Antibacterial and mechanical properties of honeycomb ceramic materials incorporated with silver and zinc

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\textbf{Abstract}

The antibacterial and mechanical properties of heat-resistant honeycomb ceramic materials produced from red mud industrial waste and doped with Zn and Ag are determined. Excellent antibacterial effects against \textit{Escherichia coli} are obtained by the plate counting and vibration methods. When 5% and 6% Zn are added to the honeycombs doped with 0.3% Ag, the antibacterial rates reach 98.9% and 99.5%, respectively. The mechanical properties are evaluated by monitoring the bending strength, open porosity, water absorption capability, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The Zn and Ag particles are distributed uniformly in the honeycomb ceramics and the crystalline structure of the ceramic materials is not altered after Zn and Ag incorporation consequently enabling good dispersion of the antibacterial metals.

\textbf{1. Introduction}

Much attention is paid to problems associated with environmental pollution and health nowadays and antibacterial materials are needed in many fields such as sewage disposal, biomedical engineering, environmental protection and buildings\([1–11]\). Heavy metals such as silver, zinc, copper, mercury, tin, lead, bismuth, cadmium, chromium, and thallium are known to possess antibacterial properties and incorporation of these metals into zeolites produces antibacterial activity\([12]\). The in vitro antibacterial activity against multi-resistant bacteria and in vitro cytotoxicity of polymethylmethacrylate bone cement loaded with metallic silver particles with a size of 5–50 nm called NanoSilver were investigated\([13]\), and Balamurugan and Balossier\([14]\) evaluated the in vitro antibacterial and biological activity of silver-incorporated bioactive glass SiO\(_2\)-CaO-P\(_2\)O\(_5\)-Ag\(_2\)O (AgBG). Silver (Ag) was introduced into polyethylene terephthalate (PET) by the filtered cathodic vacuum arc (FCVA) technique\([15]\) and Shi et al.\([16]\) investigated the use of chitosan nanoparticles (CS NP) and quaternary ammonium chitosan nanoparticles (QCS NP) as bactericidal agents in poly(methyl methacrylate) (PMMA) bone cement with and without gentamicin. De la Rosa-Gómez et al.\([17]\) compared the effects of water disinfection between \textit{Escherichia coli} (ATCC 8739) and total coliform micro-organisms from synthetic wastewater or municipal wastewater and the anti-bacterial activity of silver-modified clinoptilolite–heulandite rich tuff (ZS Ag) was studied. Hernández-Sierra\([18]\) compared the bactericidal and bacteriostatic effects of silver, zinc oxide, and gold nanoparticles on S. Mutans by employing the liquid dilution method and determined the minimum inhibitory concentrations (MICS) using subcultures to obtain the minimum bactericidal concentrations (MBCs). The influence of particle size on the antibacterial activity of ZnO powders was investigated using different particle size ranging from 0.1 to 0.8 mm\([19]\). By measuring the change in the electrical conductivity with bacterial growth, it was found that the antibacterial activity of ZnO increased with smaller particles and larger powder concentrations. Li and Hong\([20]\) found significant improvement in the Young’s modulus and tensile strength of PU films by incorporating ZnO nanoparticles to up to 2.0 wt% and the abrasion resistance of the PU coats was greatly enhanced after addition of ZnO nanoparticles. Osinaga and Grande\([21]\) evaluated the effects of ZnSO\(_4\) addition to a conventional glass ionomer and resin-modified glass ionomer on the solubility, flexural strength, zinc and fluoride release, as well as \textit{Streptococcus mutans} growth inhibition.

The objective of this study is to determine the effects of inorganic antibacterial agents on honeycomb ceramic materials as shown in Fig. 1. The antibacterial properties and mechanical behavior are evaluated systematically.
2. Experimental procedures

Red mud (RM) was chosen as the raw materials to produce heat-resistant honeycomb ceramics containing two inorganic antibacterial agents, Ag⁺ and Zn²⁺. Based on previous results, the optimal honeycomb ceramic samples were produced. The mixtures containing the perform body and custom-made inorganic antibacterial agents in different proportions were used and an economical and efficient technique, wet ceramic powder process in conjunction with co-firing, was employed to fabricate the antibacterial ceramic materials.

The antibacterial performance was assessed on samples with dimensions of 2 mm³ and weighing 1–2 g. The experiments involving the nutrient broth culture medium (NB), nutrient agar culture medium (NA), eluent and bacteria suspension, culture preservation, and activation of culture were performed according to GB/T 21551.2-2010 [22]. Fig. 2 illustrates the antibacterial tests. The antibacterial efficacy against *E. coli* was measured by the vibration and plate counting methods. Initially, the samples, including the reference, were soaked in 70% ethanol for 1 min, washed with sterile water, and dried naturally. After high-temperature humid or dry sterilization, the samples were transferred to sterilized petri dishes to which 0.2 ml of the bacteria suspension was introduced. Three samples from each group were tested to improve the statistics. The samples were transferred to sterilized conical flasks and sealed while making good contact with the bacteria suspension in a constant-temperature 80 rpm bath oscillator for (24 ± 1) h at (37 ± 1) °C and RH (relative humidity) of over 90%. Afterwards, 20 ml of the eluent were taken to a conical flask and the samples were washed repeatedly. The eluent after gradient dilution was inoculated in the agar culture medium (NA) and cultured at (37 ± 1) °C for 24–48 h. The bacteria counting method according to GB/T 21551.2-2010 [22] was utilized to determine the number of living bacteria in the eluent. The antibacterial rate was calculated according to the following formula:

\[
R = \frac{(B - A)}{B} \times 100 \%
\]

where \(R\) is the antibacterial rate, \(A\) is the average recovery bacterial count of the sample (CFU), and \(B\) is the average recovery bacterial count of the blank control (CFU).

The compressive strength of the sintered ceramic samples was evaluated based on Chinese National Standard GB/T 4740-1999 [23], whereas the water absorption, bulk density, and apparent porosity were determined in accordance with Chinese National Standard GB/T 3810.3-2006 [24]. The structure was determined by X-ray diffraction (XRD) at 40 kV and 40 mA by measuring 2θ from 5° to 80° with a step size of 0.02° and time of 5 s per step. The powder diffraction patterns were analyzed using a software package program and microstructure of the thermally treated specimens was determined by scanning electron microscopy (SEM).

3. Results and discussion

Introduction of a larger amount of an antibacterial agent translates into a wider distribution in the honeycomb ceramic materials and stronger inhibition of bacteria. The antibacterial effects evaluated by the plate counting method against *E. coli* are shown in Figs. 3-6 and Tables 1 and 2. Fig. 3 shows that the antibacterial rate is 98.9% when the concentration is 5%. This is due to leaching of zinc ions with the opposite charge of the bacteria from the honeycomb structure and killing them. It is known that silver has more potent antibacterial effects than zinc [25] and Fig. 4 shows that 1% Ag in the honeycomb structure can kill about 98.7% of the *E. coli* in the solution. However, silver is more expensive and so it is worthwhile to study the combined effects of Zn and Ag to achieve the optimal performance and cost. The Ag and Zn incorporated materials possess excellent antibacterial properties and as shown in Fig. 5, the honeycomb with 0.5% Ag shows an antibacterial efficacy of more than 97.6% which is slightly better than that obtained with 0.3% Ag. When the 0.3% Ag materials are further doped with 5% and 6% Zn, the antibacterial rates reach 98.9% and 99.5%, respectively. It is thus obvious that the antibacterial performance can be improved by co-doping with Ag and Zn and from commercial considerations, 0.3% Ag is better than 0.5% Ag because the former is cheaper.

According to Fig. 7, the bending strength, open porosity, and water absorption properties of the antibacterial honeycomb ceramic materials are similar to those of the control. It is believed that the incorporated antibacterial agents do not affect the structure of the bulk materials thus preserving the good mechanical properties. The effects of addition of silver and zinc are investigated with XRD.
and Fig. 8 shows the broad-angle XRD patterns of the three types of antibacterial honeycomb ceramics. The typical narrow silver diffraction peaks at 2θ of 38.1°, 44.3°, 64.5°, and 77.5° correspond to the (111), (200), (220), and (311) Bragg’s reflections of face-centered cubic crystalline silver. The typical zinc diffraction peaks at 2θ of 31.77°, 34.42°, 36.25°, 56.60°, and 66.38° represent the (100), (002), (101), (110), and (200) Bragg’s reflections of face-centered cubic crystalline zinc. Furthermore, the characteristic

Table 1
Description of tested formulations in terms of the raw materials and corresponding antibacterial rates [Red mud (RM) and Antibacterial agent (AA)].

<table>
<thead>
<tr>
<th>RM:AA (Zn)</th>
<th>Antibacterial ratio (%)</th>
<th>RM:AA (Ag)</th>
<th>Antibacterial ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99:1</td>
<td>16.8</td>
<td>99.7:0.3</td>
<td>92.3</td>
</tr>
<tr>
<td>98:2</td>
<td>47.7</td>
<td>99.5:0.5</td>
<td>95.7</td>
</tr>
<tr>
<td>97:3</td>
<td>69.5</td>
<td>99.0:1.0</td>
<td>98.7</td>
</tr>
<tr>
<td>95:5</td>
<td>98.9</td>
<td>98.5:1.5</td>
<td>99.9</td>
</tr>
<tr>
<td>93:7</td>
<td>99.1</td>
<td>98.0:2.0</td>
<td>99.9</td>
</tr>
<tr>
<td>90:10</td>
<td>99.7</td>
<td>97.5:2.5</td>
<td>99.9</td>
</tr>
<tr>
<td>87:13</td>
<td>99.9</td>
<td>97.0:3.0</td>
<td>99.9</td>
</tr>
<tr>
<td>85:15</td>
<td>99.9</td>
<td></td>
<td></td>
</tr>
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</table>

Fig. 3. Antibacterial ratios against E. coli (Zn²⁺-loaded).

Fig. 4. Antibacterial ratios against E. coli (Ag⁺-loaded).

Fig. 5. Antibacterial ratios against E. coli (Ag⁺ and Zn²⁺-loaded).

Fig. 6. Photographs of honeycomb ceramic materials (Ag⁺-loaded) cultured with E. coli.
Table 2
Description of tested formulations in terms of the raw materials and the corresponding antibacterial rate. Red mud (RM) and Antibacterial agent (AA).

<table>
<thead>
<tr>
<th>RM AA</th>
<th>AA (Ag)</th>
<th>Antibacterial ratio (%)</th>
<th>RM AA</th>
<th>AA (Zn)</th>
<th>Antibacterial ratio</th>
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</thead>
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<tr>
<td></td>
<td>98</td>
<td>0.3</td>
<td>1.7</td>
<td>92.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>97</td>
<td>0.3</td>
<td>2.7</td>
<td>93.3</td>
<td></td>
</tr>
<tr>
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<td>96</td>
<td>0.3</td>
<td>3</td>
<td>94.9</td>
<td></td>
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<td>4</td>
<td>97.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>95</td>
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<td>98.4</td>
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</tr>
<tr>
<td></td>
<td>94.7</td>
<td>0.3</td>
<td>5</td>
<td>98.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>93.7</td>
<td>0.3</td>
<td>6</td>
<td>99.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>92.7</td>
<td>0.3</td>
<td>7</td>
<td>99.9</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 7. Bending strength, open porosity and water adsorption of the antibacterial honeycomb ceramic materials and blank sample.

Fig. 8. X-ray diffraction patterns of honeycomb ceramic materials (A, Zn²⁺-loaded), (B, Ag⁺-loaded), and (C, Ag⁺ + Zn²⁺-loaded).

Fig. 9. SEM image and X-ray analysis of Zn²⁺-loaded antibacterial honeycomb ceramic materials.

Fig. 10. SEM image and X-ray analysis of Ag⁺-loaded antibacterial honeycomb ceramic materials.
peaks of silver and zinc imply the existence of large and crystalline silver and zinc particles in the matrix. As a result, the crystal structure of the carrier is not altered enabling good dispersion of the antibacterial metals throughout the materials.

SEM is conducted to examine the surface morphology and size distribution of the antibacterial honeycomb ceramic materials. Figs. 9–11 depict the SEM images of the Zn-doped, Ag-doped, and Ag and Zn co-doped materials, respectively. The figures reveal heterogeneity and EDS confirms the existence of Zn and Ag in the honeycomb structure with a porous surface.

4. Conclusions

Using red mud industrial waste as the raw materials, honeycomb ceramic materials are produced and subsequently endowed with antibacterial properties by doping with silver and zinc. When 5% and 6% Zn are further added to the honeycombs doped with 0.3% Ag, the antibacterial rates reach 98.9% and 99.5%, respectively. From the commercial standpoint, the use of 0.3% Ag is better than 0.5% Ag because the former is cheaper. The bending strength, open porosity, and water absorption capability of the materials are not compromised by the addition of the two antibacterial agents. Scanning electron microscopy and X-ray diffraction reveal the existence of large and crystalline silver and zinc particles in the matrix. As a result, the crystal structure of the carrier is not altered enabling good dispersion of the antibacterial metals throughout the materials.

Acknowledgements

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