

River Water Discolouration with Acid Activated Kaolinite - Rich Clays

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Abstract: Nyong waters are naturally dark brown to light brown in colour because of humic substances. In the present report, Nyong waters treatment with kaolinite rich clays has been investigated. In raw state, 8 to 9 % of the best clay materials were necessary to eliminate all humic substances from Nyong waters. The best acid activation parameters were found with a mass of solution/mass of clay ratio equal to 5: 0.48 N H₂SO₄, 60 min activation time at 97 °C. After acid treatment, the clay content necessary for total Nyong waters discolouration was consequently reduced from 8 to 1 %. The analysis of acidic sites developed during acid activation revealed the predominance of Lewis acid sites. Very low contents (< 0.7 %) of acid-activated clay could not be employed for Nyb discolouration because of sedimentation problems. Recycling of the best acid-activated clay was based on humic substances oxidation with hydrogen peroxide in an acid medium. After 15 cycles, the acid-activated clay still discoloured Nyong waters in spite of particles erosion.

Keywords: kaolinite, acid activation, humic substances, Nyong waters, recycling.

INTRODUCTION

In tropical and equatorial zones, river waters often contain humic substances (HS) which they carry along their course. For instance, the waters of Nyong River run through South Cameroon with a distance of 640 km from East to West to get into the Atlantic Ocean [1]. Nyong waters have a dark to light brown colour. With an average annual flow rate which varies between 145 and 926 m³/s, the less mineralized and less polluted waters are collected and treated (aluminum sulfate, flocculants etc.) for supply in the surrounding towns [2,3]. Humic substances generally induce a brown/yellow colour to the waters which worry the potential consumers. In addition, problems such as complex with metals and organic pollutants, mutagenic halogenated compounds formed after chlorination may also occur [4]. In the case of waters highly charged with HS, aluminum sulfate process is not efficient enough to eliminate them completely [5]. Moreover an aluminium concentration greater than 0.2 mg/dm³ in treated waters does not meet the World Health Organisation (1993) standards due to complaints by the potential consumers about discolouration and depositions.

The use of clay materials as adsorbents is becoming a very promising alternative as compared to aluminum sulfate for water treatment, since they are inexpensive, abundant and efficient. In fact clays are 20 times cheaper than activated carbon [6]. Among clay minerals, kaolinite is the most abundant phyllosilicate mineral in highly weathered soils [7]

and its hydroxyl groups located at the broken edges can be exchanged with H.S. whose overall charge is negative. They can also be adsorbed by electrostatic interaction with kaolinite acid sites. Recent publications [5] have shown that 8 to 9 % of kaolinite and magnetite rich clay were necessary for the decolouration of Nyong waters from 267 to 33 Platinum-Cobalt color scale (PtCo units). Unfortunately, the amounts of clay were too high (80 kg for 1 meter cube of Nyong waters) compared to that of aluminum sulfate (9 to 42 g /m³). Finally it was shown that the use of 1.5 % raw clay, after previous treatment with aluminum sulfate was enabled to attain a colour equal to 6 PtCo units. According to Komadel *et al.* (2006) [8], the main task of acid activation is to obtain partly dissolved material of increased specific surface area, porosity and surface acidity. These surface modifications consecutive to acid activation of kaolinite - rich clays should enhance the adsorbent capacities with respect to humic substances.

This work aims to investigate the best acid activation parameters of two kaolinite-rich clays, in order to determine the minimal quantities enabling complete extraction of humic substances from the Nyong waters. The recycling of the best acid activated clay is also studied.

MATERIALS AND METHODS

Materials

For the studies, two kaolinite-rich clays have been sampled in Mayouom, about 30 km north of Foumban town (West Cameroon), or in the Bafang region (West Cameroon). They will be denoted as Myb and Kob respectively. The main difference between these two clays (Table 1a) is the absence of quartz in Kob to the benefit of magnetite. The presence of magnetite in Kob increases Fe₂O₃ content (Table

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Table 1a. Some Clay Materials Characteristics

| Denomination | Fine Clay Fraction (<2 μ m) | Cationic Exchange Capacity (meq/100 g) | Main Minerals | Visual Colour | Density |
|--------------|---------------------------------|--|------------------------------------|---------------|---------|
| Kob | 25% | 4.8 | kaolinite magnetite goethite | dark grey | 2.60 |
| Myb | 15% | 2.4 | kaolinite quartz anatase | whitish | 2.32 |

Table 1b. Chemical Composition, Expressed as Mass Content of the Air-Dried Materials [5]

| Oxyde | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | MnO | MgO | CaO | Na ₂ O | K ₂ O | TiO ₂ | P ₂ O ₅ | L.O.I. | Total |
|-------|------------------|--------------------------------|--------------------------------|------|------|------|-------------------|------------------|------------------|-------------------------------|--------|-------|
| Kob | 32.48 | 28.12 | 21.46 | 0.20 | 0.69 | 0.09 | <D.I. | <D.I. | 3.84 | 0.685 | 11.22 | 98.67 |
| Myb | 47.52 | 29.74 | 2.22 | 0.03 | Tr. | Tr. | Tr. | 0.68 | 3.76 | 0.45 | 13.73 | 98.13 |

D.I. = detection limits; Tr. = traces; L.O.I. = loss on ignition.

1b) and explains the greatest density of Kob compared to Myb. The very low Cation Exchange Capacity of Myb (CEC = 2.4 meq/100 g) could be an indication of its low content in clay minerals.

Nyong waters (denoted Nyb hereafter) have a dark to light brown colour (245 -165 PtCo units) due to the amount of dissolved humic substances. Once treated with aluminum sulfate (Alsu), the supernatant liquid denoted Nyb-(Alsu) has a colour (refractory organic substances) that could attain 28 to 33 PtCo units.

Experimental Methods

Nyong water (Nyb) analyses: the colour (PtCo units) was measured with a spectrophotometer (HACH/DR2000) at 455 nm wavelength. Distilled water was used as standard with a colour of zero PtCo units. The electrical conductivity was determined with a calibrated CD810 Tacussel digital conductimeter. The dry mass was determined by drying one litre of filtered sample at 110°C [9]. The pH was measured with a calibrated digital pH-meter (SCHOTT GERÄTE).

River water discolouration: amounts of bulk or activated clay were dispersed in 100 ml of Nyb or Nyb-(Alsu) and stirred at room temperature for 2 h, then allowed to rest for 24 h. The supernatant liquid was filtered with an ordinary filter paper and the colour was measured.

Activation parameters: the temperature was fixed at 97 °C in a hot bath. The liquid/clay mass ratio fixed at 5 enabled the obtaining of well wetted clay, with a high probability of kaolinite abrasion and formation of fine particles when stirring [8]. The “right” acid concentration (H₂SO₄) was sought out between 0 and 0.8 N by arbitrarily fixing the activation time to one hour. A mixture of 5 g of clay, x ml of a 2 N sulphuric acid solution and (25 - x) ml of distilled water were introduced in 22 erlenmeyer flasks of 150 ml. (0 < x < 25). The mixture was afterwards agitated under reflux in the hot bath for one hour. The solid obtained was washed with distilled water until the supernatant liquid did not react anymore with Ba²⁺ ions. The solids were dried in an oven at 110 °C for 24 h before use and were denoted here as KoA and MyA corresponding to Kob and Myb

activated samples respectively. The influence of this activation procedure was assessed by measuring the capacity of activated clays to adsorb the refractory organic compounds contained in Nyb-(Alsu). 0.5 g of each activated clays sample (KoA, MyA) were tested in the discolouration reaction of 100 ml of Nyb-(Alsu). The right acid concentration was then used to find out the activation time necessary to attain a maximal activation. 5g of clay was introduced in 9 erlenmeyer flasks of 150 ml with the correct amount of acid and the volume was completed to 25 ml with distilled water. The mixture was stirred in the hot bath under reflux for 30 min or 540 min. The samples obtained were denoted KoA30 to KoA540 or MyA30 to MyA540. The influence of activation time was evaluated in the same manner as above. After HS adsorption, KoA60 was denoted KoA60-HS.

Clays analyses: the infrared spectra of clay samples were recorded between 380 and 4000 cm⁻¹, using an Alpha-P Bruker spectrometer (Attenuated total reflection method: ATR). The acidity of clay samples was measured by FTIR spectroscopy, using pyridine to probe both Brønsted and Lewis acid sites. Pyridine adsorption experiments were performed with a static experimental setup under vacuum. An IR cell made in quartz equipped with KBr windows was used. The powdered clays were pressed into self-supporting wafers of 20 mg which corresponded to 10 mg cm⁻². The samples were pretreated at 423 K under evacuation for 1 h in order to remove adsorbed water and impurities. After cooling to RT, an IR spectrum of the clay material was recorded (64 scans, 4 cm⁻¹) and referred to as background. Afterwards 1 mbar equilibrium pyridine was contacted on the wafer for 10 min. The sample was then brought up to 398 K for 10 min under vacuum in order to remove physisorbed pyridine. After cooling down to RT, an IR spectrum was measured in the 1650-1350 cm⁻¹ spectral range (background subtracted). Some recycled powder samples were studied by XRD using a D8 Advanced Bruker diffractometer. The counting step was 0.022 2 θ , the step time was 10 s and the scanned angular domain was 5° ≤ 2 θ ≤ 40°.

HS destruction by H₂O₂ in acid medium: H₂O₂ is susceptible to oxidize organic matter in hot acid medium.

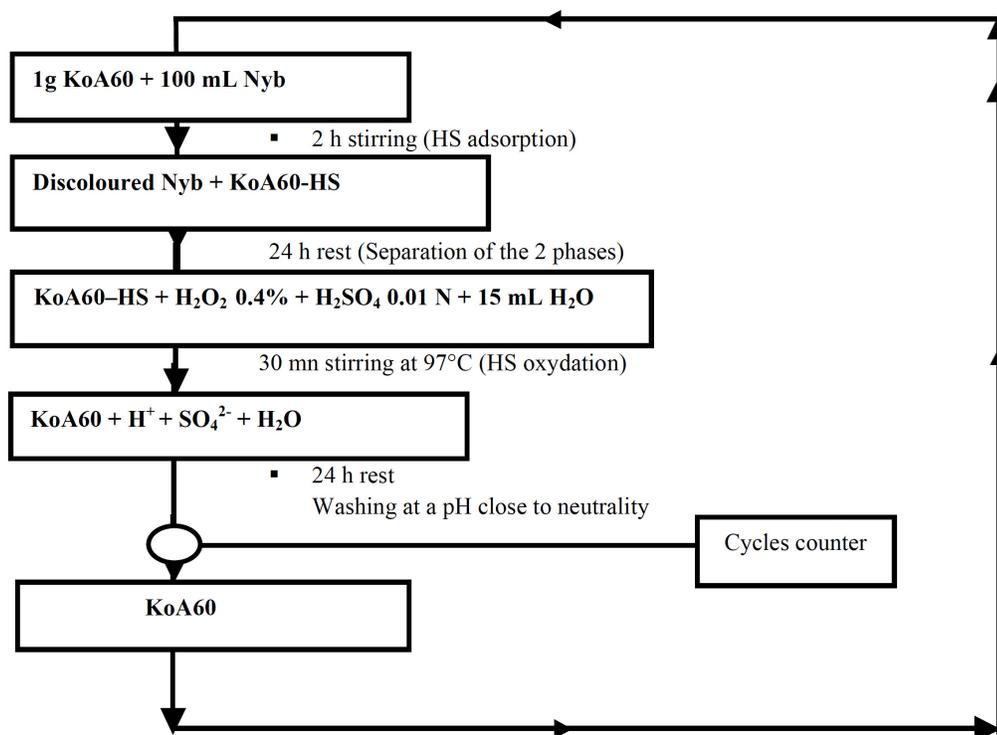
The influence of H₂O₂ concentration was the first parameter considered. In 20 beakers of 200 ml, a mixture of 100 ml of Nyb was added to 1ml of a 2 N sulphuric acid solution + x ml (0 < x < 3.5) of 20 % hydrogen peroxide aqueous solution. The mixture was stirred for two hours at 97 °C and allowed to stand for 24 h. The supernatant liquid was collected for colour measurement. The second parameter influencing the oxidation of HS was time. The selection of appropriate time of reaction was carried out at 97 °C in a 200 ml beaker. 2 ml of 20 % H₂O₂ were added to 100 ml of Nyb, plus 1ml solution of a 2 N sulphuric acid. The mixture was stirred at time intervals varying between 0 and 2 h.

Recycling of acid-activated clay: It was possible to recycle the best activated clay material: KoA60-HS (Scheme 1) by oxidizing humic substances. The stirring velocity was reduced to the minimum as possible (100 rotations/min) and

the mass ratio liquid/clay was fixed to 15 in order to limit collisions and avoid destruction of clay particles.

RESULTS AND DISCUSSION

Discolouration of Nyb by raw clays: The discolouration curves as a function of clay content (0 - 10 %) depicted similar profile (Fig. 1). Clay particles remained in suspension in Nyb till a certain concentration, above such level they gathered to settle. According to Zbik *et al.* (2008) [10], in absence of flocculant, Van der Waal’s forces in the near potential minimum could induce coagulation of clay particles if the charge barrier could be overcome. In the raw state, clays displayed different performances. In fact, 8 to 9 % of Kob was required to eliminate all HS from Nyb. On the other hand, Myb did not discolour Nyb but introduced an additional colouration, which actually was due to the very



Scheme 1. Recycling of KoA60-HS.

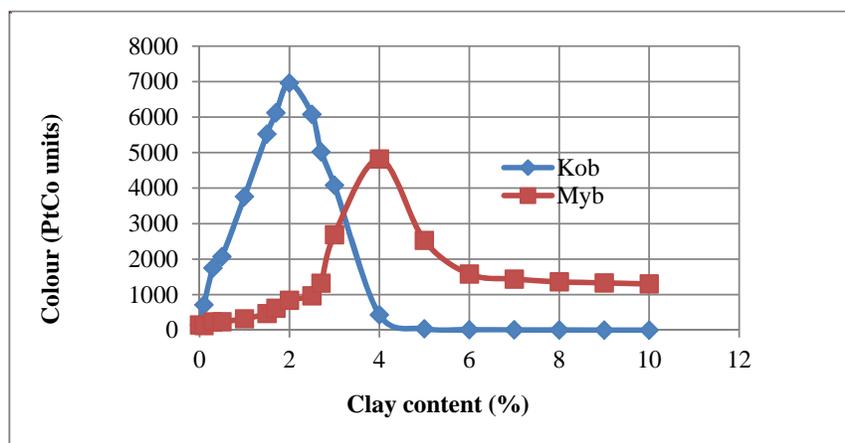


Fig. (1). Nyb discolouration as a function of raw clays content (in %).

fine clay particles that did not settle. Superposition of IR spectra from the two raw clays (Fig. 2) showed very similar absorption bands: O-H stretching bands ($3690/3620\text{ cm}^{-1}$) from silanol groups and characteristic of kaolinite. The bands at 1003 and 909 cm^{-1} corresponded to the symmetric stretching frequencies of the Si-O bonds. Bands between 400 and 527 cm^{-1} could also be attributed to Si-O bending [11]. The absorption bands of Kob had intensity generally superior to that of Myb and the decolorizing capacity of Kob was higher compared to Myb. This could be explained by higher kaolinite and hydroxyl groups content in Kob.

Activation Parameters

Effect of acid concentration: KoA and MyA discolouration was maximal with H_2SO_4 concentrations of 0.48 N ($x = 6\text{ ml}$) and 0.56 N ($x = 7\text{ ml}$) respectively (Fig. 3).

Effect of activation time: Activation was optimal after 60 min and 90 min for KoA and MyA respectively (Fig. 4). These samples were thus denoted KoA60 and MyA90. The superposition of IR spectra from Kob, KoA60, KoA540 samples (Fig. 5a) and Myb, MyA60, MyA540 samples (Fig. 5b) permitted to take notice on the effect of a good activation (KoA60 and MyA90) and a poor one (KoA540

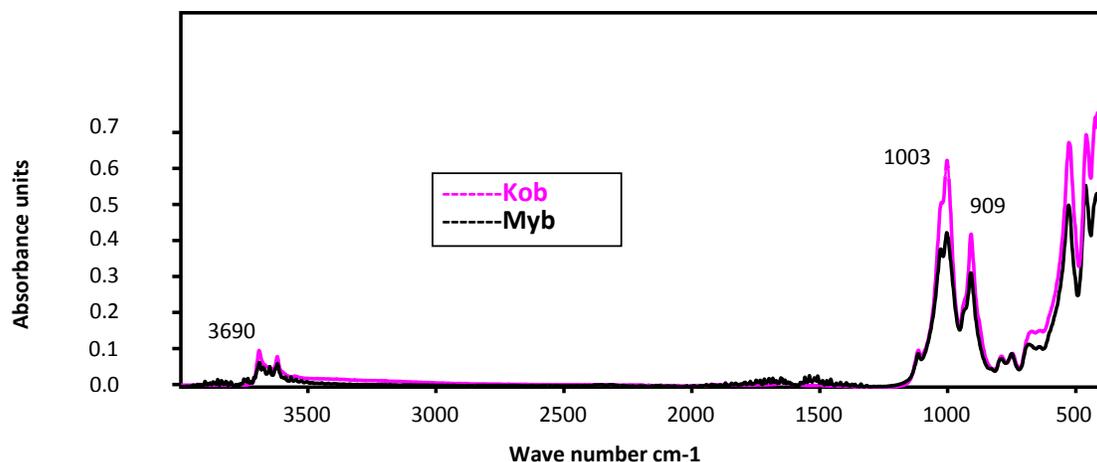


Fig. (2). Infrared spectrum of raw clays (Kob and Myb).

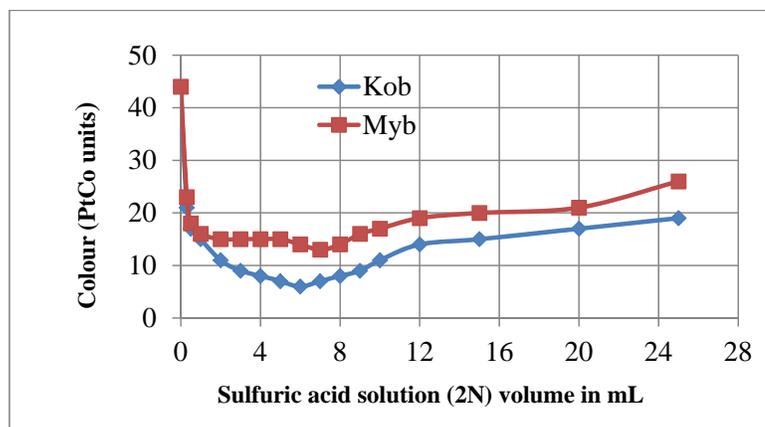


Fig. (3). Effect of acid concentration on Nyb discolouration.

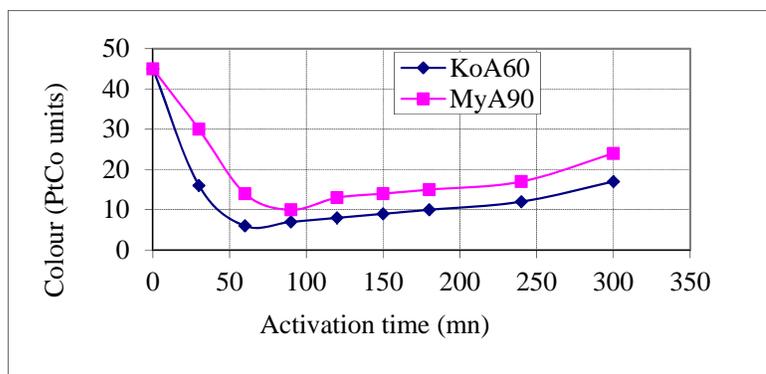


Fig. (4). Effect of activation time on Nyb discolouration.

and MyA540) on the intensities of absorption bands. The intensities of absorption bands corresponding to KoA60 and MyA90 appear to be slightly improved, compared to Kob and Myb respectively. Acid activation induced division of kaolinite into fine particles and the consequence was the apparition of additional aluminol and silanol groups [12]. Chemical reactions between protons and hydroxyl groups from broken edges were made. A longer activation time (540 min) caused the destruction of kaolinite layers, indicated by a decrease of all absorption bands with respect to the raw material. Similar observations were made by Panda *et al.* (2010) [13]. Acid activation of kaolinitic clays required weaker acid concentrations (0.50 N vs 0.70 N) and less long activation durations (60 min vs 300 min) than those of smectitic clays [14].

Acidity of clay samples (Kob, KoA60; Myb, MyA90):

Pyridine adsorption (Fig. 6) on the 4 different clay materials led to the occurrence of 5 IR bands at 1621, 1609, 1545, 1490 and 1454 cm^{-1} . The spectroscopic components found at 1621, 1609 (MyA90 sample) and 1454 cm^{-1} were assigned to pyridine on Lewis acid sites. The band at 1490 cm^{-1}

corresponded to pyridine adsorbed on both Lewis and Brønsted acid sites, while the IR feature at 1545 cm^{-1} was the signature of pyridine adsorbed on Brønsted acid sites. The concentrations of Brønsted and Lewis acid sites for each clay material were obtained after integration of the absorbance values (a.u.) found in the 1575-1525 and 1470-1435 cm^{-1} ranges respectively (Table 2). Molar extinction coefficients of 1.67 and 2.22 $\text{cm}^2/\mu\text{mol}$ were used for Brønsted and Lewis acid sites respectively [15]. Raw materials had practically similar Brønsted acid sites concentration (13 and 15 $\mu\text{mol/g}$). However, the number of Lewis acid sites was larger for Kob than for Myb (178 against 78 $\mu\text{mol/g}$). At the activated state, these two materials developed a greater Lewis acidity than the Brønsted one. Greatest adsorption of HS after acid activation was in agreement with the increase of Lewis acids sites concentration. During acid activation, exchangeable cations are replaced by protons and a part of dissolved octahedral cations, giving rise to unsatisfied valencies and creating new acidic sites in the structure [16]. On the broken edges, protons could react with hydroxyl groups to form $-\text{OH}_2^+$ onto which HS could be adsorbed [7]. Brønsted and Lewis acid sites are associated with the interlamellar region

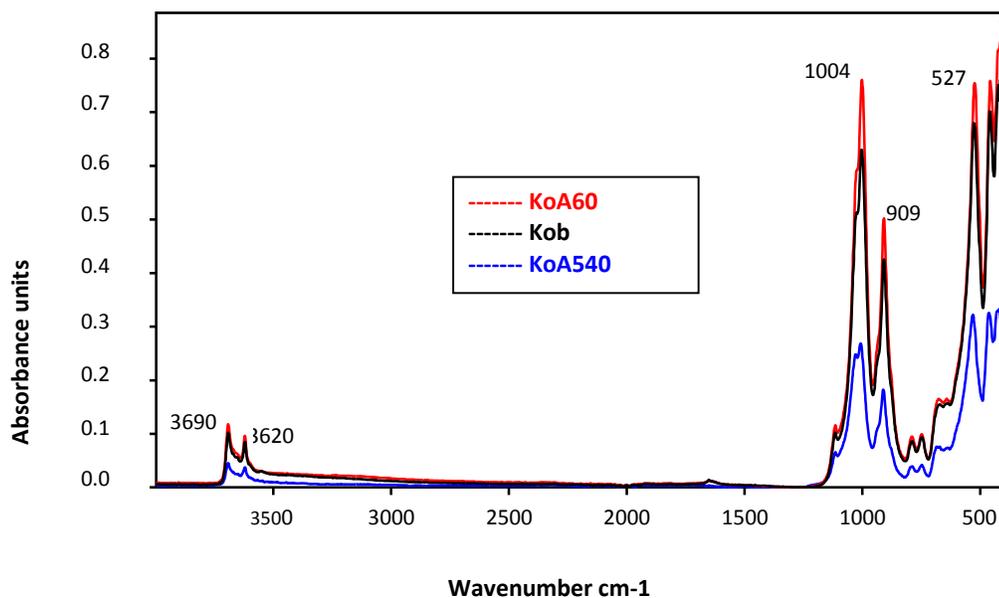


Fig. (5a). Effect of activation time on Kob absorption bands.

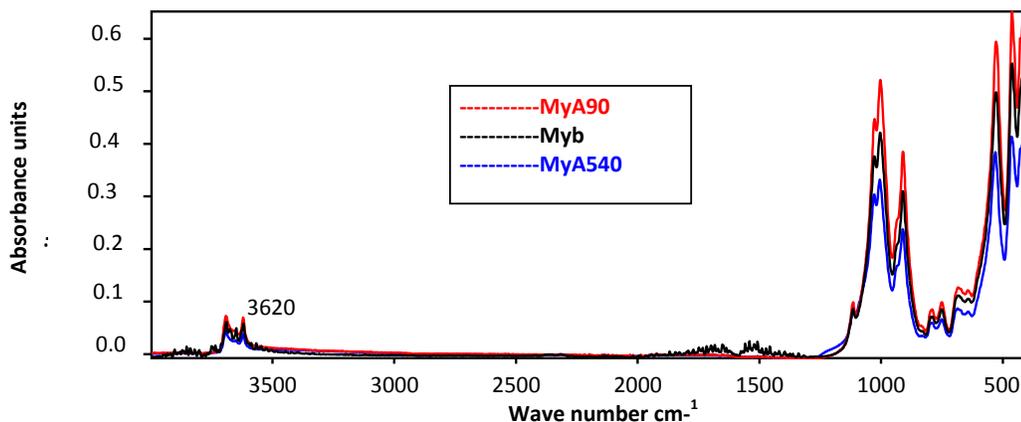


Fig. (5b). Effect of activation time on Myb absorption bands.

and the edge sites of clays respectively. The exchange of the interlayer cations by protons resulted in the increase of Bronsted acid sites [12]. According to Srinivasan [6] (2011), the Lewis acidity arises from exposed trivalent cations, mostly Al^{3+} at the edges, or Al^{3+} arising from rupture of Si-O-Al bonds. Fe^{3+} dissolved from magnetite could interchange the exchangeable cations and exhibit some of the strongest Lewis acid sites described by many workers [17]. These Lewis acid sites could then adsorb refractory organic substances from Nyb-(Alsu).

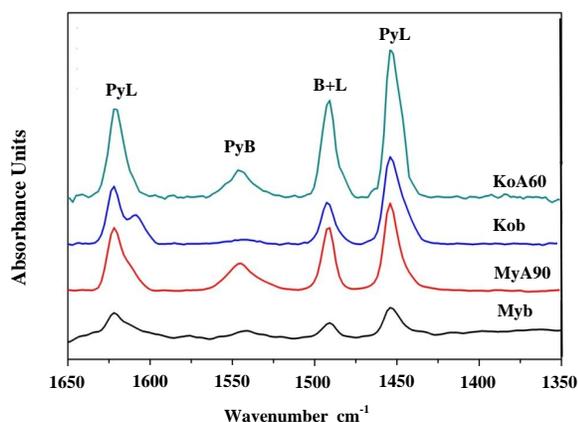


Fig. (6). IR spectra of pyridine adsorbed on Myb, MyA90, Kob and KoA60 clays at RT. (PyL = pyridine onto Lewis site; PyB = pyridine Bronsted site onto; B+L = Bronsted + Lewis sites).

Discolouration of Nyb with activated clays: The discolouration of Nyb was total with only 1 % of KoA60 while about 8 % of MyA90 was required to reach the same result (Fig. 7). Complete discolouration of Nyb-(Alsu) was obtained with 0.7% of KobA60 and 5 % of MyA90. After discolouration with acid activated clays, Nyb waters became slightly acidic (pH 3.80 and 3.95; Table 3). This could be explained by an exchange of the protons of activated clays by some Nyb cations susceptible to accommodate between clay minerals interlayer. The electrical conductivity of Nyb changed from 58.2 to 165.1 and 152.5 $\mu S/cm$ probably due to the dissolution of amorphous minerals contained in the activated clays. The little increase of dry residue observed after the elimination of HS could also confirm the dissolution of amorphous minerals arising from activated clays. The use of 8 % MyA90 produced a dry residue mass practically double of that generated by 1 % of KoA60. At very low concentrations (0 - 0.3% for KoA60 and 0-1% for MyA90) clay particles dispersed in Nyb, did not settle but introduced an additional color (Fig. 7). Higher contents of clay particles (0.5 % for KoA60 and 1.3 % for MyA90) promoted interactions between clay particles, their aggregation and sedimentation. In general, clays used at low contents (≤ 0.7 %) for Nyb discolouration were problematic with dispersion and sedimentation.

Comparison of discolouration methods: One cubic meter of Nyb with an initial colour of 149 PtCo units could be treated by aluminum sulfate, raw or activated clays (Table 4). Only 42 g of aluminum sulfate were necessary to attain a colour equal to 29 PtCo units. Raw clay materials were not efficient because the amounts used to attain colours as 33

Table 2. Quantitative Estimation of Bronsted and Lewis Acid Sites Concentrations, Observed on the Different Samples

| | Area PyL | Lewis ($\mu mol.g^{-1}$) | Area PyB | Bronsted ($\mu mol.g^{-1}$) | Ratio L/B |
|-------|----------|----------------------------|----------|-------------------------------|-----------|
| KoA60 | 0,496 | 447 | 0,144 | 172 | 2.60 |
| Kob | 0,198 | 178 | 0,011 | 13 | 13.69 |
| MyA90 | 0,254 | 229 | 0,135 | 162 | 1.41 |
| Myb | 0,087 | 78 | 0,013 | 15 | 5.20 |

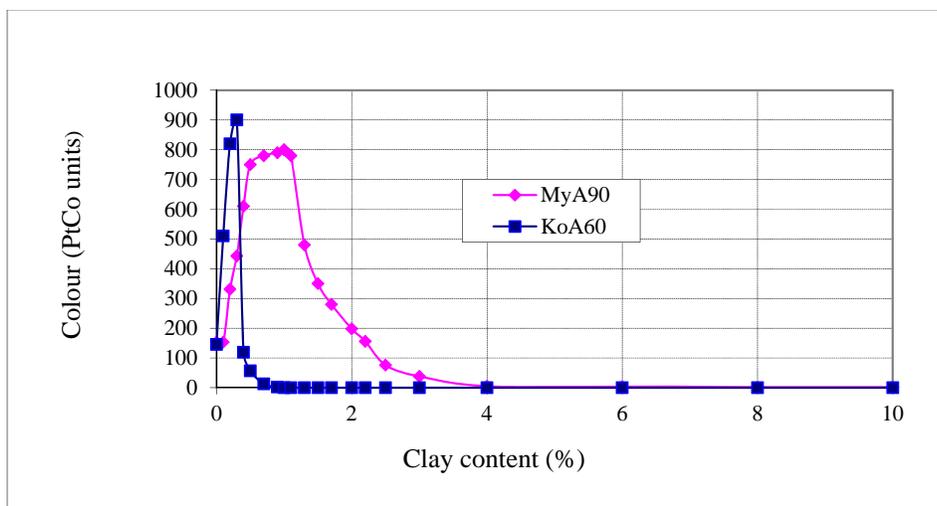


Fig. (7). Nyb discolouration with activated clays.

Table 3. Nyb Characteristics Before and After Elimination of HS by Activated Clays

| | pH | Conductivity ($\mu\text{S/cm}$) | Dry mass (mg/L) |
|------------------------|------|-----------------------------------|-----------------|
| Nyb | 6,16 | 58,2 | 62 |
| Nyb treated with MyA90 | 3,80 | 165,1 | 140 |
| Nyb treated with KoA60 | 3,95 | 152,5 | 76 |

Table 4. Comparison of Various Discolouration Methods

| Bleaching Material | Average Mass Necessary to Discolour One Meter Cube of Nyb | Average Colour of Treated Water (PtCo Units) |
|--------------------|---|--|
| Aluminum sulfate | 42 g | 29 |
| Kob | 90 kg | 33 |
| Myb | 720 kg | 1322 |
| KoA60 | 10 kg | 0 |
| MyA90 | 80 kg | 0 |

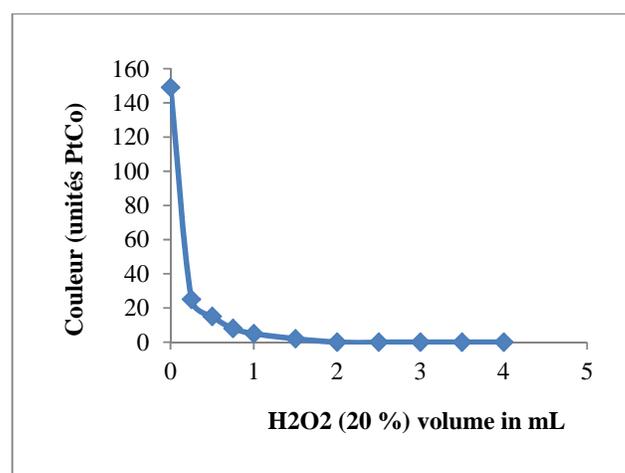
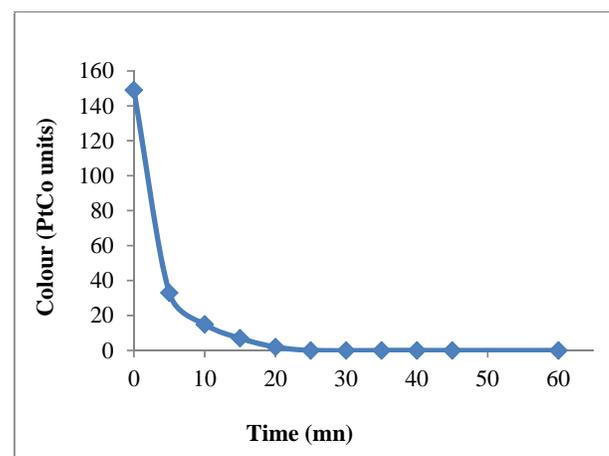
PtCo units were very large (90 kg for Kob). 10 kg of KoA60 or 80 kg of MyA90 were necessary for complete discolouration of 1 m³ of Nyb. A kaolinite richer clay material would minimize the total amount of clay necessary.

HS destruction by H₂O₂ in acid medium: HS from Nyb were completely removed (Fig. 8a) by 0.4 % hydrogen peroxide in hot (97°C) acid medium (0.01N). Under the operating conditions described above, 30 min was necessary for the oxidation of total amount of HS (Fig. 8b). HS present in Nyb could not be oxidized at room temperature.

Recycling of the best activated clay material (KoA60): After 15 cycles, Nyb was completely discoloured (within 24 h rest) by KoR15. The intensities of IR bands assigned to the hydroxyl groups (Fig. 9a) decreased as a function of cycles. From the fifth to the tenth cycle, the intensity of the absorption bands decreased only by approximately 25%. The intensity of bands from KoR₁₅ sample was almost 50 % weaker than that from KoR₀. This could be explained by a progressive destruction of the clay layers. Examination of the main diffraction peak (*d*₀₀₁) from kaolinite (reflection centred at 7.20 Å) for the samples KoR₀, KoR₅, KoR₁₀ and KoR₁₅, (Fig. 9b) showed a good crystallinity of the material in spite of the 15 cycles. The study showed that the recycling of KoA60 could be used more than 15 times despite the gradual erosion, the increase of fine particles and longer settling time.

CONCLUSION

In the raw state, only the kaolinite richest clay (Kob) was able to eliminate HS from Nyb. The optimal acid activation parameters were determined after fixing: (i) the temperature to 97 °C and the liquid/clay mass ratio to 5, (ii) sulfuric acid concentrations to 0.48 and 0.56 N, (iii) activation times to 60 and 90 min for Kob and Myb respectively. IR spectroscopy permitted to display the decrease of absorption bands intensities (hydroxyl groups concentration) following a poor acid activation. The acidity measurements before and after acid activation of clays showed a prevalence of Lewis acid sites compared to Bronsted acid sites. Acid activation of

**Fig. (8a).** Effect of H₂O₂ concentration on the oxidation of HS.**Fig. (8b).** Oxidation of HS as a function of time.

Myb permitted to obtain the discolouration of Nyb with 8 % of MyA90. Only 1 % of KoA60 were necessary to attain the same result. Very low contents (< 0.7 %) of acid-activated

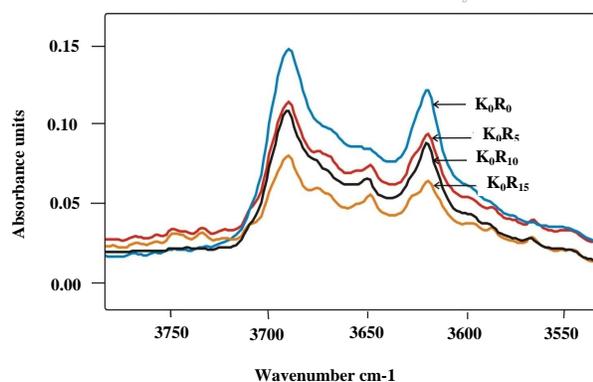


Fig. (9a). Intensity of hydroxyl groups during KoA60 recycling.

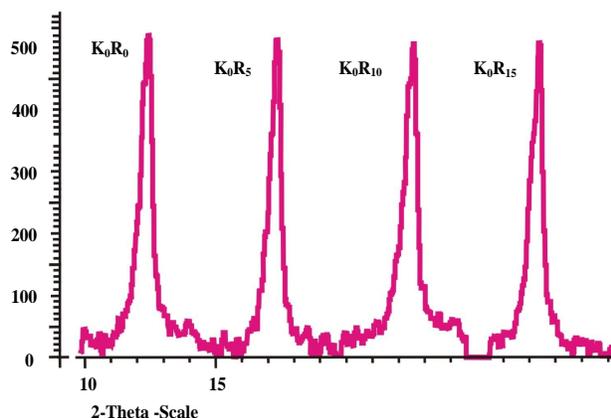


Fig. (9b). Evolution of the main kaolinite reflection during recycling.

clay were not usable for Nyb discolouration because of sedimentation problems. Recycling KoA60 was based on HS oxidation with hydrogen peroxide in an acid medium. After 15 cycles, KoA60 still discoloured Nyb in spite of particles erosion. 1% of KoA60 applied to the discolouration of one cubic meter of Nyb represented a mass of 10 kg. Applying KoA60 to a daily production of about 10 to 20 cubic meters of water could be considered since the masses of clay (100 to 200 kg) to handle remained reasonable.

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CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflicts of interest.

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