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Carboxymethyl Cellulose -Polyaniline Composites as Efficient Corrosion Inhibitor for Q235 Steel in 1 M HCl solution

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Polyaniline has a wide application in the field of corrosion protection, the poor solubility of polyaniline limited its application as a corrosion inhibitor. Water-soluble carboxymethyl cellulose -polyaniline composites was synthesized by chemical oxidation polymerization in a mild way without other inorganic or organic acids added. Corrosion inhibition performance of composites was evaluated for Q235 steel corrosion in 1 M HCl corrosive solution using weight loss and electrochemical measurements at various concentrations. The results show that carboxymethyl cellulose -polyaniline composites exhibit good inhibition properties and the remarkable increase in inhibition efficiency, i.e., 94.24% is achieved while the maximum concentration of the experiment is 1000 ppm. The composites in corrosive solution suppress the cathodic hydrogen evolution reactions and anodic metal dissolution of the substrate. Adsorption of the inhibitor on the steel surface follows a Langmuir adsorption isotherm.

Keywords: corrosion; inhibitor; polyaniline; water-soluble; cellulose

1. INTRODUCTION

Corrosion is worth to be investigated and prevented in refinery, because corrosion accounts for a large part of the total costs, which triggers the damage and premature failure of the equipment, increases the maintenance cost and wastes the resources. Appropriate suppress corrosion deterioration can avoid many potential accidents which may cause catastrophe failure including life property loss, negative social impacts, water resource and environment pollution and so on. The use of inhibitors has proven to be useful in relation to protection of metals and alloys against corrosion in different corrosive media that can be used in circulating water and cooling water system in refinery and so on. Inorganic corrosion inhibitors, such as chromate, nitrite, phosphate, have a degree of toxicity and contamination to the environment and hazards on human health. The development and application of environment-friendly and natural compounds has become a very important research direction, most of which are biodegradable and do not contain heavy metals or other toxic compounds. Organic molecules contains N, O, S, P and other heteroatom is used in the research of corrosion inhibitors which can adsorbed on the metal surface [1]. Polymer compounds has more adsorption activity center and can form a single layer or multi-layer dense protective film more easily. Corrosion protection of these polymer compounds which are widely used as corrosion inhibitors are more superior compared with low molecular compound [2].

The application of conducting polymers, e.g., polyaniline [3], polypyrrole[4, 5], polythiophene[6], and polycarbazole[7], which are well known for their electrical and electronic properties, as excellent corrosion inhibitors or coating ingredients was elaborately evaluted[8]. Polyaniline has been widely studied by reason that unique characteristics, including low cost and simple preparation, remarkable environmental stability, corrosion resistance to scratch and pitting, passivate metal substrate. That has better corrosion resistance and is considered to be the most promising conducting polymers [9]. However, the special structure of polyaniline contribute to its poor solubility in water, it just can dissolve in a few organic solvents, such as methyl pyrrolidone, dimethyl formamide, this restrict the application of that as corrosion inhibitor. Polyaniline has unique doping mechanism. Doping it can improve the water solubility of polyaniline that bring new improvement as corrosion inhibitor [10]. Using macromolecular water-soluble polymers poly (vinyl alcohol), polyacrylamide, polyvinyl pyrrolidone or acid doped polyaniline can get water-soluble polyaniline composites[11-13]. Syed, et al[14]dissolved polyacrylic acid in HCl solution and added ammonium persulfate antioxidant, prepared water-soluble polyaniline-acrylate composite materials by chemical oxidative polymerization with aniline monomers, surveyed the corrosion ability of 316 stainless steel in 0.5 M HCl solution. Corrosion inhibition efficiency reached 91.6% when the optimal concentration of 200 ppm. Polyacrylic acid compound not only improved the water solubility of polyaniline, at the same time limited the accumulation of polyaniline. Karthikaiselviet, et al[15]also prepared poly(vinyl pyrrolidone-methylaniline) composite materials with chemical oxidative polymerization, the Optimum inhibition efficiency of 87.01 % was obtained from weight loss method while the highest concentration of inhibitors was 2000 ppm in 1.0 M HCl. Similarly, polyaniline composites with good water solubility were synthesized by the same method using poly(vinyl alcohol) [16-17].

But to the best of our knowledge, there has been relatively little scientific study of the application of carboxymethyl cellulose -polyaniline composites (PANI/CMC composites) as an efficient corrosion inhibitor for Q235 steel in corrosive medium. Cellulose is widely used in corrosion inhibitor which is the most abundant polysaccharide in nature and that is bio-degradable and non-toxic[18-19], including water-soluble carboxymethyl cellulose (CMC) [20-21] and hydroxyethyl cellulose [22]. The aim of the present work was to synthesize PANI/CMC composites and to study the inhibitive behavior of that for Q235 steel. We used carboxymethyl cellulose as a doped acid which was gained by means of oxidation of hydroxypropyl methyl cellulose (HPC) to prepare PANI/CMC composites. The inhibition efficiency of that was studied and the surface coverage, adsorption isotherm and inhibition mechanism of the composites over Q235 steel substrates in corrosive solution was also discussed.

2. EXPERIMENTAL

2.1. Materials

All reagents were analytical reagent and used without further purification except aniline. Hydroxypropyl methyl cellulose was provided by Aladdin biochemical technology co.LTD. Aniline, ethanol, hydrochloric acid and acetone were provided by Tianjin DaMao chemical reagent factory. Ammonium persulphate was provided by Yantai ShuangShuang chemical co.LTD. For electrochemical tests were carried out by using Q235 steel (weight % composition, C: 0.17%, Mn: 0.46%, Si: 0.46%, S: 0.017%, P: 0.05% and remainder Fe) measuring 10×10×4 mm prepared from China National Chemical Corporation. The steel sheets were polished with a series of emery papers (400, 600, 800, 1000, 1500 and 2000 grit) and then ultrasonically degreased in acetone and ethyl alcohol, successively, for 10 min. Washed with distilled water and dried in a cold air stream.

2.2. Synthesis of PANI/CMC composites

Aniline was distilled under vacuum prior to use. The optimum conditions were determined by orthogonal experimentals, and a special case was given to illustrate the experimental process. Firstly, 5 g hydroxypropyl methyl cellulose was well dissolved in 100 ml water and 4.56 g (0.02 mol) ammonium persulfate was added to the solution, reacted at 60℃ as a certain time described in the literature[23]. After the reaction completely, cooled to room temperature and transferred to the drip funnel. Then added it dropwise to aniline solution which has dissolved 3ml aniline in 50ml water, ultrasonic dispersed to form uniform solutions and cooled to 0~-5℃. The solution immediately become transparent faint yellow. This demonstrated that generated the aniline salt with acid-base reaction between aniline and carboxymethyl cellulose. Polymerization was allowed to carry out under constant stirring for 12 h at 0~-5℃ and a deep-green-colored solution of PANI/CMC composites were gained. Filtered the reaction product and then washed with anhydrous ethanol and acetone to remove impurities. Dried the resulting composites in an air oven at 60℃for 8 h. Before determining the inhibition efficiency of the inhibitor, add corrosion inhibitors with different concentrations (0, 300, 500, 700 and 1000 ppm, respectively.) to 100 ml 1M HCl solution and conduct ultrasonic dispersion for 5 min. The characteristics of the samples were identified by Fourier transform infrared spectra (FT-IR) technology in the spectral range 4000 – 400cm^{-1} on a Nicolet 5700 spectrometer.

2.3. Gravimetric Measurements

Carbon steel coupons measuring 50×25×3 mm were used for the weight loss tests that exposed total area of 29.5 cm^2. Three parallel specimens were performed to ensure the reliability of results. The coupons were immersed in 100 mL 1 M HCl solutions for 4 h with and without the addition of different concentrations of inhibitors. After immersion, the specimens were withdrawn, washed with distilled water, dried thoroughly and accurately weighed.

The inhibition efficiency (I.E.%) and surface coverage (θ) was computed from the equation:

$$I.E.(\%)=\frac{\mathrm{m}_{\mathrm{blank}}-\mathrm{m}_{\mathrm{inhibitor}}}{\mathrm{m}_{\mathrm{blank}}}\times 100\% \qquad \theta=\frac{\mathrm{m}_0-\mathrm{m}_1}{\mathrm{m}_0}$$

where $\mathrm{m}_{\mathrm{blank}}$ and $\mathrm{m}_{\mathrm{inhibitor}}$ is weight (g) of Q235 steel specimens before and after immersion, respectively.

2.4. Electrochemical measurements

Electrochemical experiments were carried out using a conventional three-electrode cell assembly. Q235 steel specimens was used as the working electrode which was machined into square specimens and then embedded in polytetrafluoroethylene (PTFE) with an exposed surface area of 0.78 cm^2 to contact the corrosive solution. The platinum sheet was used as the counter electrode (PE), and the saturated calomel electrode (SCE) was used as the reference electrode, respectively, the area of the working electrode and counter electrode Pt sheet are both 1 cm^2. The polarization and impedance measurements were conducted using a computer-controlled CHI660E electrochemical workstation at room temperature in open air. The working electrode was allowed to immerse in the 1.0 M HCl solution for about 30 min to attain stable potential before carrying out electrochemical measurements.

Potentiodynamic polarization studies were performed from cathodic potential of -300 mV vs. SCE to anodic potential of +300 mV vs. SCE with respect to the open circuit potential at a sweep rate of 1 mV/s. The anodic and cathodic curves of the Tafel plots were extrapolated to obtain corrosion current densities ($\mathrm{I}_{\mathrm{inhibitor}}$). The inhibition efficiency was calculated using the following equation:

$$I.E.(\%)=\frac{I_{\mathrm{blank}}-I_{\mathrm{inhibitor}}}{I_{\mathrm{blank}}}\times 100\%$$

Where, $\mathrm{I}_{\mathrm{blank}}$ and $\mathrm{I}_{\mathrm{inhibitor}}$ are the corrosion current densities in absence and presence of inhibitors, respectively.

Electrochemical impedance spectroscopy (EIS) studies were carried out for the frequency spectrum from 100 kHz to 0.01 Hz with an amplitude of 5 mV peak to peak. The results were interpreted with Zview software. We obtained the values of charge transfer resistance (R_{ct}) from the Nyquist plots. Then, the inhibition efficiency was determined from the R_{ct} using the following equation:

$$I.E.(\%)=\frac{R_{\mathrm{ct}}-R'_{\mathrm{ct}}}{R_{\mathrm{ct}}}\times 100\%$$

where, Rct and R′ct denote the charge transfer resistance values in the absence and presence of inhibitors, respectively.

2.5. Metal surface morphology

The surface morphology of Q235 steel immersed in corrosive solution, with or without the presence of the inhibitor, was observed by a scanning electron microscopy (SEM, S-4300, Hitachi Co., Ltd. Tokyo, Japan) coupled with X-ray energy dispersive spectrum (EDS) which was used to analyze the composition of the steel surface.

3. RESULTS AND DISCUSSION

3.1. FT-IR studies

The FT-IR spectrum of PANI/CMC composites with KBr in tablet form is shown in the Fig.1.

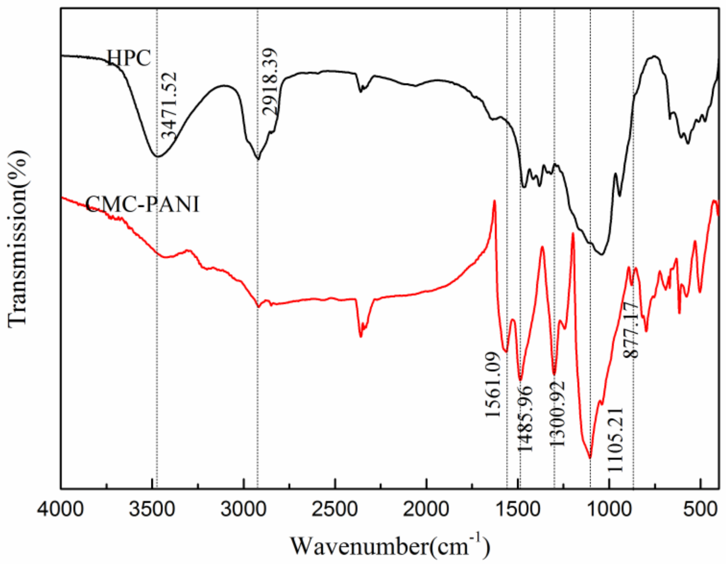

Figure 1. FT-IR spectra of PANI/CMC composites and hydroxypropyl methyl cellulose

The characteristic absorption peaks of hydroxypropyl methyl cellulose, at 3471.52 cm^{-1} is assigned to the stretching vibration peak of hydroxyl, the absorption peak at 2918.39 cm^{-1} is belong to the characteristic absorption peak of C-H, and the absorption peak at near 1041.03 cm^{-1} belongs to C-O-C frame vibration peak of main chain from cellulose. The absorption bands at 1485.96 cm^{-1} and 1561.09 cm^{-1} correspond to the C=C ring-stretching vibrations of the quinone and benzenoid ring of polyaniline, respectively. The absorption peak at 1300.92 cm^{-1} is the C-H vibration peak on benquinone ring. Peaks observed at 877.17 cm^{-1} is attributed to the para-substituted aromatic rings in PANI. The diminished band concerned with the O−H vibration of (−COO−) group of cellulose in the composites confirmed the formation of a composites of polyaniline with cellulose [11]. Meanwhile, the absorption of C-O-C hypsochromic shifts to around 1105.21 cm^{-1} manifested that cellulose doped with polyaniline[24-25]. As a consequence, these results confirm the formation of PANI/CMC composites.

3.2. Weight loss studies

So as to evaluate the average dissolution rate of steel samples in acid solution with different concentration of corrosion inhibitors and determine the adsorption property of the composites on the Q235 steel surface, weight loss studies were performed in room temperature in 1 mol/L hydrochloric acid medium with different concentrations (0~1000 ppm) of the composites. The inhibition efficiency (I.E.%) for different concentrations of inhibitor is shown in Table 1.

Table 1. Weight loss parameters for steel in 1.0 M HCl solution with different concentrations of inhibitors

Inhibitor	concentration (ppm)	Weight loss (g)	I.E.%	θ
PANI/CMC composites	Blank	0.0745	–	–
	300	0.0311	58.25	0.5825
	500	0.0203	72.88	0.7288
	750	0.0105	85.86	0.8586
	1000	0.0042	94.24	0.9424

We can clearly see that the inhibition efficiency increases with the increase of concentration of the inhibitor, which is attribute to the inhibitor molecules adsorb on the Q235 steel surface to form a shielding layer that hinder the diffusion of corrosive ions to metal surface. When the maximum concentration of the experiment is 1000 ppm, the inhibition efficiency can reach 94.24%.

3.3. Potentiodynamic polarization

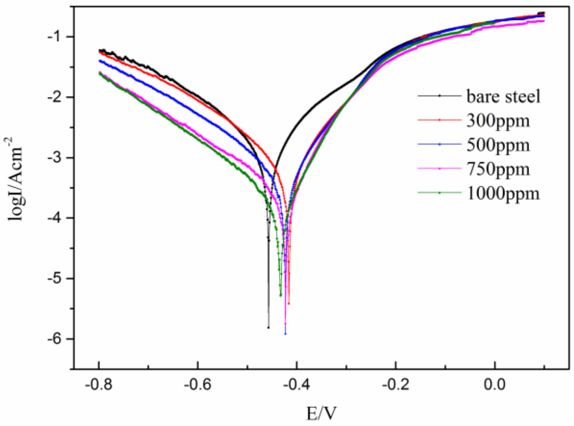

Figure 2. Polarization curves of mild steel electrode in 0.1 M HCl in absence and presence of PANI/CMC composites.

Fig.2. shows the polarization curves for Q235 steel in 1.0 M HCl with different concentration of composites. The electrochemical corrosion kinetic parameters such as corrosion current densities

(I_{corr}), corrosion potential (E_{corr}) and inhibition efficiency(I.E.%), obtained by extrapolation of Tafel lines are summarized in Table 2.

Table 2. Corrosion kinetic parameters for corrosion of mile steel in 1 M HCl containing different concentrations of PANI/CMC composites.

Concentration	Ecorr (V vs SCE)	Icorr A/cm^2	I.E.(%)	θ
Blank	-0.457	1.26×10-3	—	—
300	-0.416	6.39×10-4	49.3	0.493
500	-0.423	4.71×10-4	62.6	0.626
750	-0.423	2.45×10-4	80.5	0.805
1000	-0.433	1.54×10-4	87.7	0.877

The polarization curves indicate that the addition of composites reduce the corrosion current densities(I_{corr}) and increases the surface coverage. This is due to the composites molecules adsorbed on the steel surface that blocked the corrosive ion erode Q235 steel. It has been observed that added the inhibitor to the corrosive media not only affected the anodic metal dissolution, but also affected the cathodic hydrogen evolution reactions. More than anything else, anodic Tafel slopes increases with the concentration of composite. Therefore, we infer that PANI/CMC composites are inhibitor of anodic type. The higher inhibition performance of composites is attributed to the imine group (C=N) and hetero atoms in the polyaniline. Inhibition efficiency increases with increase of composites concentration in acid. When the concentration of PANI/CMC composites is 1000 ppm in 1 M HCl, the E_{corr} is the largest and Icorr is the smallest, and its corrosion inhibition efficiency can reach 87.7%.

3.4. EIS studies

EIS measurements were carried out to gain insight into the characteristics and kinetics of electrochemical processes occurring at the solution/metal interface. Impedance spectra as exemplified by Nyquist plots obtained for Q235 steel in corrosive media without or with different concentrations of PANI/CMC composites are shown in Fig.3.

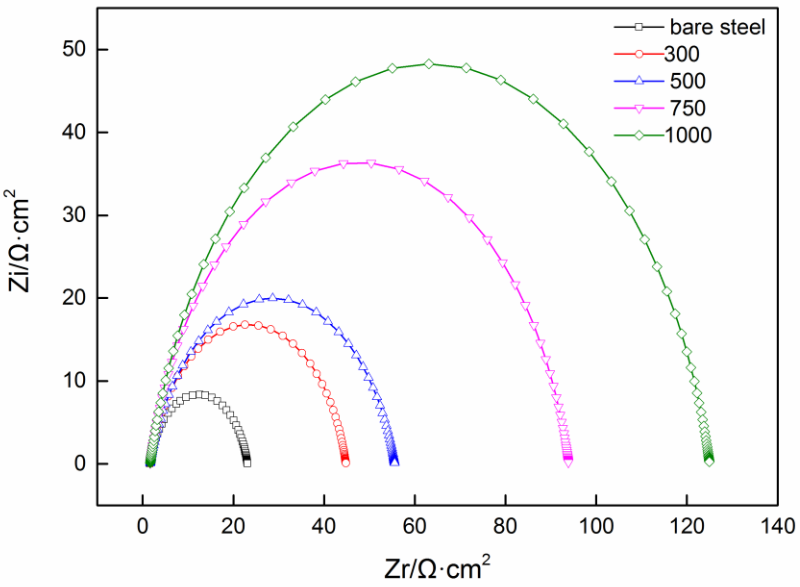

Figure 3. Nyquist plots of Q235 steel without or with different concentrations of PANI/CMC composites

Can be seen from the diagram, impedance spectroscopy are single semicircle capacitive reactance arc probably due to the frequency dispersion of interfacial impedance, this shows that the corrosion system of Q235 steel is primarily dominated by the charge transfer. It is apparent from these plots that the capacitive reactance arc radius increases gradually with the increase of the concentration. This demonstrate that the corrosion reaction charge transfer resistance increases and the corrosion rate retards. According to the characteristics of the above impedance spectrum, we used the following equivalent circuit model (shown in Fig. 4.) to analyze the impedance spectra.

Figure 4. The equivalent circuit model used to fit experimental date

where R_s is the solution resistance and R_t is the charge transfer resistance that can represents the corrosion rate of carbon steel in corrosive media solution.

In order to quantitatively evaluate the corrosion inhibition effect of inhibitor, ZSimpWin software was used to simulate and analyze EIS spectrogram. And the obtained equivalent circuit parameters are listed in Table 3.

Table 3. Nyquist diagrams for Q235 steel in 0.1 M HCl containing different concentration of PANI/CMC composites.

concentration /ppm	Rs Ω•cm2	Rct Ω•cm^2	CPE F/cm^2	n	I.E.%
Blank	1.582	21.54	4.601×10^{-3}	—	—
300	1.697	43.26	2.810×10^{-4}	0.832	50.2
500	16.35	53.94	2.525×10^{-4}	0.742	60.1
750	16.44	91.86	1.570×10^{-4}	0.860	76.6
1000	1.642	123.00	1.296×10^{-4}	0.726	82.49

It is found that the equivalent circuit of the n value is greater than 0.5, that at 0.75~0.87 and indicated that the interface of hydrochloric acid solution/carbon steel is characterized by double layer capacitance. It is observed that capacitance decreases from 4.6×10^{-3} F/cm^2 to 1.296×10^{-4} F/cm^2 with increase of inhibitor concentration from 0 to 1000 ppm, which shows that inhibitor molecules squeezed away the water molecules that with higher dielectric constant. So more amount of inhibitor molecules adsorb on the Q235 steel surface. It is not hard to see that the impedance of inhibited substrate increases with increase the concentration of inhibitor, indicated that the compactness of protective layer on the carbon steel electrode surface increase, which further improves the corrosion inhibition efficiency. Optimum inhibition efficiency can reach 82.49 %. And this is consistent with the results of polarization curve method.

The results of weight loss and electrochemical measurement at different concentrations show that the PANI/CMC composites has good corrosion inhibition performance. When the maximum concentration in 1 M HCl solution is 1000 ppm, the corrosion inhibition efficiency is significantly improved, reaching 94.24%. Compared with poly (vinyl pyrrolidone methyl) composites[15], it has better corrosion inhibition efficiency at the same concentration. But compared with water-soluble conducting polyaniline-sulfonated naphthalene formaldehyde nanocomposites, which has the inhibition efficiency for 316ss in 1M HCl solution was 97.9% at the concentration of 50ppm[26]. The author synthesized the inhibitor by one-step in-situ polymerization method, after the polymerization and dried it for 24h directly. However, we washed with anhydrous ethanol and acetone, and it may be that some active ingredients are lost during flushing, which leads to a higher corrosion inhibition efficiency at a higher concentration.

3.5 SEM observation

The surface morphologies of polished Q235 steel specimen and these immersed in 1.0 M HCl solution (without PANI/CMC composites and with 500 ppm PANI/CMC composites) were studied by using SEM and the images are displayed in Fig. 5.

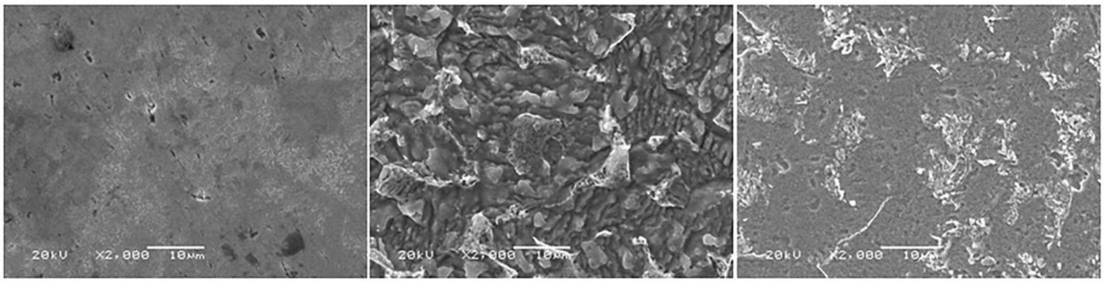

Figure 5. SEM images of (a) polished Q235 steel, (b) the Q235 steel immersed in HCl solutions without inhibitor for 4 h at 25 ºC and (c) the Q235 steel immersed in 1.0 MHCl solutions with 500 ppm inhibitor for 4 h at 25 ºC.

The chemical composition of the specimen which immersed in HCl solutions with inhibitor was analyzed using EDS. Elemental composition of inhibitor protected sample are listed in Table 4.

Table 4. Elemental composition of inhibitor protected sample

inhibitor	Fe(%)	C(%)	Cl(%)	N(%)
composites	95.08	4.24	0.23	0.44

It can be seen from SEM images that the surface of the polished steels is smooth, but a small amount of pits are observed because of occurred a slight corrosion during the placement. However, the steel sample without inhibitor protection is seriously corroded after immersed and getting cracks due to the acid corrosion. On the contrary, the surface of steel sample with corrosion inhibitor protection is smaller and smoother than that of steel sample without corrosion inhibitor protection. The Q235 steel surface was much less damaged, which further confirms that a protective adsorption layer formed on steel surface.

As seen in the Table, the sample surface was mainly composed of Fe, C, Cl and N elements, and the presence of N and C on the surface showed that PANI/CMC composites were adsorbed on the steel surface.

3.6. Adsorption isotherm and inhibition mechanism

The interaction and effectiveness of the inhibitor with the steel surface depends mainly on its adsorption capacity[27]. Nevertheless, the factors affecting the efficiency and adsorption properties of these organic inhibitors are the type of electrolyte, the charge on the metal surface and its properties[28].

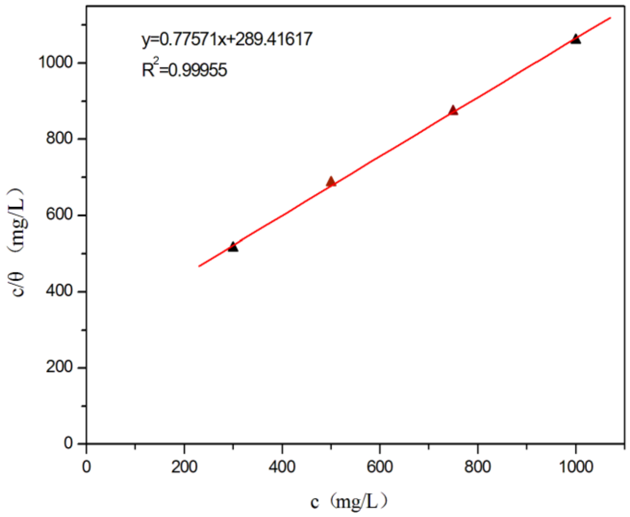

Figure 6. Langmuir adsorption isotherm for polyaniline composites in corrosive media

On account of the adsorption isotherm can provide basic information about the interaction of the corrosion inhibitor with the metal surface. The application of the adsorption isotherm is very important. We can use the following equation (θ=IE%/100) to calculate the surface coverage degree θ from weight loss studies measurements [29]. The surface coverage as a function of inhibitor concentration was drawn and verified by fitting to the Langmuir adsorption isotherm as per the equation [30]:

$$C/\theta=C+1/K_{ads}$$

where C represents the concentration of inhibitor and K_{ads} represents the adsorption equilibrium constant.

The plot of C/θ against C with $R^2 \geq 0.99955$ correlation coefficient is shown to be linear in Fig. 6. As a consequence, the adsorption of polyaniline composites is fitted well and follows the Langmuir adsorption isotherm. The preferred corrosion inhibition properties of polyaniline composites was ascribed to its excellent adsorption properties on steel surfaces. The θ values indicate that better surface coverage is gained when the concentration of corrosion inhibitor is 1000 ppm.

The data of corrosion inhibition efficiency show that inhibitor retard steel corrosion via adsorption on the steel surface to form a protective film. The adsorption route is generally considered to be an alternative process between the organic inhibitor in the aqueous solution and water molecules adsorbed at the metal surface[31]. There are two proposed possible adsorption mechanism of corrosion inhibitors an steel surface. N atoms, π electrons, aromatic rings in polyaniline conjugated with empty d orbital that on the steel surface, and form coordinate bond, so the molecules adsorb on the steel surface, form a protective film which separates the steel surface from the corrosive medium[32-33]. At the same time, the carboxymethyl cellulose mainly increases the solubility of corrosion inhibitor, and the oxygen atoms of that has lone pair electrons will promote the chemical adsorption of PANI/CMC composites[34].

4. CONCLUSION

(1) Soluble PANI/CMC composites were synthesized by chemical oxidation polymerization without other inorganic or organic acids added.

(2) The synthesized composites exhibited good inhibitory effect on Q235 steel corrosion in 1.0 M HCl solution. The inhibition efficiency was found to increase with increase in concentration of inhibitor. Optimum inhibition efficiency, i.e., 94.24 % was obtained while the maximum concentration of the experiment is 1000 ppm. The prepared composites can be used for corrosion protection of carbon steel under acidic conditions, and can also be added to the anti-corrosion coating as a functional material.

(3) Polarization results revealed that PANI/CMC composites in 1.0 M HCl solution suppressed the cathodic hydrogen evolution reactions and anodic metal dissolution of the substrate and mainly suppressed anodic processes. Impedance data specified that electrochemical corrosion reaction of Q235 steel was prevented by the adsorption of composites on its surface and adsorption of that on the steel/solution interface obey the Langmuir adsorption isotherm model.

(4) The SEM images clearly shown that Q235 steel corrosion was retarded obviously due to the adsorption of PANI/CMC composites on the mild steel surface.

CONFLICTS OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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