

Assessment of organo-mineral fraction during storage of oil refinery sludge

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Abstract

The biotransformation during storage of petroleum refinery sludge was evaluated by physicochemical and spectroscopy analyses. The abatement rate of organic matter has reached 50.5% after 14 months of storage. The humic substances have decreased of about 49% at the end of storage indicating that the OM was mineralized into inorganic compounds (CO₂, N₂...). The XRD of dried samples shows the presence of a large proportion of silica (SiO₂), carbonate (CaCO₃), Hercynite (Al₂FeO₄) and hemihydrate calcium sulphate (2CaSO₄.H₂O). Hematite (Fe₂O₃) and anhydrite (CaSO₄) were found as a new appeared phase. Pb, Cd, Cr, Cu, Ni and Zn were the most identified heavy metals in the petroleum samples. Their increase at the end of storage was explain by the organic matter degradation. FTIR analysis show that the carbonate, sulphate and silica are the most identified compounds beside the organic matter.

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1. Introduction

Petroleum refinery effluents (PRE) are wastes originating from industries primarily engaged in refining crude oil and manufacturing fuels, lubricants and petrochemical intermediates [1]. These petroleum effluents are a major source of aquatic environmental pollution [2]. They are composed of oil and grease along with many other toxic metallic and organic compounds such as phenols and cresols with small amounts of non-acid species like esters, amides and ketones. Petroleum refining in Morocco produces about 2000 tons per year of contaminated soil, including waste water from the treatment plant, land paraffin treatment units, residues of bacs bottom, in addition to the cumulative stock of soils contaminated by hydrocarbons estimated at 22,000 t [3]. The PRE undergoes physico-chemical treatment: oil separation, sedimentation and coagulation-flocculation, and biological treatment using activated sludge that purifies effluent emerging from the physico-chemical treatment [4]. The collected biological oily sludge is dried and stored to be incinerated. Due to sludge production which increases growing, landfilling cannot be considered as a sustainable approach to sludge management. Among the disadvantages of landfilling, it's only a temporary solution (contaminants remain in the environment) and permanent monitoring is necessary. Also, agricultural recycling strongly prohibits the use of untreated sludge on agricultural land, unless they check all limit values for heavy metals and organic compounds. On the other hand, the importance of organic matter contained in the refinery wastes is well known for its calorific value [4]. Several options have been studied for the treatment or disposal of these wastes, namely incineration in cement kilns, on-site biological treatment and incineration on site [3; 5]. Available information in the literature regarding the effluents treatment in petroleum refineries is scarce and confidential. This complicates the knowledge of the constituents added during the treatment process and the true nature of the sludge chemical composition. To date, no studies on sludge from oil refineries in Morocco were conducted. The characterization of organic/inorganic materials and heavy metal concentration are prerequisites for estimating the toxicity of the sludge in order to provide answers about the possibility of their treatment. In addition, the heavy metals (HMs) leach and organic matter transformation (hydrocarbons, humic substances) are dynamic processes that deserve a qualitative and quantitative study of their behaviour in relation to the aging of the sludge. HMs extraction from the sludge in various stages of storage, accounts the ability to release / capture of the sludge and thus the HMs mobility. In the present investigation, we studied the biological oily sludge stored in the landfill of the petroleum refinery. This will allow us to better assess the effectiveness of storage process to organo mineral matter evolution by using different physico-chemical and spectroscopy analysis.

2. Materials and methods

2.1. Sampling

Samples were taken at different points of the storage basins, they are homogenised and quartered them. Samples were excavated using a stainless excavators following the protocol Cedric Durand [6]. At the sampling, the basin was filled to 2/3 of its capacity. Three sludge batches were taken at different periods of storage: June 22th 2014 (raw matter); October 19th 2014 (sludge stored for 4 months); and August 18th 2015 (sludge stored for 14 months). Samples were placed in plastic bags and filed in a refrigerator at -20°C.

2.2. Organic matter and humic substance extraction

The organic matter is measured by loss on ignition of the sample after calcination at 550 ° C in an oven. The total organic carbon content is determined by assay of organic carbon by oxidation sulfochromic according to NF ISO 14235. The humic substances (HS) were extracted from 30 g of fresh sample. It was treated three times with 40 ml of distilled water to extract the water-soluble non-humic substances (sugars, proteins, etc.) [7]. Then, the humic

substances were extracted with 40 ml NaOH (0.1M). This was repeated several times until the extract obtained was colorless. The supernatant obtained was centrifuged at 4000 g for 15 min. The concentration of HS was determined by the MnO_4 oxidation method [8].

2.3. Heat treatment and heavy metals (HMs) analyses

The effect of heat treatment on the dropping of metals has been conducted by heating the aged sample in a laboratory furnace during 2h. To avoid changes in the composition of heavy metals likely to volatilize, the heating was performed at 600 °C (temperature lower than the volatilization of the most volatile metal Cd which occurs at 650 °C). The resultant products were ground in a mortar and then sieved below nominal aperture of 45 μm . [9]. The HMs were extracted by digestion with acid mixture ($\text{VHCl}/\text{VHNO}_3/\text{VHF} = 3/1/1$) [10] in PTFE beakers and heated on a hot plate. All the samples were kept in 4°C before analysis. HMs concentration from sludge was performed by using an ICP-AES (type PANORAMA).

2.4. XRD analysis

Dried samples at 105°C were milled and analysed using the diffractometer Philips X'PERT, a copper anticathode wavelength $\lambda = 1.540560 \text{ \AA}$ operating at 40kV and 40mA. The data acquisition is carried out by a control unit for angles 2 theta (2θ) between 5 and 70°. XRD was indexed by comparison with those of the database ASTM (American Society for Testing and Materials). The database used for the identification of the phases is PDF2 (2004) Converted High Score-Banc.

2.5. Fourier transform infrared spectroscopy (FTIR) analysis

Dried samples at 105°C was mixed with dried potassium bromide (sample/ KBr, 2:200 mg). The mixture was then compressed under vacuum. The pellets were analysed covering a frequency range of 4000-450 cm^{-1} using a Bruker Vertex 70 FTIR spectrometer equipped with a DTGS detector and OPUS software 6.5 (128 scans at a resolution of 2 cm^{-1} were carried out).

3. Results and Discussions

3.1. XRD mineralogical analysis

Given the complexity and heterogeneity of the samples, which can contain various mineral phases with overlap of XRD peaks, the indexing of each phase was performed only when three diffraction peaks (the most intense peaks and those located at larger values of θ) coincide with those of the ASTM database. However, the XRD of the dried (105°C) sludge presents a slightly raised background between 20 and 40° (2θ) which indicates the presence of an amorphous phase. This amorphous phase seems to be rich in organic matter because the XRD profile, of heated sample at 600°C (figure 1), becomes characteristic of well crystallized phases [9]. The XRD of dried sample at 105°C, shows the presence of a large proportion of silica (SiO_2), carbonate (CaCO_3), Hercynite (Al_2FeO_4) and hemihydrate calcium sulphate ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$). When the sample is heated at 600°C, we noted the presence of hematite (Fe_2O_3) as a new phase and anhydrite (CaSO_4). It is likely that the hematite already existed in the fresh sample with a low composition making it undetectable, and appears on the XRD when the sample is heated at 600°C, since, at this temperature, total or partial degradation of the organic matter occurs and hematite composition in the sample increases. Compared to the peak of silica, the carbonate decreases but remains present at this temperature. The presence of a hemihydrate in the fresh sample is justified because when the sample is heated to 600°C, the X-ray diffraction shows the peak of the anhydrite which is the dehydrated phase of the hemihydrate.

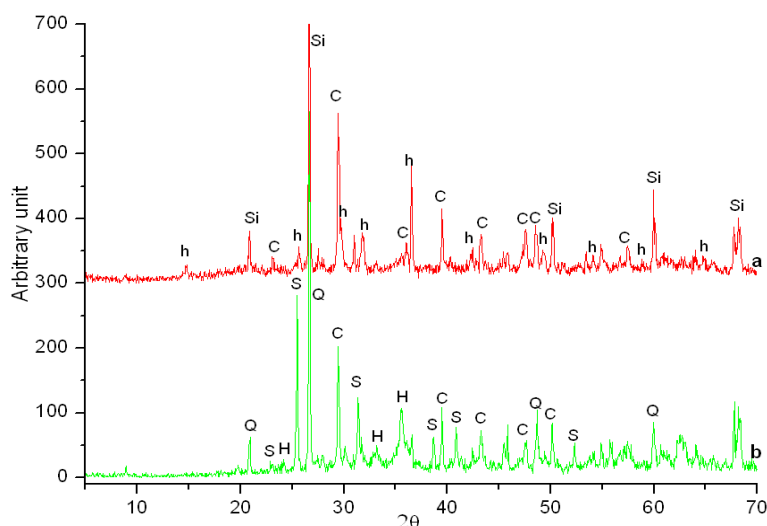


Figure 1. XRD Mineralogical analysis of sludge from petroleum refinery

a: sample dried at 105°C and b: sample heated at 600°C

3.2. Heavy metals (HMs) analyses

Level of heavy metal during biodegradation can increase due to organic matter decomposition, release of carbon dioxide and mineralization process. We proceed with normalization of all measurements by referring to the amount of ash, to correct this increase. According to [11] normalized values are obtained from the following formula:

$$C_{ash} = C_i \times \frac{a_0}{a_t}$$

C_i : value of heavy metal expressed per kg of dry matter; a_0 : level of ash in initial sample; a_t : level of ash in each selected time. The concentrations of HMs in sludge at different storage periods are shown in table 1 and compared with the target values and intervention of the Dutch standard for polluted soils [12], and the values set from Pollution from heavy metals in a settling tank which retains road runoff [13]. Concentration analysis of HMs shows that the raw matter is very rich in Pb (45.81 ppm), Cd (2.43 ppm), Cr (53.66 ppm), Cu (89.35 ppm), Ni (167.98 ppm) and Zn (4238.49 ppm). The evolution of the extraction of these metals in relation with the sludge aging shows that after 4 months of storage, except for the zinc and cadmium, the rate of extraction of other metals increases when the pH decreases (pH varying from 8.02 to 6.86). This behaviour is in agreement with the decrease in the retention capacity by the sludge when the pH decreases. Thing confirmed after 14 months of storage, when the pH stabilizes at a substantially neutral value (pH = 7.08), the extraction rate of all HMs, except Pb, is lower than that of the fresh sludge.. For these metals, the results of static leaching test of the sludge (chemical analysis of eluates after 24 hours) showed respectively a release of about 3,5 and 5% by mass relative to the initial contents in the sludge. These data are consistent with the geochemical behaviour of HMs which show that the leaching of metals in the environment is classified in decreasing mobility order: Zn > Cd > Pb > Cu > Ni < Cr [6]. Furthermore, heating of sample stored during 14 months at 600° C accentuates releasing and gives a better extraction of all metals. It is difficult to specify the mechanism, which induces the increase in the extraction of HMs by heat treatment and even less the fraction in sludge which induces this increase. Once in the soil, HMs are adsorbed by initial fast reactions (minutes, hours), followed by slow adsorption reactions (days, years) and are, therefore, redistributed into different chemical forms with varying bioavailability and mobility [14; 15]. This distribution is believed to be controlled by reactions of HMs such as precipitation, dissolution, ion exchange, adsorption, desorption, aqueous complexation and biological immobilization/mobilization and plant uptake [16]. Particularly, in the case of contaminated dredged sediment treated

at intermediate temperatures (120–350°C), the extraction showed a sharp increase in metal leachability of Cd, Pb, Zn, Fe and Mn [17]. It is suggested that binding energy changes within the fractions rather than shifts between chemical forms account for the observed leaching behaviour. Moreover, the polymerization of particles around oil sediment is well known in the refinery sludge [18]. According to these considerations, by equating the sludge aged of 14 months to a system consisting of soil contaminated by metals and deposition of crude oil which are both in the form of salts dissolved in water, in suspension or in the form of organometallic compounds and metal soaps. The deposit can be derived from the polymerization of some particules around oil sediments and it has the power to solidify gradually. We can explain the extraction increase by heating at higher temperature, by the thermal degradation which accentuate gradually the de-polymerization/degradation of these particles around the sediment and reduce the storage capacity.

Table 1. Evolution of HMs and OM concentrations in sludge at different storage periods.

	pH	Cd (mg/kg)	Ni (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	HS (g/kg)	OM (%)
Raw matter	8.02	2.43	167.98	53.66	89.35	45.81	4238.49	210.45	77.96
4months storage	6.86	1.68	189.16	64.32	107.03	54.63	2850.28	247.5	76
14months storage	7.08	0.33	88.7	23.68	67.99	54.08	914.9	107.25	38.6
Sludge at 600°C	7.02	1.41	374.99	120.29	269.97	208.97	3626.76		
Spierenburg et al. [12]	-	0.8-12	35-210	100-380	36-190	85-530	140-720		
Legret et al. [13]	-	1-4	20-30	39-80	84-208	300-819	683-1980		

3.3. Organic matter and humification process during storage of sludge

The quantitative analysis of the organic matter (OM) shows that the OM undergoes a decrease from 2.5% to 50.5% after 4 and 14 months of storage respectively. In parallel, the amount of HS extracted after 14 months is lower than that extracted after 4 months of storage. These results are consistent with the establishment of a process occurring under natural conditions during the first four months of storage, over which the rate of OM decreases and the HS increases. Stopping this process while the MO continues to downfall may be due to the formation of unstable HS or to an accumulation of polycyclic molecules such as HAs.

3.4. FTIR analysis

3.4.1. Inorganic matter spectrum

The FTIR spectrum (Figure 2) show bands located at 1450, 875, and 713 cm^{-1} which recalls the presence of the calcium carbonates. This is confirmed by the shoulder at 2515 cm^{-1} attributed to the combination mode [19]. The two bands located at 1155 and 1123 cm^{-1} which correspond exactly to the frequencies observed by [20] and at few cm^{-1} of [21; 22]. It was assigned to $\nu_3(\text{F}_2)$ vibration mode in sulphate form [23]. Table 2 gives a full overview of the main observed bands and their attributions to the phases present in the sludge in comparison to reported spectra in the literature of OM, sulphates, carbonates and related minerals. Finally, the argument that quartz may be present in our sample is justified by the presence of bands at around 1040 and 472 cm^{-1} which characterise Si-O stretching and O-Si-O bending vibration modes respectively.

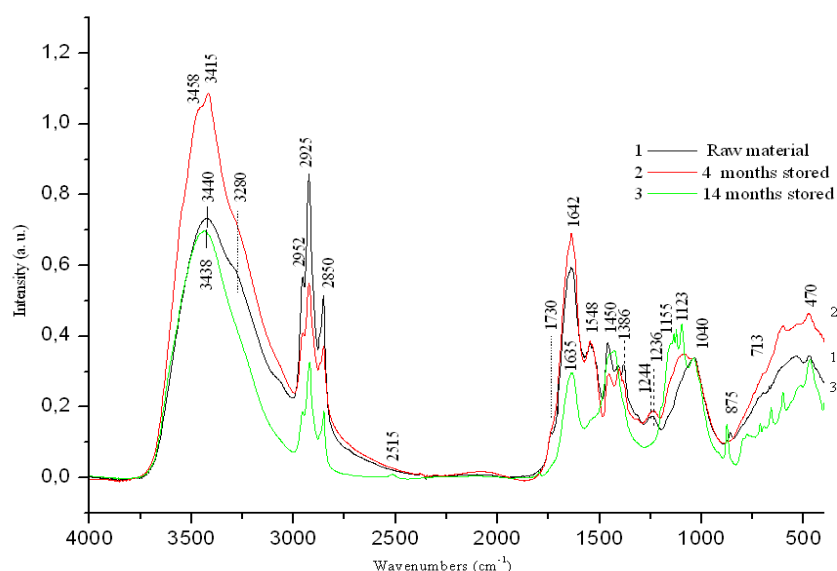


Figure 2. FTIR spectrum of sludge at different storage times.

(1): Raw material; (2): 4 months stored; (3): 14 months stored

3.4.2. Organic matter spectrum

The FTIR spectra of samples at different storage stages are just a few details that will be discussed in the sequel, typical of sludge rich in organic matter (figure 2). All spectra show the main characteristic of OM absorption bands situated at: $\nu = 3465\text{--}3415\text{ cm}^{-1}$ (hydroxyl groups H-bonded), $\nu = 2950\text{--}2850\text{ cm}^{-1}$ (aliphatic C-H stretching), $\nu = 1540\text{ cm}^{-1}$ (C=N, stretching, amide II band), carboxylic group $\nu = 1730\text{ cm}^{-1}$ (C=O stretch in COOH), $\nu = 1640\text{ cm}^{-1}$ (COO⁻ stretch of ionised COOH groups) [24; 25]. The greater intensity of the bands situated at $\nu = 2900\text{--}2800\text{ cm}^{-1}$ region indicate the presence of aliphatic chains which are common groups in hydrocarbon compounds or may also indicate the presence of fatty acids which are common metabolites in anaerobic sludge [26]. Comparatively to the FTIR spectrum of the fresh sludge, the one stored over 4 and 14 months show a decrease in band intensities situated in the $2950\text{--}2850\text{ cm}^{-1}$ region and change in intensity of band situated around (1642-1635), 1730, 1544, 1386 and (1246-1236) cm^{-1} with a slight shifts of some peaks towards low wavenumbers. These behaviours are typical of formation (by Humification/Fermentation process) of the so-called humic substances in sewage sludge [27]. The enhancement of the absorption band at 1642 cm^{-1} after 4 months of storage as well as the disappearance of the characteristic band of carboxylic groups at 1730 cm^{-1} after 14 months of storage can be an evidence of increase of content of ionized carboxylic groups which can bind to metals present in humic acids. The same observations were noted on the FTIR spectrum of HA extracted from sludge after fermentation, humic acids extracted from raw sewage sludge and from sewage sludge after the digestion process. This result points to COOH group dissociation to COO⁻ and to the formation of the transition metal complexes during sewage treatment. However, it confirms the presence of complexes of metals with humic substances which is in agreement with the analysis of EPR spectra characteristic for iron, manganese and copper complexes [28; 29]. Moreover, on FTIR spectra of sludge collected after 14 months of storage, a fairly intensive band at 1548 cm^{-1} with a deformation of nitrogen functional groups NH is observed but its intensity decreases. There the band at frequencies characteristic for groups C–OH in phenols (1236 cm^{-1}) is absent, which can be a proof for connections between the hydroxyl group from phenols and metals [29-32]. The possible connections of humic acids with metals can be confirmed by the presence of absorption band at $1378\text{--}1380\text{ cm}^{-1}$, which was

attributed to the shifted absorption band of vibrations at 1236 cm^{-1} of C–O carboxylic groups connected with metals [31].

Table 2. FTIR Characteristic Bands and their attribution to the different phases present in the sludge.

$\nu\text{ (cm}^{-1}\text{)}$	Attribution	Corresponding Phase
3438	$\nu_{\text{O-H}}$ groups	
3282	$\nu_{\text{N-H}}$	
2952-2855	$\nu_{\text{C-H}}$ Aliphatique	OM
2515	Combination mode	Calcium Carbonate
1730		OM
1640		OM
1540	$\nu_{\text{Amide II}}$	OM
1450		Calcium Carbonate
1236	$\nu_{\text{C-OH}}$	OM
1155	$\nu_3(\text{F}_2)$	Sulphate
1123	$\nu_3(\text{F}_2)$	Sulphate
1040	$\nu_{\text{Si-O}}$	silicate
875 ν_2		Calcium Carbonate
713 ν_{4a}	ν_{4a}	Calcium Carbonate
470	$\delta_{\text{O-Si-O}}$	Silicate/Quartz (SiO_2)

4. Conclusion

XRD Mineralogical analysis of petroleum refinery sludges shows the presence of carbonates, silica, sulphates and hematite. The Concentration of HMs shows that the samples are very rich in Pb, Cd, Cr, Cu, Ni and Zn. The evolution of metal extraction in relation with the sludge aging shows that after 4 months of storage, except for the zinc and cadmium, the rate of extraction of Pb, Cu, Cr and Ni increases when the pH decreases. On other hand, after 14 months of storage, while the pH stabilizes at a substantially neutral value, the extraction rate of of HMs is lower than that in the fresh mud, but the Pb behave differently because their release increases with storage. This increase of amount of Pb extracted after 14 months storage, shows that the Pb can be easily release even with a neutral pH. Finally, FTIR spectrum of the fresh sludge and the one stored over 4 months show a decrease in band intensities situated in the $2950\text{--}2850\text{ cm}^{-1}$ region and an increase of the band situated at 1640 cm^{-1} . These behaviours are typical of formation (by Humification/Fermentation process) of the HS and are consistent with a biological degradation process of the MO that takes place during the 4th first months of storage and which appears to be then stopped.

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