₅
C	285.0	34.52	22.88	28.07	18.57
Na	1072.0	13.84	14.37	14.76	26.48
O	531.5	42.85	43.70	43.31	41.23
S	168.3	4.39	3.01	5.38	13.71
Ca	347.0	3.22	0.57	2.41	–
Si	102.7	1.18	12.30	5.52	–
B	192.7	–	3.16	–	–
Fe	711.3	–	–	0.55	–

from 710 to 630 cm⁻¹, indicating the presence of ethyl mercaptan substrate. Moreover, the appearance of a band around 660 cm⁻¹ which could be linked either to the extensional vibration of the (C–S) bond in the CH₃–S– group or to the extension of the (S–S) bond of the disulfides, allows us to deduce that all solids could contain either a salt of methyl mercaptan or a salt of a disulfide or both compounds. S₁ also has elongation bands at 541 and 466 cm⁻¹ which correspond to the (S–S) bond characteristic of the polysulfides. The solids S₂ and S₃ have bands that correspond to the elongation of the (S–H) bond, around 2463 cm⁻¹. Their spectra also show, at around 1650 cm⁻¹, the characteristic band of elongation vibration of the carbonyl group (C=O), as well as the band which is due

to the stretching of the (C–S) bond, around 1440 cm⁻¹. Vibration bands due to (S=O) bonds, both in sulfoxide SO₂ and sulfate groups SO₄²⁻, are also recorded, respectively, at wavelengths ranging from 1070 to 995 cm⁻¹ and 700 to 600 cm⁻¹. With regard to the solid S₄, with the exception of the characteristic band of the S–H bond, we find all the other bands (C–S, S–S, S=O, and C=O) mentioned before. Finally, the solid S₅ has all the bands described for the first three solid, this result, therefore, allows us to assign the same composition as S₁, S₂, and S₃. All of these results are in agreement with that found in XPS, thus confirming the fact that sulfur is present in different oxidized states in all of the solids fractions. These results indicate that the solids contain mainly mercaptans, disulfides and carbonate compounds such as Na₂CO₃ from the extraction of CO₂ from LPG.

Filtrate analysis

It is worth mentioning that the study of the caustic soda effluent filtrate is also an important step. In this context, its pH-metric, as well as potentiometric titrations, have been undertaken.

The evolution of pH = f(V_{HCl}) in Fig. 5 suggest the presence of different basic forms such as S²⁻, RS⁻, CO₃²⁻, HS⁻ in addition to hydroxyl ions. Using the method of Gran, lead us to conclude the concentration of basic compounds other than OH⁻ [C]_{basic compounds} = 2.238 mol L⁻¹. On the basis of the reported titration method, the effluent soda

Fig. 3 High-resolution spectrum of S_{2p} , solid S_1 , S_2 , S_3 and S_5

High-resolution spectrum of S_{2p} , solid S_1 , S_2 , S_3 and S_5

Table 3 Assignments of the deconvoluted signals of S_{2p}

Peaks	Solids	Band energy (eV)		Attribution
		Experimental	Reported	
A	S_2	161.65	162.9 [6]	$Na_2S_2O_3$
	S_3	161.83	168.4 [7]	$S^+SO_3^-$
	S_5	161.99		
B	S_2	162.88	162.90 [7]	$Na_2S_2O_3$
	S_3	163.10	163.90 [7]	$gpt (S_4O_6)^{2-}$
	S_5	163.28		$gpt (S_4O_6)^{2-}$ 2nd pic
C	S_1	162.73	162.30 [7]	$Na_2S_2O_3$
	S_5	166.70	166.60 [7]	
	S_2	166.48	166.9 [8]	Na_2SO_3
	S_3	166.40		
D	S_2	168.06	168.00 [9]	RSO_3^-
	S_3	167.97		
	S_5	168.11		
	S_1	164.19	164.10 [10]	RS_2O_2R
E	S_2	169.35	169.00/169.50	SO_4^{2-}
	S_3	169.25	[11]	
	S_5	169.51		
	S_1	165.47	165.00 [12]	RSOR

filtrate and two solutions of fresh caustic soda containing Na_2S and C_2H_5SH having a concentration $10^{-1} \text{ mol L}^{-1}$ have been studied. Figure 6 shows there are three potential jumps which are located respectively around a volume of reagent

IR absorption spectra of solids S_1 , S_2 , S_3 , S_4 , and S_5

Fig. 4 IR absorption spectra of solids S_1 , S_2 , S_3 , S_4 and S_5

titrant of 20 cm^3 for the first (-1235 mV at -263 mV), 40 cm^3 for the second (-263 and -107 mV) and 50 cm^3 for the last jump (-107 mV to $+60 \text{ mV}$). The first jump of potential which is quite important is relative to the dosage of the S^{2-} ions, whereas the second one can be attributed to the dosage of the HS^- ions, which gives in the presence of Ag^+ ions the $AgSH$ complex, which can be transformed

Table 4 Assignments of infrared absorption bands, solids S_1 , S_2 , S_3 , S_4 and S_5

Bond	Absorption bands/cm ^{−1}					Reported [13, 14]
	Observed					
	S ₁	S ₂	S ₃	S ₄	S ₅	
S–H	2522–2463	2463	2463	–	2496	2600–2450
C=O	1641	1641	1641	1641	1635	1650–1750
C–S and S=O	1409–1448	1409–1448	1409–1448	1409–1448	1441	1410–1440
de SO ₄ ^{2−}	660 – 705	669	669	669	673	600–700
S=O (sulphoxides)	1066	1066	1066	1066	–	1070–1030
	998	998	998	998	998	995
S–S	466	466	466	466	496	400–500

Fig. 5 $\text{pH} = f(V_{\text{HCl}})$ dosing curve of $V = 10$ mL fresh sodium hydroxide and $V = 10$ mL spent sodium hydroxide, with a hydrochloric acid solution $\text{HCl } 2 \text{ mol L}^{-1}$ **Fig. 6** Potential difference of an $\text{Ag}_2\text{S}/\text{Ag}$ electrode with respect to a sulphate electrode, in contact with a $V = 20 \text{ cm}^3$ studied solutions as a function of the added volume of $\text{AgNO}_3 \text{ } 0.2 \text{ mol L}^{-1}$

into $\text{Ag}(\text{HS})_2^-$. In case of a solution containing only ethyl mercaptan, we observe two successive potential jumps, the first which is by far the most important, is due to the jump of potentiometric from -1.05 V to -0.075 V , it corresponds to a volume of silver nitrate solution of the order of 7 cm^3 . Subsequently, a second rather weak jump ($\approx 0.050 \text{ V}$) appears after adding a volume of the order of 14 cm^3 of the solution, after the second equivalence point the potential stabilizes at -0.060 V . The intense peak observed is attributed to the assay of the existing $\text{C}_2\text{H}_5\text{S}^-$ anion in the solution. The rather weak peak could be due to the dosage of a more complex form.

The method steps the potentiometric dosage of the filtered washing solution gave three jumps of potential, we locate the first jump of potential, which corresponds to the passage of -1091 mV to -245 mV , to 40 cm^3 of added solution. While the second jump which is less important (from -245 mV to -106 mV), corresponds to a volume of the order of 65 cm^3 .

Finally, the third jump after which the potential stabilizes towards $+84 \text{ mV}$ indicating the end of the dosage, appears around 97 cm^3 .

The comparison of the dosage curve of spent soda, on the one hand to those which correspond to the determination of sodium sulphide and ethyl mercaptans, on the other hand, to the method (UOP209-69 T) [15], allows us to conclude that the spent soda solution contains mainly sodium sulphide Na_2S and mercaptans as ethyl mercaptans in the form of salt $\text{C}_2\text{H}_5\text{SNa}$. We can also estimate the presence of other mercaptans in the washing solution and which can be determined without being able to distinguish them on the curve of dosage. At the end of the dosage, the characteristic bad smell of the sulphides already present in the spent soda solution disappears completely.

To explain the shape of the curve $\Delta E = f(V_{\text{AgNO}_3})$ plotted during the determination of the used soda solution, by potentiometry at zero current, we proposed to examine the variation

of the current as a function of the potential imposed on a silver electrode covered with a deposit of Ag_2S . This was then immersed in a series of three prepared solutions of sodium hydroxide with $\text{pH}=13$, containing only sodium sulphide for the first, that of ethyl mercaptan for the second, to finally go to the filtrate. The shape of the curve recorded in contact with a solution of Na_2S is illustrated in Fig. 6. By going towards the more negative potentials, this one is delimited by a wall of reduction which is manifested by a fairly important decrease of the current starting from a potential of the order of -1.17 V . This potential barrier is due to the gain of an electron pair by the solid Ag_2S of the indicator electrode following the half-reaction:

Towards the most positive potentials, and more precisely towards -0.3 V , we are witnessing a rather rapid increase in current. This potential barrier corresponds to the loss of an electron by the silver element of the $\text{Ag}_2\text{S}/\text{Ag}$ electrode to form, in the presence of ammonia, the $\text{Ag}(\text{NH}_3)_2^+$ complex according to the reaction mechanism:

[16]

Moreover, this curve presents two successive waves in oxidation. The first one, located around -1.17 V , corresponds to the formation of silver sulphide (solid Ag_2S), in this case, the silver forming the electrode oxidizes to combine with the sulphide ion which diffuses from the solution to the electrode and limit the current. The reaction mechanism of this step corresponds to the inverse of that of the reduction wall (reaction 1), we can write it as follows:

During this step, we consume the electrode metal that goes in the direction of the formation of Ag_2S on the surface of the electrode. Now, the complete recovery of the latter causes the growth of the deposit to stop, since the interface between the two silver/silver sulphide electronic conductors can not be the seat of the electrochemical reaction. Also, we are witnessing a decrease in the current limit of this wave which is quite remarkable in Fig. 7.

At around -0.60 V , we observe a rather complex variation of the anode current, which could be attributed to the diffusion of HS^- ions towards the electrode to react with the silver of the electrode following the half reaction:

Fig. 7 Curves $i=f(E)$ to an $\text{Ag}_2\text{S}/\text{Ag}$ electrode in contact with a solution of Na_2S $10^{-3}\text{ mol L}^{-1}$ in NaOH ($\text{pH}=13$), when assayed with a solution of AgNO_3 0.2 mol L^{-1} , the reference electrode is sulfates

when assaying this solution with AgNO_3 0.1 mol L^{-1} , the voltammetric study at the solid electrode of $\text{Ag}_2\text{S}/\text{Ag}$, allows us to see, as soon as the ten first milliliters of the titrant reagent, the disappearance of the two oxidation waves due to the diffusion of ions S^{2-} and HS^- . As dosing progresses, we observe the variation of the potential at zero current ($E_{i=0}$) which becomes more and more positive. We can deduce as qualitative predictions from this voltammetric study, that

the potential at zero current undergoes a first jump from the first quantity of reagent titrant added (10 cm³), it then passes from −1.17 V/at −0.29 V. Subsequently, there is a second and a third potential jump since it goes respectively to −0.1 V then 0.6 according to the volumes of Ag added. These variations seem quite comparable to those obtained during the potentiometric assay Fig. 6.

In Fig. 8, we have illustrated the potential current curve that characterizes the electrochemical behavior of an Ag₂S/Ag solid electrode in the presence of a basic solution of ethyl mercaptan, [C₂H₅SH] = 10^{−3} mol L^{−1}, which we have prepared in our laboratory. On this curve we can see the presence of the reduction wall to −1.13 V which is due to the reaction:

On the other hand, and since the solution is free of sulphide ions, the curve does not present the wave that we observed during the study of the Na₂S solution:

Fig. 8 Curves $i=f(E)$ to an Ag₂S/Ag solid electrode in contact with a solution of C₂H₅SH 10^{−3} mol L^{−1} in NaOH (pH=13), when dosing with a solution of AgNO₃ 0.1 mol L^{−1}, the reference electrode is sulfates

which corresponds to the silver oxidation in the presence of S^{2−} ions. Subsequently, there is a fairly complex variation of the current as a function of the potential, especially with the appearance of a rather large peak to −0.920 V. This behavior could be attributed to adsorption, and/or decomposition and/or oxidation of C₂H₅SH on the surface of the electrode. Such electrochemical processes, known by mercaptans, have been described in the literature [17, 18]. We have shown the curves $i=f(E)$ recorded at each addition of 10 mL of titrant reagent. According to these, we note the disappearance of all the waves observed before the assay. Moreover, and although these curves have fairly complex paces, which may originate electrochemical behavior of adsorption, oxidation or decomposition of mercaptans, we can distinguish, when adding a quantity of reagent to the other, a variation of the potential at zero current. This one shows a look quite similar to that observed in potentiometry (Fig. 6), although the second potential-jump was not recorded.

In Fig. 9 we have shown the curve $i=f(E)$ obtained by voltammetry at an Ag₂S/Ag electrode in contact with the filtrate of spent soda, and whose pH was set at a value equal to 13. The latter presents a rather complex variation of intensity as a function of potential. The current passes by a peak then it decreases. This leads us to suggest the intervention of several rather complex electrochemical phenomena, such as oxidation reactions, adsorption or decomposition that the filtrate can manifest on the surface of the electrode. The recorded curve leads us to think that the content of the solution considered sulphide can only be important.

The determination of the washing solution with AgNO₃ 0.2 mol L^{−1}, which is followed by voltammetry, made it possible to draw the curves $i=f(E)$ of Fig. 9. This shows quite different trends with, in particular, the disappearance of the peak of anodic currents to −1.2 V that we observed just before the assay and which correspond to S^{2−} ions. We are also witnessing the disappearance of the anode wave due to HS[−] ions, which should be located near −0.6 V to 50 cm³ of added solution.

The curves of the curves $i=f(E)$ are quite complex and difficult to interpret, although their evolutions present rather remarkable differences from one addition to the other of the titrant reagent. However, it seemed useful to determine the potential at zero current for the different dosage stages. This shows two jumps of potential whose volumes are quite close, since the first corresponds to addition between 80 and 90 cm³, while the second appears when the volume is located around an average value of 100 cm³. The curve shows a fairly similar appearance to that observed in potentiometry (Fig. 5). Indeed, although the determination of zero current potentials is not precise enough, at least two jumps of potentials are recorded.

Fig. 9 Curves $i=f(E)$ to an $\text{Ag}_2\text{S}/\text{Ag}$ electrode in contact with a filtered spent sodium hydroxide solution when it is assayed with a solution of AgNO_3 0.2 mol L^{-1} , the reference electrode is sulfates

All these results, obtained at the end of the study of the filtered solution of spent soda, show the presence of the S^{2-} , HS^- ions as well as the mercaptans as sulfur-containing entities.

Nevertheless, it would be interesting to resume the voltammetric study at different stages of the assay by improving the operating conditions. In particular, using a solid electrode $\text{Ag}_2\text{S}/\text{Ag}$ rotating, replacing the magnetic stirring of the solution used in all of these studies.

Conclusions

The analysis of the content of the spent soda solution discharged by a petroleum refining station located in Tunisia required at the first stage of the work, separation by vacuum filtration, the solid phase of the liquid effluent solution. In a second step, we subjected the recovered solid and the filtrate to an analysis by various techniques such as X-ray induced photoelectron spectroscopy (XPS), IR absorption spectroscopy, PH-metry, potentiometry, and stationary voltammetry. These techniques show that solids (S_1 , S_2 , S_3 , S_4 , and S_5) and liquid (the filtrate of spent soda) phases essentially contain carbon, sulfur, sodium and oxygen under various chemical combinations (Na_2S , NaSH , $\text{C}_2\text{H}_5\text{SNa}$, $\text{Na}_2\text{S}_2\text{O}_3$, Na_2SO_3 , $\text{RS}_2\text{O}_2\text{R}$, RSOR); R is an alkyl group. All these compounds, contained in the rejected effluent, are undesirable because they constitute a source of pollution with harmful effects on the ecosystem.

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Compliance with ethical standards

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