Synthesis and properties of composite antibacterial agent containing copper and zinc ions

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The medical stone is a type of natural stone which is rich in Silicon and many metal and trace elements.[1]The composite antibacterial agents were prepared with “medical stone” containing Cu^{2+} and Zn^{2+} by liquid ion-exchange reaction. The ion exchange capacity of the medical stone composite antibacterial agents (MSAA) were investigated by Inductively Coupled Plasma Atomic Emission Specrometry(ICP-AES), and the antibacterial activities of these agents were tested by bacteriostasis ratio and the structures were characterized by X-Ray Diffractomer(XRD) and Scanning electron microscope(SEM). The results show that the conditions of preparation, such as pH, concentrations of copper and zinc ions, reaction time and reaction temperature, have important influences on the ion exchange of MSAA. The maximum ion exchange capacity have been obtained when 0.2 mol/L Cu^{2+} and 0.6 mol/L Zn^{2+} reacted with medical stone in the solution with pH of 8 for 8 hours at 50 ºC. Meanwhile good antibacterial activities and safety are also gained. The reasons for causing the above results are that copper and zinc ions can enter into the framework of medical stone by ion exchanging and adsorption, and are slowly released owing tostone porosity.

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1. Introduction

Harmful bacteria exist anywhere in the world such as air, water, soil, surfaces of objects, skin, etc. They have seriously threatened the health of human beings. For this reason, much attention has been paid to restraining and killing the harmful bacteria. In order to build a healthy environment, the antibacterial materials as ecological functional materials have been developed and how to prepare these materials and to investigate their properties have become one of the hot topics in the fields of functional materials researches [2-3].

The antibacterial materials are divided into organic and inorganic groups according to their structure. Compared with organic antibacterial materials, the inorganic antibacterialones have a good prospect in applications, such as ceramic, plastic, fiber, building material, coating, etc., due to their heat resistance, chemical stability, safety, durability, wide range of antibacterial properties and so on [4,5]. Currently, most of inorganic antibacterial agents are produced with high porosity materials, such as zeolite, silica gel, calcium phosphate, siallite, activated carbon, etc., used as carriers to firmly support metal ions, such as silver, copper and zinc ions, by physical absorption or ion exchanging reaction [6,7]. There is little works done using medical stone as an antibacterial carrier. Medical stone [8] assumes a silicate framework with uniformly distributed cavities and a large internal surface area due to long-term weathering. We have prepared a novel medical stone antibacterial agent carrying silver ions with excellent antibacterial activities [9], but the price of silver is so high that it is difficult to popularize them. So, in this paper, the composite antibacterial agents were prepared using medical stone as carrier and Cu^{2+} and Zn^{2+} as antibacterial ions, by liquid ion exchanging reaction.

2. Experimental

2.1 Preparation of MSAA

After preparing the solutions by dissolving copper and zinc nitrate into deionized water, the medical stone in size of 45 μm were put into beaker and mixed with the solutions together, and then were stirred for some hours using a magnetic mixer. Afterward, the mixtures were filtered in a centrifugal filter and washed by deionized water for several times. Being dried in oven at temperature of 120 ºC, the MSAA containing Cu^{2+} and Zn^{2+} were obtained.

2.2 Testing and characterization of MSAA

The antibacterial activities and the safety of the as-prepared MSAA were tested according to HG/T 3794-2005 defined by Chemical Industry Department of China.

The ion exchanging capacity of the MSAA were analyzed by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES: type ICPS-7510) at the power of 1.2 kW. The microstructure of raw medical stone and the MSAA were determined by X-ray diffraction (XRD, X’Pert MPD) with Cu Kα radiation (λ = 0.015418 μm) and scanning electron microscopy (SEM: Type JSM-5610LV) with an accelerating voltage of 20 kV.

3. Results and discussions

3.1 The ion exchange capacity of MSAA

Table 1 shows the testing results of the ion exchange capacity of MSAA. The results revealed that the ion exchanging capacities were influenced by four factors including pH, ions concentration in solution, reaction time and temperature. Among them, the first two are the key factors. It is also found that the ion exchanging capacity of sample 5 # is the biggest among all the samples. The sample 5# was prepared when 0.2 mol/L Cu^{2+} and 0.6 mol/L Zn^{2+} reacted with medical stone in the solution with pH of 8 for 8 hours at 50 ºC.

Table 1. The results of orthogonal array experiment.

No.	pH value	Ion concentration /(mol/L)		Reaction time /h	Reaction temperature /℃	Ion exchange capacity /(wt%)	
		Cu^{2+}	Zn^{2+}			Cu^{2+}	Zn^{2+}
1#	5（1）	0.1（1）	0.3（1）	4（1）	50（1）	0.74	3.12
2#	5（1）	0.2（2）	0.6（2）	6（2）	80（2）	1.81	4.70
3#	5（1）	0.5（3）	1.5（3）	8（3）	90（3）	1.89	4.54
4#	8（2）	0.1（1）	0.3（1）	6（2）	90（3）	1.64	4.71
5#	8（2）	0.2（2）	0.6（2）	8（3）	50（1）	2.50	5.65
6#	8（2）	0.5（3）	1.5（3）	4（1）	80（2）	2.46	5.44
7#	10（3）	0.1（1）	0.3（1）	8（3）	80（2）	0.61	2.86
8#	10（3）	0.2（2）	0.6（2）	4（1）	90（3）	1.09	3.02
9#	10（3）	0.5（3）	1.5（3）	6（2）	50（1）	1.17	3.49
K_1	4.44/12.36	2.99	10.69	4.29/11.58	4.41/12.26		
K_2	6.60/15.80	5.40	13.37	4.62/12.90	4.88/13.00		
K_3	2.87/9.37	5.52	13.47	5.00/13.05	4.62/12.27		
R	3.3/6.43	2.41	2.78	0.71/1.47	0.47/0.74		

3.2 Antibacterial activities and safety properties of MSAA

Fig. 1 shows the antibacterial activity of the MSAA. It reveals that all the samples have a certain degree of antibacterial activity, and that of sample 5#, whose bacteriostasis ratio reached 99.71 % (for *Escherichia coli*) and 98.14 % (for *Staphylococcus aureus*), is the best among them. The mechanism is discussed later.

It is well known that medical stone has the capacity of producing a moderate content of elements which are good for our health [10], which are necessary to bioactivity. Therefore, it has been widely used in the fields such as medical science and environmental hygienics. The safety properties of sample 5# were tested according to HG/T 3794-2005. The result shows that LD_{50} (LD denotes lethal dose, LD_{50} denotes statistically derived dose that is expected to cause death in 50 % of the treated animals) is above 5 g/kg and has no stimulation on rabbits. Meanwhile, the result of Ames test of big white rat shows negative effort compared with our traditonal theory. These indicated that sample 5# also has a good safety property.

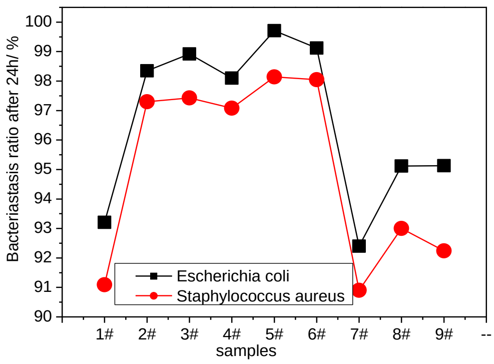

Fig. 1. The antibacterial activity of MSSA.

3.3 XRD *results*

Fig. 2 shows the XRD patterns of the pure medical stone and the MSAA of sample 5#. It can be seen that the raw medical stone and the sample 5# are both composed of the same crystal phases and there is no new diffraction peak in the MSAA. The XRD result indicates that there are no corresponding hydroxides occurring and no change of the structure of medical stone containing Cu and Zn ions, which show that Cu^{2+} and Zn^{2+} are completely combined with the stone [11].

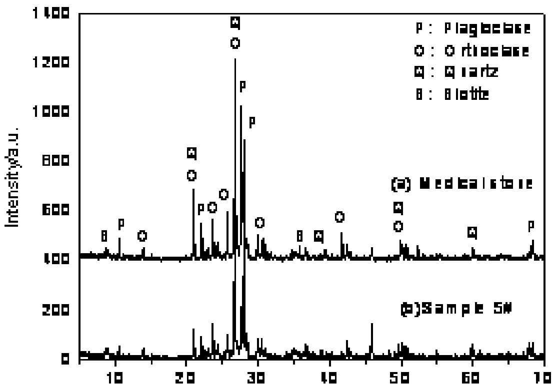

Fig. 2. XRD patterns of the MSSA and Medical stone.

3.4 SEM results

The morphology of the raw medical stone and the sample 5# are displayed in Fig. 3. From Fig. 3 (a), we can see that there are many pores with the size of tens of nanometers in the structure of raw medical stone. After containing Copper and Zinc ions, as shown in Fig. 3 (b), the structure of the antibacterial agent, exhibits a significant decrease in pore size. The SEM result indicates that Cu^{2+} and Zn^{2+} had been entered into the structure of medical stone by the ion-exchange or adsorption.

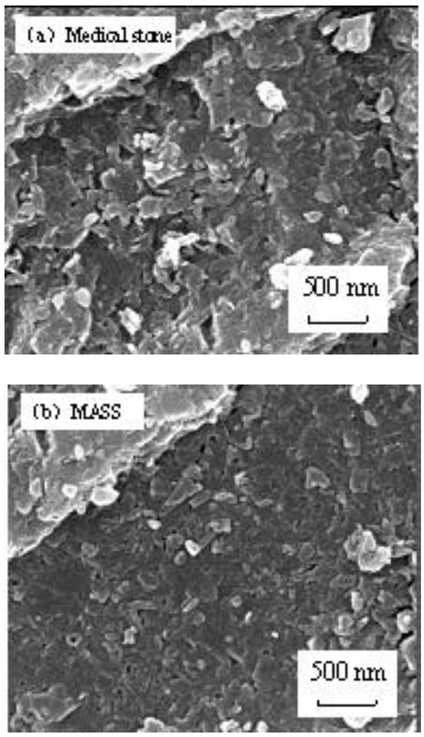

Fig. 3. The SEM photograph of the raw Medical stone and the MSAA.

3.5 Analysis of the antibacterial mechanism

As discussed before, the main reason of medical stone used as antibacterial carrier is due to its high porosity. The uniformly distributed opening cavities [8] in the stone can easily adsorb Cu^{2+} and Zn^{2+}. Moreover, medical stone [12] is made up of SiO_4 tetrahedrons, the oxygen atom at the shared apex belonging to two neighboring tetrahedrons. There is a negative charge on the Si-O tetrahedron when one aluminum atom replace one of the silicon atoms and cations, such as K^+, Na^+, Ca^{2+} and Mg^{2+}, will enter into the framework of the medical stone to maintain the tetrahedron electrically neutral. These cations could be substituted by Cu^{2+} and Zn^{2+} by ion exchanging reaction. Therefore the main antibacterial mechanism is consisting in Cu^{2+} and Zn^{2+} entering the medical stone framework and their slow release to kill bacteria leading thus to antibacterial activity of MSAA.

4. Conclusions

The MSAA carrying Cu^{2+} and Zn^{2+} are prepared by liquid ion-exchanging technology. When 0.2 mol/LCu^{2+} and 0.6 mol/L Zn^{2+} reacted with medical stone in the solution with pH of 8 for 8 hours at 50 ºC, the MSAA with excellent antibacterial activities and safety is obtained. The antibacterial mechanism of the product consists in Cu^{2+} and Zn^{2+} entering the medical stone framework by ion exchanging and adsorption and slow release of these ions that are killing the bacteria.

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