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ARTICLE

Corrosion Studies of Mild Steel in Organic Acid/Chloride Media

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ABSTRACT

This study investigated the corrosion behaviour of mild steel immersed in 0.5 M organic acid media and in 90 %/10 % 0.5 M organic acid media/ 3.5 % NaCl by surface observation and weight loss technique. In all the solutions (0.5 M organic acid and the organic acid containing 3.5 % NaCl), mild steel corroded more in acetic acid compared to other solutions, while NaCl was lowest. The corrosion rate of mild steel immersed in 90 % organic acid contaminated with 10 % of 3.5 % NaCl was lower than that found when the steel samples were immersed in 100 % organic acid. It can be suggested that an increase in pH of organic acid media as NaCl was added to the organic acids increased the passivity of the mild steel in the solutions. Scanning electron microscope (SEM) was used to examine and characterize the mild steel surface before and after its immersion in the respective media. The elemental composition on the corroded surface of mild steel was detected with the SEM coupled with electron dispersive spectroscopy (EDS). The SEM and the physical observation results showed corrosion products, which were confirmed to be oxide films on the surface of mild steel studied in 100 % organic acid solutions. Meanwhile, morphology of the mild steel after corrosion in organic acids containing NaCl showed that corrosion products were the protective oxide films. The oxides of Fe, Mn, Na, and Si were mostly detected on the surface of mild steel after corrosion.

KEYWORDS

INTRODUCTION

Corrosion is the deterioration of a material by a chemical attack or electrochemical reaction under the influence of its surrounding. For a corrosion process to occur, anodic and cathodic reactions must be present to transmit current flow. Anodic reaction received electrons from cathodic reaction through the electrolyte. Thus, the reaction between organic acids and mild steel products could cause damage in terms of human safety, financial cost and environment [1].

Organic acids serve as important precursors for the synthesis of many chemicals. Unlike strong inorganic acids, organic acids are weak acids and do not dissociate completely in water however, organic acids provide sufficient protons to act as inorganic acids towards metals because most of the organic acids are neither oxidizing nor reducing to metals such as copper, which does not displace hydrogen from acids [2]. Lower molecular weight

organic acids are miscible in water, but higher molecular weight organic acids are insoluble in molecular form [3]. In chemical industries, organic acids are used as process mixtures with other acids, solvents, salts, *etc.* thereby making the corrosive action of organic acids complicated [3].

Acetic acid is the best known organic acid and usually produced in the largest volume. However, other organic acids are vital for the preparation of compounds used in fields of pharmaceuticals, plastics and fiber [2]. Acetic acid is reported to be slightly less corrosive than formic acid which is the most aggressive among all pure organic acids and both acids play major roles in certain corrosion systems [4]. However, some studies on the corrosion of copper in organic acids have reported the corrosivity of acetic acid to be higher than that of formic acid with the mechanism of degradation of copper in the acids involving the formation of a basic copper acetate and hydrated copper acetate and copper formate [5,6]. The corrosive behaviour of other organic acids like oxalic acid and citric acid have also been reported with varying corrosive degrees [7].

Mild steel is widely applied in various industries due to its availability and good physical properties. It is cheaper than wrought iron while being more workable than cast iron. It is used in the fabrication of reaction vessels and storage tanks for industries that either manufacture or use various organic acids as reactants. Although, mild steel has different industrial applications its use and lifespan is under restriction in acidic environment as a result of its susceptibility towards corrosion [8]. There is limited data on corrosion studies of mild steel in mixtures of organic acids and sodium chloride, hence this study evaluates the corrosion behavior of mild steel in organic acids-sodium chloride mixtures of various concentrations.

E X P E R I M E N T A L

AR grade glacial acetic acid (99 %), formic acid (85 %), citric acid (99.5 %), oxalic acid dihydrate (99 %) and sodium chloride (99 %) were used for weight loss studies. Double distilled water was used to prepare 0.5 M solutions of the organic acids and 3.5 % NaCl solution. Mild steel specimens of size 3.5 cm × 1 cm were cut, grinded, degreased by immersing in acetone and stored in a vacuum desiccator. Table-1 shows the elemental compositions of the mild steel used.

TABLE-1
CHEMICAL COMPOSITIONS OF MILD STEEL

Elements	Fe	C	Mn	P	S	Si
Weight (%)	Balance	0.15	1.00	0.035	0.035	0.30

Weight loss and corrosion rate: The experimental set up involved a set of 100 % organic acid and another set of 90 % organic acid and 10 % NaCl solution. Weight loss studies involved the samples immersed in 50 mL test solution in glass beakers in static conditions for 21 days. The samples were kept in the beaker in such a way that the surface were in contact with the solution. The samples were taken out at the interval of 3 days, washed in distilled water & acetone and weighed. The corrosion rate was determined from the difference in weight of the samples before and after conducting the corrosion study using the formula:

$$\text{Corrosion rate (mm/yr)} = \frac{87.6W}{A\rho t} \quad (1)$$

where W is the weight loss (mg), A is the surface area of mild steel (cm^2), ρ is density of mild steel (g/cm^3) and t is time of immersion (h).

Microstructural studies: The morphology of corroded samples was studied using scanning electron microscopy (SEM; Tescan HRSEM, South Africa). Samples were carbon coated prior to morphological studies to avoid charge effect and to obtain clear images. The elemental compositions of the samples were obtained using electron dispersive spectroscopy coupled with the SEM measurement instrument. Generated micrographs were used in studying corroded areas at microstructure levels by identifying their elemental compositions which confirmed that oxides were formed on the surface of samples and illustrating structural changes.

R E S U L T S   A N D   D I S C U S S I O N

Weight loss: The weight loss measurement has been identified as one of best of corrosion techniques for metal corrosion evaluation in an immersion test [9]. The weight loss study of mild steel in different medium including 0.5 M organic acids (acetic acid, formic acid, citric acid and oxalic acid), 3.5 % NaCl and double distilled water have been studied over a period of 21 days. In this study, weight loss technique was used to evaluate corrosion behaviour of mild steel samples in these solutions.

From Fig. 1, there is decrease in weight loss of mild steel samples over the entire exposure time with a sharp decrease in the first five days. It was also observed that mild steel sample immersed in acetic acid exhibited the highest weight loss over the first 10 days of the study. On the other hand, the sample immersed in water shows the lowest weight loss compared to all other mild steel samples in 100 % organic acids. The study showed that the corrosive order of media used in the study was initially acetic acid > citric acid > formic acid > oxalic acid > 3.5 % NaCl solution. It is important to note that even though the mild corroded very fast in acetic acid, the rate decreased significantly in 9 days as compared to others. This is due to the formation of passive oxide film.
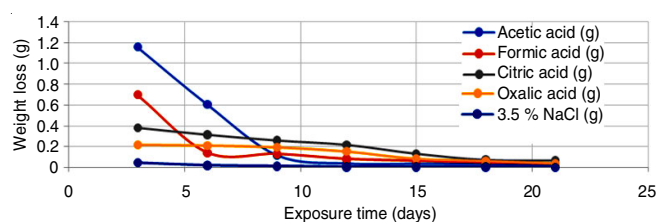

Fig. 1. Weight loss against time over the period of 21 days for 100 % organic acid and NaCl solutions

Fig. 2 represents the weight loss of mild steel samples in different organic/10 % NaCl media during the course of study. The weight loss of mild steel samples was found to decrease with increasing of exposure time. Weight loss of mild steel samples was recorded and the order of media corrosiveness was found to be as follow: formic acid > acetic acid > citric acid > oxalic acid > water over the first 6 days of the study. Generally, sodium chloride addition accelerates the corrosion of
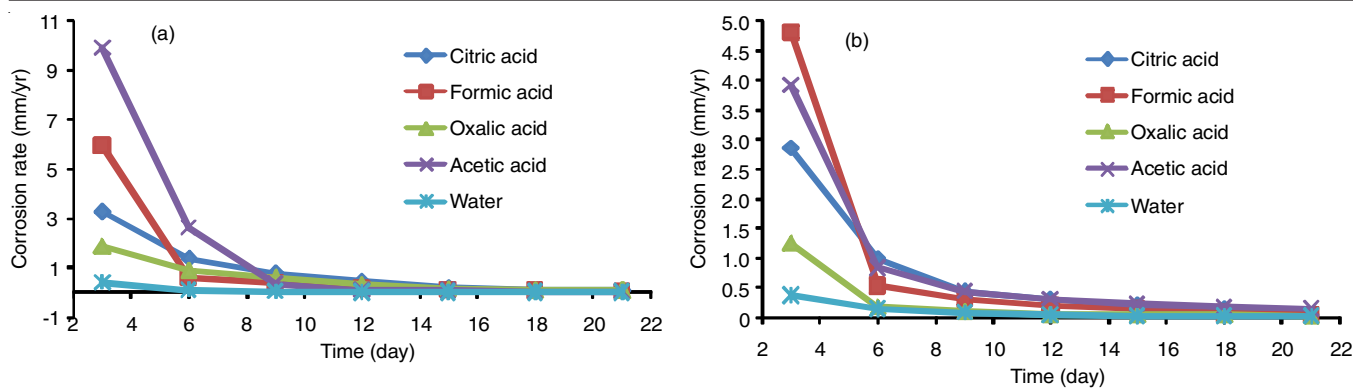
Fig. 3. Corrosion rates of mild steel in (a) media without NaCl (b) media with NaCl after 21 days
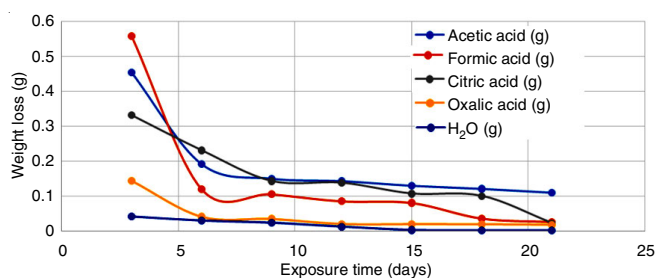

Fig. 2. Weight loss against time over the period of 21 days for 90 % organic acid and 10 % NaCl solutions

immersed steel by increasing chloride ions in the solution which penetrate in and leads to pit corrosion [10]. The pitting corrosion of the mild steel in the chloride media was however not studied.

Corrosion rates: Fig. 3 represents the corrosion rate of mild steel in pure organic acids and in organic acids mixed with 10 % NaCl solution. It is observed that the samples shown in (a) exhibits an initial sharp decrease in corrosion rate over the first 5 days compared to the corrosion rate of samples in (b), but both show a gradual decrease in corrosion rates after 6 days onwards. The corrosion rates were observed to decrease with increase in the time of exposure. The addition of NaCl solution generally leads to the decrease in corrosion rates of mild steel in the media studied. The average corrosion rates were in the order of acetic acid > formic acid > citric acid > oxalic acid > 3.5 % NaCl. The average corrosion rates also showed that the addition of NaCl to oxalic acid increased the corrosion rate of mild steel in this solution unlike in the other solutions with NaCl.

The pH of organic acids used (acetic acid, citric acid, formic acid and oxalic acid) were 2.3, 1.59, 1.63 and 0.94, respectively. These pH values increased to 2.5, 1.75, 1.70 and 1.03, respectively when NaCl solution was added to these organic acids. At high pH, hydrogen evolution is usually reduced and there is possibility of protective film formation to increase, thus as the time of exposure time increased the rate at which the samples corrode will reduced [11]. It was reported that the higher the alkalinity of a solution, the lower the corrosion rate in the solution [12]. The corrosion reaction of mild steel in aerated media can be written as:

$$4Fe + 2H_2O + 3O_2 \longrightarrow 2Fe_2O_3 \cdot 2H_2O \qquad (2)$$
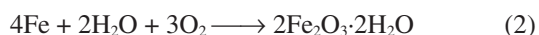
It was reported that at initial stage of attack on mild steel in an aerated media, the corrosion rates of the mild steels increased

[11]. However, as the exposure time increased, ferrous hydroxide film which serves as barrier to oxygen diffusion is formed on the surface of mild steel and iron(II) hydroxide is converted to iron(III) hydroxide with increase in the time of exposure thus leading to an increase in pH of the media and decrease in corrosion rates.

Microstructural studies

Surface observations: Surface images presented in Figs. 4 and 5 show that all the mild steel samples immersed in 100 % organic acid and organic acid/10 % NaCl media suffered corrosion on the surface of the metal samples. Sample in Fig. 4b which was treated with formic acid did not form a stable oxide film on the enter surface when it was immersed in 100 % formic acid. This caused it to have a high corrosion rate comparing to the situation observed on same sample (b) in Fig. 5 after being contaminated with NaCl solution. Likewise, samples in Figs. 4(a) and 4(d) showed inadequate formation of protective oxide film which was the opposite of the observations made when NaCl solution was added [Fig. 5(a) and 5(d)]. For sample (d) represented in Fig. 5 suffered a moderate corrosion on the whole surface. Mild steel sample (c) treated with oxalic acid showed formation of powdery structure in 100 % acid solution which was not stable enough to mitigate corrosion. The addition of NaCl to oxalic acid made the medium less corrosive [Fig. 5(c)].

Fig. 4. Pictures of mild steels after corrosion in (a) 0.5 M acetic acid (b) 0.5 M formic acid (c) 0.5 M oxalic acid (d) 0.5 M citric acid (e) water

Fig. 5. Pictures of mild steel after corrosion in solutions containing (a) 10 % NaCl/90 % 0.5 M acetic acid (b) 10 % NaCl/90 % 0.5 M formic acid (c) 10 % NaCl/90 % 0.5 M citric acid (d) 10 % NaCl/90 % 0.5 M oxalic acid (e) 10 % NaCl/90 % water

Scanning electron microscopy and EDS analyses: SEM and EDS results provide corrosion engineers with useful information about corrosion mechanisms, process by which material of interest would corrode and properties of corrosion inhibitors. Micrographs taken with an aid of the SEM system are used to explain changes such as pits, cracks, fractures undergone by the corroded surface [1]. In this study, microstructure of the samples was examined under SEM to investigate the effects of medium on the structure of mild steel sample. The obvious observations made are the presence of porous, powdery microstructure and cracks along grain boundaries of corroded mild steels which were due to corrosion stresses. Additionally, more cracks are clearly noticeable in sample (e) which was treated in acetic acid and (f) in citric acid. These results confirm severity of acetic acid and citric acid medium as shown in Fig. 7.

Moreover, it was also revealed that passive oxide film (of whitish colour) appeared on SEM image (c) and (e). The conspicuous passive oxide film on corroded areas is due to the oxidation reaction and prevents further attacks at the surface of mild steel samples as observed (Figs. 2 and 5) after 10 days. It is the oxidation reaction that occurred first before it further protects the sample from further deterioration. On the other hand, passive films on images (Fig. 6e) and (Fig. 6f) were not effective at the same rate as that on aforementioned images. Finally, image (Fig. 6b) of the sample immersed in water does not corrode much and has less protective oxide film among others samples.

It was observed in Fig. 6 before contamination of organic acids with 10 % NaCl solution, SEM analysis of steel samples showed quite similar behavior after contamination of the media (Fig. 7). Morphological changes were observed on all the mild steel samples as it can be seen by comparing grain arrangement of mild steel sample before corrosion study (Fig. 6a) and all samples after study in Fig. 4. Whitish oxidative film was detected on the SEM of samples in Fig. 7(a), (b), (c) and (e) but they were not stable enough to significantly reduce corrosion rate. Furthermore, sample treated in acetic acid showed development of powdery microstructure. Some cracks were observed on the sample immersed in NaCl solution, but they were not as intense as that observed on the sample in this particular medium before contamination [Fig. 3(e)].

EDS analyses were also carried out to determine the elemental composition of corroded areas. Furthermore, the EDS elemental composition analyses in Fig. 8 revealed five main elements on all images which are Fe, Mn, Na, O, and Si and Cl as minor elements. The oxides of these elements formed were iron(II) oxide, manganese(II) oxide and trace of silicon oxide. Moreover, the presence of some amount of chlorine on image (c) shows that Cl^- ions is present and might have mixed with oxalic acid. In addition, the appearance of sodium indicates that sodium chloride added was present in the organic/chloride media.
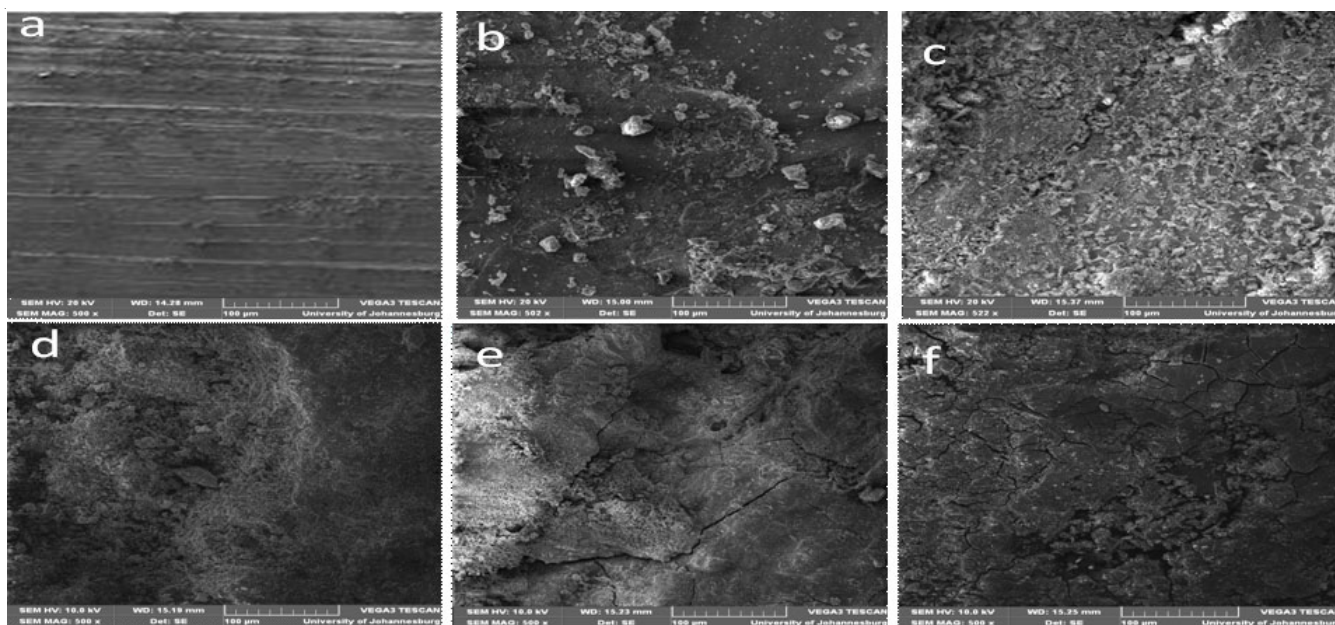

Fig. 6. Micrographs of mild steel (a) before corrosion test (b) 10 % NaCl/90 % water (c) 10 % NaCl/90 % 0.5 M formic acid (d) 10 % NaCl/90 % 0.5 M oxalic acid (e) 10 % NaCl/90 % 0.5 M acetic acid (f) 10 % NaCl/90 % 0.5 M citric acid
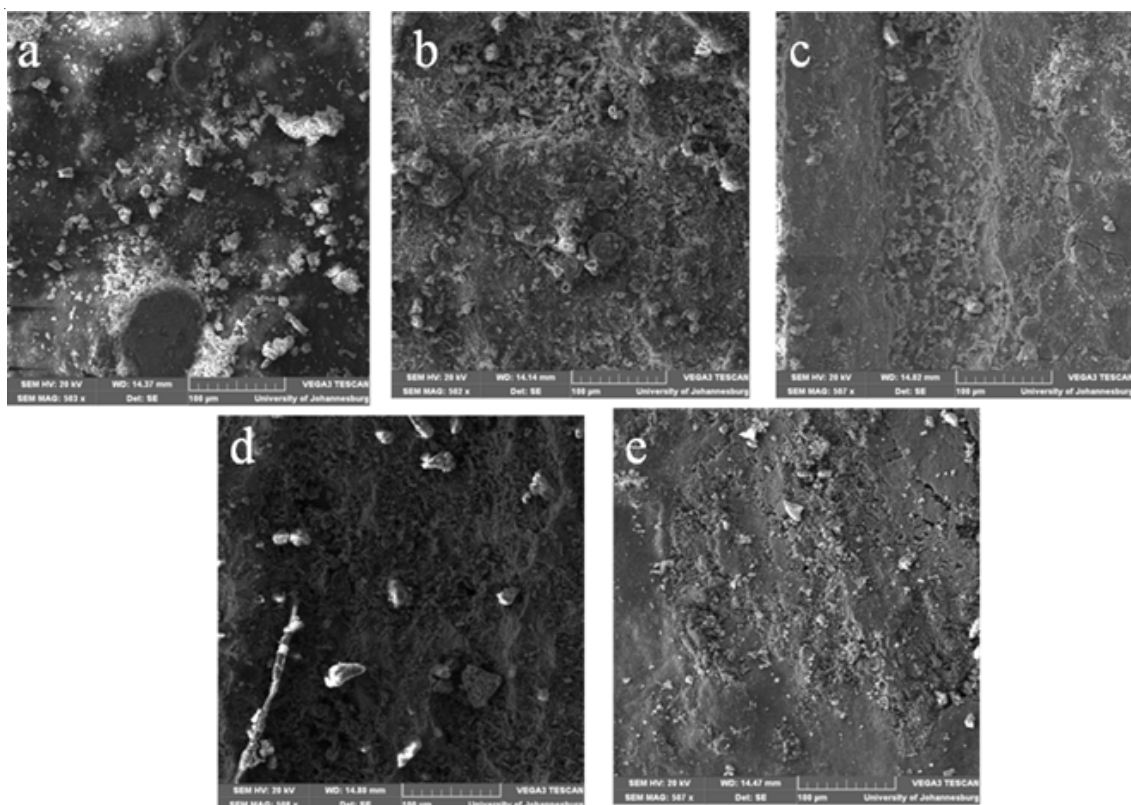
Fig. 7. Micrographs of mild steel after corrosion in solutions of (a) 0.5 M oxalic acid (b) formic acid (c) acetic acid (d) citric acid (e) 3.5 % NaCl
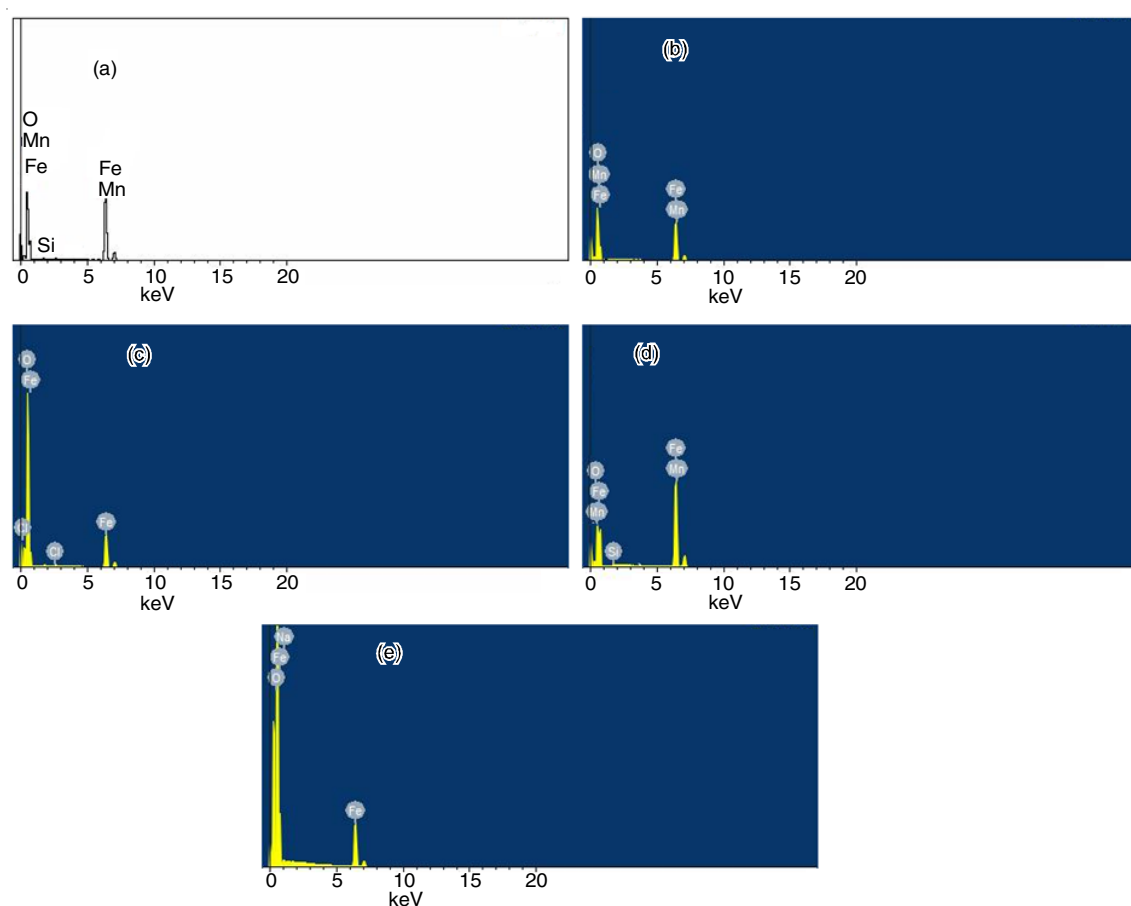

Fig. 8. Electron dispersive spectra of mild steel after corrosion in solutions containing 10 % NaCl and 90 % of (a) water (b) formic acid (c) oxalic acid (d) acetic acid (e) citric acid
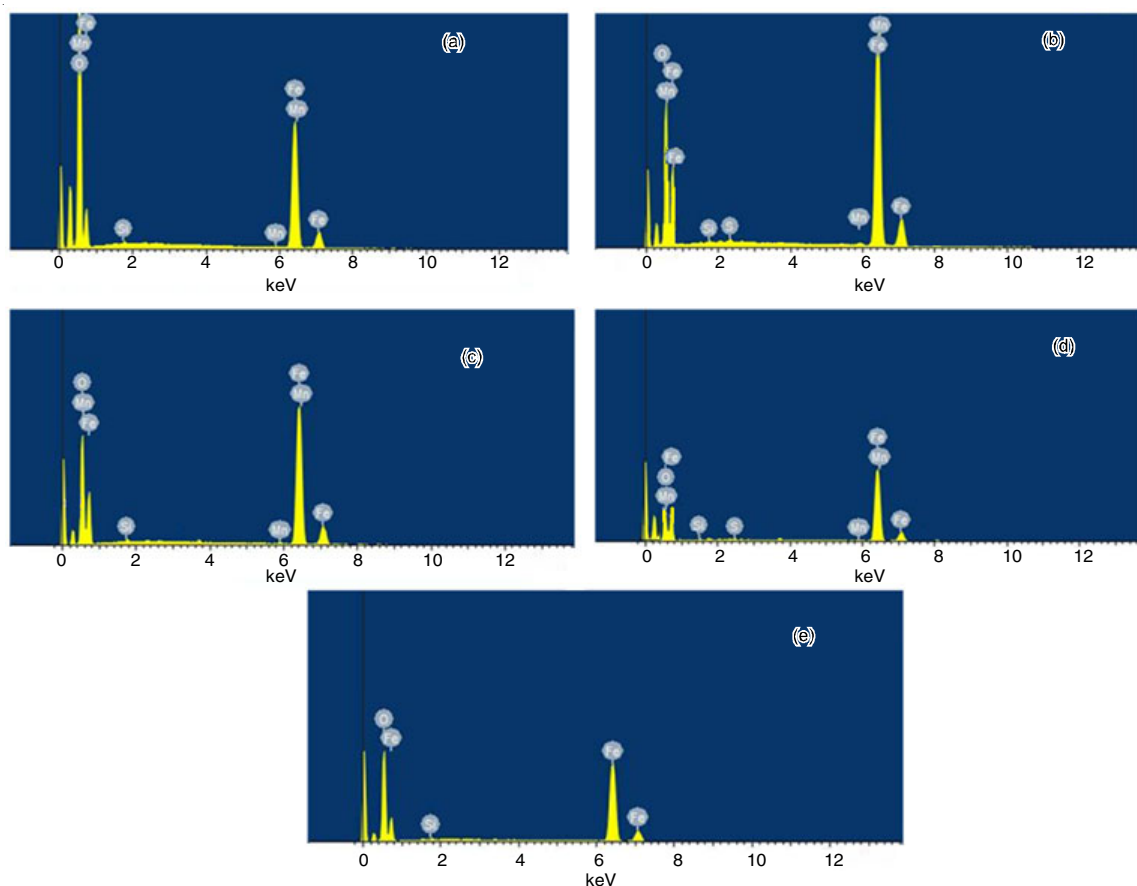
Fig. 9. Electron dispersive spectra of mild steel after corrosion in solutions of (a) 0.5 M oxalic acid (b) formic acid (c) acetic acid (d) citric acid (e) 3.5 % NaCl

Electron dispersive spectra elemental composition analysis after corrosion of mild steel immersed in 100 % organic acids (0.5 M) (Fig. 9) detected three major elements *i.e.*, Fe, Mn and O. Additionally, minor elements such as Si in all spectra and S (in spectra b and d) were also found. These imply that the oxide film layers formed are those of iron, manganese and silicon. In the EDS spectra analysis (Fig. 9), no chloride or sodium ions were detected which may be due to the fact that no sodium chloride was added in the organic acids.

Conclusion

The corrosion behaviour of mild steel in organic acids-sodium chloride mixtures of various concentrations and its corrosion rate were studied by weight loss measurement and microstructural analysis. The results obtained showed that the rate of corrosion was lower for mild steel immersed in organic acids containing 3.5 % NaCl than when they were immersed in 100 % organic acids. The corrosion behaviour of the mild steel in the organic acid solutions containing 3.5 % NaCl suggests the presence of free Cl⁻ ions in the solution which was confirmed by the EDS and pH results. The major oxides on mild steel surface were found to be those of Fe, Mn and Si.

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