New coumain derivatives as corrosion inhibitor

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Abstract. Electrocoagulation can be considered as a simple and an efficient method for treating both wastewater and water. In this work, a synthetic bentonite suspension water was treated using this technique to reduce turbidity caused by solid particles pollutants. This process was carried out in a batch glass reactor of 1000 ml operated with aluminium electrodes with and without agitation. The removal efficiency as a turbidity removal procedure has been examined using bentonite clay as a turbidity source. The effects of some parameters such as contact time, and electrolyte concentration on the removal efficiency were investigated and compared. The mixing effect over the range (0–800 rpm) on the removal efficiency was also evaluated. The process was found to achieve excellent turbidity removal with mild mixing (550 rpm). In addition, the effect of using Ultrasonic as a mixing source has also been studied. The lowest residual turbidity was found to be 1.0 NTU for the samples with initial turbidities of 500 NTU. Similar final turbidity of 1.0 NTU was obtained after 25 min with initial turbidity of 200 NTU. This was obtained at a current of 750 mA, a contact time of 60 min, and a calculated dissolved aluminium concentration of 10 mg/l.

1. Introduction

Temperature greatly affects the rate of metal electrochemical corrosion. If there should arise an occurrence of corrosion in a nonpartisan arrangement, the expansion of temperature favorably affects the over capability of oxygen depolarization and the rate of oxygen dissemination, however it prompts a decline of oxygen solvency. If there should be an occurrence of corrosion in a corrosive medium, the consumption rate increments with temperature increment in light of the fact that the hydrogen advancement over potential abatements. Temperatures impacts on acidic erosion, regularly in sulphuric and hydrochloric acids, have been the protest of an extensive number of examinations [1-10].

Corrosion is continuous annihilation of materials typically metals, by concoction response with its condition which implies electrochemical oxidation of metals in response with an oxidation, for example, oxygen. Consumption happens in metals as well as in non-metals like plastics and glass [11]. Corrosion inhibitor is a synthetic aggravates that diminishes the corrosion rate of a material when added to a fluid or a gas [12].

The normal system for hindering corrosion includes development passivation, covering which forestalls access of the substance to the metal. Inhibitors are added to numerous frameworks, for example, cooling frameworks, concoction, oil and gas creation unit, boilers and refinery unit to forestall corrosion. By and large, the compelling inhibitors utilized contain a heteroatom, for example, oxygen, nitrogen, sulfur, and numerous bonds in their structure through which they are adsorbed on
the surface of the metal [13]. That adsorption depends exclusively on certain physiochemical properties of the inhibitor gatherings, for example, useful gatherings, electronic skeleton of the particles and electron thickness at the contributor iota [14]. Recent studies have demonstrated that natural compound containing polar useful gatherings are very productive in limiting the impact of consumption notwithstanding the heterocyclic compound containing π-electrons and polar gatherings. The design of coumarin compounds has consisted of NH₂, carbonyl, and π-electron, which feasibly add to the hindrance of mellow steel consumption in acidic media. The proposed structure of the novel synthesized as corrosion inhibitor is appeared in scheme 1.

![Scheme 1](image)

Reagents and Conditions: a = Tetrabutylammonium bromide (TBAB) / reflux; b = diammonium hydrogen phosphate (DAHP) / reflux; c = hydrolysis; d = benzene / reflux; e = H₂SO₄ / reflux.

**Scheme 1.** Reaction of the new coumarin compounds

### 2. Experimental Section

#### 2.1. General Information

The compounds and solvents utilized were provided by Sigma/Aldrich. The IR spectra of prepared molecules have been done by Nicolet 6700 spectrophotometer and the qualities are communicated in cm⁻¹. NMR spectra were recorded utilizing an AVANCE III 600 MHz spectrometer (Bruker, Billerica, MA, USA), utilizing DMSO-d6 as an interior standard. Elemental analysis was done on an Elementary Vario El III Carlo Erba 1108 basic analyzer (Italy).

#### 2.2. Chemistry

##### 2.2.1. Synthesis of 2-amino-4-(4-bromophenyl)-5-oxo, 5-dihydropyran-3, 2-c chromene-3-carbonitrile (1)

**a. Synthesis of COMP.(1) by using Tetrabutylammonium Bromide (TBAB) as catalyst**

4-hydroxy-2H-chromen-2-one (0.162 g; 10 mmol) was refluxed with 4-bromobenzaldehyde (5 mmol), malononitrile (15 mmol) and tetrabutylammonium bromide (10 mol %). Then, cooled the mixture at 25°C. Then filtered solid mass, dried and recrystallized from ethanol [15]. Then the compound was characterized by spectroscopic and physical data, yields 75%. M.P (222-224°C).

**b. Synthesis of compound (1) by using Diammonium Hydrogen Phosphate (DAHP) as catalyst**
In 50 ml of aqueous ethanol (50% ethanol; 50% water), with 4-hydroxy-2H-chromen-2-one (0.162 g; 10 mmol), 4-bromobenzaldehyde (10 mmol), malononitrile (12 mmol), (DAHP) (26.4 mg, 10 mol%), were mixture (4 hr). at 25°C. when the time was finished, the product was filtered then washed with ethanol and water [16]. Then the compound was characterized by spectroscopic and physical data., yields 70%. M.P (221-223°C); 1H-NMR: δ 4.26 (s, 1H, CH), δ 7.84 (dd, 2H), δ 7.45 (dd, 2H), δ 7.41-7.83 (m, 1H, C-H benzen ring), δ8.5 (s, NH2); FT-IR: 3381.5 cm⁻¹ (NH2), 3183.0 cm⁻¹ (C-H aromatic), 1705.4 cm⁻¹ (C=O, lactone), 221 cm⁻¹ (C=O, lactone); Analysis: The theoretical calculation for C₁₉H₁₁BrClNO₅: C 57.7 % H 2.81 % N 7.09 %, while the experimental calculation shows C 57.4% H 2.5% and N 7.01%.

2.2.2-Synthesis of 2-amino-4-(4-bromophenyl)-5-oxo-4, 5-dihydropyran (3; 2-c) chromene-3-carboxylic acid (2)

Aqueous solution of (NaOH) (1 M, 0.3 ml) was heated with compound (1) for 5 min at 140°C. Then we added HCl(1 M, 0.3 ml) to neutralized the reaction and we got compound (2) at 19–20 min. After fulfillment of the reaction, the product was filtered and washed with ethanol and water, [17], yields 45%. M.P (235-237°C); 1H-NMR: δ 3.83 (s, 1H, CH), δ 7.14 (dd, 2H), δ 7.77 (dd, 2H), δ 7.10-7.60(m, 1H, C-H aromatic ring), δ8.3 (s, NH2), δ 11.0 (s, OH); FT-IR: 3220(NH), 3309 cm⁻¹ (OH); 3085.4 cm⁻¹ (C-H aromatic), 1652 cm⁻¹ (C=O, lactone), 1710 cm⁻¹ (C=O, carboxylic), 1625.9 cm⁻¹ (C=C aromatic); Analysis: The theoretical calculation for C₁₉H₁₁BrNO₅: C 55.09 % H 2.92 % N 3.38 %, while the experimental calculation shows C 55.01% H 2.81% and N 3.29%.

2.2.3-Synthesis of 3-amino-2-(((4-bromophenyl)(2-oxo-2H-chromen-3-yl)methyl)acrylic 2-chloroacetic anhydride (3)

In 100 ml RBF, (0.02 mol) of compound (2) in 4ml ethanol was mixed on the attractive stirrer for 10 min. Four equivalent of chloroacetylchloride (0.02 mol) was included drop shrewd for 1 hr. Response blend was kept for mixing for 24 squirm response blend was cooled, filled super cold water (50 ml) containing a drop of pyridine and mixed until the point when the oil sets. Unrefined item was sifted, washed with icy water and dried. The product was recrystallized from ethanol [18], yields 40%. M.P (277-279°C); 1H-NMR: δ 3.55 (s, OH) δ 4.39 (s, 1H, CH), δ 6.54(s, 1H, CH) δ 7.01(s, 1H, CH), δ 7.11 (dd, 2H), δ 7.81 (dd, 2H), δ 7.4-7.79 (m, 1H, C-H benzen ring), δ8.3 (s, NH2); FT-IR: 3431 cm⁻¹ (NH2), 3050 cm⁻¹ (C-H aromatic), 1650 cm⁻¹ (C=O), 1611.5 cm⁻¹ (C=O, lactone); Analysis: The theoretical calculation for C₂₁H₁₉BrNO₅: C 55.04% H 3.52% N 3.06%, while the experimental calculation shows C 54.9% H 3.11% and N 2.9%.

2.2.4-Synthesis of 7-(4-bromophenyl)-10-(chloromethyl) -6H-chromeno [3', 4': 5,6] pyrano [2,3-d][1,3] oxazine-6,8(7H)-dione (4)

To a solution of 2 mmol of compound (3) in 50 mL of anhydrous methanol was added concentrated sulphuric acid (80 ml). The mixture was refluxed on a water bath for 3-4h. Subsequent to cooling, the response content was filled ice-water blend. The precipitated solid was collected by filtration, washed with water and recrystallized from methanol to obtain compound (4) [19], yields 25%. M.P (215-217°C); 1H-NMR: δ 3.29 (s,2H,CH₂Cl), δ 4.39 (s, 1H, CH), δ 7.11 (dd, 2H), δ 7.79(dd, 2H), δ 7.3-7.79 (m, 1H, C-H aromatic ring); FT-IR: 3180.5 cm⁻¹ (C-H aromatic), 1670.2,1613.2 cm⁻¹ (C=O, lactone), 1571.3 cm⁻¹ (C=C aromatic); Analysis: The theoretical calculation for C₂₁H₁₁BrCINO₅: C 53.36 % H 2.35 % N 2.96 %, while the experimental calculation shows C 52.91% H 2.1% and N 2.88%.
2.3 Gravimetric Experiments

2.3.1 Mild steel specimens.

All through this investigation with the dynamic surface zone of 4.5 cm² the Mild steel examples got from the Metal Samples Company were utilized as the working anodes. The piece (wt%) of the mellow steel was as per the following: Fe, 99.21; C, 0.21; Si, 0.38; P, 0.09; S, 0.05; Mn, 0.05; and Al, 0.01. The estimations were coordinated in flowed air through, non-blended 1.0 M HCl arrangements containing distinctive convergences of coumarin compound.

2.3.2 Weight Loss Method

The specimens in duplicate were suspended in the test solution (200 mL), with the four compounds and without the four compounds. Corrosion Inhibitor of different concentration (0x10⁻² mM, 5x10⁻² mM, 10x10⁻² mM, 15x10⁻² mM, 20x10⁻² mM, 25x10⁻² mM and 50x10⁻² mM), for 1, 2, 3, 4, 5, 10, 24, 48 and 72 hr. at room temperature, [20] The weight of the specimens before and after immersion was determined. Inhibition efficiency of the mild steel was determined using the average of the duplicate value using the equation:

Inhibition Efficiency (IE %) = (1-W₂/W₁) X100

Where, W₁ and W₂ are weight loss of the mild steel without and with the four compounds Inhibitor respectively.

3. Results and Discussion

3.1 Weight Loss Method

Table (1-4) shows the inhibitor efficiency for various concentrations of coumarin compounds (1-4) in 1M HCl at various time interim. It demonstrates that as the inhibitor fixation expands, level of inhibitor proficiency additionally builds which implies inhibitor effectiveness is specifically relative to inhibitor focus at a specific time. It likewise uncovered that at a predefined fixation, rate inhibitor proficiency is conversely corresponding to time that is as time expands, rate inhibitor productivity diminishes. The ideal inhibitor productivity was around 91.2% which relates to 50x10⁻² mM grouping of compound (2) in 1.0M HCl at 72 hours [21].

| Concentration of compound (1) | IE at % |
|-----------------------------|---------|
|                             | 1hr.    | 3 hr. | 24 hr. | 48 hr. | 72 hr. |
| 0x10⁻² mM                   | 0.00    | 0.00  | 0.00   | 0.00   | 0.00   |
| 10x10⁻² mM                  | 10      | 15    | 26     | 33     | 38     |
| 15x10⁻² mM                  | 13      | 16    | 28     | 34     | 39     |
| 20x10⁻² mM                  | 15      | 18    | 29     | 40     | 41     |
| 25x10⁻² mM                  | 16      | 20    | 31     | 42     | 45     |
| 50x10⁻² mM                  | 17      | 31    | 36     | 44     | 50     |
Table 2: Inhibitor efficiency %IE of compound (2) in 1.0M HCl

| Concentration of compound (2) | IE at % |
|-------------------------------|---------|
|                               | 1 hr.   | 3 hr.   | 24 hr.  | 48 hr.  | 72 hr. |
| 0x10^{-2} mM                  | 0.00    | 0.00    | 0.00    | 0.00    | 0.00   |
| 10x10^{-2} mM                 | 20      | 26      | 34      | 41      | 52     |
| 15x10^{-2} mM                 | 23      | 28      | 36      | 44      | 54     |
| 20x10^{-2} mM                 | 26      | 29      | 40      | 49      | 57     |
| 25x10^{-2} mM                 | 29      | 33      | 45      | 51      | 60     |
| 50x10^{-2} mM                 | 54      | 66      | 76      | 85      | 91.2   |

Table 3: Inhibitor efficiency %IE of compound (3) in 1.0M HCl

| Concentration of compound (3) | IE at % |
|-------------------------------|---------|
|                               | 1 hr.   | 3 hr.   | 24 hr.  | 48 hr.  | 72 hr. |
| 0x10^{-2} mM                  | 0.00    | 0.00    | 0.00    | 0.00    | 0.00   |
| 10x10^{-2} mM                 | 22      | 25      | 34      | 41      | 50     |
| 15x10^{-2} mM                 | 24      | 29      | 35      | 47      | 51     |
| 20x10^{-2} mM                 | 25      | 30      | 41      | 48      | 52     |
| 25x10^{-2} mM                 | 30      | 32      | 46      | 55      | 61     |
| 50x10^{-2} mM                 | 53      | 62      | 74      | 81      | 90.3   |

Table 4: Inhibitor efficiency %IE of compound (4) in 1.0M HCl

| Concentration of compound (4) | IE at % |
|-------------------------------|---------|
|                               | 1 hr.   | 3 hr.   | 24 hr.  | 48 hr.  | 72 hr. |
| 0x10^{-2} mM                  | 0.00    | 0.00    | 0.00    | 0.00    | 0.00   |
| 10x10^{-2} mM                 | 9       | 13      | 20      | 30      | 38     |
| 15x10^{-2} mM                 | 11      | 14      | 25      | 34      | 39     |
| 20x10^{-2} mM                 | 13      | 18      | 27      | 39      | 40     |
| 25x10^{-2} mM                 | 14      | 20      | 30      | 40      | 40.5   |
| 50x10^{-2} mM                 | 15      | 23      | 33      | 40.3    | 41     |

Figure 1,2,3,4 demonstrates the chart of rate inhibitor proficiency against inhibitor focus for different time for compound 1,2,3,4 respectively. The results of the experiment have shown that compounds 2 and 3 decreased the corrosion rate as high as around 91.2 %, 90.3% for this specific investigation. The inhibitor proficiency is enabling and this can be used in the ventures as a substitute for the imported synthetic inhibitors. Abdul Amir et.al new coumarin derivative was synthesized and the IE was investigated on the corrosion of MS in 1.0 M HCl but the yield of these compounds is very low and the cost of synthesis is very high compared with our prepared compounds [22].
Figure 1: Chart of % IE for compound (1) against concentration at different time

Figure 2: Chart of % IE for compound (2) against concentration at different time

Figure 3: Chart of % IE for compound (3) against concentration at different time
3.2 Scanning Electron Microscopy (SEM) Analysis

The SEM test was directed at the Electron Microscopy Unit of applied science department. Figure 5 shows the mild steel without corrosion inhibitor and Figure 6 shows that the corrosion inhibitor (compound 2) given security to the mellow steel from the erosion assault brought about by HCl.

Figure 5. The SEM micrographs 5000X, for MS in 1.0 M HCl
Figure 6. The SEM micrographs 5000X, for MS in 1.0 M HCl with 0.5 mM of the compound (2)

3.3 Proposed Mechanisms Actions of Synthesized Compound as Corrosion Inhibitor

Chemically the inhibitor is adsorbed on the metal surface and structures a defensive thin film or synthetic bonds frame by response between the inhibitor and metal. The adsorption segment of regular inhibitors can proceed by methods for one of these courses. first, the cooperation between unpaired electrons and the metal surface. second, charged atoms and metal pull in electrostatic-ally. third, cooperation between π-electrons and the metal surface [23-27]. The restraint effectiveness of our erosion inhibitor against the consumption of mellow steel in 1M of (HCl) can be uncovered by the amount of charge thickness, adsorption locales, sub-atomic size, method of association with the metal surface and capacity of arrangement of metallic insoluble complex. The π electrons for the twofold bonds and free electrons on the oxygen and nitrogen molecules shape synthetic bonds with the metal surface as showed up Figure 7 and Figure 8.

Figure 7. The proposed mechanism of compound(2) as inhibitor
4 Conclusions
This study has shown that compound (1-4) can be utilized as consumption inhibitor. As the convergence of inhibitor delivered expands, the consumption rate diminishes and the inhibitor has an ideal effectiveness of about 91.2% and 90.3 % for mixes 2, 3 individually which showed that its utilization in the process ventures will diminish unquestionably the erosion rate.

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