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Antimicrobial behavior of ion-exchanged zeolite X containing fragrance

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ABSTRACT

Microporous zeolites are aluminosilicates composed of silicon, aluminum, and oxygen in a framework with cations. The cation contents can be exchanged with metal ions in order to add antimicrobial (antibacterial, anticandidal, and antifungal) properties. Zeolites has also recently been acquainted with fragrance applications to tailor products with controlled release properties. Here, a new application of ion exchanged zeolite X combined with adsorption properties is presented. In this study, zeolite X crystals were ion-exchanged with Zn^{2+} and Cu^{2+} ions and encapsulation of a fragrance molecule, triplal, was studied using ion-exchanged zeolite X as a fragrance carrier. The antimicrobial behavior of ion-exchanged zeolite X before and after encapsulation were investigated by disc diffusion method. Zn^{2+} and Cu^{2+} loaded zeolite samples showed excellent antimicrobial activities against three bacteria *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa*, a yeast *Candida albicans* and a fungus *Aspergillus niger*. Ion-exchanged zeolite X samples containing triplal sustained antimicrobial activities after the encapsulation process.

1. Introduction

Zeolites are crystalline hydrated aluminosilicates with three-dimensional structures consisting of $[AlO_4]^{5-}$ and $[SiO_4]^{4-}$ sharing their oxygens. The substitution of Al^{3+} for Si^{4+} results in negatively charged aluminosilicate lattice, which needs to be balanced by extraframework cations, generally Na^+, K^+, and Ca^{2+}. These cations are movable and exchangeable by other metal ions [1–3].

Zeolites are used extensively as catalysts, ion-exchangers, molecular sieves and adsorbents [4,5]. Recent studies have been suggesting that the zeolite crystals can encapsulate/trap a large number of small molecules in their channels or cage-like structures for application of as a perfume delivery system [6–8]. These studies asserted that after washing process, zeolites continue to release fragrance when exposed to heat and/or humidity.

It has been long known that heavy metals such as silver, zinc, copper, mercury, tin, lead, bismuth, cadmium, chromium, and thallium have antibacterial properties. In the last two decades, several investigations concerning the use of zeolites have shown that zeolites ion-exchanged with these metals add antibacterial activity to both synthetic and natural zeolites [9]. Silver, zinc, copper and other antibacterial metals loaded onto zeolites are released slowly and act as inorganic bactericide and disinfectants, which are excellent in terms of safety and thermal stability when compared to organic ones [10]. Especially, silver, zinc and copper exchanged zeolites have been under investigation in recent years. Rivera-Garza et al. reported that silver loaded Mexican clinoptilolite-heulandite reduced the pathogenic microorganisms, *Escherichia coli* and *Streptococcus faecalis* from water [11]. Apart from natural zeolites, synthetic zeolites have also been targeted for antibacterial use by cation exchange process. Antimicrobial activity of faujasite (FAU) zeolites (NaY and NaX) loaded with silver was reported by Ferreira et al. [12]. However, there are some disadvantages of Ag^+ exchanged mineral as antimicrobial material. It is expensive and, Ag^+ is not stable in aqueous solution and tends to be reduced to Ag^0 when exposed to light or heat. Ag^+ also reacts with anions commonly present in water, and forms insoluble compounds, which may result in loss of its antibacterial activity [13].

As an alternative to silver exchanged forms of zeolites, zinc and copper loaded zeolites have also significant effects against the microorganisms. Zinc is a vital antioxidant and anti-inflammatory agent in the human body. Although a small quantity of zinc ion is essential for numerous metabolic activities, it becomes toxic for

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Table 1
Properties of commercial zeolite X[a].

SiO_2/Al_2O_3	Mean particle size (μm)	Surface area (BET, m^2/g)	Pore volume (cm^3/g)
2.4	3–5	593–699	198

[a] Data is provided by Luoyang Jianlong Chemical Industrial Co.

Table 2
Summary of ion exchange procedure.

Cation source	Concentration of ion-exchange solution (M)	Amount of ion-exchange solution (mL)	Amount of zeolite X (g)	Mixing rpm	Mixing time (h)
$ZnCl_2$	1	1000	125	500	24
$CuSO_4 \cdot 5H_2O$	1	1000	80	500	24

most of the living organisms at higher concentrations [14–16]. Zinc-exchanged zeolites have been used in biomedical applications due to their wound healing and bactericidal properties. Cerri et al. used clinoptilolite-rich rock with exchanged zinc as active carrier for antibiotics in anti-acne therapy [17,18].

Similar to zinc, copper is an essential metal for living organisms at low concentrations, but it is toxic to most microorganisms and reduces bacterial growth at high concentrations [19,20]. Hence, copper compounds such as $CuSO_4$ and $Cu(OH)_2$ are widely used inorganic antibacterial materials [13].

Escherichia coli is an indicator of fecal contamination of water [12]. *E. coli* leads to inflammation of the colon and cause diarrhoea and abdominal pain with bloody stools [21]. *Pseudomonas aeruginosa* and *Staphylococcus aureus* are prevalent nosocomial pathogens generally implicated in colonization of medical devices including vascular lines, endotracheal tubes and urinary catheters [22]. Antibacterial activities of the Cu^{2+} and Zn^{2+} exchanged natural zeolites against *Escherichia coli* and *Staphylococcus aureus* were tested by Hrenovic et al. [23]. It was reported that Cu^{2+} and Zn^{2+} exchanged natural zeolites reduced the bacterial numbers for six orders of magnitude in effluent water. Ag^+, Zn^{2+}, and Cu^{2+} forms of natural zeolite, clinoptilolite, were examined for the antibacterial activity against *Escherichia coli* and *Pseudomonas aeruginosa*. Ag^+, Zn^{2+}, and Cu^{2+} exchanged Na-clinoptilolite showed inhibitive effect against those microorganisms [24].

Similar to antibacterial effect, antifungal activity of Ag^+, Zn^{2+}, and Cu^{2+} exchanged montmorillonite was explained by Malachová et al. [25] based on the interactions of released metal ions with the bacteria and fungus. Most recently, antimicrobial (antibacterial, anticandidal, and antifungal) properties of zeolite X and A, ion exchanged with Ag^+, Zn^{2+}, and Cu^{2+} ions were studied by Demirci et al. [26]. They tested the antimicrobial characteristics of various synthetic zeolites exchanged with Ag^+, Zn^{2+}, and Cu^{2+} ions against bacteria, yeast, and mold.

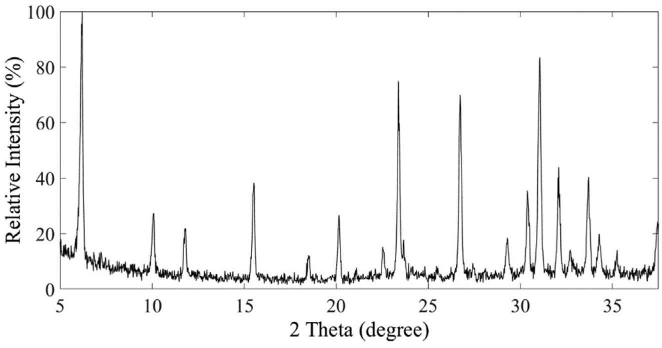

Fig. 1. XRD patterns of commercial zeolite X.

Triplal is a powerful green odorant widely used in fragrance, beauty care, soap, laundry care, and household products to enrich grassy notes. Triplal, with an IUPAC name 2,6-dimethylcyclohex-2-ene-1-carbaldehyde, is a colorless liquid and exhibits high volatility [27,28]. The three-dimensional model of triplal was generated using the Spartan08 Software [29]. Geometry of the specie was pre-optimized by using semi-empirical calculations based on PM3 method [30]. Triplal molecule and quantitative structure–activity relationship (QSAR) properties are given in Table 1 [29]. The maximum distance between atoms of triplal was measured to be ~6.9 Å [31]. Faujasite (FAU)-type zeolite X has a considerable potential in adsorption applications due to its large pore size with a diameter 7.4 Å [31–33]. For this reason, zeolite X crystals may be suitable hosts for triplal molecules.

Within the scope of this study, a new application of ion-exchanged zeolite X combined with adsorption properties is presented. Product purity was confirmed using X-ray powder diffraction (XRD) and crystal/particle morphology and size distribution were determined using scanning electron microscopy (SEM) before the ion-exchange and encapsulation experiments. Zeolite X crystals were ion exchanged with Zn^{2+} and Cu^{2+} ions and antimicrobial behavior of ion-exchanged form of zeolite samples were investigated by disc diffusion method against 3 bacteria including *Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus*, 1 yeast *Candida albicans* and 1 fungus *Aspergillus niger.*

2. Materials and methods

2.1. Materials

Zinc chloride anhydrous, $ZnCl_2$ (Carlo Erba Reagents), copper sulfate pentahydrate, $CuSO_4 \cdot 5\ H_2O$, (BDH), commercial zeolite X, (Luoyang Jianlong Chemical Industrial Co.), triplal (EPS Fragrances).

2.2. Ion-exchange of zeolite X

1 M $ZnCl_2$, and 1 M $CuSO_4 \cdot 5\ H_2O$ ion exchange solutions were prepared. Zeolite X samples were put into contact with these solutions, separately and mixed for 24 h at room temperature. Experimental parameters were shown in Table 2. Cation exchanged zeolites were dried at 90 °C and were ground using a mortar and pestle. Ion exchange process for copper and zinc zeolites can be expressed as the following equations:

$$\mathrm{Na-Z+ZnCl_{2(aq)} \rightarrow Zn-Z+NaCl} \tag{1}$$

$$\mathrm{Na-Z+CuSO_4 \rightarrow Cu-Z+Na_2SO_4} \tag{2}$$