

## IDENTIFICATION AND QUANTIFICATION OF THE ORGANIC MATTER IN THE FOULING INDUSTRIAL OF WET PHOSPHORIC ACID PROCESS

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**Abstract.** The organic matter of rock phosphate has been the subject of numerous studies. The valuation and resolution of some problems, such as fouling, encountered in the industrial production of phosphoric acid are of great interest, and enable better production yields of phosphoric acid. The solid deposits formed in the production of wet process phosphoric acid were characterized and revealed the malladrite, gypsum, trace metals, and the presence of organic matter. The identification of the organic matter was carried out in the fouling samples using FT-IR and Raman spectroscopies. The quantitative determination of the total organic matter content of the fouling samples was performed using the Walkley-Black and calcination methods. The knowledge of the organic matter in the fouling layers allows a better understanding of phenomena in processes.

**Keywords:** phosphoric acid process, fouling, characterization, organic matter.

### 1. Introduction

In the production of wet process phosphoric acid, the phosphate bearing rock reacts with sulfuric acid in aqueous solutions to produce phosphoric acid and phosphogypsum, depending on the used process and the quality of phosphate.<sup>1,2</sup> The phosphate rocks are rich in fluoride, contained in about 4 % (w/w), as well as in other ions.<sup>3</sup> The sedimentary layers of phosphates consist mainly of apatite and contain the organic matter.<sup>4-6</sup> In the process, the fluoride, in the form of HF and SiF<sub>4</sub>, combines with the other impurities such as silica SiO<sub>2</sub> contained in the acid phase to give rise to other aqueous and solid chemical species; the formed solid phases can induce the fouling.<sup>7-10</sup> One of the major problems of the wet process

of production of phosphoric acid (WPA) is related to the formation of hexafluoridosilicate scale deposits, together with other solids as gypsum, on the filters, pipelines and evaporators. There are natural phosphates which have organic matter trapped in their framework during their geological formation that gives the phosphate a grey color. The origin and composition of this matter are similar to those of all fossil fuels which have not undergone complete decay. The organic matter (OM) of rock phosphate has been the subject of numerous studies.<sup>11-14</sup> Their elimination and thermal decomposition were investigated. The temperature and residence times of calcination were studied to optimize the expenditure related to energy destined to burn the organic matter.<sup>13</sup> On the other side, the OM has been characterized in the phosphogypsum of the WPA to know its chemical composition and its physical and thermal characteristics.<sup>14,15</sup>

In the WPA, fouling is the one of the serious problems facing the chemical phosphate processing industry. Fouling produces losses of production and productivity due to the stops required for washing and the reduction in volumes and the production areas it produces. Various studies were reported to understand and characterize this phenomenon in order to reduce its impact on the performance of phosphoric acid and fertilizer production units and on the environment.<sup>15-17</sup>

The main objective is to evaluate the organic matter in the solid deposits formed in the production of wet-process phosphoric acid. The literature indicates that significant deficiencies studies exist in the OM in the solid deposits in the phosphate industry. Indeed, the knowledge of the OM in the fouling layers and their mixing in different steps of wet process allows a better understanding of the mechanisms governing such complex thermodynamic equilibria and the reaction paths. Various techniques were used to evaluate the OM in the fouling layers formed during the phosphoric acid production cycle at the phosphate attack reactor. Their quantitative characterization in the fouling samples was also performed.

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## 2. Materials and Methods

### 2.1. Samples

The solid deposits were formed during a production cycle at the phosphate attack reactor. The taken sample is a representative of the facies of deposits formed at the wet transformation reactors of the phosphates. The deposit was formed during a production cycle of 16 months and appears as a multilayer fouling which covers the entire inner surface of the reactor with considerable thicknesses.<sup>18</sup> The solid phases are formed predominantly of malladrite and gypsum and their chemical composition and some of their physical characteristics evolve over time and are impacted by the nature and quality of the processed phosphate.<sup>19</sup> The preparation of the fouling sample includes all the steps performed in the laboratory to make a sample in a form suitable for chemical analysis. Proper sample preparation generates sub-samples representative of the entire samples of the fouling A, B, C, and D. Crushing, grinding and dry sieving were used for the finest treatment of particles each covering a range of sizes its own.

### 2.2. Methods and analysis technics

Various techniques as well as characterization methods were used to identify the organic matter. The experimental protocols were described to detect OM. Analyses of solid residues of fouling were carried out using Raman and IR spectroscopies. The FT-IR spectra were recorded by Shimadzu FTIR 8400 in the range from 400 to 4000  $\text{cm}^{-1}$  with the resolution 4  $\text{cm}^{-1}$ . The Raman spectra were measured using a "Thermo Scientific DXR<sup>TM</sup>3 SmartRaman spectrometer which was equipped with fine laser power, controlled and reported at samples in 0.1 mW increments excitation Laser at 532 nm. The instrument was calibrated with emission lines and the uncertainty in the measured frequency shifts high-resolution grating is less than 2.0  $\text{cm}^{-1}$ .

The pH of the aqueous solution of the dissolution of fouling sample was determined, the ratio of the sample mass to the volume of water varies according to standard NF X 31-103.<sup>20</sup> The dissolution of the fouling samples in aqueous solutions was performed. For each sample, 10 g of sample was dissolved in a volume 25  $\text{cm}^3$  of bi-distilled water. The mixture was stirred for 60 min and kept at the temperature of  $298 \pm 0.1$  K. The stirring makes it possible to suspend the entire sample and thus obtain a balance between the two solid and liquid phases. The obtained mixture is left to stand for two hours. The pH measurements of the solutions resulting from the dissolution of the fouling samples were carried out using a Consort C 861

type pH meter with 0.1 % accuracy at the temperature 298 K.

The quantitative determination of the total organic matter content of the fouling samples will be carried out using two methods: the wet one such as the Walkley and Black method, and the other dry by calcination. The determination of OM content is generally made by hot wet method according to that of Springer-Klee,<sup>21</sup> and also by the cold wet analysis at room temperature, that of Walkley and Black (WB).<sup>22</sup> The latter is widely used and has the advantage of using relatively simple equipment with good precision.

The evaluation of OM was carried out from the determination of organic carbon (O.C) that is one of principal constituents. Thereafter, from the O.C according to Eq. (1) the OM was estimated as:

$$\%O.C.e = O.M\% \quad (1)$$

The organic matter of the fouling samples was determined according to the procedure described above. The sample mass is about 1g, the titration volume of each sample was carried out by potassium dichromate  $\text{K}_2\text{Cr}_2\text{O}_7$ . The titration of a blank witness was performed by potassium dichromate and sulfuric acid (without carbon). Each value is an average of six assays with an uncertainty of  $\Delta V (\pm 0.01)$ . 100  $\text{cm}^3$  of sulfuric acid is added to the fouling sample in solution, the mixture will be titrated with potassium dichromate. From the results, the percentage of organic carbon present in the fouling samples is calculated by Eq. (2)

$$\%O.C = V_B . V_E \frac{1.794}{p} \quad (2)$$

From the volume of the blank titration B and the sample E (VB, VE) with a normality of iron sulfate (p), the carbon percentage in the fouling samples was determined. Then, the amount of organic matter is calculated from Eq. (1).

The evaluation of OM content using dry method is based on the calcination process. The treatment consists in the combustion of OM that gives the mass loss at temperature 823 K, and determines the amount of OM contained in the fouling sample. Indeed, the fouling samples sieved to 63  $\mu\text{m}$  with the mass  $m_i=4.0001$  g were placed in an oven at 373 K for 24 hours, the mass loss is P. These samples are gradually brought to 823 K for four hours and are cooled, the mass loss is noted Q. The humidity of the fouling samples is determined by Eq. (3)

$$H \% = \frac{m_i - P}{m_i} 100 \quad (3)$$

The rate calcination allows us to evaluate the OM using Eq. (4).

$$OM \% = \frac{P - Q}{P} 100 \quad (4)$$

where P is mass initial loss (g) at 373 K; Q is mass loss (g) after calcination at 823 K.

### 3. Results and Discussion

#### 3.1. Identification of the organic matter in the fouling samples

The physico-chemical properties are useful for the recognition and identification of organic and inorganic compounds. The solid deposits are generally complex mixtures of macromolecules and structurally heterogeneous. These properties of minerals allow to know the phenomena and/or mechanism of the solubility or dissolution, humidity, and color of these compounds. The characterization of the fouling sample is a fundamental step to the knowledge of the phenomena governing the deposit formation. However, different techniques and protocols have been carried out to identify the solid deposits. In particular, it is to know the composition responsible for the color of the fouling layers, especially their level in organic mat-

ter. In our previous work, the fouling samples were homogenized and prepared on the micro-scale using a particle size fractionation.<sup>18</sup> The mineral deposits during attack-filtration and concentration operations were characterized using complementary techniques XRF, XRD, and IR. The elemental analyses have been performed for the fouling layers. The observed solid phases in the fouling layers are principally composed by the mallardite ( $\text{Na}_2\text{SiF}_6$ ) form and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) minerals.<sup>17,18</sup> The FT-IR spectra confirm the presence of mallardite and gypsum phases and reveal a supplementary band that has been assigned to C–O vibrations in acids, esters, or ethers. This appearance indicates the possibility of the organic matter in the fouling layer.

##### 3.1.1. FT-IR spectroscopic analysis

Infrared transmittance spectroscopy is used primarily to identify functional groups of compounds. The FT-IR spectra of the fouling layers A, B, C, and D show some functional groups (Fig. 1a).

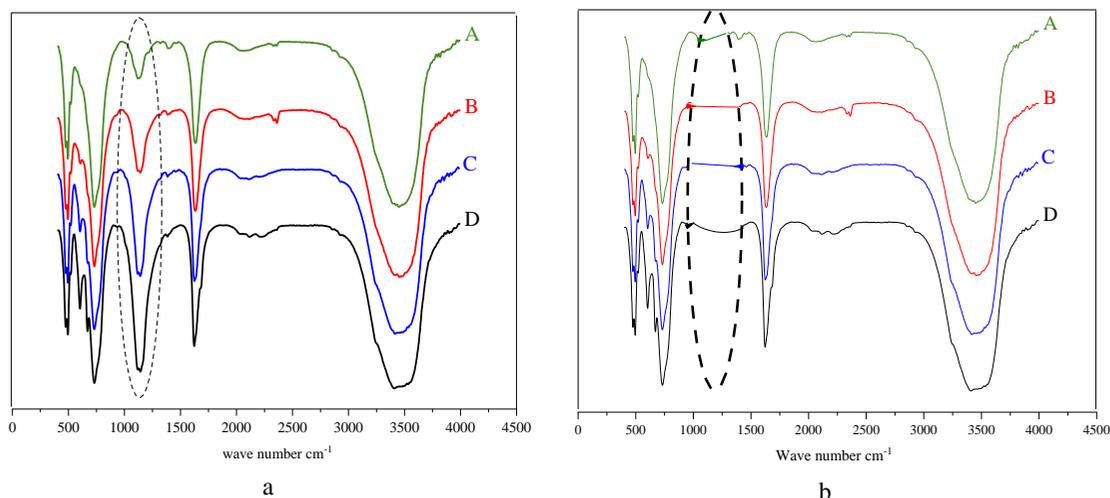


Fig. 1. Infrared spectra of the fouling samples (a) and solid residues obtained after dissolution (b)

The analysis IR spectra can be expressed in bands at  $3448\text{ cm}^{-1}$ , the elongation bands of the main O–H groups. The intense bands observed at  $733\text{ cm}^{-1}$  and  $477\text{--}496\text{ cm}^{-1}$  have been assigned as Si–F stretching vibrations, which is the main character of  $\text{Na}_2\text{SiF}_6$ .<sup>23,24</sup> The band at  $603\text{ cm}^{-1}$  is attributed to at the  $\text{SO}_4$  elongation which is relatively at gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).<sup>25–27</sup> The appearance of band at  $1130\text{--}1134\text{ cm}^{-1}$  has been assigned to C–O as vibrations in acids, esters or ethers.<sup>28–31</sup> Moreover, there is a possibility of the presence of OM in the fouling layer. The intensity of this band increases being from sample A to D. IR spectra of the samples were similar, which means that they were formed by the same type of functional groups. Various techniques were used to identify and characterize the fouling layers A, B, C, and D. The analysis reveals the presence of mallardite, gypsum, trace metals, and the organic matter.

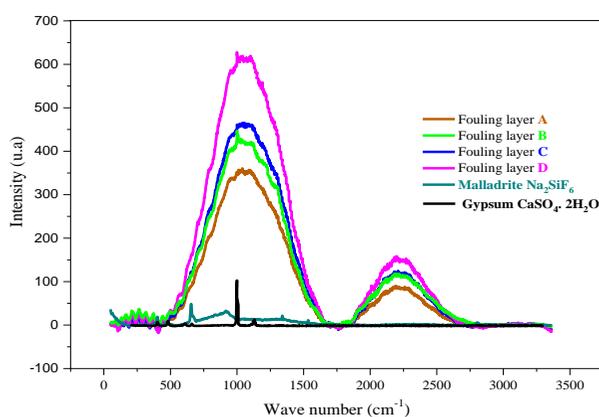
##### 3.1.2. Raman spectroscopic analysis

The vibrational spectra of the fouling layers A–D show two bands: one medium is between  $2000$  and  $2500\text{ cm}^{-1}$ , the other very strong intense one is located in the interval  $500\text{--}1500\text{ cm}^{-1}$ . The spectra of pure mallardite and gypsum were also presented in the same Fig. 2. Their comparison indicates that the two medium bands ( $1000$ ;  $2250\text{ cm}^{-1}$ ) are not among those of mallardite and gypsum. The examination of these spectra shows a clear difference between those of the fouling samples and those corresponding to pure mallardite as well as gypsum.<sup>23,32,33</sup> Consequently, they could be attributed to those of OM. To better identify the nature of this matter, we used a method of deconvolution of the band profile by means of a Fourier transform analysis. The deconvolution of the band using specific software (peak fit), the results obtained are shown

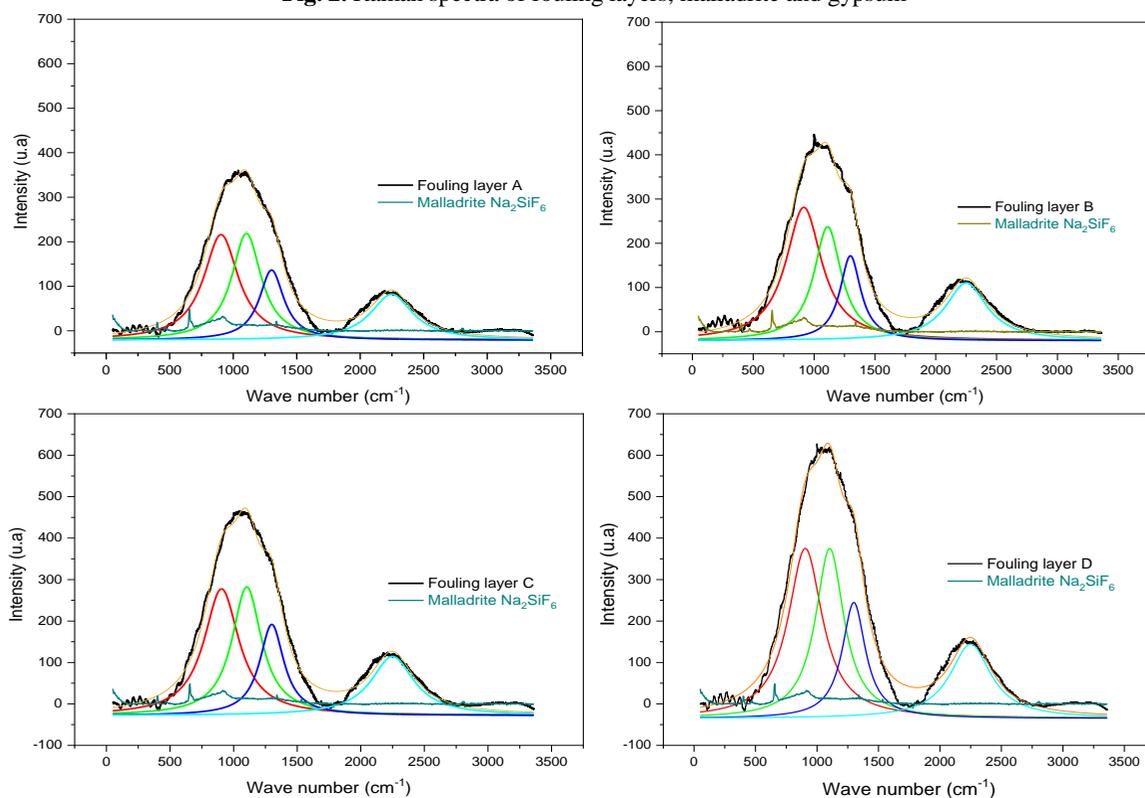
in the Fig. 3. In the interval  $2000\text{--}2500\text{ cm}^{-1}$  there shows only A band at  $2250\text{ cm}^{-1}$ .

However, the analysis performed for the strong band on the spectral region  $500\text{--}1500\text{ cm}^{-1}$  shows three bands at  $964\text{ cm}^{-1}$ ,  $1008\text{ cm}^{-1}$ , and  $1239\text{ cm}^{-1}$ . The intensity of these bands increases in the fouling layers from A to D. Based on frequency data relating to organic groupings in the literature, the analysis of these bands was performed and summarized in Fig. 4. Consequently, the band located at  $2250\text{ cm}^{-1}$  corresponds to the C=C, R-C=CH groupings. The bands of frequencies  $964\text{ cm}^{-1}$ ,  $1008\text{ cm}^{-1}$ , and

$1239\text{ cm}^{-1}$  have been attributed to the presence of groups aromatic =CH bonds, C=O groups of the bonds present in acids, esters or ethers.<sup>34-36</sup>. From the fouling layers, the FT-IR and Raman techniques are complementary and have allowed us to characterize and identify the different groups present in the organic matter. These vibrational techniques also have the advantage of being able to analyze mineral compounds included in an organic matrix. The bands Raman of frequencies attribute to the presence of groups aromatic =CH bonds, C=O groups of the bonds present in acids, esters or ethers.



**Fig. 2.** Raman spectra of fouling layers, malladrite and gypsum



**Fig. 3.** Deconvolution of Raman bands of fouling layers

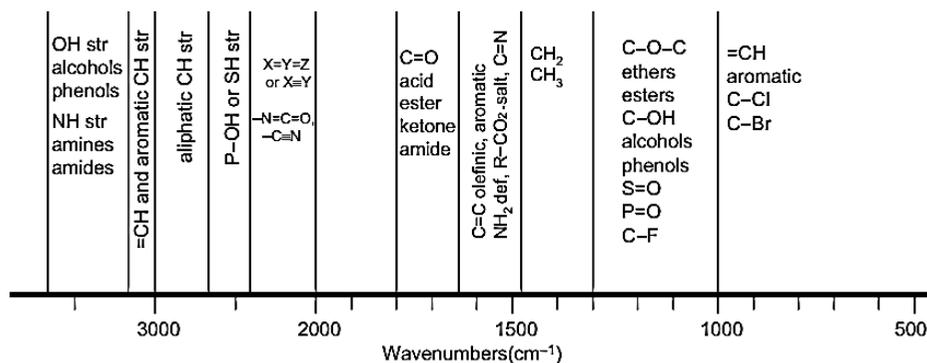
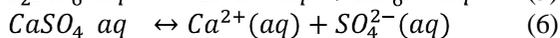
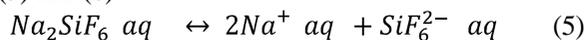


Fig. 4. Vibrational Raman bands of some organic groupings

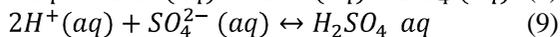
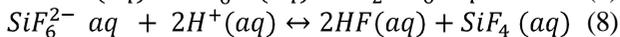
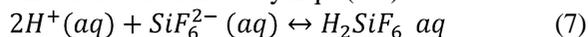
## 3.2. Dissolution of the fouling samples in aqueous solutions

### 3.2.1. pH measurements

The condition optimization requires an exhaustive and exact determination of the solid mineral's origin of the fouling. Measuring pH of the aqueous solution of fouling samples gives an indication of the acid-base nature of the solution containing dissolved species of the solids. Indeed, it is an essential parameter to describe the reactivity, the mobility, and the speciation of the chemical species within a solution. The dissolution of the fouling samples in aqueous solutions was performed. From these solutions, the pH measurements were carried out at the temperature 298 K. The pH values of the solution for different fouling layers A-D are between 2.47 and 2.01 with average  $2.26 \pm 0.01$  and follows this order:  $pH_A (2.47) > pH_B (2.35) > pH_C (2.21) > pH_D (2.01)$ . Indeed, the dissolution of mallardite (and gypsum with low content) in aqueous solutions, the fluoride and sulfate are therefore assumed to be present as  $SiF_6^{2-}$  and  $SO_4^{2-}$  form in the liquid phase. The equilibrium reactions are given by Eqs. (5) and (6).



In solutions,  $H^+$  and  $SiF_6^{2-}$  in pure water or ( $SO_4^{2-}$ ) can form acidic solutions as by Eqs. (7-9).



The pH measurements of the dissolution of fouling layers in aqueous solutions show a slight difference. The values are around two, thus showing the acidity of the dissolving solution of the different fouling layers. The acidic solution confirms the presence of the  $H^+$  ions, these can be free or exchangeable, much more abundant, fixed in equilibrium of the fouling and solution. In the context

of this study, the used method for the separation of organic matter in the fouling samples is based on that of their dissolution in aqueous solutions. The solutions after dissolution reach an equilibrium between the solid phases and liquid. Indeed, the dissolution of mallardite (and gypsum with low content) in aqueous solutions allows the fluoride and sulfate in the liquid phase. The pH is determined mainly by the species presence of  $H^+$ ,  $SiF_6^{2-}$ ,  $SO_4^{2-}$  and their nature. However, the pH value could be sparsely affected by the presence of OM. The obtained mixture shows that the color of the precipitated solid phase becomes white and that of the aqueous solution turns brown. This observation allows us to claim that this solution could contain OM. As a result, it is argued that the OM dissolved in the aqueous phase, and the mallardite remains in the solid phase.

### 3.2.2. Analysis of solid fouling residues

The main objective is to study the presence of organic matter in the fouling layers. The characterization of OM from samples requires an estimate of the amount of substances and their nature. It was possible to distinguish this matter for the fouling samples studied. The analytical protocol for extracting the total substances was developed and implemented for the fouling samples (Fig. 5). The analyses of residues were carried out by FT-IR and Raman spectroscopy. From the dissolution of the fouling samples, the residue spectra  $R_A$ ,  $R_B$ ,  $R_C$ , and  $R_D$  (Fig. 6) show only a weak line of frequency  $659 \text{ cm}^{-1}$ , which has been attributed to mallardite. For the sample (D) an additional line is observed around  $1013 \text{ cm}^{-1}$ , which is assigned to the gypsum. For comparison, the initial spectra of the fouling samples, before the treatment, were also presented in the same figure. The two bands of the fouling layers observed at medium frequencies  $1000 \text{ cm}^{-1}$  and  $2250 \text{ cm}^{-1}$  were attributed to the organic matter disappeared after treatment according to the protocol (Fig. 5). The FT-IR analyses of the solid residues obtained after

treatment and the fouling samples (Fig. 1b) show that the peak corresponding to the OM in the fouling samples disappears after dissolution, only that of malladrite remains. The obtained results using FT-IR and Raman spectroscopy clearly reveal the presence of organic matter.

### 3.3. Quantitative characterization of the organic matter in the fouling samples

#### 3.3.1. Evaluation of the organic matter content by wet method

The quantitative determination of the total organic matter content of the fouling samples will be carried out using two methods: the wet one such as the Walkley and Black method, and the other dry by calcination. The obtained results are presented in Fig. 7, with an uncertainty of  $10^{-4}$ . Indeed, the OM in the fouling samples increases

from layer A to D and that is observed by the variation of color in different fouling layers.

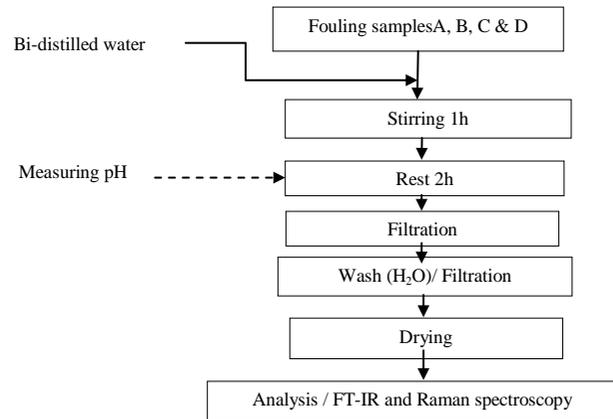


Fig. 5. Layer staining separation protocol of the fouling samples

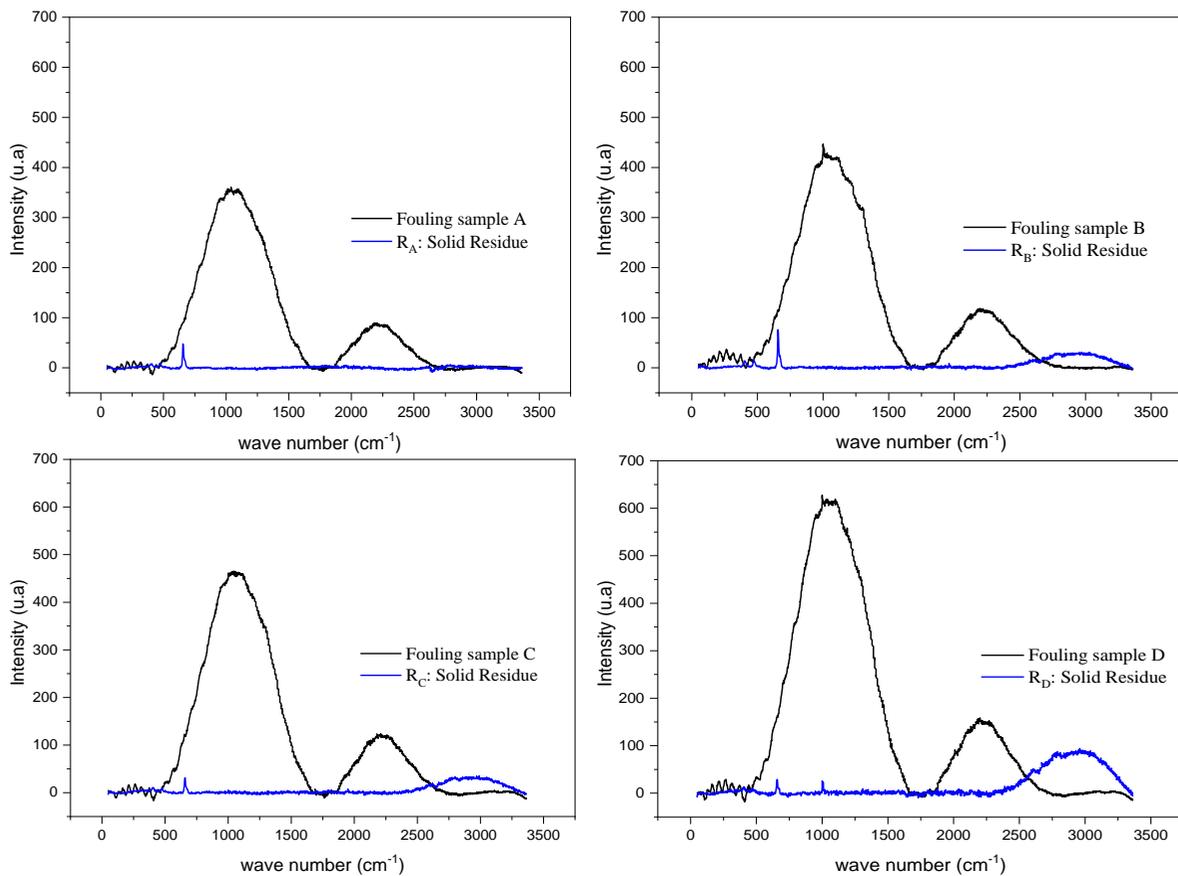


Fig. 6. Raman spectra of the fouling samples and solid residues obtained after dissolution

#### 3.3.2. Assessment of organic matter content by dry method

The evaluation of organic matter content using dry method is based on the calcination process. The fouling

samples with the mass  $m_i=4.0001$  g were placed in an oven at 373 K for 24 hours, then the mass is  $P$ . These samples are gradually brought to 823 K for four hours and are cooled, the mass loss is  $Q$ . The mass loss of the OM is then evaluated by the Eq. (4) (Table 1, Fig. 8). The hu-

midities were also determined for the fouling samples A-D using Eq. (3) and are between 11.74 % and 13.43 %, respectively.

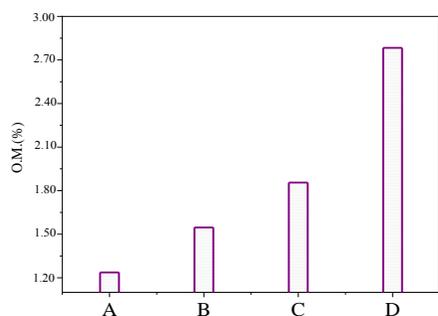
A comparative study of two methods, the wet one by W-B and the dry one by calcination, shows a similar development. Indeed, a regression according to Eq. (10), confirmed the equivalence between the results of the OM % determined by the W-B method and that obtained by calcination (are between 1.81 % and 3.34 %), with coefficients  $a = 0.9932$  and  $b = 0.5870$ .<sup>22,37</sup>

$$OM \%_{(\text{calcination})} = a \cdot OM \%_{(\text{W,B})} + b \quad (10)$$

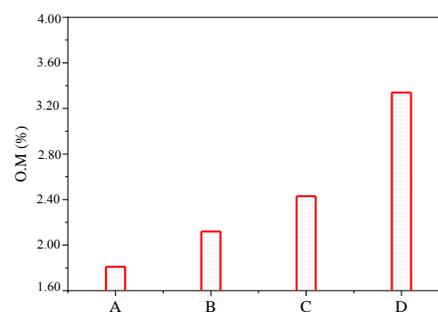
**Table 1.** Organic matter content by calcination process

Sample	$P$	$Q$	$H$ %	$OM$ %
A	3.5304	3.4664	11.74	1.81
B	3.5152	3.4406	12.12	2.12
C	3.4783	3.3937	13.04	2.43
D	3.4628	3.3786	13.43	3.34

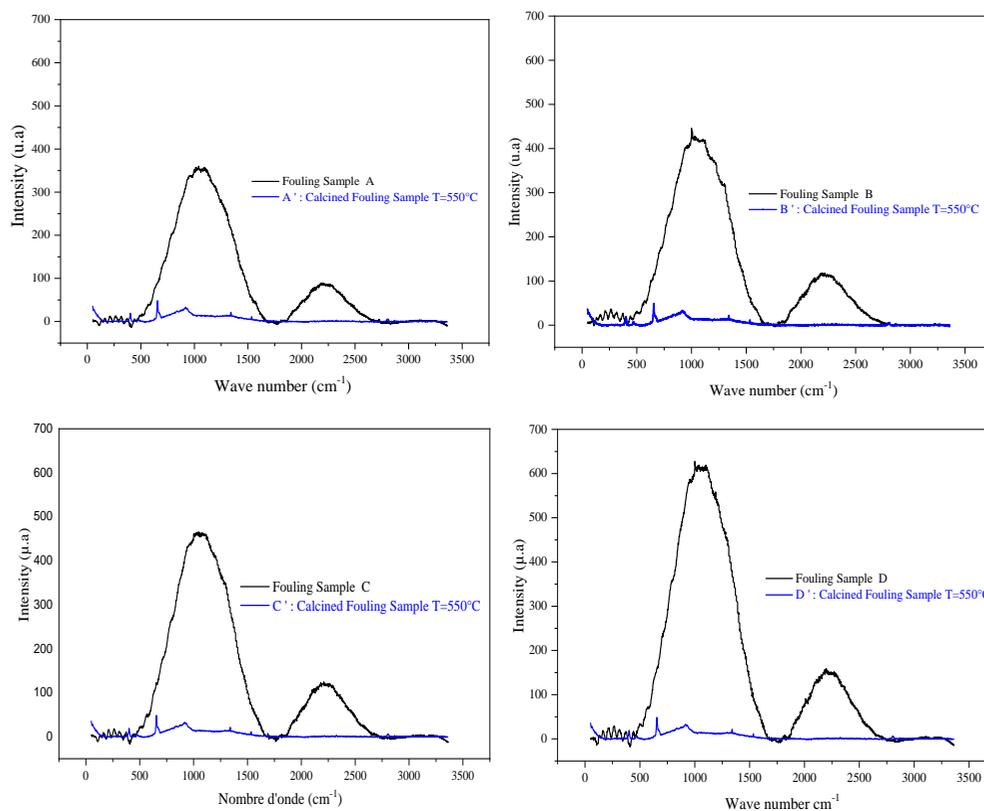
Sample mass  $m_i = 4.0001\text{g}$ ;  $P$ : mass loss (g) at 373 K for 24 hours;  $Q$ : mass loss (g) after calcination at 823 K



**Fig. 7.** Organic matter content of fouling samples



**Fig. 8.** Content of organic matter in fouling samples obtained by calcination at  $T = 823$  K



**Fig. 9.** Raman spectra of raw and calcined fouling samples at  $T = 823$  K

The residues obtained from the calcination of samples were analyzed by Raman spectroscopy (Fig. 9), for comparison, the initial samples spectra were also presented in the same figure. The bands at 1000 and 2250  $\text{cm}^{-1}$  relating to the presence of the OM of the fouling samples disappeared after calcination. However, the OM was eliminated by combustion at  $T = 823$  K. The spectrum of the obtained residue was analyzed and shows only two peaks with a shoulder that are attributed to those of the mallardite form.

## 4. Conclusions

The organic matter was identified in the solid deposits formed in the production of wet process phosphoric acid. The analytical techniques reveal the compounds of mallardite, gypsum, trace metals, and the presence of organic matter. The organic matter of the fouling layers was characterized using FT-IR and Raman spectroscopies. The IR spectra have bands at 3448  $\text{cm}^{-1}$ , the elongation bands of the main O–H groups. The intense bands observed at 733  $\text{cm}^{-1}$  and 477–496  $\text{cm}^{-1}$  have been assigned as Si–F stretching vibrations, which is the main character of  $\text{Na}_2\text{SiF}_6$ . The band at 603  $\text{cm}^{-1}$  is attributed to the  $\text{SO}_4$  elongation which is occurring in  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . The appearance of band at 1130–1134  $\text{cm}^{-1}$  has been assigned to C–O as vibrations in acids, esters or ethers. This appearance indicates the possibility of the organic matter in the fouling layer. However, the Raman vibrational spectra of the fouling layers show two bands at 2000–2500  $\text{cm}^{-1}$  and 500–1500  $\text{cm}^{-1}$ . The two medium bands (1000  $\text{cm}^{-1}$ ; 2250  $\text{cm}^{-1}$ ) are not among those of mallardite and gypsum and they could be attributed to those of OM. The deconvolution of the band using specific software shows the band located at 2250  $\text{cm}^{-1}$  corresponds to the C=C, R–C=CH groupings and those frequencies 964  $\text{cm}^{-1}$ , 1008  $\text{cm}^{-1}$  and 1239  $\text{cm}^{-1}$  have been attributed to the presence of groups aromatic =CH bonds, C=O groups of the bonds present in acids, esters or ethers.

The quantitative determination of the total organic matter content of the fouling samples was performed using two methods: the wet one such as the Walkley & Black method, and the dry one by calcination. A comparative study of two methods shows a similar development. Indeed, the equivalence is obtained between the results of the OM % determined by the W-B method and that obtained by calcination (1.81–3.34 %), with a regression of coefficients  $a = 0.9932$  and  $b = 0.5870$ . The knowledge of the organic matter in the fouling layers and their mixture in the different steps of the wet process will allow us to study the influence of this OM on the mechanisms governing these complex thermodynamic equilibria and the reaction paths.

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## ІДЕНТИФІКАЦІЯ І КІЛЬКІСНЕ ВИЗНАЧЕННЯ ОРГАНІЧНОЇ РЕЧОВИНИ В ПРОМИСЛОВИХ ВІДХОДАХ ВИРОБНИЦТВА ФОСФОРНОЇ КИСЛОТИ ЕКСТРАКЦІЙНИМ СПОСОБОМ

**Анотація.** Органічні речовини у фосфоритах були предметом численних досліджень. Оцінювання і вирішення деяких проблем, таких як забруднення, що виникають під час промислового виробництва фосфорної кислоти, становлять великий інтерес і дозволяють отримати кращі виходи фосфорної кислоти. Тверді відкладення, що утворюються під час виробництва фосфорної кислоти екстракційним способом, були охарактеризовані, і в них виявили маладрит, гіпс, сліди металів і наявність органічних речовин. Ідентифікацію органічних речовин проводили в зразках забруднення за допомогою ІЧ- та раман-спектроскопії. Кількісне визначення загального вмісту органічних речовин у зразках забруднень здійснено за допомогою методів Воклі-Блека та кальцинування. Знання про вміст органічних речовин у шарах забруднення дає змогу краще зрозуміти явища в процесах.

**Ключові слова:** виробництво фосфорної кислоти, забруднення, характеристика, органічні речовини.