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New Unsymmetrical Schiff base as Inhibitor of Carbon steel Corrosion and Antibacterial Activity

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Abstract

New unsymmetrical Schiff base namely (2-hydroxy-3-((E)-(2-((E)-(4-oxo-4H-chromen-3-yl) methyleneamino) phenylimino) methyl) Benzoic acid) was prepared and characterized by IR, HNMR,C^{13}NMR and EI-mass .The inhibition effect on the corrosion of carbon steel in industrial water have been investigated at different temperature using weight loss and Tafel polarization measurements. The effect of time and temperature on activity were studies and compared with standard commercial inhibitor also the antibacterial activity of synthesized Schiff base against four types of bacteria which is commonly known in oilfield were tested.

Keywords: unsymmetrical Schiff base, Tafel polarization, antibacterial, 3- formylsalcylic acid, 1, 2-phenylene diamine.

Introduction

Schiff base are organic compounds possessing azomethine group which resulted from condensation of amine with aldehyde or ketone. Condensation products ofaldehydes with only one amine group of diamine compounds give aso called half units which can react with another aldehydes or ketones giving unsymmetrical Schiff base[1-4]. Schiff base derived from aromatic amine and aromatic aldehydes have a wide variety of application such as biological activity, catalytic activity and also used as ligands to obtain metal complexes[5] because of their excellent abilities of this type of Schiff base are widely used as anticorrosion for different metals in different media[6,7]. Schiff base containing more than one hetero atoms beside π-electrons exhibit high inhibiting properties by providing electrons to interact with metal surface. In this paper we report the preparation of a new unsymmetrical Schiff base derived from o-phenylenediamine and two different aldehydes and study of their inhibitor efficiency and the bacterial activities.

Methodology

Material: 3- formylsalcylic acid was prepared according to the Duff procedures[8] 3-formyl chromoe (sigma), 1, 2-phenylene diamine (Merck). Were used forsyntheses. The industrial water which are used in drilling (TDS 1280–1800 PPm) used as a medium of the study.

Instruments: The IR spectrum was recorded as KBr pellets on a Shimadzu. The[1] HNMR, [13] CNMR were recorder on a Brucker (400 MHz for proton and 100 MHz for[13] CNMR). The spectra recorded in DMSO – d_6, TMS as internal standard, EI – mass was recorded on Agilent, Tafel plots was recorded on Bank eieiktornkk intellgent CONTROLS Type MLab 200.

Synthesis of Schiff base: 10 mmole (I.66 g) of 3-formylsalcylic acid in 25 ml of absolute ethanol. To this an ethanolic solution of 15 mmole (excess) 1,2-phenylenediamine was added drop wise with constant stirring ,and then the mixture was refluxed for 3 hrs. The solid product which obtain after cooling were filtered, washed with water and recrystallizedfrom ethanol.

The second stage: 5 mmole of the resulting product from stage one was dissolved in chloroform (20 ml), crystals of PTSA was added as catalyst, 5 mmole of 3-formyl chromone in 20 ml ethanol was added and the mixture was refluxed for 4 hrs. Cooled and filter and the green crystal which obtain washed with chloroform and recrystallized from ethanol , to afford a yellow crystal m.p. 215 – 217 ^oC, yield 63%.

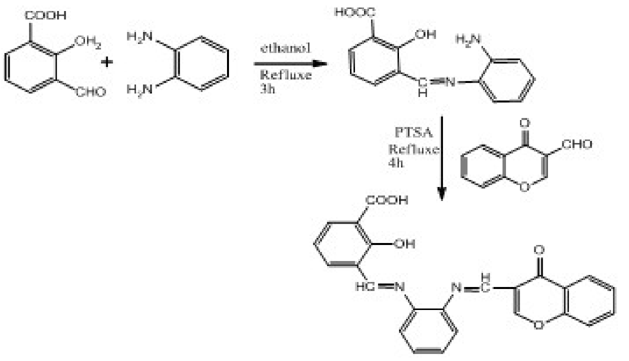
Weight loss method: Carbon stillspecimens of dimensions 2*1.5*0.3 cm were used in this method. The specimens were polished using Buhler sheets (120, 200, 300, 600, 1200) grade to remove adhering impurities and then wash with acetone and dried. The specimens were immersed in 50 ml of the experimental solution contained different concentration of inhibiter to choose the ideal concentration also the experiments repeated at that concentration in different temperature and also at different time.

Antibacterial activity: The Antibacterial activity of the prepared concentration was tested invetro against Gram (+ ve) (*Staphylococcus Aureus* (S.A), *Staphylococcus Saprophytic us* (S.S)) and Gram (-ve) (*Escherichia Coli* (E.C), *Psphclomahas Aeruyinose (P.A)* by diffusion method were socked in different concentration of concentration in DMSO.

The nutrient agar plates and incubated for 24 hrs at 37 ^oC. The diameter of on inhibition zone was measured.

Results and Discussion

Scheme-1 show the two steps of synthesis of Schiff base:



Scheme-1
Two steps of synthesis of Schiff base

The final product (unsymmetrical Schiff base) was characterized by IR, ^{1}HNMR, C^{13}NMR and mass spectrometry. The IR spectrum exhibits a broad band at 3427 cm^{-1} attributed to intermolecular hydrogen bonding OH[9] .The strong broad band centered at 1633 cm^{-1} attributed to a combined two C=O groups stretching. Also another combined band centered at 1583 cm^{-1} attributed to azomethine groups. Figure-3. ^{1}HNMR spectrum figure-4, show a signal at 3.16 ppm attributed to carboxylic proton , a signal at 9.2 ppm attributed to phenolic proton[10], two signals appear at 8.17 and 8.28 attributed to non equivalent azomethines protons .The aromatic protons at the reign 6.77 – 7.98 ppm. C^{13}NMR spectrum show a two singlet at 174.6 and169,2 ppm attributed to C=O (chromone moiety) and C=O of carboxylic groups respectively , also a two signal at 158.19 ppm and 155.54 ppm attributed to the two non equivalent azomethines groups[11], figure-5.

EI-mass spectrum of Schiff base show the molecular ion at m/z 412 , with relative abundance equal (2 %) figure-6 which is agreement with formula and in equivalent to its molecular weight

Corrosion study: Weight loss method: In weight loss method four different concentration of inhibitor (0.1, 0.01, 0.001, 0.0001 M) were tested (table-1).

Table-1
Effect of concentration on weight loss at one hour

Concentration	0.1M	0.01 M	0.001M	0.0001M	Industrial water
Weight loss	0.0004 g	0.0004g	0.0006 g	0.0007g	0.0011g

Inhibitor efficiency increases with concentration and reached a maximum efficiency at 0.1M,the effect of concentration can be ascribed to blocking of active sites of metal surface[12]. The Inhibitor efficiency increases were measured at this concentration at (30, 40, 50) (table-2).

Table-2
Effect of temperature on IE

Temperature	30 °C	40 °C	50 °C
Efficiency	63.75 %	65.20 %	60.31 %

The results indicate that the efficiency reach a maximum 65.2 % at 40°C and then decrease at 50°C, also the Inhibitor efficiency were test at different time, also Inhibitor efficiency were test at different time (1, 2, 3, 4 hrs) at different temperature (30–50°C) at the best concentration of inhibitor (0.01 M). The result tabulated in table-3.

Table 3
Effect of time on IE

Temperature	**Efficiency**			
	Time 1h	**Time 2h**	**Time 3h**	**Time 4h**
30 °C	63.75 %	67.11%	73.53 %	81.96 %
40 °C	65.20 %	70.87 %	78.37 %	85.47 %
50 °C	60.02 %	65.32 %	72.77 %	80.13 %

It can be seen from the date the Inhibitor efficiency increases with time and decreasewith increases in temperature, this can be explained that the increase in time allowed to inhibitor to film formed on the carbon steel surface and decrease in efficiency with increases the temperature this may be attributed to the partially decomposition of the film and separated from the carbon steel surface[13].

This Inhibitor efficiency was compared with the starting material (Aldehydes and Amine) and a commercial inhibitor that is used in oil industry namely potassium dichromate, at 30 °C. The results showed Schiff base is more effective.

This may be explained due to increase the functional groups (C=O, C=N, hetero atoms and rings), so the density of electron increase[14].

The Inhibitor efficiency of Schiff base was investigated by electrochemical after4 hrs at 30°C. Table-4.

Tafel plot method: Tafel plots of carbon steel in presence of Schiff base (0.01 M) and inhibited and without inhibitor, the Inhibitor efficiency was calculated by using corrosion current density as follow[15]:

$$IE \% = (1 - (I_{inh} / I_i) \times 100$$

I_{in} = the current in presence of the inhibitor, I_i =the current without inhibitor. The calculated IE from this method was found 88.o4%. The Tafel polarization curves of carbon steel are show in figues-1, 2:

Table 4
Comparison of Inhibition efficiency of Schiff base with starting materials

Objects	M1	1, 2-phenylene diamane	3-formyl chromoe	3-formylsalcylic acid	potassium dichromate
Efficiency	85.47 %	79.73 %	73.08 %	69.74 %	80.11 %

Figure-1
Tafel plot without inhibitor

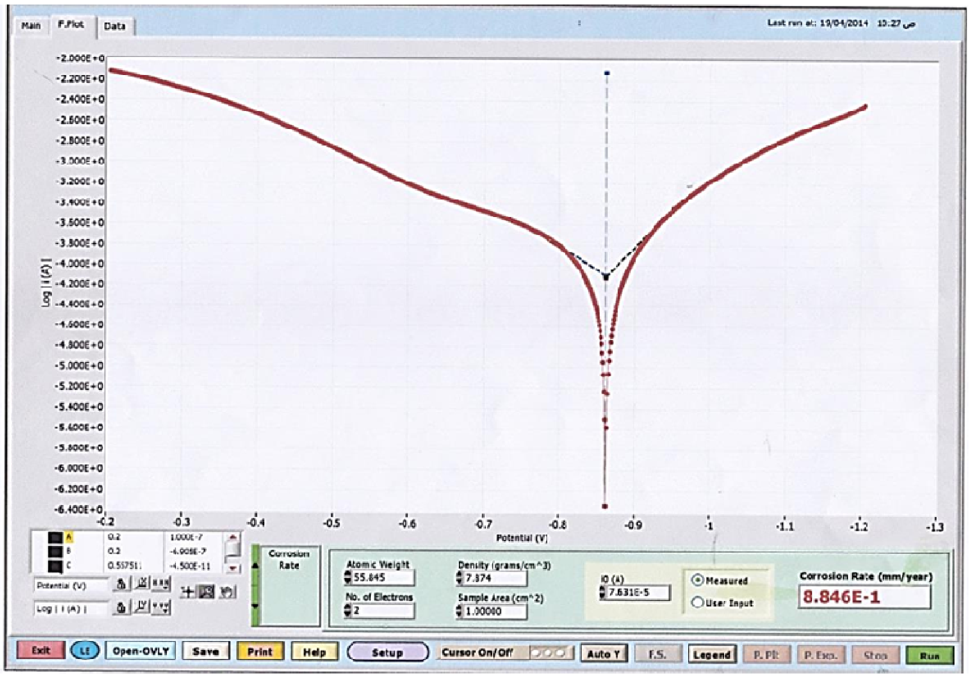


Figure-2
Tafel plot in presence Schiff base

Antibacterial activity: Bacterial sensitivity of 4 type of bacteria against prepared unsymmetrical Schiff base were recorded in table-5.

Table 5
Effect of concentration on Antibacterial activity

Concentration	**Tape of bacteria**			
	S.A	E.C	P.A	S.S
0.1 mg/ml	17 mm	17 mm	18 mm	20 mm
0.01 mg/ml	14 mm	15 mm	15 mm	18 mm
0.001 mg/ml	13 mm	12 mm	13 mm	15 mm

Moderate sensitivity was observed with concentration (10 mg/ml) and the inhibitionzone increase with elevated concentration (100 mg/ml). Table-6.

Table 6
Comparison of antibacterial activity of Schiff base with standards

Tape of bacteria	Objects			
	M1	X3	X4	X5
S.A	13 mm	13 mm	33 mm	15 mm
E.C	12 mm	13 mm	20 mm	14 mm
P.A	13 mm	19 mm	17 mm	21 mm
S.S	15 mm	13 mm	22 mm	15 mm

X3 = 1,2-phenylene diamine. X4 = potassium dichromate. X5 = Amoxicillin.

Conclusion

The unsymmetrical Schiff base can be synthesized in two steps, the first step conditions required an excess of amine to control the condensation of aldehyde with one amine group.

Inhibited corrosion of carbon steel explained by the interaction between the functional groups of Schiff base and metal surface.IE increase with increased inhibitor concentration, also the IE increase with time. The in vitro studies against four type of bacteria show a moderate activities. This compound can be used as a novel compound to reduce the corrosion in oil fields.

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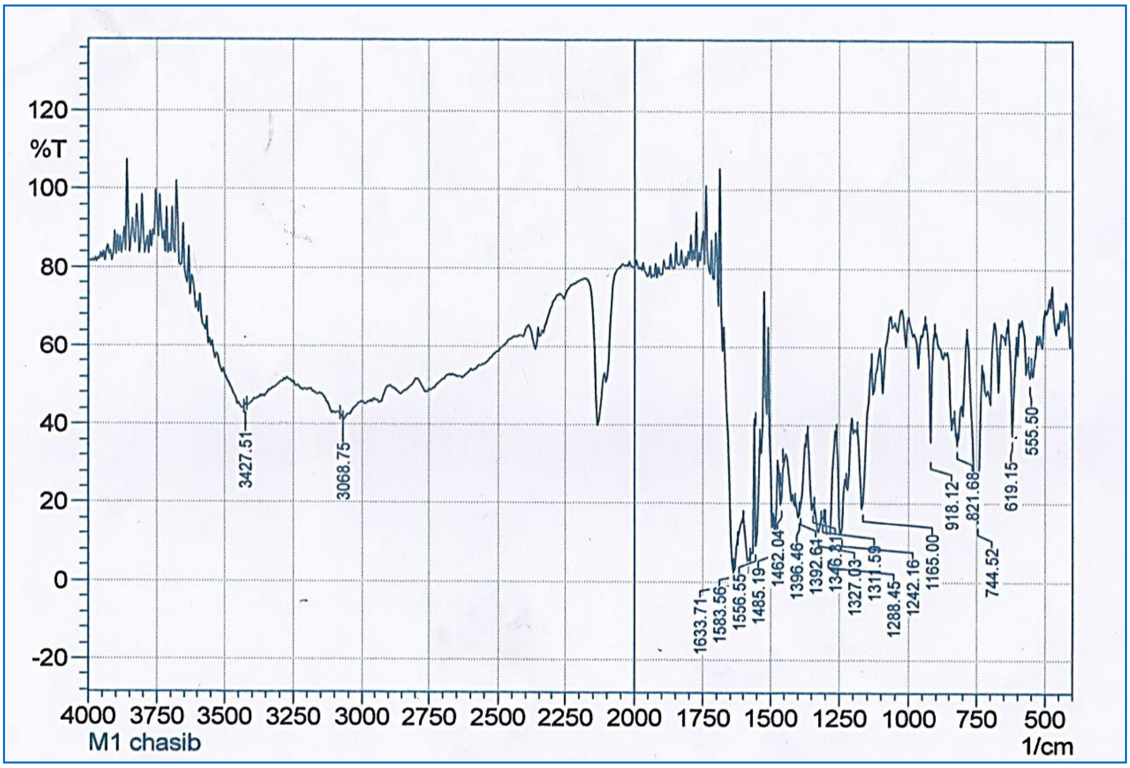

Figure-3
IR spectrum of Schiff base (KBr disk)

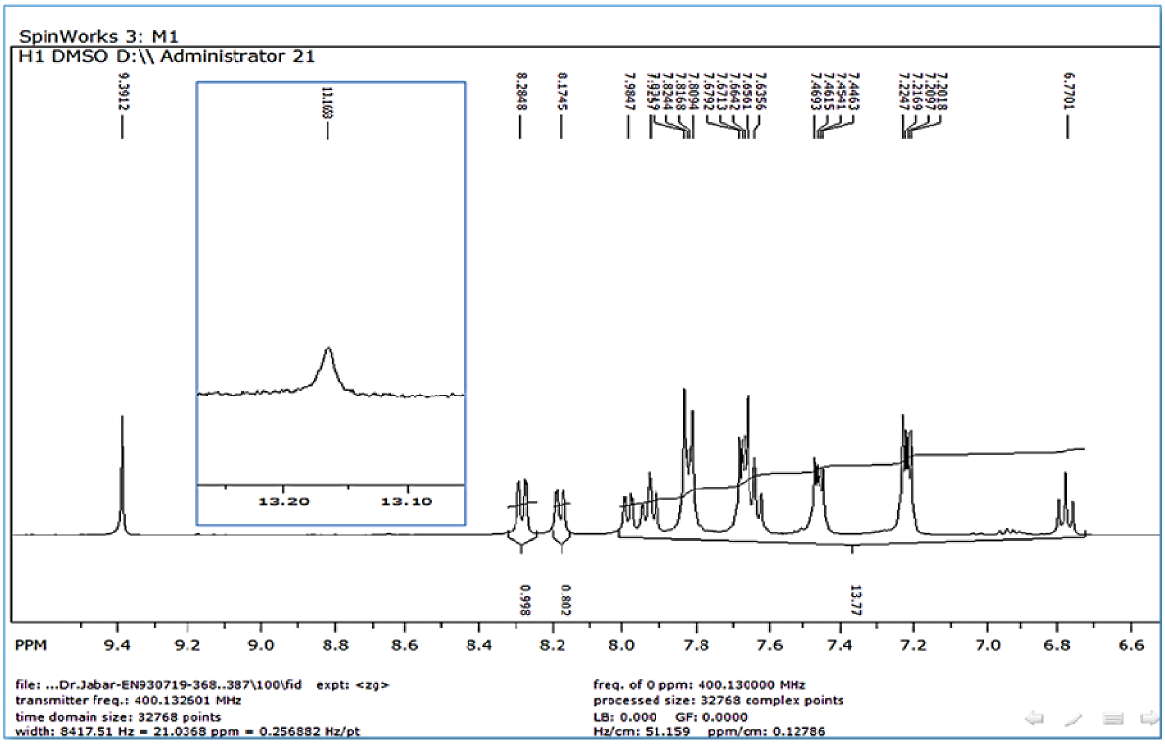

Figure-4
[1]HNMR spectrum of Schiff base

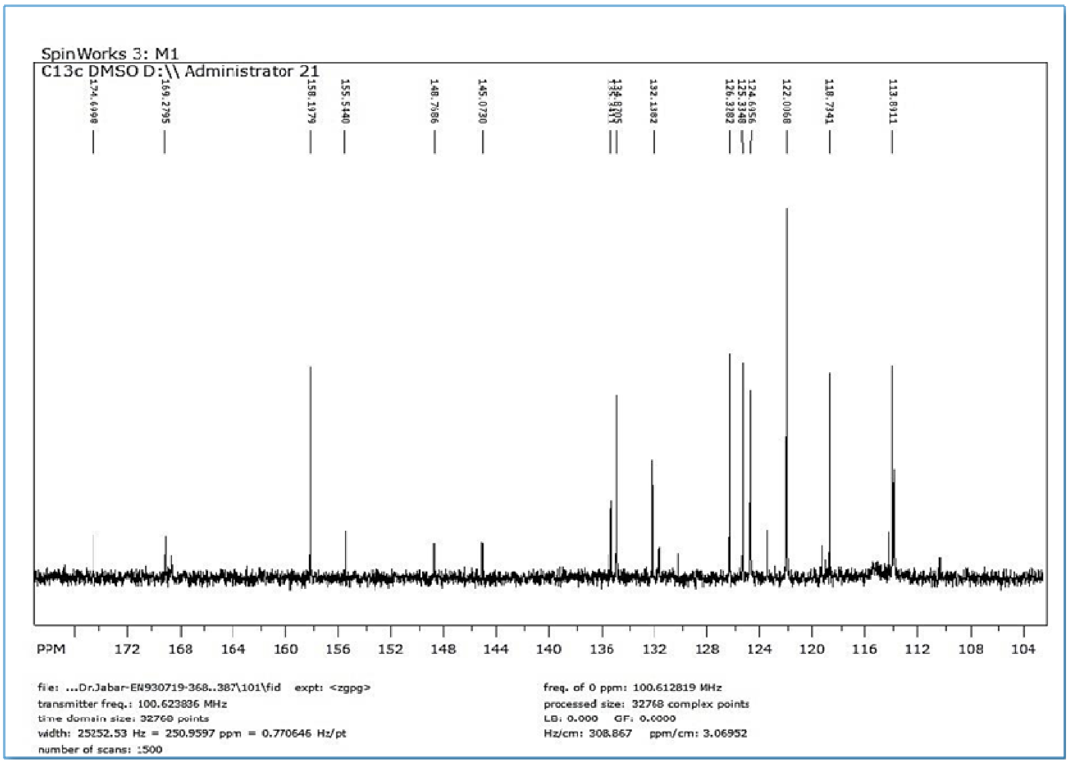

Figure-5
[13]CNMR spectrum of Schiff base

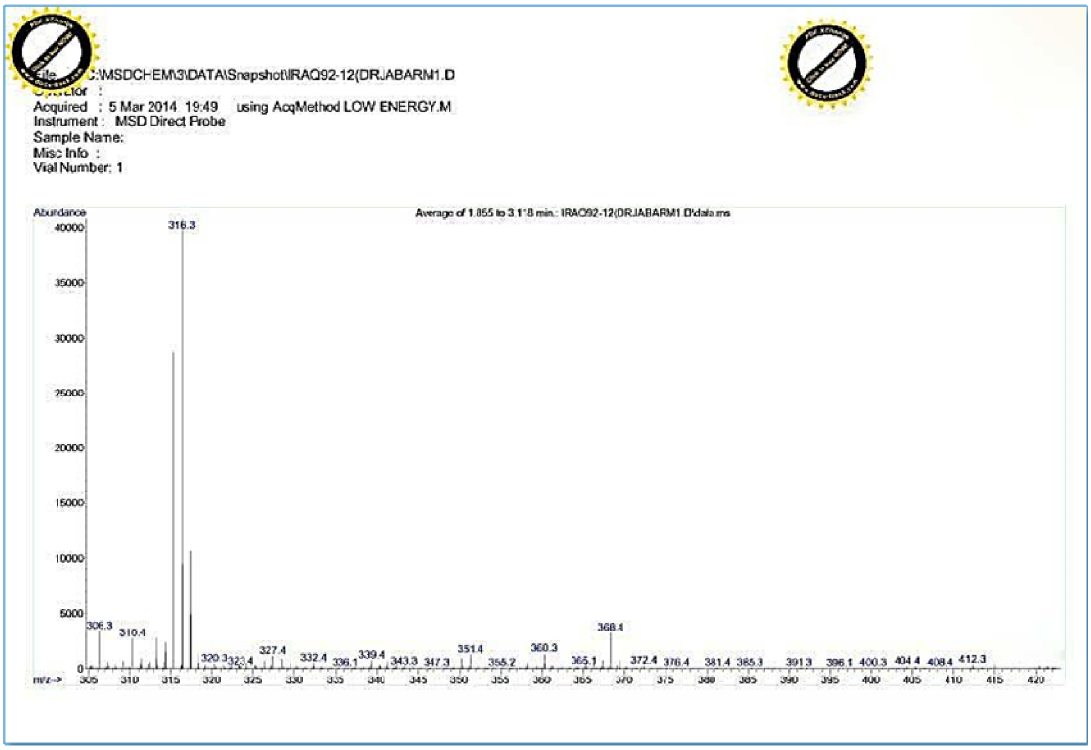

Figure-6
EI – mass (70 eV) of Schiff base

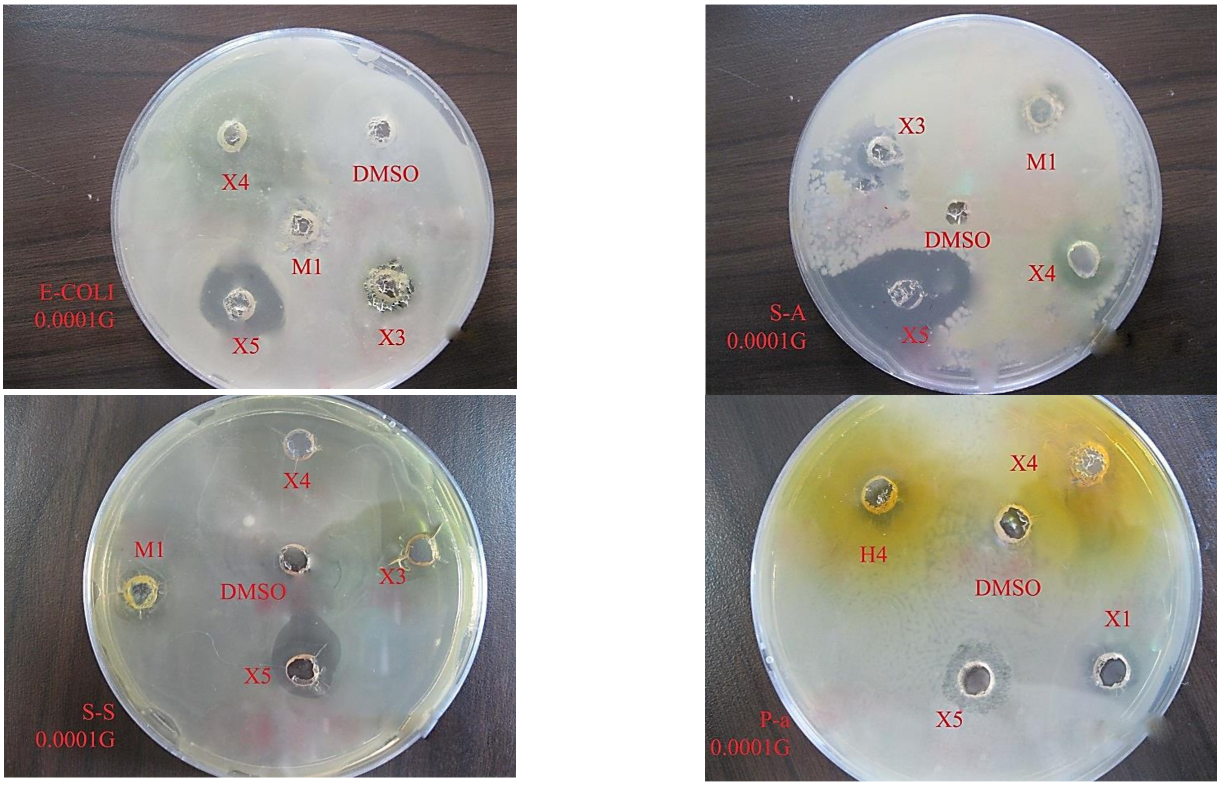

Figure-7
Antibacterial activity of Schiff base

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