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Influence of inhibitors on the adhesion of SRB to the stainless steel in circulating cooling water

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ABSTRACT

Influence of the surface characteristics of three stainless steels (SS304, 316L and 317) and presence of scale inhibitors on adhesion kinetics of sulfate reducing bacteria (SRB) in circulating cooling water, were investigated by evaluating surface free energy, adhesion kinetic constants in a parallel plate flow chamber. Results show that the surface free energy values of SS317, SS316L and SS304 are −31.69, −24.18 and −13.92 mJ m^{-2}, respectively. SS317 surface had higher surface hydrophobicity than SS316L and SS304. In the process of bacteria cells adhesion onto SS surfaces, electrostatic interaction for SS is slightly more than hydrophobic interaction. The number of adhering bacteria and the adhesion kinetic constants are different on the three types of stainless steel. The adhesion kinetic constants for SS317 and 316L are greater than that for SS304, which are 0.0354, 0.0282 and 0.0190 min^{-1}, respectively. Scale inhibitors of hydrosy ethyl fork phosphonic acid (HEDP) and phosphono butane-1, 2, 4-tricarboxylic acid (PBTCA) have a certain influence on the initial adhesion of bacteria cell and adhesion kinetics constants are reduced in the presence of HEDP and PBTCA.

1. Introduction

Due to the freshwater scarcity in Northern part of China, the reclaimed water from municipal wastewater discharge has been widely adopted for circulating cooling systems in power plants [1] as an alternative for surface and ground water sources. The environmental conditions in cooling water systems, such as temperature, nutrients are amiable to microbial growth. Bacteria could reside in the tubes of heat exchangers tubes and form biofilms [2].

Biofilms are interface–associated colonies of microorganisms embedded in a self-produced organic polymeric matrix [3] containing molecules derived from the aqueous phase and/or corrosion products of the metal substrata. Biofilm formation could increase heat transfer resistance in cooling water systems [4] and microbiologically influenced corrosion (MIC) [5,6].

Bacterial adhesion is considered as the initial stage in the formation of a biofilm. Previous study showed that bacterial adhesion onto the surfaces of stainless steel 304 and 316L in 30 s [7,8]. Bacterial adhesion may be influenced by many factors, including the surface properties of metal materials (hydrophobicity, chemical composition and roughness) [9] and environmental conditions (pH, ionic strength, shear stress and static magnetic field) [10–12]. E. Vanhaecke indicated that bacterial cell surface hydrophobicity was the major parameter influencing the adhesion rate constant for the first 30 min of adhesion [8]. Bacterial cell adhesion forces are enhanced by increasing surface hydrophobicity of substrate [13,14]. However, some studies reported a decrease in bacterial adhesion to metallic surfaces with the increase of hydrophobicity [15].

Xiaoxia Sheng [16] found that stronger ionic strength in the solution results in a larger bacterial-metal adhesion force due to stronger electrostatic between bacterial cell and stainless steel surface. Adhesion force at pH 9 were higher than at pH 7. F.A. Lopes [17] found that adhesion of D. desulfuricans is more significant on Ni surface than on SS surface. Some authors [18,19] investigated bacterial adhesion and growth on a polymer based-coating to reduce bacterial adhesion and biofilm formation on stainless steel. Results identified that bacterial adhesion are significantly reduced on the hydrophobized stainless steel conditioned with poly (ethylene oxide)-poly(propylene oxide)-poly (ethylene oxide) (PEO–PPO–PEO) [25]. Surface free energy is a kind of direct embodiment of intermolecular forces that directly influence bacterial adhesion. Liquid or solid surface molecule is affected by the imbalance of intermolecular forces, compared with internal molecules, with additional energy [20]. The total free energy includes electrostatic interaction free energy, Lifshitz-vander Waals interaction free energy and van Oss-Chaudhury-Good polarity interaction free energy, etc. And surface free energy is generated by electrostatic force, Vander Waals

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force, Hydrophobic gravity and water repulsion, etc. [21].

SRB have been commonly identified as a major group of bacteria responsible for metal corrosion in cooling water systems. The colonization of SRB on stainless steels could cause micro-pitting corrosion [22,23], with a characteristic feature of iron (Fe) depletion and enrichment of chromium (Cr) [24].

In practice, many chemicals such as scale inhibitors, were used in cooling water system. Some studies show that main mechanisms of corrosion inhibition for many inhibitors are: (i) adhesion on the molecules or its ions on anodic and/or cathodic sites. (ii) increasing in cathodic and/or anodic over voltage.(iii) formation of a protective barrier film [25–27]. In solution, the initial adhesion of inhibitor compounds could be affected by surface active molecules. These inhibitors actually reduce corrosion on the surface of a metal depend on adhesion of their moieties on the metal surface, either by physical forces or chemical bond.

From the mid-1970s to 2000s, phosphonates were developed and extensively used as scale and corrosion inhibitors in a variety of fields including circulating cooling systems in power plants, industrial equipment cleaning, and industrial water treatment [28].

The quantitative relationship between molecular structure and corrosion efficiency of various inhibitors is studied by various quantum chemical calculation methods. Xia et al. studied the mechanism of phosphonate scale inhibitors against calcium carbonate scales [29]. Results identified that the following order of inhibitor effectiveness: HEDP, PBTCA, ATMP and EDTMP and ion bonds between the phosphonate functional groups or carboxylic acid groups of inhibitors and the Ca^{2+} of calcite play the dominant role in their adhesion. Zhang et al found that the mixture of HEDP, PBTCA and DETPMP was a high efficient, low phosphorus, partly biodegradable water treatment agent, which had better scale and corrosion inhibition than that of polyaspartic acid [30]. Cui et al found that the trend of the action between Fe and the electron of corrosion inhibitors supplied was bigger than the trend of the action between Fe and the electron of corrosion inhibitors accepted [31].

Nevertheless, most previous studies focused only on the SS304 and 316L, and no information about the bacterial adhesion on SS317 has been reported. Few experimental studies investigating the effects of agents, e.g. PBTCA/HEDP, on bacteria adhesion have been performed.

The aim of this work is to comparatively study the influence of surface hydrophobicity characteristics of different stainless steel substrata (304, 316L and 317) on the kinetics of SRB adhesion. Bacterial adhesion to PBTCA/HEDP -modified stainless steel substrata surfaces was also examined to investigate if the stainless steel conditioned with PBTCA/HEDP could reduce SRB adhesion and biofilm formation. The parameters, such as surface free energy, surface roughness, hydrophobicity and zeta potential, were discussed with respect to the influence on the bacteria–stainless steel interaction.

2. Materials and methods

2.1. Circulating cooling water

The circulating cooling water, collected from the circulating cooling system in Gaobeidian Thermal Power Plant, was used as the aqueous medium in SRB adhesion experiments. The main water quality characteristics of the cooling water are as follows: pH 7.31; conductivity 750 μs cm^{-1}; total hardness 244.8 mg $CaCO_3$ L^{-1}; Cl- 108.1 mg L^{-1}; SO_4^{2-} 177.0 mg L^{-1}; NO_3^- 97.7 mg L^{-1}; PO_4^{3-} 1.14 mg L^{-1}; NH_4^+ 1.69 mg L^{-1}; COD_{Cr} 55.7 mg L^{-1}; turbidity 1.89 NTU. Prior to use, the water sample was filtered through membranes (pore size 0.22 μm, Millipore, USA) to remove particulate solids and microorganisms.

2.2. Stainless steel coupons

Three types of stainless steel substrata (SS304, SS316L and SS317) were selected in the present study. The element composition of each substrate is listed in Table S1. Materials were machined to obtain stainless steel coupons (1 cm × 1 cm × 0.1 cm). Sample surfaces were ground (1200 grit sand-paper) and polished with diamond-paste (1 μm). The polished coupons were cleaned with 70% ethanol solution, then degreased by sonication with 100% acetone, and finally cleaned by 100% ethanol. To study the antifouling effect of scale inhibitors, SS surfaces were coated with scale inhibitors (hydroxy ethyl fork phosphonic acid, HEDP and phosphono butane-1, 2, 4- tricarboxylic acid, PBTCA) by incubation in sterile cooling water containing 5 mg L^{-1} HEDP or PBTCA, respectively, at room temperature for 24 h. After incubation, the SS coupons were rinsed with sterile distilled water for 30 min, and stored in a desiccator overnight until use.

2.3. Bacterial strain and culture conditions

The sulfate reducing bacterium was used in the study, which has been frequently reported to be involved in microbiologically influenced corrosion. The cultivation of bacteria was performed anaerobically in an anaerobic incubator [32]. Several colonies of SRB grown on a Postagte medium E [33] agar plate was inoculated in 10 mL modified Postgate medium C [33] at 37 °C. After 24 h, the 10 mL culture was transferred to 200 mL modified Postgate medium C and incubated at 37 °C for 16 h. Bacterial cells were pelleted by centrifugation (J2-MC, Beckman Coulter, Inc., Brea, CA, USA) for 5 min at 6500 rpm and resuspended in 10 mL phosphate buffer saline (PBS) (5 mM K_2HPO_4, 5 mM KH_2PO_4, 0.15 M NaCl, pH 7.0). Centrifugation was done twice in order to remove all traces of growth medium. Finally, the cells were suspended in sterilized circulating cooling water to a number concentration of 3×10^6 cells mL^{-1}, as determined in a Bürker-Türk counting chamber [34].

2.4. Surface characteristics of substrata and bacteria

The surface roughness of three SS substrata was determined by an AFM (SPM-9500J3; SHIMADZU, Japan) in contact mode under ambient conditions. The cantilevers were made of silicon nitride (Si_3N_4) with a spring constant of $k = 0.06$ N m^{-1}. The surface roughness was represented as the root mean squared roughness.

The hydrophobicity of SS surface was determined by contact angle measurements with water, formamide, and diiodomethane as the liquids of different hydrophobic levels. (JCZ000C; zhongchen digital technic apparatus co. ltd, shanghai, China). Briefly, each liquid (l.0 μL) was dropped on the polished SS coupon with a micro-pipette, forming a drop in diameter of 1–2 mm. The contact angle between the liquid and SS surface was provided by the image processing system equipped with the instrument. At least, 20 measurements were performed for each substratum.

The hydrophobicity of bacteria was measured according to the protocol reported by [35]. Briefly, bacteria cells in the mid-exponential phase were pelleted through centrifuging at 8000 r/min. The pellets were washed with PBS twice as described above to remove trace nutrients in culture medium. Bacterial suspension (5.0×10^8 cells mL^{-1}) was then filtrated through 0.22 μm pore diameter filter to form bacterial lawns. The filter was maintained in Petri dishes containing 1% (w/v) agar with 10% (v/v) glycerol for 30 min to establish constant moisture contents. Finally, the filter was fixed on a glass slide for the contact angle measurements.

2.5. Surface tension and surface free energy

The surface tensions of each stainless steel materials were calculated according to the approach of Van Oss et al. [36], using the values of the contact angles formed by water, formamide and diiodomethane on each material surface.

The surface tension and its relatedparameters were estimated by

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