Corrosion Inhibition by Potassium Chromate-Zn^{2+} System for Mild Steel in Simulated Concrete Pore Solution

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Abstract

The inhibition efficiency (IE) of potassium chromate -Zn^{2+} system in controlling corrosion of mild steel immersed in simulated concrete pore solution SCPS prepared in well water has been evaluated by weight loss method. The formulation consisting of 100 ppm of K_2CrO_4 and 50 ppm of Zn^{2+} provides 98% of IE. FTIR spectra reveal that the protective film consists of Fe^{2+} - chromate complex and $Zn(OH)_2$. Polarization study confirms the formation of a protective film on the metal surface .AC impedance spectra also revealed that a protective film formed on the metal surface. The inhibitor system controls the anodic reaction predominantly. The reactions are diffusion controlled process.

Keywords: Concrete corrosion, simulated concrete pore solution, mild steel, potassium chromate, well water.

Introduction

Metals are extracted from their ores by reduction process. When metals come in contact with the environment, especially oxygen and moisture, they deteriorate. This process, we call, corrosion. Corrosion is the desire of pure metals to go back to its original state of ores. Corrosion is a natural, spontaneous and thermodynamically stable process. The process of corrosion can be controlled but it cannot be prevented.

Carbon steel reinforcement in concrete structures are in passive conditions that they are protected by a thin oxide layer promoted by the concrete alkalinity. Corrosion can iniate only when passivity is destroyed. This occurs in two ways: carbonation of concrete, the reaction of atmospheric CO_2 with cement paste, that lowers pH and causes general corrosion; the presence of chlorides at the steel surface in concentration higher than a critical threshold, generally considered in the range of 0.4 – 1 % by a cement weight[1,2]. Among available methods, corrosion inhibitors seem to attractive because of their low cost and easy handling, compared with other preventive methods. Inhibitors can be divided in two groups: admixed inhibitors, added to fresh concrete for new structures, and migrating inhibitors, which can penetrate into the hardened concrete and are usually proposed in repair system.

While admixed inhibitors are commercially available since 70's, migrating corrosion inhibitors for concrete structures were proposed in the last 15 -20 years[3]. Nowadays, there are several admixtures available on the market: inorganic compounds based on nitrites, especially used as additives[4-8] and sodium mono-fluoro-phosphate used as migrating inhibitors[9-10] organic compounds based on mixtures of alkanolamines, amines or amino acids, or based on an emulsion of unsaturated fatty acid,

proposed both as admixed and migrating inhibitor[11]. Other non-commercial inhibitors, both inorganic and organic were studied: zinc oxide[12], molibdates and borates[13], stannates[14], carboxylate ions, quaternary ammonium salts and many other organic compounds[15].

Ormellese. *et al* also have been used the above inhibitors for chlorides induced corrosion in Reinforced concrete structures[16]. Nitrite based inhibitors are considered the most effective products available on market: they were studied from 60's both in laboratory and in field tests and several applications confirmed their efficiency. Nitrite act as a passivator, due to its oxidizing properties, and its inhibitive effectiveness is related to the $[NO^-]/[Cl^-]$ molar ratio, that should be higher than 0.8 – 1 to prevent corrosion[3]. Concerns are with their toxicity, solubility and possible increase of corrosion rate in case of low dosage or in the presence of concrete cracks[3-8]. The corrosion inhibition studies of mild steel[17], aluminium[18], Zinc[19], Galvanized steel and SS316L[20] etc., in various environment and simulated concrete pore solution medium have been studied.

The present work in undertaken i. to evaluate the inhibition efficiency of Potassium chromate Zn^{2+} systemin controlling corrosion of mild steel in SCPS prepared in well water, ii. to analyse the protective film by FTIR spectroscopy and iii. to study the mechanistic aspects of corrosion inhibition by polarization study and AC impedance spectra. Results are discussed in terms of ability of the corrosion inhibitors to prevent corrosion occurrence or to corrosion rate, once corrosion started.

Methodology

Preparation of Simulated Concrete pore solution (SCPS): Simulated concrete pore solution is mainly consisted of

saturated calcium hydroxide (Ca(OH)$_2$, sodium hydroxide (NaOH) and potassium hydroxide (KOH) with the pH~13.5[21-22]. However in numerous studies of rebar corrosion, saturated Ca(OH)$_2$ has been used as a substitute for pore solution[23]. A saturated calcium hydroxide solution is used in present study, as SCP solution with the pH ~ 12.5.

Preparation of the specimens: Mild steel specimen was used in the present study. (Composition (wt %): 0.026 S, 0.06 P, 0.4 Mn, 0.1 C and balance iron. The dimension of the specimen was 1 x 4 x 0.2cm were polished to a mirror finish and degreased with trichloroethylene and used for the weight-loss method and surface examination studies. The environment chosen is well water and the physic-chemical parameter of well water is given in table 1.

Table–1
Physico- chemical parameters of well water

Parameters	Value
pH	8.38
Conductivity	1770$\mu\Omega^{-1}cm^{-1}$
Chloride	665 ppm
Sulphate	214 ppm
TDS	1100 ppm
Total hardness	402 ppm
Total Alkalinity	390 ppm
Magnesium	83 ppm
Potassium	55 ppm
Sodium	172 ppm
Calcium	88 ppm

Weight Loss Method: Determination of Surface Area of the specimens: The length, breadth, and the thickness of mild steel specimens and the radius of the holes were determined with the help of vernier calibers of high precision, and the surface areas of the specimens were calculated.

Weighing the specimens before and after Corrosion: All the weighing of the mild steel specimens before and after corrosion was carried out using Shimadzu balance, model AY62.

Determination of Corrosion Rate: The weighed specimens in triplicate were suspended by means of glass hooks in 100mL SCPS prepared in well water containing various concentration of potassium chromate in the presence and absence of Zn^{2+} for one day, the specimen were taken out, washed in running water, dried, and weighed. From the change in weights of the specimens, corrosion rates were calculated using the following relationship:

CR = [(Weight loss in mg) / (Area of the specimens in dm^2 × Immersion periods in days)] mdd   (1)

Corrosion inhibition efficiency (IE, %) was then calculated using the equation:
I.E =100[1-(W$_2$/W$_1$)] %   (2)

Where, W1 = corrosion rate in the absence of the inhibitor, and W$_2$ = corrosion rate in the presence of the inhibitor,

Surface Examinations study: The mild steel specimens were immersed in various test solutions for a period of one day, the specimens were taken out and dried. The nature of the film formed on the surface of metal specimen was analyzed by various surface analysis techniques.

Potentiodynamic Polarization: Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, Model 660A. A three-electrode cell assembly was used. The three electrode assembly is shown in figure-1. The working electrode was mild steel. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. From the polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes (anodic = *b*a and cathodic =*b*c) and Linear polarization resistance (*LPR*) were calculated. The scan rate *(V/S)* was 0.01.Hold time at (E_{fcs}) was zero and quit time(s) was two.
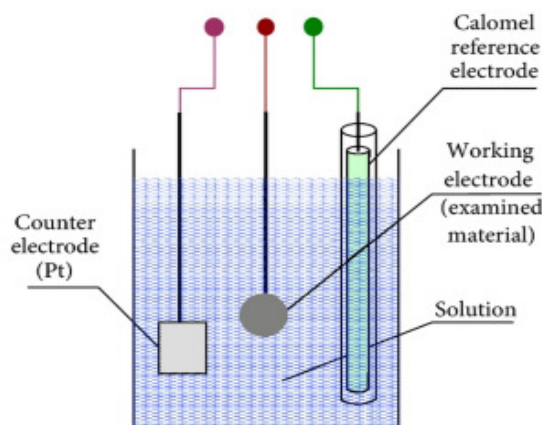

Figure-1
Circuit diagram of three- electrode cell assembly

AC impedance spectra: AC impedance spectral studies were carried out in a CHI – Electrochemical workstation with impedance, Model 660A. A three-electrode cell assembly was used. The working electrode was one of the three metals. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. Values of the charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculate. The equivalent circuit diagram is shown in figure-2.
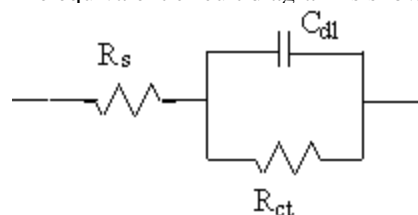

Figure–2
Equivalent circuit diagram: R_s is solution resistance, C_{dl} is double layer capacitance, R_{ct} is charge transfer resistance

Fourier Transform Infrared Spectra: These spectra were recorded in a Perkin-Elmer -1600 spectrometer using KBr pellet. The spectrum of the protective film was recorded by carefully removing the film, mixing it with KBr and making the pellet.

Results and Discussion

Analysis of Results of Weight loss method: The corrosion resistance of mild steel immersed in SCPS prepared in well water in the absence and presence of potassium chromate and Zn^{2+} are given in table 2. It is observed that when 50 ppm of potassium chromate is added to SCPS the inhibition efficiency increases from 68% to 92%. Similarly when 100 ppm potassium chromate is added the inhibition efficiency increases from 68% to 98%.
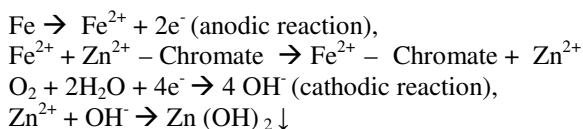
Table-2
Corrosion rates (*CR*) of mild steel immersed in Simulated Concrete Pore Solution (SCPS) prepared in well water and the inhibition efficiency (IE) obtained by weight loss method

System	*IE* %	*CR* (mdd)
Well Water	-----	25
SCPS	68	8
SCPS + K_2CrO_4 50 ppm	92	2
SCPS + K_2CrO_4 100 ppm	94	1.5
SCPS + K_2CrO_4 50 ppm + Zn^{2+} 50 ppm	96	1
SCPS + K_2CrO_4 100 ppm+Zn^{2+} 50 ppm	98	0.5

Immersion period: One Day; *CR* =Corrosion Rate; *IE* =Inhibition Efficiency, mdd = milligrams per square decimeter per day.

Influence of Zn^{2+} on the corrosion inhibition efficiency: It is observed that when 50 ppm Zn^{2+} is added, the inhibition efficiency increases in the both the cases. The formulation consisting of SCPS+ 100 ppm of potassium chromate and 50 ppm of Zn^{2+} has 98% corrosion inhibition efficiency.

In presence of Zn^{2+} more amount potassium chromate is transported towards metal surface. On the metal surface Fe-chromate complex is formed on the anodic sides of the metal surface. Thus the anodic reaction is controlled. The cathodic reaction, the generation of OH^- is controlled by the formation of $Zn(OH)_2$ on the cathodic sites of the metal surface. Thus, the anodic reaction and cathodic reaction are controlled effectively.

$Fe \rightarrow Fe^{2+} + 2e^-$ (anodic reaction),
$Fe^{2+} + Zn^{2+} - Chromate \rightarrow Fe^{2+} - Chromate + Zn^{2+}$
$O_2 + 2H_2O + 4e^- \rightarrow 4 OH^-$ (cathodic reaction),
$Zn^{2+} + OH^- \rightarrow Zn (OH)_2 \downarrow$

Analysis of Polarization Curves: When mild steel is immersed in simulated concrete pore solution prepared in well water the corrosion potential was -661 mV vs SCE (saturated calomel electrode). When K_2CrO_4(100 ppm) and Zn^{2+} (50 ppm) were

added to the above system the corrosion potential shifted to the anodic side -615 mV vs SCE; that is noble side. This indicates that the K_2CrO_4 - Zn^{2+} system control anodic reaction predominantly. This indicates that the passive film is formed on the metal surface in presence of inhibitor. The shifting of corrosion potential towards anodic side in presence of inhibitors has been reported by several researchers[24-25].
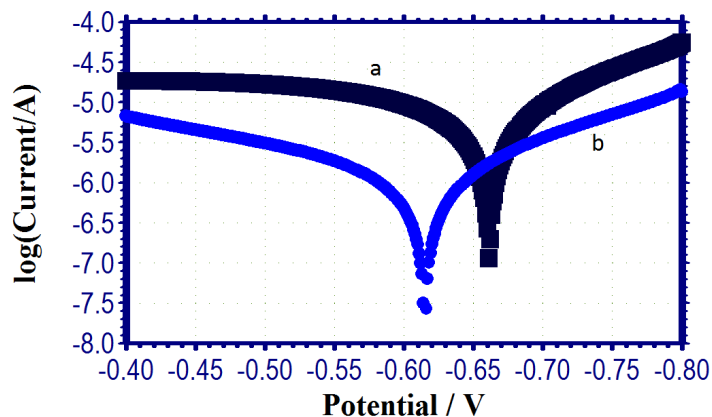

Figure–3
Polarization curve of mild steel immersed in SCPS prepared in water a) SCPS b) K_2CrO_4 100 ppm+ Zn^{2+} 50 ppm

Table-3
Corrosion parameters of mild steel immersed in SCPS prepared in well water in the absence and presence of inhibitor system obtained from Potentiodynamic Polarization Study

System	E_{corr} mV vs SCE	b_c mV/ decade	b_a mV/ decade	*LPR* ohmcm^2	I_{corr} Acm^{-2}
SCPS	-661	143	313	5103.1	8.389 x 10^{-6}
SCPS + K_2CrO_4 100 ppm + Zn^{2+} 50 ppm	-615	152	229	30226.9	1.312x 10^{-6}

Further, the *LPR* value increases from 5103.1 ohm cm^2 to 30266.9 ohm cm^2; the corrosion current decreases from 8.389x10^{-6} A/cm^2 to 1.312x10^{-6} A/cm^2 .When a passive film formed on mild steel surface, in presence of inhibitor system, the electron transfer from the metal surface towards the bulk of the solution is difficult and prevented. So rate of corrosion decreases and hence corrosion current decreases in presence of inhibitor system.

Analysis of AC Impedance spectra: AC impedance spectra (electro chemical impedance spectra) have been used to confirm the formation of protective film on the metal surface. If a protective film is formed on the metal surface, charge transfer resistance (R_t) increases; double layer capacitance value (C_{dl})

decreases and the impedance log (z/ohm) value increases[26-27]. The AC impedance spectra of mild steel immersed in SCPS prepared in well water in the absence and presence of inhibitors (K_2CrO_4- Zn^{2+}) are shown in figure 4. (Nyquist plots) and figures 5 and 6. (Bode plots). The AC impedance parameters namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plots are given in table 4 .The impedance log (z/ohm) values derived from Bode plots are also given in table 4.
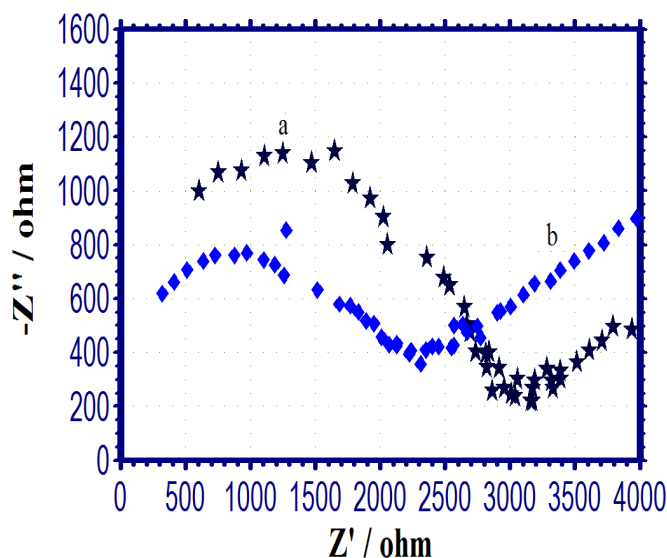

Figure-4
AC Impedance curves of mild steel immersed in various test solution (Nyquist plots) a) SCPS b) K_2CrO_4 100 ppm+ Zn^{2+} 50 ppm
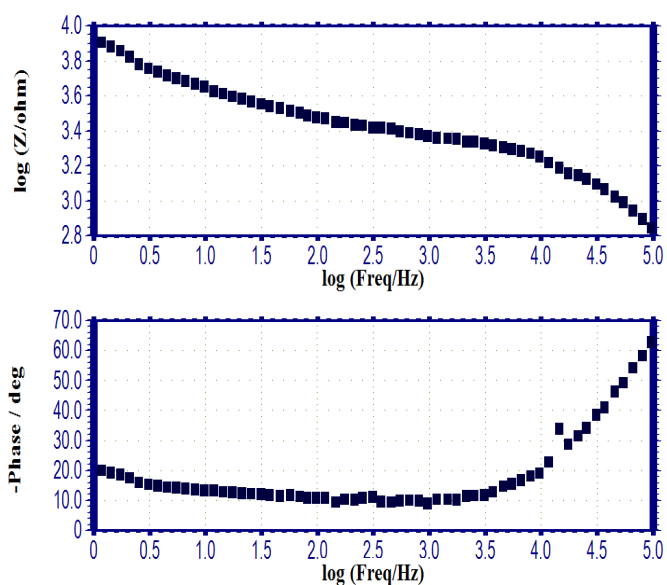

Figure-5
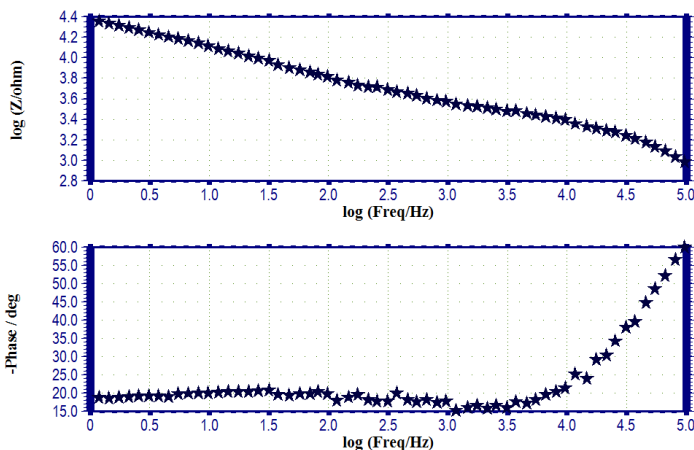**AC impedance spectrum of mild steel immersed in SCPS (Bode plots)**

Figure-6
AC impedance spectrum of mild steel immersed in SCPS 100 ppm K_2CrO_4 + 50 ppm Zn^{2+} (Bode plots)

Table–4
Corrosion parameters of mild steel immersed in SCPS prepared in well water in the absence and presence of inhibitor system obtained from AC impedance spectra

| System | Nyquist plot | | Bode plot |
	R_t, ohm cm^2	C_{dl} F/cm^2	Impedance value log (z/ohm)
SCPS	3339.8	1.527×10^{-9}	3.87
SCPS+ K_2CrO_4 100 ppm + Zn^{2+} 50 ppm	3658.5	1.394×10^{-9}	4.35

It is observed that when the inhibitors K_2CrO_4 (100ppm) + Zn^{2+} (50 ppm) are added, the charge transfer resistance (R_t) increases from 3339.8 ohm cm^2 to 3658.5 ohm cm^2. The C_{dl} value decreases from 1.527×10^{-9} F /cm^2 to 1.394×10^{-9} F /cm^2. The impedance values [log (z/ohm)] increases from 3.87 Z/ohm to 4.35 Z/ohm. These results lead to the conclusion that a protective film is formed on the metal surface.

It is observed from Nyquist plot that the systems are formed to be diffusion controlled process. The equivalent circuit diagram for the above system is shown in the figure 7.
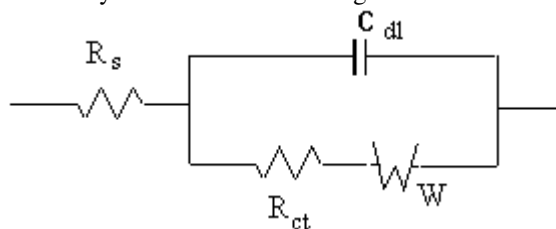

Figure–7
Equivalent circuit diagram for diffusion controlled process, R_s is solution resistance, C_{dl} is double layer capacitance, R_{ct} is charge transfer resistance, W is Warburg diffusion resistance

Analysis of FTIR spectra: Earlier researchers have confirmed that FTIR spectrometer is a powerful instrument that can be used to study inhibitors adsorbed on the metal surface. FTIR spectra were used to analyze the protective film formed on metal surface[28].

The FTIR (KBr) spectrum of pure potassium chromate is given in figure 8. The CrO_4^{2-} stretching frequency appears at 1124 [29]. The FTIR spectrum of the film formed on the metal surface after immersion in SCPS prepared in well water conning 100 ppm of K_2CrO_4 and 50 ppm of Zn^{2+} is shown in figure 9. The CrO_4^{2-} stretching frequency of K_2CrO_4 shifted from 1124 to 1349 cm^{-1}. This confirms that the oxygen atom of the chromate has coordinated with Fe^{2+} resulting in the formation Fe^{2+} - chromate complex on the metal surface. Also there in possibility of anchoring of Chromate on the layer of consisting CaO, $Ca(OH)_2$, $CaCO_3$.

Peak appears at 1382 cm^{-1} is due to Zn–O stretching. The - OH stretching frequency appears at 3430.39 cm^{-1}. These observations indicate the presence of $Zn(OH)_2$ formed on the metal surface Peak appears at 1593, 765 and 1349 cm^{-1}. These peaks confirm the presence of calcium carbonate, calcium oxide, calcium hydroxide and on the metal surface[30].

Conclusion

The present study leads to the following conclusions: i. The formulation consisting of 100 ppm of K_2CrO_4 and 50 ppm of Zn^{2+} offers 98% IE to mild steel immersed in simulated concrete pore solution prepared in well water. ii. Polarization study reveals that K_2CrO_4 system controls the anodic reaction predominantly. iii. AC impedance spectra reveal that the formation of protective film on the metal surface, and the reactions are diffusion controlled process. iv. FTIR spectra reveal that the protective film consists of Fe^{2+} - chromate complex and $Zn(OH)_2$.
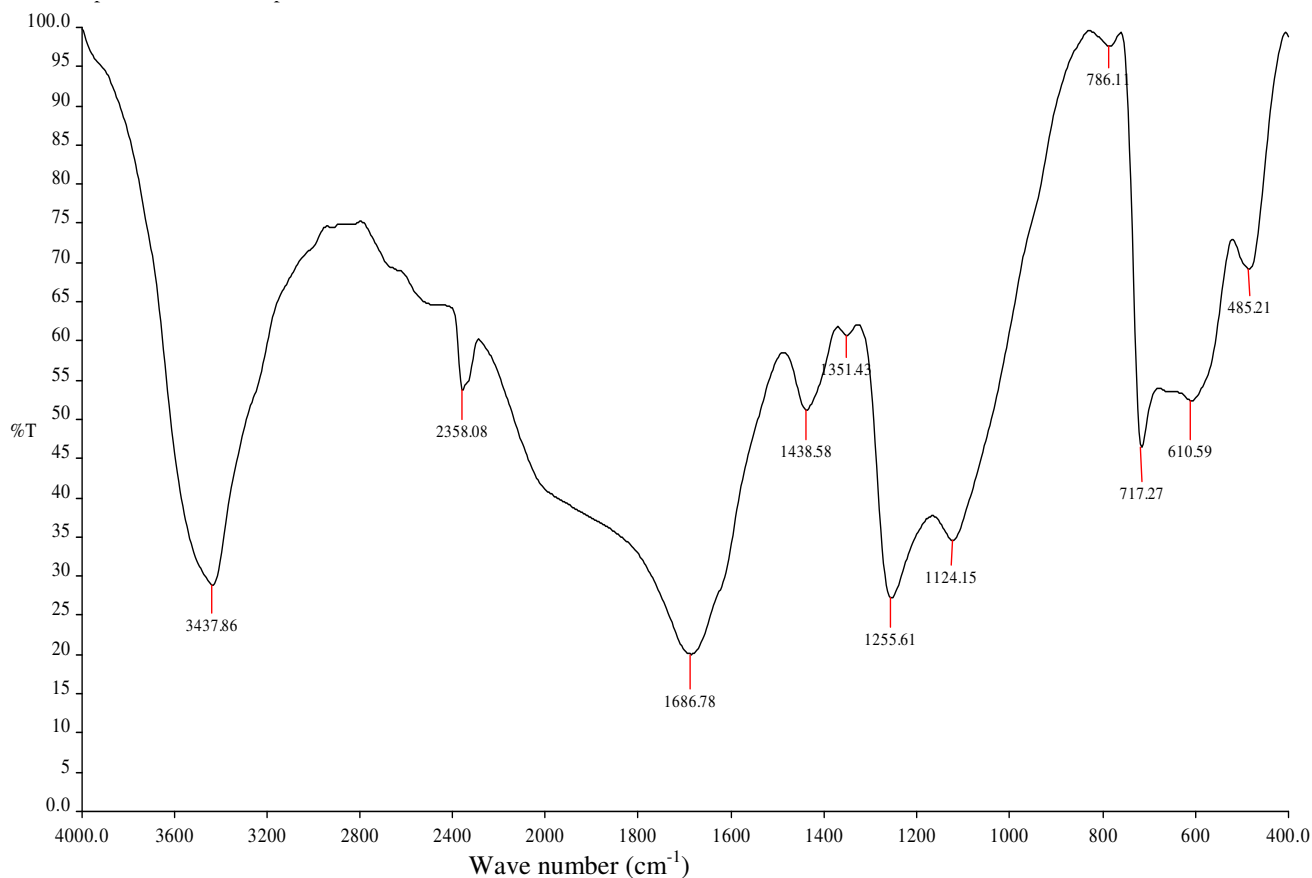

Figure-8
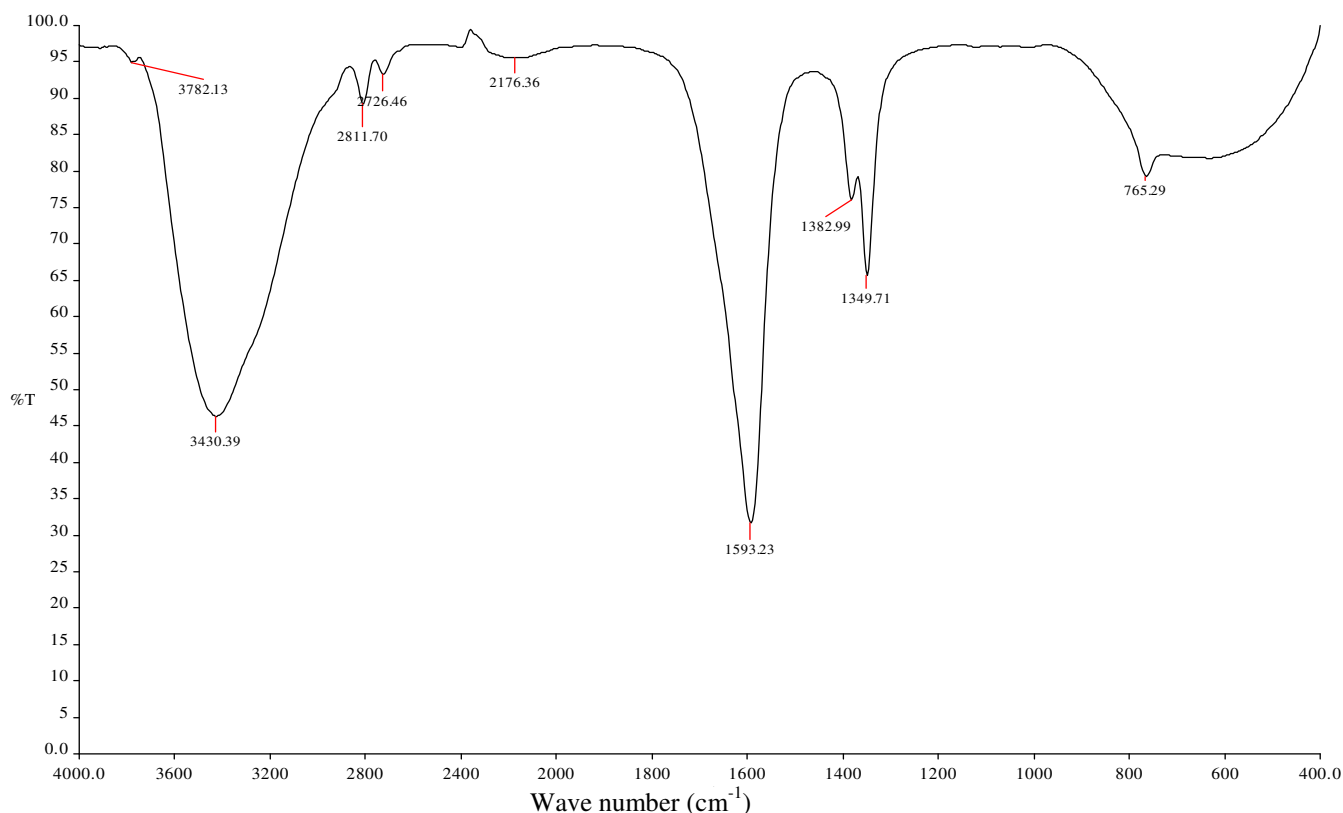**FTIR spectrum of Pure Potassium Chromate**

Figure-9
FTIR spectrum of the film formed on the metal surface after immersion in SCPS prepared in well water containing 100 ppm of K_2CrO_4 and 50 ppm of Zn^{2+}

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