Review article

An overview about synthetic high charge micas and their uses

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ABSTRACT

Synthetic micas are materials with interesting properties that combine high charge (high cation exchange capacity) with swelling capacity. Among the various methods for synthesizing this clay, the "NaCl-melt method" is the most widely used, producing a material with excellent crystallinity. Furthermore, synthetic micas are also susceptible to modifications with a wide range of compounds, mainly organic compounds, which further increases their reactivity. Thus, this Review addresses the properties and syntheses of this clay. The types of modifications used and the changes that occur in the properties of this clay are reported, in addition to applications in the removal of contaminating compounds that can be found in water. Research to date has demonstrated that synthetic mica-based adsorbents are versatile in the adsorption of various contaminants, such as metals, pharmaceuticals and others. Therefore, this material can be promising in the adsorption and release of drugs, bioactive compounds, enzymes, proteins, etc., thus increasing its field of application.

1. Introduction

The search for materials that can act in different fields of application, such as health, cosmetics, food, and even environmental remediation remains a constant demand both at the academic level and in industry. Among the materials that can be used are clays/clay minerals with and without prior modification due to their characteristics and structural properties (Komadel, 2016; França et al., 2020a, 2020b; de Oliveira et al., 2021, 2022, 2023).

Among clay minerals, synthetic mica (Na-Mica-x) has gained prominence in recent years (Pazos et al., 2015, 2017; Martín et al., 2018, 2019; Pavón et al., 2019; Orta et al., 2020; Osuna et al., 2020, 2023; Osuna et al., 2021a, 2021b). Na-Mica-x is a synthetic fluoro-mica that has high purity, high cation exchange capacity (CEC), absence of secondary phases as can occurs in natural clays, and swelling capacity (Alba et al., 2006; Pavón et al., 2019; Osuna et al., 2023). Furthermore, due to its high interlaminar charge, with values of up to 2, 3 or 4 per unit cell, Na-Mica-x is called a highly charged synthetic mica. (Park et al., 2002a; Alba et al., 2006; Orta et al., 2019). It has a high cation exchange capacity, with values up to 468cmol(+)/Kg and a high expansion capacity. These properties make Na-Mica-x excellent candidates to interact with

various organic compounds (Pazos et al., 2015, 2017; Alba et al., 2019; Osuna et al., 2020) or inorganic (José García-Jiménez et al., 2016; Osuna et al., 2017; Osuna et al., 2019a, 2019b; Osuna et al., 2021a, 2021b). In this way, Na-Mica-x becomes a promising material to act in several areas such as cosmetics, in the immobilization of bioactive molecules, in the delivery of drugs, in addition to its use in the removal of pollutants, etc.

Although systems containing high charge synthetic mica have attracted significant attention in recent years, to the best of our knowledge, no comprehensive review on the subject is available. Therefore, the main objective of this review is to compile data from published studies of micas of different Na-Mica-x loadings, their synthesis methods, characterization, and applications. A brief description of the differences in structure and properties between natural and synthetic micas is provided. Furthermore, types of modifications of synthetic micas with organic molecules are covered, such as surfactants, amino compounds, silane agents and polymers, as well as the applications of this clay.

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2. Structure and properties of mica (natural and synthetic)

Mica belongs to a group of clays with a 2:1 structure, with a formula depending on the type of mica (Brigatti and Guggenheim, 2002). Mica is mostly of natural origin, which can be further classified as true and brittle micas, dioctahedral or trioctahedral (Brigatti and Guggenheim, 2002; Brigatti et al., 2013). The structure of natural micas, in general, consists of two sheets containing Si^{4+}, Al^{3+}, or Fe^{3+} cations, coordinated tetrahedrally with oxygen atoms, joined by an octahedral sheet containing Mg^{2+}, Al^{3+}, Fe^{2+}, or Fe^{3+} cations, with OH groups in some vertices (Brigatti and Guggenheim, 2002; Brigatti et al., 2013), whose structure is shown in Fig. 1. However, highly charged synthetic micas, or fluorophlogopites, with the idealized formula $Na_n(Si_{8-n}Al_n)(Mg_6)O_{20}F_4$, are trioctahedral micas that have only Si^{4+} and Al^{3+} cations in the tetrahedral sheets, Mg^{2+} cations in the octahedral sites and groups F^- at its edges of the octahedral sheets, replacing the hydroxyl present in natural micas (Osuna et al., 2019a, 2019b; Taruta et al., 2022), Fig. 1.

Isomorphic substitutions provide a negative lamellar charge to these materials with values close to 1 for true micas and close to 2 for brittle micas (Brigatti et al., 2013). On the other hand, higher charges are found in synthetic micas, derived from isomorphic substitution at the tetrahedral site, that is, the replacement of Si^{4+} by Al^{3+}, which violates Lowenstein's rule (Pavón et al., 2014a, 2014b; Pavón et al., 2019) and provides a layer charge of 2, 3 or 4 (Osuna et al., 2023), originating the nomenclatures Na-Mica-2, Na-Mica-3 or Na-Mica-4.

In both natural and synthetic micas, the negative charge is counterbalanced by interlayer ions, typically K^+ and Na^+ for natural and synthetic mica, respectively (Brigatti and Guggenheim, 2002; Pavón et al., 2017), which can result in CEC synthetic micas of up to 468 cmol (+)/kg, and even high swelling capacity (Park et al., 2012; Pavón et al., 2017).

3. High charge mica synthesis

Synthetic micas are materials that have a unique structure and high exchange capacity (Alba et al., 2006; Shimizu et al., 2006; Perdigón et al., 2013; Osuna et al., 2021a, 2021b). Mica synthesis methods are varied, from its first synthesis of Na-Mica-4 mica by to the reaction of augite with a mixture of NaF and MgF_2 in a 1:1 ratio, under heating at 900 °C (Gregorkiewitz and Rausell-Colom, 1987). The mica formed with the formula $Na_{4.0}(Mg_{6.0}Ti_{0.05})[Fe_{0.1}Al_{3.4}Si_{4.5}O_{20.7}F_{3.3}]$ was obtained with low yield, with a mass of around 20 mg.

Almost a decade later, in the mid-1990s, Na-Mica-4 mica was produced by the sol-gel process, by mixing $Al(NO_3)_3 \cdot 9H_2O$ and $Mg(NO_3) \cdot 6H_2O$ in ethanol and subsequent addition of tetraethylorthosilicate, $Si(OC_2H_5)_4$, in a proportion to obtain a stoichiometric composition of $3MgO-Al_2O_3-2SiO_2$ (Paulus et al., 1992). NaF was the source of sodium and fluorine used, and the main limitations of this synthesis were, in addition to the long reaction times, the need for extensive washings with boric acid to remove insoluble salts from the final sample. In another study, the authors used this same sol-gel method in several stages for the synthesis of mica Na-Mica-4 so that they were successful in terms of the presence of impurities (Franklin and Lee, 1996).

Subsequently, Na-Mica-4 was obtained from metakaolin, MgO and NaF (Kodama and Komarneni, 1999). For synthesis, MgO and metakaolin were initially mixed to a final stoichiometric composition of $3MgO-Al_2O_3-2SiO_2$. Then equal mass amounts of $3MgO-Al_2O_3-2SiO_2$ and NaF were added in a platinum crucible and heated at 890 °C for 6, 12 and 24 h. The authors concluded that there was no distinction in the prolonged crystallization period, indicating that in the heating times used (6-24 h), it was possible to obtain Na-Mica-4. This same procedure was adopted by other studies in the production of Na-Mica-3 micas with an ideal composition of $Na_{2.94}(Mg_{5.55}Ti_{0.07}Fe_{0.04})_{oct}(Al_{2.07}Si_{5.83})_{tet}O_{20}F_4 \cdot 1.72H_2O$, Na-Mica-2 with an ideal composition of $Na_2Mg_6Al_2Si_6O_{20}F_4 \cdot xH_2O$ and also Na-Mica-4 with an ideal composition of $Na_4Mg_6Al_4Si_4O_{20}F_4 \cdot xH_2O$ (Kodama et al., 2000, 2002, 2003, 2004; T. Kodama et al., 2001a, 2001b; Shimizu et al., 2004, 2006). However, this method employs excessive amounts of NaF and requires exhaustive washings with boric acid solution to remove non-reactive fluorides, which still provides for the possible replacement/exchange of Na^+ by H^+ ions of boric acid.

In a new method, Park et al. (2002a) synthesized Na-Mica-4 with other precursors, replacing NaF with NaCl and MgF_2, thus avoiding excess NaF, the so-called NaCl-melt method. Additionally, fly ash was used (Park et al., 2002b), and the mass amounts of these components were mixed and added to a platinum crucible and heated to 890 °C for 24 h. The limitation of this method was that it was only aimed at the preparation of Na-Mica-4 micas, which was not used in the preparation of micas from other fillers such as Na-Mica-2 and Na-Mica-3.

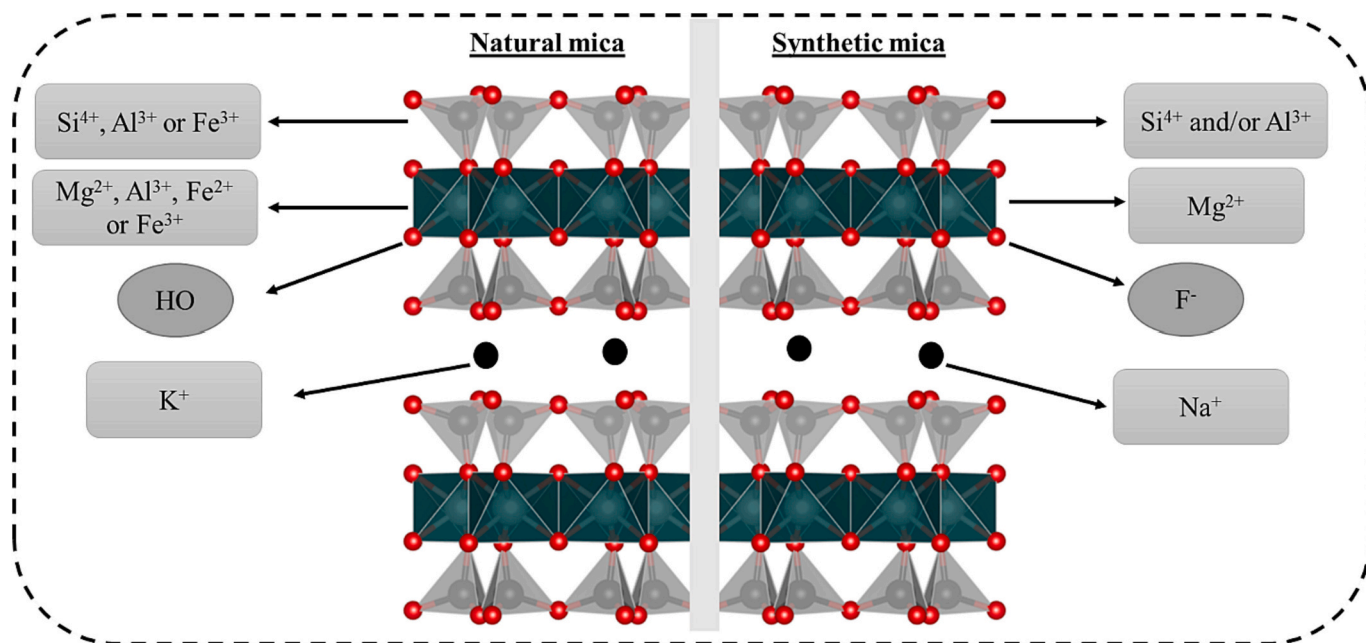Na-Mica-x micas were obtained (Alba et al., 2006), adopting a

Fig. 1. Mica structure and differences between natural and synthetic mica (Figure generated with the program VESTA 3-Free program (Momma and Izumi, 2011)).

procedure similar to that used by (Park et al., 2002a), from an almost stoichiometric powder mixture of SiO_2, $Al(OH)_3$, MgF_2 and NaCl with molar composition (8-n)SiO_2, (n/2)$Al(OH)_3$, $6MgF_2$ and (2n)NaCl, where n represents the charge of mica (2, 3 or 4). In the synthesis, all powdered reagents are mixed, deagglomerated and subsequently heated in a platinum crucible at 900 °C. This method produces micas with excellent crystallinity and is the most widely used and investigated so far to obtain high-load micas (Alba et al., 2011a, 2011b, 2019; Pavon et al., 2013; Pavón et al., 2014a, 2014b; Naranjo et al., 2015; Osuna et al., 2017, 2018a, 2018b, 2020; Pavón et al., 2017; Martín et al., 2018, 2019; Orta et al., 2018; Osuna et al., 2019a, 2019b; Osuna et al., 2021a, 2021b; Martín-Rodríguez et al., 2019; Osuna et al., 2021a, 2021b). Alteration of the method also uses precursors such as bentonite (Osuna et al., 2018a) and rice ash (Mouchet et al., 2021).

4. Synthetic mica modifications

One of the great advantages of using clay minerals is, in addition to their properties, the possibility of modifications, thus expanding the applications, increasing the reactivity and versatility of these materials (He et al., 2013; Ewis et al., 2022). Among these modifications, the incorporation of organic molecules with different functionalities, such as surfactants and amines, can be highlighted (Brito et al., 2018; Orta et al., 2019; França et al., 2020a, 2020b), silanes (He et al., 2013; Queiroga et al., 2019), polymers (da Silva et al., 2021; Ramos-Torres et al., 2021), etc. A summary of mica modifications is presented in Table 1. In the following sections, these modifications and the impact they have on these materials will be briefly described.

4.1. Interaction with surfactants

Modification of clay and clay minerals with surfactants has been widely studied (Brito et al., 2018; Shen and Gao, 2019; Barakan and Aghazadeh, 2021; Z. Liu et al., 2021a). The interaction can occur by insertion of the protonated group into the interlamellar region of the

clay mineral through an ion exchange reaction, that is, the exit of the interlamellar ion for the entry of the protonated group (Barakan and Aghazadeh, 2021; Z. Liu et al., 2021a). Depending on the amount of surfactant, ion pair intercalation may occur, usually when the value exceeds the CEC. This type of modification can often depend on the CEC of the clay and the pH of the reaction medium (Alba et al., 2011b; Martín et al., 2019; Z. Liu et al., 2021a), being able to cause changes to the clay mineral, by activating its surface due to the presence of nonpolar alkyl chains; expansion of the interlamellar space or even hydrophobization (Brito et al., 2018; Pesquera et al., 2018; Martín et al., 2019; Orta et al., 2019; França et al., 2020a, 2020b; Z. Liu et al., 2021a).

In addition to montmorillonites (Brito et al., 2018; França et al., 2020a, 2020b) and vermiculites (Wang et al., 2018; Jin et al., 2022), high charge swelling synthetic micas are also modified with surfactants. Due to the high charge of synthetic micas, the basal spacing values obtained for organomica are generally higher than for organophilic montmorillonites (Orta et al., 2019). Hydrophobization has been described for ODA-modified Na-Mica-4 mica (Orta et al., 2019). Although Na-Mica-4 exhibited a contact angle of 33°, the value for organomica was 110°, characteristic of hydrophobic materials (Wang et al., 2020).

Studies report the effects of chain length (Alba et al., 2011b), head group type (Komarneni et al., 2013) and amount of surfactants (Orta et al., 2019), beyond the load of synthetic mica lamella (Pazos et al., 2012; Komarneni et al., 2013) in organomica preparation.

For example, Na-Mica-4 was modified with n-alkylammonium cations (RNH_3^+) with different alkyl chain lengths (R = C_{12}, C_{14}, C_{16} and C_{18}) (Alba et al., 2011b). For the synthesis, an amount of surfactant corresponding to 200% of the CEC of the clay mineral was added. The XRD results showed a high value of basal spacing, with a maximum of 4.60 nm for the sample as a surfactant with a C18 chain, indicating that the packaging of the surfactants occurred in the form of a paraffin-like bilayer with a structure in trans conformation, Fig. 2. Measurements ^{13}C and ^{29}Si NMR indicated the surfactant configuration.

The charge effect of synthetic mica ($Na_nSi_{8-n}Al_nMg_6F_4O_{20} \cdot XH_2O$,

Table 1
Examples of modifications in Na-Mica-x micas.

Sample	Modifier compound	Modification	Characterization	Ref
Na-Mica-2 and Na-Mica-4	MEA, EA, ODA	ionic exchange	XRD, TG/DTG, TSSA, Zeta potencial	Osuna et al. (2019a, 2019b)
	MPTMS, MEA and BAL	Silylation and ionic exchange	ICP, XRD, FTIR, ^{13}C, ^{29}Si, ^{27}Al NMR and XPS	Osuna et al. (2020)
	Chitosan	Ionic exchange	TG, XRD, FTIR, ^{29}Si, ^{23}Na MAS-NMR and Zeta potential.	Alba et al. (2019)
Na-Mica-3 and Na-Mica-4	n-octylammonium and Fe_2O_3	Ionic exchange and pillarization	XRD, TEM and N_2 adsorption	Shimizu et al. (2006)
Na-Mica-2 and Na-Mica-3	ODTMA and PEI	Ionic exchange	XRD	Komarneni et al. (2013)
Na-Mica-2, Na-Mica-3 and Na-Mica-4	ODTMA and dodecylammonium		XRD, TG/DTA and ^{13}C, ^{29}Si and ^{27}Al NMR	Pazos et al. (2012)
Na-Mica-2 and Na-Mica-3	Tetradecylammonium		XRD, TG/DTA, FTIR and ^{13}C, ^{29}Si and ^{27}Al NMR	Pazos et al. (2015)
Na-Mica-2	Octylamine, MPTMS and polyhydroxy aluminium	Ionic Exchange, pillarization and Silylation	XRD and FTIR	Pazos et al. (2020)
Na-Mica-4	Octylamine	Ionic exchange	XRD, TG and Zeta potential.	Martín et al. (2019)
	ODA, hexadecylamine, Tetradecylamine and dodecylamine		XRD, TG, FTIR, ^{13}C, ^{29}Si NMR	Alba et al. (2011b)
Na-Mica-3 and Na-Mica-4			XRD, TG and FTIR	Pazos et al. (2017)
Na-Mica-4 and Mt	Octadecylamine and ODTMA		XRD, TG, TSSA, particle size distribution, contact angle	Orta et al. (2019)
Na-Mica-4	ODA		XRD, Zeta potential, TG, DSC, specific surface area and TEM	Martín et al. (2018)
	Hexadecylamine and dimethylhexadecylamine		XRD and TEM	Aguado et al. (2021)
Na-Mica-2 and Na-Mica-4	EA and MEA		XRD, TG, ^{13}C and ^{23}Na NMR	Osuna et al. (2021a, 2021b)

MPTMS: 3-mercaptopropyl trimethoxysilane; MEA: 2-mercaptoethylammonium; BAL 2,3-dimercapto-1-propanol; ODTMA: Octadecyltrimethylammonium; PEI: Polyethylenimine; XRD: X-ray diffraction; FTIR: Infrared spectra; TG: Thermogravimetric analysis; TEM: Transmission electron microscopy; NMR: Nuclear magnetic resonance spectroscopy; TSSA: The total specific surface area; DSC: differential scanning calorimetry; ODA: Octadecylamine; EA: ethylammonium;
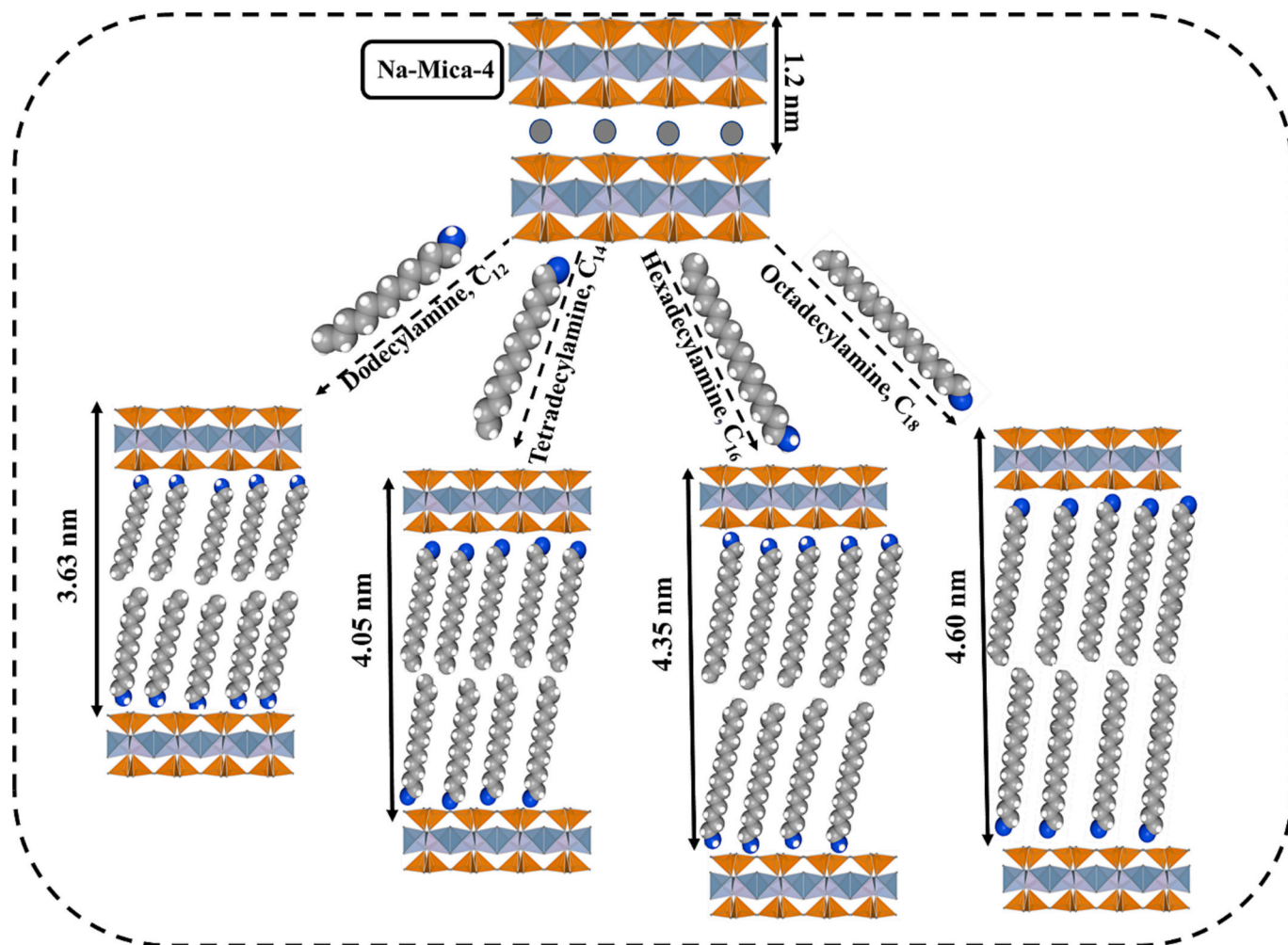
Fig. 2. Representation of the configuration of surfactants of different alkyl chains in the interlayer space of synthetic Na-Mica-4.
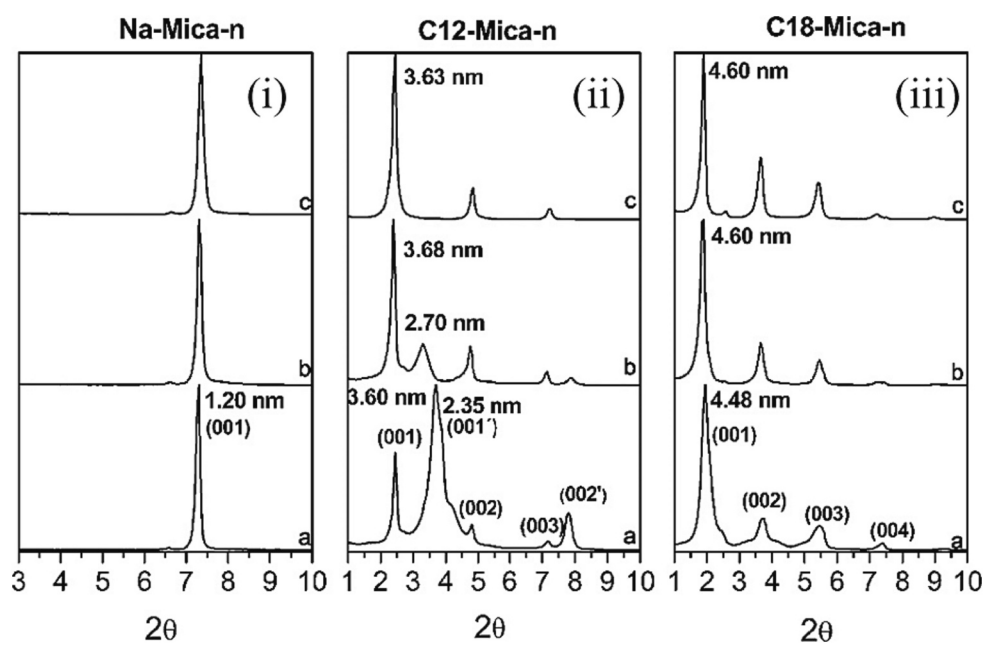

Fig. 3. Organomica XRD patterns for: (i)(a) Na-Mica-2, (b) Na-Mica-3, and (c) NaMica-4, (ii) (a) C12-Mica-2, (b) C12-Mica-3, and (c) C12-Mica-4, and (iii) (a) C18-Mica-2, (b) C18-Mica-3 and (d) C18-Mica-4. "Reprinted with permission from Pazos et al. (2012). Copyright 2023 American Chemical Society."

where *n* = 2, 3, and 4) on the intercalation of surfactants dodecyl-lammonium and octadecylammonium was also monitored (Pazos et al., 2012). Organomicas were prepared using an amount of organic cations that corresponds to twice the amount of alkylammonium salt necessary to satisfy the total layer charge 2, 3, and 4 per unit cell of Na-Mica-2, Na-Mica-3 and Na-Mica-4, respectively. XRD results (Fig. 3) showed that the charge of the clay mineral lamella mainly influenced the samples modified with the surfactant with the lowest alkyl chain length, dodecylammonium, whose d001 values suggested the existence of paraffin-like arrangements in monolayer and bilayer. When the longest chain cation was used, only the paraffin-like bilayer arrangement was observed. Complete intercalation of octadecylammonium in Na-Mica-4 was also observed by TEM imaging (Fig. 4) (Martín et al., 2018).

However, when the surfactant head group was changed, different results were observed. Octadecyltrimethylammonium (ODTMA) was used in a ratio equivalent to 2 CEC of each Na-Mica-x, for x = 1, 2, 3 and 4. Despite the size of the organic cation chain, complete intercalation only occurred in the mica with the lowest charge, for x = 1 and 2, demonstrating the surfactant relationship between the head group and the mica charge (Komarneni et al., 2013). For the other samples, the XRD results showed the presence of the original mica reflection (1.20 nm), which demonstrated that the intercalation was not complete.

This effect was even more pronounced with decreasing proportion of surfactant used. Another study investigated the influence of the concentration of octadecyltrimethylammonium (ODTMA) or octadecyl-amine (ODA) on the modification of Na-Mica-4 (Orta et al., 2019). Montmorillonite (Mt) was also used and modified with the same compounds. Two compositions were evaluated in relation to the amount of ammonium salt, which corresponds to 50 and 100% of the CEC value of the clay mineral. Mica modified with ODTMA at 50% and 100% CEC showed basal distances of 3.5 and 3.9 nm, respectively, while for the samples modified with ODA the d001 values obtained were 4.7 and 5.0 nm in proportions corresponding to 50% and 100 % CEC, respectively. However, the XRD results (Fig. 5) also showed the presence of the original mica reflection (1.22 nm), mainly in the samples modified with ODTMA whose peak intensity was more intense due to incomplete intercalation.

4.2. Silylation

The silylation reaction is based on the covalent anchoring of different species derived from the silyl group, mainly trimethylalkoxysilyl and triethylalkoxysilyl, in clay minerals, which can occur in the inter-lamellar region and/or in the edges that contain available and reactive hydroxyl groups (He et al., 2013; Bee et al., 2018). The covalent clay/silylating agent interaction allows the immobilization and non-leaching of these organic compounds, thus producing more chemically and thermally stable organofunctionalized solids (He et al., 2013; Bee et al., 2018).

The organosilanes most commonly used are bifunctional, chemically represented by $(RO)_3Si(CH_2)nX$, where (RO), in this case, refers to the alkoxy group, which hydrolyzes easily when dispersed in an aqueous medium (He et al., 2013; Su et al., 2013). The X component, present at the end of the molecule, represents the species of interest for each silylating agent. Therefore, depending on its reactivity, this fraction can be the key point for the desired application (Santos et al., 2016; Tao et al., 2016; González et al., 2017).

Silylation reactions have been carried out with several clay minerals, such as montmorillonite (Queiroga et al., 2019; Dumitru et al., 2022), vermiculite (do Nascimento et al., 2016; Santos et al., 2016), palygorskite (Liu et al., 2018; Pei et al., 2020), halloysite (Peixoto et al., 2016; Park et al., 2022), and also synthetic micas (Osuna et al., 2020). Synthetic fluorophlogopites with different charges per layer Na-Mica-x (x = 2 and 4) reacted with 3-mercaptopropyl trimethoxysilane (MPTMS) by silanization reaction and with 2-mercaptoethylammonium (MEA) and 2,3-dimercapto-1-propanol (BAL), by ion exchange (Osuna et al., 2020). Mica silanization was carried out in protic (water, ethanol, methanol) and aprotic (toluene) solvents and under different pH conditions (1.0, 7.0 and 13). Measurements of ICP, XRD, FTIR, ^{13}C, ^{29}Si, ^{27}Al NMR and XPS indicated that the reaction was pH dependent. At pH 1.0, the amount of groups incorporated into Mica-2 and M-4 micas was 2.1 and 1.9 mmol S per gram of solid, respectively, suggesting that the
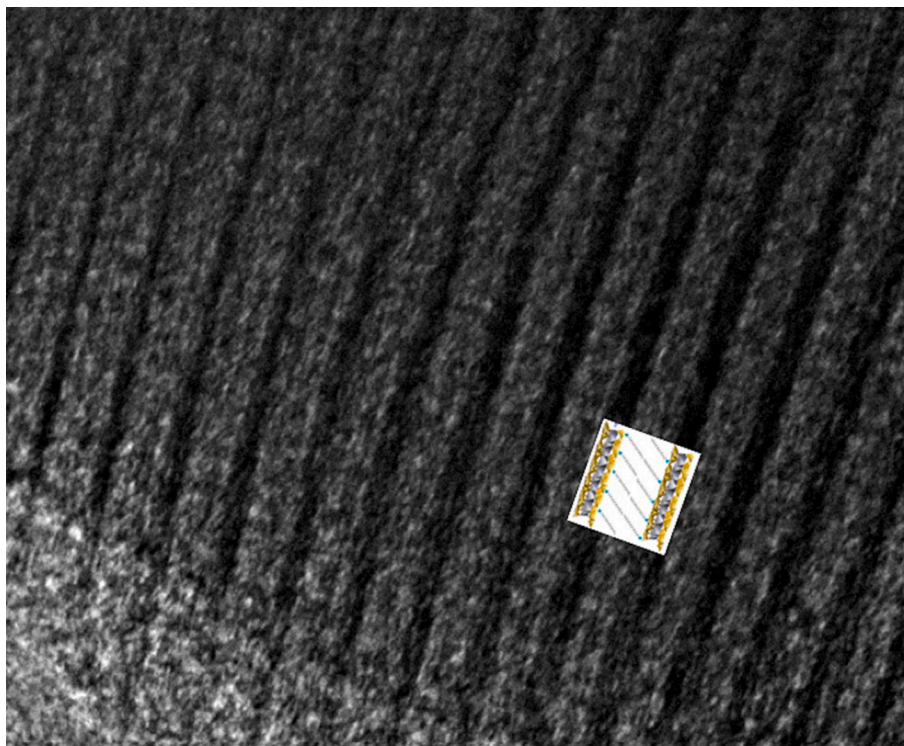

Fig. 4. Transmission electron microscopy picture of C18-Mica-4. Reprinted from Martín et al. (2018). Copyright (2023) with permission from Elsevier.
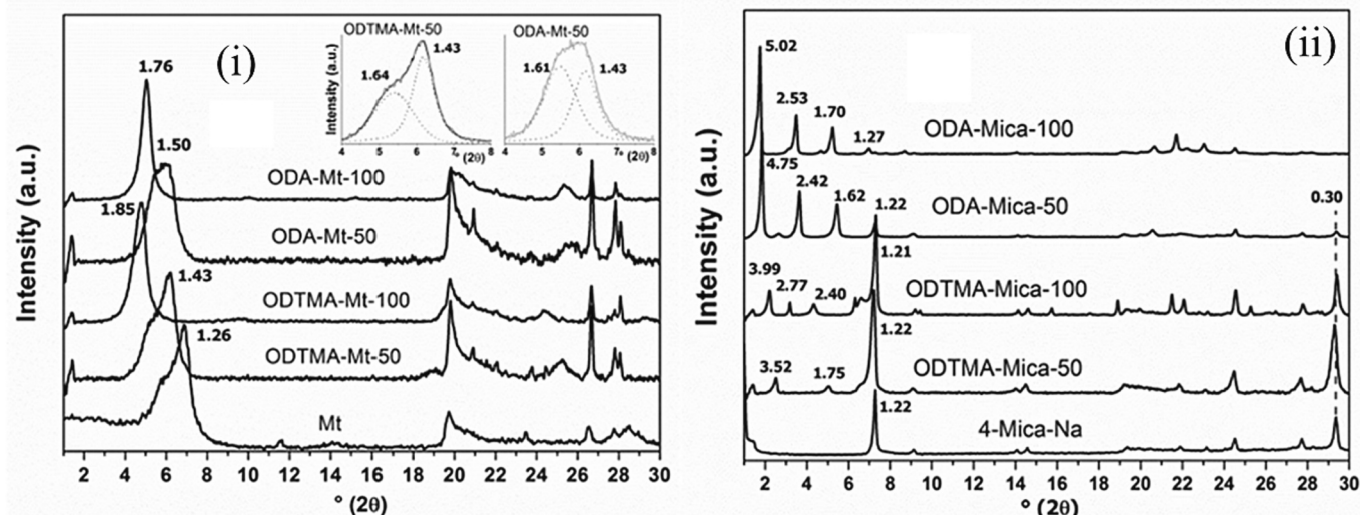
Fig. 5. XRD patterns of (i) Mt. and (ii) Na-Mica-4 and the respective samples loaded with ODA/ODTMA. Insets: deconvolution of the 001 peak for indicated samples. Reprinted from Orta et al. (2019). Copyright (2023) with permission from Elsevier.

M-2 matrix was more stable than Mica-4. The ^{29}Si RMN measures indicated the presence of T1 and T2 groups in silanized micas that were associated with the covalent immobilization of organic groups. Although the XRD data did not indicate structural changes in solids obtained at acidic pH, clay minerals in an acid medium can exchange interlayer ions for H_3O^+ and still suffer attacks on their structure, by leaching cations from octahedral and tetrahedral sites (Osuna et al., 2020).

4.3. Interaction with polymers

The interaction of polymers with clay minerals, mainly biopolymers, results in the formation of bionanocomposites that have a great impact in several fields, such as environmental, medical, etc. (Ruiz-Hitzky et al., 2013; Orta et al., 2020; de Lima et al., 2022). The economic and environmental value and the reactivity added to these biomaterials make them excellent candidates for several applications, such as contaminating species adsorption (Hu et al., 2017; Orta et al., 2020), drug release (Ruiz-Hitzky et al., 2013; de Lima et al., 2022), among others. One of the main biopolymers used to form bionanocomposites with clay minerals is chitosan, a polysaccharide derived from the deacetylation of chitin, found in the exoskeleton of crustaceans, insects, and fungi (Kurita, 2006).

The entry / conjugation of chitosan into the clay mineral structure leads to an improvement in the adsorption capacity of the clay mineral, forming biodegradable and ecologically correct materials (Darder et al., 2003; França et al., 2020a, 2020b). The chitosan/clay mineral interaction is mainly due to electrostatic attraction between the positive charge
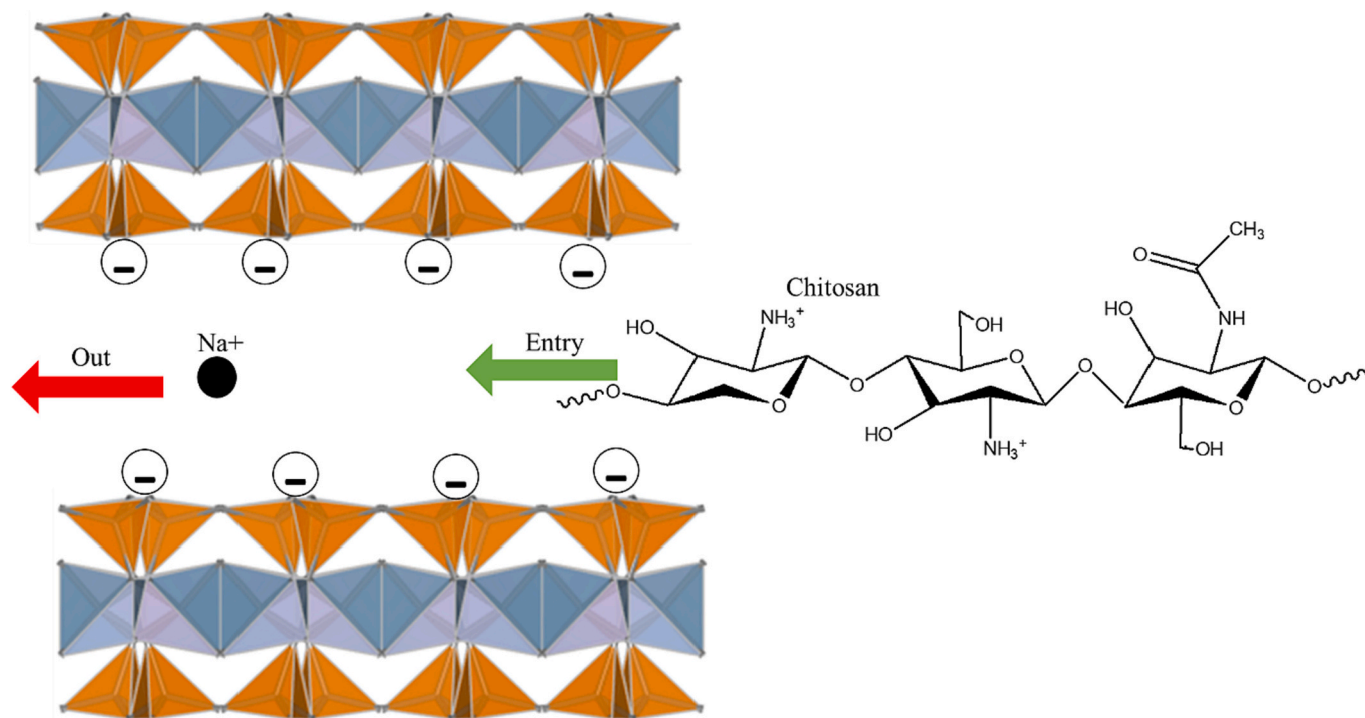

Fig. 6. General scheme of the intercalation of chitosan with mica Na-Mica-x.

of the protonated amino groups and the negative charge of the clay, Fig. 6 (Darder et al., 2003; França et al., 2020a, 2020b). Futhermore, expandable clay minerals are also targets for this type of modification, including montmorillonite (Hu et al., 2017; França et al., 2020a, 2020b; de Lima et al., 2022).

In the case of highly charged swelling micas, bionanocomposites based on chitosan and highly charged swelling synthetic fluoro-phlogopites, Na-Mica-2 and Na-Mica-4 were obtained at pH 4.9, a condition in which the chitosan amino groups (pKa 6.5) are predominantly protonated (Alba et al., 2019). The bionanocomposite was formed with different proportions of chitosan with 0.5 g of each mica. The maximum amount of chitosan in the bionanocomposite was 103 mg per gram of Na-M-4, the CEC of which was 468 cmol(+)/kg, respectively. The XRD measurements indicated that the interaction of mica with chitosan could not reach the total intercalated state since the increase in the basal spacing of the samples (0.17 nm) was lower than that of the chitosan film (0.38 nm), suggesting that the polymer was partially intercalated, and still incorporated into the surface and edges of the mica, also confirmed by FTIR, ^{29}Si and ^{23}Na MAS-NMR.

5. Application of high charge mica

The use of adsorbents capable of effectively removing contaminants found in water is still one of the most effective strategies to separate pollutants (Ewis et al., 2022; Varsha et al., 2022). The choice is made for adsorbents with a high affinity for different contaminants, as is the case with high charge synthetic micas. In fact, micas with different Na-Mica-x

charge are widely applied in the adsorption of organic and inorganic contaminants, as summarized in Fig. 7. In this review, emphasis will be placed on high charge synthetic mica for removal of a range of contaminants found in water, whose results are listed in Table 2.

5.1. Removal of perchlorate and non-ionic compounds

One of the most persistent inorganic compounds that cause serious damage to human health is perchlorate (Ye et al., 2012). Found in wastewater, this compound, because it is similar in size to iodide ions, can be taken up in place of iodide ions by the mammalian thyroid gland and can disrupt thyroid hormone production and metabolism in the human body, causing significant effects mainly in pregnant women and fetuses (Ye et al., 2012; Komarneni et al., 2013). With this in mind, the adsorption of perchlorate in Na-M-x micas (x = 1, 2, 3 and 4) modified with octadecyltrimethylammonium (ODTMA) and polyethyleneimine (PEI) was evaluated and compared with the performance of aluminium oxide-capped montmorillonites (Komarneni et al., 2013). The best adsorption capacities occurred for Na-Mica-2 and Na-Mica-3 modified with ODTMA, whose values were 0.436 and 0.269 mmol/g, respectively. The mechanism of interaction between perchlorate and ODTMA/Na-Mica-x was attributed to the exchange with chloride ions of the intercalated neutral surfactant during the cation exchange process, Fig. 8. Clays prepared with PEI and pillared clays showed little or no adsorption of perchlorate.

Other wastewater contaminants derived from oil refineries are non-ionic hydrocarbons such as benzene, toluene, and phenol. These
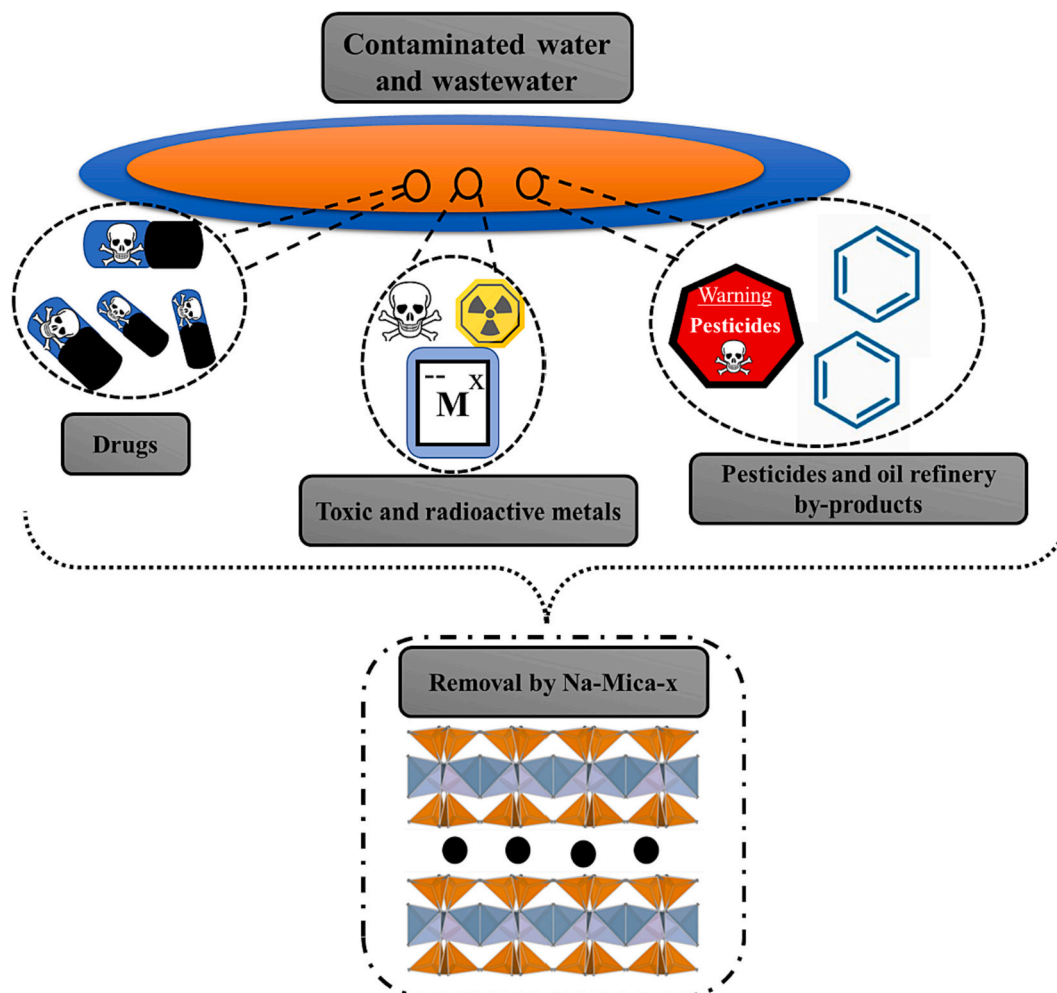

Fig. 7. Types of contaminants studied in high charge mica removal.

Table 2
Systems based on high charge micas and modified high charge micas for contaminant removal.

Sample	Target compound	Results	Ref
Na-Mica-2 and Na-Mica-4	Ra^{2+}	Na-Mica-4 adsorbed 95% of Ra^{2+}.	Komarneni et al. (2001)
Na-Mica-2 and Na-Mica-3 modified with ODTMA and PEI	perchlorate	Improved adsorption capacity for ODTMA/Na-Mica-2 and ODTMA/Na-Mica-3 with values of 0.269[a] and 0.436[a] meq/g, respectively.	Komarneni et al. (2013)
Na-Mica-2, Na-Mica-3 and Na-Mica-4	Hg^{2+}	Higher absorption capacity for Na-Mica-3 with 59%[b] of Hg^{2+} compared to the theoretical CEC of the clay.	Noh and Komarneni (2011)
	Sr^{2+} and Ba^{2+}	Best results in 84 and 95%[b] removal of Sr^{2+} and Ba^{2+} for Na-Mica-2, respectively.	Noh et al. (2013)
Na-Mica-4	Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}	–	Kim et al. (2014)
Na-Mica-2 modified with octylamine, MPTMS and polyhydroxy aluminium	Zn^{2+} and MCPA	The maximum adsorption capacities were 11.7[b] and 0.517[c] mmol/g of Zn^{2+} and MCPA.	Pazos et al. (2020)
Na-Mica-4 and Mt. modified with octamine	Ibuprofen	Rapid (60 min) adsorption of ibuprofen in modified Na-M-4 was concentration dependent and the removals were 99 and 68%[c] at concentrations of 0.1 and 80 mg/L, respectively.	Martín et al. (2019)
Na-Mica-4 and Mt. modified with ODA and ODTMA	Pyrimethanil	Organomodified mica with both organic compounds showed a removal of less than 10%[c] of the 80 mg/L concentration.	Orta et al. (2019)
Na-Mica-4 modified with ODA	Methylparaben, propylparaben, perfluorobutanoic acid, perfluoroheptanoic acid, perfluorooctanoic acid, perfluorooctane sulfonic acid, nonylphenol, dodecyl sulfate, octadecyl sulfate, diclofenac, ibuprofen, salicylic acid, trimethoprim, carbamazepine, propranolol, caffeine, clofibric acid, and gemfibrozil	100%[c] removal capacity for perfluorooctane sulfonic acid, non-ylphenol, dodecyl sulfate, octadecyl sulfate, diclofenac, ibuprofen, salicylic acid, clofibric acid and gemfibrozil by organomodified micas.	Martín et al. (2018)
Na-Mica-4 and Na-Mica-4 modified with octadecylamine	LAS	The highest removal capacity (98%[c]) was for the modified mica.	Orta et al. (2018)
Na-Mica-3 and Na-Mica-4 modified with octadecylamine, hexadecylamine, Tetradecylamine and dodecylamine	benzene, toluene, and phenol	Maximum adsorption capacity for C18-Mica-4 with values of 1500, 750 and 100[d] mmol/Kg for toluene, benzene, and phenol, respectively.	Pazos et al. (2017)
Na-Mica-4 modified with hexadecylamine and dimethylhexadecylamine	Cyclohexylamine and Eu^{3+}	The maximum amount absorbed of cyclohexylamine was 16%[e].	Aguado et al. (2021)
Na-Mica-2 and Na-Mica-4	Eu^{3+}	–	Martín-Rodríguez et al. (2022)
Na-Mica-2			Martín-Rodríguez et al. (2017) (Martín-Rodríguez et al. (2019)
Na-Mica-2 and Na-Mica-4		Maximum adsorption capacity of 84.8%[f] and 81.3%[f] for Na-Mica-4 and Na-Mica-2, respectively.	José García-Jiménez et al. (2016)
	Cs^{+}	Maximum adsorption capacity of 224.2[f] meq/100 g for Na-Mica-2 at a temperature of 300 °C.	Osuna et al. (2018b)
		Maximum adsorption capacity of 80%[f] for Na-Mica-4.	Osuna et al. (2018b)
	Pb^{2+}, Hg^{2+} and Cd^{2+}	Maximum adsorption followed the trend $Hg^{2+} > Pb^{2+} > Cd^{2+}$.	Osuna et al. (2019a, 2019b)
Na-Mica-2 and Na-Mica-4 modified with EA and MEA		Better removal capacities for Na-Mica-2 in the adsorption of Pb^{2+} and Cd^{2+} and MEA-Mica-2 for Hg^{2+}, with values of 3500, 4000 and 5000 meq/Kg[f], respectively.	Osuna et al. (2021a, 2021b)
Na-Mica-4	Sr^{2+}	Maximum holding capacity 43%[f].	Tatsuya Kodama et al. (2001)
Na-Mica-4 and Na-Mica-2 modified with octadecylamine and dodecylamine	I⁻	Maximum adsorption for Na-Mica-2 modified with octadecylamine, with 30%[f] removal.	Osuna et al. (2021a, 2021b)

a: quantification by ion chromatograph; b: quantification by atomic absorption; c: quantification by HLPC; d: quantification by UV–Vis; e: quantification by TG; f: quantification by ICP-MS; ODTMA: Octadecyltrimethylammonium; ODA: Octadecylamine; PEI: Polyethylenimine; MCPA: 2-methyl-4-chlorophenoxyacetic acid; Mt.: montmorillonite; EA: ethylammonium; MEA: mercaptoethylammonium; LAS: linear alkylbenzene sulfonates.

compounds can also cause serious damage to health and the environment. Therefore, the removal of some nonionic hydrocarbons by Na-Mica-x (x = 3 and 4) and modified surfactants of different alkyl chains (C_{12}, C_{14}, C_{16} and C_{18}) was investigated. Pazos et al. (Pazos et al., 2017). The ability to remove contaminants depended on the length of the alkyl chain and the organization of the surfactants in the clay, whose values were 1.50, 0.75 and 0.10 mmol of toluene, benzene, and phenol per gram of C_{18}-Mica-4.

5.2. Drugs removal

Effluents from the pharmaceutical industry and increased use of drugs can contribute significantly to water pollution, causing serious toxicity problems for both humans and the environment (Bielen et al., 2017; França et al., 2022; González-González et al., 2022).

Several classes of drugs, including antibiotics and anti-inflammatory agents, have been found in the aquatic environment, even at low
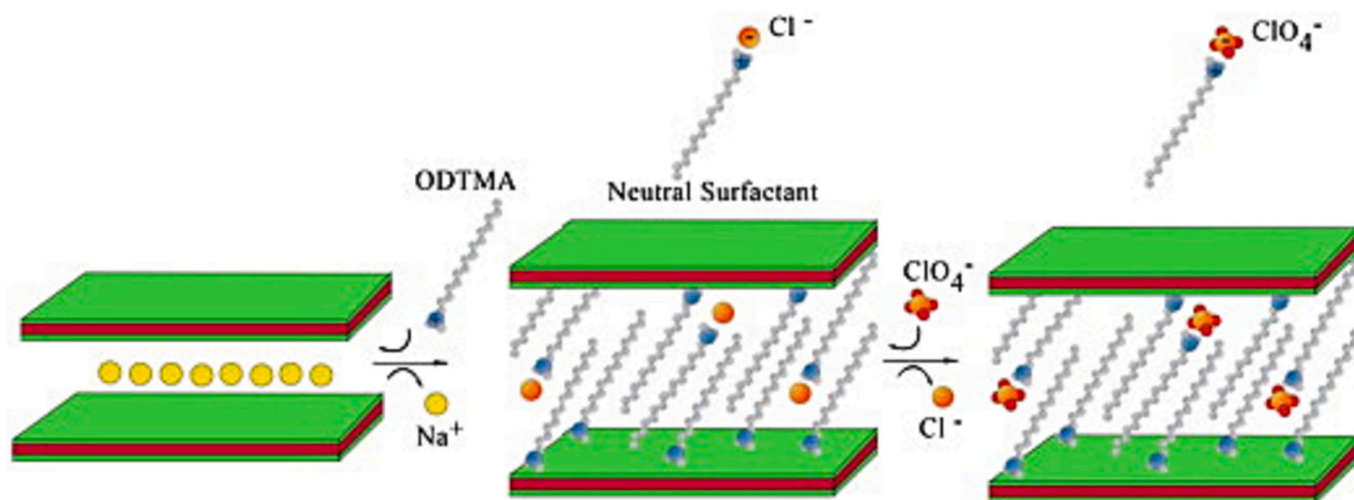
Fig. 8. Schematic of perchlorate uptake by organomicas Reprinted from Komarneni et al. (Komarneni et al., 2013), Copyright (2023) with permission from Elsevier.

concentrations (Bielen et al., 2017; González-González et al., 2022). For example, ibuprofen is a drug in the group of non-steroidal anti-inflammatory drugs, which can be sold without a prescription in some countries and has been found in wastewater almost everywhere in the world (Ben Maamar et al., 2017; Ocampo-Perez et al., 2019; Patel et al., 2019). Ibuprofen, even at apparently low concentrations, can cause the death of aquatic species such as *Oryzias latipes* fish, which could not resist a concentration of 100 ng/L of ibuprofen (Han et al., 2010).

Synthetic mica Na-Mica-4 and montmorillonite modified with octadecylamine were applied to remove ibuprofen (Martín et al., 2019). The study observed a dependence of drug concentration on the adsorption rate of modified Na-Mica-4, whose drug removals were 99 and 68% at a concentration of 0.1 and 80 mg/L, respectively, in 60 min.

5.3. Toxic metal removal

Water pollution by toxic metals has been a major environmental concern, due to its high toxicity and low or no biodegradability, which can cause various types of diseases to live beings (Na Nagara et al., 2022). Different adsorbents are used to remove toxic metals from water (Na Nagara et al., 2022), clay minerals have been applied considering that they can adsorb metals by different mechanisms involving the formation of inner and outer complexes (Liu et al., 2021b). In recent years, high charge synthetic micas have gained prominence, as shown in Table 2. The removal of Hg^{2+} by Na-Mica-x (x = 2, 3 and 4), titanosilicate-4 (Na-ETS-4) and sodium titanosilicate was investigated as a function of the ionic strength of the medium (Noh and Komarneni, 2011). The adsorption capacity of Hg^{2+} by mica was ~19%, 59% and ~30% for Na-Mica-2, Na-Mica-3 and Na-Mica-4, respectively, compared to the theoretical CEC of each clay mineral. The greater adsorption of Na-Mica-3 mica was associated with its layer charge density, which has an intermediate value in relation to other micas, which affects the availability and exchange sites with Hg^{2+}.

The removal of Hg^{2+}, Pb^{2+} and Cd^{2+} against Na-Mica-2 and Na-Mica-4 was evaluated at pH 2.5 and 6 (Osuna et al., 2019a, 2019b). Parameters such as the variation in metal concentration in relation to the CEC of micas, counter-ion and agitation were evaluated at the maximum removal capacity by cation exchange that occurred in the order $Hg^{2+} > Pb^{2+} > Cd^{2+}$ for Na-Mica-2, reaching values above the CPB of 254.18 cmol(+)/Kg. This fact was associated with a lower load on Na-Mica-2, which better provided access to the interaction sites with the entrance of metallic cations in the interlamellar region. Furthermore, the authors indicated that under the pH conditions of the medium (pH 2.5), the structure of mica may have leached, reducing some sites of interaction with the metals.

The adsorption of Hg^{2+}, Pb^{2+} and Cd^{2+} was also evaluated in Na-Mica-2 and Na-Mica-4 and modified with ethylammonium (EA: $C_2H_5NH_3^+$) and mercaptoethylammonium (MEA: $SHC_2H_4NH_3^+$) in a proportion of 200% of CEC of micas (Osuna et al., 2021a, 2021b). All adsorbents were efficient in removing metals, with better removal capacities for Na-Mica-2 in the adsorption of Pb^{2+} and Cd^{2+} and MEA-Mica-2 for Hg^{2+}, whose values were 3.5, 4.0 and 5.0 mmol per gram of solid, respectively. The main mechanisms involved in the adsorption of Pb^{2+} and Cd^{2+} were ionic exchange and interaction with the thiol groups for Hg^{2+} removal.

Another metal studied is Zn^{2+} because it can cause neurotoxicity in humans if ingested at concentrations greater than 40 mg/day (Palmer et al., 2019; Pazos et al., 2020). The elimination of Zn^{2+} removal in Na-Mica-2 modified with octylamine, pillared with Al_2O_3 and then silanized with MPTMS was monitored in the presence of 4-chloro-2-methylphenoxyacetic acid (MCPA) (Pazos et al., 2020). The highest adsorption values obtained were 11.7 and 0.517 mmol/g for Zn^{2+} and MCPA, respectively, indicating an excellent ability to remove these contaminants with heteromodified mica.

The removal of contaminants derived from the nuclear industry by highly charged synthetic micas was also evaluated, which serve as a chemical barrier for the retention and storage of radioactive materials, such as Cs (Osuna et al., 2017). Cesium isotopes, such as ^{135}Cs and ^{137}Cs with t1/2 of 2.6×10^6 and 30 years, respectively, are one of the main constituents of wastewater effluents derived from nuclear reprocessing. Furthermore, because of their high solubility and long half-lifes, they are very hazardous radioactive waste (Castrillejo et al., 2016). Therefore, Osuna et al. (Osuna et al., 2018b), studied the immobilization of cesium in highly charged synthetic micas (Na-Mica-2 and Na-Mica-4), evaluating the influence of temperature (ambient and at 80 °C) and Cs^+ concentrations between 0.01 and 25 mmol L^{-1} for 0.2 g of clay on the adsorption capacity. Better performance was observed for Na-Mica-4 with a maximum adsorption of 80% at low concentrations of Cs^+, which decreased with increasing initial concentration, even with increasing temperature. SEM and XRD results indicated the permanence of the morphology after adsorption and reflections compatible with a base spacing of 1.20–1.22 nm, indicating that Cs^+ formed a hydration complex in the mica interlayer space.

6. Conclusions

Synthetic Na-Mica-x micas have interesting properties as adsorbents. Various methods are employed in the synthesis of this clay, with the intention of achieving a high yield and crystallinity. Studies have shown that synthetic mica can interact with several organic molecules,

increasing their reactivity. Therefore, these high-charge clays have proven to be promising materials for diverse applications, including the adsorption of contaminants found in water. As impurity-free materials, their properties and capacity to interact with a wide range of organic molecules make high-charge mica a material suitable in various fields of application, such as health, food or even cosmetics, with the possibility to adsorb/release bioactive compounds, medicines, proteins/enzymes, etc.

CRediT authorship contribution statement

Luís H. Oliveira: Writing – original draft, Formal analysis, Data curation. **Denise B. França:** Writing – original draft. **Alan I.S. Moraes:** Writing – original draft. **Santiago Medina-Carrasco:** Writing – original draft. **Maria G. Fonseca:** Writing – review & editing. **Josy A. Osajima:** Writing – review & editing, Supervision, Conceptualization. **Edson C. da Silva-Filho:** Writing – review & editing, Supervision, Conceptualization. **María del Mar Orta:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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