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A novel and innovative method for reduction of mild steel corrosion in water by activated carbon from prosopis juliflora

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ABSTRACT

The activated carbon (prosopis juliflora) is used to reduce the amount of dissolved oxygen present in water. This prevents the rate of corrosion in industrial water supply. Experiments were carried out by changing the temperature and pH. The amount of dissolved oxygen removal is high as the mass of activated carbon increases. The inhibition efficiency of mild steel is calculated by weight loss, polarization and impedance techniques in distilled water. The inhibition efficiency at room temperature was 72.95% and for 60^0C the efficiency was 86.88% in 100ml distilled water for 300 mg of prosopis juliflora. When the pH increases the activated carbon becomes more effective. The inhibition efficiency reported in weight loss method was 74.59% in 100 ml distilled water for 300 mg of prosopis juliflora at pH=3. In basic conditions inhibition efficiency was 87.70% in 100 ml distilled water for 300 mg of prosopis juliflora at pH=12. The inhibition efficiency increases with increase in the mass of activated carbon. The surface morphology was carried out by FT-IR and SEM techniques. The adsorption of activated carbon follows Langmuir adsorption isotherm.

KEYWORDS

Activated carbon;
Mild steel;
Dissolved oxygen;
Prosopis Juliflora.

INTRODUCTION

Mild steel is used as a constructional material in industries, in fabrication reaction vessels, storage tanks, petroleum refineries, petro chemical process devices, boiler drums, flow lines, transmission pipeline and heat exchangers[10]. The usage of mild steel is more because of mechanical properties, high susceptibility and low cost. Acidic solution is widely used in industry for pickling, desaling, cleaning, oil well acidifying etc. Because of strong corrositivity in acidic solution, mild steel undergoes dissolution in acidic medium. The corrosion of metals is scientific problem in the world. To prevent corrosion, certain organic compounds as inhibitors are introduced in corrodent system[5]. Application of corrosion inhibitor is most economical and practical method to mitigate electrochemical corrosion. Corrosion inhibitors usually have electron – rich elements such as Nitrogen, Oxygen, Sulphur, Phosphorous and aromatic rings.

The activated carbon is an excellent adsorbent due to its high surface area and porosity[4,9]. The activated carbon which is used must be non-toxic and eco-friendly[6]. It absorbs colour, odour, taste, dissolved

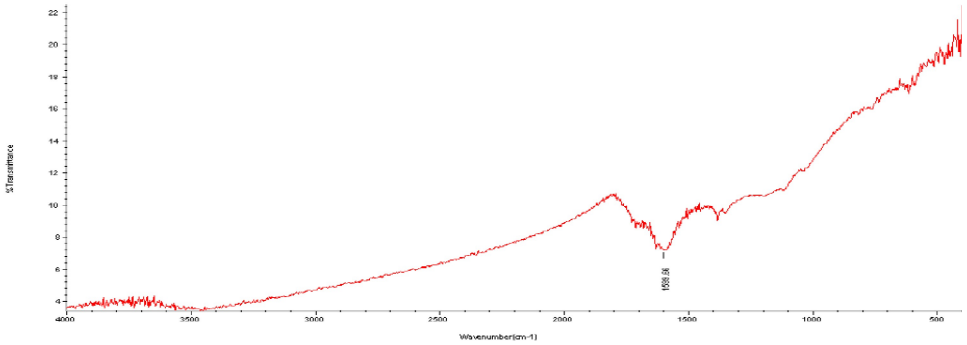

Figure 1 : FT-IR spectrum for Activated carbon

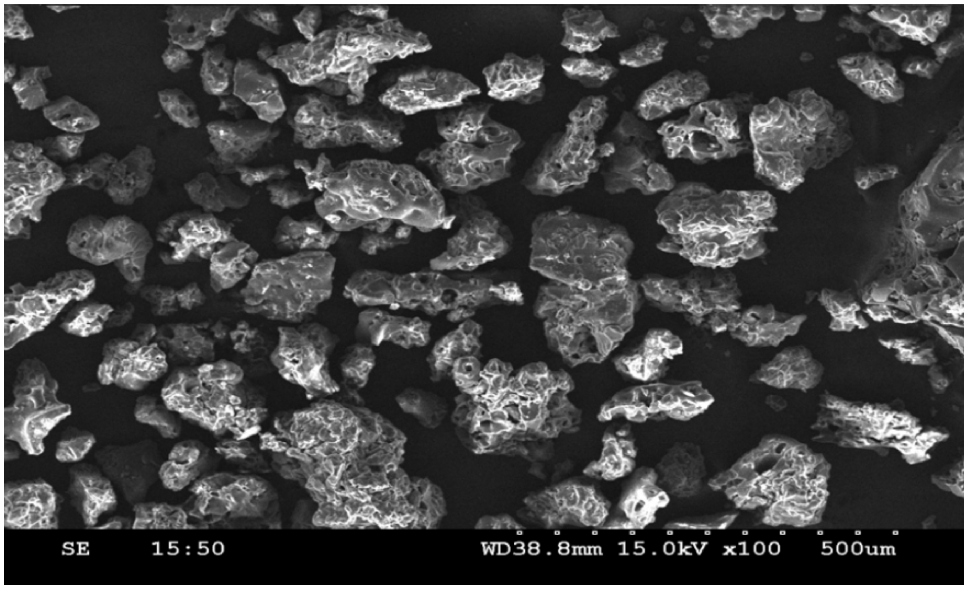

Figure 2a : SEM micrograph of Activated carbon 500 um mesh

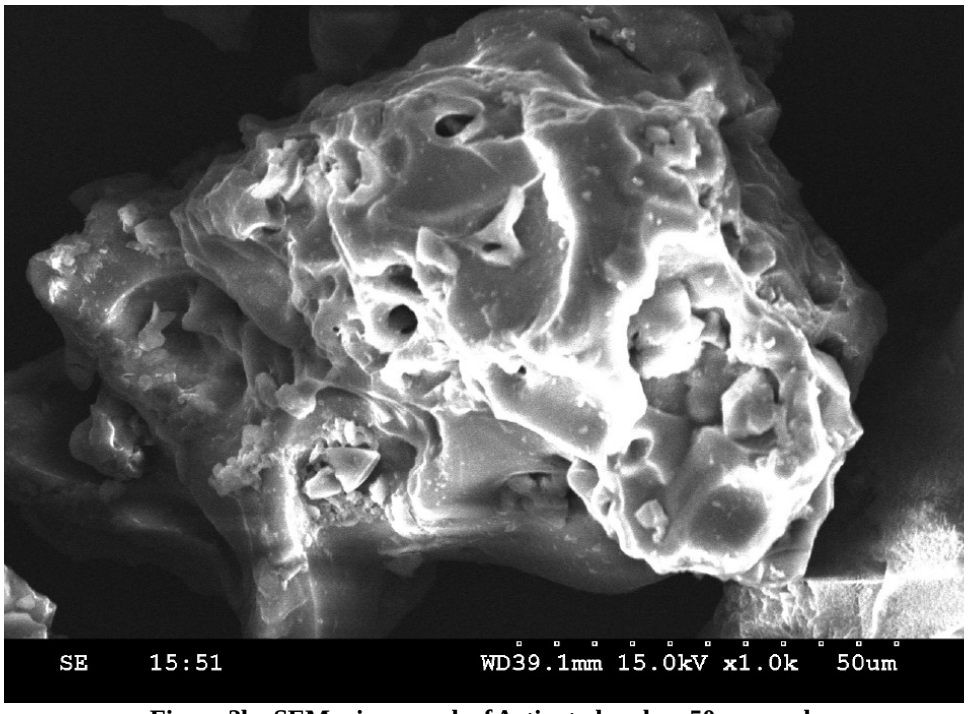

Figure 2b : SEM micrograph of Activated carbon 50 um mesh

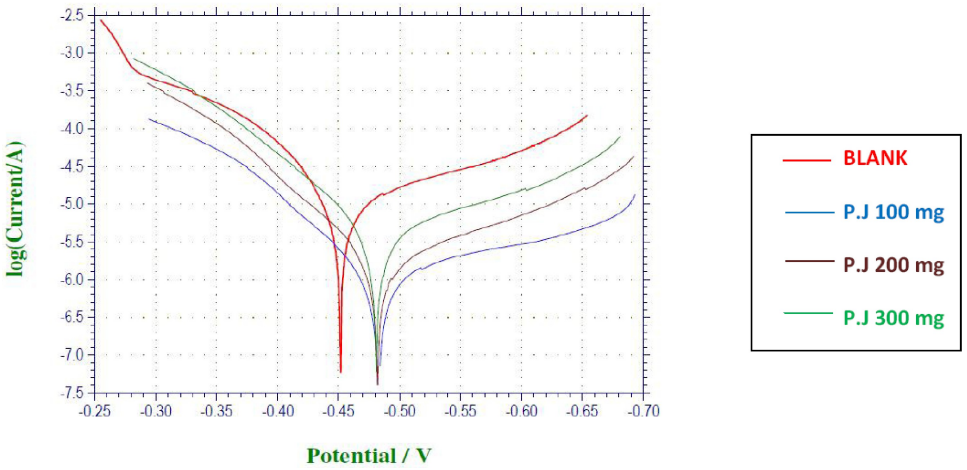

Figure 3a : Potentiodynamic polarisation curves of Prosopis Juliflora for mild steel in distilled water at 60^{0}C

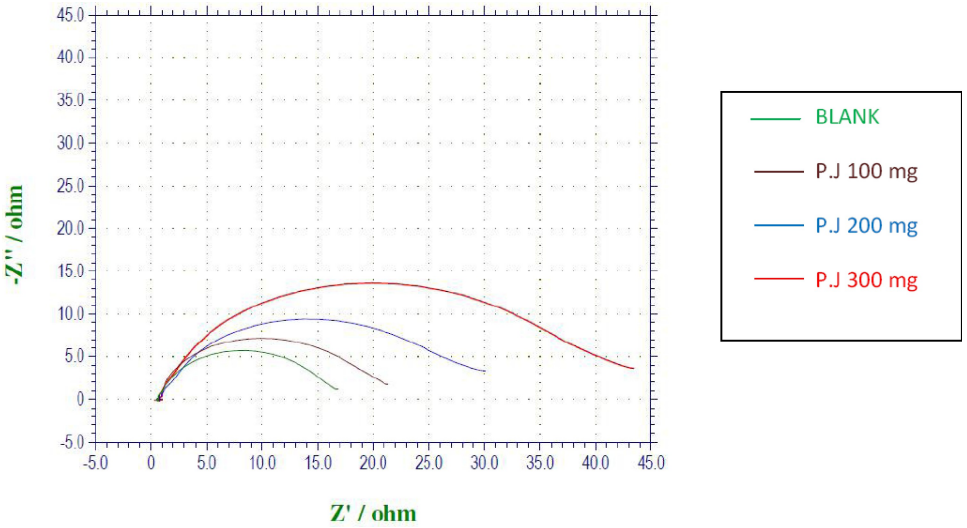

Figure 3b : AC impedance curves of Prosopis Juliflora for mild steel in distilled water at 60^{0}C

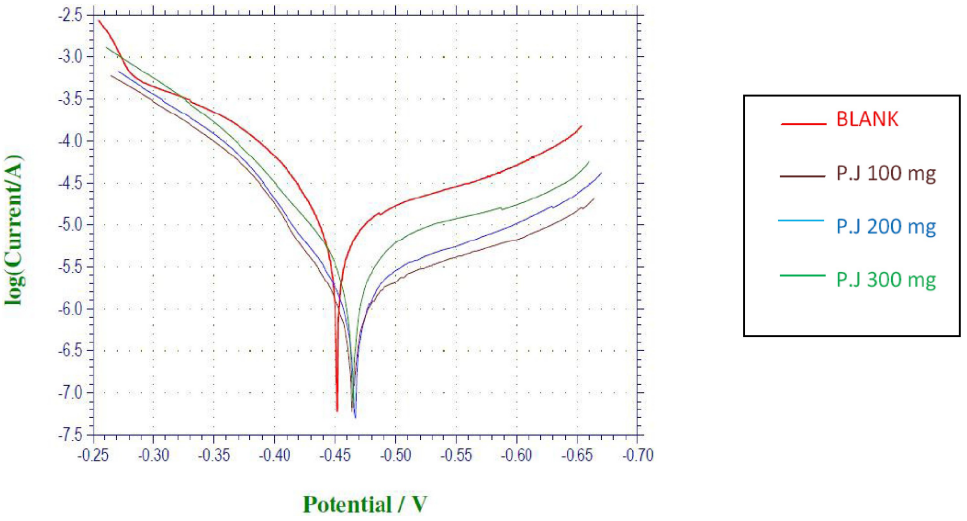

Figure 4a : Potentiodynamic polarisation curves of Prosopis Juliflora for mild steel in distilled water at room temperature

oxygen, organic compounds, heavy metals, herbicides and dyes among other toxic and hazardous compounds in the treatment of waste water, heavy metals, boiler corrosion and solvent recovery. In this present study, activated carbon is used as a adsorbent to remove the amount of dissolved oxygen present in water. The main

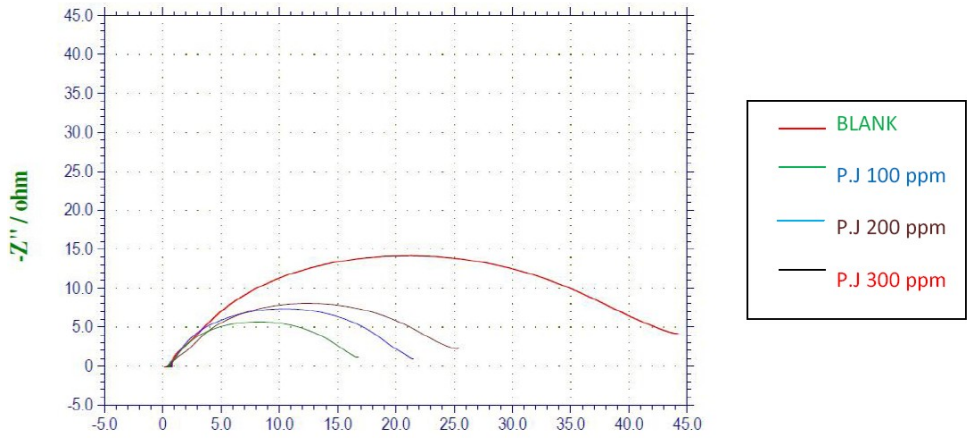

Figure 4b : AC impedance curves of Prosopis Juliflora for mild steel in distilled water at room temperature

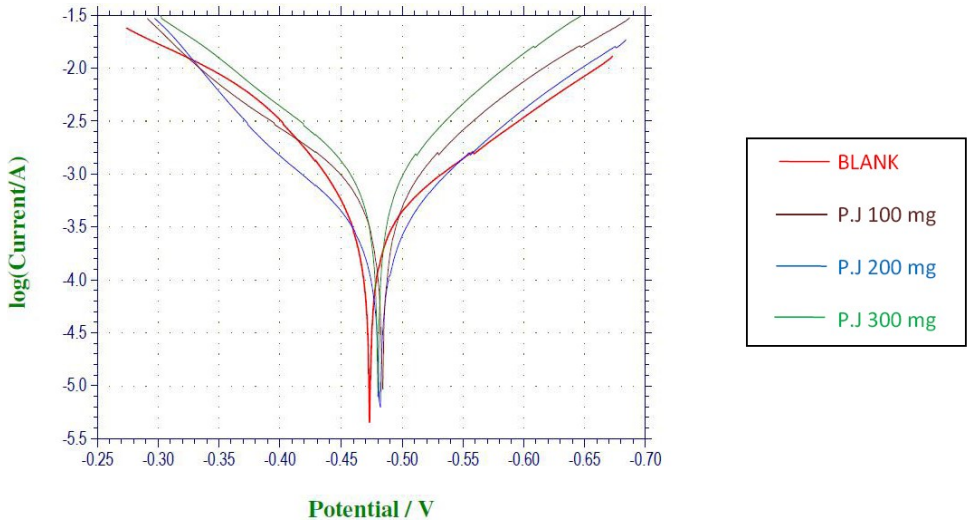

Figure 5a : Potentiodynamic polarisation curves of Prosopis Juliflora for mild steel in distilled water at pH = 3

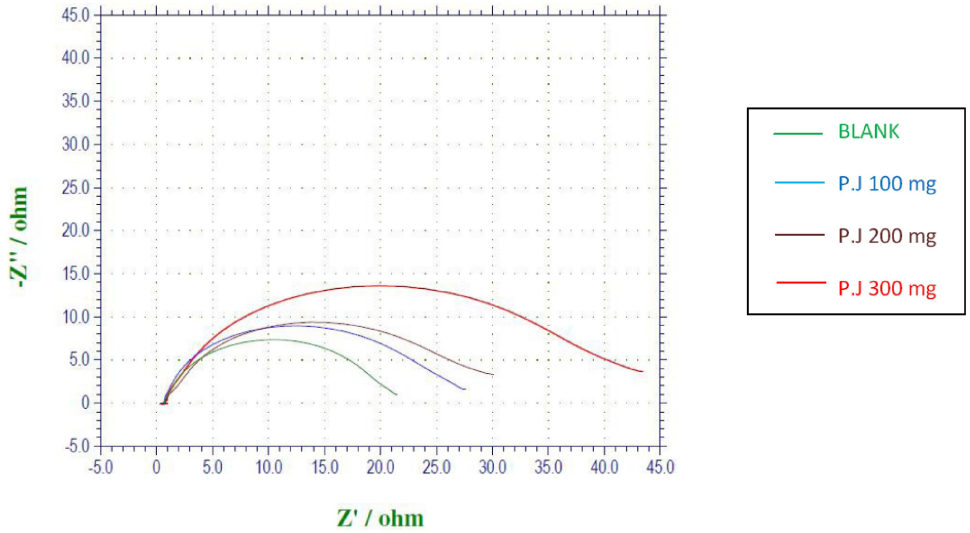

Figure 5b : AC impedance curves of Prosopis Juliflora for mild steel in distilled water at pH = 3

problem in industries is the dissolved oxygen present in water which enhances the rate of corrosion. This can be minimised by adding the activated carbon[7].

There are two main types of carbon activation procedure - physical and chemical. In the physical activation process - pyrolysis of the compound is done

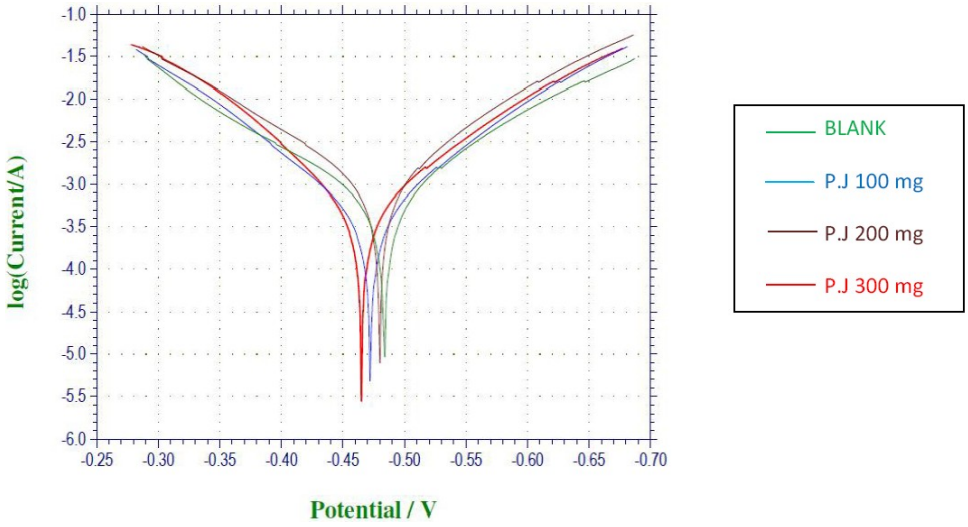

Figure 6a : Potentiodynamic polarisation curves of Prosopis Juliflora for mild steel in distilled water at pH = 12

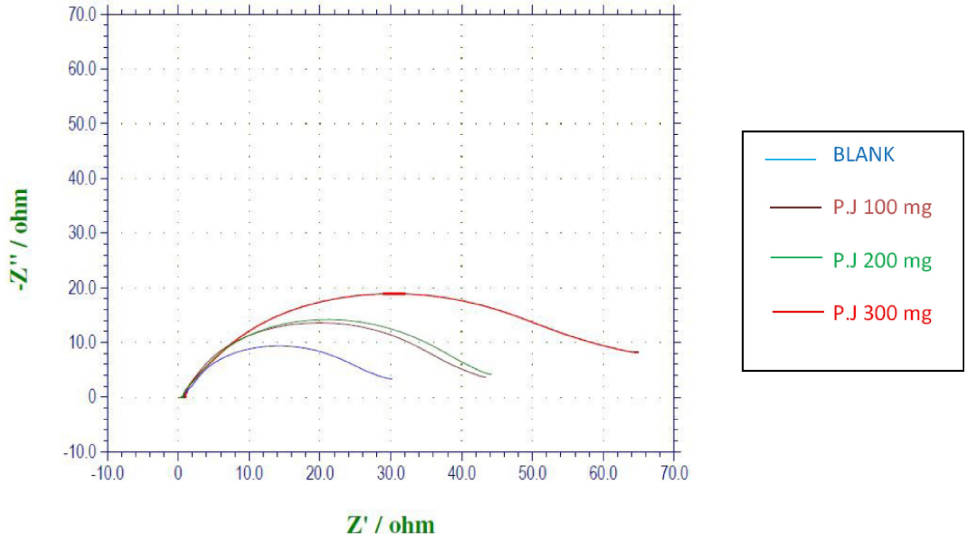

Figure 6b : AC impedance curves of Prosopis Juliflora for mild steel in distilled water at pH = 12

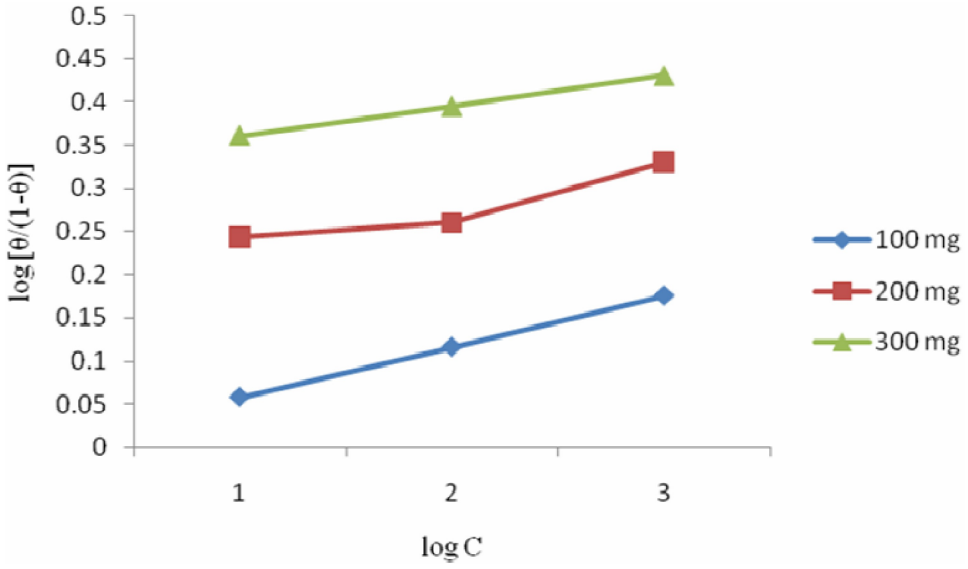

Figure 7a : Langmuir adsorption isotherm for mild steel in distilled water with Prosopis Juliflora at room temperature

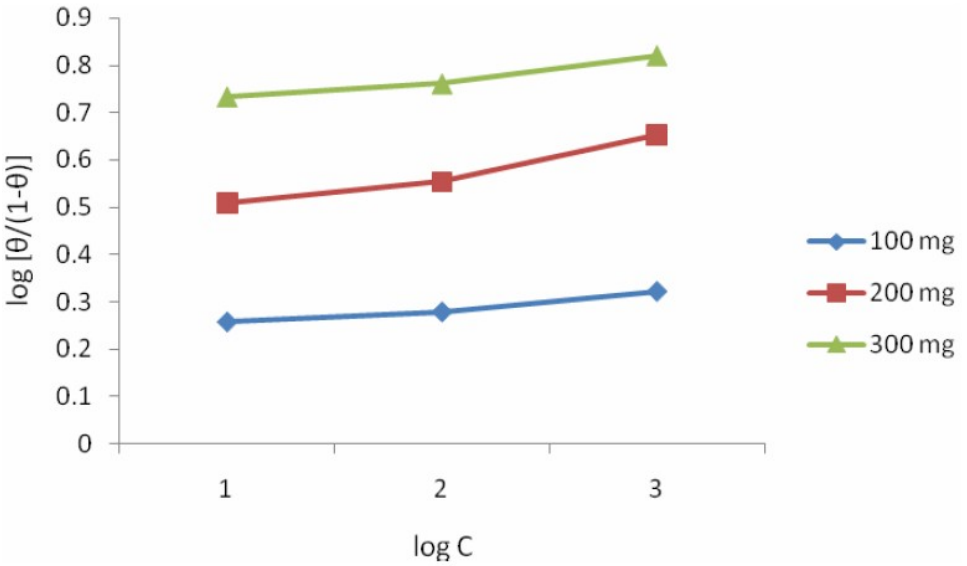

Figure 7b : Langmuir adsorption isotherm for mild steel in distilled water with Prosopis Juliflora at 60^{0}C

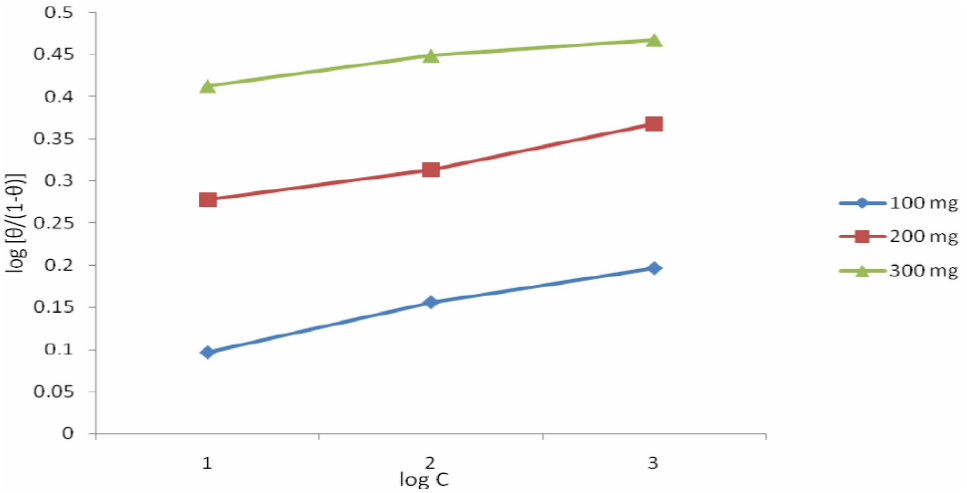

Figure7c : Langmuir adsorption isotherm for mild steel in distilled water with Prosopis Juliflora at pH = 3

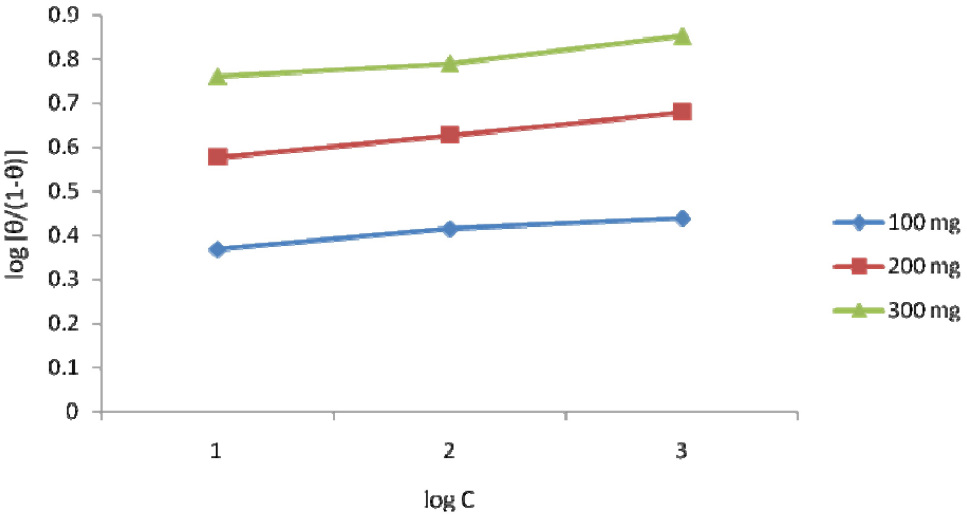

Figure 7d : Langmuir adsorption isotherm for mild steel in distilled water with Prosopis Juliflora at pH= 12

in presence of inert gases like nitrogen or carbon dioxide. In chemical activation process, activation is done by

TABLE 1 : Weight loss "W and inhibition efficiency (η %) for mild steel in distilled water with activated carbon at room temperature

Mass of activated carbon	100 ml Distilled water					200 ml Distilled water					300 ml Distilled water				
(mg)	ΔW (mg)	DO	θ	$\log\frac{\theta}{1-\theta}$	I.E (η %)	ΔW (mg)	DO	θ	$\log\frac{\theta}{1-\theta}$	I.E (η %)	ΔW (mg)	DO	θ	$\log\frac{\theta}{1-\theta}$	I.E (η %)
Blank	122	4.8	-	-	-	110	6.2	-	-	-	90	9.8	-	-	-
100	37	3.8	0.6967	0.3611	69.67	40	4.9	0.6363	0.2429	63.63	42	6.4	0.5333	0.0579	53.33
200	35	3.1	0.7131	0.3954	71.31	39	4.5	0.6454	0.2600	64.54	39	5.1	0.5666	0.1163	56.66
300	33	2.6	0.7295	0.4308	72.95	35	4.1	0.6818	0.3309	68.18	36	4.6	0.6000	0.1760	60.00

TABLE 2 : Weight loss ΔW and inhibition efficiency (η %) for mild steel in distilled water with activated carbon at 60^{0}C

Mass of activated carbon	100 ml Distilled water					200 ml Distilled water					300 ml Distilled water				
(mg)	ΔW (mg)	DO	θ	$\log\frac{\theta}{1-\theta}$	I.E (η %)	ΔW (mg)	DO	θ	$\log\frac{\theta}{1-\theta}$	I.E (η %)	ΔW (mg)	DO	θ	$\log\frac{\theta}{1-\theta}$	I.E (η %)
Blank	122	3.2	-	-	-	110	4.0	-	-	-	90	6.0	-	-	-
100	19	2.9	0.8442	0.7338	84.42	26	3.8	0.7636	0.5092	76.36	32	4.1	0.6444	0.2581	64.44
200	18	2.4	0.8524	0.7615	85.24	24	3.2	0.7818	0.5542	78.18	31	3.2	0.6555	0.2793	65.65
300	16	1.8	0.8688	0.8209	86.88	20	2.8	0.8181	0.6529	81.81	29	2.0	0.6777	0.3227	67.77

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	100 ml Distilled water					200 ml Distilled water					300 ml Distilled water				
(mg)	ΔW (mg)	DO	θ	$\log\frac{\theta}{1-\theta}$	I.E (η %)	ΔW (mg)	DO	θ	$\log\frac{\theta}{1-\theta}$	I.E (η %)	ΔW (mg)	DO	θ	$\log\frac{\theta}{1-\theta}$	I.E (η %)
Blank	122	3.6	-	-	-	110	4.2	-	-	-	90	5.3	-	-	-
100	34	2.9	0.7213	0.4129	72.13	38	3.9	0.6545	0.2774	65.45	40	4.9	0.5555	0.0968	55.55
200	32	2.4	0.7377	0.4490	73.77	36	3.6	0.6727	0.3128	67.27	37	4.4	0.5888	0.1559	58.88
300	31	1.8	0.7459	0.4676	74.59	33	3.0	0.7000	0.3679	70.00	35	3.8	0.6111	0.1962	61.11

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	100 ml Distilled water					200 ml Distilled water					300 ml Distilled water				
(mg)	ΔW (mg)	DO	θ	$\log\frac{\theta}{1-\theta}$	I.E (η %)	ΔW (mg)	DO	θ	$\log\frac{\theta}{1-\theta}$	I.E (η %)	ΔW (mg)	DO	θ	$\log\frac{\theta}{1-\theta}$	I.E (η %)
Blank	122	5.0	-	-	-	110	5.3	-	-	-	90	5.7	-	-	-
100	18	4.6	0.8524	0.7615	85.24	23	3.9	0.7909	0.5777	79.09	27	3.3	0.7000	0.3679	70.00
200	17	4.2	0.8606	0.7905	86.06	21	2.8	0.8090	0.6269	80.90	25	2.6	0.7222	0.4149	72.22
300	15	3.2	0.8770	0.8530	87.70	19	2.2	0.8272	0.6800	82.72	24	2.1	0.7333	0.4392	73.33

TABLE 5 : Corrosion parameters of mild steel in distilled water with Prosopis Juliflora by potentiodynamic polarisation method at 60^{0}C

Mass of activated carbon (mg)	E_{corr} (mv)	Tafel slopes (mV/dec)		I_{corr} (μA/cm^2)	Inhibition efficiency (%)
		ba	bc		
Blank	-236	97.4	84.1	1246.0	-
100	-314	130.1	45.3	294.20	76.38
200	-326	128.7	51.6	268.10	78.48
300	-372	118.6	60.2	208.01	83.30

either using acid as 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 from the physical methods has functional group which can interact with the adsorbate and also the surface area of the activated carbon is also superior than 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 this work the activated carbon is prepared from the seeds of Prosopis juliflora by dehydrating with sulphuric acid.

EXPERIMENTAL PROCEDURE

Preparation of activated carbon

25g of sieved samples of Prosopis juliflora (Tamil name - velikathan) were soaked in 50 ml of sulphuric acid (the ratio being 1:2) for 24 hours with constant stirring in a fume hood. The liquid portion was then decanted carefully and the solid portion are then taken in a ceramic hood and heated to 160°C in an air oven for 24 hours. The temperature of the oven is increased by 5°C every 15 minutes. 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 105°C for 1 hour. The activated carbon is then stored in cool dry place (desiccator) for further analysis.

Specimen preparation

Mild steel having a composition of Fe: 99.75%, Mn: 0.01%, Cu: 0.01%, Si: 0.02%, P: 0.02% and C: 0.18 % is used in this work. The specimens of dimension 5 cm 1.5 cm width are used. The specimens were polished using 1/0,2/0, 3/0 and 4/0 grade emery papers and pickling solution were used to wash the mild steel till the metal is clear and washed with distilled water, acetone and kept in oven, for immediate usage.

Batch studies

Batch studies were preformed in a closed plastic container (500 ml capacity) with 100 ml, 200 ml and 300 ml distilled water. Different adsorbent mass were also used (0.1g, 0.2g and 0.3g). Constant shaking of the solution was done using orbital shaker at the rate of 150 rpm. The constant temperature throughout the experiment was maintained at 45°C. The samples are shaken for 1 hour and then the supernatant liquid is filter as discussed earlier. pH of the solution was also adjusted with 1N HCl and 1N NaOH. A blank was also carried out by shaking distilled water without activated carbon.

Weight loss method

Mild steel is used here because the percentage of iron is more in mild steel, which enhances the corrosion rate in industries. Here by adding activated carbon the dissolved oxygen present in water is reduced and rate of corrosion is minimised. Weight loss methods are carried out by weighing the specimens before and after immersion in (100 ml, 200 ml and 300 ml) solutions for 2 hours in the absence and presence of activated carbon. From the initial and final mass of the specimen, the weight loss was calculated. From this weight loss value, inhibition efficiency (IE) and corrosion rate were determined[1,8].

Electrochemical studies

The surface of electrode is prepared by taking mild steel specimen of an area of 1 cm and embedded with Teflon coating. The coated mild steel was polished with1/0, 2/0, 3/0 and 4/0 grade emery papers and degreased with acetone before usage.

Electrode cell assembly

Electrochemical workstation Model 600 D Series was used for polarization and AC Impedance studies. Three electrode systems was used for this purpose, Platinum electrode acts as a auxiliary electrode, saturated calomel electrode (SCE) act as a reference electrode and mild steel of an area of 1cm was used as working electrode.

Procedure and calculation

In Electrochemical workstation Tafel and Electrochemical Impedance (EI) was carried out and the readings were recorded for polarization and impedance, for water treated with and without activated carbon, from this values the percentage of inhibition efficiency was calculated[2].

TABLE 6 : AC impedance parameters for corrosion of mild steel in distilled water with prosopis Juliflora at 60^{0}C

Mass of activated carbon (mg)	R_{ct} (Ω cm$^{2)}$	C_{dl} (μF/cm^2)	Inhibition efficiency (%)
Blank	70.60	51.18	-
100	72.31	44.33	84.42
200	90.65	40.26	85.24
300	98.42	39.04	86.88

$$\text{I.E (or) } \eta\ \% = \frac{\Delta W_u - \Delta W_i}{\Delta W_u} \times 100$$

Where,

ΔW_u = Weight loss of the metal in distilled water without activated carbon.

ΔW_i = Weight loss of the metal in distilled water with activated carbon.

$$\theta = \frac{\Delta W_u - \Delta W_i}{\Delta W_u}$$

Where,

The degree of surface coverage θ by inhibitor can be calculated as[3].

Where,

ΔW_u = Weight loss of the metal in distilled water without activated carbon.

ΔW_i = Weight loss of the metal in distilled water with activated carbon.

Temperature and pH

Experiment was carried out with two different temperature and pH. pH of the water sample were maintained at 3 and 12. Temperature was maintained with a thermostat at 60^0 C and 25^{0}C (room temperature).

Dissolved oxygen

Three methods that were most commonly used to measure the dissolved oxygen (DO) present in water are colorimetric, titrimetric and polographic method. In this work titrimetric method is used because colorimetric method may show some irregular results and it is very rapid, they are used for screening low oxygen content. In polographic method large amount of samples is required within a short period. Winkler method is used for measuring the amount of dissolved oxygen present in the water sample.

SURFACE ANALYSIS

The activated carbon is characterized by SEM and FT-IR (Lambda FT-IR-7600). The Fourier Transform Infrared spectroscopy picture of activated carbon is shown in Figure 1. In FT-IR a sharp peak is obtained at a wavelength 1599^{cm-1}. This indicates that there is an asymmetric CO and NO stretching. The scanning electron microscope picture of the activated carbon at 500 micrometer and at 50 micrometer is shown in Figure 2a and 2b. The SEM images clearly differentiate the effect of the size of the activated carbon.

RESULTS AND DISCUSSION

Weight loss method at room temperature

The amount of dissolved oxygen decreases with increase in amount of activated carbon at room temperature. Dissolved oxygen, inhibition efficiency and surface coverage with various mass of Prosopis Juliflora in distilled water at room temperature were shown in TABLE 1. It indicates that the inhibition efficiency increases with increase in the mass of the activated carbon used in the batch studies. The maximum inhibition efficiency of Prosopis Juliflora was found to be 72.95% in 100 ml distilled water for 300 mg of prosopis juliflora at room temperature. This can be attributed to the fact that there is a decrease in the dissolved oxygen for that solution.

Weight loss method at 60^{0}C

As the temperature increases the amount of dissolved oxygen content is less compared to room temperature. With increase in the temperature there would be less dissolution of oxygen in the water. The inhibition efficiency, surface coverage and dissolved oxygen for mild steel with various mass of prosopis juliflora in distilled water at 60^{0}C were shown in TABLE 2. The maximum inhibition efficiency of prosopis juliflora was found to be 86.88% at 60^{0}C in 100 ml distilled water with 300 mg of prosopis juliflora at 60^{0}C . It clearly indicates that with temperature increase, the corrosion decreases and the dissolved oxygen present in distilled water also decreases.

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Weight loss method at pH= 3

In acidic medium the removal of dissolved oxygen is less but there is a change in value of inhibition efficiency and surface coverage for various mass of prosopis juliflora in distilled water. The inhibition efficiency increases with respect to the mass of activated carbon. The maximum inhibition efficiency of prosopis juliflora was found to be 74.59% in 100 ml distilled water for 300 mg of prosopis juliflora at pH = 3. The inhibition efficiency and surface coverage of mild steel with various mass of prosopis juliflora in distilled water at pH= 3 is shown in TABLE 3.

Weight loss method at pH = 12

In basic medium the removal of dissolved oxygen is more. While comparing all these methods the activated carbon is more effective in basic medium rather than acidic medium. The inhibition efficiency increases with respect to the mass of activated carbon. The maximum inhibition efficiency of prosopis juliflora was 87.70% in 100 ml distilled water for 300 mg of prosopis juliflora at pH = 12. The inhibition efficiency and surface coverage of mild steel with various concentration of prosopis juliflora in distilled water at pH = 12 is shown in TABLE 4.

Langmuir adsorption isotherm

Langmuir adsorption isotherm is used to study the characteristics of activated carbon. The adsorption behaviour of activated carbon on mild steel is used to understand the inhibition mechanism of corrosion. The plots of log [θ/(1- θ)] vs log C yield a straight line and provided the information that the adsorption of Prosopis Juliflora on mild steel surface in distilled water. The Langmuir adsorption isotherm was calculated by using the equation.

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

A straight line is obtained by plotting log [θ/(1- θ)] versus 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 plot was shown in Figure 7a, 7b, 7c and 7d 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 [θ/(1- θ)] also increases which indicates that the rate of corrosion is decreased.

Potentiodynamic polarisation studies

As the mass of activated carbon increases the amount of dissolved oxygen decreases. Polarisation curves of mild steel in distilled water with and without activated carbon at different temperatures and pH was shown in Figure.3a, 4a, 5a and 6a. Corrosion parameters such as corrosion potential, anodic Tafel slope and cathodic Tafel slope, corrosion current and inhibition efficiency were calculated. It implies that, addition of activated carbon to water, shifts the anodic polarisation to more positive and cathodic to more negative values. It indicates that addition of activated carbon reduces both anodic and cathodic process and the added activated carbon act as mixed type inhibitor.

In TABLE 5, the Icorr values decrease with increase in mass of activated carbon with shift of E_{corr} to more negative potential. This indicates that, activated carbon Prosopis Juliflora which decreases the dissolved oxygen content suppresses cathodic reaction predominantly than anodic process. The maximum inhibition efficiency of Prosopis Juliflora inhibitor was found to be 83.30 % in 300 mg of prosopis juliflora at 60^0C. The inhibition efficiency of Prosopis Juliflora obtained from the polarisation method is good compared with the inhibition efficiency obtained from the weight loss method.

AC Impedance study

The open circuit potential for mild steel in distilled water with and without activated carbon at different temperatures and pH was shown in Figure.3b, 4b, 5b and 6b. Impedance parameters derived from Nyquist plots were given in TABLE 6. From the TABLE, it is observed that the value of charge transfer resistance (R_{ct}) increase with increase in mass of activated carbon. But the value of double layer capacitance (C_{dl}) decreases with increase in the mass of activated carbon. The inhibition efficiency is increased with increase in mass of activated carbon. The maximum inhibition efficiency of Prosopis Juliflora was found to be 86.88 % in 300 mg of prosopis juliflora at 60^0C. The impedance diagram for solutions have almost semicircular appearance, it indicates that the corrosion of mild steel is mainly controlled by dissolved oxygen which

decreases with increase in the mass of activated carbon. The inhibition efficiency obtained from AC impedance method is in good agreement with the inhibition efficiency obtained from polarisation and weight loss method.

CONCLUSIONS

The removal of dissolved oxygen is superior by increasing the mass of activated carbon Prosopis Juliflora because the activated carbon acts as an adsorbent which reduces the rate of corrosion.

At room temperature the amount of dissolved oxygen present in water is more compared to 60^0C. The inhibition efficiency at room temperature was 72.95% in 100 ml distilled water for 300 mg of prosopis juliflora and for 60^0C the efficiency was 86.88% % in 100 ml distilled water for 300 mg of prosopis juliflora. This clearly indicates that, when temperature increases inhibition efficiency also increases due to decrease in dissolved oxygen content.

When the pH increases the activated carbon becomes more effective. The maximum inhibition efficiency reported in weight loss method was 74.59% in 100 ml distilled water for 300 mg of prosopis juliflora at pH=3. In basic conditions inhibition efficiency was 87.70% in 100 ml distilled water for 300 mg of prosopis juliflora at pH=12. This indicates that the activated carbon works better under basic medium rather than acidic medium.

Increase in the amount of prosopis juliflora decreases the I_{corr} values with shift of corrosion potential to more negative, which indicates Prosopis Juliflora behaves as cathodic type inhibitor. The maximum inhibition efficiency obtained in this method was 83.30 % in 300 mg of prosopis juliflora.

The value of charge transfer resistance obtained by AC impedance method was increased with increase in the amount of Prosopis Juliflora. The maximum inhibition efficiency obtained in this method is 86.88 % in 300 mg of prosopis juliflora.

The added activated carbon follows Langmuir adsorption isotherm which indicates that the rate of corrosion is decreased.

Inhibition efficiency obtained from AC impedance study, Potentiodynamic polarisation method was found to be good compared from conventional weight loss method.

REFERENCES

[1] Bin Xu, Wenzhong Yang, Ying Liu, Xiaoshuang Yin, Weinan Gong, Yizhong Chen; Corrosion Science, January, **78**, 260-268 **(2014)**.
[2] P.Muthukrishnan, B.Jeyaprabha, P.Prakash; JMEPEG, **22,** 3792-3800 **(2013)**.
[3] Mahendra Yadav, Debasis Behera, Sumit Kumar, Rajesh Ranjan Sinha; Ind.Eng.Chem.Res., **52(19)**, 6318–6328 (**2013**).
[4] Nutan Kumpawat, Alok Chaturvedi, Rajesh Kumar Upadhaya; Scientific research., **2**, 68-73 **(2012)**.
[5] Jamal Abdul Nasser, M.Anwar Sathiq; International journal of engineering science and technology, **2(11)**, 6417-6426 **(2010)**.
[6] Zhihua Tao, Shengtao Zhang, Weihua Li, Baorong Hou; Corrosion Science, **51**, 2588-2595 **(2009)**.
[7] Vassileios M.Matsis, Helen P.Grigoropoulou; Chemical Engineering Science., **63**, 609-621 **(2007)**.
[8] M.A.Quraishia, Ishtiaque Ahamada, Ashish Kumar Singha, Sudhish Kumar Shuklaa, B.B.Lal, B.Vakil Singh; December, **112(3),** 1035-1039 **(2008)**.
[9] Ji yang, Juan peng, Zhemin shen, Jinping Jia, Feng; Carbon, **44**, 19-26 **(2006)**.
[10] M.Sfaira, A.Srhiri, H.Takenouti, M.Marie de Ficqelmont-Loizos, A.Ben bachir, M.Khalakhil; Journal of applied electrochemistry, **31**, 537-546 **(2001)**.