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# ORGANOCLAYS AND INORGANIC-ORGANIC PILLARED CLAYS. PREPARATION, CHARACTERIZATION AND POTENTIAL USE AS ELECTRODE MODIFIER

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**ABSTRACT.** We report on the synthesis of organoclays and inorganic-organic clays obtained by inserting in natural clay hexadecylpyridinium (HDPB) bromide and HDPB plus hydroxy-aluminium, respectively. The effect of synthesis conditions on the physical, chemical, and structural properties of the products was examined by total organic carbon determination, specific surface and porosity measurement, and performing SEM and FT-IR of the surface. Glassy carbon electrodes were modified by a film of the organoclays, and utilized as the working electrode in ion-exchange voltammetry. Multistep cyclic voltammetry revealed a time dependence accumulation of anions in the clay layer, by adsorption from the supporting electrolyte. Thereby, the modified clays have been shown to be useful in analytical applications that involve high affinity ion capturing. Recorded adsorption isotherms show that these modified clays are promising materials for environmental application as adsorbents of organic pollutants such as 2,4- and 2,6-dinitrophenols.

**Keywords:** modified clays, organoclays, organic-inorganic clays, ions exchange voltammetry, and dinitrophenols.

## INTRODUCTION

Most industrial waste waters contain hydrophobic organic compounds, e.g., nitrophenol derivatives, along with oxyanions, such as chromate ions. Even when present at trace levels, these contaminants are toxic to animals and to microorganisms in the soil [1], or may act as possible mutagens and carcinogens [2]. Recovery or total immobilization of these pollutants from residual waters is a major concern, which triggers research toward developing new and more efficient adsorbents [1, 3-7].

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Smectite clay minerals are readily available crystalline materials, which can be used as less expensive adsorbents. They possess a lamellar structure, which comprises overlaid sheets, where each tetrahedral sheet is bound to the octahedral sheet. Clays possess permanent negative charges, and the presence of cations renders them electrically neutral. These interlayer $Na^+$, $Ca^{2+}$, and $K^+$ cations are exchangeable: they can be substituted by organic cations or by hydroxylmetal cations. By exchanging the original interlayer cations for organocations, one could obtain organically modified materials, known as *organoclays* [8,9]; while clays treated with inorganic ions are referred to as *pillared clays* [10, 11].

In both cases, the surface properties of the obtained materials undergo a dramatic change. As a result of the treatment, the surface of clays become organophilic, as it accommodates covalently linked organic moieties. The lamellar structure of the organoclay remains, however, analogous to the parent phyllosilicate. Owing to their great affinity for hydrophobic organic compounds, they manifest excellent adsorptive properties toward them [12]. On their turn, pillared clays are efficient adsorbents of heavy metals and oxyanions [13, 14]. Consequently, clays with an intercalated organic surfactant and a hydroxyl-metal cation, termed as *organic-inorganic clay* [15] should adsorb from aqueous solutions organic compounds and oxyanions, simultaneously.

Four procedures are described for the synthesis of organic-inorganic clays (abbreviated as IO clays) [15] termed alternatively as inorganic clay–organic cation complexes [16]. Typically, the synthetic procedure involves a controlled hydrolysis reaction, which may proceed either in solution or in the interlayer galleries of the clay. When the hydrolysis takes place in solution, the yielded amount of polycation is determined by the identity of reactants and their initial concentrations, the degree of hydrolysis, temperature, the rate at which the reactants are added, and the overall duration of the reaction [17]. Zhu and co-workers [18] demonstrated that cetyltrimethylammonium bromide (CTAB) surfactant and Al could not be both inserted in the interlayer gallery of bentonite, when added at the same time, or when CTAB was first incorporated. Conversely, when $Al_{13}$ was added first, the aluminum cations “blocked” the interlayer space, hence, the eventual insertion of CTAB becomes extremely difficult.

In this work, we synthesized an organoclay and an inorganic-organic clay via insertion of hexadecylpyridinium bromide (HDPB), and HDPB plus hydroxy-aluminium, respectively. The effect of synthesis conditions on the physical, chemical, and structural properties of the products was examined by (i) total organic carbon determination, (ii) specific surface and porosity measurements, (iii) FT-IR, and (iv) ion-exchange voltammetry. Batch adsorption experiments show that these modified clays are promising materials for environmental application, as adsorbents of hazardous 2,4- and 2,6-dinitrophenols.

## RESULTS AND DISCUSSION

### Clay modification

Modified smectites were obtained according to procedures described in the Experimental part. Sample codes and sample descriptions are listed in Table 1.

**Table 1.** Samples code and description of the natural and modified clays

| Sample | Description |
|---|---|
| Sa01 | Natural clay |
| Sa01-Na | Natural clay converted in homo-ionic form |
| O- Sa01(a) | Sa01-Na clay modified with organic substance, 0.5 time CEC |
| O- Sa01(b) | Sa01-Na clay modified with organic substance, 1 time CEC |
| O- Sa01(c) | Sa01-Na clay modified with organic substance, 2 time CEC |
| I- Sa01 | Clay modified with inorganic substance, $Al_{13}$ (10 mmol/g of clay) |
| OI- Sa01(a) | Clay modified with organic substance, 0.5 time CEC and $Al_{13}$ (10 mmol /g of clay) |
| OI- Sa01(b) | Clay modified with organic substance, 1 time CEC and $Al_{13}$ (10 mmol/g of clay) |

CEC: Cation-exchange capacity
Organic substance: hexadecylpyridinium bromide (HDPB)
Inorganic substance: hydroxy-aluminum with the formula $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, abbreviated as $Al_{13}$

### Materials characterization

TOC values obtained for the investigated samples are listed in Table 2.

**Table 2.** COT values determined for different samples

| Sample | TOC (mg C /g clay) | Carbon (%wt) |
|---|---|---|
| Sa01 | 0.87 | 0.087 |
| O-Sa01(b) | 84.0 | 8.40 |
| OI-Sa01(b) | 54.0 | 5.40 |

Data in Table 2 reveal that natural clay contains a very low quantity of carbon, which originates from the organic impurities present in the sample. The high carbon proportion determined in the other two samples originates from HDPB. The lower carbon percentage of the hybrid (OI-Sa01(b)) as compared to the organoclay (O-Sa01(b)) is a result of utilizing $Al_{13}$ in the second step of the sample treatment. This aluminum complex replaces in part HDPB present in the interlayer space, decreasing the overall carbon content of the resulting modified clay [19].

Overlaid IR spectra of samples Sa01, O-Sa01(b) and OI-Sa01(b) are shown in Figure 1. The very strong absorption band, present in the three samples around 3635 $cm^{-1}$ can be assigned to the internal OH group linked to Al or Mg in the montmorillonite sheets [20-21]. Upon examining these spectra one can notice three major changes in the two modified clays, as compared to the starting material.

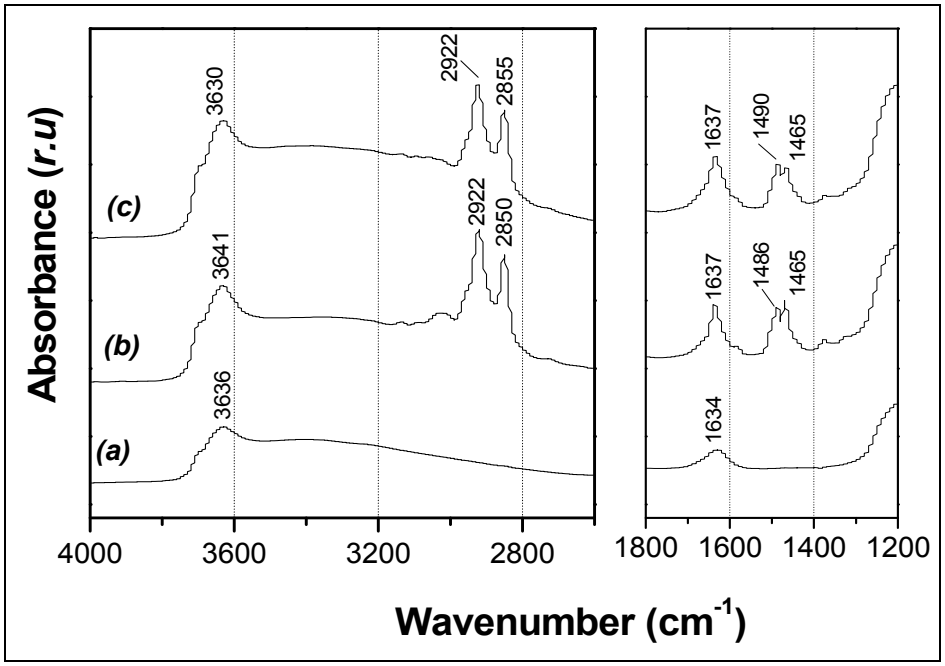


**Figure 1.** IR spectra (recorded in the range from 4000 to 1200 $cm^{-1}$) of (a): Sa01, (b): O-Sa01(b) and (c): OI-Sa01(b) materials.

Absorptions bands between at 3000 and 2800 $cm^{-1}$ present in modified materials correspond to the vibrations and symmetrical deformations of $-CH_2-$ groups. Furthermore, the absorption bands around 1490 and 1465 cm,$^{-1}$ which are not present on the spectra of the unmodified clay, can be assigned to the in-plane deformation of the C-H bond. The changes arising with the clay modification support the idea of intercalation of the organic molecules between the clay sheets.

Microphotographs recorded by SEM for samples modified and unmodified clays (Figure 2) reveal that the unmodified material, i.e., the native clay has a uniform surface with even pore distribution. These findings confirm the results of specific surface and porosity measurements, Table 3.

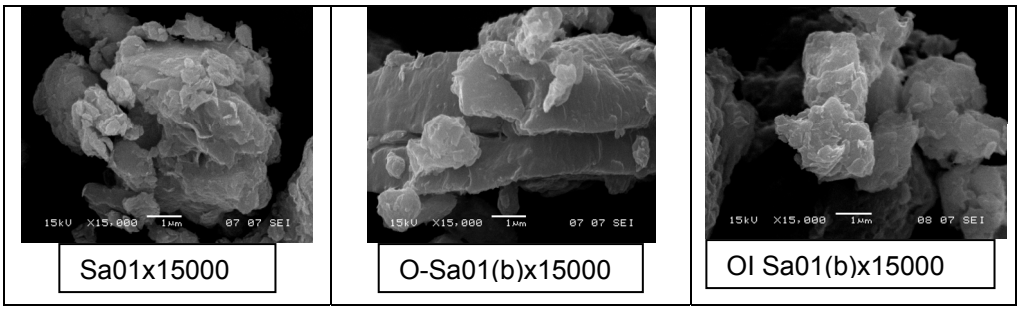


**Figure 2.** SEMs of Sa01, O-Sa01(b) and OI-Sa01(b) materials.

**Table 3.** Specific surface and pores distribution of some clays.

| Sample | Surface Area | | Pore volume ( t-plot) | Mezo- and Macropores (BJH-desorbtion) | | |
|---|---|---|---|---|---|---|
| | Single point $m^2 g^{-1}$ | BET $m^2 g^{-1}$ | Cumulative volume of pores, $cm^3 g^{-1}$ | Total area $m^2 g^{-1}$ | Total volume $cm^3 g^{-1}$ | Average pore diameter nm |
| O-Sa01(b) | 1.4954 | 1.6652 | - | 1.6216 | 0.015936 | 3.9309 |
| OI-Sa01(b) | 3.1324 | 3.3639 | - | 5.6173 | 0.030170 | 2.1484 |
| Sa01 | 59.7219 | 60.6172 | 0.00748 | 58.5195 | 0.109799 | 0.7505 |

Comparing with unmodified smectite, the specific surface of O-Sa01 and OI-Sa01 decrease and the average pore diameter increase after modification, Table 3. Thereby, the modified clays could be able to absorb the big anions such ferricyanide, chromates, etc. from the surrounding solution.

### Characterization of materials by ion-exchange voltammetry

As we intend to use the organoclays in high affinity analytical ion capturing, it was necessary to study the behaviour of a solid electrode substrate covered by these materials. Thus, some electrochemical experiments were performed through a glassy carbon (GC) electrode modified by dip-coating using a 2 %wt (organo)clay suspension (O-Sa01), and drying the film in air at room temperature. Such electrodes were scanned in the classical ferricyanide/ferrocyanide system.

As revealed by Figure 3(A), the magnitude of peak current recorded with OI clay-modified GC electrode is more than two fold greater than the signal obtained with a bare GC electrode. The greater signal, however, needs to be developed over time (see Figure 3(B)).

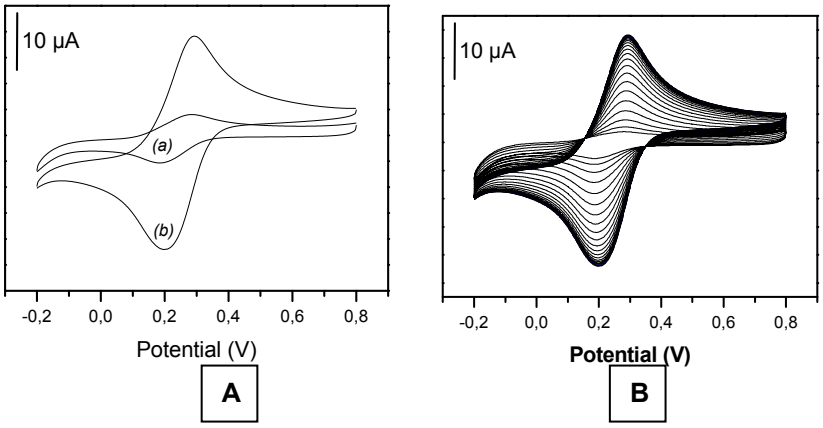


**Figure 3. (A)** Cyclic voltammetry of $10^{-3}$ M $[Fe(CN)_6]^{3-}$ in 0.1 M KCl performed with (**a**) unmodified glassy carbon (GC) electrode and (**b**) GC modified with an organic-inorganic clay film. (Scan rate: 50 mV $s^{-1}$)
**(B)** Successive scans (20 scans) of $10^{-3}$ M $[Fe(CN)_6]^{3-}$ in 0.1 M KCl performed with GC electrode modified with an organic-inorganic clay film. (Scan rate: 50 mV $s^{-1}$)

Shown in Figure 3(B) is the increase of peak currents with the number of successive scans. Very scarce Faradaic activity is noticed in the first cycle, as if the supporting electrolyte were not electroactive. This observation is a consequence of the blocking properties of the clay film located on the electrode surface. Over the next scans however, peak currents increase progressively, owing to the incorporation of electroactive species in the film. Redox species are continuously accumulated in the clay film via the replacement of counter ions of the weekly bound surfactant. By this, ion pairs are formed between the $HDP^+$ cations and the $[Fe(CN)_6]^{3-}$ anions [22]. After about 15 cycles, the peak currents stabilize at constant values, indicating that the system has reached the steady state. This observation indicates that the electrode coating enables the fixation of anions from solution. The explanation of the phenomenon is that several smectites, though negatively charged prior to being applied as a coating layer onto the GC surface, are able to absorb the anions from the supporting electrolyte, and store them in its pores, or even on the sides of the clay surface, which interact strongly with the anions [23,24].

Another possible reason for $[Fe(CN)_6]^{3-}$ build-up in the clay film is the following: during the synthesis a large number of surfactant cations ($HDP^+$) substituted by Al polycations are retained by the clay via hydrophobic interactions with their long carbon chain [25]. As a consequence, the overall positive charge of the clay increases, which is a driving force for absorbing additional ferricyanide anions from the surrounding solution.

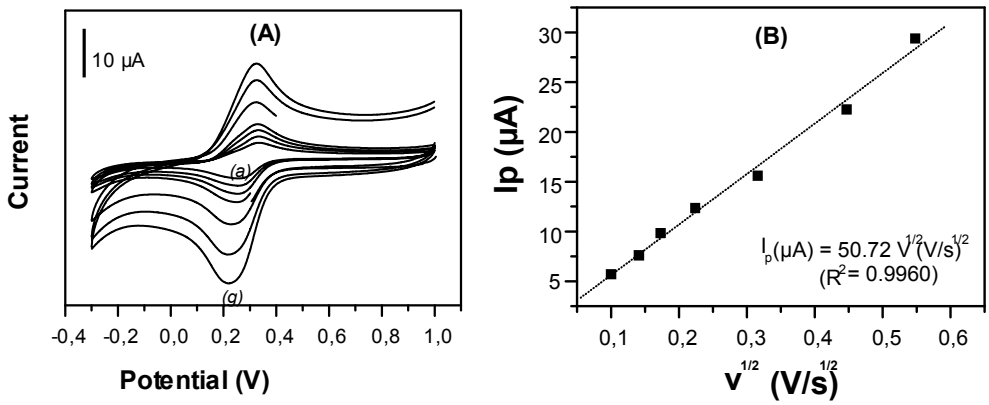


**Figure 4.** (**A**) Cyclic voltammetry performed in $10^{-3}$ M $[Fe(CN)_6]^{3-}$ in 0.1 M KCl with a GC modified with a film of OI clay, at scan rates of 10 (a), 20, 30, 50 , 100, 200 and 300 (g) mV $s^{-1}$. (**B**) Variation of peak current with the square root of scan rate.

Figure 4(A) displays the cyclic voltammograms, recorded at increasing potential scan rates from 10 to 300 mV $s^{-1}$. As one can notice, the the peak potential separation was not really affected with scan rate; however, the peak currents correlate linearly with the square root (Figure 4(B)) of the potential scan rate ($R^2$ =0.9971).

### Adsorption properties of the modified clays

In order to investigate the potential of our modified clays as adsorbents of environmental contaminants, we investigated the extent to which they retain model compounds. Because of their environmental impact we have chosen 2,4-dinitrophenol (2,4-DNP) and 2,6-dinitrophenol (2,6-DNP) The sorption isotherms were presented in Figure 5. The values of 1/*n* were obtained from the application of the Freundlich model and Langmuir [7]. Further, the slope 1/*n* between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, with the surface becoming more heterogeneous, when the value is closer to 0 [26]. As 1/*n* is less than 0.40, the materials have a heterogeneous surface. The 2,4-DNP adsorption capacities for O-Sa01 and IO-Sa01 calculated according to Langmuir isotherm are 53.48 and 54.05 mg $g^{-1}$, respectively, and 43.10 and 43.67 mg $g^{-1}$ for 2,6-DNP adsorption on O-Sa01 and IO-Sa01, respectively [27], comparable to the adsorption capacity ($q_{max}$ = 41.15mg.$g^{-1}$) of 2,6-dinitrophenol on activated carbon, obtained by Tertis and co-workers [28].

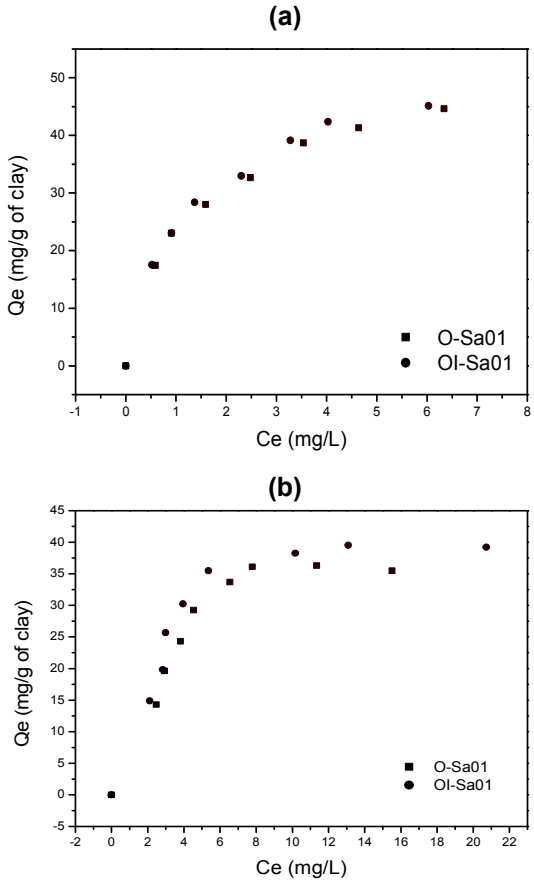


**Figure 5.** Sorption isotherms of 2.4-DNP (a) and of 2,6-DNP (b) on O-Sa01 and OI-Sa01.

No significant difference is observed on the maximum amount of adsorption during the adsorption of these derivatives between nitrophenols on O-Sa01 and IO-Sa01; however, the latter has the advantage to adsorb simultaneously hydrophobic organic compounds and inorganic substances from aqueous solution [18, 25].

## CONCLUSIONS

New organoclays (O-Sa) and inorganic-organic (OI-Sa) clays were synthesized by insertion of (HDPB) and (HDPB) plus $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, respectively. These modified smectites were characterized (SEM, FT-IR, TOC, specific surface, porosity) and were used to modify glassy carbon electrode with a clay film (GCE-CF). The (GCE-CF) was working electrode in ion-exchange voltammetry for a model ferri/ferro cyanide system.

The main conclusions are:

- Clay modification was confirmed by FT-IR, SEM and TOC determination;
- The specific surface of O-clay and OI-clay decrease and the average pore diameter increase after modification, Table 3. Thereby, the modified clay are able to absorb the anions, such ferricyanide.
- Modified clays reported here show promising properties as adsorbents of environmental pollutants, such as 2,4- and 2,6-dinitrophenols ($q_{max}$ = 53.48-54.05 mg $g^{-1}$)

As we intend to use the organoclays in high affinity analytical ion capturing, future experiments will be done to confirm the adsorption capability of modified clay for other anions.

## EXPERIMENTAL SECTION

### Materials and methods

2,4-DNP with 0.5 mL $H_2O$/g (Merck, Germany), and 2,6-DNP with purity Greater than 95% (wt.% calculated based on dry substance), moistened with 20% $H_2O$ (Aldrich, Switzerland) were used for preparing solutions with concentrations needed for our experiments. Aqueous solutions were prepared with distilled water. All reagents were analytical grade, and used without further purification.

The clay utilized in this work originates from Sabga, a locality of the North-West Region of Cameroon. Its characterization and chemical composition correspond to smectite, as reported in previous work [27]. Details on the synthesis and characterization of organo-clays and inorganic-organic pillared clays are being published elsewhere [29].

### Clay modification

First, the clay is cleaned, and dried in air, and then crushed, and sifted through a sieve of 90 µm diameter mesh. Raw clay is enriched in clay minerals by sedimentation, followed by the collection of the fine fraction (particles with diameter less than 2 µm).

### Conversion into homo-ionic form

An amount of 5 g of fine clay fraction are dispersed in 200 mL of 1M NaCl in distilled water, and stirred for 24 h. This operation is repeated three times to ensure that the clay is fully converted in the homo-ionic form. Then, the solid is collected by centrifugation, and washed with distilled water, until its silver nitrate test becomes negative.

### Intercalation of the organic surfactant

The solution of hexadecylpyridinium bromide is mixed with homo-ionic clay; the mixture is stirred for 5 h, centrifuged, washed several times with distilled water, and then the solid is dried in air, at ambient temperature.

This clay is referred to O-Sa01(a), a referring to the amount of surfactant in relation with the CEC of the clay (see Table 1).

### Modification with hydroxy-aluminum, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$

The title process is performed by adding a solution of hydroxy aluminum to a 2% suspension of O-Sa01 in distilled water, such that the Al/clay ratio is 10 mmol $g^{-1}$. Addition takes place at 60 °C, and then the mixture is stirred for 2 h at the same temperature. Again, the solid is washed with distilled water, until negative to chloride test, and then dried at 60 °C for 24 h. This modified clay is referred to under the code name IO-Sa01.

### Materials characterization

(i) *Structural characterization* was performed by $S_{spec}$, pores volume and distribution measurement (Micrometrics TriStar II 3020 V1.01), SEM (JEOL JSM 5510 LV) and FT-IR (Brucker VERTEX 70).

Porosity measurements were performed by adsoptiob/desorption of nitrogen. Prior to the measurements the materiel was degassed for eliminating the water molecules retained by physical adsoption or condensation in the pores of the clay. In work reported here we degassed the clay at 65 $^0$C for 24 h, which prevented decomposition of the hexadecylpyridinium bromide surfactant molecules (with a fusion temperature in the range of 79-82 $^0$C). Control samples, which did not contain organic surfactants, were degassed at 150 $^0$C, providing similar results.

*(ii) Organic carbon content of organic modified clays (TOC determination)*

The measurement was carried out by means of a Model LCK 385 TOC-DR 2800 Hach Lange for water quality instrument comprised of a digestion container, equipped with a TOC-5 stirrer, a thermostat, and a photometer. TOC determination involved two steps:

(a) *Sample preparation* by the elimination of total inorganic carbon, as follows: 2 mL of sample suspension were placed in the digestion container, and then the stirrer was inserted.

(b) *TOC determination*: the digestion container is heated in the thermostat at 95°C for 2 h, and then allowed to cool to ambient temperature. Then, the outer wall of the container is wiped, and inserted in the photometer for performing the measurements.

*(iii) Batch adsorption experiments*

Adsorption experiments were carried out by using the conventional batch technique. Nitrophenol solutions were prepared by dissolving required amounts of solid NP in distilled water. The initial concentrations of NP compounds was between 11.4 and 29.4 mg $L^{-1}$, for 2,4-DNP, and from 11.4 to 36.8 mg $L^{-1}$, for 2,6-DNP. The amount of clay (0.03 g) added to 0.05 L of NP solution and the temperature (25 $\pm$ 2) $^0$C were kept constant during the adsorption experiments. The concentration of adsorbed NP was determined from absorbance data [27, 28].

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