Inhibition mechanism of mild steel corrosion in acidic media by some amine compounds

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Abstract

The inhibition action of four amine compounds (e.g. p-toluidine, o-aminophenol, anthranilic acid and o-phenylenediamine) on the corrosion of mild steel in HCl solutions has been studied using weight – loss technique. The results revealed that most of the amine compounds inhibit the corrosion of mild steel. It is obvious that, at each inhibitor concentration the inhibition effect for the amine compounds increases in the following order: anthranilic acid > o-phenylenediamine > p-toluidine. The inhibition effect of anthranilic acid and o-phenylenediamine compounds could be attributed to the formation of an insoluble adsorbed complex layer onto the metal surface, while in case of p-toluidine the inhibition effect was ascribed to the formation of a link between the $-NH_2$ group and the metal surface via adsorption. On the other hand, different concentrations from o-aminophenol in HCl were found to accelerate corrosion. This stimulating action towards the corrosion of mild steel could be due to oxidative tendency of the formed adsorbed surface complex. The corrosion inhibition mechanism is discussed depending on the nature and surface charge of the metal, the type of the aggressive electrolyte and the chemical structure of the amine compounds.

Key words: Amine compounds,Mild steel, HCl, Corrosion inhibition and accelerationMechanism.

1. Introduction

Mild steel can be used in a variety of environments, including acidic media [1 – 3]. The use of inhibitors is one of the most practical methods used to protect iron and steel against corrosion in different acidic solutions [4 - 8].

Most of the efficient inhibitors in acidic media are organic compounds containing functional nitrogen, sulfur and/or oxygen atoms. The inhibitor efficiency has been attributed [9, 10] to adsorption of the inhibitor molecules onto the metal surface forming a protective layer. The extent of adsorption of an inhibitor depends on various factors such as the nature of the metal, the chemical structure of the inhibitor, the type of the aggressive medium and the metal surface condition [11 – 15].

Although, the inhibition effect of many organic compounds such as amines on the corrosion of iron and steel in acid medium were studied [14, 16], the mechanism for their action is as yet not completely clarified. Generally, a study of the mechanism of the action of corrosion inhibitors has relevance both from the point of view of the search for new inhibitors and also for their use [7].

The aim of the present investigation is to study the inhibiting action of some amine compounds (e.g. p-toluidine, o-phenylenediamine, o-aminophenol and anthranlic acid) on the corrosion of mild steel in acidic media. Weight loss technique is used for this study. Also, a corrosion inhibition mechanism was discussed.

2. Experimental
2.1. Materials

The chemical composition (%) of the mild steel used was 0.13 C, 0.032 S, 0.14Si. 0.025 P, 0.48 Mn and the remainder iron. For weight loss measurements, rectangular samples of total surface area measuring 4 cm^2 were used. Before use, strips were polished with different grades of emery papers, degreased by acetone and washed thoroughly with doubly distilled water. Aqueous solutions of different concentrations from HCl were prepared. Also, p-toluidine, o-phenylenediamine, o-aminophenol and anthranilic acid were added to 0.5 M HCl in different concentrations. However, all the chemicals used were of AR grade and solutions were prepared by using doubly distilled water.

2.2. Corrosion weight loss measurements

Experiments were conducted in the test solutions at 25 ± 1 ^{0}C. In each experiment, the cleaned mild steel specimen was weighted and suspended by a glass hook in 100 ml acid solution. The specimen was then taken out of the test solution, rinsed with distilled water, dried and weighted. The average weight loss for each of two identical experiments was taken. Generally, weight changes of mild steel were followed for different time intervals in different concentrations from HCl solutions and in 0.5 M HCl without and various concentrations from the amines compounds. Inhibition efficiency (% I.E) of the amines compounds are calculated as follows:
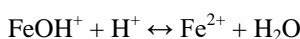
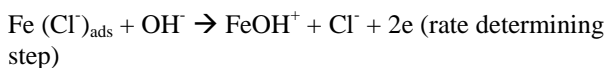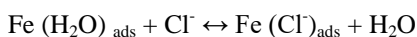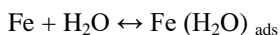$$\% \ I.\ E. = [(W - W_{inh})/\ W] \ X \ 100$$

Where W and W_{inh} are the values of the weight loss of mild steel after immersion in solutions without and with inhibitor, respectively.

3. Results and discussion
3.1. Weight loss of mild steel in different concentrations from HCl solutions

The curves of Figure 1 represent the variation of weight loss of mild steel with time in different

concentrations from HCl solutions. It can be clearly seen that as the acid concentration increase, the weight loss increases with time. This behavior could be attributed to the mild steel dissolution under the effect of acidic medium. It is evident that in HCl solutions, iron and steel can be corroding to form Fe^{2+} cations and as the acid concentration increase, the rate of corrosion rises [17]. The following reaction sequence for the dissolution of iron and steel in HCl was proposed [18]:

$$Fe + H_2O \leftrightarrow Fe\,(H_2O)\,_{ads}$$

$$Fe\,(H_2O)\,_{ads} + Cl^- \leftrightarrow Fe\,(Cl^-)_{ads} + H_2O$$

$$Fe\,(Cl^-)_{ads} + OH^- \rightarrow FeOH^+ + Cl^- + 2e \text{ (rate determining step)}$$

$$FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2O$$

In this sequence chemisorbed Cl^- ions displace adsorbed water molecules and then interact with adjacently adsorbed hydroxide ions.

3.2. Weight loss of mild steel in 0.5 M HCl solutions containing amine inhibitors.

Figures 2 – 5 show the weight loss versus time for mild steel in 0.5 M HCl solution containing or not the amines compounds. Values of the inhibition efficiency (% I. E.) obtained are given in Table 1. It can be clearly seen that, in the presence of different concentrations from anthranilic acid, o-phenylenediamine and p-toluidine (see Figures 2 – 4) a marked decrease in the weight loss of mild steel, which is lower than that obtained in the blank solution.

This behavior would reveal that, these three amine compounds have inhibition effect on the corrosion of mild steel in 0.5 M HCl. The inhibition of mild steel corrosion by these three amine compounds could be attributed to the adsorption of the amine inhibitor molecules on the metal surface to form a protective layer [19, 20]. On the other hand, the presence o-aminophenol additive (see Figure 5) leads to increase the weight loss indicating that this amine compound can act as corrosion accelerator for mild steel in acidic media.

In conclusion, the adsorption of the amine molecules and consequently the nature of the layer formed onto the metal surface can be influenced by various factors such as the nature and surface charge of the metal surface, by the type of the aggressive medium and by the chemical structure of the amine compounds.

3.3. The inhibition mechanism

As follows from weight loss measurements, the corrosion of mild steel in 0.5 M HCl is reduced in the presence of anthranilic acid, o-phenylenediamine and p-toluidine and accelerates in the presence of o-aminophenol.

The first stage in the action mechanism of the amine compounds in HCl solution is their adsorption on the metal surface through the active group such as –NH_2, - OH and – COOH [19]. Also, the π-bond of the aromatic ring is considered as a suitable site for adsorption process [19, 21].

As shown from Figure 6, most of the constituent of the amine compounds are aromatic ring, - NH_2, – COOH and - OH group. They exist in the acidic medium as a neutral species or in the cationic form.

On the other hand it is known that [12, 19 – 23], the extent of adsorption of the organic cation molecules is affected by the nature of anions in acidic solution. Thus, in HCl solution, Cl^- anions can be adsorbing onto the metal surface, which form intermediate bridges. The negative ends of the halogen-metal dipoles being oriented toward the solution. This negative end of the metal surface can be facilitate the adsorption of the positively inhibitor cations from the solution by electrostatic interaction.

However, the adsorption of the amine molecules through the π-bond of the aromatic ring onto the mild steel surface is omitted. This is due to the fact that, mild steel surface is assumed to be negatively charged in HCl solution, in which negatively charged centers of the amine molecules are not attached to the same negatively charged metal surface. Consequently, it can be assume that the adsorption of the amine molecules is facilitated through the electrostatic interaction between the positively charged amine group and the negatively charged mild steel surface.

Also, the amine compounds may be adsorbed on the metal surface in the form of neutral molecules, to form a links between the d-orbital of iron atom, involving the displacement of water molecules from the metal surface, and the lonely sp^2 electron pairs present on the N atom of the aniline moiety and oxygen of the carboxylate or hydroxyl group as in case of anthranilic acid and o-aminophenol as well as the N atom of phenylenediamine [24]. It is well known that amine compounds containing active grope such as – COOH, – NH_2 or – OH in the ortho-position of its aniline moiety are able to form a complex compound with a transition metal cation or atom.

Thus, it is expected that a complex compound is formed to cover the metal surface. The formation of a complex between the molecules of p-toluidine and the mild steel surface is excluded and the surface coverage is expected due to the formation of link between the metal atoms and the lone pairs present on the N atom of the aniline moiety.

Since the adsorption of the amine molecules through its π-bond of the aromatic ring is omitted, thus it is reasonable to conclude that the amine molecules are adsorbed on the mild steel surface in a vertical orientation as shown from Figure 7.

For the same inhibitor concentration (see Table 1), the inhibition efficiency obtained for the amine compounds are arranged in the following order:
anthranilic acid > o-phenylenediamine > p-toluidine.

On the other hand, o-aminophenol was found to accelerate corrosion of mild steel. These results could be explained depending on the type of the substituent group and the number of the functional adsorption group in the aniline moiety as well as the oxidative properties of the formed surface layer.

The protective ability of anthranilic acid and o-phenylenediamine comes first but anthranilic acid is the better restrainer and more strongly adsorbed than o-phenylenediamine. This should be due to the fact that the carbonyl group ($- C = O$) which included in the $-$ COOH group of the anthranilic acid is considered as electron withdrawing group. Consequently, the acidity of the $-$ OH attached to this carbonyl group is increased (i.e., give proton easily). Thus, the oxygen atom of this $-$ OH group could be strongly adsorbed to the metal surface as compared to the adsorption of the nitrogen atom included in the $-$ NH$_2$ of the aniline moiety of o-phenylenediamine.

In case of p-toluidine, the presence of $-$ CH$_3$ group attached to the aniline moiety in the para position (electron donating group) leads to increase the π - electron density of the aromatic ring. Consequently, the positive charge density of the cationic form of the aniline moiety is decreased causing decrease of the inhibition effect. Moreover, it appears that in case of p-toluidine one adsorption center (e.g. $-$ NH$_2$ group) is participate in the adsorption process as compared to the adsorption centers of both anthranilic acid (e.g. $-$ NH$_2$ group and the $-$ OH of the carboxyl group) and o-phenylenediamine (e.g. two $-$ NH$_2$ groups). Accordingly, it is assumed that the presence of two active groups in the inhibitor molecule make its inhibition action against corrosion more effective than that contain one active group. Thus, the inhibition effect of p-toluidine compound is lower than of both anthranilic acid and o-phenylenediamine compounds.

The stimulating action of o-aminophenol towards the corrosion of mild steel in HCl solution could be explained on the basis of a formation of a surface complex. In this case, the presence of strongly adsorbed Cl$^-$ anions forms a surface complex according to;

$$Fe + Cl^- \leftrightarrow (Fe\ Cl^-)_s$$

where s represents an ion or compound on the surface. In the presence of protonated o-aminophenol, it is adsorbed on the sites of the surface where the anion is chemisorbed [25] as:

$$(Fe\ Cl^-)s + o\text{-}OHC6H4NH_3^+ \leftrightarrow (Fe\ Cl^- \cdots\cdots\ o\text{-}OHC6H4NH_3^+)_s$$
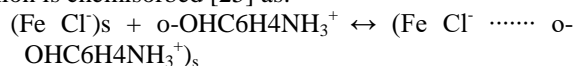
Thus, it is believed that the presence of different concentrations from o-aminophenol, the complex (Fe Cl- $\cdots\cdots$ o-OHC6H4NH3-)$_s$ is formed on the mild steel surface. The corrosion acceleration of o-aminophenol could be related to the oxidative tendency of the surface complex [25, 26]. It takes place until the complex is adsorbed. When the charge transfer occurs, a complex ion undergoes desorption and hence the inhibitor will function as a stimulator (i.e., enhances the corrosion process).

4. Conclusions

1. The inhibition effect for the three amine compounds increases in the following order: anthranilic acid > o-phenylenediamine > p-toluidine while 0-aminophenol was found to accelerate corrosion of mild steel in HCl solution.

2. anthranilic acid and o-phenylenediamine inhibit corrosion most probably due to the formation of an insoluble adsorbed complex layer onto the mild steel surface, while the acceleration of corrosion could be related to a formation of a soluble (desorbed) complex as in case of o-aminophenol.

3. Both the type and position of the substituent group, the number of the functional adsorption atoms of the amine molecules and the nature of the metal surface were found to play an important role in the inhibition process.

Table (1) Inhibition efficiencies of mild steel corrosion in 0.5 M HCL solutions in the absence and presence of different concentrations of the amine compounds at 25 ± 1 °C after 8 hours.

Inhibitor type	Concentration (M)	Inhibition efficiency (% IE)
Blank	-	-
Anthranilic acid	10^{-6}	68.79
	$5*10^{-6}$	75.18
	10^{-5}	78.01
	10^{-4}	79.43
	10^{-2}	82.98
	10^{-1}	85.11
o-phenylenediamine	10^{-6}	9.68
	10^{-5}	12.90
	10^{-4}	16.13
	10^{-3}	22.58
	10^{-2}	29.03
	10^{-1}	38.71
P-Toluidine	10^{-6}	11.11
	10^{-5}	14.81
	10^{-4}	18.52
	10^{-3}	22.22
	10^{-2}	25.93
	10^{-1}	29.63
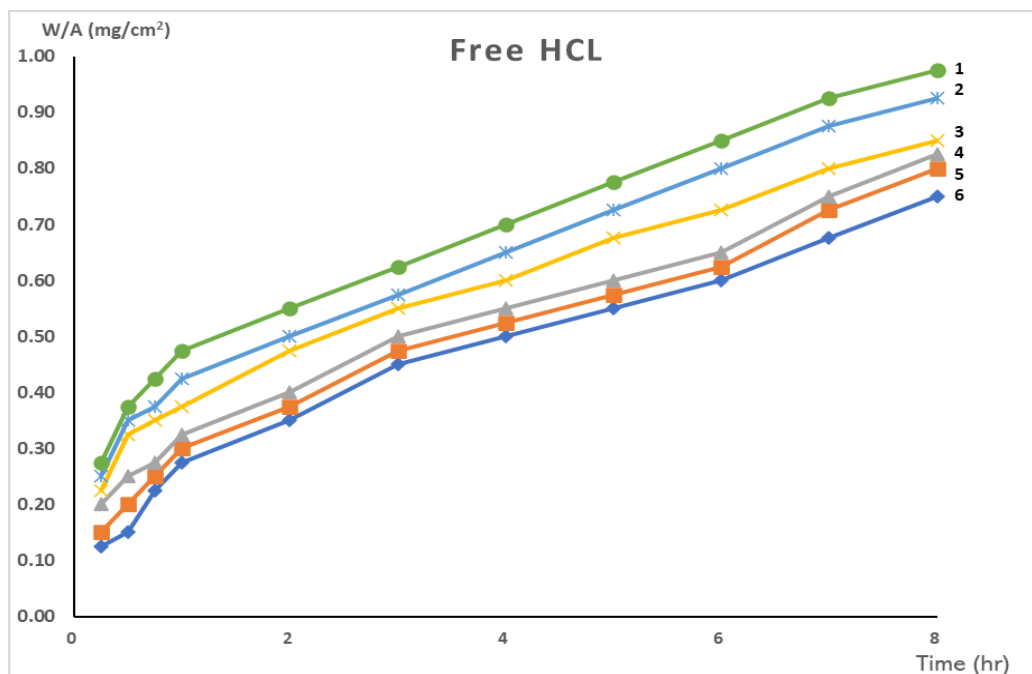
Fig. (1) Weight loss as function of time of mild steel in different concentrations from HCL solutions: (1) 1.5, (2) 1.25, (3) 1, (4) 0.75, (5) 0.5, (6) 0.25 M.
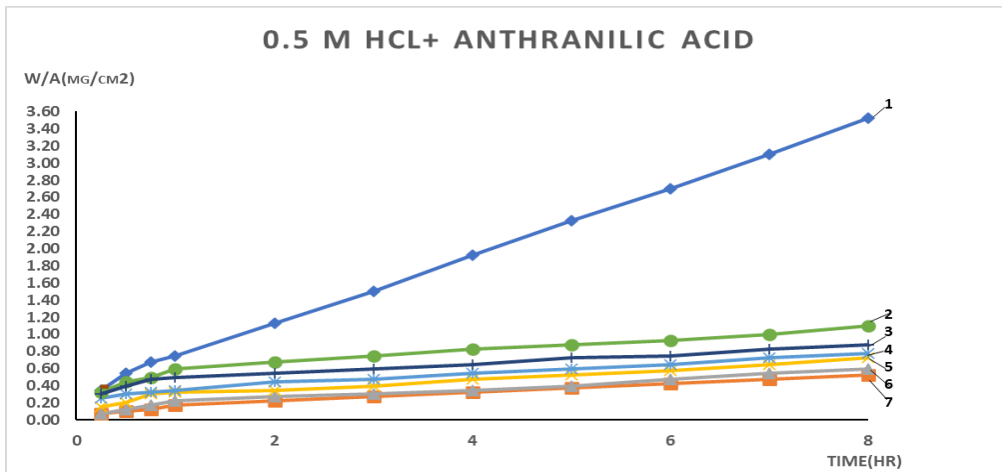
Fig. (2) Weight loss as function of time of mild steel in 0.5 M HCL without and with different concentrations of anthranilic acid: (1) blank, (2) 10^{-6}, (3) $5*10^{-6}$, (4) 10^{-5}, (5) 10^{-4}, (6) 10^{-2}, (7) 10^{-1} M.
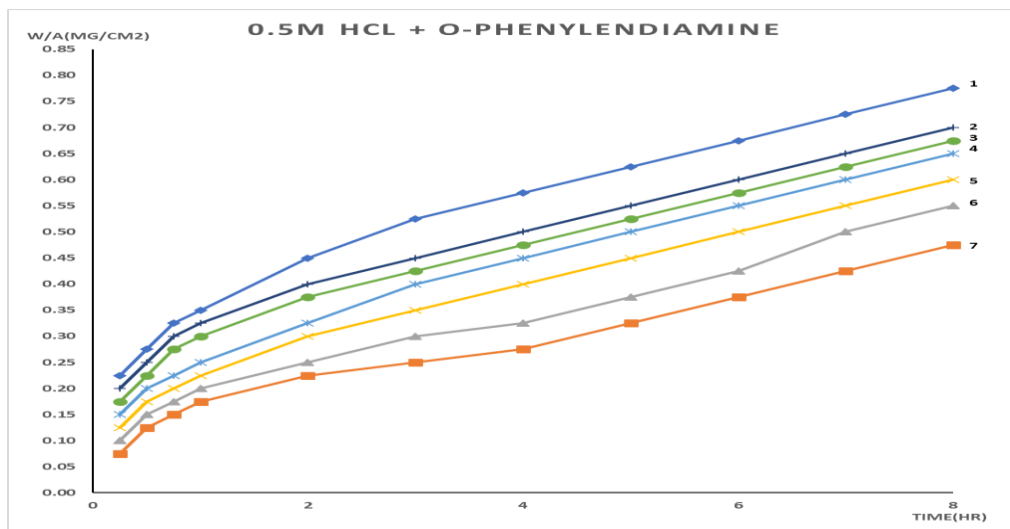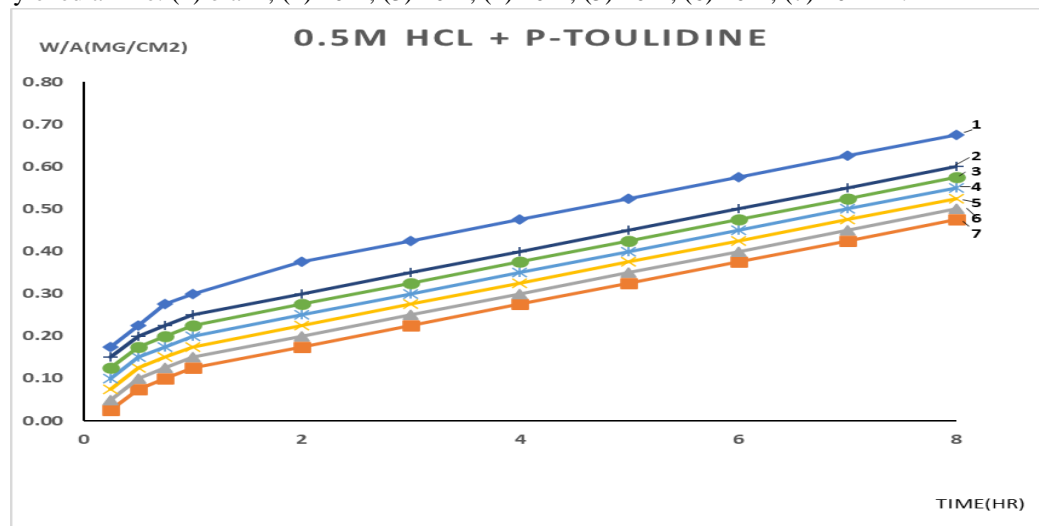

Fig. (3) Weight loss as function of time of mild steel in 0.5 M HCL without and with different concentrations of o-phenylenediamine: (1) blank, (2) 10^{-6}, (3) 10^{-5}, (4) 10^{-4}, (5) 10^{-3}, (6) 10^{-2}, (7) 10^{-1} M.

Fig. (4) Weight loss as function of time of mild steel in 0.5 M HCL without and with different concentrations of p-toluidine: (1) blank, (2) 10^{-6}, (3) 10^{-5}, (4) 10^{-4}, (5) 10^{-3}, (6) 10^{-2}, (7) 10^{-1} M.
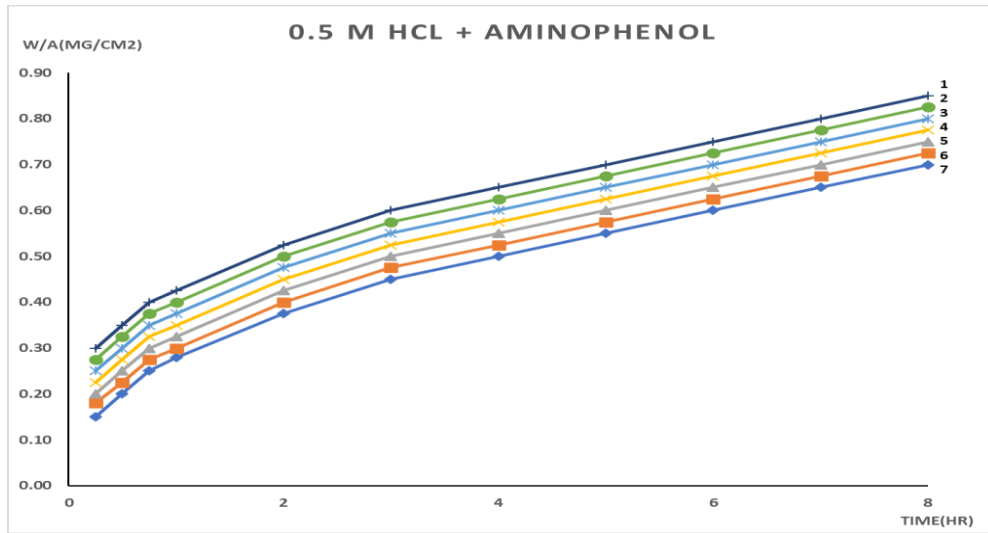
Fig. (5) Weight loss as function of time of mild steel in 0.5 M HCL without and with different concentrations of o-aminophenol: (1) 10^{-6}, (2) 10^{-5}, (3) 10^{-4}, (4) 10^{-3}, (5) 10^{-2}, (6) 10^{-1}M, (7) blank.
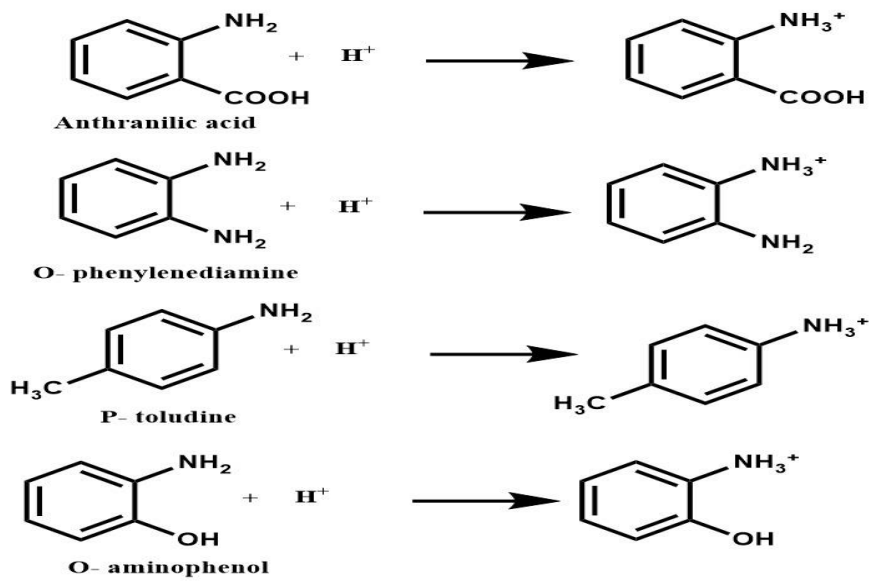

Fig. (6) Chemical formula of the investigated amine compounds in both the molecular and cationic forms.

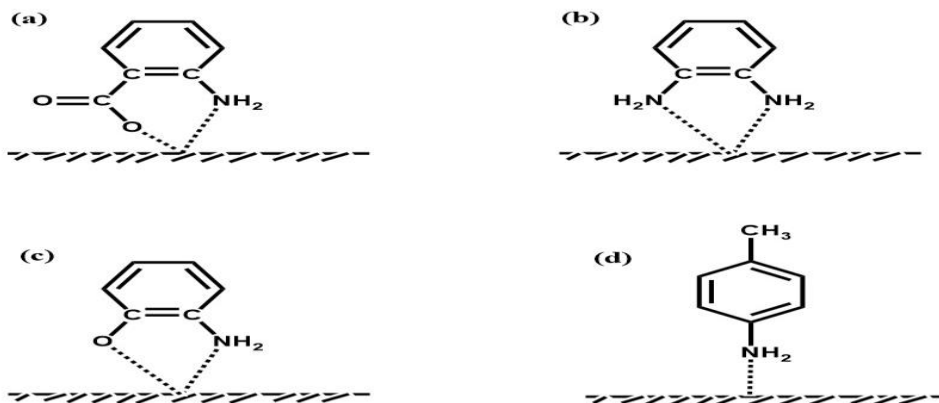**Fig. (7)** Schematic representation of the mode of adsorption of (a)anthranilic acid, (b) o-phenylenediamine, (c) o-aminophenol and (d) p-toluidine

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