Contents lists available at ScienceDirect

Comptes Rendus Chimie

Account/Revue

Organoclay applications and limits in the environment

Régis Guégan

Faculty of Science and Engineering, Global Center for Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

ABSTRACT

This article gives an overview of the preparation, applications, and limits of organoclay materials in the environment field. Organoclays are obtained by the combination of clay minerals and surfactants (quaternary alkyl ammonium salts and others) and are appropriate candidates for the adsorption of organic contaminants such as pesticides, herbicides, and pharmaceuticals that are more and more found in the water resource despite wastewater treatments. This review article focuses on novel organoclay preparation methods based on the use of nonconventional nonionic surfactants and the interest and limits of these hybrid materials for the adsorption of organic compounds at both batch equilibrium and dynamical percolation experimental conditions.

© 2018 Académie des sciences. Published by Elsevier Masson SAS. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Organoclay materials are defined as hybrid materials resulting from the association of clay minerals (swelling ones such as montmorillonite [Mt], vermiculite, and saponite) with surfactants and/or other various organic compounds [1—3]. With the incorporation of the surfactants in their internal structure through different chemical and physical processes, the obtained materials combine a large specific surface and a hydrophobic behavior, enhancing the applications of clay minerals in various fields. A large volume of the research work focused on and pointed out the use of organoclays as reinforcers in polymer nanocomposites, starting materials for photophysical films, rheological agents, and as adsorbents for organic pollutants in soil and aquatic environments [1—9].

The final characteristics of organoclays mainly depend on the type of inorganic layered materials used and the chemical nature of the surfactant for the surface modification. Among the expandable clay minerals, Mt was the most popular material for preparation of organoclays because of its singular properties: charge density, cation exchange capacity (CEC) and swelling ability, its abundance in the ground, and thus its low cost [1—9]. Cationic surfactants were principally used for the modification of clay minerals where the mechanism for adsorption implies a cation substitution of the inorganic hydrated cations located within the interlayer space leading to the intercalation of surfactant aggregates of which arrangements depend on both the length of the alkyl chains and the concentration of the amphiphilic molecules [1—5]. In the past few years, with a permanent exploration in the development of novel modification methods, some alternatives were proposed with the use of nonconventional nonionic [10—21] and zwitterionic surfactants [8,22]. Although these surfactants involve other interaction mechanisms, it leads to the proper intercalation of surfactant aggregates with similar arrangements as their cationic analogous but with singular adsorption properties allowing their uses for possible applications in water remediation [2,12,13,18].

The aim of this article was to provide new insights based on the literature not only about alternative preparation methods of organoclays including nonionic and zwitterionic surfactants in contrast to the conventional quaternary

E-mail address: regis.guegan@aoni.waseda.jp.

ammonium halides showing a moderate toxicity, but also their interests and limitations in the field of the adsorption of organic pollutants in environmental science.

2. Organoclay preparation

2.1. Structure and interaction mechanisms of Mt

The layered molecular structure of a sheet of Mt such as the one from Wyoming, obtained from the Source Clay Minerals Repository, consists of an octahedral layer intercalated between two tetrahedral layers, which primarily consist of $Al_4(OH)_{12}$ and SiO_4 entities, respectively (Fig. 1). Isomorphic substitution of AlO_6 by MgO_6 moieties in the octahedral layer or to a lesser extent of SiO_4 by AlO_4 moieties in the tetrahedral layers leads to negatively charged clay sheets [23]. With the presence of inorganic cations such as Na^+, Ca^{2+}, or Mg^{2+} in the interlayer space, the charge balance is equilibrated. In water, the interactions between the silicate layers and the cations are strongly modified, leading to the expansion of the interlayer space. This allows the adsorption of several layers of water molecules with the solvation of cation which can be easily replaced by both inorganic and organic cations such as cationic surfactants for organoclay preparation but also the adsorbtion of pollutants [1,2,4,24—26].

Mt and more generally clay minerals can interact with various organic compounds through different interactional mechanisms as displayed in Fig. 1. Depending on the nature of the organic molecules, several interactional mechanisms can be involved such ion—dipole interaction, hydrogen bonds, acid—base reactions, charge transfer, electrostatic

interaction, and van der Waals forces for the adsorption. Thus, Mt showed its efficiency to adsorb and intercalate organic cations and polar molecules but was not relevant for the adsorption of hydrophobic molecules [2,3,18,27,28]. These mechanisms of reactions, which clay minerals can do, were highlighted through their singular properties for the adsorption of both organic and inorganic molecules for remediation or material preparation purposes [2].

2.2. Organoclay preparation in aqueous solution

Organoclays can be synthesized through different routes in dried states by solid—solid interaction without the use of any solvents [2,29]. However, despite the intercalation of the compounds (cationic or polar molecules), confirming by an expansion of the interlayer space identified by following the 00l reflection through X-ray diffraction (XRD), the dry process leads to heterogeneous exchanged organoclays [2]. The easiest way for organoclay preparation, which was reported in many studies, is surely in aqueous solution. Indeed, in solution the presence of water surrounding the exchangeable cations amplifies the repulsive forces at long-range order leading to an exfoliation of the phyllosilicate sheets offering a total access to the entire specific surface area, making easier the adsorption and interaction with surfactants of which chemical nature control the properties of the organoclays [16,17].

2.2.1. Cationic organoclays

Organoclays are mainly obtained by intercalating cationic surfactants such as quaternary ammonium compounds through ion exchange with the inorganic cations
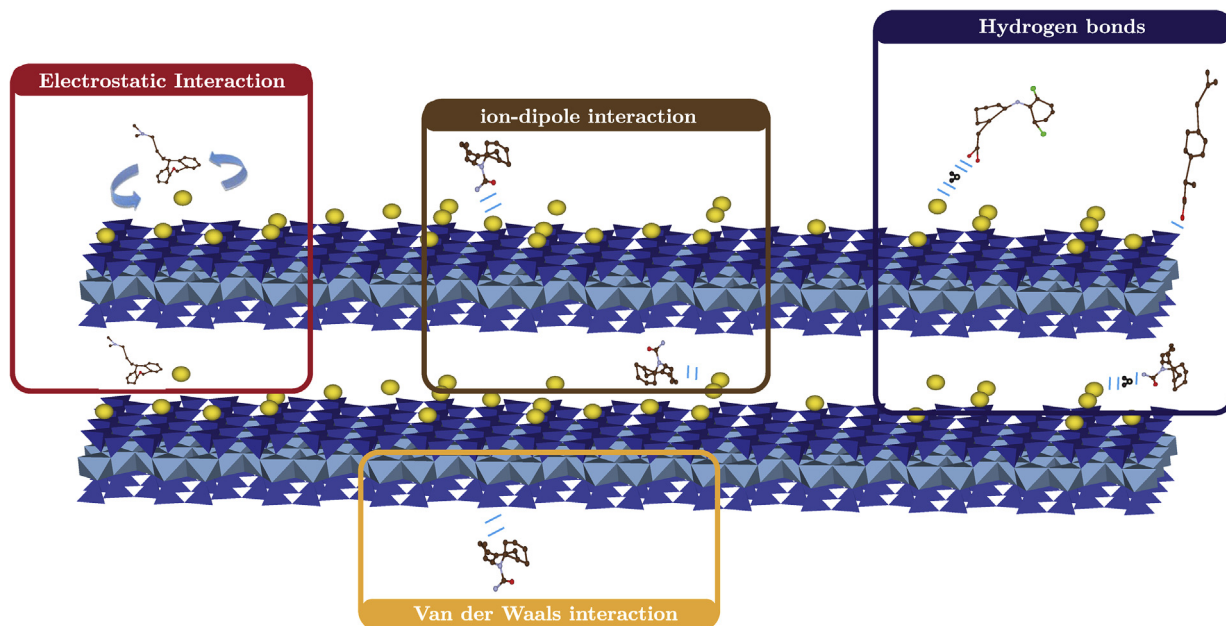

Fig. 1. Layered structure of a montmorillonite showing tetrahedral—octahedral—tetrahedral layers of which surface is negatively charged because of isomorphic substitution in the octahedral sheet. The charge is compensated by the introduction in the interlayer space of inorganic exchangeable cations (yellow). The possible reaction mechanisms in montmorillonite among many others depending on the nature of the chemical compounds involve electrostatic interaction, ion—dipole interaction, hydrogen bonds, and van der Waals forces.

within the interlayer space. Such process switches the chemical nature of the starting layered material from hydrophilic to hydrophobic. Depending on the length of the alkyl chains of the cationic surfactants, cationic organoclays can be divided into two main groups. For short alkyl chain surfactants such as trimethylammonium or benzyltrimethylammonium (BTA) (Fig. 2), the intercalation is limited to one layer in respect to one time the CEC of the clay minerals (i.e., concentration at which the all inorganic cations are expelled), expanding the interlayer space to a limited value of about 1.4 nm (Fig. 3) and the adsorption line shapes show a Langmuir-type profile [1—4,24]. The resulting organoclays were called adsorptive organoclays because they display well-localized specific adsorption sites with the introduction of organic cations. In contrast, for long alkyl chain surfactants such as hexadecyltrimethylammonium (HDTMA) or benzyldecyltrimethylammonium (BDTA), the surfactant loading linearly increases as a function of the CEC due to the stoichiometric exchange with the inorganic cations and reaches a saturation limit, which corresponds to or is larger than the CEC value, where additional organic cations can be intercalated through hydrophobic interaction between the alkyl chains. In this way, with the increase in the concentration of the long alkyl chain surfactants, different arrangements of the organic cations can be formed within the interlayer space: lateral monolayer(s), bilayer(s), and a paraffin structure (normal bilayer) (Fig. 3) based on complementary data obtained from different techniques, XRD, Fourier transform infrared spectroscopy, and solid state nuclear magnetic resonance (NMR) spectroscopy, among the most used techniques to characterize layered materials in these past years [1—4,24,27,28].

2.2.2. Zwitterionic organoclays

Because cationic surfactants are moderately nonenvironmental friendly compounds, some research works switch toward the use of other surfactants for organoclay preparation. Zwitterionic surfactants are biodegradable and biologically safe compounds showing excellent water solubility. At all pH ranges, these surfactants such as 3-(*N,N*-dimethyldodecylammonio)propane sulfonate (SB12) (Fig. 2) display both positively (alkylammonium moieties) and negatively (sulfonate moieties) charged groups. Although owning antagonist electric charges, it appears that the concentration of surfactants controls their arrangements in the clay galleries and the line shape of the adsorption isotherms appears identical to those of the long alkyl chain cationic surfactants. However, the adsorption follows two distinct steps in regards to the concentration: (1) below the CEC, surfactants are intercalated through ion exchange as their cationic analogous and probably by ion—dipole as shown in a recent article; and (2) at concentration exceeding the CEC, surfactant aggregates are self-assembled not only in a paraffin arrangement onto the organoclay particle but also in the internal structure with the incorporation of additional molecules implying hydrophobic (between the alkyl chains) and electrostatic interactions (between the antagonist electric charges moieties), expanding the interlayer space at large distance [22,26].

2.2.3. Nonionic surfactants

As zwitterionic compounds, nonionic surfactants display interesting properties: a good biodegradability, thermal and chemical stabilities, and a low toxicity or at least far less reduced comparatively to the cationic analogous [12—18,20]. Here, only pure nonionic surfactants are considered, that is, those which do not own any electric charge for the whole pH range and thus remain exclusively nonionic in aqueous solution. In contrast, molecules as ethoxylated tallow amines or other derived amine species, despite being labeled as nonionic surfactants in the literature, can be assimilated as cationic like compounds because they express a positive electric charge for particular pH conditions and follow an equivalent adsorption process as the cationic surfactants [30]. For the pure neutral surfactants such as polyoxyethylenic (TX100), polyethylene glycol
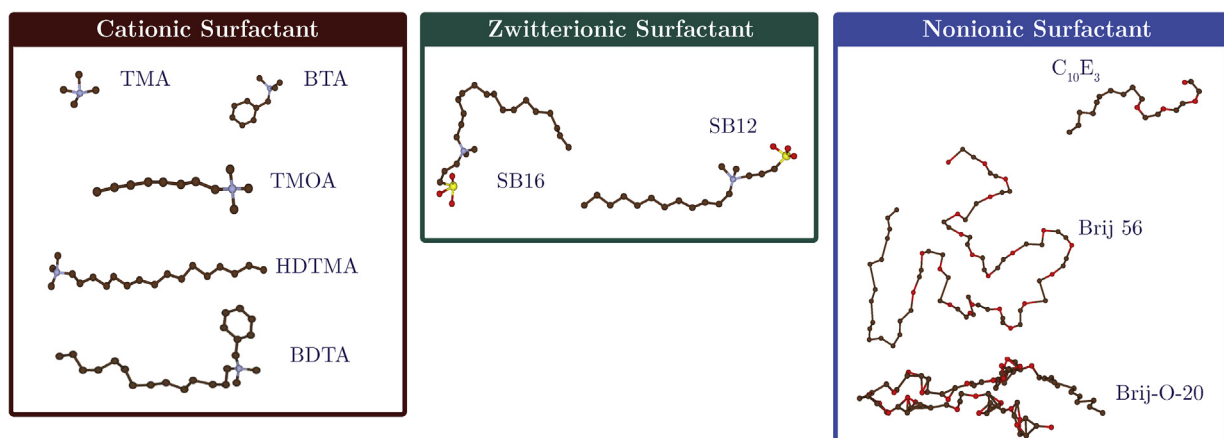

Fig. 2. List of examples for selected cationic, zwitterionic surfactants on the exchange reactions, and nonionic surfactants for organoclay preparation. SB16, 3-(*N,N*-dimethylpalmitylammonio)propane sulfonate; TMA, tetramethylammonium; TMOA, trioctylmethylammonium.
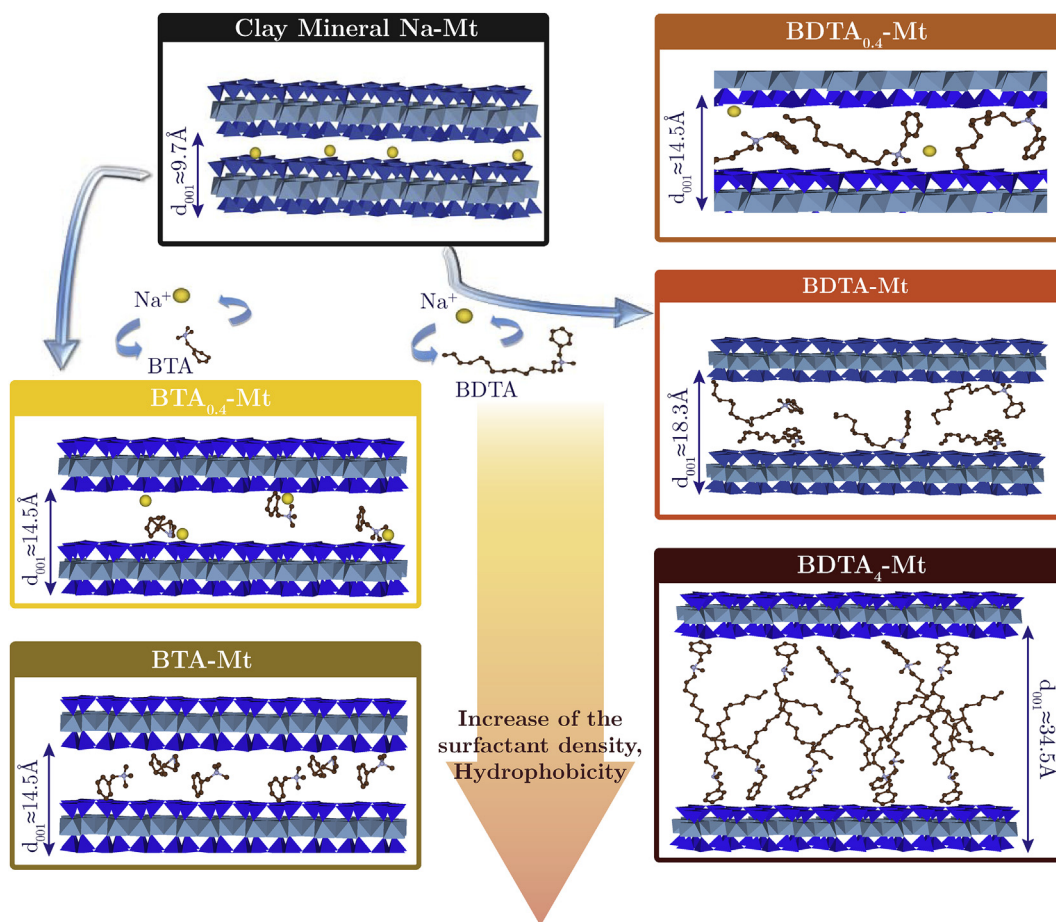
Fig. 3. Schematic representation of synthesis through ion exchange of the cationic surfactants. The final arrangement and properties of the organoclays mainly depend on the length of the alkyl chains: for short alkyl chain compounds, only a monolayer arrangement is observed leading to adsorptive clays, whereas for long alkyl chain compounds, lateral to normal bilayer arrangement is formed within the interlayer space enhancing the hydrophobic behavior, an important feature for the further adsorption of organophilic chemicals.

(PEG), polyoxyethylene alkyl ethers series (C_nE_m), and other similar amphiphilic compounds (Fig. 2), the adsorption on hydrophilic clay mineral differs from electrostatic interaction or ion exchange and keeps in the clay mineral structure the inorganic exchangeable cations, which play an important role for the adsorption of neutral compounds [12—18,20]. The main driving force for the adsorption between ion—dipole interaction and hydrogen bonds was a subject of debate for nonionic compounds with clay minerals [12—18,20]. With the use of infrared spectroscopy and by focusing not only on the CH stretching and deformation modes but also on the OH stretching wavenumber window of both surfactants and the layered materials, a previous study pointed out the role of H bonds or possible substitution of cations' hydration water molecules in the adsorption of PEG onto clay mineral surface [14]. A recent work using solid state NMR for the characterization of the surfactant aggregates made of a $C_{10}E_3$ (triethylene glycol mono-*n*-decyl ether) on a synthetic clay mineral, obtained through a hydrothermal process allowing one to get a layered material without any iron in its structure in contrast to the natural analogous, attests that H bonds play

a minor role in regards to (1) the low density of both silanol and aluminol groups (mainly located on the edge of the phyllosilicate sheets and could not be observed in the synthetic Mt) and (2) Na^+ cations appear to be solvated in this case by the hydrophilic fractions of the surfactant molecules, highlighted from [23]Na signals emphasizing the extreme mobility of the inorganic cations (i.e., sodium ions were not affected by the presence of the surfactant as they were solvated by them either water molecules) [20]. Thus, with H bonds likely being absent and without any positive charge in the headgroups of $C_{10}E_3$, ion—dipole interaction (Fig. 4) mainly seems to govern the adsorption of nonionic compounds allowing one (if we can generalize this observation to the all nonionic compounds) to preserve the exchangeable inorganic cations after adsorption onto clay minerals, which confer a dual hydrophilic/hydrophobic behavior of the organoclays.

Although involving the same interaction mechanism for the adsorption (ion—dipole), Brij, TX100, and PEG surfactants lead to the intercalation of only lateral monolayer and bilayer arrangements (Fig. 4), expanding the interlayer space at limited values, typically from 1.2 to 1.8 nm
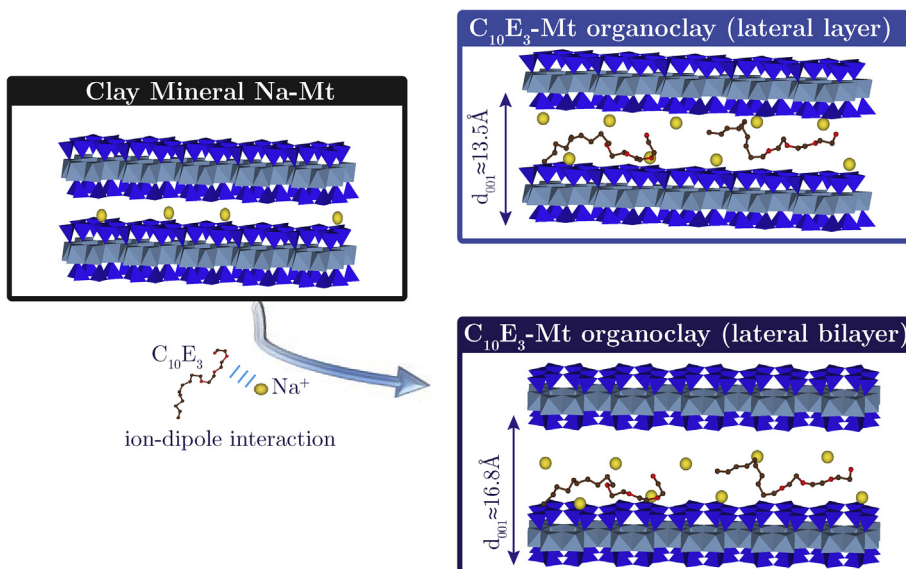
Fig. 4. Schematic representation of synthesis of the nonionic surfactants. The nonionic surfactants and probably the all nonionic compounds are adsorbed and intercalated through ion–dipole interaction as a recent solid state NMR work highlighted, leading once the surfactant is in a single molecule form (i.e., below its cmc) to lateral monolayer(s) and bilayer(s) arrangement(s) within the interlayer space.

[2,10–13,21], whereas for particular condition, $C_{10}E_3$ could self-organize in a paraffin arrangement because of its bulk lamellar phase aggregation expanding the interlayer space at much larger values of about 3.6–4.2 nm (Fig. 5) [15,16,20,31].

2.2.4. Micelle aggregation

Above both the critical micelle concentration (cmc) and the Krafft point (minimum temperature for the formation of micelle), surfactants can self-assemble in various micelle shapes and lyotropic liquid crystalline phases, which were used as a template system for the synthesis of mesoporous-based silica materials [31–34]. Previous organoclay preparation restrained the concentration range below or near cmc, where for most surfactants the maximum of adsorption was reached [11,21]. The related adsorption isotherms displayed a Langmuir-type equation. However, for singular cationic surfactants showing low cmc values, as polyhedral
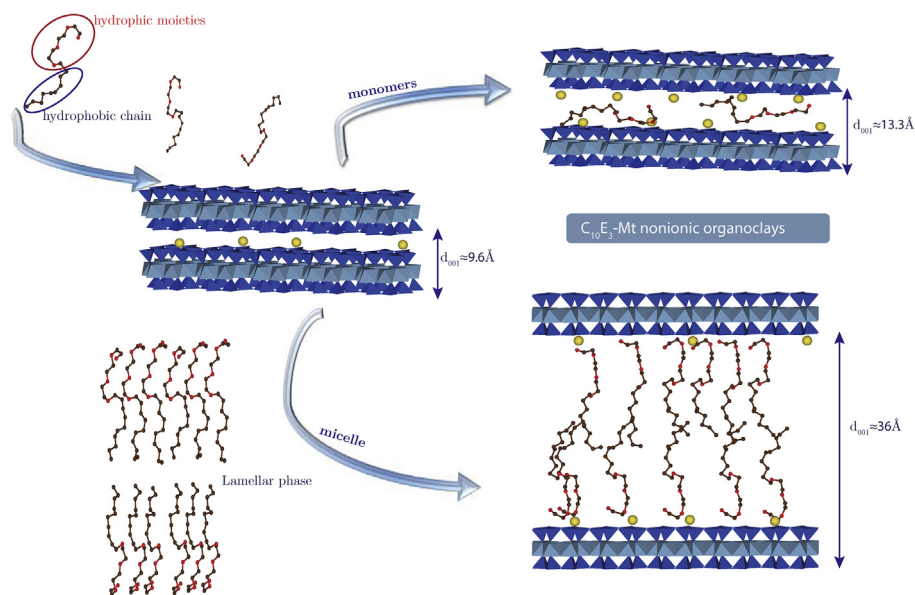

Fig. 5. Different ways of intercalation for surfactants, case of a nonionic surfactant, the $C_{10}E_3$ in a monomer or single molecule form (below the cmc) leading to the intercalation of a lateral monolayer(s) or bilayer(s) and above the cmc with self-organization in a lamellar phase driving to the aggregation of a bilayer arrangement expanding the interlayer space at large values.

oligomeric silsesquioxane (POSS) imidazolium compound exhibits, the packing of surfactants in a paraffin arrangement can be formed and observed at a concentration far below the CEC [35—37], which does not follow the expected sketch shown in Fig. 3 for quaternary ammonium compounds. Without any clear understanding about the relationship between the bulk molecular structures of POSS in solution and the way they pack within the interlayer space of organoclays, it tends that the surfactant state in solution plays a preponderant role on the structure of the resulting surfactant aggregates. For nonionic surfactants and those of the C_nE_m series, the main driving force (ion—dipole) for the adsorption is one order of magnitude lower than electrostatic interaction and thus almost equivalent to those ensuring the cohesion in micelles, leading to the formation of hemimicelles or bulk like micelle aggregates, which were observed on various substrates of different hydrophobic and hydrophilic nature including clay minerals [32,34,38]. In this way, a $C_{10}E_3$ bilayer arrangement could be confined in the internal structure of a Mt, enlarging the interlayer at a value that matches the thickness of the bilayer of a bulk lamellar phase (about 3.6 nm), and thus corroborating its proper aggregation [15,16,19,20]. This observation strongly contrasts to previous organoclay preparation based on the use of nonionic surfactants (Section 2.2.3), but as studies working on POSS stressed out, it confirms the role of the surfactant (single molecules vs liquid crystalline phase) in the aggregate structures and final arrangements and the adsorption properties, and opens new alternative routes for the preparation of organoclays.

3. Interests and limits of organoclays in the environment field

The adsorption properties of the sorbent systems including raw clay minerals and organoclays are usually characterized in solution through batch experiments. The resulting adsorption isotherms at equilibrium and the parameters derived from a fiiting procedure with the use of Langmuir or Freundlich models give important information about the the affinity of each single analyte to the layered materials. If these batch experiments make sense at a laboratory scale and allow one to emphasize the adsorption properties with an easy control of the all parameters (temperature, pH, ionic strengths, competition of pollutants, etc.), the situation is somehow quite different at an industrial scale where the dispersion of sorbent materials in contaminated water cannot be extended for technical implementation and economical reasons, in addition to the lack of control or fluctuations of the experimental conditions, and thus traditionally percolation protocols were designed.

Clay minerals are well-known materials for their outstanding adsorption properties and were used in that context as adsorbents for water remediation and as sealing or geotechnical layers below waste deposits. Despite showing a hydraulic conductivity that meets the standards, clay minerals once interacting for a long time with organic compounds show varying sensitivity to their adsorption properties, which may affect the durability of the clay liners [25]. Thus, a combination of sandwich-like assemblies of a liner composed of different clays and organoclays was

suggested for the improvement of the durability of the geotechnical layers, where unfortunately few studies were devoted to the behavior of organoclays through percolation experiments or infiltration of contaminated solution.

In this study, the adsorption behaviors in batch experiments of clay minerals and both cationic and nonionic organoclays as well as the combination of micelle—clay systems (i.e., association of both clay minerals or organoclays and surfactants in solution) and also through percolation protocols are tackled with a critical discussion on the interests and limits of each system based on several published works in the field.

3.1. Batch experiments or particles in suspension with pollutants (contaminated water)

3.1.1. Clay minerals

Adsorption onto porous materials represents certainly the most appropriate easy way to remove both inorganic and organic micropollutants [18,39]. Clay minerals show following appropriate features to be used as adsorbents: a large specific surface area, CEC, swelling and hydration properties, and multiple adsorption sites with a large panel of interactional mechanisms leading to an excellent affinity to various micropollutants [2,4,18,27,28,39]. If untreated clay minerals were successfully used as sorbents in drinking water treatment for the removal of several micropollutants, mainly toxic trace elements in their cationic forms and organic cations (organic cations other than the surfactant can be adsorbed and intercalated through a similar reaction mechanism up to more than the CEC depending on the chemical nature of the organic compounds) and polar organic molecules, they, nevertheless, turned out not only to be ineffective for the adsorption of nonpolar hydrophobic organic contaminants (and the most often, also persistent and recalcitrant products) but also anionic compounds [2,4,18,27,28,39]. Thus, because of their hydrophilic characteristics and charges, clay minerals display adsorption sites for the sequestration of cationic pollutants through the electrostatic interaction such as paraquat, a herbicide, since 2007 forbidden in the European Union (and to a lesser extent cationic detergents), and through an ion—dipole interaction, the dimethyl phthalate, a polar molecule released from plastics, but was not relevant for benzene for instance (Fig. 6). In the case of paraquat, because this organic compound does not interact through van der Waals force, only a monolayer arrangement was formed for which all of the inorganic cations were exchanged and expelled. On the basis of the literature, Fig. 6 sums up and illustrates the kind of chemical pollutants clay minerals are able to adsorb, mainly cationic and polar species exhibited by the paraquat and the dimethyl phthalate, respectively [2—4,27,28,39—41].

3.1.2. Cationic organoclays

The improvement in the adsorption capacity of hydrophobic compounds can be achieved by the chemical modification of the clay mineral surface by cationic surfactants. Because zwitterionic and cationic organoclays (i.e., organoclays prepared with their respective surfactants) show similar properties and procedure for their
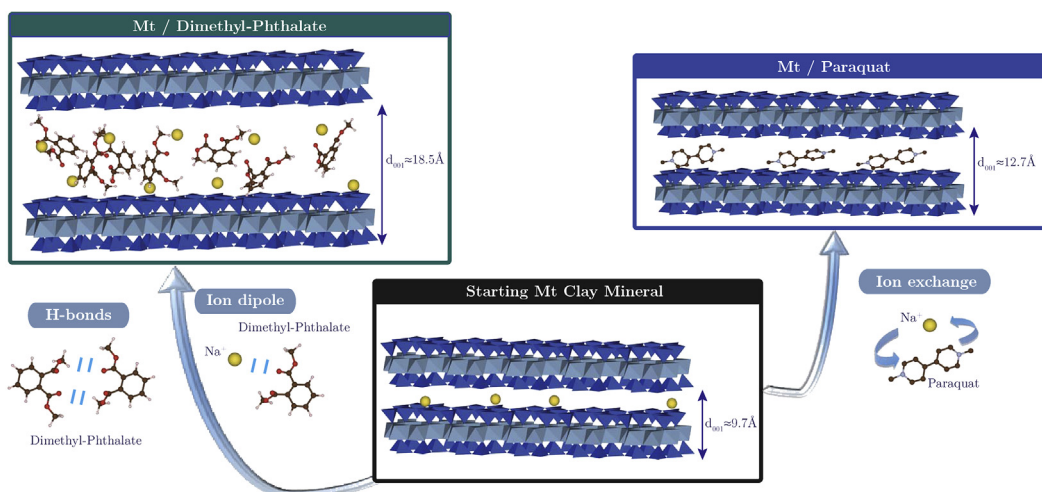
Fig. 6. Possible adsorption mechanisms in an untreated Mt for the adsorption of paraquat, an organic herbicide cation (ion exchange), and dimethyl phthalate compound (ion—dipole and H-bonds interaction).

preparation, only the adsorption properties of cationic organoclays will be discussed here and probably also because of a lack of studies on characterization of the adsorption properties of zwitterionic organoclays.

The resulting organoclay materials at high loadings display a hydrophobic surface while showing a wide opening of the interlayer spaces, enhancing significantly not only the adsorption of different hydrophobic, aromatic, phenolic organic compounds [42] but also pesticides, herbicides, and daily life products (i.e., pharmaceuticals and others, classified as emerging pollutants that are quite frequently found in aquatic environments) [2—4,27,28,39—41]. Nevertheless, the improvement in the sequestration mainly depends on both the chemical nature and the structural organization of the intercalated surfactants [2,3,18,27,28]. Thus, surfactants showing long alkyl chains such as HDTMA create an appropriate organic environment within the inorganic frame for the adsorption of alkanes or hydrophobic compounds, whereas modifiers such as BDTA or BTA owing aromatic rings show an excellent affinity with aromatic compounds such as phenols, dyes, and other chemicals (Fig. 7) [2,3,18,27,28].

At high loadings of surfactants (i.e., for a density of surfactant above one time the CEC), cationic organoclays own an excess of positive charge offering additional adsorption sites for the adsorption of negative species. Thus, cationic organoclays show an ability to adsorb both inorganic (for instance, nitrate and chromates [43,44]) and organic anions (diclofenac, an anti-inflammatory pharmaceutical product [24,25]) as layered double hydroxides do without, however, the restrictions (pH condition, affinity to carbonates, etc.) of these synthetic layered materials, mainly designed for laboratory experiments or other technological applications[2,3,18,27,28].

Nevertheless, organoclays at high loadings show some limitations. The first one implies the stability of the complexes resulting after the adsorption of the pollutants. Indeed, because numerous organophilic compounds are intercalated through hydrophobic interaction, which is a low energy molecular force (typically about 2 kJ mol^{-1}), some pollutants easily can be released or expelled from the layered structure of organoclays. This was even suggested as a potential application for a controlled release of pesticides from organoclays to plants to reduce the amount of chemicals in the agriculture. For similar reasons, another leak from organoclays concerns intercalated cationic surfactants (with probably the organic contaminants at the same time), leading to potential pollution and problems in the environment because of their chemical nature and toxicity for some of them (possibility of irritation for some cationic surfactants). However, the release of surfactants, which is undertaken under specific conditions (high stirring for instance), will reach a threshold with the conservation of at least lateral monolayer(s) or bilayer(s) configuration for which cationic surfactants were intercalated through electrostatic interaction. In other words, the expelling of the cationic surfactants in organoclays mainly concerns those that are intercalated through hydrophobic interaction, the others remain in the structure but limit nevertheless the interests or possibility of cationic organoclay uses. Indeed, because these cationic surfactants were introduced by strong electrostatic forces, no further ion exchange can be performed and thus in the environment field, it indicates that both organic and inorganic cations cannot be adsorbed or intercalated onto cationic organoclays (for organoclays prepared with a surfactant density of 1 CEC) [2,3,18,27,28].

3.1.3. Nonionic organoclays

As explained previously, nonionic surfactants for organoclay preparation show multiple interests: (1) a low toxicity and biodegradability; (2) a preservation of the inorganic exchangeable cations after adsorption onto clay minerals, leading to a dual hydrophobic/hydrophilic character enhancing the possibilities for the adsorption of
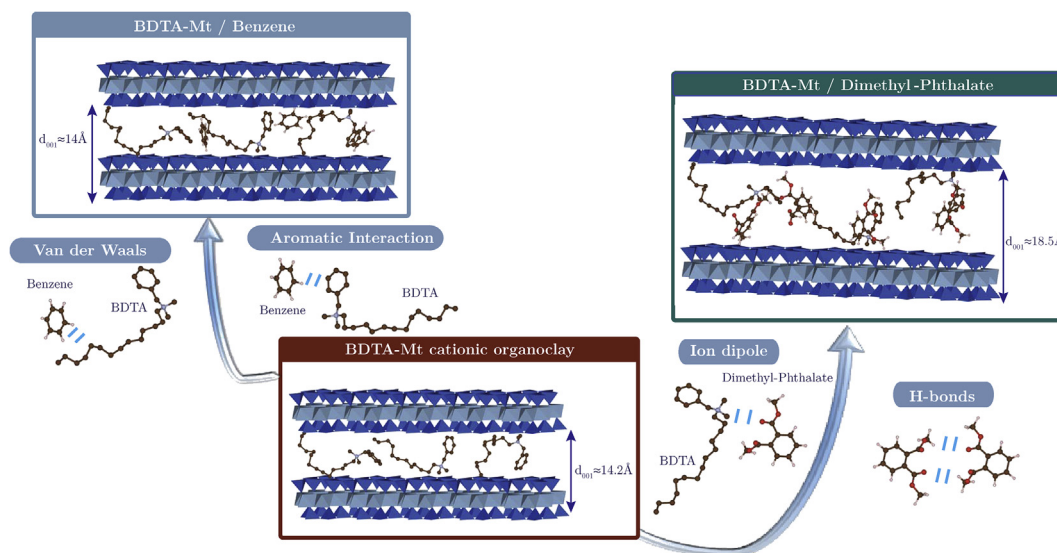
Fig. 7. Possible adsorption mechanisms in a BDTA-Mt cationic organoclay showing a lateral surfactant arrangement involved in the sequestration of benzene, a nonpolar hydrophobic organic compound (hydrophobic interaction), and dimethyl phthalate compound (ion—dipole and H-bonds interaction).

different nature chemicals; (3) the possibility to still perform some ion exchanges; and (4) aggregates of which structure a result from the bulk surfactant state leading to wide openings in the interlayer space favoring the intercalation/adsorption of pollutants.

Thus, these nonionic organoclays due to their multiple properties, in particular the one prepared with $C_{10}E_3$ showing a lateral monolayer arrangement, can adsorb and intercalate contaminants of different nature, that is, cationic, hydrophobic, and polar species, based on a set of data obtained by complementary techniques, Fourier transform infrared, XRD, and adsorption isotherms at the equilibrium [18]. However, the extent of the adsorption is rather limited in contrast to untreated clay minerals and cationic organoclays for cationic and hydrophobic pollutants, respectively. Indeed, it appeared that only 30% of the inorganic exchangeable cations participated in the adsorption of the paraquat for instance [18]. Nevertheless, such nonionic organoclay, although its behavior was not investigated so far for different pH and ionic strength conditions, appears as a versatile material and another sorbent option than the association of both cationic organoclay and untreated clays in the field of water remediation.

3.1.4. Combination of surfactants and layered materials in solution

Surfactants in aqueous environments self-assemble in lyotropic liquid crystalline phases, which form complex three-dimensional structures that can be used as a vector system for the release of organic compounds such as drugs. Simple spherical micelles in the L_1 phase act as solvent for greasy or hydrophobic compound. This principle is well known in a washing-up machine process and highlights the interest of surfactants in the detergency field among many others. Thus, on the basis of this idea, cationic surfactants

were used in their micelle forms as trapping systems for the removal of contaminants: hydrophobic and anionic compounds. The generated organic complexes can be in a second step intercalate through electrostatic intercalation in clay mineral (Fig. 8) [27,40,41]. This leads to high loadings of adsorbed pollutants or removal efficiencies, better than activated carbon can show, typically a removal of emerging pollutants, antibiotics: tetracycline, sulfamethoxazole, sulfisoxazole achieved a percentage in the range of 89—99.9% and 45—59% for the combination of micelle—clay and activated carbon, respectively. The differences between the two methods are exacerbated in the presence of humic acids, which strongly reduce the adsorption on activated carbon without disturbing that one of the micelle—clay [40,41]. In addition, with this method, clay minerals are able to adsorb anionic compounds.

Clay minerals can be substituted to organoclays as host matrices and then combined with surfactants in interaction with organic contaminants. Organoclays used as sorbents make sense with the level of concentration of detergents in wastewater that probably causes an underhand contamination (especially the anionic surfactants). Moreover, in the case of the clay—micelle combination, it is highly probable that once clay minerals are introduced, they selectively interact with surfactants driving to organoclays, which then trap through hydrophobic interaction of the pollutant—surfactant complex. In this way, the coupled action of a cationic organoclay and micelle acts as an efficient method without any restriction for the removal of a recalcitrant and persistent emerging pollutant: the diclofenac, an anti-inflammatory drug showing discharge concentration up to 1000 ng L^{-1} in wastewater influents [27]. Besides showing potential interests in water remediation strategies, such method suffers from the impossibility or the difficulty to recover the porous materials associated with pollutants because it implies to perform a filtration or
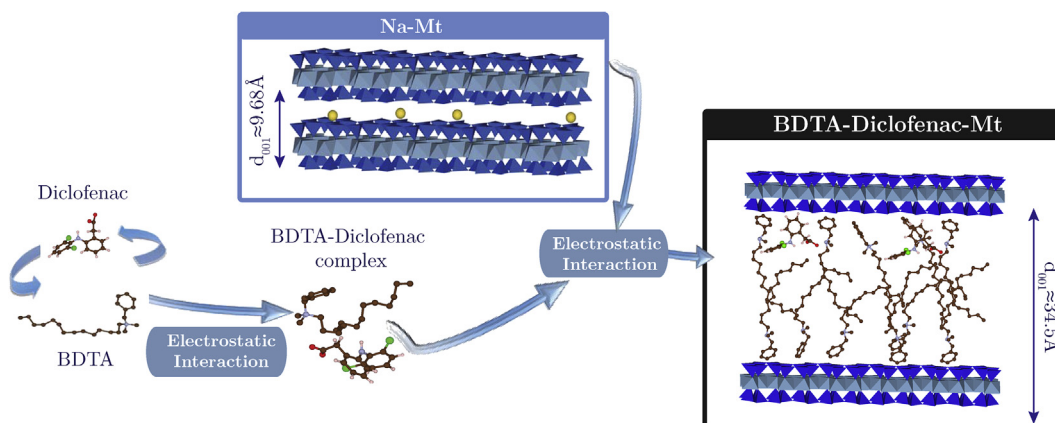
Fig. 8. Schematic representation of the possible adsorption mechanisms for diclofenac with a dual micelle–clay system forming a hybrid material incorporating in its structure BDTA (the cationic surfactant), diclofenac, and Mt.

centrifugation, which cannot be upscale for an industrial water treatment purpose.

3.2. Percolation experiments or infiltration of pollutants through materials as engineering applications

In contrast to batch equilibrium adsorption experiments allowing one to determine pertinent thermodynamical parameters, dynamical percolation experiments consist to a fine balance between the affinity and the contact time of the analytes (pollutants the most often case) with a sorbent material. Thus, the hydraulic behavior of the sorbents, their permeability, or their ability to retain an analyte turn out to the most important points to be considered [45–47]. Therefore, before any characterization of the infiltration of a contaminated solution through a clay mineral or organoclay layer, it is first worth to determine their hydraulic behaviors (i.e., with only water).

Percolation experiments can be performed with the use of a column filled with slightly compacted porous materials. A solution with contaminants or water is added on the top of the column and time evolution of the eluate or leachate volume is then measured allowing one to determine the ability through a dynamical process of the porous material to retain a pollutant or analyte or the hydraulic conductivity, respectively [45–47]. Another way of investigation consists of using oedometer cells, the principle of which is basically similar to the previous one, developed for simulation of the behavior of a material with a control of the pressure, temperature, and injection at a laboratory scale. These two methods allow an easy recovery of the sorbent material after an experiment or water treatment process and were principally used to mimic geotechnical liners composed of clay layers [25].

The resulting data obtained with these two methods consist of the representation of the volume of the leachate along with the time (Fig. 9). The permanent hydromechanical regime can be defined by the volume of leachate and the strain equilibrium allowing the calculation of a hydraulic conductivity through Darcy's law. When organic cations replace the exchangeable inorganic cations, the
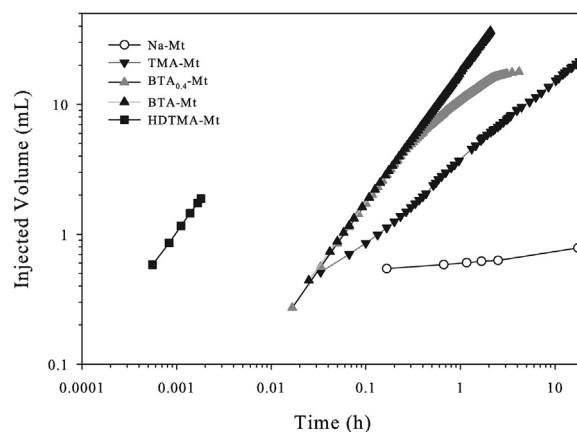

Fig. 9. Log-scale representation of the solute intake during percolation experiments of water in Na–Mt and a series of cationic organoclays: TMA-Mt, BTA-MT (short alkyl chain surfactants—see Fig. 2) and HDTMA-Mt (long alkyl chain).

hydraulic conductivity of the cationic organoclays for water is on the magnitude of 10^{-8} m·s^{-1}, still low, but really different Na–Mt (10^{-12} m·s^{-1}). Thus, hydrophobic character of the cationic organoclays investigated displays a hydraulic behavior quite different from an untreated sodium exchanged Mt, leading to 3–4 orders of magnitude [47] difference in the hydraulic coefficient and an increase in the permeability of the organoclays that behave as the most hydrophobic ones like sandy materials, which obviously represent a critical issue if one think to use these materials in water remediation or for environmental application purposes.

4. Conclusions

This review article describes the different ways of preparation of organoclays with the use of conventional quaternary alkylammonium cationic surfactants and exotic surfactants such zwitterionic and nonionic ones. For

cationic and zwitterionic surfactants, organoclays are obtained by the replacement of the inorganic cations through cation exchange, whereas these exchange hydrated cations are kept in the case of nonionic compounds, leading to hybrid materials with a dual hydrophilic hydrophobic behavior. This literature review highlighted also the importance of the surfactants in solution (micelle or single molecules) in the surfactant aggregates within the interlayer space that play on the final properties of the prepared organoclays.

Organoclays can be used in numerous applications including sorbent systems in the environmental field. These materials display interesting adsorption properties for numerous organic compounds, especially hydrophobic chemicals. Nonionic organoclays are revealed as a versatile sorbent material with their abilities to sequestrate a large number of chemicals of different nature without, nevertheless, reaching to similar adsorption extent as cationic organoclay and untreated clay minerals for hydrophobic and organic cations, respectively. Despite showing potential interests in environment applications, it appears the use of organoclays is restricted to batch experiments where some experimental conditions such as ionic strength were not investigated so far and may reduce the efficiency of adsorption. Percolation experimental setup, which can be assimilated as the one that may be industrially upscale, pointed out the decrease in impermeability of cationic organoclays, which may represent a critical issue if one thinks to use these materials in water remediation or for environmental application purposes.

References

[1] H. He, L. Ma, J. Zhu, R.L. Frost, B.K.G. Theng, F.Ø. Bergaya, Appl. Clay Sci. 100 (2014) 22−28.
[2] L.B. de Paiva, A.R. Morales, F.R. Valenzuela Díaz, Appl. Clay Sci. 42 (2008) 8−24.
[3] Y. Park, G.A. Ayoko, R.L. Frost, J. Colloid Interface Sci. 354 (2011) 292−305.
[4] F. Bergaya, G. Lagaly, in: F. Bergaya, B.K.G. Theng, G. Lagaly (Eds.), Developments in Clay Science, Elsevier, 2006, pp. 1−18. https://www.elsevier.com/books/handbook-of-clay-science/bergaya/978-0-08-044183-2.
[5] E. Ruiz-Hitzky, P. Aranda, M. Darder, M. Ogawa, Chem. Soc. Rev. 40 (2011) 801−828.
[6] P. Huang, A. Kazlauciunas, R. Menzel, L. Lin, ACS Appl. Mater. Interfaces 9 (2017) 26383−26391.
[7] U.C. Ugochukwu, C.I. Fialips, Chemosphere 174 (2017) 28−38.
[8] J. Zhu, P. Zhang, Y. Qing, K. Wen, X. Su, L. Ma, J. Wei, H. Liu, H. He, Y. Xi, Appl. Clay Sci. 141 (2017) 265−271.
[9] K.J. Shah, S.-Y. Pan, A.D. Shukla, D.O. Shah, P.-C. Chiang, J. Colloid Interface Sci. 529 (2018) 90−99.
[10] C. Breen, G. Thompson, M. Webb, J. Mater. Chem. 9 (1999) 3159−3165.
[11] J.M. Cases, F. Villieras, Langmuir 8 (1992) 1251−1264.
[12] Y. Deng, J. Dixon, G.N. White, Colloid Polym. Sci. 284 (2006) 347−356.
[13] Y. Deng, J. Dixon, G.N. White, Clay Clay Miner. 51 (2003) 150−161.
[14] E. Finocchio, I. Baccini, C. Cristiani, G. Dotelli, P. Gallo Stampino, L. Zampori, J. Phys. Chem. A 115 (2011) 7484−7493.
[15] R. Guegan, Soft Matter 9 (2013) 10913−10920.
[16] R. Guégan, Langmuir 26 (2010) 19175−19180.
[17] R. Guégan, M. Gautier, J.-M. Beny, F. Muller, Clay Clay Miner. 57 (2009) 502−509.
[18] R. Guégan, M. Giovanela, F. Warmont, M. Motelica-Heino, J. Colloid Interface Sci. 437 (2015) 71−79.
[19] R. Guegan, K. Sueyoshi, S. Anraku, S. Yamamoto, N. Miyamoto, Chem. Commun. 52 (2016) 1594−1597.
[20] R. Guégan, E. Veron, L. Le Forestier, M. Ogawa, S. Cadars, Langmuir 33 (2017) 9759−9771.
[21] P. Levitz, Langmuir 7 (1991) 1595−1608.
[22] J. Zhu, Y. Qing, T. Wang, R. Zhu, J. Wei, Q. Tao, P. Yuan, H. He, J. Colloid Interface Sci. 360 (2011) 386−392.
[23] S. Cadars, R. Guégan, M.N. Garaga, X. Bourrat, L. Le Forestier, F. Fayon, T.V. Huynh, T. Allier, Z. Nour, D. Massiot, Chem. Mater. 24 (2012) 4376−4389.
[24] G. Alther, Waste Manag. 22 (2002) 507−513.
[25] L. Le Forestier, F. Muller, F. Villieras, M. Pelletier, Appl. Clay Sci. 48 (2010) 18−25.
[26] R. Zhu, J. Zhao, F. Ge, L. Zhu, J. Zhu, Q. Tao, H. He, Appl. Clay Sci. 88−89 (2014) 73−77.
[27] T. De Oliveira, R. Guégan, Environ. Sci. Technol. 50 (2016) 10209−10215.
[28] T. De Oliveira, R. Guégan, T. Thiebault, C.L. Milbeau, F. Muller, V. Teixeira, M. Giovanela, M. Boussafir, J. Hazard. Mater. 323 (2017) 558−566.
[29] N. Khaorapapong, K. Kuroda, M. Ogawa, Clay Clay Miner. 50 (2002) 428−434.
[30] J.L. Alves, P.d.T.V.e. Rosa, A.R. Morales, Appl. Clay Sci. 132−133 (2016) 475−484.
[31] R. Guégan, J. Colloid Interface Sci. 358 (2011) 485−490.
[32] M. Jaschke, H.J. Butt, H.E. Gaub, S. Manne, Langmuir 13 (1997) 1381−1384.
[33] P. Levitz, H. Van Damme, D. Keravis, J. Phys. Chem. 88 (1984) 2228−2235.
[34] M.J. Rosen, Surfactants and Interfacial Phenomena/Milton J. Rosen, Wiley, NY, 1978.
[35] D.M. Fox, P.H. Maupin, R.H. Harris, J.W. Gilman, D.V. Eldred, D. Katsoulis, P.C. Trulove, H.C. De Long, Langmuir 23 (2007) 7707−7714.
[36] C.L. Toh, X. Li, S.K. Lau, K.P. Pramoda, Y.C. Chua, X. Lu, J. Phys. Chem. B 114 (2010) 207−214.
[37] C. Wan, F. Zhao, X. Bao, B. Kandasubramanian, M. Duggan, J. Phys. Chem. B 112 (2008) 11915−11922.
[38] H. Heinz, U.W. Suter, Angew. Chem. Int. Ed. 43 (2004) 2239−2243.
[39] T. Thiebault, R. Guégan, M. Boussafir, J. Colloid Interface Sci. 453 (2015) 1−8.
[40] T. Polubesova, S. Nir, D. Zadaka, O. Rabinovitz, C. Serban, L. Groisman, B. Rubin, Environ. Sci. Technol. 39 (2005) 2343−2348.
[41] T. Polubesova, D. Zadaka, L. Groisman, S. Nir, Water Res. 40 (2006) 2369−2374.
[42] Y.-H. Shen, Colloids Surf. A Physicochem. Eng. Aspects 232 (2004) 143−149.
[43] Y.-C. Lee, W.-K. Park, J.-W. Yang, J. Hazard. Mater. 190 (2011) 652−658.
[44] B. Sarkar, Y. Xi, M. Megharaj, G.S.R. Krishnamurti, D. Rajarathnam, R. Naidu, J. Hazard. Mater. 183 (2010) 87−97.
[45] S. Akbulut, Z.N. Kurt, S. Arasan, Y. Pekdemir, Sadhana 38 (2013) 317−329.
[46] M.R. Stockmeyer, Appl. Clay Sci. 6 (1991) 39−57.
[47] Q. Zhao, S.E. Burns, Environ. Sci. Technol. 47 (2013) 2769−2776.