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Research Article

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Application chitosan derivatives as inhibitor corrosion on steel with fluidization method

Suyanto*, Handoko Darmo Koesoemo, Ratih Ruriyanti and Leo Satya Anggara

Department of Chemistry, Faculty of Science and Technology, Airlangga University, Surabaya, Indonesia

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ABSTRACT

Chitosan derivatives are carboxy methyl chitosan-benzaldehyde (CMChi-B) and carboxy methyl chitosan-urea-glutaric acid (CMChi-UGLU) were synthesized from chitosan. CMChi-B and CMChi-UGLU have been used as new corrosion inhibitor on steel with fluidization method. In this research, corrosion media was NaCl 2% solution and value of maximum inhibition efficiency for CMChi-B and CMChi-UGLU respectively were 80,82% and 80.62%.

Keywords: carboxy methyl chitosan -bezaldehyde, carboxy methyl chitosan-urea-glutaric acid, fluidization, new inhibitor.

INTRODUCTION

Industry development increases in economic growth, but it also produces waste industrial, such as sulphur dioxide and nitrogen oxide. If sulphur dioxide and nitrogen oxide react with rain water, they lead to sulphite acid and nitric acid. The acids known as acid rain and corrosive to equipments which is made from metal [1]. The disadvantages of corrosion are replacing industrial equipment, bridge and construction maintenance, disturbing of production process and transportation [2].

Corrosion is material (metal/alloy and non metal) damage process caused by chemical phenomenon or electro chemical reaction with its environmental or electrochemical reaction of material with oxygen or by thermodynamically reaction on metal and alloy in corrosive media [3-5]. Various methods can be using as corrosion control such us material choice, coating/electro plating inhibiting, cathodic protection, design, material up grading, process control, passivating the surface, raising pH by alkaline beyond pH 10.5**,** lowering potential [6-10].

Chemical compounds in little quantities minimize can inhibit/decrease or prevents corrosion on metal known as an inhibitor corrosion [11-14]. Hetero atom such as oxygen, nitrogen, sulphur and an electron π (in an organic compounds are most effective as excellent inhibitors, unsaturated bond and hetero atom on this compounds are causes an adsorption process take place on the metal surface [15-32].

In acidic media, inhibitor can use to against corrosion [33], the efficiency and effectively the inhibitors depend on some factors such as density of electron donor on the atom in molecule inhibitor [34], size and molecule structure[35], aromatic properties, electronic structure, steric hindrance, area of molecule, molecular weight of inhibitor, functional group, properties of electron π **[**36-45**].** Benzyl Triethyl Ammonium chloride 0,5M have been

evaluated as steel inhibitor corrosion in hydrochloric acid corrosion medium. Inhibition efficiency of benzyl triethyl ammonium chloride was 74,22% in 7 days contact with solution[46].

Process or operation where fine particles convert to fluid-like properties, which fine particles contact with liquid or gas known as fluidization [47,48]. In the fluidization bed, gas or liquid flows from the bottom of the bed. In the solid-liquid-gas system, with certain gas rate, solid particles is flowing with gas and apart from others, experience circulation flows from bottom to the top and return to the bottom of the bed. Solid particles contact with solution/liquid completely and increase the power of inhibiting on to the corrosion rate. Corrosion rate was determined by polarization linier and analyzed with potentiostatic autolab PGSTAT 302N.

EXPERIMENTAL SECTION

Material: chitosan commercial, chloroacetic acid, glutaric acid, benzaldehyde, glacial acetic acid, urea, NaOH, ethanol, isopropanol pro analysis.

Equipment: AAS, Air Pump, FTIR, Potentiostatic Autolab PGSTAT 302N, EDX

Procedure:

1. Synthesis Carboxymethyl chitosan (CMChi)

Amount 10 g chitosan was diluted in 100 ml. Acetic acid 2% was added, then 13,5 g NaOH was added. The mixture was heated on 50^0 C and was stirred during 1 hour. Drop wise solution of 15 g chloroacetic acid in 20 ml isopropanol was added. This mixture was refluxed at 50^0C during 4 hours. The reaction was stopped when 200 ml ethanol 70% was added [49]. The CMChi product was analyzed with FTIR.

2.Synthesis Carboxy methyl Chitosan-Benzaldehyde

Carboxy methyl chitosan- Benzaldehyde (CMChi-B) was synthesized by [50]**:** 10 g CMChi was diluted in 200 ml distillate water, and 15 ml benzaldehyde in ethanol (1/1) was added. The mixture was refluxed at 60^0C for 5 hours. The precipitate was washed with ethanol until filtrate was colorless. Finally, the precipitate was dried in oven at 50^0 C until it was completely dried. The product was analyzed with FTIR.

3.Synthesis Carboxy methyl Chitosan-urea-glutaric acid

Carboxy methyl Chitosan-Urea- Glutaric acid (CMChi-UGLU) was synthesized by [51]**:** 2 g urea was diluted in 60 ml of distillate water and 4 g glutaric acid was added. The mixture was refluxed at 100^0C during 3 hours. This solution was added with drop wise of 2,72 g CMChi in 60 ml distillate water, then the solution was stirred for 4 hours at 60^0C. The product was CMChi-UGLU and it was washed with 0.1 M NaOH, distillate water, acetone, and dried in oven. The product was characterized with FTIR.

4. Test of corrosion inhibition power CMChi-B and CMChi-UGLU on steel

100 ml NaCl 2% was filled in fluidized bed and 0.25 g CMChi-B was added. Steel plate (2cm x 1 cm x 1 mm) was flowed with fluidized bed flow rate from the bottom bed for 30 hours and it was soaked in bed for 42 hours. The plate was replaced from bed and it was washed with distillate water. The last, it dried in oven. The rate corrosion was analyzed with linier polarization potentiostatic and it will be evaluated with AAS.

RESULTS AND DISCUSSION

CMChi from chitosan was synthesized, it was characterized with FTIR. FTIR spectra were shown in Table 1. Data in Table 1 was shown that CMChi synthesis product is similar with literature. It means that synthesis of CMChi in this research was successful. Synthesis of CMChi-B was analyzed with FTIR. The FTIR spectra of CMChi-B is shown in Table 2. The spectra shown that groups of imin, phenyl, carboxyl and C-O-C exist in this compound, it means that synthesis of CMChi-B in this research was successful.

Table 1. FTIR spectra of CMChi synthesis product

Function Group	Wave Number of CMChi-B Synthesis product (cm^{-1})	Wave Number [52] (cm^{-1})
C-O-C	1151.42	1150 - 1070
N-H bending	1587.31	1650 - 1560
COO^-stretching	1407.94	1420 - 1300
CO stretching	1078.13	1150 - 1040
OH bending	1323.08	1410 - 1260
OH stretching	3404.13	3600 - 3200

Table 2. FTIR Spectra of CMChi-B

Function Group	Wave Number of CMChi-B Synthesis product (cm^{-1})	Wave Number [52] (cm^{-1})
C= N imin	1639	1645
Benzene	1554	1600 - 1450
C-O-C	1153	1150 - 1070
COO	1383	1420 - 1300

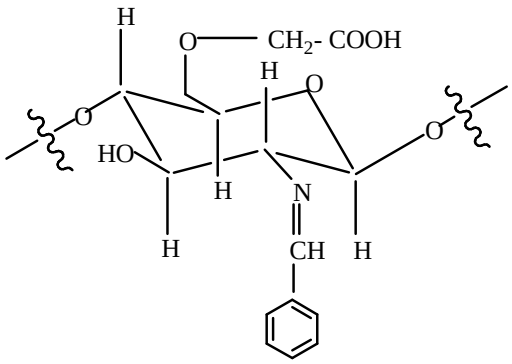

Figure 1. The molecule structure of CMChi-B

The synthesis of CMChi-UGLU was analyzed with FTIR. The spectra of CMChi-UGLU is shown in Table 3. Table 3 shown that synthesis of CMChi-UGLU was successful. Steel analysis with EDX (electron diffraction X-ray) obtained data which shown in Table 4. Steel inhibition efficiency of CMChi-B and CMChi-UGLU with corrosion media variation using fluidization method shown in Table 5.

Table 3. Wave Number of CMChi-UGLU synthesis product

Functional Group	Wave Number CMChi-UGLU synthesis product (cm^{-1})	Wave Number Literatur (cm^{-1})
CO (NH)	3442	3460 - 3440
CO (NH) solid	1668	1680 - 1630
N (CO) N	1668	1660
C - O - C	1114	1151
COOH	2509	3000 - 2500
C-OH stretching	1058	1150 - 1040

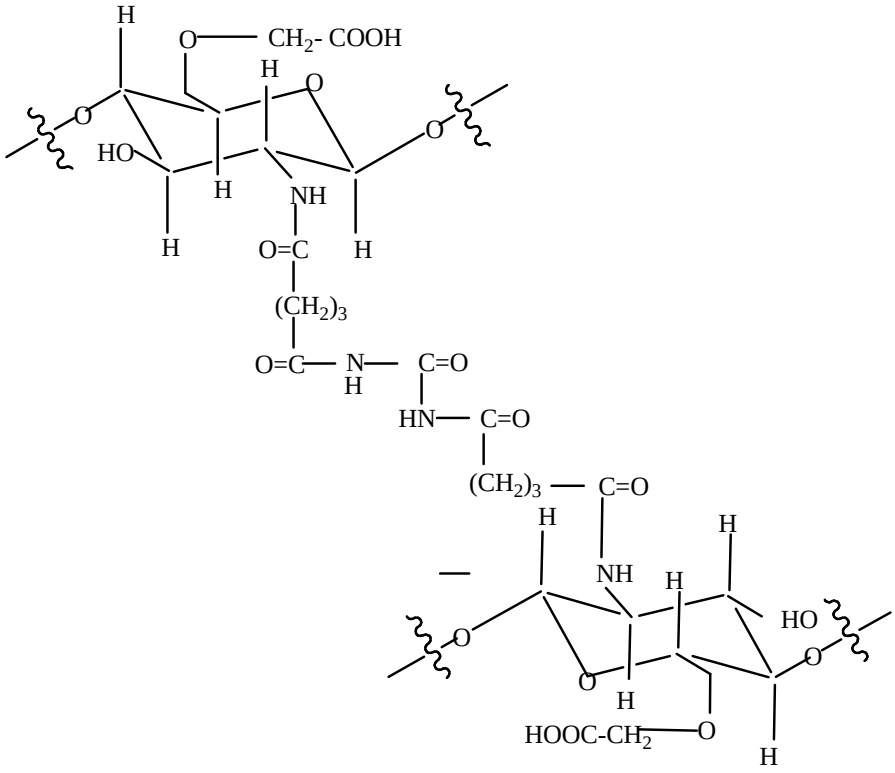

Figure 2. The molecule structure of CMChi-UGLU

Table 4. Composition of steel which was applied in this research

Elemen	Fe	C	Cr	Mn	Co
Atom (%)	92.47	4.11	0.18	0.31	2.93
Mass (%)	95.41	0.91	0.17	0.32	3.19

The rate corrosion in this research was determined with linier polarization potensiostatic analysis using formula: [3] v corrosion = (0.13 x I cor x EW) : d, where v corrosion = rate corrosion (mm per year); Icorr = corrosion current(micro Ampere per cm^2), EW = weight equivalent is mass of atomic/ valence (gram); corrosion current was obtained using tafel analysis with attracted tangent line on plot log current intensity for cross anode and cathode current. Using instrument potensiostatic Autolab (PGSTAT 302 N), the rate corrosion can be obtained automatically. Rate corrosion of blank was also evaluated, thus the inhibition efficiency could be calculate with equation:

Inhibition efficiency = (rate corrosion blank - rate corrosion sample)/rate corrosion blank

The maximum inhibition corrosion of inhibitor CMChi-B and CMChi-UGLU on steel in media NaCl 2% with fluidization method respectively were 80.82% and 80.62 %. The hypotheses of mechanism steel corrosion inhibition by CMChi-B in HCl media shown in Figure 3. In HCl solution media, proton is surrounded the steel. The free electron from N atom is catched proton and leads to formation of $-N^+$ on CMChi-B. Because the proton is catcher by CMChi-B, the proton is not reacting with Fe and the rate of corrosion is inhibited. Without the present of CMChi-B,

the corrosion takes place with following reaction:

$$Fe + 2\,H^{+} \longrightarrow Fe^{2+} + H_2$$

Table 5. The maximum inhibition corrosion on steel in various media

Inhibitor	Method	Corrosion media	Inhibition Efficiency (%)
CMChi-B	Fluidization	HCl 1M	76.55
		HCl 2M	79.71
		HCl 3M	54.36
		NaCl 2%	80.82
CMChi-UGLU	Fluidization	HCl 1M	68.68
		HCl 2M	39.96
		HCl 3M	26.26
		NaCl 2%	80.62

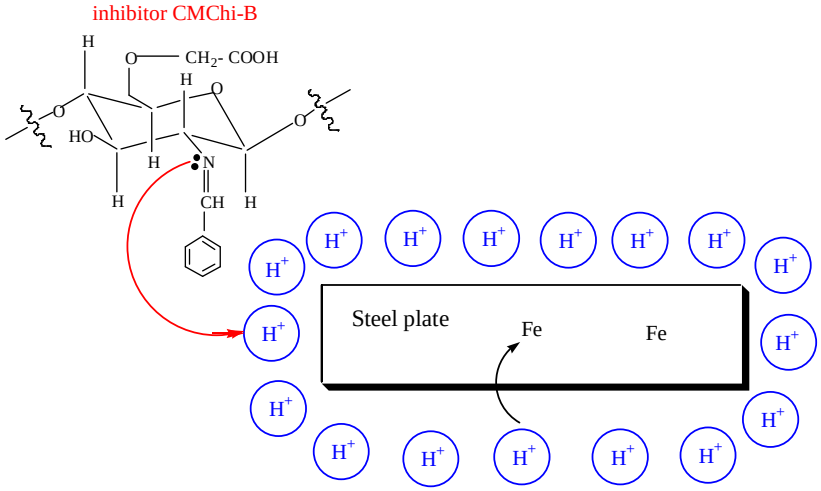

Figure 3. The hypothesis of mechanism steel inhibition corrosion by CMChi-B in HCl media

In this research, maximum inhibition efficiency using fluidization method in NaCl 2% media was 80.82 % for inhibitor CMChi-B and 80.62% for inhibitor CMChi-UGLU. In fluidization method, every particles of inhibitor was transformed into a fluid through suspension in gas and liquid [47, 48]. Each particle flies, rotates, and circulates in the bed, so particle-solution contact was very good and it leads to the increasing of efficiency inhibition. The synthesis product was comparing with TEBA (Tri Ethyl Benzyl Ammonium Bromide), which was using soaking method and HCl as media corrosion. TEBA inhibition efficiency was 74,22 % [46]. Comparing the method, inhibitor, and media corrosion, inhibition efficiency of CMChi-B and CMChi-UGLU were higher than inhibition efficiency of

TEBA, because in CMChi-B containing hetero atom N, O and electron π, whereas CMChi-UGLU containing hetero atom N and O, whereas in TEBA only contain hetero atom N, so CMChi-B has maximum inhibition efficiency more higher than CMChi-UGLU and TEBA

CONCLUSION

Carboxymethyl chitosan- benzaldehyde (CMChi-B) and carboxymethyl chitosan-urea-glutaric acid (CMChi- UGLU) which was synthesized can be used as new steel corrosion inhibitor. Fluidization was a new method to inhibit the corrosion process. Inhibition efficiency of CMChi-B and CMChi-UGLU were respectively 80.82% and 80.62%. The both inhibitor could inhibit steel corrosion in NaCl 2% as corrosion media solution.

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