Preparation of a Novel Nano or Submicron Tourmaline Ceramic and Its Ability to Inhibit the Activity of the Sulfate-Reducing Bacterium

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Abstract. In this study, novel nano- or submicron-scale tourmaline bacteriostatic ceramics in which nano or submicron tourmaline is one of the central materials, together with nano-zinc oxide, are prepared using ion exchange and solid-phase synthesis techniques. The material is then examined with IR, XRD and XPS and is tested for the ability to inhibit the activity of the sulfate-reducing bacterium (SRB). The calcination temperature of the ceramic is 600 °C, and the main components are present at 11.17% for Si2p, 3.12% for Mo3d, 3.47% for Zn2p3, 2.86% for Mn2p and 2.35% for Cu2p. Additionally, the density of this material is 1.4-3.5 g/cm³, and its compressive strength exceeds 5.2 MPa, meeting the requirements of ceramic standards. Consequently, the bacteriostatic ceramic inhibits the activity of the sulfate-reducing bacterium effectively without inhibiting the removal of COD and NO_3^-. These results indicate that the sulfate-reducing bacterium maintains its functional metabolism, apart from its sulfate reduction potential, when using this bacteriostatic ceramic, thus achieving the goal of inhibiting the action of the sulfate-reducing bacterium.

1. Introduction

In China, the SRB[1] contained in the Daqing Oilfield wastewater has vastly increased its reproduction in the past decades, which increases the amount of sulfide and the suspended solids, causing serious accidents during production, such as the collapse of the electric field, and leading to losses every year due to the corrosion of approximately RMB 2.5 billion. Balancing the killing and the inhibition of the SRB has been a topic of interest for both researchers and workers [2]. New observations suggest that the SRB serves as the main supportive bacterium in the reservoir system, while it negatively affects the ground system of the oilfield. Thus, the focus lies in controlling the sulfate-reducing function appropriately to inhibit its sulfate-reducing activity while taking advantage of the useful aspects of this bacterium[3-5].

The goal of this research was to develop a novel nano or submicron tourmaline bacteriostatic ceramic; nano or submicron tourmaline was added to a ceramic to combine the characteristics of the tourmaline and nano materials, to enlarge the contact area and to strengthen the electrodes and the piezoelectricity of the tourmaline. Meanwhile, several metal salts and nano-zinc oxide with a high bactericidal capacity for the SRB were tested to reduce the cost, using mixed shale and zeolite as the carrier. The new bacteriostatic ceramic and its inhibition of the SRB are evaluated.

2. Materials and methods

2.1. Preparation of nano or submicron tourmaline bacteriostatic ceramic

Five grams each of nano or submicron tourmaline, zeolite and shale was added to 50 mL of deionized water at a 6:3:1 ratio and then stirred uniformly using a magnetic stirrer. A nitrate solution was prepared (0.03 mol/L) and adjusted to a specified pH value (4-8); molybdate (1%), silver chloride (0.5%), copper sulfate (0.5%) and nano zinc (2%) were added, and the solution was stirred in the dark with the dispersant. The mixture was then decompressed, pumped, filtered, separated and cleaned with deionized water; it was then dried in a thermostatic oven at 105°C. Then, pore-forming agents (CS) (5%), binder (SF) (1%) and enamel agent (15%) were added to the sludge in the dried sample and were ground for 10 min to form a ball. The samples dried naturally and were then calcinated at 600°C for 4 h to produce the finished product, which was then stored in a dry place[6-7].

2.2. SRB activity inhibition experiment

The experimental sludge taken from an anaerobic UASB reactor contained a large amount of SRB, with 135 mg/L, 135 mg/L and 500 mg/L of SO_4^{2-}, NO_3- and COD, respectively, and an alkalinity of 500 mg/L. The sludge was placed into a 500-mL bottle of serum and high-purity nitrogen was introduced to the culture, which was incubated on a shaker for 24 h. Then, 10 g of bacteriostatic ceramic was added to the culture. The sample was removed after 12 h to measure the activity of the sulfate reductase against SO_4^{2}-、NO_3-、pH、ORP and S^{2-}. The culture was incubated on a shaker (speed of 125 rpm and temperature of 36±1°C) and was sampled regularly.

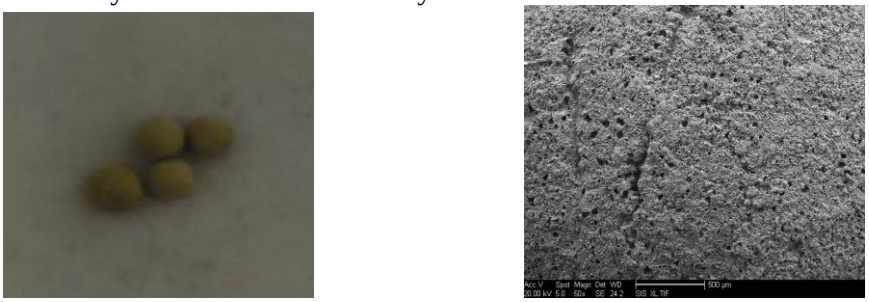
2.3. Analysis and characteristics

Nano or submicron tourmaline was imported from the United States. The following techniques and equipment were used: Infrared Spectroscopy: Spectrum One B (FT-IR spectrometer); ICP: 5300DV (PE) and other plasma emission spectroscopy; X-ray photoelectron spectroscopy (PH15700), X-ray diffraction (D-MAX/rB rotating anode X-ray diffraction instrument), sulfate concentration: the application of ion determination of Shimadzu, Japan; the measurement of sulfate reductase activity; the Ostrowski method; and pH and oxidation-reduction potential (ORP): measurement with WTW-in lab.

3. Results and discussion

3.1. Characteristics of copper-carrying nano or submicron tourmaline

3.1.1. Ceramic characteristics. Figure 1 shows that the diameter of the nano or submicron tourmaline bacteriostatic ceramic is between 5~8 mm. The scanning electron micrograph of the surface indicates a honeycomb structure with many voids and an even distribution.



A. The finished ceramic product B. The surface of the bacteriostatic ceramic after calcination

Figure 1. The characterization of the tourmaline bacteriostatic ceramic.

3.1.2. Infrared Spectroscopy (IR). The complicated bacteriostatic ceramic consists of nano or submicron tourmaline, shale, zeolite, zinc oxide, copper chloride, manganese chloride and molybdate, among others, producing an extremely complex infrared spectrum (IR).

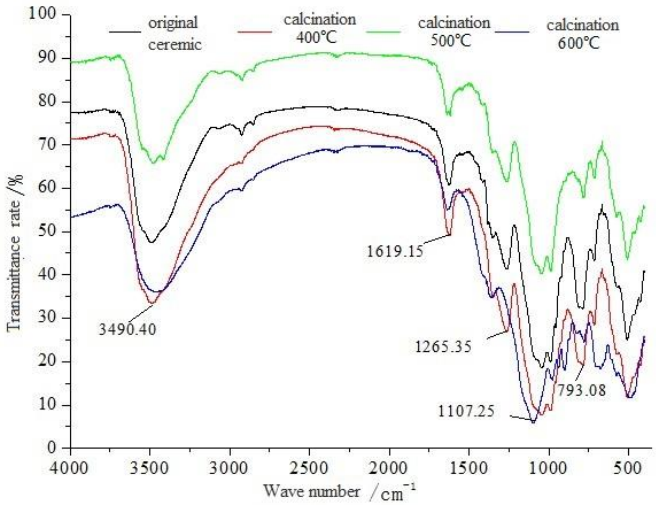


Figure 2. The IR map of the ceramic product at different temperatures.

Figure 2 shows that the OH stretching vibration absorption emerges at 3556.84 cm^{-1} for the tourmaline during calcination. The adsorption peak of the bacteriostatic ceramic is found between 3495 and 3470 cm^{-1} as the calcination temperature increases. The peak of the OH stretching vibration shifts, indicating that the ceramic experiences the association of hydroxy compounds during the preparation.

3.1.3. X-ray diffraction (XRD) analysis. The changes in the XRD spectrum were analyzed for the different calcination temperatures because of the complex elements of the bacteriostatic ceramic (Figure 3). The crystal form changes prominently and \ more intensely during the entire process. Based on the hardness of the ceramic and the nature of the tourmaline, 600 ℃ was identified as the calcination temperature.

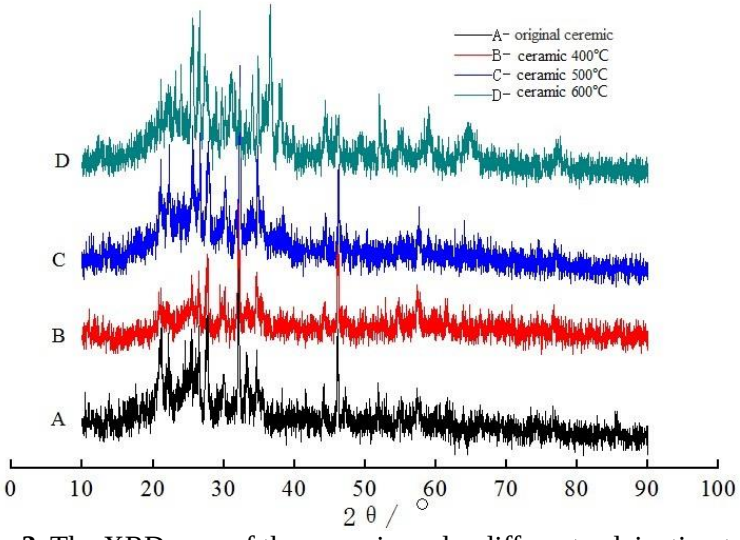


Figure 3. The XRD map of the ceramic under different calcination temperatures.

3.1.4. X-ray photoelectron spectroscopy (XPS). The whole ceramic is dominated by the nano or submicron tourmaline and is supplemented by the relevant bacteriostatic elements—nano-zinc oxide, copper chloride, manganese chloride, molybdate and the synthesis glazes and sludge generated during the formation of the ceramic with complexing factors. Figure 4 shows the main bacteriostatic elements in the ceramic by spectroscopy, which mainly includes Mo3d、Zn2p3、Mn2p and Cu2p (11.17% for

Si2p, 3.12% for Mo3d, 3.47% for Zn2p3, 2.86% for Mn2p and 2.35% for Cu2p). The strong inhibition ability of the individual elements of the ceramic indicates the stronger power of the nano or submicron tourmaline.

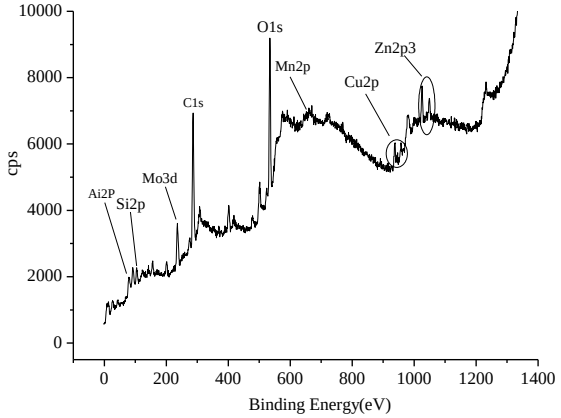


Figure 4. The XPS graph of the bacteriostatic ceramic.

3.2. Effectiveness of the ceramic at inhibiting SRB activity

3.2.1. Inhibition of SRB activity by the ceramic. The activity of the sludge gradually increases without the bacteriostatic ceramic, reaching 1.05 U/mL after 48 h. When the sulfate is almost entirely consumed, the activity begins to decrease. In comparison, the sludge treated with the bacteriostatic ceramic shows inhibited activity of the sulfate sludge: no hydrogen sulfide gas is generated or sulfate reduction occurs, achieving the desired effect.

3.2.2. The ORP of the bacteriostatic ceramic on the sulfate-reducing sludge and its influence on pH. Figure 5 indicates that the ORP increases immediately after adding the bacteriostatic agent, reaching -26 mV when the activity of the sulfate reductase is inhibited completely by the bacteriostatic ceramic. After 60 h, the ORP remains stable at 6.1 mV, and the ORP of the sulfate reductase was unable to grow. The bacteriostatic ceramic could improve the ORP significantly and could inhibit the growth of the SRB to stop the sulfate reduction. There is no major change in the pH compared with the original sample.

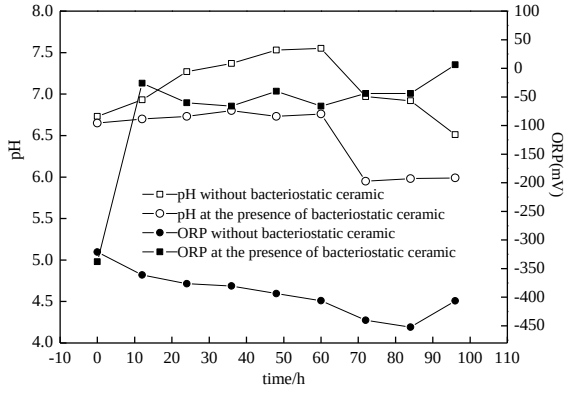


Figure 5. The influence of the bacteriostatic ceramic on the ORP and pH of the sulfate-reducing sludge.

3.2.3. Influence of the bacteriostatic ceramic on SO_4^{2-} *and sulfide.* Figure 6 shows that the concentration of SO_4^{2-} for the sample decreases to 7.6 mg/L from 134.2 mg/L and that the removal rate is 94.33% after 96 h; conversely, the concentration of S^{2-} rises from 5.2 mg/L to 30.7 mg/L. However,

the concentration of SO_4^{2-} for the culture medium with the ceramic decreases to 116 mg/L from 134 mg/L without significant fluctuations, with a removal rate of 13.4%.

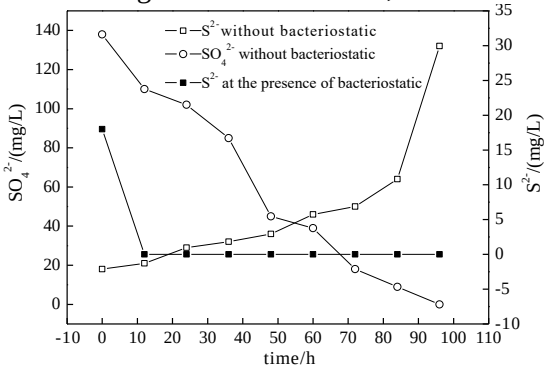


Figure 6. The influence of the bacteriostatic ceramic on the levels of SO_4^2 and sulfides.

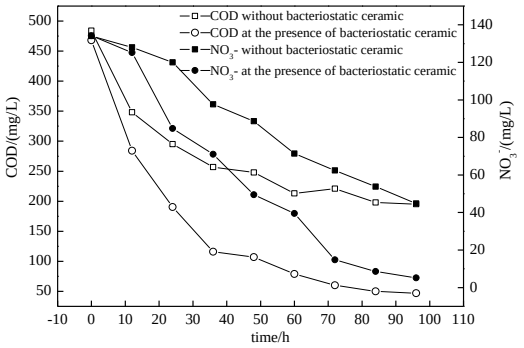


Figure 7. The influence of the bacteriostatic ceramic on the levels of COD and NO_3^-.

3.2.4. Influence of the ceramic on COD and NO_3^-. Figure 7 shows that the concentration of COD in the sample is reduced to 195 mg/L from 484 mg/L, with a removal rate of 59.71%. In comparison, the COD of the sample with ceramic is reduced to 47 mg/L from 468 mg/L at a rate of 89.95%. The concentration in both samples is reduced, but the ceramic sample has a faster removal rate; for comparison, the concentration of NO_3 in the untreated sample drops to 44.8 mg/L from 134 mg/L for a removal rate of 66.56%, while the NO in the ceramic-treated sample is reduced to 5.2 mg/L from 134.2 mg/L, an effective rate of 96.13%. The values of both the COD and NO_3^- are lower, indicating that only the sulfide is inhibited.

4. Conclusions

The novel nano or submicron tourmaline bacteriostatic ceramic, which uses nano or submicron tourmaline as one of the central materials, together with nano-zinc oxide, was prepared using ion exchange and solid-phase synthesis techniques.

1) The calcination temperature of the ceramic is 600 °C, and the content of the main components are 11.17% for Si2p, 3.12% for Mo3d, 3.47% for Zn2p3, 2.86% for Mn2p and 2.35% for Cu2p. Additionally, the density of this ceramic is 1.4-3.5 g/cm³, and the compressive strength exceeds 5.2 MPa, which meets the requirements of ceramic standards.
2) The bacteriostatic ceramic inhibits the activity of the sulfate-reducing bacterium effectively without generating hydrogen sulfide gas. The efficient removal of COD and NO_3^- indicates that the sulfate-reducing bacterium maintains its functional metabolism, apart from the inhibition of its sulfate reduction ability, creating a targeted inhibition of SRB activity.

Acknowledgements

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