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Research paper

Layered titanosilicates JDF-L1 and AM-4 for biocide applications

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ABSTRACT

JDF-L1 and AM-4 are porous layered titanosilicates that can be modified by ion exchange while keeping the crystallinity. In this study, JDF-L1 and AM-4 were exchanged with Ag^+, Zn^{2+} and Cu^{2+} ions and characterized by XRD and TEM. JDF-L1 exchanged titanosilicate preserved the crystalline structure while AM-4 exchanged titanosilicate showed a certain loss of crystallinity. In the case of Ag-exchanged samples, the Ag nanoparticles were distributed at the edges of the JDF-L1 crystals whereas they were distributed around the AM-4 particles. The antimicrobial activity was tested with *Staphylococcus aureus*. All the exchanged titanosilicates showed good antimicrobial activity against the bacteria and the most active was Ag–AM-4.

1. Introduction

Metal cations and especially silver ions were long used to prevent or treat infections. Around 1000 B.C., silver was used to produce potable water (Castellano et al., 2007; Richard et al., 2002). In the 18th century, silver nitrate was employed for the treatment of different microbial infections such as venereal diseases, fistulae from salivary glands, bone and perianal abscesses (Klasen, 2000; Landsdown and Williams, 2007). In 1800, silver nitrate was also applied to remove granulation tissues. This allowed epithelization to take place and the formation of a crust on the surface of wounds. Moreover, silver nitrate was also recognized as a good tool to treat fresh burns (Castellano et al., 2007; Klasen, 2002). During World War II, penicillin was widely introduced and the use of silver as antimicrobial agent diminished (Demling and DeSanti, 2001; Hugo and Russell, 1982). Nevertheless, due to the emergence of antibiotic-resistant bacteria and the stronger control of the use of antibiotics (Chopra, 2007; Gemell et al., 2006), silver recently regained importance as an antimicrobial.

Different forms of silver were found in the literature. Silver nanoparticles showed antimicrobial properties that were size-dependent. The smaller they were, the greater their bactericidal effect due to their better ability to penetrate the bacteria (Morones et al., 2005; Panacek et al., 2006). Silver sulfadiazine was reported as a good reservoir from which silver was slowly released (Rai et al., 2009). The action mechanism of silver ions is not yet well known. Although different mechanisms were proposed, silver ions on bacteria effected several morphological and structural changes in the cells: (i) by interacting with the peptidoglycan and lipids of the cell membrane, silver inhibited the respiration chain and, in this way, reactive oxygen species (ROS) were generated, which could damage the bacterial cell itself (Matsumura et al., 2003); (ii) by binding of the silver ions to DNA phosphate groups the functions of replication and transcription could be lost. When the silver ions penetrated inside the bacterial cell, the DNA molecule turned into a condensed form to protect itself limiting of the replication ability and finally leading to cell death (Feng et al., 2000); and (iii) silver ions interacting with thiol groups to proteins and enzymes inhibiting their functions (Matsumura et al., 2003).

Clay minerals are abundant and versatile materials that can be assembled in nanometer scale to a large diversity of organic compounds yielding nanostructured hybrid materials, by mechanisms ranging from ion exchange to covalent bonding, with growing applications in environment and biomedicine (Ruiz-Hitzky et al., 2010).

Other antimicrobial materials used were TiO_2, ZnO and copper nanoparticles. TiO_2 was used as a semiconductor catalyst activated by UV radiation and, in this way, producing ROS, so that the antibacterial action was inhibited (Kikuchi et al., 1997). ZnO nanoparticles also showed a wide range of antibacterial activity on a large amount of bacteria but their mechanism is yet less understood than that of silver and silver ions (Sawai, 2003). Copper nanoparticles were embedded in particles of sepiolite but the anti-bacterial activity was lower than that of silver nanoparticles (Dastjerdi and Montazer, 2010).

Other antimicrobial materials were silver-exchanged zeolites (Lalueza et al., 2011; Matsumura et al., 2003), where even very low concentrations, such as 0.2 mass % silver in silver-exchanged ZSM-5, caused bactericidal activity (Lalueza et al., 2011). Other zeolite

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related materials like titanosilicate ETS-10 (Lv et al., 2009) were reported, where the antibacterial action could be produced by both factors mentioned above. Novel titanosilicate frameworks such as JDF-L1 and AM-4 are microporous lamellar materials, the structure consists of layers with Na^+ exchangeable cations situated in the interlayer space (Lin et al., 1997; Rocha and Anderson, 2000). JDF-L1 was used in mixed matrix membranes improving the H_2/CH_4 separation but showing a barrier effect when performing in the separation of O_2/N_2 mixtures (Galve et al., 2011). These titanosilicates could have potential application in active antimicrobial food packaging, as other nanoclays have (Sanchez-Garcia et al., 2010).

JDF-L1 is an unusual non-centrosymmetric tetragonal layered solid that contains five-coordinated Ti(IV) ions in the form of TiO_5 square pyramids in which each of the vertices of the base is linked to SiO_4 tetrahedra $[TiOO_4(SiO_3)_4]$ to form continuous layers (Roberts et al., 1996) (Fig. 1A).

AM-4 is built of TiO_6 (M) octahedra and SiO_4 (T) tetrahedra that form layers perpendicular to [001]. Each layer consists of a five-tier sandwich of T–M–T–M–T. Between the layers there are Na^+ cations and water molecules. The Na^+ ions are also found in small cages within the layers. The major features of the structure are zig-zag chains of edge-sharing TiO_6 octahedra running along the [100] direction that are connected by corner-sharing pyroxene-type SiO_4 tetrahedra (Dadachov et al., 1997) (Fig. 1B).

The corresponding ion exchange process could be improved by using small sized crystals of these materials. The size of the crystals of both JDF-L1 and AM-4 was reduced in the laboratory by secondary growth methods, by varying seeding, Ti source and shortening the synthesis time (Casado et al., 2011; Rubio et al., 2009). In general, the ion exchange process is low cost and easily scalable.

Metal particles were used for different applications: (i) water disinfection and microbial control (Li et al., 2008); (ii) impregnation of medical devices and surfaces (Wilcox et al., 1998); (iii) wound dressing, by releasing silver in different concentrations (Chopra, 2007); and (iv) textile fibres prepared with silver nanoparticles were able to produce antibacterial action against *Staphylococcus aureus* (*S. Aureus*) (Durán et al., 2007).

The bacteria more commonly used in antibacterial assays are *Staphylococcus epidermidis, S. Aureus, Pseudomonas aeruginosa,* and *Escherichia coli.* All of them are opportunistic pathogens. Particularly, *S. Aureus* strains cause biofilm formation. Biofilms consist of communities of bacteria that have colonized a surface and lived imbued in extracellular polymeric substances that protect them from antibiotic effects (Monteiro et al., 2009). The use of metal ions could thus be a good strategy to eliminate infections.

In this study, the porous layered titanosilicates JDF-L1 and AM-4 were modified by ion exchange with Ag^+, Zn^{2+}, and Cu^{2+}. The antimicrobial capacity was tested against *S. Aureus*.

2. Experimental

2.1. Synthesis of JDF-L1

JDF-L1 was synthesized as reported elsewhere (Rubio et al., 2009) by hydrothermal crystallization at 230 °C for 24 h in a 35-mL Teflon lined stainless steel autoclave. A typical synthesis procedure was as follows: the silicon source, sodium silicate solution (10.05 g, 27 mass % SiO_2, 8 mass % Na_2O, Merck), deionized water (1.65 g), NaOH (1.43 g, 99.0 wt.%, Scharlab) and 8.24 g of $TiCl_3$ solution (20 mass% in 3 wt.% HCl, Alfa Aesar) were added under continuous mechanical agitation. The reaction mixture was seeded by 0.5 mass% seeds (107 mg), which were obtained by grinding a previously synthesized JDF-L1 prepared with the same gel composition at 230 °C for 96 h. Once the precursor solution was homogenous, it was introduced into an ultrasound bath before being placed in an autoclave. The product was washed 3 times with distilled water in a centrifuge (Beckman Coulter Allegra(R) X-15R centrifuge) at 9500 rpm for 15 min each. The samples were dried overnight at 90 °C. An amount of 3.5 g JDF-L1 was obtained.

2.2. Synthesis of AM-4

AM-4 was synthesized from the same silicon source as JDF-L1 with TiO_2 anatase (nanopowder<25 nm, Aldrich) as the titanium source, as reported elsewhere (Casado et al., 2011). The procedure was as follows: 10.05 g sodium silicate solution was mixed with 6.55 g deionized water, 1.43 g NaOH (99 mass%, Scharlab) and 0.85 g TiO_2 anatase, under mechanical agitation until homogeneity was achieved. The synthesis gel was seeded by 0.45 mass% of previously made and carefully ground AM-4 crystals (85 mg). The precursor solution was dispersed in an ultrasound bath for a few minutes before being placed in the autoclave for hydrothermal synthesis. The reaction proceeded at 230 °C for 6 h. The product obtained was washed and dried overnight at 90 °C. An amount of 2.4 g of AM-4 was recovered.

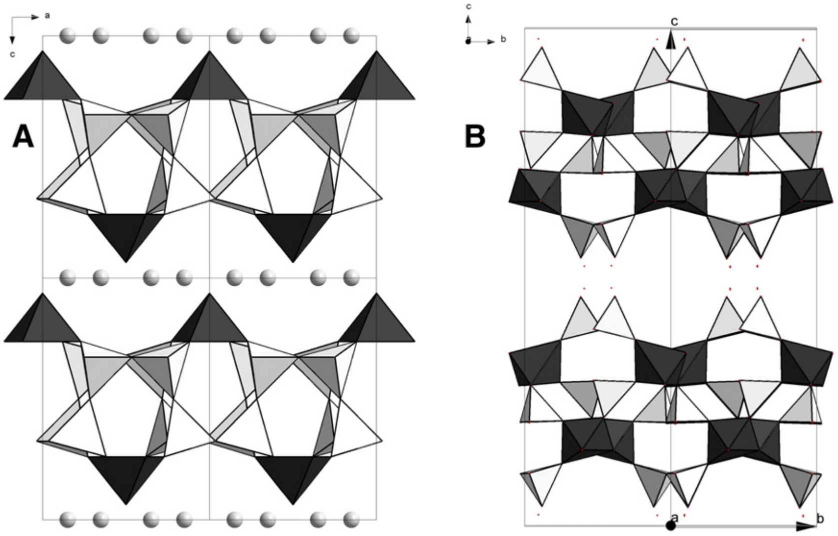

Fig. 1. (A) Projection of the JDF-L1 structure along the [010] direction and (B) projection of the AM-4 structure along the [100] direction. Si atom, white; Ti atom, dark grey: O, light grey; the exchangeable Na^+ ions were omitted for clarity (drawn using DIAMOND 3.2, with the required crystallographic data from the literature (Dadachov et al., 1997; Roberts et al., 1996)).