สารสกัดจากเปลือกถั่วลิสงสำหรับการเป็นสารยับยั้งการกัดกร่อนของโลหะสังกะสีในสภาวะกรด

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บทคัดย่อ

วัตถุประสงค์ของงานวิจัยนี้คือเพื่อศึกษาประสิทธิภาพการยับยั้งการกัดกร่อนของสารสกัดจากเปลือกถั่วลิสงซึ่งเป็นสารสกัดทางธรรมชาติสำหรับการยับยั้งการกัดกร่อนของโลหะสังกะสีในสภาวะต่างๆ ได้แก่ ปริมาณสารสกัดจากเปลือกถั่วลิสง เวลาในการแช่โลหะสังกะสี ความเข้มข้นของกรดไฮโดรคลอริก และอุณหภูมิ สำหรับการเตรียมตัวอย่างนั้นโลหะสังกะสีขนาดกว้าง 1 เซนติเมตร ยาว 3 เซนติเมตร ถูกขัดด้วยกระดาษทรายและทำความสะอาดโดยการล้างด้วยอะซิโตน ค่าประสิทธิภาพการยับยั้งการกัดกร่อนของสารสกัดจากเปลือกถั่วลิสงสำหรับโลหะสังกะสีที่สภาวะต่างๆ ถูกศึกษาโดยเทคนิคการชั่งน้ำหนักก่อนและหลังการทดลองเพื่อเปรียบเทียบน้ำหนักที่เปลี่ยนแปลงไป และเทคนิคเคมีวิเคราะห์เชิงไฟฟ้า จากผลการวิจัยพบว่าสารสกัดจากเปลือกถั่วลิสงสามารถเป็นสารสกัดจากธรรมชาติที่ยับยั้งการกัดกร่อนของโลหะสังกะสีได้ ข้อมูลจากเทคนิค FT-IR แสดงให้เห็นว่าสารสกัดจากเปลือกถั่วลิสงมีโครงสร้างที่ประกอบด้วยอะตอมของออกซิเจนและวงอะโรมาติก ทั้งนี้ประสิทธิภาพการยับยั้งการกัดกร่อนของสารสกัดจากเปลือกถั่วลิสงสำหรับโลหะสังกะสีมีค่าเพิ่มขึ้น เมื่อปริมาณสารสกัดจากเปลือกถั่วลิสงสูงขึ้น เวลาในการแช่โลหะสังกะสีนานขึ้น และความเข้มข้นของกรดไฮโดรคลอริกต่ำลง ณ อุณหภูมิที่ต่ำลง

คำสำคัญ: การกัดกร่อน / ประสิทธิภาพการยับยั้งการกัดกร่อน / สังกะสี
สารสกัดจากเปลือกถั่วลิสง

Peanut shell Extract as Green Corrosion Inhibitor for Corroded Zinc in Acidic Solution

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Abstract

The objectives of this research were to investigate the inhibition efficiency of peanut shell extract acted as environmental friendly corrosion inhibitor for zinc corroded at different conditions of the amount of peanut shell extract, immersion time, hydrochloric acid concentration, and temperature. For sample pretreatment, zinc platform with 1 x 3 cm dimension was scrubbed and cleaned using sandpaper and acetone, respectively. The inhibition efficiency of peanut shell extract for zinc corrosion at various conditions was performed using weight loss measurement and electrochemical study. The results showed that peanut shell extract could be applied as green corrosion inhibitor for zinc corrosion. FTIR data presented that there are oxygen atoms and aromatic rings in its structural component. The percent inhibition efficiency of peanut shell extract for zinc corrosion was increased at higher concentration of peanut shell extract, longer immersion time, lower HCl concentration, and also lower temperature.

Keywords: Corrosion / Inhibition efficiency / Zinc / Peanut shell extract

Introduction

Metal corrosion is one of the significant problems for various industries such as petroleum, transport, and construction industries because metals are widely used as raw material. Some metal properties, especially strength, and safety can be reduced by corrosion of metal. Factors such as acidity and temperature can affect metal corrosion. Zinc (Zn), a silvery-white metal of the periodic table, is naturally presented as calamine (zinc silicate) and zinc blende (zinc sulfide). Zn is applied for automobile, electrical and hardware industries in die-casting process. It is also mixed with other metals (nickel, silver, and aluminium) to be alloy for many applications. Therefore corroded zinc is the significant topic to concern in many researchers. Corrosion inhibitor method has been popularly used to reduce metal corrosion because of its simplicity and low cost. Effective corrosion inhibitor generally contains nitrogen (N), sulfur (S), oxygen (O), or aromatic ring in its chemical structure. Heteroatoms (N, S, and O) and aromatic ring in charged corrosion inhibitor molecule can produce electrostatic attraction with metal ions. Furthermore organic inhibitor can provide lone pair electron or electron from heteroatoms (N, S, and O) and aromatic ring for unoccupied metal ion. Organic inhibitor can be divided into two types including green and synthetic inhibitors. Although synthetic inhibitor successfully mitigates corroded zinc, they are toxic and expensive. Nowadays green corrosion has been focused instead. It is specified as eco-friendly and cheap corrosion inhibitor. Various plants such as *Eucalyptus globules* (Blue gum) [1], *Centaurea cyanus* (Blue bottle) [2], Seaweed [3], *Tagetes erecta* (Marigold flower) [4], *Tinospora crispa* (Petawali) [5], *Pisum sativum* (Green pea) [6], and *Mansoa alliacea* [7] were studied as successful green corrosion inhibitor for carbon steel, mild steel, and zinc metal. In this work, peanut was selected as natural corrosion inhibitor for corroded zinc because of its nontoxic, inexpensive, and easily found in Thailand. The peanut, edible seeds, is mainly grown for human and animal because there is high oil content and essential nutrients. However peanut shell as agricultural waste was ignored after consumption. To increase its value, peanut shell was extracted to be crude and studied the efficiency to be used as a corrosion inhibitor.

In this work the peanut shell extract as friendly corrosion inhibitor for zinc in acidic solution was studied using weight loss measurement and also electrochemical study to confirm the inhibition efficiency of peanut shell extract. Moreover functional group of peanut shell extract was described by Fourier Transform Infrared Spectrometry (FTIR).

Materials and Methods

All chemicals (acetone, 37% w/w hydrochloric acid – HCl, 98% w/w sulfuric acid – H_2SO_4, and sodium hydroxide – NaOH) used in this experiment were analytical grade ordering from Quality Reagent Chemical (QRëC, New Zealand). Deionized (DI) water was obtained from Nanopure® Analytical Deionization Water with an electrical resistant $\geq$ 18.2 MΩ/cm. Platform shape Zn specimens were cut 1 x 3 cm. They were prepared by polishing with sandpapers, rinsing with deionized water, and then degreasing in acetone in an ultrasonic bath (Elmasonic S 30 H, DKSH, Thailand) for an hour. Subsequently, they were dried in oven (UM, Memmert, Germany) at 80 °C for 30 min, and then stored in desiccators before using. The various concentrations of hydrochloric acid solutions (0.5, 1.0, 1.2, and 1.5 M HCl) were used as the tested solution in this work by dilution of 37% w/w HCl with deionized water. Peanut shell extract was prepared using the procedure mentioned in earlier publication [8]. Peanut shells were cleaned and dried. Subsequently, they were ground to size between 70-120 mesh. The grinded peanut shells were subjected to an alkaline extraction by 7.5% w/v NaOH (1:10 (w/v)) with constant stirring while keeping the temperature at 90-100 °C for 6 hours. After gravity filtration, the filtrate was acidified by 5 M H_2SO_4 to pH 5.5. The hemicelluloses and cellulose were isolated by adding 1.35 L of ethanol (C_2H_5OH, QRëC, New Zealand) and settling for 30 min. The filtrate was separated using vacuum filter. Subsequently, it was acidified by 5 M H_2SO_4 to pH 1.5 and left overnight. The precipitation (lignin) as peanut shell extract was isolated by vacuum filter, cleaned using 1% v/v H_2SO_4, and dried in oven at 125 $^{\circ}$C for 24 hours.

Weight loss measurement was observed using a sensitive balance (Mettler Toledo, Switzerland). The initial weight of Zn platform was measured prior corrosion study. After immersion, it was removed from the tested solution, then washed with 100 cm^3 of ethanol and dried in oven at 80 $^{\circ}$C for 30 min before reweighed. Various factors of content of peanut shell extract (0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 g), immersion time (15, 30, 60, 120, and 240 min), acid concentration (0.5, 1.0, 1.2, and 1.5 M), and temperature (30, 40, 50, 60, and 70 $^{\circ}$C) were focused in this work. All experiments were triplicated measurements to obtain mean value. The inhibition efficiency was calculated by using the equation $\%IE = \frac{(\Delta m_i - \Delta m_u)}{\Delta m_u} \times 100$, where Δm_i and Δm_u are the mass loss of Zn with and without peanut shell extract, respectively for weight loss measurement and $\%IE = \frac{(R_{ct} - R^0{}_{ct})}{R_{ct}} \times 100$, where R_{ct} and $R^0{}_{ct}$ are the charge transfer resistance of Zn with and without peanut shell extract, respectively for electrochemistry as mentioned in earlier publication [9].

An electrochemical study was applied using Potentiostat Electrochemical Analyzer (AMETEK Scientific Instruments, VersaStat 3 Potentiostat Galvanostat). In electrochemical cell, Zn plate acts as a working electrode, platinum wire acts as an auxiliary electrode, and silver-silver chloride as a reference electrode. The polarization measurements were performed at open circuit potential (OCP) in a frequency range of 100,000 – 0.01 Hz with a single amplitude of 10 mV. Charge transfer resistance values at various conditions were observed in triplicated detections for all experiments to determine the inhibition efficiency as mentioned in earlier publications [9-11].

The identification of the functional groups of peanut shell extract was studied using Fourier Transform Infrared Spectroscopy (FT-IR) (PerkinElmer, Frontier FT-IR, USA) at wavenumbers of 4000 – 400 cm^{-1}. Attenuated total reflectance (ATR) mode was applied to confirm functional group in this study.

Results

Effects of content of peanut shell extract, immersion time, acid concentration, and temperature on the inhibition efficiency of peanut shell extract for corroded Zn were investigated using weight loss and electrochemical experiment. Table 1 showed the inhibition efficiency (%IE) of peanut shell extract with various peanut shell extract concentration at 1.2 M HCl.

Table 1 The inhibition efficiency of peanut shell extract with various peanut shell extract concentration at 1.2 M HCl

Content of peanut shell extract (g)	%IE from weight loss study	%IE from electrochemical study
0.5	26.80 ± 2.75	25.22 ± 1.05
1.0	35.25 ± 2.99	34.05 ± 1.09
1.5	42.48 ± 3.04	41.18 ± 1.04
2.0	82.48 ± 2.24	81.38 ± 0.99
2.5	85.48 ± 3.04	83.05 ± 1.02
3.0	83.48 ± 1.04	82.10 ± 1.12

The results (Table 1) clearly show that the inhibition efficiency of Zn corrosion was increased with enhancing peanut shell extract content. The optimum concentration of peanut shell extract was observed to be 2.0 g because it produced more than 80% IE. Immersion times at 15, 30 60, 120, and 240 min depending on the inhibition efficiency were showed in Table 2.

Table 2 The inhibition efficiency of 2.0 g of peanut shell extract with various immersion times at 1.2 M HCl

Immersion time (min)	%IE from weight loss study	%IE from electrochemical study
15	15.35 ± 2.55	14.05 ± 0.95
30	40.80 ± 2.75	39.95 ± 1.05
60	82.48 ± 2.24	81.38 ± 0.99
120	83.08 ± 2.09	82.85 ± 1.55
240	81.48 ± 1.64	80.40 ± 1.04

The results indicate that the inhibition efficiency increases with the longer immersion time. Moreover, %IE was found to be more than 80 above 60 min of immersion time.

Table 3 The inhibition efficiency of 2.0 g of peanut shell extract at 60 min of immersion time with various concentration of HCl

Concentration of HCl (M)	%IE from weight loss study	%IE from electrochemical study
0.5	90.35 ± 1.95	89.05 ± 1.05
1.0	85.80 ± 2.05	84.95 ± 0.95
1.2	82.48 ± 2.24	81.38 ± 0.99
1.5	70.15 ± 3.65	68.45 ± 1.15

Table 3 showed the inhibition efficiency of peanut shell extract with various concentration of HCl. It is observed that the inhibition improvement is more pronounced after decreasing of HCl concentration. Eventually more than 80% IE was obtained with reducing the content down to 1.2 M.

Table 4 The inhibition efficiency of 2.0 g of peanut shell extract with various temperatures at 1.2 M HCl and 60 min of immersion time

Temperatures (°C)	%IE from weight loss study	%IE from electrochemical study
30	82.48 ± 2.24	81.38 ± 0.99
40	60.72 ± 2.75	59.11 ± 1.18
50	44.31 ± 2.89	42.69 ± 1.09
60	35.07 ± 2.83	32.73 ± 1.55
70	28.11 ± 3.24	25.45 ± 0.98

Effect of temperature on the inhibition efficiency of peanut shell extract is demonstrated in Table 4. The result provided that the inhibition ability significantly decreased with increasing temperature. The optimum temperature condition was 30 °C because they produced more than 80% IE of both studies.

Furthermore, the functional group of the peanut shell extract was characterized using FT-IR. Wavenumbers presenting as main functional groups of peanut shell extract were in the region of 3639-3030 cm^{-1} (O-H stretching of aromatic group) and the region of 1500-1400 cm^{-1} (aromatic structure and C-H in lignin [12-13]). These results implied that the active component for zinc corrosion inhibitor of peanut shell extract was lignin compound.

Discussion

In this work, the main chemical component of peanut shell extract was lignin compound as mentioned in the earlier publication [14]. There are active components for corrosion inhibitor such as oxygen atom and aromatic ring in lignin [15-17]. These active groups could be neutralized Zn^{2+} to Zn (reduce Zn(II) to Zn(0)) [18-21]. Therefore, peanut shell extract could be applied as eco-friendly corrosion inhibitor for Zn corrosion. Trends of the inhibition efficiency of peanut shell extract for corroded Zn from weight loss measurement and electrochemical studies are quite close. This experiment revealed that the ability of peanut shell extract as green corrosion inhibitor obtained by different techniques is in good agreement. It could be assumed that peanut shell extract was adsorbed as a layer on the Zn surface. Hence there is no significant increasing of %IE for 2.0-3.0 g peanut shell extract and 60-240 min immersion time also. This was due to the saturation of peanut shell extract on the Zn surface. However peanut shell extract could be decreased its inhibition ability or %IE with factors of acidic media and temperature. In the condition of high acid content and temperature, the molecular structure of peanut shell extract was degraded. Under these conditions the stability of peanut shell extract was destroyed as mentioned in the earlier publication [8].

Conclusion

Peanut shell extract shows the good inhibition efficiency for the corrosion of zinc plate under acidic condition. 2.0 g of peanut shell extract was a minimum amount for performing the high percentage of inhibition efficiency up to 80% under immersion in 1.2 M HCl for 60 min at ambient temperature. This study provides fundamental knowledge of corrosion inhibition of zinc by peanut shell extract and could develop for further application.

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