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INTERACTION OF TOURMALINE MINERAL POWDERS WITH SEA WATER AND ITS ANTI-MICROBIAL PROPERTIES

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Abstract

The interaction of tourmaline mineral powders with de-ionized water and seawater and the inhibiting growth activity of marine bacteria and diatoms were investigated. The results show that negative ion release rate of tourmaline powders are somewhat reduced immersing in seawater for 24h. When tourmaline powders is added into de-ionized water or seawater, electric conductivity of the de-ionized water is increased with time under the static state, their pH tend to be 7, solution oxygen of de-ionized water keeps to be about 139% of the initial 4.9mg/L and solution oxygen of seawater tends to be its initial value under stirring. For the capability of inhibiting the growth activity of marine bacteria and diatom, lithium tourmaline is the strongest in the three type of tourmaline powders with similar size, magnesium tourmaline is slightly lower than lithium tourmaline, but iron tourmaline is extremely lower than the other two types. The capability of inhibiting the microbe activity increases with reducing the size of tourmaline particles and adding the content of tourmaline powders. Tourmaline mineral materials are prospective to use as an additive to antifouling coatings from this work.

Introduction

Tourmaline is a kind of complex borosilicate mineral belonging to the trigonal space group[1] including magnesium tourmaline, iron tourmaline, lithium tourmaline and manganese tourmaline [2]. The general chemical formula of tourmaline is written as XY3Z6(T6O18)(BO3)3V3W where X = Ca, Na, K, vacancy; Y = Li, Mg, Fe2+, Mn2+, Zn, Al, Cr3+, V3+, Fe3+, Ti4+, vacancy; Z = Mg, Al, Fe3+, Cr3+, V3+; T = Si, Al, B; B = B, vacancy; V = OH, O; and W= OH, F,O[3]. Tourmaline exhibits spontaneous surface electric fields in the order of 104 – 107V/m especially in small granules with a diameter in the range of several microns to nano-scale[4,5]. The tourmaline crystal generates an electric potential difference that results in the ionization of the surrounding air and conversion of the adjacent water and oxygen molecules into negative oxygen ions[6]. The oxygen ions move in the air and transfer negative charges to dust particles, smoke particles and water droplets, resulting in purification of the air. Therefore, as it possesses excellent functional and environmental properties[7,8]. It is reported that tourmaline could promote the growth activity of sulfate reducing bacteria, nitrite bacteria, nitrobacteria and aerobic denitrifying bacteria [9-13]. Tourmaline also possesses antibacterial properties[14-18]. Tourmaline powders were used an additive of antifouling paint to reduce the

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adhesion of marine organisms[19]

In many marine industries, the colonization of submerged surface is a major problem. It is estimated that the world fleet consumes an additional 300 million tons of fuel annually as a result of hull fouling[20]. The historical paradigm for controlling marine biofouling was to use biocidal products within coating systems to kill colonizing organisms. With the legal implementation of the International Maritime Organisation Treaty on biocides in 2008 the use of components such as tributyltin (TBT) will be increasingly restricted. It is to urgent developing environmentally benign fouling-resistant products to fill the gap in the market. After solid surface immersed in sea water, organic molecules of proteins, polysaccharides, glycoproteins and others become first physically adhered to the surface, subsequently bacteria and single-cell diatom are adsorbed to the surface that provides sufficient food to allow the fixing of spores of microalgae and the increased capture of more particles and organisms, such as larvae of marine macroorganisms[21-14].

In this work, we investigate the interaction of tourmaline mineral powders with de-ionized water and seawater and effects of tourmaline powders on growth activity of marine bacteria and diatoms to understand the application of tourmaline material in marine antifouling paint.

Material and methods

Materials: Tourmaline powders were purchased from Tianjin Hongyan Co., Ltd which were produced by air current and wet grinding Xinjiang tourmaline ore. The color, type and granularity of these powders were listed Table 1. Granularity, zeta potential and Negative ion release rate of the powders were measured by JL-1177 particle size analysis-Laser, JS94H micro-electrophoresis instrument and COM-3010PRO ion tester, respectively.

Table 1. Type, particle size and zeta potential of tourmaline

Powder	Color	Type	Granularity (μm)	zeta potential (mv)
A1	Pink	Lithium tourmaline	0.534	-45.962
A2	Pink	Lithium tourmaline	1.470	-33.02
B	White	Magnesium tourmaline	1.533	-30.92
C	Grey	Iron tourmaline	1.276	-30.30

Test of pH, electric conductivity and solution oxygen of de-ionized water and seawater contained mineral tourmaline powders: Adding 2 gram of tourmaline powders (A2) into 250ml of de-ionized water or seawater, which are stirred by FA25 emulsifying machine for 5 minutes, then test the pH, electric conductivity and solution oxygen of the water using SevenMulti™ S40K meter under a static state and a stirring static made by magnetic stirring apparatus, respectively.

Estimation of bacterial cells in seawater: Fresh nature seawater were fetched from Dalian seas and filtered. Tourmaline powder was added into 200 ml of fresh nature seawater that were oscillated for 24 hours. 0.1ml of the dilution of the seawater is spread across the surface of a 2216E nutrient agar plate and incubated for 4 days at 25°C. Then the bacterial cell numbers on the plate were counted and the cfu/ml of the original is deduced mathematically, factoring in the amount plated and its dilution factor.

Estimation of diatom activity: The diatoms (*Navicula perminuta*) were isolated from Dalian seas microbial mats. Species identification was based on morphological features. Cells of *Navicula perminuta* were cultured in 250 ml conical flasks in an illuminated incubator at 18°C in F/2 medium with a light/dark cycle of 12/12 h. After 3 days, the cells were washed three times in fresh medium, filtered through 20 mm nylon mesh and diluted to give a suspension with a chlorophyll a content of approximately 0.3μg/ml. Tourmaline powder was added into the suspension of 200ml that were oscillated for 24 hours in an illuminated incubator. Then the chlorophyll a of the diatom suspension was measured by the spectrophotometric method.

Results and discussions

The zeta potential of tourmaline powders were shown in Table1 from which zeta potential of three type tourmaline A2, B and C with a close size are -33.02mv, 30.92mv and 30.3mv, respectively in which the difference is very small. The zeta potential of lithium tourmaline is decreased to -45.962mv from -33.02mv with the average diameter of tourmaline particles diminished from 1.47nm to 0.534nm. Therefore, the surface zeta potential of tourmaline powders mainly depend on the particle size, and the zeta potential become more negative with reducing the diameter of tourmaline particle. However, negative ion release rate of tourmaline powders are related to both tourmaline type and particle size of tourmaline (Fig1). Negative ion release rate of lithium (A2) and magnesium (B) tourmaline are twenty and nineteen times larger than that of iron tourmaline, respectively. Negative ion release rate of A1 with a diameter of 0.534μm exceeds that of A2 with a diameter of 1.47μm by 15%. Negative ion release rate of tourmaline powders have no obvious change after immersing in de-ionized water for 24h, bud that are somewhat reduced after immersing in seawater for 24h.

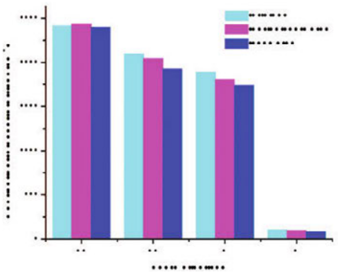

Fig.1. Negative ion release rate of tourmaline powders

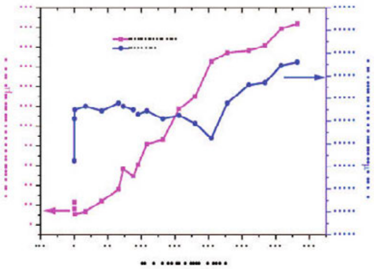

Fig.2. Effect of tourmaline A2 on the electric conductivity of de-ionized water and sea water under the static state

Fig.2, Fig.3 and Fig.4 show respectively the variation of electric conductivity, pH and solution oxygen of de-ionized water and seawater contained lithium tourmaline powders with time. The electric conductivity of de-ionized water decreases to 16.04 from the initial 22.9 μS/cm after stirring 5 minutes, next decreases to 10.43 after 1 hour and begin to increase continuously, and increases to 204 after 332 hour. The electric conductivity of seawater increases rapidly to 60200 from the initial 56500 μS/cm after stirring 5 minutes, and then increases slowly to 65200 after 332 hour (Fig.2). The pH of de-ionized water increases to 8.2 from the initial 7.07 after stirring 5 minutes, then decreases and increases alternately in the vicinity of 7.3 after the following 100 hour under the static state, and the pH of seawater has no obviously change (Fig.3a). Under stirring continuously (Fig.3b), the pH of de-ionized water increases firstly to 7.48 from the initial 7.07 after stirring 1 minutes, then decreases slowly to 7.11 in the following 120 minutes, and the pH of seawater has no obviously change in the vicinity of 7.9 before the 60 minutes, then decreases quickly and approaches to 7 . The solution oxygen of de-ionized water increases firstly to 7.19mg/L from the initial 4.9mg/L after stirring 5 minutes, next decreases rapidly 6.09mg/L after 1 hour, then decreases and increases alternately in the vicinity of 4.5mg/L after the following 332 hour under the static state, and the solution oxygen of seawater increases firstly to 5.68mg/L from the initial 4.19mg/L after stirring 5 minutes, then decreases and increases alternately in the vicinity of 5mg/L after the following 332 hour under the static state (Fig.4a). Under stirring continuously (Fig.4b), the solution oxygen of de-ionized water increases quickly to 6.83mg/L from the initial 4.9mg/L after stirring 1 minutes, then has no obviously change in the vicinity of 6.8mg/L in the following 120mg/L minutes, and the solution oxygen of seawater increases rapidly to 8.72mg/L from the initial 4.19mg/L after stirring 1 minutes, then decreases continuously to 3.79mg/L in the following 120 minutes.

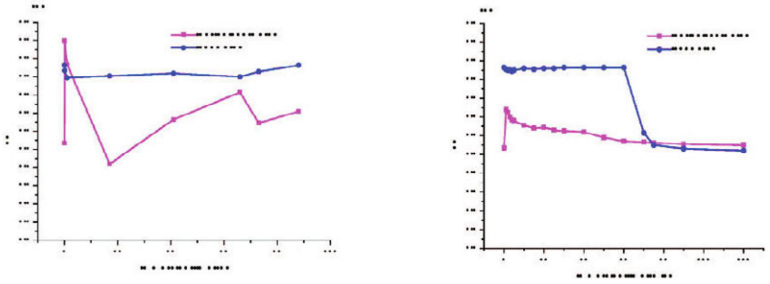

Fig.3. Effect of tourmaline A2 on the pH of de-ionized water and sea water under the static state (a) and the stirring state (b)

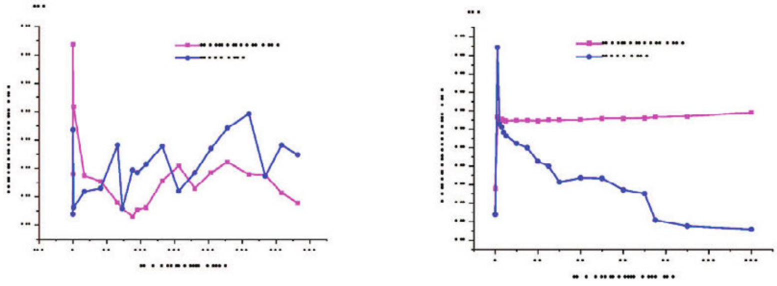

Fig.4. Effect of tourmaline A2 on the solution oxygen of de-ionized water and sea water under the static state (a) and the stirring state (b)

The bacterial cell number in fresh nature seawater are correspondingly reduced by 96%, 78%, 32% and 24% when adding 1g/L, 2g/L, 3g/L and 4g/L tourmaline A2 into the sea water, respectively (Fig2a), and correspondingly reduced by 25%, 32%, 36% and 89% when adding 3g/L tourmaline A1, A2, B and C , respectively (Fig2b). The chlorophyll a of *navicula perminuta* solution are correspondingly diminished by 88%, 73%, 60% and 49% when adding 2.5g/L, 5g/L, 10g/L and 15g/L tourmaline A2 into the sea water, respectively (Fig2c), correspondingly diminished by

54%, 60%, 63% and 85% when adding 3g/L tourmaline A1, A2, B and C , respectively (Fig2d). Accordingly, the capability of lithium tourmaline is the strongest in the three type tourmaline powders with similar size for inhibiting the growth activity of marine bacteria and diatom, magnesium tourmaline is slightly lower than lithium tourmaline, but iron tourmaline is extremely lower than the other two types. The capability of tourmaline inhibiting the microbe activity increases with reducing the size of tourmaline particles and adding the content of tourmaline powders.

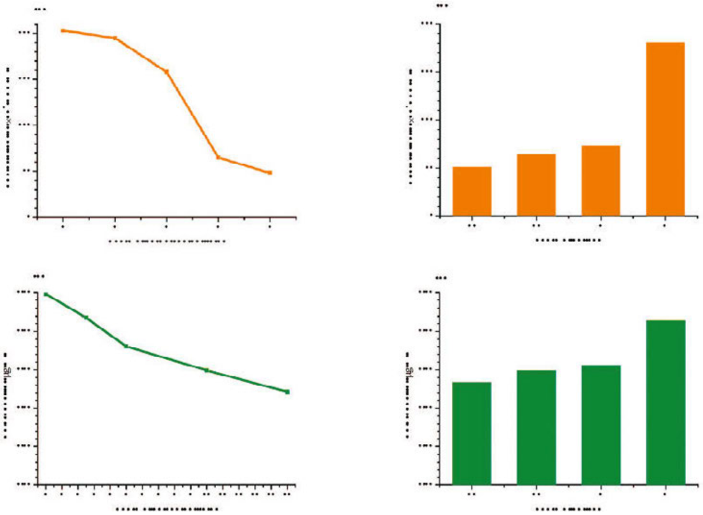

Fig.2 Effects of tourmaline powders on the growth activity of marine bacteria(a and b) and diatom(c and d)

Conclusion

In summary, we have studied the interaction of three types of tourmaline mineral powders with de-ionized water and seawater and the inhibiting growth activity of marine bacteria and diatoms. It is found that negative ion release rate of tourmaline powders have no obvious change after immersing in de-ionized water for 24h, bud that are somewhat reduced in seawater for 24h. When tourmaline powders is added into de-ionized water or seawater, under the static state pH, solution oxygen and electric conductivity of the de-ionized water and the seawater have no obvious changes except for increasing electric conductivity of de-ionized water with time, moreover under stirring pH and solution oxygen are rapidly increased initially except pH of seawater, then their pH tend to be 7, solution oxygen of de-ionized water keeps to be about 139% of the initial 4.9mg/L and solution oxygen of seawater tends to be its initial value. The capability of lithium tourmaline for inhibiting the growth activity of marine bacteria and diatom is the strongest in the three type of tourmaline powders with similar size, magnesium tourmaline is slightly lower than lithium tourmaline, but iron tourmaline is extremely lower than the other two types. The capability of tourmaline inhibiting the microbe activity increases with reducing the size of tourmaline particles and adding the content of tourmaline powders.

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