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Research paper

ZnAl layered double hydroxides impregnated with eucalyptus oil as efficient hybrid materials against multi-resistant bacteria

Marta Lobo-Sánchez[a], Gisel Nájera-Meléndez[a], Gilberto Luna[a], Verónica Segura-Pérez[a], José Angel Rivera[b], Geolar Fetter[a,*]

[a] Benemérita Universidad Autónoma de Puebla, Facultad de Ciencias Químicas, Blvd. 14 Sur y Av., San Claudio, Ciudadela Universitaria, 72570, Puebla (PUE), Mexico
[b] Yachay Tech, The School of Chemical Sciences and Engineering, Yachay City of Knowledge, 100119 Urcuqui, Ecuador

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ABSTRACT

Bacterial contamination poses a serious hazard for human health. The use of bactericidal materials, such as layered double hydroxides, might constitute a way to reduce the risk of diseases. In this work, ZnAl layered double hydroxides were synthesized by microwave irradiation at different pH values and various metal molar ratios to be tested against multi-resistant bacteria. The synthesis conditions were chosen to form, in some cases, a composite containing zincite (ZnO), as both materials, zincite as well as the layered double hydroxide, are well known to be efficient antimicrobials.

Eucalyptus extracted oil, which is a bactericidal compound, was extracted from eucalyptus leaves and used to impregnate some layered double hydroxide–zincite composites. The materials were characterized by X-ray diffraction, infrared spectroscopy, nitrogen physisorption and scanning electron microscopy. The samples were tested against *Staphylococcus* sp. and *Pseudomonas aeruginosa*, which are multi-resistant bacteria. It was found that Zn/Al molar ratio, pH and inclusion of eucalyptus oil in the layered double hydroxides synthesis determined the bactericidal activity. The best performing samples were those containing eucalyptus oil, which, at very low concentrations, were able to kill *Staphylococcus* sp. and inhibit the *Pseudomonas aeruginosa* growth.

1. Introduction

Recent epidemiological studies have shown a continuous increase in infections caused by multi-resistant bacteria. The bacterial resistance has been recognized by the OMS as one of the greatest threats to human health. These microorganisms, immersed in dust or aerosol particles, can be present in the atmosphere, having the possibility to move easily from one place to another and remain alive during long periods of time (Höppe and Martinac, 1998). The bacteria most frequently isolated from the air are *Pseudomonas* sp. and *Staphylococcus* sp. These bacteria have the genetic ability to transfer and acquire resistant genes to antimicrobials among other chemical bactericides. They are not altered by penicillin and some strains are methicillin-resistant (Boucher and Corey, 2008). Furthermore, these bacteria are able to grow on fuels such as kerosene or diesel, since they are microorganisms able to nourish from hydrocarbons (Margesin et al., 2003). *Staphylococci* and *Pseudomonas aeruginosa* can produce infections related to joint or vascular prostheses, catheters and other medical devices. They can cause diseases as meningitis, endocarditis or pneumonia (Fahlgren et al., 2010; Liang et al., 2013).

The common control methods to remove bacteria from air are physical methods, such as ultraviolet or ionizing radiation, but they are costly and they can produce ozone and radicals causing harmful effects to humans (Cheng et al., 2012). Chemical methods, such as chlorine and its derivatives, are often used, but they may form toxic and carcinogenic by-products (Poyatos et al., 2010). Currently, inorganic solids as zeolites, clays, mesoporous silica or metal oxides impregnated with heavy metals, such as silver, zinc or copper have become widely used against pathogenic microorganisms. (Ballarin et al., 2015; De la Rosa-Gómez et al., 2008; Demirci et al., 2014; Kim et al., 2002; Raghupathi et al., 2011; Salim and Malek, 2016; Savvova, 2014). These solids exhibit high bactericide properties due, in part, to their high surface areas that provide a good contact with microorganisms; however, the main factor is their chemical composition (Qu et al., 2013; Rai et al., 2009). It has been shown that the inorganic supports also contribute to bacterium elimination, especially when the supports present a basic character (Huang et al., 2005; Tousley et al., 2012). Layered double hydroxides (LDH), also referred as hydrotalcite-like compounds or hydrotalcites, are anionic clays and, consequently, are basic materials. They are constituted by the stacking of layers which are charged

* Corresponding author.
E-mail address: geolarfetter@yahoo.com.mx (G. Fetter).

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positively due to isomorphs substitutions of some M^{2+} by M^{3+} metals. Between layers, anions, usually hydrated, are present to neutralize the charge of the layers. The general chemical formula is:

$$[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2](X^{m-})_{x/m}\cdot nH_2O$$

where M^{2+} and M^{3+} are divalent and trivalent metals, respectively. X^{m-} is a compensating anion with charge m^-; x represents the metal ratio $M^{3+}/(M^{3+} + M^{2+})$ and n is the number of water molecules.

The M^{3+} and M^{2+} nature and its ratio are important factors that determine the LDH properties (Rivera et al., 2007). Indeed, depending on their cationic sizes, there is a great number of cations that can form LDH. There are almost no limits to the types of anionic species that can integrate the structure, due to the layer expansion ability of these clays (Evans and Slade, 2006). Thus, many bactericidal compounds can be integrated to the LDH as interlayered species or adsorbed on their surfaces to form hybrid materials.

As bactericidal materials, layered double hydroxides have several advantages if compared to other compounds, the most important being the basic character, due to the hydroxides (OH^-), and the nature of the metallic cations, where Zn^{2+} is one of the most active one, due to its strong oligodynamic feature (Malachová et al., 2011; Santo et al., 2008). The Zn^{2+} ions have a significant effect on the nourishment transport inhibition as well as on the bacterium metabolism. Furthermore, these ions can cause the disruption of the cell wall and membrane (Huang et al., 2008). Hydroxide ions are strong oxidant species that show extreme reactivity against several microorganisms. Its lethal activity is thought to cause protein denaturation and damage in the bacterium DNA or in the cytoplasmic membrane (Siqueira and Lopes, 1999). Also, hydroxides can absorb water to create hydroxyl radicals and, in presence of oxygen, generate superoxide ions that damage the bacterium cell (Buzea et al., 2007).

In spite of the possible applications of the LDH as bactericidal materials, publications on this subject are scarce. Sunayama et al. (2002) reported the use of layered double hydroxides containing antimicrobial metals (copper or zinc) against *Escherichia coli*, *Staphylococcus aureus* and *phage Q β* in water medium. The activity depended on the basicity and the M^{2+} metal nature, Cu-LDH was very active against *E. coli* but not against *S. aureus* which is a very resistant bacterium. Even the Zn-LDH had a low activity with a survival rate for *S. aureus* of only 95% using 16.7 mg of Zn-LDH per mL of water, after 120 min of exposure time. These results indicate that their Zn containing LDH possessed a slight disinfection effect against *S. aureus*. More recently, Rocha Oliveira et al. (2015) reported the performance of chlorophyllin-copper LDH against bacteria present in industrial waste-water. The bactericide effect of these materials depended on the copper released from the LDH structure to the bactericidal medium, as well as on the chlorophyllin and LDH basicity. Note that the activity of the LDH increases when a bactericide compound is adsorbed on its surface. In this sense, the eucalyptus oil and its main component, the eucalyptol (1,8-cineole), are highly active against bacteria, virus or fungi. (Bachir and Benali, 2012; De Vincenzi et al., 2002; Hendry et al., 2009; Morcia et al., 2012; Pereira et al., 2014). The eucalyptus oil is an important ingredient in soaps, cosmetics or drug formulations and can be easily extracted from eucalyptus leaves (Baratta et al., 1998; Sacchetti et al., 2005). In this sense, this organic compound should increase the bactericidal activity when integrated to LDH materials.

In this work, ZnAl-layered double hydroxides were synthesized in presence of microwave irradiation at various Zn/Al molar ratios and precipitation pH values. Some samples were prepared in presence of eucalyptus oil extracted from eucalyptus leaves to promote the LDH anti-bacterial activity. The samples were tested against *Staphylococcus* sp. and *Pseudomonas aeruginosa,* multi-resistant bacteria which are very dangerous to human health.

2. Experimental

2.1. Eucalyptus oil

Fresh eucalyptus leaves were washed and dried in an oven at 50 °C for 3 days. They were grounded in a food processor and the resulting flakes were then mixed with ethanol (Alpha 99%) or acetone (Aldrich, 99%). Acetone and ethanol differ in their polarity degree and consequently in their extraction features; thus, different oil compositions could be expected. The mixtures were maintained under stirring at room temperature for 3 days. The eucalyptus essence oils were separated from the solid leave waste by filtration. They were stored in amber flasks to protect them from light.

2.2. Layered double hydroxides synthesis

2.2.1. Materials

Magnesium (Sigma-Aldrich, 99%), zinc and aluminum nitrates (Sigma-Aldrich, 98%) were used as the reactants to synthesize the layered double hydroxides. Sodium hydroxide (Merck, 99%) was used as the precipitating agent.

2.2.2. Samples

2.2.2.1. ZnAl layered double hydroxides. Three samples were synthesized by dropping simultaneously a Zn- and Al-nitrate aqueous solution (2.5 mol L^{-1}) and a sodium hydroxide solution (2.0 mol L^{-1}), adjusting the dropping flow of each solution to maintain a constant pH of 7.5. The solution amounts corresponded to Zn/Al molar ratios of 2, 3 and 4. The resulting mixtures were treated in a microwave autoclave (MIC-I, Sistemas y Equipos de Vidrio S.A. de C.V.) operating at 2.45 GHz for 10 min. The microwave equipment consists of a glass reactor of 500 mL, which fits in a microwave chamber. An impeller-type stirring mechanism is adjusted to the reactor so that the temperature turns out to be the same all over; it is controlled through an infrared radiation sensor. The power was fixed at 200 W and the temperature at 80 °C. After, the solids were recovered by decantation and washed with distilled water until the pH of the supernatant water was 7. The solids were dried overnight in an oven at 70 °C. They were labeled as ZnAl-2, ZnAl-3 and ZnAl-4 after their Zn/Al molar ratios. A fourth sample was prepared similarly to the ZnAl-3 only differing in the co-precipitation pH; in this case, it was 10, sample ZnAl-3-10. It is known that the synthesis of ZnAl layered double hydroxides is highly dependent on the co-precipitation pH and it has to be lower than 9 to obtain almost pure layered double hydroxides. With higher pH values, ZnO is formed (Cavani et al., 1991). In the present work, the ZnAl-3-10 sample was deliberately prepared at pH 10 to form a solid composed by layered double hydroxides and a high amount of zinc oxide, indeed, this compound was reported to be an efficient bactericidal material (Raghupathi et al., 2011; Xie et al., 2011) and thus, it could increase the activity of the HDL.

2.2.2.2. Hybrids eucalyptus oil-ZnAl layered double hydroxides. Two samples were synthesized by dropping simultaneously a Zn and Al nitrate solution (2.5 mol L^{-1}), a sodium hydroxide solution (2.0 mol L^{-1}) and 50 mL of the eucalyptus oil in ethanol or acetone dissolvent. The amount of eucalyptus essence oil corresponded to *ca.* 5.0 mg g^{-1} of the layered double hydroxides and was calculated following the considerations reported in previous works (Rocha Oliveira et al., 2015; Sommer Márquez et al., 2014). The pH was maintained constant at 10 by adjusting the flow of each solution. The obtained slurry was treated in an ultrasound vessel at 25 °C for 20 min. This treatment was already reported to crystallize LDH (Paredes et al., 2011) and it was used here instead of the microwave method to avoid eucalyptus essence degradation. The solids were recovered by precipitation, washed and dried at the same conditions described above. The hybrid samples were labeled Euc/et-ZnAl and Euc/ac-

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