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INNOVATIVE METHOD FOR REDUCTION OF MILD STEEL CORROSION IN WATER BY ACTIVATED CARBON FROM OCIMUM TENUIFLORUM

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Abstract. The activated carbon prepared from the bark of *Ocimum Tenuiflorum* reduces the amount of dissolved oxygen (DO) present in distilled water, which in turn reduces the rate of corrosion. The effects of DO, temperature and pH on the rate of mild steel corrosion were discussed. The inhibition efficiency of corrosion on mild steel was estimated by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The inhibition efficiency increases with increase in temperature, pH and the mass of activated carbon. The adsorption of activated carbon follows Langmuir adsorption isotherm. The surface morphology of activated carbon was analysed by FT-IR and SEM.

Keywords: activated carbon, mild steel, dissolved oxygen, *Ocimum Tenuiflorum*, SEM, FT-IR.

1. Introduction

Corrosion is the main problem for industrial water supply and circulation system. Protection against corrosion was carried out by adding inhibitors in acidic medium. These inhibitors have electron-rich elements such as nitrogen, oxygen, sulphur, phosphorous and aromatic rings which cause adsorption on the metal surface. They are not eco-friendly, expensive and non-renewable sources which influence metal corrosion of the equipment. Nowadays combating metal corrosion with non polluting inhibitors was developed. Plant extracts are organic in nature; they contain tannins, alkaloids and amino acids and can be extracted by simple procedure with low cost [1].

Mild steel is widely used as a constructional material in industries due to its mechanical properties, high susceptibility and low cost. Dissolution of mild steel takes place under acidic condition due to desalting, acidifying and pickling [2]. They cause corrosion and steel can be protected in different forms like surface treatment, coatings, sealants, and by adding inhibitors. It can be also protected by reducing the amount of dissolved oxygen (DO) present in industrial water supply with enhances corrosion [15].

The activated carbon is the most promising adsorbent due to its unique structure and characteristics such as surface area, specific functional group and high adsorption capacity. It absorbs DO, organic compounds, heavy metals and other physical properties like colour, odour and taste in the treatment of waste water, boiler corrosion and solvent recovery. Activated carbon is commercially available and it is widely used in different fields like waste water treatment, electronic industry and biologically medical treatment [14]. The main problem in industries is the amount of DO present in water which enhances the rate of corrosion. This can be minimised by adding the activated carbon [11].

There are two main types of carbon activation procedure – physical and chemical one. In the physical activation process – pyrolysis of the compound is done in the presence of inert gases like nitrogen or carbon dioxide. In chemical activation process activation is done by either using acid as a dehydrating agent or by using compounds of Zn, Ni or Cd. The acid used may be sulphuric acid, phosphoric acid, *etc*. Chemical method has its own advantage over the physical methods, activated carbon prepared by the physical methods has a functional group which can interact with the adsorbate and the surface area of the activated carbon is also superior to that of the activated carbon done by pyrolysis. The application of a gaseous stream such as air, nitrogen or argon is carried out which generates a better development of materials porosity. In the present study the activated carbon from the stem of Tulsi (*Ocimum Tenuiflorum*) was prepared by dehydrating with sulphuric acid [5, 6].

Literature survey has shown that no work has been reported on the use of activated carbon for inhibition of corrosion. The aim of our study is to use the activated carbon from the stem of *Ocimum Tenuiflorum* for the removal of DO from distilled water and reduction of corrosion. Chemically activated carbon was prepared from the stem of *Ocimum Tenuiflorum* and the batch process is carried out for the removal of DO. EIS, polarization and weight loss methods are used for the study of corrosion inhibition.

2. Experimental

2.1. Preparation of Activated Carbon

25 g of sieved samples of Tulsi (*Ocimum Tenuiflorum*) were soaked in 50 ml of sulphuric acid (the ratio being 1:2) for 24 h under a constant stirring in a fume hood. The liquid portion was then decanted carefully and the solid portion is then taken to a ceramic hood and heated to 433 K in an air oven for 24 h. The temperature of the oven is increased by 5 K for every 15 min. The mass is then thoroughly washed with water until the filtrate pH coincided with distilled water pH used. Washed activated carbon is then dried at 378 K for 1 h. The activated carbon is then stored in a cool dry place (desiccator) for further analysis.

2.2. Specimen Preparation

The chemical composition of the working electrode, a mild steel electrode was (%): Fe 99.75; Mn 0.01; Cu 0.01; Si 0.02; P 0.02 and C 0.18. The specimens of the dimension 5 and 1.5 cm width are used. It was mechanically ground with1/0, 2/0, 3/0 and 4/0 grade emery papers, washed in acetone, double distilled water and kept in the oven for immediate use.

2.3. Batch Studies

Batch studies were performed in a closed plastic container (500 ml capacity) with 100, 200 and 300 ml of distilled water. Different adsorbent masses were also used (0.1, 0.2 and 0.3 g). Constant shaking of the solution was done using an orbital shaker at the rate of 150 rpm. The constant temperature throughout the experiment was maintained at 318 K. The samples are shaken for 1 h and then the supernatant liquid is filtered as discussed earlier. pH of the solution was also adjusted with 1 N HCl and 1 N NaOH. A blank was also carried out by shaking distilled water without activated carbon.

2.4. Weight Loss Method

The weighed specimens were suspended by means of glass hooks in 100 ml beakers containing 100, 200 and 300 ml of double distilled water for 5 h in the absence and presence of activated carbon. After the immersion the specimens were taken out, washed in running water dried and weighed. From the weight loss measurements, inhibition efficiency (*IE*) and corrosion rate were determined [3]. The inhibition efficiency was calculated in terms of percentage (Eq. 1) and the degree of surface coverage θ gives the information about adsorption of activated carbon using Langmuir adsorption isotherm.

$$IE \text{ or } h = \frac{\Delta W_u - \Delta W_i}{\Delta W_u} \cdot 100\% \quad (1)$$

where ΔW_u and ΔW_i – weight loss of the metal in distilled water without and with activated carbon, respectively.

2.5. Electrochemical Measurement

A three electrode system consisting of mild steel as a working electrode, a platinum counter electrode and saturated calomel electrode as reference electrode was used for electrochemical measurements. Experiments were carried out under atmospheric condition. In electrochemical measurements, a stabilization period of 30 min was allowed, which is enough to attain stable E_{corr} value [7].

2.6. Potentiodynamic Polarization

Polarization studies were carried out in electrochemical workstation Model 600 D/E series. From these study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and tafel slopes (anodic b_a and cathodic b_c) were calculated. The inhibition efficiency was calculated by Eq. (2):

$$IE \text{ or } h = \left(1 - \frac{I'_{corr}}{I_{corr}}\right) \cdot 100\% \quad (2)$$

where I'_{corr} and I_{corr} are the corrosion current density of mild steel in the absence and presence of activated carbon, respectively.

2.7. AC Impedance Measurement

AC impedance was carried out in electrochemical workstation Model 600 D/E series. AC frequency was varied from 100 MHz to 100 KHz. The real part (*Z*') and imaginary part (*Z*'') of the cell impedance were measured in Ohms for frequencies. The charge transfer resistance (*Rct*) and double layer capacitance (*Cdl*) values were calculated using the relationship (3):

$$Cdl = \frac{1}{2 \cdot 3.14 \cdot f_{\max} \cdot Rct} \quad (3)$$

2.8. Temperature, pH and Dissolved Oxygen

Two different temperatures and pH were maintained. Temperature was maintained with a thermostat at 333 and 298 K (room temperature). pH of the water sample was maintained at 3 and 12. The DO present in water was measured by a titrimetric method (Winkler method).

3. Results and Discussion

3.1. Surface Analysis

The activated carbon was characterized by SEM and FT-IR (Lambda FT-IR-7600). The Fourier Transform Infrared spectroscopy picture of activated carbon is shown in Fig. 1. In FT-IR a sharp peak is obtained at a wavelength of 1588cm^{-1}. This indicates that there is an asymmetric CO and NO stretching. The scanning electron microscope (SEM) picture of the activated carbon at 500 and 50 μm is shown in Fig. 2a and 2b, respectively. The SEM images clearly differentiate the effect of the activated carbon size.

3.2. Weight Loss Method

3.2.1. Weight loss method at room temperature

At room temperature the amount of DO present in water decreases with increase in the mass of activated carbon. In Table 1 inhibition efficiency, DO and surface coverage with various mass of *Ocimum Tenuiflorum* in distilled water at room temperature are shown. It implies that the inhibition efficiency increases with increase in the mass of the activated carbon used in the batch studies. The maximum inhibition efficiency of *Ocimum Tenuiflorum* was found to be 80.97 % in 100 ml of distilled water for 300 mg of *Ocimum Tenuiflorum* at room temperature [4]. From this it is clear that there is decrease in DO.

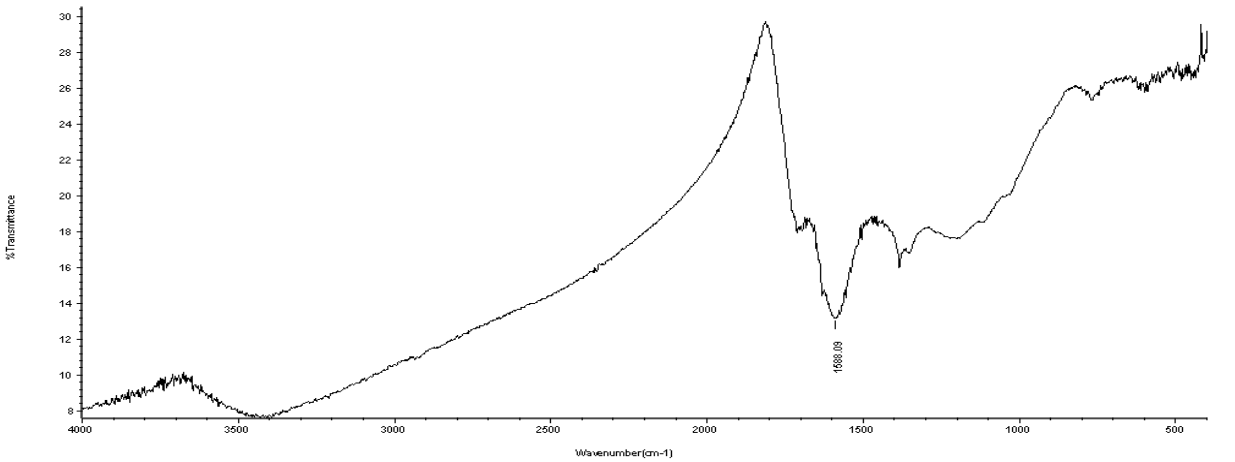
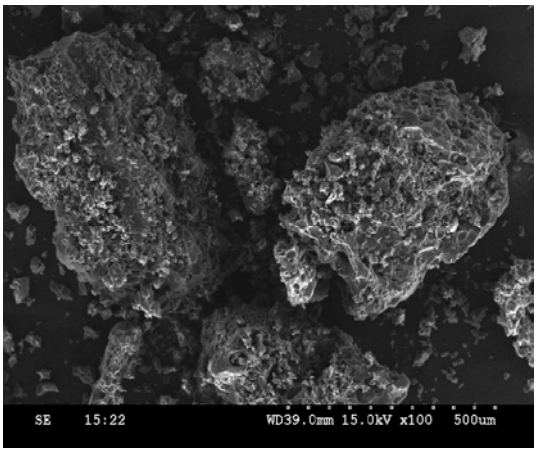
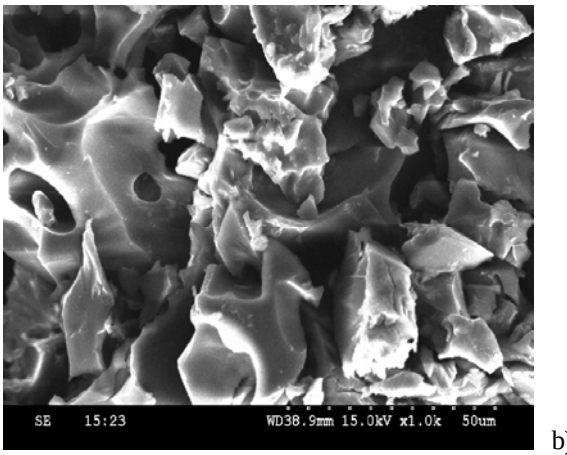


Fig. 1. FT-IR spectrum for activated carbon



a)



b)

Fig. 2. SEM images of activated carbon: 500 μm mesh (a) and 50 μm mesh (b)

3.2.2. Weight loss method at 333 K

At 333 K the amount of DO removal is less compared to room temperature. When the temperature increases the dissolution of oxygen is less. In Table 2 inhibition efficiency, surface coverage and DO for mild steel with various mass of *Ocimum Tenuiflorum* in distilled water at 333 K are shown. The maximum inhibition efficiency of *Ocimum Tenuiflorum* was found to be 82.06 %, which implies that when temperature increases the corrosion rate and the amount of DO present in distilled water decreases.

3.2.3. Weight loss method at pH = 3

The removal of DO present in water is less when pH = 3. But there is a change in inhibition efficiency and surface coverage for various mass of *Ocimum Tenuiflorum* present in distilled water. As the mass of activated carbon increases the inhibition efficiency also increases. The maximum inhibition efficiency of *Ocimum Tenuiflorum* was found to be 72.82 % in 100 ml of distilled water for 300 mg of *Ocimum Tenuiflorum* at pH = 3. In Table 3 inhibition efficiency, DO and surface coverage of mild steel with various mass of *Ocimum Tenuiflorum* in distilled water at pH= 3 are shown.

3.2.4. Weight loss method at pH = 12

When pH increases the removal of DO is greater. It indicates that the activated carbon is more efficient in basic medium rather than acidic medium. The inhibition efficiency increases with respect to the mass of activated carbon. The maximum inhibition efficiency of *Ocimum Tenuiflorum* was found to be 83.69 % in 100 ml of distilled water for 300 mg of *Ocimum Tenuiflorum* at pH = 12. In Table 4 inhibition efficiency, DO and surface coverage of mild steel with various concentration of Ocimum Tenuiflorum in distilled water at pH = 12 are shown.

3.3. Langmuir Adsorption Isotherm

Langmuir adsorption isotherm is used to study the surface area of the activated carbon available for the adsorption on mild steel which was determined from the isotherm data. The inhibition mechanism of corrosion is known by the adsorption of activated carbon. A graph is plotted between $\log[\theta/(1-\theta)]$ *vs*. $\log C$; it gives information about the adsorption of activated carbon *Ocimum Tenuiflorum* in distilled water. The Langmuir adsorption isotherm was calculated by using Eq. (4):

$$\log[\theta/(1-\theta)] = \log A + \log C - [Q/2.303RT] \quad (4)$$

A straight line is obtained by plotting $\log[\theta/(1-\theta)]$ *vs.* $\log C$,where A is a temperature independent constant, C is the bulk concentration of the inhibitor (percentage) and Q is the heat evolved during adsorption. The plots are shown in Fig. 3 with different mass of activated carbon by varying the temperature and pH. It is observed that as the mass of activated carbon increases the value of $\log[\theta/(1-\theta)]$ also increases which indicates that the rate of corrosion is decreased [8].

Table 1

Weight loss ΔW and inhibition efficiency η for mild steel in distilled water with activated carbon at room temperature

Mass of activated carbon, mg	100 ml of distilled water				200 ml of distilled water				300 ml of distilled water			
	ΔW, mg	DO	θ	IE (η), %	ΔW, mg	DO	θ	IE (η), %	ΔW, mg	DO	θ	IE (η), %
Blank	184	5.0	–	–	152	5.9	–	–	124	6.3	–	–
100	44	4.8	0.7608	76.08	49	5.2	0.6776	67.76	54	5.6	0.5645	56.45
200	41	3.9	0.7771	77.71	46	4.7	0.6973	69.73	53	5.4	0.5725	57.25
300	35	3.4	0.8097	80.97	37	3.6	0.7565	75.65	51	4.9	0.5887	58.87

Table 2

Weight loss ΔW and inhibition efficiency η for mild steel in distilled water with activated carbon at 333 K

Mass of activated carbon, mg	100 ml of distilled water				200 ml of distilled water				300 ml of distilled water			
	ΔW, mg	DO	θ	IE (η), %	ΔW, mg	DO	θ	IE (η), %	ΔW, mg	DO	θ	IE (η), %
Blank	184	3.8	–	–	152	4.2	–	–	124	5.3	–	-
100	40	3.1	0.7826	78.26	49	3.7	0.6776	67.76	53	5.0	0.5725	57.25
200	38	2.8	0.7934	79.34	43	3.4	0.7171	71.71	45	4.6	0.6370	63.70
300	33	2.6	0.8206	82.06	32	3.2	0.7894	78.94	29	4.3	0.7661	76.61

Table 3

Weight loss ΔW and inhibition efficiency η for mild steel in distilled water with activated carbon at pH = 3

Mass of activated carbon, mg	100 ml of distilled water				200 ml of distilled water				300 ml of distilled water			
	ΔW, mg	DO	θ	*IE* (η), %	ΔW, mg	DO	θ	*IE* (η), %	ΔW, mg	DO	θ	*IE* (η), %
Blank	184	3.4	–	–	152	4.4	–	–	124	5.1	–	-
100	58	3.0	0.6847	68.47	60	4.1	0.6052	60.52	61	4.7	0.5080	50.80
200	54	2.8	0.7065	70.65	59	3.8	0.6118	61.18	53	4.4	0.5725	57.25
300	50	2.5	0.7282	72.82	56	3.3	0.6315	63.15	51	3.7	0.5887	58.87

Table 4

Weight loss ΔW and inhibition efficiency η for mild steel in distilled water with activated carbon at pH = 12

Mass of activated carbon, mg	100 ml of distilled water				200 ml of distilled water				300 ml of distilled water			
	ΔW, mg	DO	θ	*IE* (η), %	ΔW, mg	DO	θ	*IE* (η), %	ΔW, mg	DO	θ	*IE* (η), %
Blank	184	5.9	–	–	152	6.5	–	–	124	6.8	–	–
100	39	4.5	0.7880	78.80	45	6.2	0.7039	70.39	57	6.4	0.5403	54.03
200	36	4.0	0.8043	80.43	42	5.8	0.7236	72.36	55	6.0	0.5564	55.64
300	30	2.9	0.8369	83.69	34	5.6	0.7763	77.63	52	5.5	0.5806	58.06

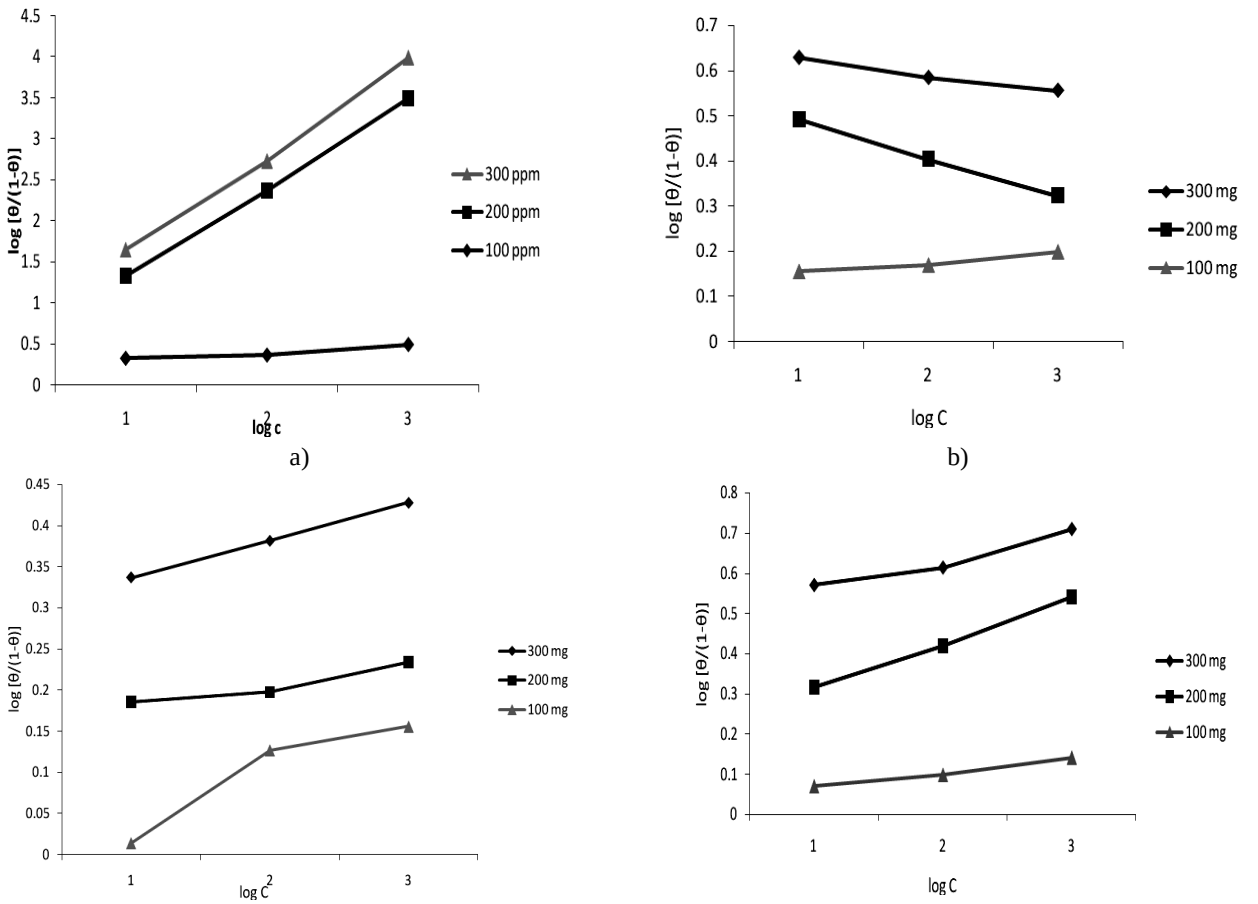


Fig. 3. Langmuir adsorption isotherm for mild steel in distilled water with *Ocimum Tenuiflorum*: at room temperature (a); at 333 K (b); at pH = 3 (c) and pH = 12 (d)

Table 5

Corrosion parameters of mild steel in distilled water with *Ocimum Tenuiflorum* by potentiodynamic polarisation method at 333 K

Mass of activated carbon, mg	E_{corr}, mV	Tafel slopes, mV/dec		i_{corr}, μA/cm^2	Inhibition efficiency, %
		ba	Bc		
Blank	-242	103.0	89.2	1349.20	–
100	-338	146.3	72.3	301.60	68.10
200	-349	154.1	59.4	286.10	75.45
300	-386	188.2	48.6	206.22	81.89

Table 6

AC impedance parameters for corrosion of mild steel in distilled water with *Ocimum Tenuiflorum* at 333 K

Mass of activated carbon, mg	*Rct*, Ohm·cm^2	*Cdl*, μF/cm^2	Inhibition efficiency, %
Blank	73.16	56.12	–
100	75.44	49.52	82.51
200	83.78	40.91	85.18
300	92.24	33.74	86.11

3.4. Potentiodynamic Polarisation Studies

The amount of DO in water decreases when the mass of activated carbon increases. Polarisation curves of mild steel in distilled water with and without activated carbon at different temperatures and pH are shown in Figs. 4a, 5a, 6a and 7a. Corrosion parameters such as corrosion potential, anodic tafel slope and cathodic tafel slope, corrosion current and inhibition efficiency were calculated. It implies that, when activated carbon is added to water, the anodic polarisation shifts to more positive and the cathodic one – to more negative values. It indicates that the activated carbon acts as a mixed type inhibitor because the activated carbon reduces both anodic and cathodic values [13].

In Table 5 it can be seen that as the mass of activated carbon increases the I_{corr} values decrease with the shift of E_{corr} to more negative potential. The decrease in DO content of activated carbon suppresses the cathodic reaction predominantly than the anodic process. The maximum inhibition efficiency of *Ocimum Tenuiflorum* was found to be 81.89 % in 300 mg of *Ocimum Tenuiflorum* at 333 K. The inhibition efficiency of *Ocimum Tenuiflorum* obtained by the polarisation method is better compared with the inhibition efficiency obtained by the weight loss method [9].

3.5. AC Impedance Study

The open circuit potential for mild steel in distilled water with and without activated carbon at different temperatures and pH is shown in Figs. 4b, 5b, 6b and 6b. In Table 6 impedance parameters derived from Nyquist plots are shown. It is observed from Table 6 that the value of charge transfer resistance (*Rct*) increases with increase in the mass of activated carbon. But the value of double layer capacitance (*Cdl*) decreases with increase in the mass of activated carbon. The inhibition efficiency is increased with increase in the mass of activated carbon [12].

The maximum inhibition efficiency of *Ocimum Tenuiflorum* was found to be 86.11 % in 300 mg of *Ocimum Tenuiflorum* at 333 K. The impedance diagram for solutions has almost a semicircular appearance; it indicates that the corrosion of mild steel is mainly controlled by DO which decreases with increase in the mass of activated carbon. The inhibition efficiency obtained by AC impedance method is in good agreement with the inhibition efficiency obtained by polarisation and weight loss methods [10].

4. Conclusions

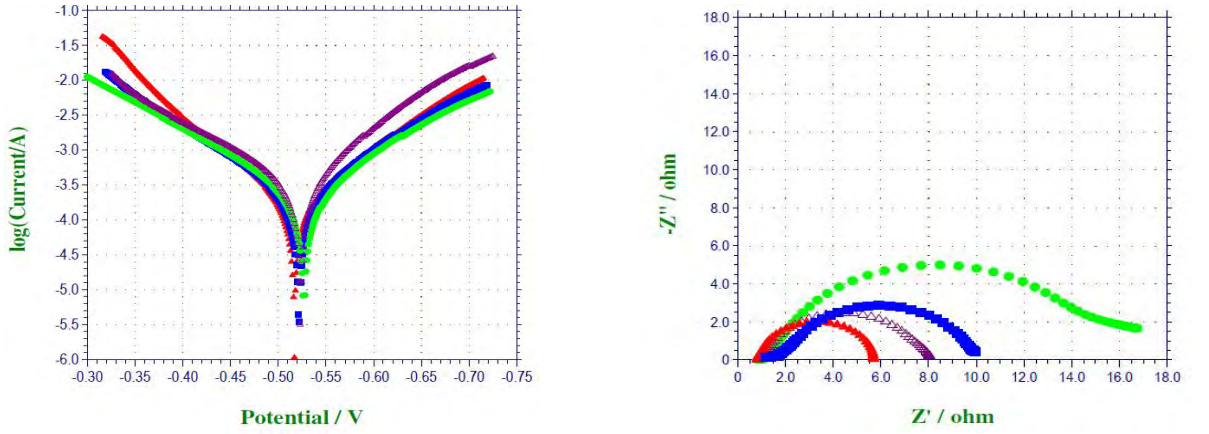
The activated carbon (*Ocimum Tenuiflorum*) acts as an adsorbent which reduces the rate of corrosion. The inhibition efficiency at room temperature was 80.97 % and for 333 K the efficiency was found to be 82.06 % in 100 ml of distilled water for 300 mg of *Ocimum Tenuiflorum*. It indicates that when the temperature increases the inhibition efficiency also increases due to decrease in dissolved oxygen.

The maximum inhibition efficiency of *Ocimum Tenuiflorum* reported by the weight loss method was 72.82 % at pH = 3. Under basic conditions the inhibition efficiency was 83.69 % in 100 ml of distilled water for 300 mg of *Ocimum Tenuiflorum* at pH = 12. It indicates that activated carbon is more efficient in basic medium rather than in acidic one.

The maximum inhibition efficiency obtained by polarisation method was found to be 81.89 % in 300 mg of *Ocimum Tenuiflorum*. The activated carbon acts as a mixed type inhibitor because it reduces both cathodic and anodic values.

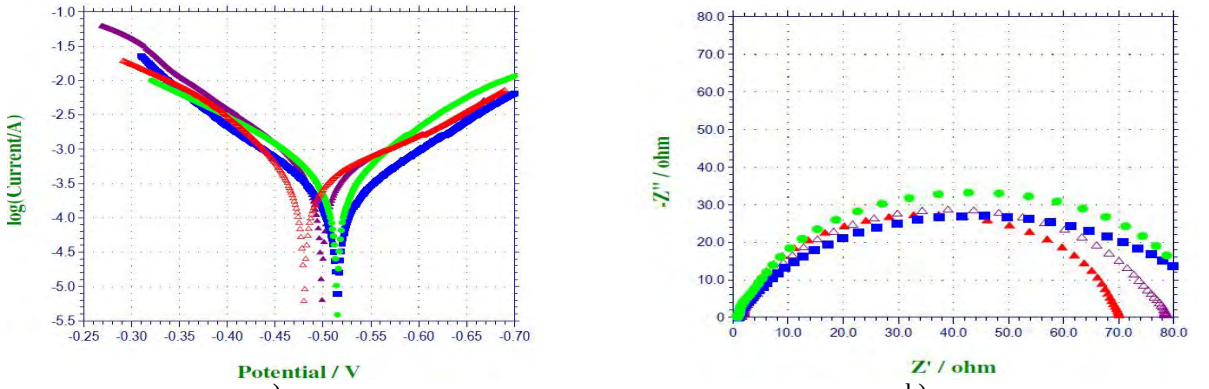
The maximum inhibition efficiency obtained by AC impedance method was found to be 86.11 % in 300 mg of *Ocimum Tenuiflorum*.

As the mass of activated carbon increases the rate of corrosion decreases and it follows Langmuir adsorption isotherm. If we compare all methods, the inhibition efficiency obtained by AC impedance study and potentiodynamic polarisation method was found to be better compared to the conventional weight loss method.



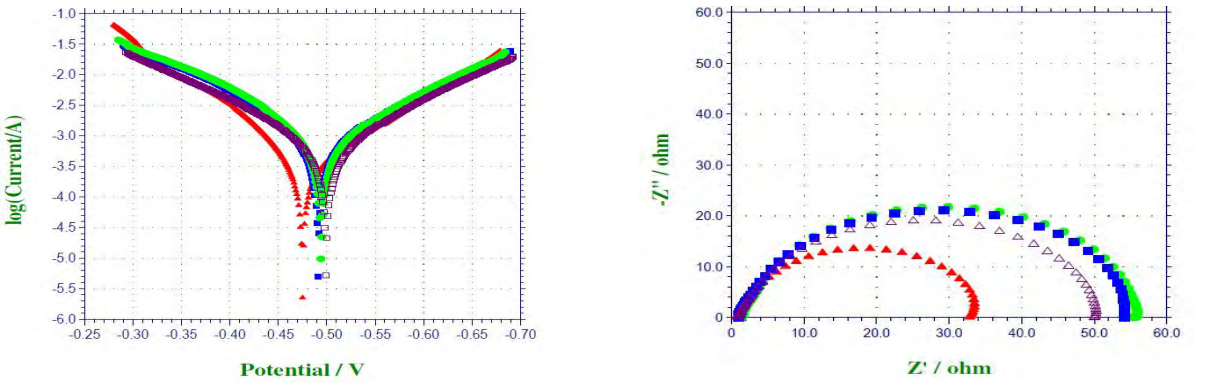
a) b)

Fig. 4. Potentiodynamic polarisation curves (a) and AC impedance curves (b) of *Ocimum Tenuiflorum* (OT) for mild steel in distilled water at 333 K: blank (▲); OT 100 mg (△); OT 200 mg (■) and OT 300 mg (●)



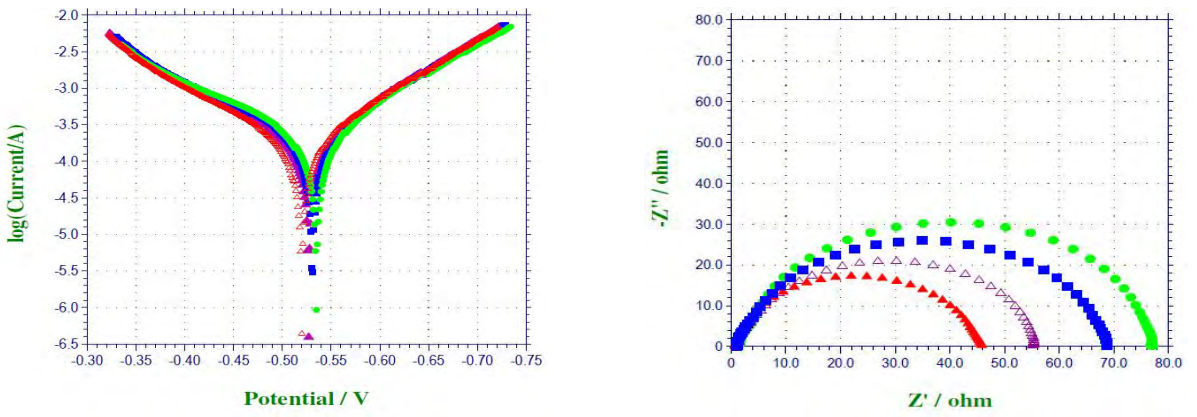
a) b)

Fig. 5. Potentiodynamic polarisation curves (a) and AC impedance curves (b) of *Ocimum Tenuiflorum* (OT) for mild steel in distilled water at room temperature: blank (▲); OT 100 mg (△); OT 200 mg (■) and OT 300 mg (●)



a) b)

Fig. 6. Potentiodynamic polarisation curves (a) and AC impedance curves (b) of *Ocimum Tenuiflorum* (OT) for mild steel in distilled water at pH = 3: blank (▲); OT 100 mg (△); OT 200 mg (■) and OT 300 mg (●)



a) b)

Fig. 7. Potentiodynamic polarisation curves (a) and AC impedance curves (b) of *Ocimum Tenuiflorum* (OT) for mild steel in distilled water at pH = 12: blank (▲); OT 100 mg (△); OT 200 mg (■) and OT 300 mg (●)

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ІННОВАЦІЙНИЙ МЕТОД ЗНИЖЕННЯ КОРОЗІЇ М'ЯКОЇ СТАЛІ У ВОДІ АКТИВОВАНИМ ВУГІЛЛЯМ З *OCIMUM TENUIFLORUM*

Анотація. *Показано, що активоване вугілля, яке отримують з кори туласі (Ocimum Tenuiflorum), зменшує кількість розчиненого кисню, присутнього в дистильованої води, і, як наслідок, швидкість корозії. Досліджено вплив розчиненого кисню, температури і pH на швидкість корозії м'якої сталі. За допомогою вагового, електрохімічного та імпедансного методів визначено інгібуючий ефект активованого вугілля. Показано, що ефективність інгібітування зростає з підвищенням температури, pH і маси активованого вугілля. Адсорбцію активованого вугілля описано ізотермою адсорбції Ленгмюра. Морфологія поверхні активованого вугілля визначена за допомогою Фур'є-спектроскопії та скануючої електронної мікроскопії.*

Ключові слова: *активоване вугілля, м'яка сталь, розчинений кисень, Ocimum Tenuiflorum, СЕМ, Фур'є-спектроскопія.*