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Corrosion, inhibition and biological evaluation investigations of Schiff bases derived from formyl chromone

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ABSTRACT

Three new schiff bases derived from 3- Formyl chromone with Sulfapyrdazine (K3), 3-formyl-6-methyl chromone with Sulfamethoxeypyrdazine (H3) and 3- formyl-6-methyl chromone with Sulfaproxylene (H4) were Synthesized. The structures were confirmed by IR, ^{1}H and $^{13}CNMR$, and EI-mass Spectrometry. Corrosion inhibition of these compound on carbon steel in industrial water have been investigated using weight loss and Tafel polarization methods. The effect of temp. and concentration were investigated. The compounds were screened for their in vitro antimicrobial activities against four types of bacteria which commonly known in oilfield.

Keywords: Formyl chromone, Sulfa drug, Corrosion inhibition, antimicrobial activities.

INTRODUCTION

Sulfa drug and their Schiff bases are important compounds owing to their wide rang application , these classes of compounds are well known organic corrosion inhibitions of different metals [1] as well as these compounds are widely used as antimicrobial[2] , anti-tumor and antifungal[3] . For the literature review compounds possessing hetero atoms, functional groups beside azomethine group are reported as effective corrosion inhibitors for mild steel, Al, Zn, and Cu. Compared with the corresponding aldehydes and amines[2,4]. The present article was undertaken the corrosion inhibition and biological activities of three new schiff bases toward carbon steel in industrial water.

MATERIALS AND METHODS

Material: The 3- formyl chromone and 3- formyl-6-methyl chromone were purchased from Sigma, Sulfamethoxey pyrdazine and Sulfaproxylene from Himedia.

Instruments:
Melting points were recorded in open capillaries in thermo scientific melting points apparatus, IR Spectra were recorded as KBr pellets on shimadzu FT-IR Spectrphotometer, NMR Spectra were recorded on Brucker 400 ($400MH_Z$for^{1}Hand $100MH_Z$for^{13}C) using DMSO-d6 as a solvent and TMS as internal reference. Tafel polarization analyses were done by DY 230 Series potenisostat –Digi-IVY instrument.

Synthesis:
Synthesis of N-(6-methoxypyribazin-3-yl)-4-((4-oxo-4H-chromen-3-yl) methylene amino) benzene sulfonamide (K3):3- Formyl chromone (1.74 g 10mmol) dissolved in 20ml of absolute ethanol was mixed with (2.31g 10mmol) 0f Sulfamethoxepyrdazine in 20ml of the same solvent to this solution ,crystals of p-toluene sulfonic acid was added. The reaction mixture was refluxed for 3hrs, the mixture after that was cooled to room temperature and the resulting yellow precipitate was filtered and washed with cold ethanol and recrystallized from mixture of ethanol and water (1:1). The product isolated as a yellow powder m.p 183-185^{o}C, yield 58%. IR (KBr/cm^{-1})[5]: 3236νN-H,

1656νC=O, 1595νC=N. ^{1}HNMR (DMSO-d6, δ ppm)[6] : 11.8(1H, NH), 8.94(1H, HC=N), (7.08-8.16 Ar-H), 6.5, 6.93(2H, Pyridizinemethoxy), 3.86(3H, OCH_3). EI-mass: $\{M+1\}^+$436 1.6%.

Synthesis of N-(6-methoxypyridazin-3-yl)-4-((6-methyl-4-oxo-4H-chromen-3-yl)methylene amino)benzene sulfonamide (H3): by the same procedure of K3, H3 was synthesized from equal molar of 3- Formyl-6-methyl chromone and the mixture was refluxed for 5hrs. The product isolated as yellow crystal in 68% yield, m.p 117-119^{o}C. IR (KBr/cm^{-1}): 3194 νN-H, 1651νC=O, 1595νC=N. ^{1}HNMR (DMSO-d6, δ ppm): 11.82(1H, NH), 8.91(1H, HC=N), (7.08-8.18 Ar-H), 3.86(3H, OCH_3), 2.3(3H, CH_3).

Synthesis of 4-isopropoxy-N-(4-((6-methyl-4-oxo-4H-chromen-3-yl) methylene eamino)phenylsulfonyl) benzamide (H4): Sulfaproxylene(1.74g, 10mmol)dissolved in 20ml of warm absolute ethanol was mixed with (2.31g 10mmol) from3- formyl-6-methyl chromone dissolved in 20ml of warm absolute ethanol ,to this solution , crystals of p-toluen sulfonic acid was added, The mixture was refluxed for 4hrs and then cooled to room temperature, filtered the precipitate was washed with cold ethanol and dried at 50^{o}C, the yellow crystal product m.p. 153-157^{o}C, yield 75%. IR (KBr/cm^{-1}): 3265νN-H, 1652νC=O, 1595νC=N. ^{1}HNMR (DMSO-d6, δ ppm): 12.1(1H,NH), 8.9 (1H,HC=N), (6.95-8.22 Ar-H),2.29(3H,CH_3). EI-mass: M^+504, 5%.

Weight loss method:

Carbon still specimens type A-510 (C;0.31, Mn;0.9, S;0.05, P;0.04, Fe;98.70) [7] of dimensions 6.65∗3∗0.3cm were used in this method after abraded with emery sheet , wished with water and acetone then dried and weighted. Beakers of 100ml capacity were labeled 1-5 .no.1 was reserved as blank (industrial water). The remaining beakers contained the schiff base at concentration 0.1, 0.01, 0.001 and 0.0001M. After immersed the specimens removed, wished with water and acetone dried and reweighted. This procedure was done in one hour time at 303K. The weight loss was calculated by the relation [8] :

$$CR=WL*K /A*D*t$$

Were CR the rate of corrosion, WL is the weight loss in mg, K constant (534), A is the surface area ofspecimen in inh^2, D density of specimens and t is the time in hours.

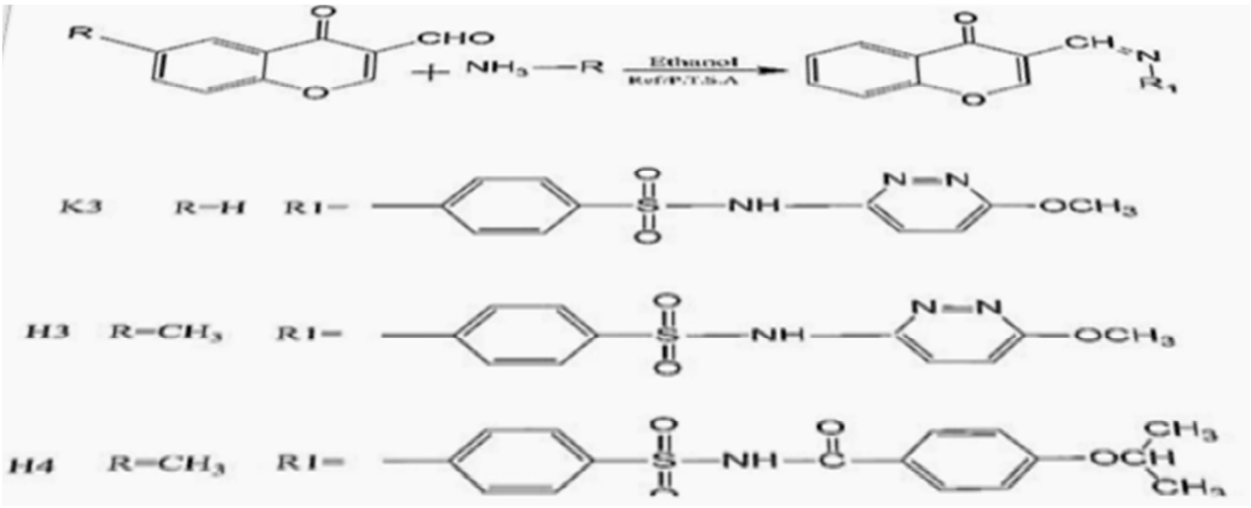
The efficiency of the inhibitor was calculated using the following eq.

$$IE\% = (CR_o - CR_i / CR_o)* 100$$

Were CR_o and CR_i are the corrosion rate of uninhibited and inhibited respectively[9].

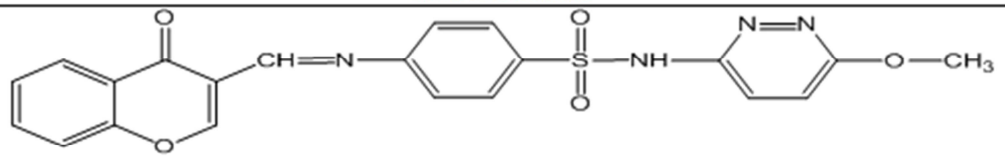
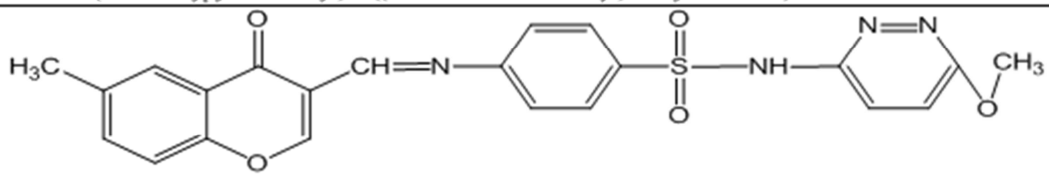
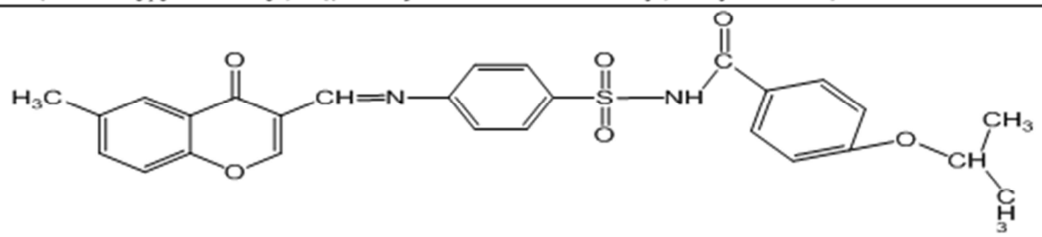
RESULTS AND DISCUSSION

Scheme-1 Show the method of preparation of schiff bases, the final product are stable in air until 100^{o}C. The name and structures are listed in table-1.



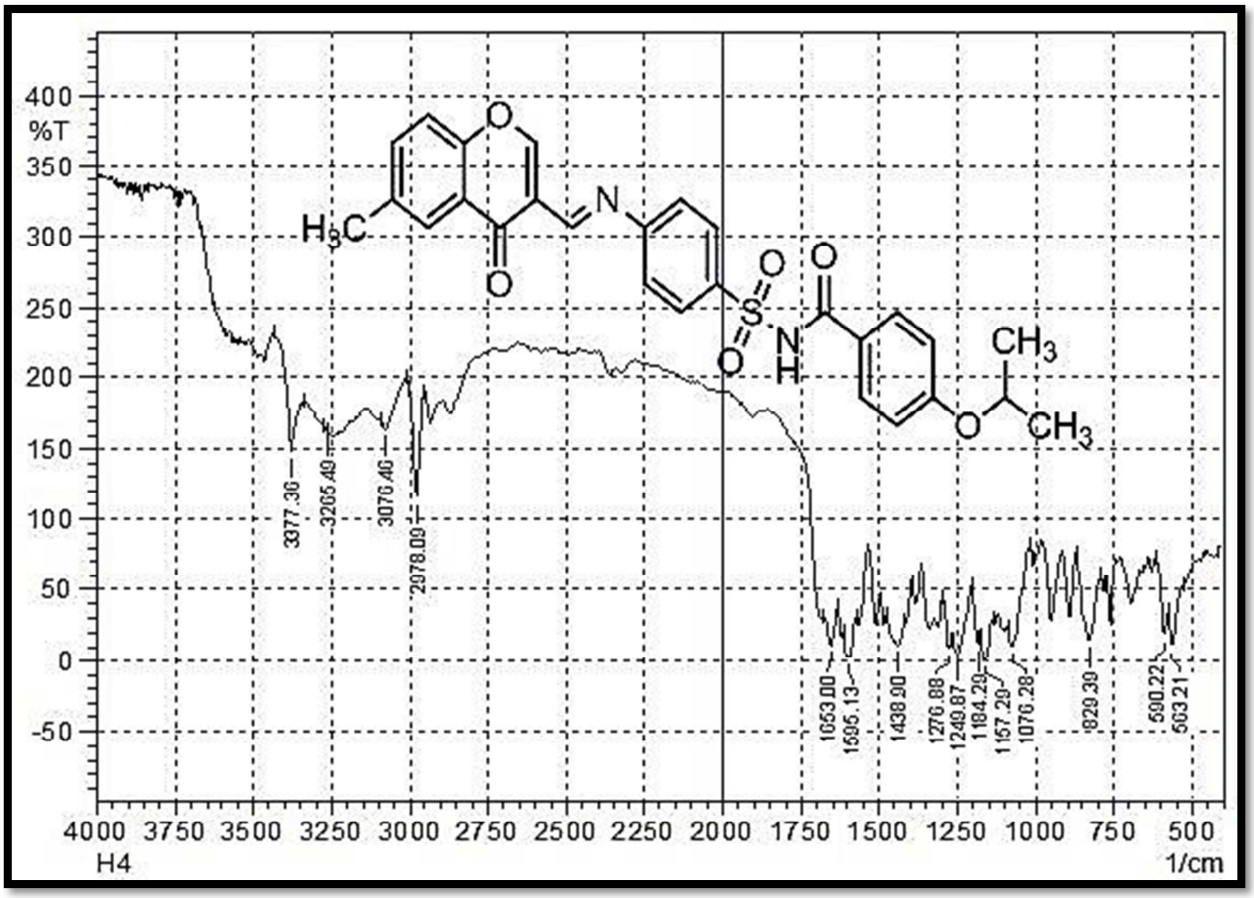
Scheme-1 synthesis of Schiff base

Table-1 the name and structures of prepared compounds

symbol	name and structure
K3	 *N*-(6-methoxypyridazin-3-yl)-4-((4-oxo-4*H*-chromen-3-yl)methyleneamino)benzenesulfonamide
H3	 *N*-(6-methoxypyridazin-3-yl)-4-((6-methyl-4-oxo-4*H*-chromen-3-yl)methyleneamino)benzenesulfonamide
H4	 4-isopropoxy-*N*-(4-((6-methyl-4-oxo-4*H*-chromen-3-yl)methyleneamino)phenylsulfonyl)benzamide

Infrared spectra:

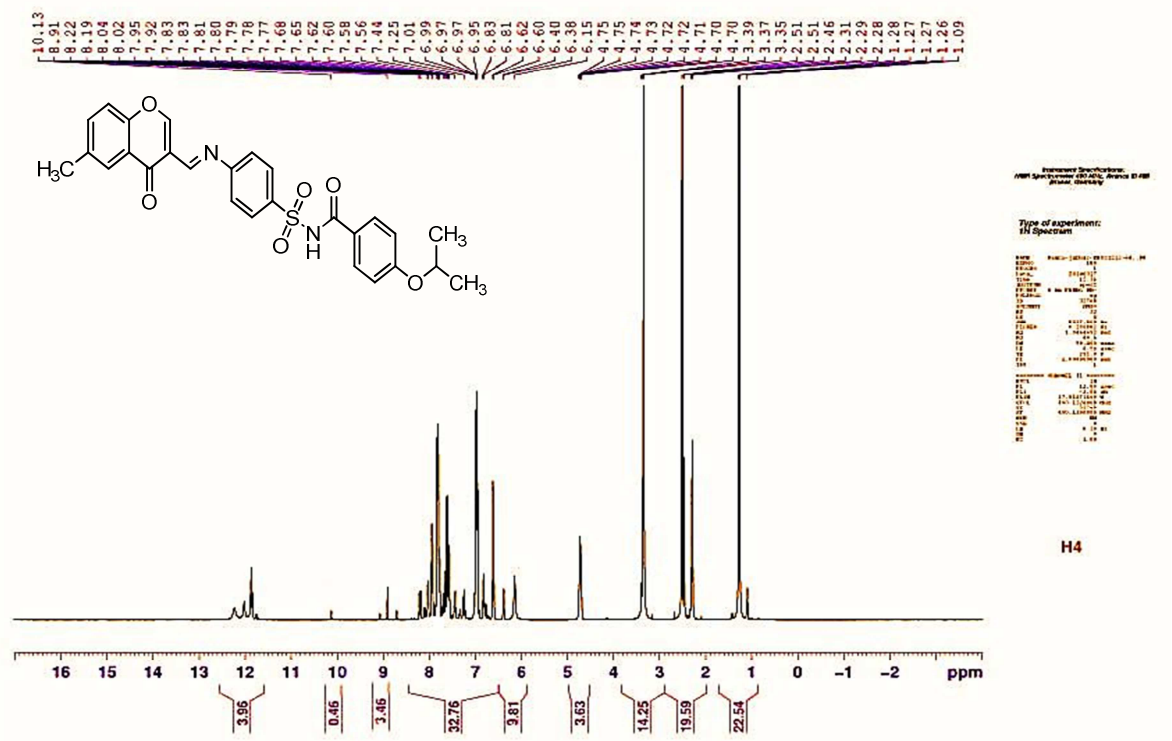
Formyl chromone one of the beta ketoaldehyde shows two strong bands in carbonyl region , the first one at~ 1700cm^{-1}attributed toformyl carbonyl and the second at 1650cm^{-1}attributed to chromone form[10]. The IR spectra of all compound shows the totally absence of the formyl chromone while the carbonyl of chromone ring remain an effected, this clearly indicated the condensation between sulfa and formylchromones take place on formyl carbonyl group. In addition the anew band at 1595cm^{-1} attributed to C=N, indicate the schiff base formation Fig-1.



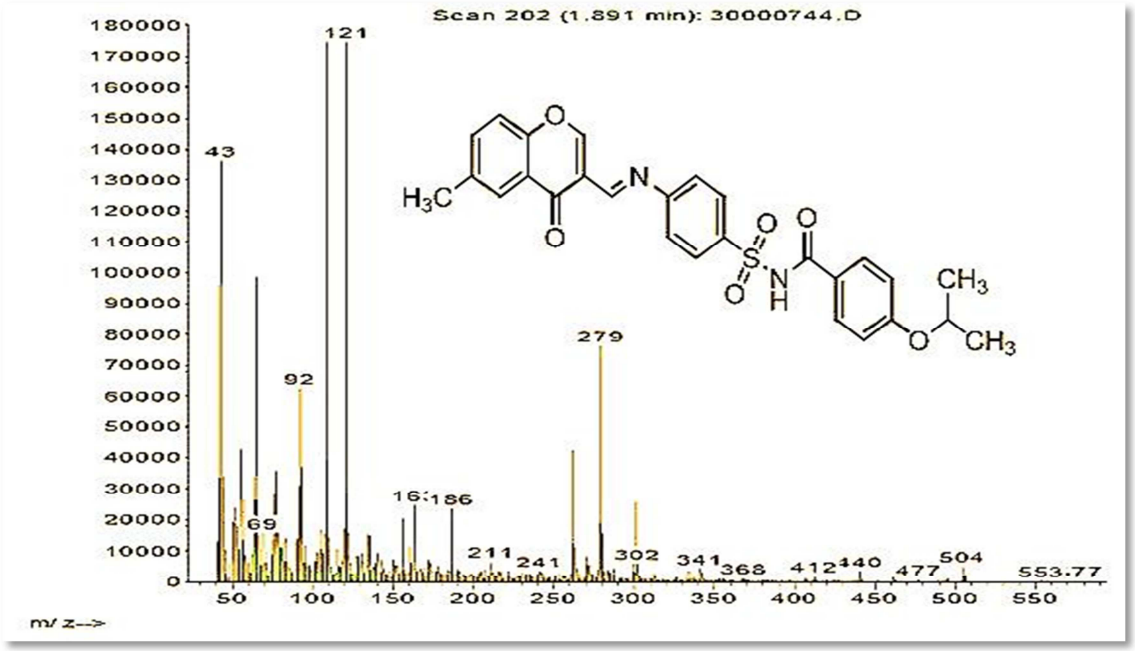
(Fig 1) IR Spectrum of compound H4

^{1}H NMR: All compound show a signal attributed to azomethine proton at δ 8.9-8.92 ppm (Fig -2). The signal at δ 11.2-12.1ppm were due to N-H proton of sulfa moiety. In addition ,a singlet signal at δ 3.86ppm in K3and H3compounds spectra a attributed to methoxy protons. The methyl proton of aldehyde moiety in compoundH3 and H4 appear as asinglet signal at δ 2.38ppm.The two methyl protons of sulfaproxylene moiety in compound H4 appear as a doublet signal at δ 1.2ppm while the CH proton appear as a multiplet signal at δ 4.86ppmThe aromatic protons appear in expected region(δ6.95- 8.22ppm)[11].

.EI-mass: the mass spectra of compound K3 show a peak at 436m/z which is with agreement with M+1, while compound H4 show the molecular ion at 504m/z with relative abundance 5% (Fig-3).



(Fig -2)^{1}HNMRSpectrum of compound H4



(Fig -3)EI-mass Spectrum of compound H4

Corrosion Study:

Weight loss method: The corrosion rate and inhibition efficiencies for carbon steel at different time of immersion (1-4hrs) ,and different concentration of inhibitor were tested (0.1, 0.01, 0.001, 0.0001 M). The results are tabulated in Tables 2-3.

Table- 2 weight loss results of the corrosion tested

symbol	Rate of Weight loss			
	0.1 M	0.01 M	0.001 M	0.0001 M
industrial water	0.0034 g	0.0034 g	0.0034 g	0.0034 g
H3	0.0004 g	0.0007 g	0.0009 g	0.0008 g
H4	0.0007 g	0.0007 g	0.0007 g	0.0008 g
K3	0.0003 g	0.0006 g	0.0008 g	0.0008 g

Table- 3 The corrosion rate at 303, 313, 323 K

Temperature (K)	TIME (hrs)	corrosion rate (mpy)			
		Industrial water	K3	H3	H4
303	1	7.0350	7.0350	3.0315	5.0250
	2	8.0411	2.0100	2.5125	3.5175
	3	8.3751	2.3450	2.3450	2.8720
	4	8.5426	2.0203	2.0203	2.5277
313	1	9.0451	7.0350	4.0200	5.0250
	2	9.5476	4.0200	3.5175	3.5175
	3	10.0501	3.3500	2.6800	2.8003
	4	10.8038	2.5003	2.2612	2.3731
323	1	9.3493	6.6812	6.0772	6.1773
	2	10.5526	6.1595	4.8740	5.1382
	3	11.3915	4.3303	3.7417	3.8843
	4	12.0601	3.0111	2.7637	2.8093

The IE increase with immersion time for all inhibitor concentration and the IE of all compounds increase with concentration, this might be due to the long time allowed to inhibitor to film formed on the carbon still surface and this is with agreement with the effect of concentration Where the IE increase with concentration. The IE of K3 and H3 higher than H4 due to the effect of methoxy pyridiazine moiety which consider an activated group (OCH_3) and two nitrogen atoms in general the high IE of all studies compounds are due to the effect of substituents OCH_3, C=O, hetro atoms which activate the aromatic ring and the presence of many groups contain ion pairs of electrons, which increase the electron density[11,12].The results are tabulated in Table 4.

.

Table- 4 the IE andθ at 303, 313, 323 K

Inhibitor	Temperature (K)	symbol	TIME (hrs)			
			1	2	3	4
K3	303	IE	0	75.00	71.99	76.35
		θ	0	0.7500	0.7199	0.7635
H3		IE	56.90	68.75	71.99	76.35
		θ	0.5690	0.6875	0.7199	0.7635
H4		IE	28.37	56.25	65.70	70.41
		θ	0.2837	0.5625	0.6570	0.7041
K3	313	IE	22.22	57.89	66.66	76.85
		θ	0.2222	0.5789	0.6666	0.7685
H3		IE	55.55	63.15	73.33	79.07
		θ	0.5555	0.6315	0.7333	0.7907
H4		IE	44.44	63.15	72.13	78.03
		θ	0.4444	0.6315	0.7213	0.7803
K3	323	IE	28.53	41.63	61.98	75.03
		θ	0.2853	0.4163	0.6198	0.7503
H3		IE	34.99	53.81	67.15	77.08
		θ	0.3499	0.5381	0.6715	0.7708
H4		IE	33.92	51.30	65.90	76.70
		θ	0.3392	0.5130	0.6590	0.7670

Tafel method: Tafel polarization analysis were done by pleating anodic and cathode curves to the potential axis to obtain corrosion current and the IE were calculated by the eq[13,14].

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

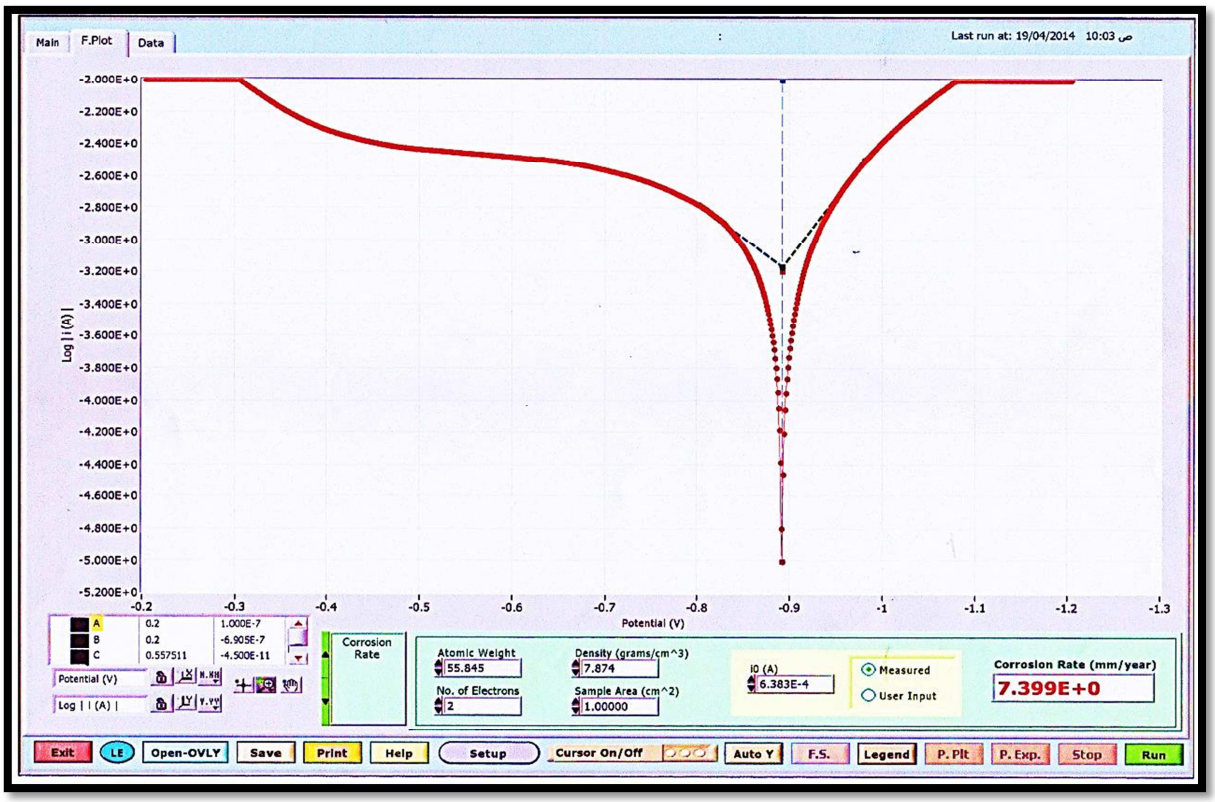
Where $I_{inh,}$ I_i the current in presence of inhibitor, and without respectively

(Figs 4-7).

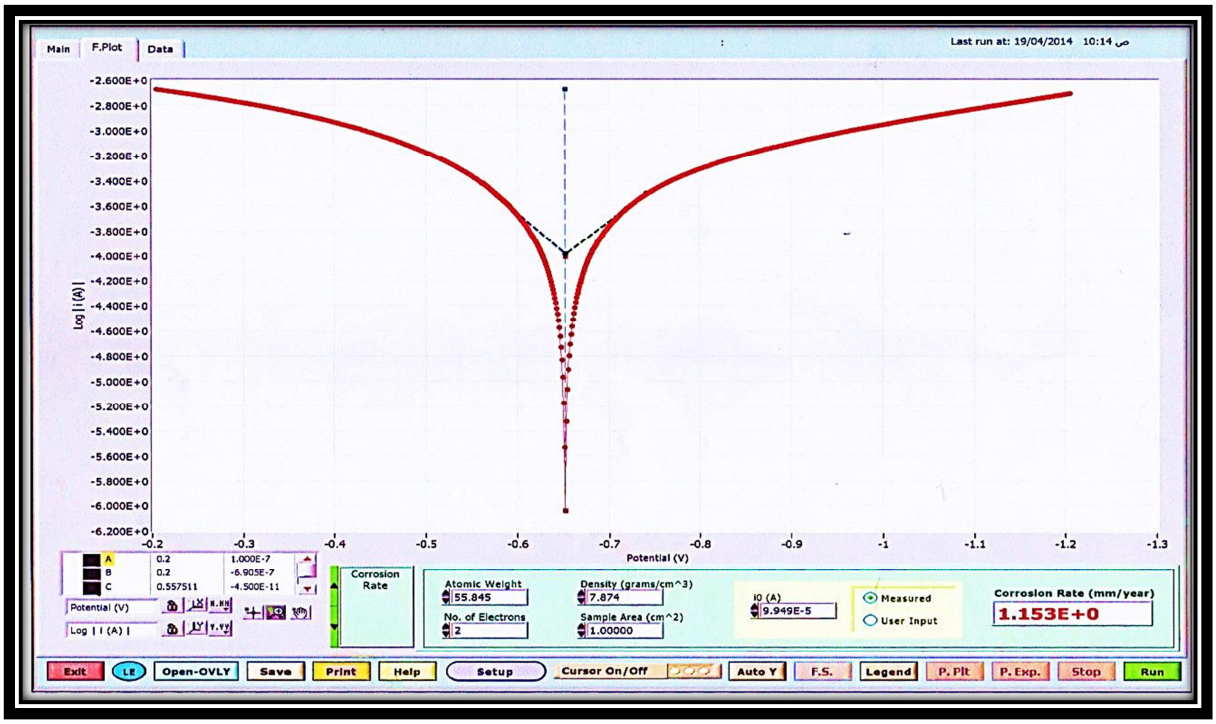
The IE obtained from Tafel plot was found 86.86% for K3, 84.41% for H3 and 73.50% for H4.

Table- 5 Tafel Plot of carbon still in presence of inhibitor, and without

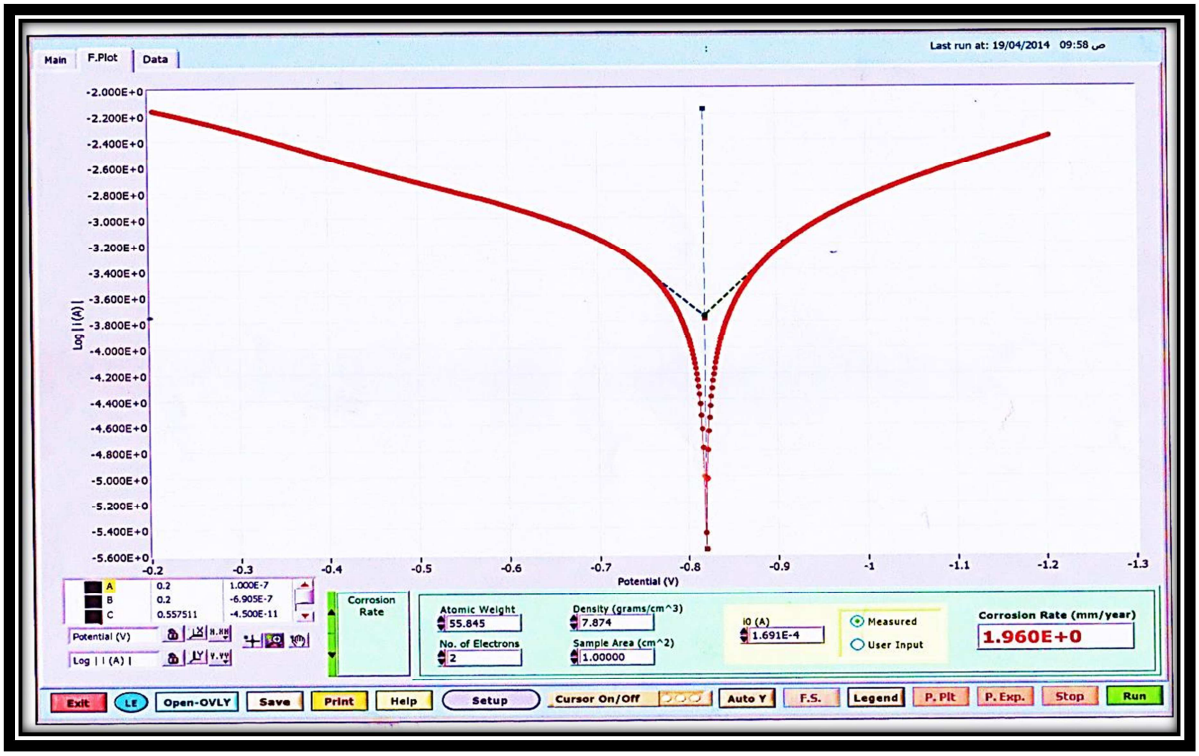
symbol	CR (mpy)	%IE	Icorr. A/cm^2	Ecorr. Volt	θ
industrial water	7.399	___	0.0006380	0.889-	____
H3	1.153	84.41	0.0000994	0.652-	0.8441
H4	1.960	73.50	0.0001691	0.821 -	0.7350
K3	0.971	86.86	0.0000838	0.801-	0.8686



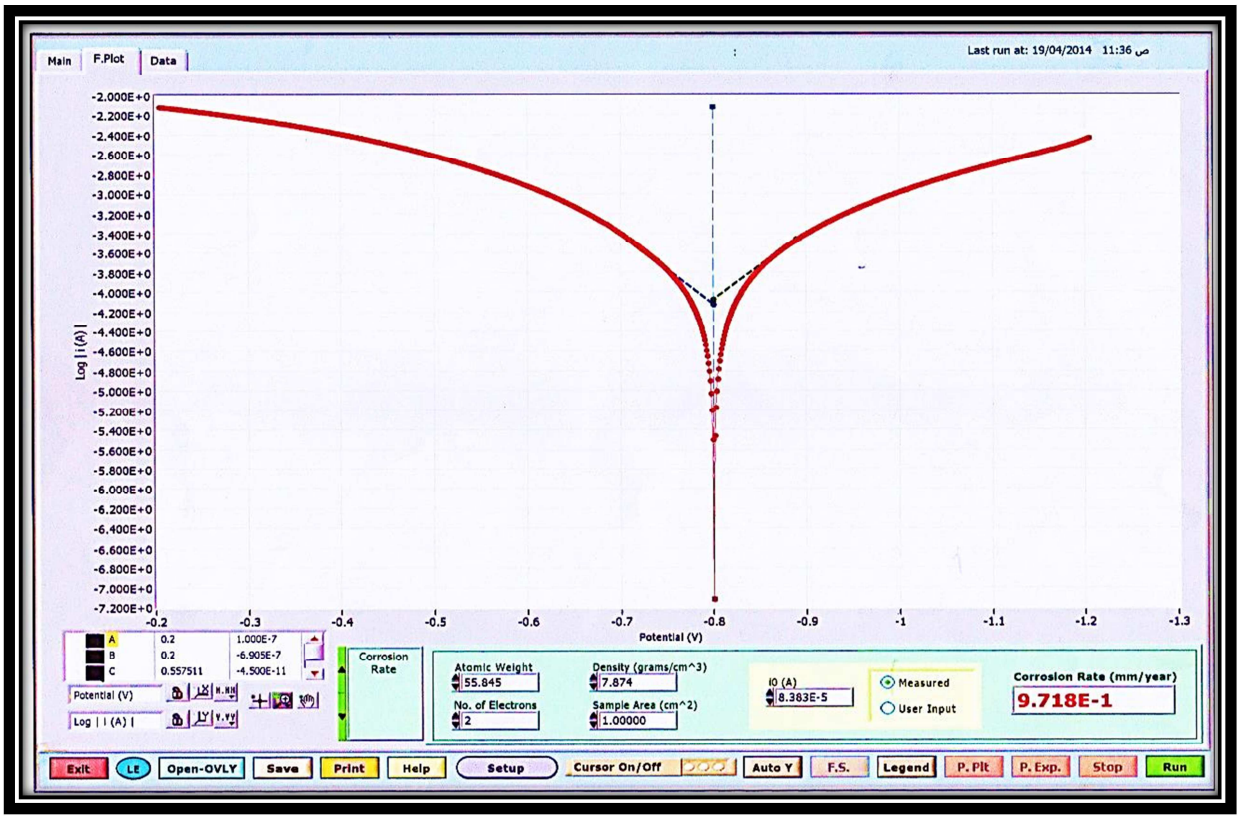
(Fig- 4) Tafel Plot of carbon still in industrial water



(Fig- 5)**Tafel Plot of carbon still in presences of compound H3**



(Fig- 6)Tafel Plot of carbon still in presences of compound H4



(Fig- 7)Tafel Plot of carbon still in presences of compound K3

Antimicrobial Activity: The three compounds were tested in vitro against four type of bacteria[15,16] *Staphylococcus aureuse (S.a), Escherichia coli(E.C), Staphylococcus Saprophyticus (S.S) and Pseudomonas aeruginosa (P.a).*This results are listed in Tables(6,7), H3 shows allow activity against S.a compound with starting materials ,amoxicillin (X5) and potassium dichromate (X4), in case of E.c the H3 show moderate activity equal to the standard drugs. While H3 shows allow lowest activity to wards P.a.

K3 shows a high activity against S.s and S.a compared with sulfamethoxy pyridiazine (X2) and potassium dichromate (X4), also shows a high activity against P. a compared with sulfamethoxy pyridiazine (X2) and lowest activity against E.c.

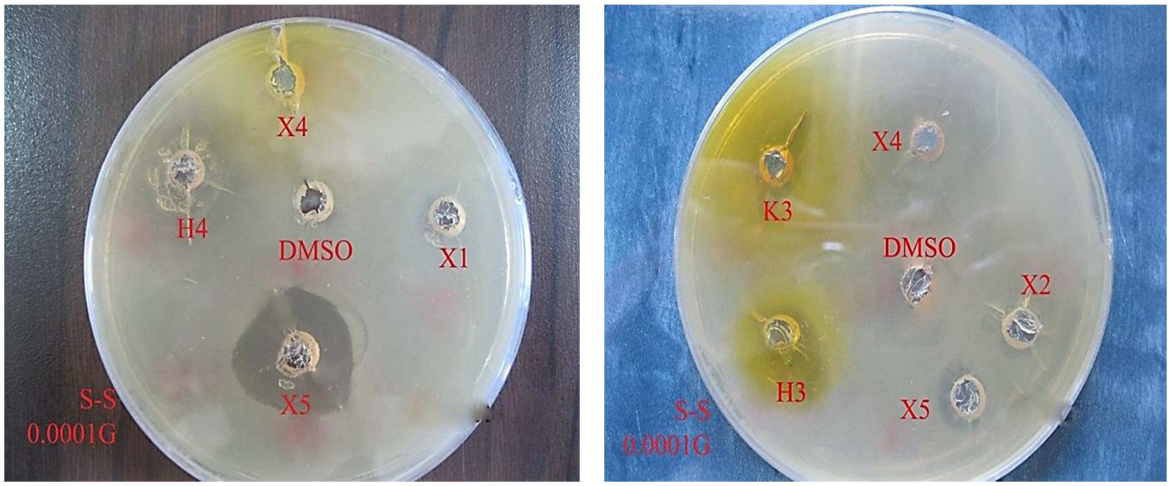
H4 shows a high activity against S.a and S.s compared with sulfaproxylene (X1) and potassium dichromate (X4) but less than amoxicillin (X5). against E.c H4 shows a lowest activity in case of P.a, H4 show a high activity compared with sulfaproxylene (X1) but less than potassium dichromate (X4) and amoxicillin (X5). Figs(8-11).

Table (6) Antimicrobial test in concentration 0.001 and 0.0001g/m

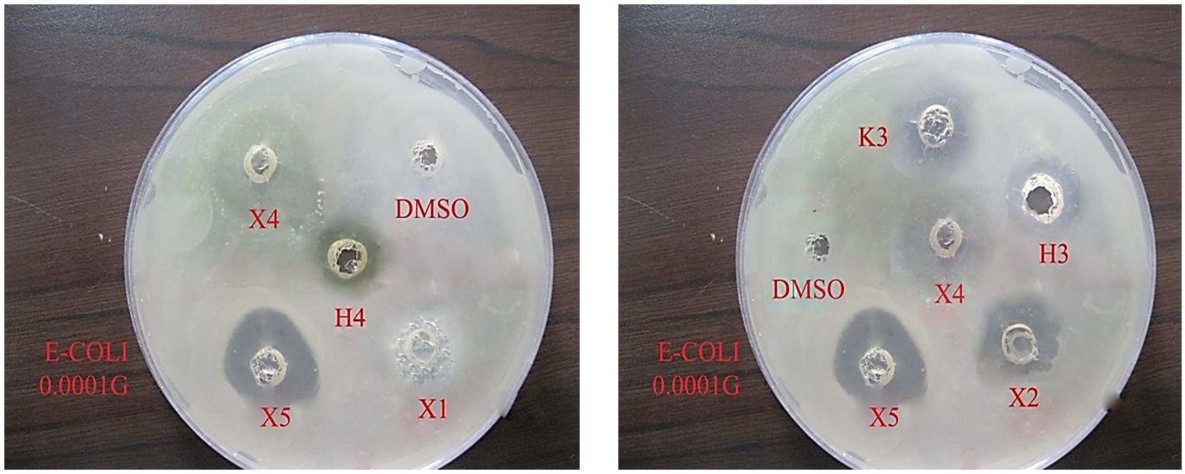
Inhibitor	Concentration g/ml	inhibition zone (mm)			
		S.a	S.s	E.c	P.a
K3	0.001	16	16	14	18
H3		14	15	14	12
H4		19	18	13	13
K3	0.0001	14	14	13	16
H3		13	14	14	11
H4		15	16	12	12

Table (7) A comparison of prepared compounds and standards

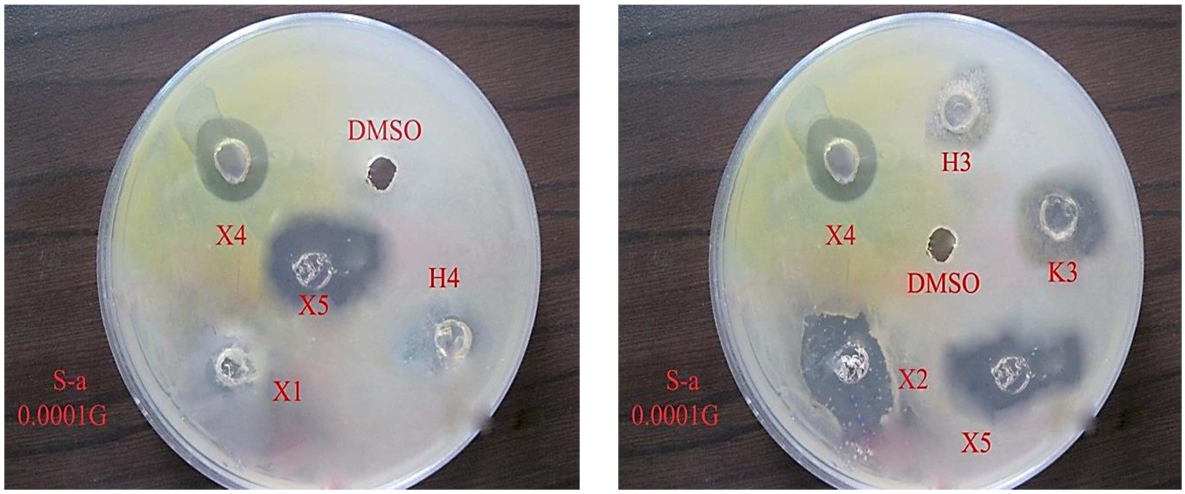
inhibitor	inhibition zone (mm)			
	S.a	S.s	E.c	P.a
K3	14	14	13	16
X2	15	12	14	13
X4	14	12	17	13
X5	20	22	16	24
H3	13	14	14	11
X2	15	12	14	13
X4	14	12	17	13
X5	20	22	16	24
H4	15	16	12	12
X1	13	13	13	11
X4	14	14	17	13
X5	20	22	16	21



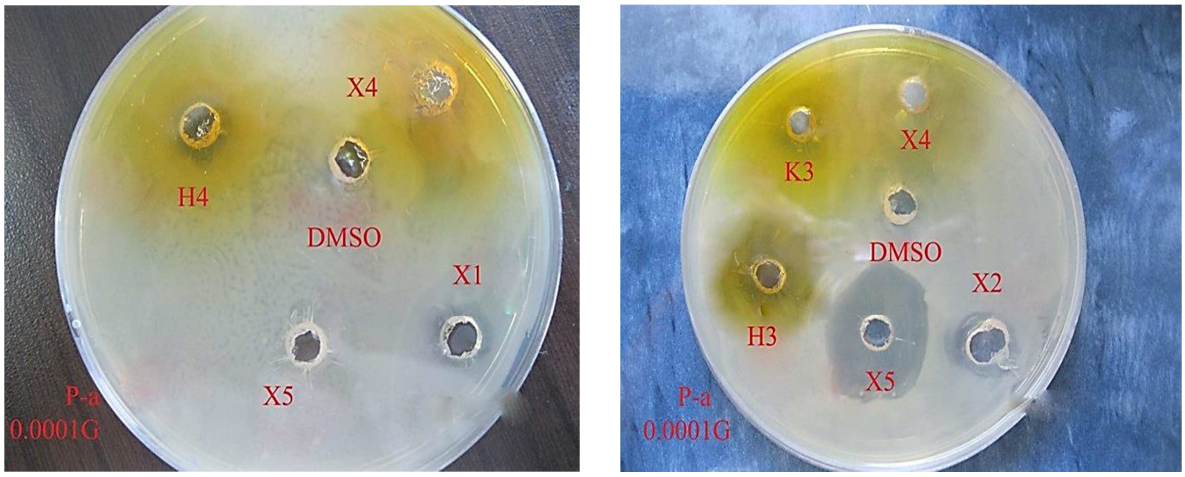
(Fig- 8)



(Fig- 9)



(Fig- 10)



(Fig- 11)

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