Preparation of Phytic Acid and its Characteristics as Copper Inhibitor

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Abstract

The aim of this study was to optimize a process of phytic acid extract for the rice bran and into test on the corrosion inhibition of copper H62. Phytic acid was extracted by using combined process technology of microwave and ultrasonic wave from rice bran, and this work present the results of the microwave and ultrasonic wave studies of Phytic acid extracted. Orthogonal experiment was used to study the optimum extraction process of phytic acid. The Phytic acid on copper H62 was evaluated by weight-loss measurements, metallographic microscopic analysis and electrochemical methods. The results demonstrated that ultrasonic treatment time was 20min, microwave treatment time was 3min, acid leaching time was 1.5h, the ratio of raw material and solution was 1:9, the extraction rate of phytic acid was 6.75%; Generation plant power circulating water system was simulated, the inhibition rate of copper H62 was 94.16% when phytic acid concentration was 5mg/L.

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Keywords- Rice bran; Phytic acid; Ultrasonic wave; Microwave; Copper corrosion inhibitor

1. Introduction

Phytic acid is a light yellow or light brown liquid paste. Molecular composition is C$_6$H$_{18}$O$_{24}$P$_6$. Molecular weight is 660.08. Molecular formula is C$_6$H$_6$(OP(OH)$_2$)$_6$[1]. Scheme1 is the molecular structure of phytic acid. The structure performance of phytic acid is similar to that of ethylene diamine four ethanoic acid (EDTA), however, phytic acid is characterized by a wide range of pH values with the chelating ability [2].

Figure 1. Molecular structure of phytic acid
Rice bran is a solid residue from rice polishing that is used in animal nutrition and rice oil production [3]. The traditional preparation methods of phytic acid have chemical synthesis, microbial fermentation and solvent extraction etc. [4]. However, phytic acid extracted by a combined process technology of microwave and ultrasonic wave from rice bran has not been reported till now.

The main objective of present study is to investigate the optimum extractive conditions of phytic acid from rice bran and its characteristics as copper inhibitor. Some factors such as ultrasonic treatment time, microwave treatment time, acid leaching time, the ratio of raw material and solution were studied. The effect of phytic acid as copper inhibitor was evaluated.

2. Materials and Methods

2.1 Materials and Reagents

Rice bran, phytic acid was purchased from National Pharmaceutical Group Chemical Reagent Co., Ltd, HCl, 001×7 resin, NaOH(98%), Ca(OH)_2, C_2H_5OH, CH_3COCH_3, and other chemicals were of analytical grade and used without further purification.

2.2 Preparation Methods of Phytic Acid

Diagram1 shows the extractive process of rice bran. Rice bran was crushed and sieved; the rice bran below 120 mesh was firstly treated with 0.1mol/L HCl for 30min, then treated with MDS-6 microwave device (Shanghai New Instrument)) and KQ-500DB ultrasonic wave (Kunshan Ultrasonic Instrument) for some time respectively; finally treated with LXJ-Ⅱ centrifugal sedimentation machine (Lianshui Telecommunications Motor Factory ) to get the mixed solution. The mixed solution was neutralized with 10% Ca(OH)_2 to pH=3-4, then with 1mol/L NaOH to pH=7 to form the precipitation of calcium phytic acid, which was separated, washed and finally acidified with 001 × 7 resin to get phytic acid.

2.3 Analytical Methods

Qualitative determination of phytic acid was according to ammonium molybdate method [5]. Quantitative determination of phytic acid was according to ferric trichloride method, the absorbance of the solution was measured using a UV-7504 Spectrophotometer (Shanghai Xin Mao Instrument) at 570nm [6].

2.4 Copper Inhibition Test Methods

1) Weight-loss measurement

Corrosion performance testing was carried out according to the HG/T 2159-1991 experimental method [7]. The weight method was measured using a RCC-I Type rotating hanging strip test apparatus (Qinyou Instrument Company) at 45 ± 1 ºC. The ratio of solution volume and sample size was 30mL/cm^2. The concentration of rice bran extract stock solution was 3mg/L, 4mg/L, 5mg/L, 6mg/L, 7mg/L, 8mg/L respectively. The experimental period was 72 h.

2) Surface morphology metallographic analysis

Surface morphology of specimens before and after experiment was observed by Metallographic microscope (DMM-200C, Shanghai Cai Kangguang Science Instrument, China), and the surface characteristics of specimens was analyzed and evaluated.

3) Critical determination of pitting breakdown potential
Constant potential/current Instrument (PS-I, Beijing Zhongfu, China) was used to determine the electrochemical property of phytic acid, the working electrode was copper H62 sealed by epoxy resin with the area of 0.25 cm². The auxiliary electrode and the reference electrode were Pt electrode and saturated calomel electrode respectively. The working electrode and saturated calomel electrode were connected by 0.1mol/L of saturated potassium chloride salt bridge.

The concentration rice bran extract stock solution were prepared to 3mg/L, 4mg/L, 5mg/L, 6mg/L, 7mg/L, 8mg/L as the tested liquid. The cleaned working electrodes were immersed in the phytic acid for 5 hours in order to form the full uniform film. The same amount of besides brine was used as a blank experiment.

3. Results and Discussion

3.1 Optimization of extraction conditions of rice bran

The results showed that: Ultrasonic wave and microwave treatments were obviously affected on the extraction rate of phytic acid. The treatment effect was best when ultrasonic time was 20 min and microwave time was 3 min. In addition, influence factors of extraction also had acid type and acid consumption, etc. These factors research were relatively mature so this study did not discuss the affect of acid type and acid consumption in detail. On the basis, done orthogonal experiment based on the leaching time, microwave processing time, ultrasonic processing time and liquid ratio of four factors, through experimental analysis of various factors on the extraction rate of rice bran to determine optimum reaction. Table 1 was shown that orthogonal table and range analysis.

Table I. Orthogonal Experiment Table of Phytic Acid Extraction

<table>
<thead>
<tr>
<th>Serial Number</th>
<th>A (Minute)</th>
<th>B (Minute)</th>
<th>C (Hour)</th>
<th>D</th>
<th>E (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>2</td>
<td>0.5</td>
<td>1.8</td>
<td>5.42</td>
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<tr>
<td>2</td>
<td>15</td>
<td>3</td>
<td>1</td>
<td>1.9</td>
<td>6.05</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>4</td>
<td>1.5</td>
<td>1:10</td>
<td>5.58</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>2</td>
<td>1</td>
<td>1:10</td>
<td>5.73</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>3</td>
<td>1.5</td>
<td>1:8</td>
<td>6.75</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>4</td>
<td>0.5</td>
<td>1:9</td>
<td>6.34</td>
</tr>
<tr>
<td>7</td>
<td>25</td>
<td>2</td>
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<td>5.57</td>
</tr>
<tr>
<td>8</td>
<td>25</td>
<td>3</td>
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<td>1:10</td>
<td>5.74</td>
</tr>
<tr>
<td>9</td>
<td>25</td>
<td>4</td>
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<td>4.98</td>
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<td>K₁</td>
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<td>5.83</td>
<td>5.72</td>
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</tr>
<tr>
<td>K₂</td>
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<td>6.18</td>
<td>5.59</td>
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<tr>
<td>K₃</td>
<td>5.43</td>
<td>5.63</td>
<td>5.97</td>
<td>5.68</td>
<td></td>
</tr>
<tr>
<td>Extreme Difference</td>
<td>0.84</td>
<td>0.61</td>
<td>0.38</td>
<td>0.31</td>
<td></td>
</tr>
</tbody>
</table>

A: Time of ultrasonic processing; B: Time of microwave processing; C: Time of acid leaching; D: The ratio of raw material and solution; E: Extraction rate of phytic acid; Note: The extraction time included ultrasonic processing time; extracting solution was 0.1mol/L hydrochloric; The ratio of raw material and solution was mass ratio; for each test electromagnetic stirring time, centrifugation time, speed, ion exchange were the same.

Table 1 showed that: Factors affecting phytic acid extraction A>B>C>D, the best level: A₂B₂C₃D₂, which the ultrasonic treatment time was 20 min, microwave treatment time was 3 min, acid leaching time was 1.5 h, The ratio of raw material and solution was 1:9.

3.2 Result of weight method experimental

Phytic acid which extracted under optimum condition was carried on the copper inhibition performance test under the identical condition (Experimental method was showed in Fig. 1). Result was shown in Fig. 1.
Figure 1. Phytic acid concentration influence on the corrosion rate Operational initial conditions: $T=45^\circ C$, [phytic acid]=3-8 mg/L, pH=7.4.

As shown in Fig. 1, phytic acid content was too high or too low all affected the corrosion rate, phytic acid formed film incomplete at low phytic acid concentration and led to corrosion rate lowly. With the increase of the concentration of phytic acid inhibition was significantly increased, however, the phytic acid concentration was too high, which corrosion rate would decrease. Over this study, inhibition effect was best when phytic acid concentration was about 5mg/L. The best inhibition rate was up to 94.16%.

3.3 Metallography microscopic analysis

Copper sheets surface morphology were observed by metallographic microscope (DMM-200C Metallographic microscopic) which amplified 100 times. Fig.2 a and c exhibit the images of uniform surface without pitting and intercrystalline corrosion of copper H62 surface. Fig.2 b and d show the metallography microscopic results of corroded copper H62 in the blank and Phytic acid solution, respectively.

Figure 2. Metallographic microscope photographs. a: The sheet copper before the blank of experiment; b: The sheet copper after the blank of experiment; c: The best conditions of copper corrosion test before the experiment metallographic photos; d: The best conditions of copper corrosion test after the experiment metallographic photos.
We may know that through the contrasted of the copper preview surface contours: Surface of sample a, c were smooth, color uniform. Sheet copper H62 after 72 h weightlessness experiment, Surface of sample b corrosion phenomena obviously, corrosion pore size relatively large, Surface of sample d was no significant surface corrosion; only a small number of corrosion holes on surface of sample.

3.4 Critical pitting potential test results

Tested pitting corrosion potential of corrosion inhibitor by PS-I type constant potential/constant current device. Tested solution of phytic acid concentrations were 4mg/L, 5mg/L, 6mg/L, besides brine was used to blank reagent, the result was shown in Fig. 3.

As shown in Fig. 3, breakdown potential (Φb) of copper sample was -256mv, -148mv, -203mv, when they were passivated by the measure liquid of phytic acid concentration for 4mg/L, 5mg/L, 6mg/L, Φb was enhanced distinctly after phytic acid treatment, test sample Φb of the passivated measure liquid for 5mg/L is the highest, It showed that under the condition of the phytic acid for concentration 5mg/L, the phytic acid can form good protective film that has the shielding and quite complete compact properties, can prevent the corrosive medium effectively to diffuse to the metal surface and can slow down the corrosion rate.

3.5 Phytic acid corrosion inhibition performance comparison experiment

To further study the extraction of phytic acid on copper H62 corrosion inhibition properties, compared it with commonly used corrosion inhibitor BTA, MBO and TTA, result was shown in Fig. 4.
The result showed that the phytic acid inhibition rate was 94.16% when dosage of phytic acid was 5mg/L. The phytic acid respectively high 1.1%, 9.2%, 0.3% compared to BTA, MBO, TTA when they were the same dosage. Fully illustrated that the phytic acid inhibition performance surpassed BTA, MBO, TTA.

4. ConclusionS

(1) A kind of low-cost, non-toxic and efficient green corrosion was extracted using a new processing which is taking rice bran of agricultural products as raw material in this article.

(2) The best dosage of corrosion inhibitor that was good at inhibition performance of copper H62 which was determined by the traditional weightlessness experiment was 5mg/L.

(3) The best technological conditions of tests: the ultrasonic wave processing time was 20min, the microwave processing time was 3min, the extraction time was 1.5h, Ratio of raw material and solution was 1:9.

(4) Corrosion inhibition performance was the best when phytic acid concentration is 5mg/L, the inhibition rate can reach 94.16%.

(5) Using the metallographic microscope analysis and taking the electrochemical corrosion test of critical hole also demonstrated the conclusions.

Acknowledgments

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