




Original Research Article

Synergistic effect of common fertilizer with potassium chromate on the corrosion inhibition of mild steel in 1 M HCl

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NPK₁

Urea

NPK₂

K₂CrO₄

DAP

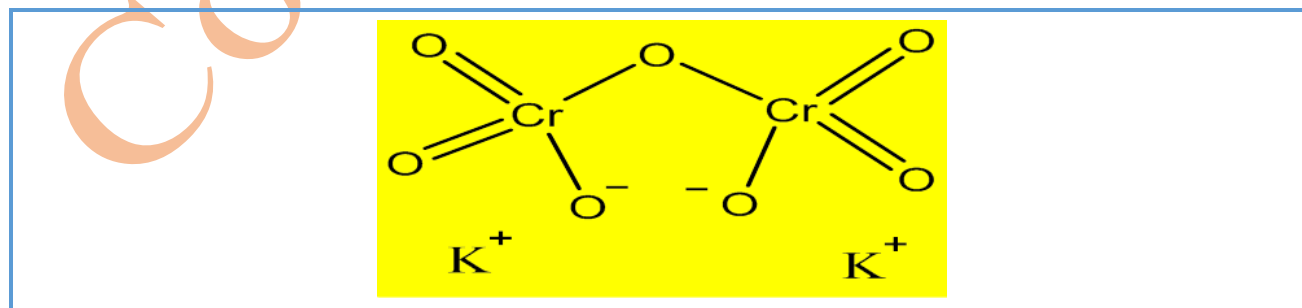
Mild Steel and Acid

ABSTRACT

Mild steel is an affordable engineering material used for various applications, including the mild acidic environment with some precautions. The (NPK₁, Urea, DAP, and NPK₂), inhibition efficiency in the control of the carbon steel corrosion in solution that contains 1M HCl in the absence and presence of the potassium chromate (K₂CrO₄) as one of the oxidizing agents were assessed through the weight loss. and spectrophotometer. Results have exhibited that the formulation consisting of 100 ppm from every one of (Urea, NPK₁, DAP, and NPK₂) and 100 ppm K₂CrO₄ presents 81.08%, 92%, 90% and 97%, respectively efficiency of inhibition. Whereas 100 ppm from every one of the Urea, NPK₁, DAP, and NPK₂, offers 63.27%, 69.93%, 76.56% and 71.69%, respectively efficiency of inhibition and 100 ppm of K₂CrO₄ had given 76% efficiency of inhibition. Fe²⁺/Fe³⁺ concentration in the solution is decreased with the increase in the concentration of the inhibitor. The inhibitor's properties of the adsorption were found to be obeying the isotherm of Langmuir adsorption.

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Graphical Abstract



Introduction

The acid solutions are typically utilized in industry, with industrial acid cleaning, acid pickling, oil well acidification and acid decaling being the most considerable application area [1]. It has been identified that nitrogen and the organic compounds containing the sulfur have resulted in the inhibition of the carbon steel dissolution conduct in the acidic [2]. Those compounds include-donating groups, reducing the corrosion rate through increasing hydrogen overvoltage on corroding metals [3]. Using compounds that contain the nitrogen as corrosion inhibitor is quite widespread. By the transfer of the electrons, those compounds have the ability of attaching to the surfaces of the metals for the purpose of forming a coordinate bond and thereby, a sufficient iron inhibition [4, 5]. Most effective and efficient inhibitors have π -bonds and heteroatoms (P, S, N, and O) with lone pair electrons that can inhibit the corrosion of metal in aqueous acid solutions [6]. The present study has been intended for the exploration of synergistic impact of a number of the organic fertilizer types in presence and absence of the potassium chromate (K_2CrO_4) as one of the oxidizing agents on the method of the weight-loss and the spectrophotometer inhibition of the corrosion of the carbon steel in 1 M of the HCl.

Experimental

Preparation of specimen

In the present study, mild steel coupons (with the dimensions of 4.5×2×0.3 cm) with composition presented in Table 1 were utilized. For the purpose of preparing polished surface for every one of the tests, the coupon surface was abraded in a sequential manner with the emery grit paper between 400 and 1,000

grades. Coupons were cleaned with the double distilled water following the process of the polishing; de-greased by the use of the acetone and finally dried prior to being utilized in the stream of warm air.

Inhibitor

There fertilizer types were utilized in the present research, which are; (phosphorus, potassium and nitrogen) (NPK) of a purity equal to 99%; Di-ammonium phosphate ($(NH_3)_2HPO_4$) of 98% purity, and Urea (CH_4N_2O) of 99% purity were used as it has been acquired from manufacturers. In addition to that, 99% purity K_2CrO_4 has been utilized as an agent of oxidation alone and with every one of the fertilizers as mentioned. All inhibitors' chemical structure draw by Chem. Office is illustrated in Figure 1.

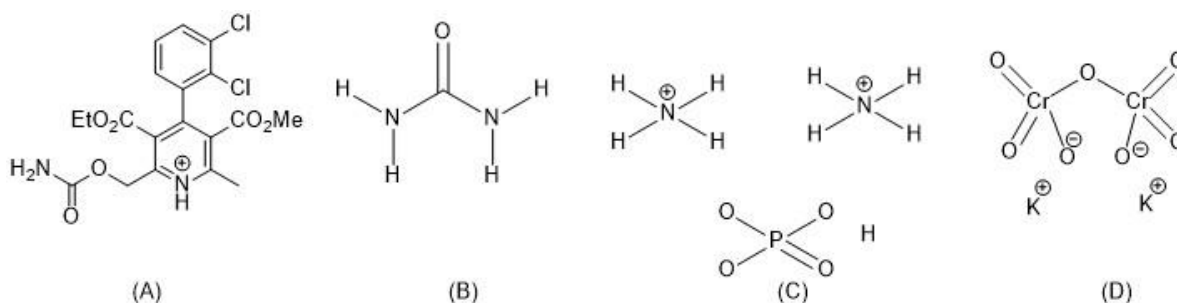
Aggressive solutions, 1M HCl have been produced from the distilled water through diluting the analytical grade (37%) hydrochloric acid. The utilized range of the inhibitor concentration was between (50 ppm and 100 ppm).

Approach of weight loss

The ASTM designation G 31-72 performed experimentations of immersion. In presence and absence of K_2CrO_4 for at 25 °C 1 day, samples that were already weighted, have been separately immersed in 500 mL of 1 M of the solutions of the HCl, which comprise the distinct levels of the inhibitor. Samples have been removed, washed, dried then re-weighed once more following the elapsed moment. According to the weight loss information that has been measured, the equations below have been utilized for the calculation of the rate of corrosion (in mpy), coverage of the surface (θ) and effectiveness of the inhibition (%IE) [7].

Table 1. composition of mild steel as it has been analyzed with optical emissions' spectrometer

Element	C	Mn	Si	S	P	Cr	Ni	Fe	Mo	Cu
Wt.%	0.207	1.050	0.940	0.050	0.110	0.170	0.080	Bal.	0.010	0.10

**Figure 1.** The researched chemical structures of inhibitors. (a) NPK (b) Urea (c) DAP (d) Potassium Chromate

$$CR = \frac{KW}{A \times T} \quad (1)$$

K represents the constant (534) A represents the area (in^2) W represents the weight loss (mg) D represents the mild steel density (7.86 g/cm^3) T represents the time (h)

$$\theta = \frac{CR_o - CR_i}{CR_o} \quad (2)$$

CR_o & CR_i represent the rates of the corrosion in presence and absence of the inhibitor.

$$\%IE = \theta \times 100 \quad (3)$$

Metal Ion solution analysis

The evaluation was carried out with the use of the UVvis spectrophotometer for the purpose of determining total ions ($\text{Fe}^{+2}/\text{Fe}^{+3}$) that have been entered in test solution of corrosion.

Result and Discussions

Weight loss evaluation

Weight-loss studies were performed 1 M of the HCl acid in a presence and absence of a variety of the levels of the inhibitor ranging between (50 ppm and 100 ppm). From Equation 1, Equation 2 and Equation 3; the corrosion rate, inhibition effectiveness and

coverage of inhibitor surface have been computed, then listed in Table 2. Adding any studied inhibitors to 1 M of the HCl was found to result in decreasing the corrosion rate, whereas the inhibition effectiveness had increased. Figures 2a-d indicates corrosion variations with inhibitor levels, whereas Figure 3a-d have demonstrated the inhibition effectiveness variations with the inhibitor levels. The optimal (NPK-1, NPK-2, DAP and Urea) concentration has been found 100 ppm with the maximal effectiveness of inhibition (69.93%, 71.69%, 76.56 %, and 63.27%); for 1 day of the time of immersion, respectively. Those outcomes have shown that the inhibitors of the medium may be behaving like a sufficient corrosion inhibitor for the mild steel. Which can be considered as an indication of the fact that the response of inhibitor on the surface of mild steel had reached a state of the equilibrium.

As seen in Figure 1, NPK-1, NPK-2, DAP, and Urea have a complex compound, containing heteroatoms in its molecules like the nitrogen, oxygen and sulfur. Mild steel corrosion inhibition may be ascribed to the adsorption of the component via those atoms, and that has been taken under consideration as an

adsorption center on the surface of the metal [8, 9].

Figure 2 and Figure 3 demonstrate that ($K_2CrO_4 + NPK_1$), ($K_2CrO_4 + NPK_2$), ($K_2CrO_4 + Urea$) and ($K_2CrO_4 + DAP$) have exhibited preferable synergistic impacts for the purpose of avoiding mild steel corrosion, which results from the adsorption and the metal surface protective film's shape. In addition to that, potassium chromate has been known as one of the sufficient oxidizing anodic inhibitors, protecting mild steel from the corrosive media of the HCl through making it in passive state, resulting in the prevention of the passive oxide breakdown that may result in the uniform corrosion [10].

Figure 4 illustrates that the effectiveness of the submission at distinct potassium chromate levels has been increased with the increase in potassium chromate concentration and reached a maximal 100 ppm (76.68%) value.

Table 2, includes as well the value of the absorbance that has been acquired at distinct inhibitor levels from spectrophotometer. The significance of the reduction of absorbance with the concentration of the incremental inhibitors of every studied inhibitor has been noted. It implies that in the presence of the inhibitor the concentration of electrons (Fe^{+2}/Fe^{+3}) has been decrease in the solution.

Table 2. parameters of corrosion that has been obtained for 1 day from the mild steel weight loss in 1 M of the HCl that contains a variety of the levels of inhibitor at a temperature of 25 °C

Compounds	Concentrations (ppm)	ΔW	CR	%IE	θ	abc
NPK ₁	0	0.0296	2.1309	0	0	0.287
	50	0.0114	0.8207	61.486	0.6148	0.176
	60	0.0107	0.7703	63.851	0.6385	0.168
	70	0.0101	0.7271	65.878	0.6587	0.155
	80	0.0098	0.7055	66.892	0.6689	0.128
	90	0.0095	0.6839	67.905	0.6790	0.116
	100	0.0089	0.6407	69.932	0.6993	0.102
NPK ₂	0	0.0265	1.9077	0.0	0.0	0.298
	50	0.0122	0.8783	53.962	0.5396	0.197
	60	0.0098	0.7055	63.019	0.6301	0.179
	70	0.0092	0.6623	65.283	0.6528	0.171
	80	0.0084	0.6047	68.302	0.6830	0.168
	90	0.0077	0.5543	70.943	0.7094	0.157
	100	0.0075	0.5399	71.698	0.7169	0.126
Urea	0	0.0373	2.6852	0.0	0.0	0.212
	50	0.0174	1.2526	53.351	0.5335	0.092
	60	0.0156	1.1230	58.177	0.5817	0.087
	70	0.0147	1.0582	60.590	0.6059	0.061
	80	0.0144	1.0367	61.394	0.6139	0.055
	90	0.0141	1.0151	62.198	0.6219	0.049
	100	0.0137	0.9863	63.271	0.6327	0.036
DAP	0	0.0431	3.103	0.0	0.0	0.205
	50	0.0211	1.519	51.044	0.5104	0.076
	60	0.0194	1.397	54.988	0.5498	0.069
	70	0.0157	1.130	63.573	0.6357	0.059
	80	0.0135	0.972	68.677	0.6867	0.055
	90	0.0102	0.734	76.334	0.7633	0.042

	100	0.0101	0.727	76.566	0.7656	0.027
	0	0.0276	0.0126	0.0	0.0	0.283
	50	0.0064	0.0029	76.8116	0.7681	0.0367
NPK ₁ +	60	0.0047	0.0021	82.971	0.8297	0.0321
K ₂ CrO ₄	70	0.0041	0.0019	85.1449	0.8514	0.0276
	80	0.0031	0.0014	88.7681	0.8876	0.0258
	90	0.0029	0.0013	89.4928	0.8949	0.0202
	100	0.0021	0.0010	92.3913	0.9239	0.0115
	0	0.0376	0.0172	0.0	0.0	0.298
	50	0.0105	0.0048	72.074	0.7207	0.092
NPK ₂	60	0.0097	0.0044	74.202	0.7420	0.071
+	70	0.0047	0.0021	87.500	0.8750	0.062
K ₂ CrO ₄	80	0.0035	0.0016	90.691	0.9069	0.053
	90	0.0022	0.0010	94.149	0.9414	0.049
	100	0.0011	0.0005	97.074	0.9707	0.032
	0	0.0573	0.0262	0.0	0.0	0.393
	50	0.028	0.0128	50.963	0.5096	0.121
Urea	60	0.0258	0.0118	54.816	0.5481	0.094
+	70	0.0228	0.0104	60.070	0.6007	0.089
K ₂ CrO ₄	80	0.0199	0.0091	65.149	0.6514	0.071
	90	0.0145	0.0066	74.606	0.7460	0.059
	100	0.0108	0.0049	81.086	0.8108	0.033
	0	0.0571	0.0261	0.0	0.0	0.215
	50	0.0187	0.0085	67.250	0.6725	0.037
DAP	60	0.0167	0.0076	70.753	0.7075	0.031
+	70	0.0144	0.0066	74.781	0.7478	0.028
K ₂ CrO ₄	80	0.0112	0.0051	80.385	0.8038	0.022
	90	0.0082	0.0037	85.639	0.8563	0.017
	100	0.0053	0.0024	90.718	0.9071	0.013
	0	0.0296	0.1352	0.0	0.0	0.321
	50	0.0113	0.0516	61.824	0.6182	0.072
	60	0.0105	0.0480	64.527	0.6452	0.064
K ₂ CrO ₄	70	0.0101	0.0461	65.878	0.6587	0.061
	80	0.0095	0.0434	67.905	0.6790	0.057
	90	0.0085	0.0388	71.284	0.7128	0.045
	100	0.0069	0.0315	76.689	0.7668	0.031

Isotherm of adsorption

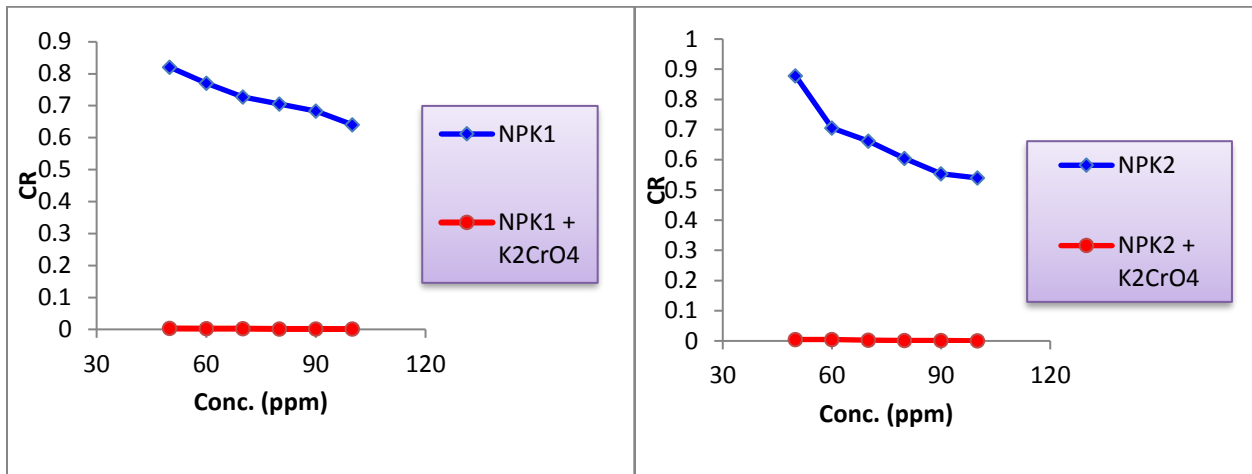
The isotherm of the adsorption has the ability to provide the basic data concerning interactions of inhibitor with the surface of the mild steel. Numerous attempts were made for the purpose of accommodating a variety of the isotherms, which include the Frumkin, Freundlich, Temkin, Flory-Huggins, Bockriss, and Langmuir isotherms [11]. Results were best

equipped with the Langmuir's isotherm of adsorption in this study. Based on this isotherm, the coverage of the surface (θ) is associated with the concentration of the inhibitor (C) by [12, 13]:

$$\frac{\theta}{1-\theta} = K_{ads} \cdot C \quad (4)$$

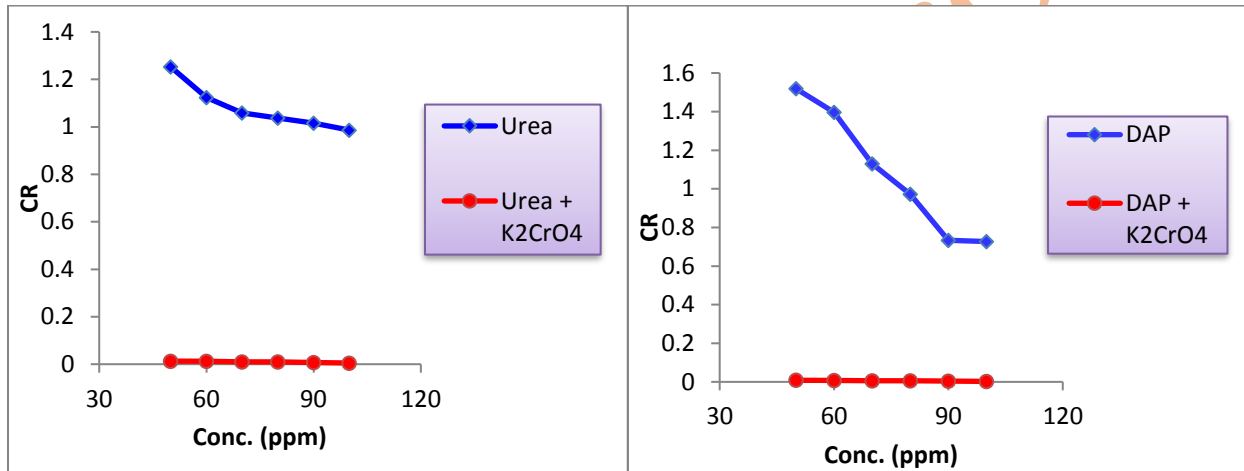
Re-arranging eq4 will give:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (5)$$



(a) NPK₁

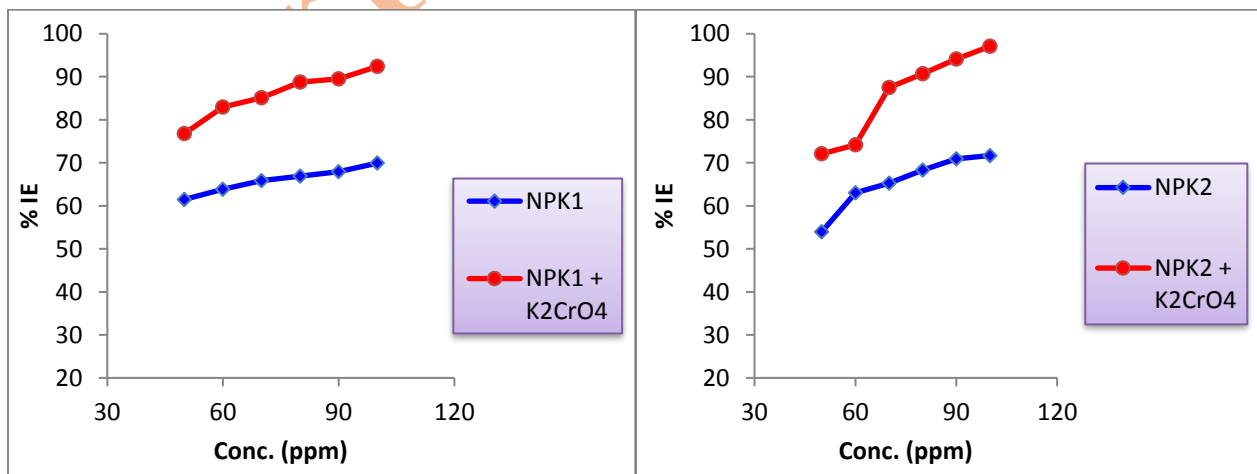
(b) NPK₂



(c) Urea

(d) DAP

Figure 2. Corrosion rate variations with inhibitor concentrations in 1M of the HCl on the surface of the mild steel at 25 °C



(a) NPK₁

(b) NPK₂

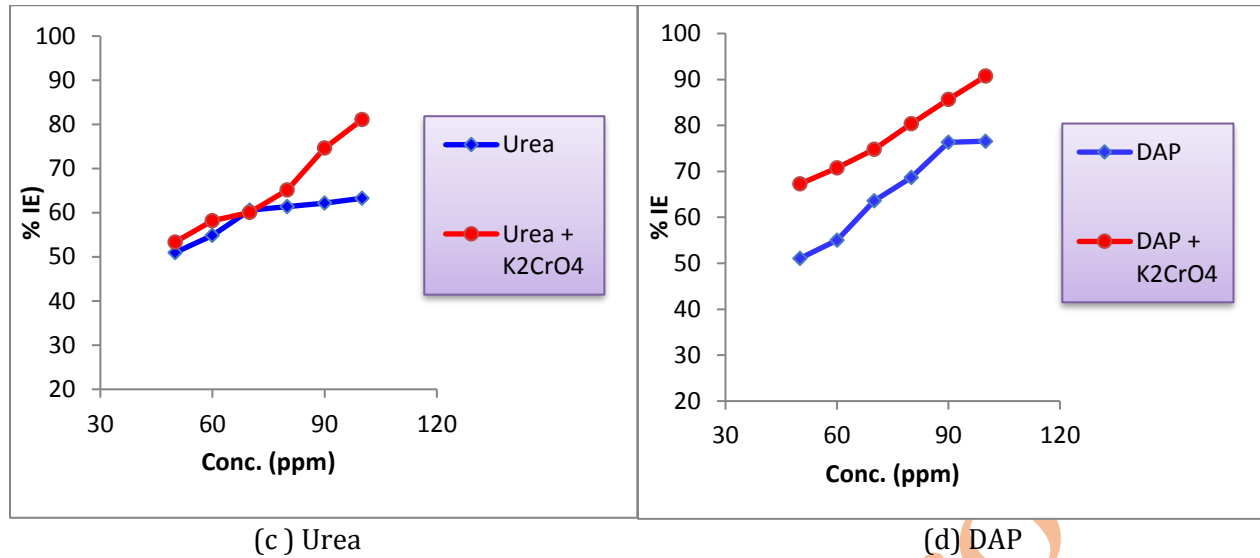


Figure 3. Inhibition efficiency variation with the concentration of the inhibitors in 1M of the HCl on the surface of the mild steel at 25 °C

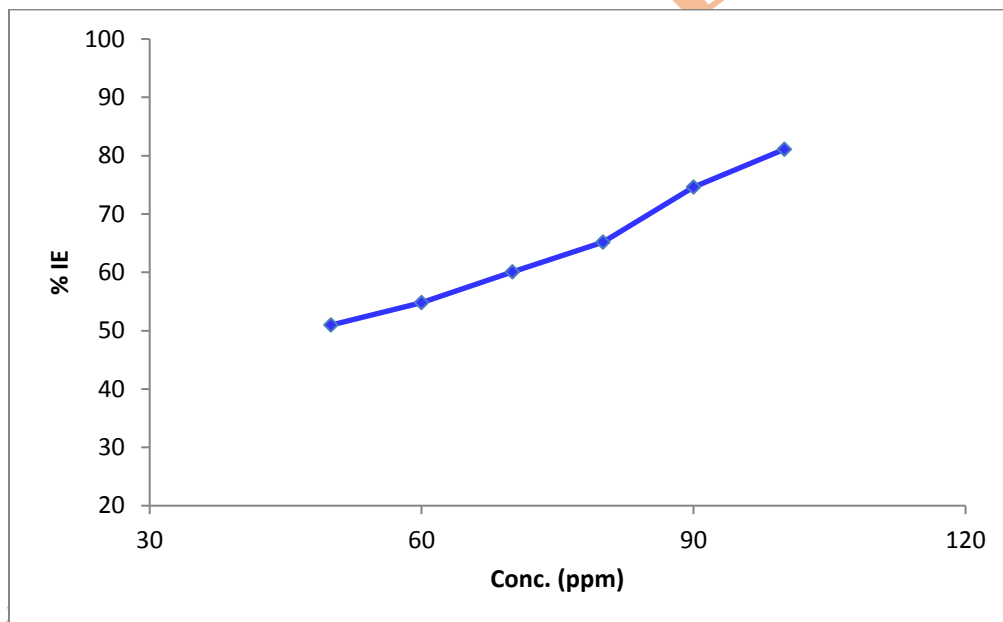


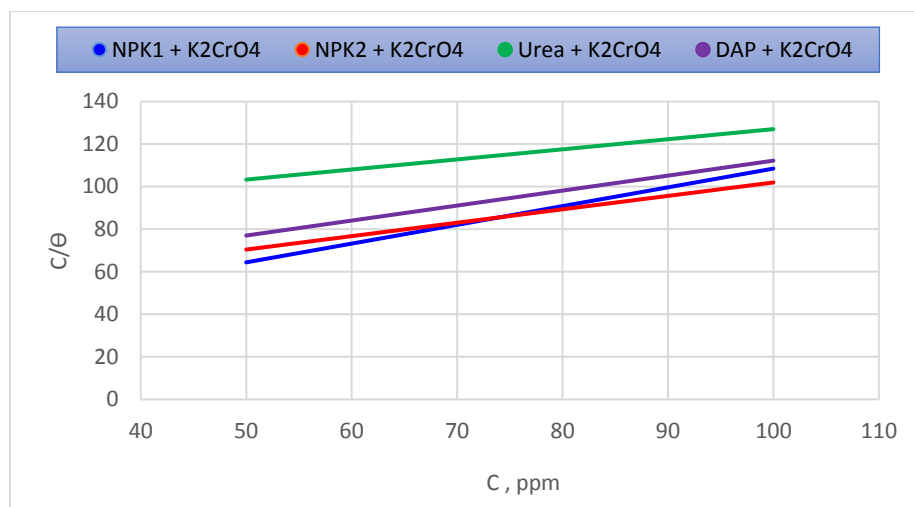
Figure 4. Inhibition efficiency variation with the concentration of the inhibitors for the potassium chromate in 1 M of the HCl on the surface of the mild steel at 25 °C

A fitted straight line with the slopes near 1, as can be observed in, was obtained from C/θ vs. C plots as shown in Figure 5, and all parameters are tabulated in Table 3. The powerful relation (R^2 higher than 0.90) is an indication of the fact that Langmuir's isotherm of adsorption has been succeeded with the

adsorption of the inhibitor on the surface of the mild steel. As can be seen in Table 3, the maximal value of the constant of adsorption equilibrium (K_{ads}) for ($K_2CrO_4 + NPK2$) in (ppm-1) is an indication of the fact that inhibitors had the tendency of desorb on the surface of the mild steel [14, 15].

Table 3. Adsorption parameters for the inhibitors that have been obtained from the adsorption of Langmuir isotherm

Additive	R ²	Parameter of Adsorption		
		Slope	Intercept	K _{ads} (ppm ⁻¹)
NPK ₁ + K ₂ CrO ₄	0.9589	0.6304	38.8990	0.0250
Urea + K ₂ CrO ₄	0.8188	0.4740	79.6010	0.0120
NPK ₂ + K ₂ CrO ₄	0.9980	0.8811	20.3460	0.0490
DAP + K ₂ CrO ₄	0.9776	0.7036	41.8330	0.0230

**Figure 5.** model of Langmuir's isothermic adsorption of the synergistic inhibitor in 1M HCl on a mild metal surface at 25 °C

Conclusions

The conclusions below may be obtained from this research study:

1. Combining (K₂CrO₄ + NPK₁), (K₂CrO₄ + Urea), (K₂CrO₄ + NPK₂), and (K₂CrO₄ + DAP) inhibitors have resulted in the production of an increased efficiency of the inhibition in 1 M of the HCl with the mild steel. This resulted from the synergistic impact of the inhibitors on mild steel in that medium.
2. Synergistic inhibitor adsorptions on the surface of the mild steel were found to be following Langmuir's isotherm from the experimental information fit at every studied concentration.
3. Fe²⁺/Fe³⁺ concentrations in the solution were reduced with increasing the concentration of the inhibitor for any utilized inhibitor.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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