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Assessment of Potassium Chromate Inhibition and Adsorption on Type A513 Mild Steel in Simulated Contaminated Media

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Abstract

The effect of potassium chromate (K_2CrO_4) compound on the inhibitive performance of type A513 mild steel was studied using linear and open circuit polarization technique with μ Autolab PGstat101. The structural degradation tendency was observed with high resolution optical microscope. Data obtained from Tafel plot showed that the organic compound performed effectively in acid/chloride solution at all concentration of (K_2CrO_4) with average inhibitor efficiency above 60%. The outcome of the OCP showed a significant correlation with the LPR trend. The massive influence of the inhibitive compound on steel was seen as a chemisorption mechanism in which the corrosive anions and particulate were suppressed significantly. The adsorption of the compound was determined and was found to obey the Langmuir isotherm model. The structural properties generally were affected with high aggressiveness of the acid/chloride ion mix with uniform corrosion propagation observed along the entire interface.

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1. Introduction

Apart from the physical and mechanical properties of mild steel in service which make it outstanding among other metallic alloy, its versatility in engineering field is enormous owing to its considerable interest for industrialist

in term of cost and production output among others [1-3]. To national development, mild steel is of significant important to national economy growth, yet it continuous challenge in terms corrosion degradation has also been a concern to national GDP [4].

In service, contaminated waste from production beverages tanks, contain jointed part which carries salty water and sulphide ion. Corrosion by salty water is an aqueous corrosion, is an electrochemical process and steel when in contact with salty water having a specific electrical potential. Salty water is an aqueous solution of salts with salinity equals approximately 3.5 % and composition of artificial ocean water according to ASTM D1141-98 [4]

The presence of H^+ , SO_4^{2-} within contamination waste water aids severe degradation causing hydrogen influenced corrosion [5, 6]. Thus, the consequence of chloride-acid attack or failure due to general corrosion had been widely reported. Corrosion is a plight that faces everyone who works with metallic materials [6, 7]. With several effort and method to address this challenges over time, the replacement of detrimental effect of waste water acid chloride contamination in the industries, has also not be fully minimized due to production processes hence, the need for continuous searching for corrosion inhibitor of mild steel in acid/chloride conditions become needful [8-12].

The mechanism of corrosion inhibition may be by film formation [13] on the substrate that could be effective if the film is continuous and tenacious and if otherwise could aggravate localised or pitting corrosion [14]. Inhibitors could also form salt particles of the aggressive ions in the solution thereby reducing the mobility and the rate of attack of the negative ions on metallic substrate [15].

Potassium chromate is inorganic substances that are available in the market among other metallic salts [16]. Its choice is on the fact that they are not poisonous in small quantities and when in ionic form can form positive polar region for the attraction of negative ions. Potassium chromate may also serve for neutralisation of other harmful metals in the salty/sulphide environment [17, 18]. Chloride ions had been reported as being less hydrated than sulphate ions that have a stronger tendency to adsorb on the metal by creating excess negative charge towards the solution phase, which favours synergetic adsorption on the metal surface [18]. Therefore, this study aimed at investigating the inhibitive characteristics of potassium chromate on corrosion behaviour of the mild steel contaminated acid/chloride media.

2. Experimental Procedures

2.1. Sample Preparation

Selected mild steel samples were sectioned into coupons with spectrometer chemical composition in (wt %) showed in Table-1. The dimensions were (30 x 20 x 2) mm before mounted with an epoxy resin. The coupons were polished to a mirror-like nature with emery papers and cleaned in acetone. It was further dried and weighed with an analytical balance. Each sample weight was recorded and labelled correctly. The chemicals used were of analytical reagent grade which were prepared using distilled water. Concentrations of acid were prepared by using double distilled water and the concentration range of inhibitors was 2-10 ml in each of 40 ml 0.5 M HCl mixed with 3.65% NaCl solution. The molecular structure of the prepared inhibitor is presented in Figure 1. The electrochemical investigation was performed at 25 0C.

Table 1: Chemical composition of mild steel sample immersed in acid/chloride medium

Element	C	Mn	Si	P	S	Al	Ni	Fe
Wt %	0.18	0.45	0.18	0.01	0.031	0.005	0.008	99.19

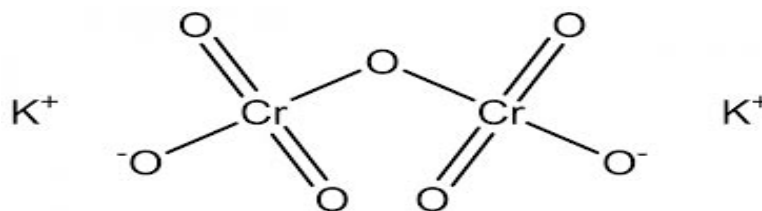


Fig. 1: Chemical structure of Potassium Dichromate [18]

2.2. Linear polarization Resistance

The sectioned mild steel coupon was mounted with resin, with a surface area of 1cm² and connected with electrode cell containing 40 ml of chloride electrolyte in an attempt to study the linear potential resistance using Autolab PGSTAT 101 Metrohm potentiostat/Galvanostat. Graphite rod was used as auxiliary electrode and silver chloride electrode (SCE) function as a reference electrode. Linear potentiodynamic potential scan range was from -1.5V to +1.5 mV at scan rate of 0.0012V/s. The corrosion potential (E_{corr}), and current density (j_{corr}) data were evaluated from the Tafel plots. The surface coverage (θ) and the percentage inhibition efficiency (% IE) were calculated with equation 1 and 2.

$$\Theta = 1 - \frac{j_{corr}}{j_{corr_0}} \quad (1)$$

The percentage inhibition efficiency (% IE) was calculated from corrosion current density values using the equation.

$$I.E\% = 1 - \frac{j_{corr}}{j_{corr_0}} \times 100 \quad (2)$$

2.3. Morphological Characterization

The sectioned samples mounted with cold resins sample was prepared mechanically using grade of SiC grit of 80, 150, 400, and 1200 grits before polishing to 9 μ m with Pen Struers diamond paste. Thereafter cleansed with deionized water and placed in a desiccator before used for potentiodynamic polarization according to ASTM standard G1-03(2011). The obtained samples under investigation were then analysed and examined with the help of ME 600T polarising optical microscope with built in camera.

3. Results and discussion

3.1. Potentiodynamic Polarization Study

The anodic and cathodic polarization curve of the effect of K₂CrO₄ inhibitor on the corrosion of A513 mild steel in 0.5 M HCl + 3.65%NaCl is shown in Fig. 2. The open circuit potential plots of the electrochemical influence of K₂CrO₄ inhibitor on the corrosion of mild steel in its contaminated media is presented in Fig. 3. Table 2 shows linear polarization Tafel scan result. From the observed Tafel plots data in Table 2 a significant change in the corrosion rate and potential was noticed with K₂CrO₄ inhibitor and uninhibited steel samples.

Table 2: Linear polarization data of admix potassium chromate in varying concentration in solution of 0.5M HCl+ 3.65%NaCl medium with immersed low carbon steel

Sample	E_{corr} , Obs (V)	j_{corr} (A/cm ²)	CR (mm/year)	Surface Coverage	Inhibitor Efficiency
Control	-1.532	210E-02	3.1200	-	-
2.5	-0.862	110E-05	1.1621	0.062	62
5.0	-0.831	110E-05	0.9962	0.068	68

7.5	-0.851	110E-05	1.1270	0.0.64	64
10	-0.842	110E-05	1.0257	0.0.67	67

There is severe deterioration at 0% K₂CrO₄ with 3.1200mm/yr corrosion rate. This is an indication of an anodic dissolution as a result of Cl⁻ and H⁺ within the acid and chloride media initializing the corrosion progression that occurred on the steel interface. In the case of inhibited sample a drastically reduction in corrosion rate occurred with inhibited concentration from 2.5 -10 % inhibitor. The highest corrosion rate among the protected steel was found with the least concentration of 2.5% mix in 0.5 M HCl + 3.65% NaCl solution at 1.1621mm/yr an indication of twice in reduction of the control sample. Surely, there are several reasons for this progressive retardation of penetration of chloride/acid influence. Among others is redox diffusion of the adsorbed species of K₂CrO₄ into the active corrosion anions, the insoluble films of the metal surface as a result of the insoluble compounds which deposited and causes hindrances to metallic ion. This mechanism promotes active passivation of the steel through adsorption and hinders progression of deterioration.

The maximum potential change in the E_{corr} is -0.831V at 5% K₂CrO₄ and the as-received is -1.532V. K₂CrO₄ effect donates double pair's electrons of atoms within its structure which enables the sufficient electrons to occupy the orbital cell on the steel interface thereafter yielding covalent bonds.

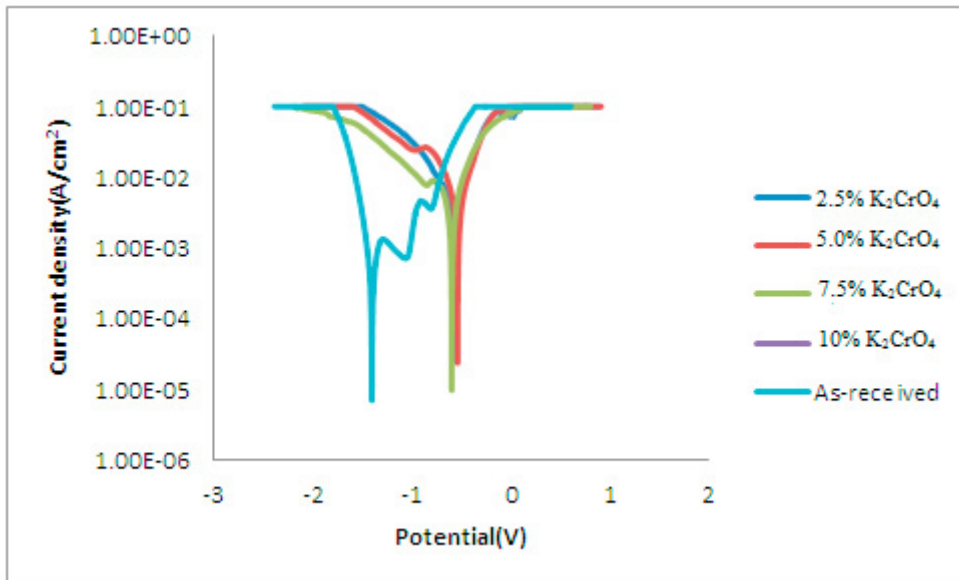


Fig. 2: Anodic and cathodic polarization curve for MS in 2.5-10% at 0.5M HCl+3.65%NaCl solution

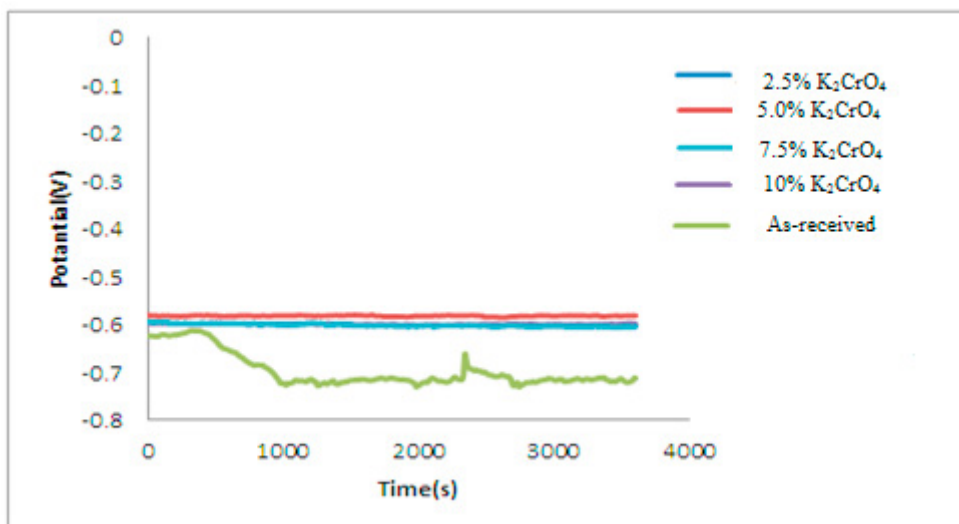


Fig. 3: Open circuit polarization studies of admix potassium chromate in varying concentration between 2.5ml-10ml in 0.5M HCl+ 3.65%NaCl medium

In Fig. 3, the potential change against time was observed from the open circuit potential curve. The electrochemical performance of K_2CrO_4 in 0.5 M HCl + 3.65%NaCl indicated that there were similar corrosion progressions of inhibitive activities linear potential effect of the steel. This implies that K_2CrO_4 instigate passivation through adsorption by reducing the active surface area prone to corrosive media. More so the suppressed corrosion anion are as a results of multiple bond and heteroatom embedded with strong polar in K_2CrO_4 .

3.2 Mechanism of inhibition efficiency and adsorption study

Fig. 4 displays the comparative chart of inhibitory efficiency (IE) on mild steel substrate K_2CrO_4 concentration in 0.5M HCl + 3.65% NaCl solution obtained in accordance with stipulated process by [1, 10]. Observed on the chat are the potentiodynamic polarization (PP-Ecorr), Potentiodynamic-corrosion current (PP-Icorr), and polarization-corrosion rates (PP-CR) it was apparent that the inhibitory efficiency from all the processes agreed. More so this confirms the phenomena of adsorption to be linked with structural activities of the molecule, ion, and the hydroxyl present.

Meanwhile, the corrosion efficiency increases with increasing concentration of K_2CrO_4 . The significant efficiency was attained with 5%, 7.5% and 10% respectively. At 2% there was slight decrease in potential and efficiency, this might be as a result of inadequate influence of the mixed inhibitor. Icorr rises to about 100 percent while the PP-Ecorr ranges around 40 % efficiency with increasing concentration of K_2CrO_4 . The Langmuir plot (Fig. 5) on the other hands shows a linear relationship with the increase in the concentration of the inhibitor this confirms a continuous adsorption of the corrosion product on the mild steel substrates and a protection on the mild steel substrate. From regression computation, correction factors (R^2) is almost unity – 0.998 which means all the surfaces of the mild steel substrate is covered with adsorbed corrosion products.

Invariably, the adsorption features of this study are centred on the molecular structure and the atom of the adsorbents inhibitor which are traced to physical adsorption between metal surface and charge atoms of the inhibitor [14]. The change in the current at both anodic and cathodic region acted increasingly with the concentration of the mixed inhibitor at the metal interface reactions.

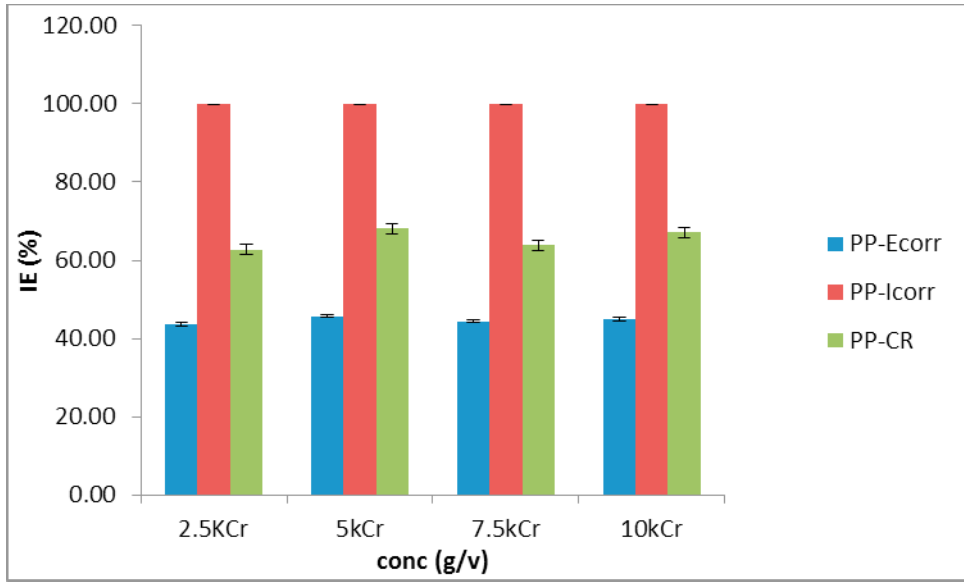


Fig. 4: Synergistic inhibitory efficiency (IE) for MS in 2.5-10% at 0.5M HCl+3.65%NaCl solution

obtained from potentiodynamic polarization (PP-Ecorr), Potentiodynamic-corrosion current (PP-Icorr), polarization-corrosion rate (PP-CR)

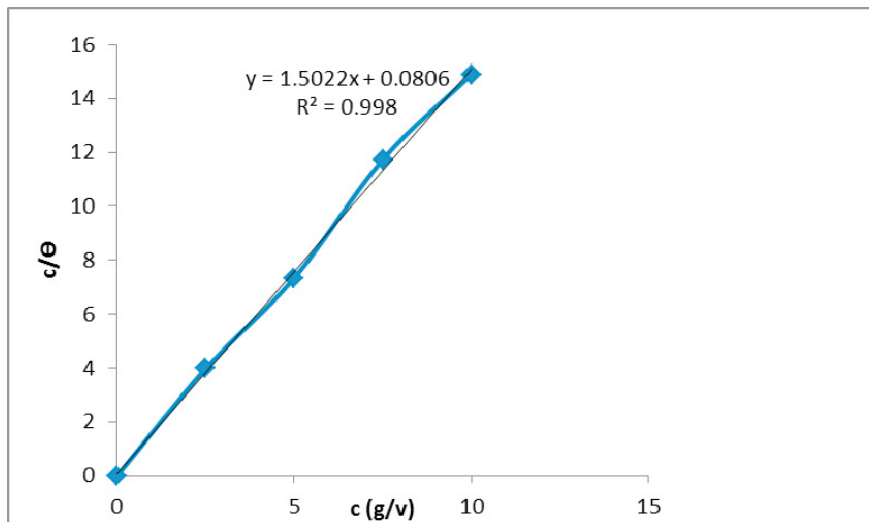


Fig. 5: Langmuir isotherm adsorption for MS in 2.5-10% at 0.5M HCl+3.65%NaCl solution

3.3 Microstructural Examination:

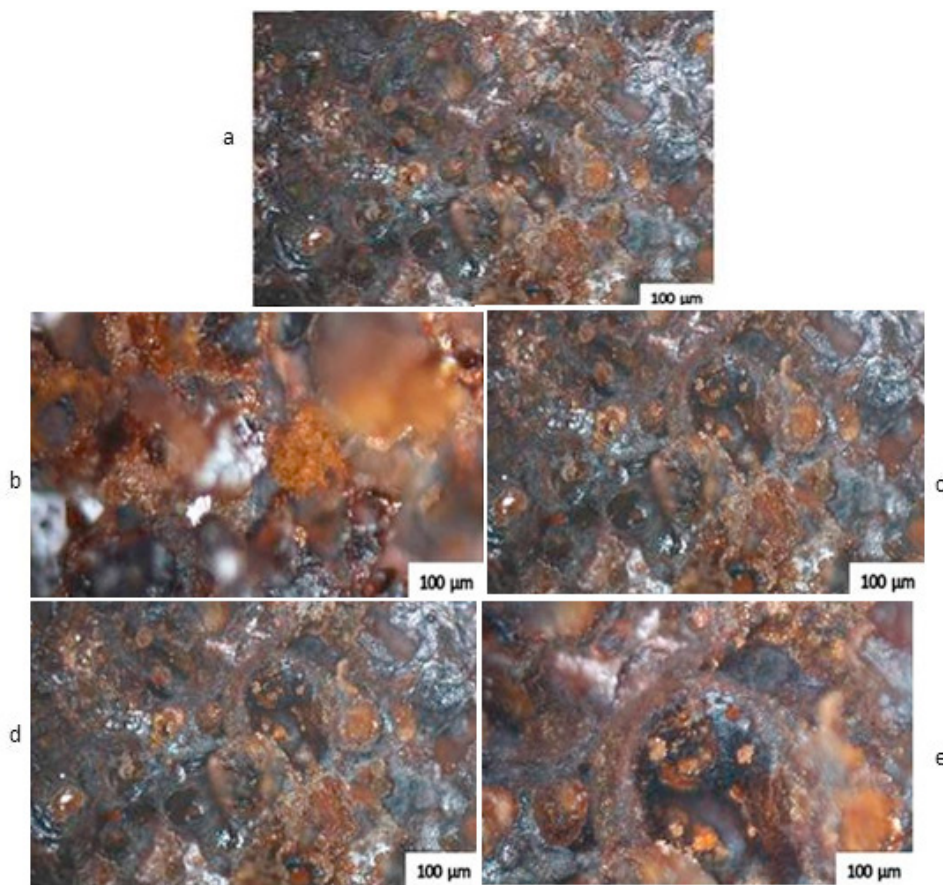


Fig. 6: Micrographs of MS after corrosion test with a) as-received b) 2.5% K₂CrO₃ inhibitor c) 5.0% K₂CrO₃ inhibitor d) 7.5 % K₂CrO₃ inhibitor e) 10 % K₂CrO₄ inhibitor in 0.5M HCl+ 3.65 NaCl medium.

The micrographs of the corroded portion of the steel under investigation are presented in Fig.6a-e. In the presence of 0.5M HCl/3.65% NaCl contaminant in K₂CrO₄ concentrations on mild steel, the images showed that there is corrosion pores at the interface with inhibitive samples but massively dominated at the as-received (uninhibited sample) [See Fig. 6a]. Although since metallic materials are heterogeneous in nature they are bound to attract reaction and quick attention to anodic dissolution [10]. This ideology is quite clear since the inhibitive influence work on time influence and the aggressiveness of the working media is also a factor in determining the extent of stability [6]. The unactive protection of the mild steel against severe corrosion attack could be explained in term of the dissolution mechanism within the medium/ surface phenomena.

4. Conclusions

The effect of K₂CrO₄ as a good inhibitive compound was seen on the potential trend with clear indication of acid-chloride as against the control sample.

K₂CrO₄ was found to be mixed type with an inhibitor efficiency of above 60 %.

It was observed that the chemisorption mechanism obey Langmuir isotherm trend with linear relationship regression coefficient of R²= 0.998 attained.

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