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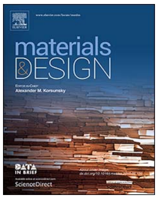

Inhibition behavior of Cu-benzoltriazole-calcium alginate gel beads by piercing and solidification

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ABSTRACT

Calcium alginate gel beads loaded with benzotriazole (defined as 'benzotriazole-calcium alginate gel beads') were successfully prepared by a piercing-solidifying method. Moreover, the insoluble Cu-benzotriazole complexes were introduced on the surface of these gel beads through the interaction between benzotriazole and Cu^{2+} to obtain Cu-benzoltriazole-calcium alginate gel beads, which act as the barrier to extend benzotriazole release time. The loading amount of benzotriazole in the Cu-benzoltriazole-calcium alginate gel beads was determined by thermo-gravimetric analysis (TGA) and the releasing process of benzotriazole was traced by UV–vis spectrophotometer. The inhibition behavior of Cu-benzoltriazole-calcium alginate gel beads for Q235 steel in 3.5% NaCl solution was investigated by polarization and electrochemical impedance spectrum techniques. The results show that complete release time of benzotriazole from benzoltriazole-calcium alginate gel beads is about 400 min, and further prolonged to dozens of hours by forming a barrier of insoluble Cu-benzotriazole complexes. In addition, Q235 steel in 3.5% NaCl solution + 5.0 g/L Cu-benzoltriazole-calcium alginate gel beads exhibit the lower corrosion current density and higher inhibition efficiency (87.06% at 24 h) than Q235 steel in 3.5% NaCl solution.

1. Introduction

Corrosion of metals is a very common and serious technological problem in the practical application. Recently, some methods including electrochemical protection, corrosion resistant material, insulating coating and corrosion inhibition, have been developed to protect metals from corrosion [1–3]. Among these above methods, the addition of inhibitor is regarded as one of the very effective methods, owing to the low cost, high efficiency and available feature.

In the early stage, chromates, phosphates and nitrites were often used as the inhibitors on account of their high inhibition efficiency. However, they were proved to be poisonous, such as chromates can cause cancer [4]. Afterwards, large amounts of attention were paid to organic corrosion inhibitors, including imidazolines, amides, amines and their derived salts [5–7]. Among these organic corrosion inhibitors, benzotriazole and its derivatives are considered as the most popular corrosion inhibitor because of the harmless to the environment and low cost. Moreover, benzotriazole can also react with metal ion to form the complex membrane, which can hinder the contact of metal and corrosive media, but its corrosion-inhibitive effect is not sufficient in the practical environment (such as seawater) due to the water-solubility [8]. Meanwhile, the adding benzotriazole into paint directly is also not effective, due to the formation of empty voids in the paint after it leaves [8].

In recent years, based on the concept of active protection, Buchheit et al. [9] and Kendig et al. [10] successfully loaded the corrosion inhibitor into the micro/nano containers by intercalating or entrapping method. The nanocontainers can be responsible with the environment changes like local pH-changes, light or mechanical force during the corrosion process. Therefore, the corrosion inhibitor loaded in these nanocontainers could be released in a controllable way to achieve the active corrosion protection. The common nanocontainers mainly include porous inorganic nanoparticles and polymer capsules. Most inorganic nanocontainers are mesoporous nanoparticles, like SiO_2 [11], ZnO [12], TiO_2 [13], halloysite nanotubes (HNTs) [14] and layered double hydroxides [15]. For example, hollow mesoporous zirconia nanospheres were synthesized by a sol–gel protection method, and loaded with corrosion inhibitor of L-Carnosine, which can demonstrate the good corrosion resistance ability in 3.5% NaCl solution [16]. Liu et al. [17] reported that a hollow porous Mn_2O_3 microsphere was synthesized by a solvothermal method, and then loaded with 8-hydroxyquinoline to produce an inhibitor delivery system. Abdullayev

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et al. [8] reported that the HNTs can effectively entrap benzotriazole under vacuum, extending the released time of benzotriazole to 30 h, and a successful drug loading reached 5–10 wt% of the HNTs weight. These inorganic containers exhibit the good encapsulation and release performances for corrosion inhibitors, but the high-cost and energy-consuming preparation methods of these inorganic containers, as well as the low encapsulation amount of inhibitors, limit their practical application. The encapsulation of corrosion inhibitors with natural macromolecule materials can solve the above problems. Besides, the natural macromolecule materials, such as alginate [18], chitosan [19], gelatin [20] and polylactic acid [21], are non-toxic, degradable and biocompatible. So far, alginate is regarded as the very potential candidates for drug encapsulation on account of its high mechanical strength and porous internal structure. Meanwhile, alginate has been proved to own certain inhibition effect on metals. For example, the corrosion inhibition on AZ31 magnesium alloy in 3.5% NaCl solution was investigated, and the results showed that it can reach to 90.00% at a sodium alginate concentration of 500 ppm [22].

In this work, benzotriazole was loaded into calcium alginate gel beads (namely 'benzotriazole-calcium alginate gel beads') by the gelation of sodium alginate with Ca^{2+}, followed by introducing the barrier of Cu-benzotriazole complexes to decrease benzotriazole release rate. Moreover, the surface morphology, structure and release behavior of obtained gel beads (defined as 'Cu-benzotriazole-calcium alginate gel beads') were observed, and the inhibition efficiency of Cu-benzotriazole-calcium alginate gel beads was investigated on Q235 steel in 3.5% NaCl solution by polarization and electrochemical impedance spectrum (EIS) measurements.

2. Experimental

2.1. Materials

Benzotriazole, sodium alginate, $CaCl_2$ and $CuSO_4{\cdot}5H_2O$ were purchased from Tianjin Yuanli chemical company. Moreover, all the regents were used as received without any post-treatments.

2.2. Preparation of benzotriazole-calcium alginate and Cu-benzotriazole-calcium alginate gel beads

Firstly, benzotriazole (0.3 g) was dissolved into distilled water (20 mL), followed by dispersed sodium alginate (0.6 g) into the benzotriazole solution and stirred to obtain the homogeneous dispersion of benzotriazole and sodium alginate. Then, as shown in Fig. 1, the resulting solution was injected into the coagulation bath by a syringe needle with the diameter size of 1.6 mm to form benzotriazole-calcium alginate gel beads. The coagulation bath was composed of 3 wt% $CaCl_2$ and 3 wt% benzotriazole aqueous solution. After coagulation for 30 min, the wet benzotriazole-calcium alginate gel beads were collected by filtration. One portion of these gel beads were washed with distilled water and dried in a freeze drying.

Another portion of these wet benzotriazole-calcium alginate gel beads were immersed into the $CuSO_4$ solution (0.08 M) for 1 min to form the barrier of insoluble Cu-benzotriazole complexes on the surface of these beads. Then these gel beads were filtrated, washed and dried in a freeze drying to produce Cu-benzotriazole-calcium alginate gel beads. The possible schematic diagram of the preparation process of Cu-benzotriazole-calcium alginate gel beads is shown in Fig. 2.

2.3. Characterization

Macro morphology of benzotriazole-calcium alginate and Cu-benzotriazole-calcium alginate gel beads was recorded by a digital camera (COOLPIX S620, Nikon, Japan).

Scanning electron microscopy (SEM) measurements for the interior, surface and cross-section of Cu-benzotriazole-calcium alginate gel beads were carried out with a S4800 microscope (Hitachi Limited, Japan).

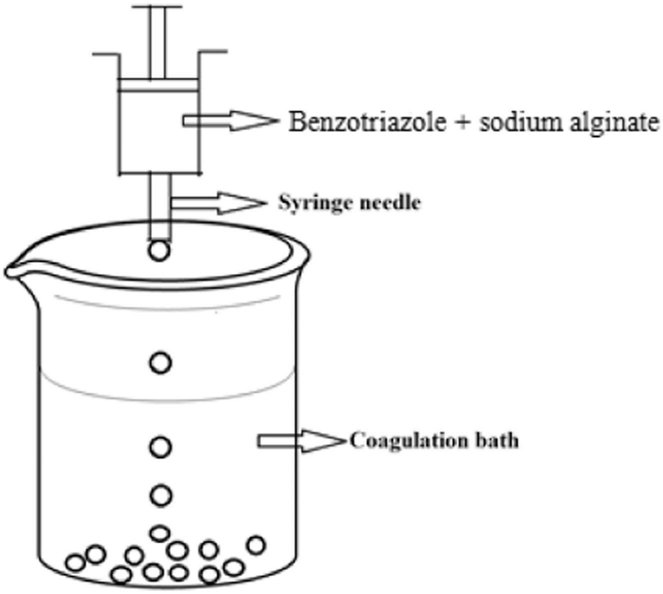

Fig. 1. Experimental process for the preparation of benzotriazole-calcium alginate gel beads.

The Fourier transform infrared (FTIR) spectra of benzotriazole, calcium alginate, benzotriazole-calcium alginate and Cu-benzotriazole-calcium alginate samples were obtained by a Perkin-Elmer Paragon-1000 FTIR spectrometer in the range of 4000–500 cm^{-1}. Each sample was taken as KBr pellets and FTIR spectrum was the average of 20 scans.

Thermo-gravimetric analysis (TGA) of benzotriazole, calcium alginate, benzotriazole-calcium alginate and Cu-benzotriazole-calcium alginate samples were performed from room temperature to 600 °C with a heating rate of 5 °C min^{-1} under N_2 atmosphere using a Rigaku-TD-TDA analyzer.

2.4. Release behavior of benzotriazole

Firstly, benzotriazole (0.1000 g) was added into distilled water (1000 mL) under continuously stirring to obtain homogeneous solution. Then the certain amounts of the above solution (2.00 mL, 5.00 mL, 8.00 mL, 10.00 mL, 12.00 mL and 15.00 mL) were diluted until 100.00 mL, respectively. These benzotriazole solutions with the known concentration were determined by UV–vis spectrophotometer and the results were shown in Fig. 3a. The maximum absorption wavelength of benzotriazole was about 259 nm. Moreover, the relationship between their absorbances and concentrations was fitted linearly to prepare the standard curve of benzotriazole (Fig. 3b).

The release tests were carried out, as follows: benzotriazole-calcium alginate gel beads (0.1 g) were immersed in distilled water (200 mL) under stirring. The dissolution medium (5 mL) was taken out at the given intervals and replaced with fresh distilled water (5 mL). The amount of the released benzotriazole was investigated using a UV2700 UV–vis spectrophotometer. As a control, the same release process was performed for Cu-benzotriazole-calcium alginate gel beads.

2.5. Electrochemical measurements

In order to estimate the anti-corrosion effect of Cu-benzotriazole-calcium alginate gel beads, the polarization curve and EIS of Q235 steel in 3.5% NaCl and 3.5% NaCl + 1.0 g/L Cu-benzotriazole-calcium alginate gel beads were conducted on Autolab 302 electrochemical workstation in a three-electrode system: a graded Q235 samples with an