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ALLOPHANE, A NATURAL NANOPARTICLE PRESENT IN ANDISOLES OF ECUADOR, PROPERTIES AND APPLICATIONS

ALOFÁN, UNA NANOPARTÍCULA NATURAL PRESENTE EN ANDISOLES DEL ECUADOR, PROPIEDADES Y APLICACIONES

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Abstract

The allophane is a natural nanoparticle present in soils from volcanic origin such as andisols, which are distributed worldwide, especially in countries that have active volcanoes. In Ecuador, andisols are in high and humid areas from the Highland/North region, constituting 30% of the territory. The allophane can be obtained from andisols through physical and chemical processes or it can be also synthesized. This nanomaterial has multiple properties for various applications in different areas; and there are studies about these nanoparticles and this kind of soil, but they have not yet been conducted in Ecuador. This article presents a review of structural characteristics, properties, formation, isolation, synthesis and uses of allophane to extend knowledge and encourage the conduction of research in these soils, which are the source of the aforementioned nanoparticle. The literature review was performed on Science Direct and Google Scholar databases using high impact articles related to natural or synthetic allophane. Allophane has characteristics that allow it to be used as an environmental remediator, bactericidal, anti-inflammatory, flame retardant, enzyme support and also in catalysis, photocatalysis and electrocatalysis. Considering the availability and the large area covered by andisols in Ecuador, research based on international investigations can be perform to take advantage of it.

Keywords: natural nanoparticle, andosol, volcanic soils, halloysite, imogolite.

Resumen

El alofán es una nanopartícula natural presente en suelos de origen volcánico como los andisoles, que se encuentran distribuidos alrededor de todo el mundo en países con actividad volcánica. En Ecuador, los andisoles constituyen el 30 % del territorio en zonas altas y húmedas de la región sierra-norte. El alofán se puede obtener de los andisoles a través de procesos físicos y químicos, o a su vez se puede sintetizar. Este nanomaterial posee múltiples propiedades para varias aplicaciones en diferentes áreas. Existen muchas investigaciones de estas nanopartículas y de este tipo de suelos, pero no se han estudiado aún en el Ecuador. En este artículo se presentan las características estructurales, propiedades, la formación, aislamiento, síntesis y usos del alofán, con el fin de generar conocimiento e incentivar la investigación de estos suelos que son fuente de la mencionada nanopartícula. La búsqueda de literatura se realizó en bases de datos de Science Direct y Google Académico, y se utilizaron artículos de alto impacto relacionados con investigaciones de alofán natural o sintético. Las características particulares que tiene el alofán le permite ser usado como remediador ambiental, bactericida, antiinflamatorio, ignífugo, soporte de enzimas, pero además se ha estudiado en catálisis, fotocatálisis y electrocatálisis. Al considerar el área cubierta por el alofán en el territorio ecuatoriano y su disponibilidad, este se puede aprovechar para realizar investigaciones basadas en los estudios internacionales que se han desarrollado para aprovechar en el área ambiental y médica.

Palabras clave: nanopartícula natural, andisol, suelos de origen volcánico, halloysita, imogolita.

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1 Introduction

Allophane is a natural nanoparticle Nishikiori2012 that is present in volcanic soils called andosols according to the global reference of the soil resource Vistoso2012 or andisols according to the Soil Taxonomy NRCS/USDA. Andosols or andisols are soils formed from volcanic materials such as ashes, through weathering processes under acidic conditions in humid climates (Cervini-Silva et al., 2015; Saeki et al., 2010), and are distributed around the world in regions with increased volcanic activity.

Allophane particle has a porous sphere shape, with a diameter between 3 and 5 nm (Henmi and Wada, 1976), and is structured by an outer layer consisting of aluminum octahedrons (Al) and an inner layer consisting of silicon tetrahedrons (Si). It has a large surface area, high porosity and variable load, allowing it to have potential applications as a cation adsorbent (Silva-Yumi et al., 2018), anions (Nishikiori et al., 2017), benzene-derived compounds, fatty acids, detergents, organochlorine compounds (Arakawa et al., 2014; Baldermann et al., 2018; Garrido-Ramírez et al., 2013), DNA and amino acids (Saeki et al., 2010), enzymes (Yu-Huang et al., 2016), in the catalysis area (Garrido-Ramírez et al., 2013), in the preparation of electrodes (Nishikiori et al., 2014), as flame-retardant (Iyoda et al., 2012; Shukla et al., 2013) as ink element for printers (Calabi-Floody et al., 2012), as anti-inflammatory and bactericidal (Calabi-Floody et al., 2012), for the purification of biodiesel (Yu-Huang et al., 2016), etc.

In Ecuador, andisoles constitute approximately 30 % of the territorial area, and these are distributed in the north-central highlands in the high and humid zones, although they extend toward the coast and the east (Calvache, 2014). Research on soils of Ecuadorian volcanic origin has focused on pedogenesis (Zehetner et al., 2003), carbon stabilization and storage (C), the effects of overgrazing on vegetation (Podwojewski et al., 2002), the short-term management effects on soil structure of hardened volcanic origin in deep layers, the variability of soils of volcanic origin and their relationship with parental material, climate and their use (Podwojewski and Germain, 2005), chemical weathering (Poncelet and Jouhannaud, 2013) and the presence of n-methyl ketones as products of n-alkane degradation (Jansen and Nierop, 2009); however, none of these articles mention or have focused on the study of allophane nanoparticles present in this type of soil, only one article published in 2007 studies the influence of allophane content and organic matter on soil properties of volcanic origin (Buytaert et al., 2007).

In 2009, an article was published about the existence of a massive allophane deposit located in the community of San José de Achotillo, in the province of Santo Domingo de los Tsatchila. Its quantification was carried out in 2010 and the presence of a high allophane content was found ($> 60\,\%$), as well as halloysite which is another natural nanoparticle with similar characteristics; iron oxides and a low organic matter content (Kaufhold et al., 2010). Since this year, several researches have emerged on allophane present in the deposit and focused on the adsorption of anions as fluoride and its comparison with other similar adsorbents (Kaufhold et al., 2010), adsorption of cations: barium, cobalt, strontium and zinc (Baldermann et al., 2018), the anti-inflammatory activity of allophane present in this deposit (Cervini-Silva et al., 2015), as well as its cytotoxicity (Cervini-Silva et al., 2014), and activation to be used as a catalyst (Vaca and Lalangui, 2018).

Studies on Ecuadorian andisols and allophane nanoparticles are limited, and research on allophane has been conducted from institutions located outside the country as seen in the literature. Although Ecuador's scientific production has increased in recent years (Araujo-Bilmonte et al., 2020), trained personnel have returned from abroad to research in this area and with higher education institutions to conduct research in nanoscience and nanotechnology (Gutiérrez Coronado, 2018). Perhaps one of the limitations is the lack of knowledge on the existence of this nanomaterial, reason for which the objective of this article is to present the characteristics, properties, formation, isolation, synthesis and uses of allophane in order to highlight the potential of this type of soil, which covers a large area of the Ecuadorian territory.

2 Methodology

The search and compilation of the articles used in the literature review was carried out between January 2018 and January 2019 through the databases: Scopus, Sciencedirect and Google Academia. The criteria were: (1) Keywords: Allophane, alofán, andisol Ecuador, andosol Ecuador, allophane Ecuador, alofán Ecuador, with boolean algorithms "and" and "with". (2) Type of articles: Research and review, (3) Inclusion and Exclusion Criteria: Articles focused on the study of allophane, articles in quartile 1 according to Scimago Journal & Country Rank for documents in English, (4) documents published in the last 10 years. 59 documents have been taken into consideration between articles and congress works, two reference documents and a patent, from which the main ideas shared in this document have been extracted. The articles have been considered based on their information about the origin, synthesis, properties and applications of allophane.

3 Andisols around the world and in Ecuador

Andisols are soils that are formed from volcanic materials such as ash, through weathering processes under acidic conditions in humid climates (FAO, 2014, 2015), and are distributed around the world in regions with significant volcanic activity. In Asia and the Pacific, these are found in Japan, Korea, the Philippines, Indonesia, Papua New Guinea and New Zealand. In Europe they are in Italy and France; in Africa and Oceania they are in Kenya, Rwanda, Tanzania, Ethiopia and the Canary Islands. In America they are located in countries around the Pacific Fire Belt: Alaska, United States, Mexico (Pérez et al., 2016), Guatemala, El Salvador, Honduras, Nicaragua, Costa Rica (Alvarado et al., 2014), Panama, Las Antilles, Colombia, Ecuador, Chile and Argentina.

Although there are several types of soils in Ecuador, andisols constitute 60593 km^2 of the Ecuadorian territory (Fig. 1), and these are distributed around the central-north highland region in high and humid zones, though they also extend to the coast and the east (Calvache, 2015; Gonzáles, 2015; González, 2010). They are the result of weathering of pyroclastic material resulting from the eruptions of numerous volcanoes located in the so-called "avenue of volcanoes", with more than 100 volcanoes, five of them active. They are soils with a low apparent density, usually with high organic matter content, low resistance to tangential cutting, good drainage, but in turn good moisture retention (Calvache, 2015; FAO, 2015; Gonzáles, 2015).

4 Formation

Allophane is formed by the rapid weathering of volcanic glass. When the pH of the soil is 5, silicon and aluminum are released from the volcanic material, thus reacting and forming allophane, imogolite and halloysite, which are other minerals present in this type of soil and which can also be formed from the hydrolysis of primary minerals. The formation and persistence of allophane, imogolite or halloysite is influenced by the organic matter content and precipitation. Allophane predominates in soils that are subjected to high precipitation, while halloysite excels in soils with a low precipitation regime. These minerals are present in soil with low organic matter content where aluminum does not exist as complexes with organic acids or humic substances but in the form of inorganic complexes (Yuan and Wada, 2012).

Allophane can be extracted from soils of volcanic origin following a process that generally involves the removal of organic matter and iron oxides, and the separation of nanometric fractions from the sand, lime and clay fractions. This nanoparticle can also be synthesized by the co-precipitation method or by the sun-gel method. The first method uses orthosilicic acid (H_4SiO_4) or sodium orthosilicate (Na_4SiO_4) and aluminum chloride ($AlCl_3$) or aluminum perchlorate ($Al(ClO_4)_3$) as precursors. The SOL-GEL method that involves hydrolysis of reagents, and condensation of the obtained products uses tetraethyl orthosilicate ($TEOS$) ($Si(OC_2H_5)_4$) and aluminum chloride ($AlCl_3$).

5 Structural characteristics

Allophane particle is shaped as a porous sphere (Fig. 2) with an external diameter between 3.5 and 5.0 nm, an internal radius between 1.0-2.0 nm and a wall with a thickness between 0.7 and 1.0 nm. It has pores with a diameter of around 0.3-0.4 nm and has a specific surface area determined by the EG-

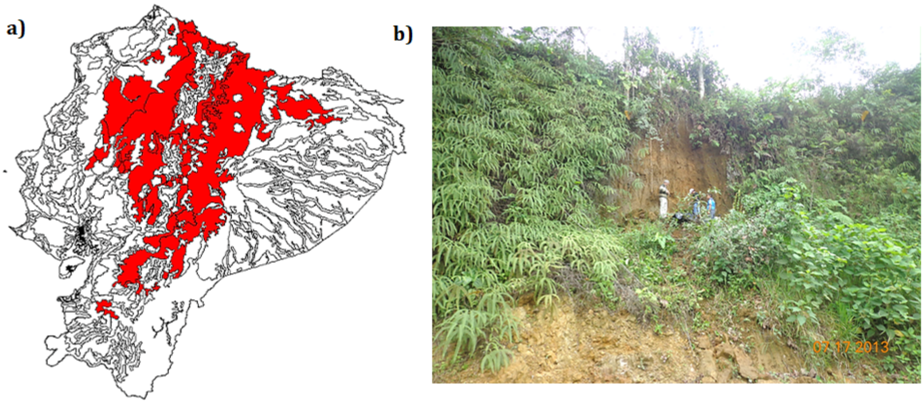

Figure 1. a) Surface area of Ecuador covered by volcanic soils taken from Calvache (2015). b) An example of area rich in allophane and located in Santo Domingo de los Tsatachilas (own image).

ME (ethylene glycol monomethyl ether) method, ranging from 400-900 m^2g^{-1}. The outer wall is composed of aluminum octahedrons, while the inner wall by silicon tetrahedrons (Fig. 2), although it is possible to find aluminum in both tetrahedrons and octahedrons.

The chemical composition of allophane changes according to the predominance of Al or Si. It is possible to find allophane rich in aluminum ($Al/Si = 2$) and allophane rich in silicon ($Al/Si = 1$), thus its chemical formula can be represented as $1-2SiO_2.Al_2O_3,5-6H_2O$. The presence of silanol groups ($Si-OH$) on the surface of the inner wall and aluminum groups ($Al-OH$) located on the outer wall allow allophane to acquire negative or positive charge (Fig. 3), depending on the conditions of the medium with the permanent or structural load it may possess, due to the isomorph replacement of Al^{3+} by Si^{4+}.

6 Application

6.1 As an absorbent for the environmental remediation

The high porosity of allophane, its large surface area and the charge it can take depending on the environment make allophane to be a potential adsorbent of positive species (cations) and negative species (anions), with internal (silanol) and external (aluminol) sites being the responsible of the process (Reinert et al., 2011). Adsorption processes can be used for treating drinking water and wastewater, as they allow contaminants (organic or inorganic species) to be retained on the surface of the material and be removed from the aqueous environment.

One of the most frequently studied processes is phosphate adsorption due to its particular fixation on allophane, although there are studies on the adsorption of molybdate (Elhadi and Henmi, 2000), arsenate, silicic acid, boric acid, chromate (Opiso et al., 2009), selenate, sulphate, oxalate, nitrate, orthylicic acid, fluoride (Kaufhold et al., 2010), citrate, among other anionic species. Adsorption of cationic species has been less studied in relation to anion species; the few species studied include zinc, cesium, copper, cobalt, cadmium, barium and strontium (Baldermann et al., 2018; Silva-Yumi et al., 2018).

Adsorption of organic species has also been of interest to scientists, including 2.4-dichlorophenol, pentachlorophenol, humic acid, benzene, benzoic acid, phthalic acid, benzaldehyde, ethyl benzoate, diethyl phthalate, acetic acid, oxalic acid, citric acid, polymers such as xanthan, detergents and fatty acids (**?**). Figure 4 shows some of the structures that correspond to the above species and how they are adsorbed on the surface of allophane. Gas adsorption has not been too studied, and only the adsorption of ammonia can be mentioned (Zaenal et al., 2013).

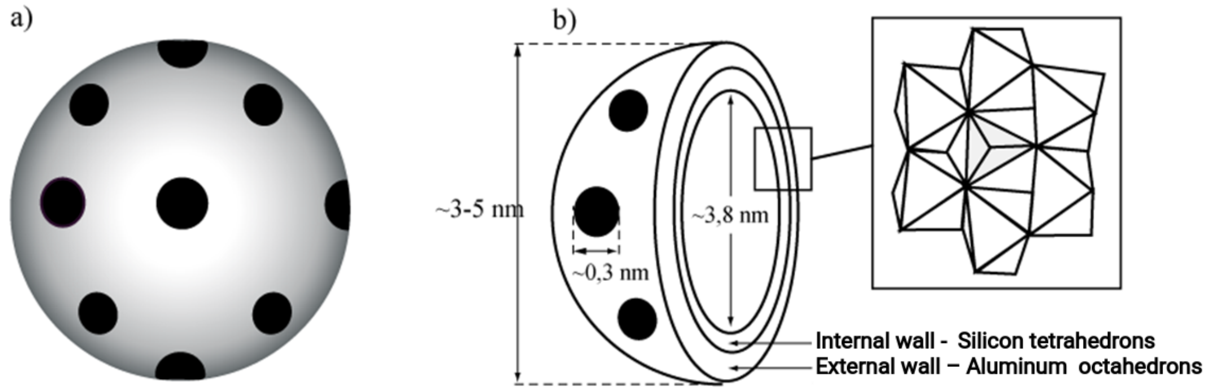

Figure 2. a) External morphology of an allophane nanoparticle. b) Detail of the internal structure.

6.2 Adsorption of essential molecules and origin of life

Understanding the processes that occur in this type of soil is possible by studies carried out, such as those of Hashizume et al. (2002; 2007) where allophane has been determined to have high affinity for nucleotides, which implies its possible role in the abiotic formation of RNA-type polynucleotides, although immobilization of these nucleotides by complexation may make it difficult to oligomerize RNA. The persistence and survival of amino acids in soils has been attributed to the adsorption and protection by clays and other minerals. For example, it has been observed that the adsorption of DL-alanine is higher on suspended allophane and it depends on the pH. A preference for L-alanyl-L-alanine is observed in the adsorption of D- and L-alanine and their dimers on allophane with different relation to Al/Si, suggesting that the size, the separation of intramolecular load and the surface orientation are the responsible factors.

In addition, the adsorption of DNA on allophane has been studied by several researchers in order to reconstruct and study past environments as well as microbial communities in soil and carbon storage (Huang and Rawlence, 2014; Matsuura et al., 2013; Yu-Huang et al., 2016). The results show that DNA adsorption is facilitated by the interaction of phosphate groups with allophane $Al-OH$ groups, although it is lower than the adsorption of adenosine-5′-monophosphate (5′-AMP), a molecule used as a reference (Matsuura et al., 2013), reason for which there is more affinity for 5′-AMP than adenine, adenosine or ribose, also due to the presence of phosphate groups that facilitate interaction with $Al-OH$ groups.

DNA adsorption is almost unaffected by the ionic strength and it decreases the presence of phosphate when the pH increases, due to the deprotonation of the $Al-OH$ groups (Matsuura et al., 2013; Saeki et al., 2010) as a result of the competition for active sites. The presence of humic acid also causes a decrease in the adsorption due to its active sites in allophane (Yu-Huang et al., 2016). DNA adsorption is higher on allophane than on silica and montmorillonite but lower on gibbbsite and goethite. The interaction of DNA and 5′-AMP with $(OH)Al(OH_2)$ groups present in the ultramicropores of allophane has also been studied through computer simulation, and has shown that DNA is elongated and that the main phosphate chain is altered after binding to allophane (Matsuura et al., 2014).

6.3 Sequestration, carbon stabilization and greenhouse control

As soils are the largest reservoir of carbon and organic matter, it is necessary to study their dynamics

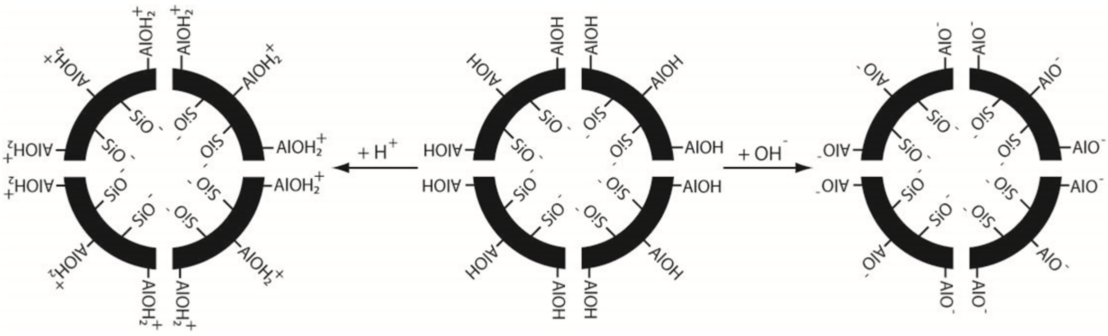

Figure 3. Superficial charge of allophane subjected to pH.

as well as their physical-chemical interactions with the main minerals present in them, due to the role as a CO_2 storage potential and key element to the greenhouse effect control (Huang and Rawlence, 2014; Triomphe and Livermore, 2005), as well as for the protection against mineralization and microbial degradation.

Carbon stabilization in allophane soils is difficult, as on the one hand it is attributed to Al^{3+} and sesquioxides, and on the other, there is a relationship between carbon and allophane content (Garrido-Ramírez et al., 2012), observing that the amount of linked organic matter is higher on imogolite material (proto imogolite, proto imogolite allophane) than on gibbbsite or non-weathered feldspar. This shows that non-crystalline (non-long range) minerals such as allophane and imogolite control the storage and movement of organic carbon in the soil (Yu et al., 2012). Stabilization of organic matter is produced by the adsorption on the specific surface area, protecting it from microbial disintegration.

In addition to surface adsorption, the entrapment of organic carbon into the fractal structure of allophane would make organic matter less accessible for microbial degradation and enzyme attack (Chevallier et al., 2010). This phenomenon is due to the mesoporous structure that occurs by the addition of allophane particles. The carbon variation in allophane is not explained by the loam and clay content; however, allophane, soil pH in water and aluminum content explains the greater carbon variation of the soil, observing an inverse relationship between the pH of the soil in water and Al (also Fe) with organic matter of the soil (Garrido-Ramírez et al., 2012).

6.4 Catalysis

6.4.1 Catalysis by Fenton-type reactions

Clays and iron oxide are an alternative to catalysts used in reactions (Fenton-type) for the decontamination of soils, water, sediment, and industrial effluents, because they are low cost, abundant and harmless. The processes of Fenton-type involve the reaction of Fe^{2+} with hydrogen peroxide, originating the formation of radical hydroxylones and Fe^{3+}. The Fe^{3+} reacts with peroxide forming Fe^{2+}, which generates more hydroxyl radicals that are highly oxidizing and capable of breaking down a wide spectrum of organic compounds. On this basis, methylene blue degradation has been studied using allophane coated with iron oxides, where allophane adsorbs methylene blue, while the interaction of the allophane Fe with hydrogen peroxide results in the formation of radicals, which break down methylene blue into smaller organic molecules (Abidin et al., 2011).

Iron oxide-coated allophane has also been evaluated for the oxidation of atrazine (1-chlorine-3-ethyl amino-5-isopropyl amino-2,4,6-triazine) in a heterogeneous electro-Fenton system, using vitreous carbon electrodes and showing greater efficiency than a heterogeneous Fenton process. Atrazine is an organic herbicide found as a pollutant in groundwater sources and drinking water supplies (Garrido-Ramírez et al., 2013). Garrido-Ramírez et al. (2012, 2016) have also evaluated the catalytic activity of iron oxides and copper oxides supported on allophane, as well as nanoparticles of Fe, Cu and bimetallic Fe-Cu for the oxidation of phenol by heterogeneous electro-Fenton reactions. In the first case, an influence of the Si/Al relationship and its structure was observed, while in the second case, a greater efficiency was evident when bimetallic nanoparticles were used compared to nanoparticles of Cu and Fe, due to a synergistic effect.

6.4.2 Photocatalysis

Photocatalysis is a remediation technique involving the adsorption of UV-visible radiation, which allows the degradation of organochlorine compounds. The degradation of trichloroethylene, a dangerous organic pollutant, and acetaldehyde in allophane-titanium composites has been studied (Nishikiori et al., 2010, 2015, 2017). The presence of allophane results in an increase in the adsorption of titanium and it inhibits the emission of phosgene ($COCl_2$) and dichloroacetyl chloride, which are intermediate products for the decomposition of trichloroethylene, which once adsorbed in the allophane are gradually degraded after moving in titanium. The photocatalytic activity of the composite improves with the treatment in the acid medium, which can be observed in the photocatalytic decomposition of gaseous acetaldehyde (Ono and Katsumata, 2014).

Hojamberdiev et al. (2014), used allophane-wakefieldite-(Ce) composites obtained by mechanical mixture and hydrothermal synthesis for the photocatalytic degradation of gaseous acetaldehyde, and found that both showed high photocatalytic activity compared to allophane or wakefieldite ($CeVO_4$)-(Ce) individually, because in the composites allophane produces an increase in the adsorption. The composite obtained by hydrothermal synthesis shows a greater photocatalytic activity than that obtained by mechanical mixture, due to a more homogeneous distribution of wakefieldite-(Ce) and allophane.

In another study, Hojamberdiev et al. (2014) use Bi_2WO_6–allophane and $BiOI$-allophane that were also obtained by mechanical mixing and hydrothermal synthesis for the photodegradation of gaseous acetaldehyde. BiOI and BiOI-allophane break down acetaldehyde completely within 5 to 7 hours, while Bi_2WO_6 and the composites obtained by mixture and synthesis break down 75.5%, 100% and 85.6% in 8 hours, respectively. Allophane also contributes to these composites due to the significant adsorption of acetaldehyde.

6.4.3 Heterogenous catalysis

The search for energy materials such as biomass is an option to fossil fuels. Polysaccharide hydrolysis is a process for obtaining monosaccharides, from which ethanol can be obtained. Okagi et al. (2011) studied hydrolysis of bamboo, silk and rice husks using sulfonated allophane. In bamboo, hemicellulose was decomposed to xylose and xylo-oligosaccharides; in silk the main products were xylose and mannose, although there was also a production of glucose, galactose and arabinose; in rice husk the main product was arabinose, although xylose and galactose were also obtained.

The degradation of compounds such as silicones or poly (dimethylsiloxane) in the presence of clays, as well as the effect of clay on the adsorption of degradation products has also been studied. In a study in which 12 different clays were used, allophane showed a lower effect on the catalytic activity compared to kaolinite, beidellite and nontronite, while degradation products were bound stronger to goethite and esmectite. The use of synthetic allophane also promotes the reduction of K_2PtCl to platinum (Pt^0) and it acts as a support for the Pt^0 nanoparticles of 2 nm, thus obtaining a composite with potential use in heterogeneous catalysis (Arakawa et al., 2014).

6.5 Photofuel cells

The use of photofuel cells to generate electricity by oxidizing combustible materials during UV irradiation is a trend in recent years. Electrodes in photofuel cells act as the phase that interacts with the combustible material. In these systems, the concentration of combustible material on the surface of the photocatalyst used is essential to improving energy conversion efficiency. One method for increasing concentration is the use of adsorbent materials. Taking advantage that allophane has a large surface area, Nishikiori et al. (2012, 2014) studied fuel cells using electrodes made from the allophane-titanium composite, and glucose and starch as combustible materials. In the first case, allophane adsorbs glucose transporting it to titanium, in which its oxidation induces the electrogeneration, in the case of starch it also improves the generation of electricity.

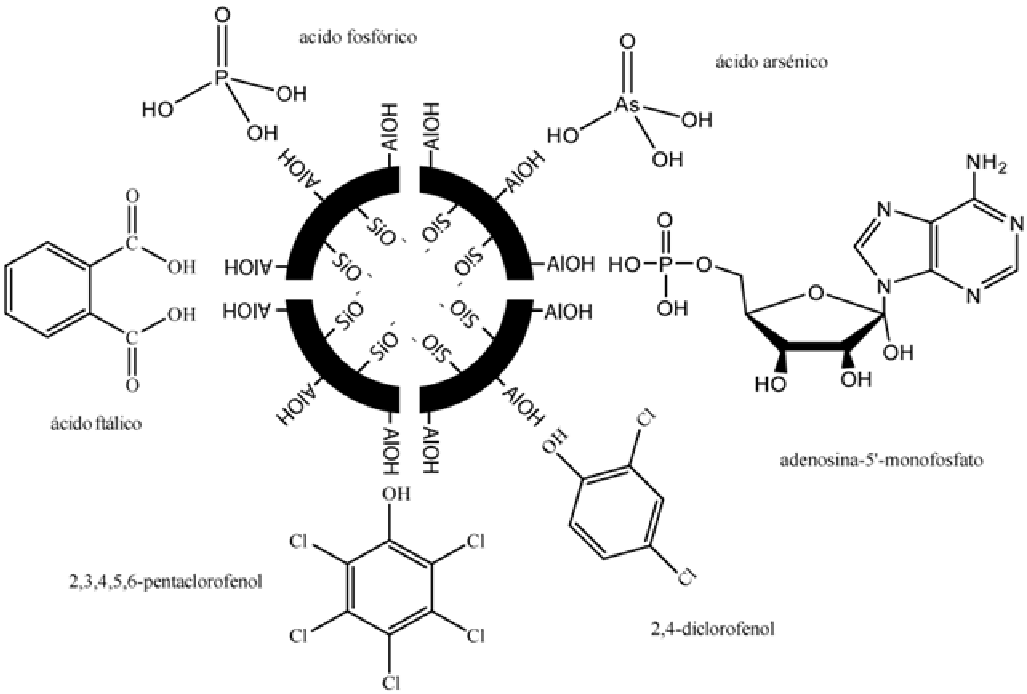

Figure 4. Diverse species adsorbed on allophane. The presence of OH groups in most of the studied species allows the exchange of ligands and the retention of allophane in the surface.

6.6 Farmacología

Clays have been used in cosmetics and industrial products, but their application is now expanding continuously in the pharmaceutical industry, tissue engineering and medical area. Since allophane is a non-toxic and biocompatible material, it is a good candidate for medical applications, as it has bactericidal properties that can be enhanced by the formation of nano-composites based on the immobilization of copper and silver nanoparticles, also with bactericidal properties. In this context, allophane has been used to support antibacterial agents such as silver nanoparticles, with strong bactericidal activity toward Escherichia coli and Staphylococcus aureus (Cervini-Silva et al., 2015). This effect is because silver exhibits strong bactericidal activity against a wide spectrum of fungal and bacterial species, in addition to low toxicity, high thermal stability and low volatility.

Allophane, and other clays such as halloysite, has anti-inflammatory properties because its application inhibits edema formation up to 39 to 60%. Even though Fe present in the allophane structure may have some role in this effect, the mechanisms have not yet been identified, hence its use for healing purposes can be recommended (Cervini-Silva et al., 2015, 2016). Natural allophane induces lipid peroxidation, oxidative degradation of lipids in cell membranes, and cytotoxicity of murine monocytes, which may be due to the presence of Fe in the surface and which may generate reactive oxygen species (Cervini-Silva et al., 2014, 2016; Toyota et al., 2017). These results have promoted studies of the cytotoxicity of natural and synthetic allophane nanoparticles against human cancer cells, with the intention of using allophane nanoparticles as a nanopower for drugs´ administration.

Kawachi et al. (2013), carried out a study of hydrogels based on DNA molecules and natural allophane, where DNA molecules adsorb on the surface, wrapping around the allophane particles and forming the hydrogel. Adsorption is facilitated by the interaction between the phosphate groups of DNAs and the groups present in the perforations of the allophane wall. The study of this type of hydrogel could be useful for the generation of new forms of drug release at specific doses.

6.7 Immobilization of enzymes

Due to its large surface area, allophane is a material that is a useful support for multiple species, including enzymes. In this way, allophane has been evaluated as a supporting material to immobilize acid phosphatase and evaluate the mineralization of organic phosphorus from decomposed cattle manure with clay complexes and nanoclay acid phosphatase. It has been observed that immobilization increases both the specific enzymatic activity and the kinetics of organic phosphorus mineralization (Calabi-Floody et al., 2012). Synthetic complexes have been obtained by the interaction between acid phosphatase, tannic acid and natural allophane in order to have a better understanding of organic phosphorus mineralization. Immobilization of phosphatase in tannic acid decreases enzymatic activity and affects kinetics, while immobilization in allophane increases the activity of the enzyme compared to the free enzyme, which would indicate that it has a protective effect on the enzyme's structure. In the case of Mn, the presence of Mn and Mo in the catalytic activity of immobilized acid phosphatase decreases the velocity compared with free phosphatase when added at the same time as the enzyme. However, no effects are observed when added after the interaction, not so for Mo, although the effect is minor when added after the clay enzyme interaction (Rosas et al., 2008).

Stabilization of the activity of two commercial microbial phytases after immobilization in synthetic allophane, iron oxide-covered allophane and natural montmorillonite have also been studied. Immobilization improves thermal stability and resistance to proteolysis, and the residual activity of both phytases was higher under acidic conditions (Menezes-Blackburn et al., 2011).

Nanomaterials have become ubiquitous materials, as there are commercial products containing some sort of nanoparticle (Heiligtag and Niederberger, 2013; Nguyen and S., 2020). In Ecuador, products containing nanomaterials are consumed, and in most of these cases these products are not generated, despite having higher education institutions capable of conducting research in this area and with a source that can provide these materials.

There is growing interest in the development of natural nanoproducts, for example, in phyto and nanotechnology, medicine, nutrition, cosmetics and agriculture (Griffin et al., 2018). In this context, allophane can be used as a reinforcement material for the design of degradable packaging; in agriculture for a controlled release of fertilizers; in medicine for the release of drugs; in the oil area as a nanofluid for the drilling of wells; as nanocatalysts in the refining of crude oil (Rashidi et al., 2018), and in the environmental area for the reduction of pollution (Wilson, 2018).

Multidisciplinary groups, lines, programs and research projects in the area of nanomaterials are needed, as well as the support of the corresponding agencies to conduct studies of this type of soil and of deposits with a significant concentration of natural nanoparticles.

7 Conclusions

National research on Ecuadorian volcanic soils has focused on issues that are not related to the allophane nanoparticle, and research on allophane has been observed in recent years. However, investigations are conducted by institutions located outside the country. Allophane has unique and versatile properties such as a big surface area, variable load, high moisture retention and high porosity. It can be extracted from natural sources, but can also be obtained by the different synthesis methods mentioned. It has application potentials for environmental remediation, oil extraction, catalysis, photocatalysis, electrocatalysis, smart packaging, nano sensors, enzyme support, drugs and fertilizers.

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