

Corrosion inhibition of acid pickling –descaling-cleaning action on mild steel using aqueous hydroxyethyl cellulose

Vincent Onuegu Izionworu ^{1,2,*}, Wan Mohd Norsani Wan Nik ², Mohammad Fakhratul Ridwan Zulkifli ², Walid Daoudi ³, Mohd Sabri Mohd Ghazali ² and Richard Victor James ⁴

¹ Chemical/Petrochemical Engineering, Faculty of Engineering, Rivers State University, Nkpolu-Oroworukwo, Port Harcourt, Nigeria Private Mail Bag 5080.

² Faculty of Ocean Engineering Technology, Universiti Malaysia Terengganu, 21030 Terengganu, Malaysia.

³ Laboratory of Materials and Environment, Dept of Chemistry, Multidisciplinary Faculty of Nador, University of Mohamed 1, 60700 Nador, Morocco.

⁴ Department of Mechanical Engineering, University of Port Harcourt, Nigeria.

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Abstract

The corrosion inhibition capability of aqueous Hydroxyethyl cellulose (HEC) on mild steel corrosion in 1 M HCl solution proposed for mild steel pickling, industrial cleaning, and descaling was evaluated at different concentrations and immersion times using gravimetric measurement. HEC demonstrated efficiency in mild steel corrosion inhibition with a maximum inhibition efficiency of 87% for a 300 ml acid pickling, industrial cleaning, and descaling solution composed of 20% aqueous solution of 0.01 M HEC and 80% of 1 M HCl solution, within an immersion time of 120 hours. The inhibition efficiency was found to increase with the increase in the concentration of HEC implying that HEC's inhibition action is concentration and time-dependent. The mechanism of adsorption of HEC was identified to be chemisorption with hydroxyl (-OH) moiety donated to the active sites of mild steel coupled with HEC molecules encapsulation of chloride ions on mild steel surface thus preventing the corrosive action of Cl ions on the mild steel.

Keywords: Corrosion; Polymers; Aqueous; Hydroxyethyl Cellulose; Pickling Action; Inhibitor; Descaling Solution; Industrial; Cleaning Solution

1. Introduction

Corrosion occurs when metals react with their environment in an electrochemical reaction, leading to the deterioration of the metal and its properties (Li et al, 2021) due to metal atoms' loss of electrons, forming metal ions, while other substances gain electrons, typically oxygen, leading to the formation of metal oxides or other compounds (American Water Works Association, 1996). The cost of corrosion is massive (Hosseinpour et al., 2021; Izionworu et al., 2020, NACE International 2016) and it affects different industries such as Infrastructure and Construction, Oil and Gas Industry, Aerospace and Aviation, Marine and Maritime and Automotive Industry (Koch et al., 2016). Other industries also affected include Electronics and Electrical Engineering, Chemical Processing - refineries, and Water and Wastewater Management. Koch et al., in a report titled "Cost of Corrosion Study Unveiled," stated that Corrosion poses a significant threat to infrastructure such as bridges, pipelines, and buildings, leading to structural failures, increased maintenance costs, and safety hazards (Koch et al., 2016).

In the Oil and Gas Industry corrosion of production facilities, pipelines, and storage tanks can lead to leaks, spills, and environmental contamination, disrupting operations and causing financial losses. When corrosion in the oil and gas

* Corresponding author: Vincent Onuegu Izionworu

industry is not adequately managed it leads to catastrophic failures (Li et al., 2021). In the Marine and Maritime industry, Sea-moving vessels, offshore platforms, and marine structures exposed to harsh met-ocean environments are also affected leading to metal fatigue, hull breaches, and eventually marine pollution (Charles et al., 2023, Charles et al., 2024). Chemical Processing plants and manufacturing facilities can fail due to the influence and effect of corrosion. There can also be leakage of hazardous chemicals leading to their release into the environment, posing risks to workers, the general public, and environmental contamination (NACE International, 2016). Corrosion also affects distribution systems for water and wastewater management such as treatment plants and sewage infrastructure, possibly leading to water quality issues, pipe bursts, and service disruptions, impacting public health and sanitation (United States Environmental Protection Agency, 1984).

The challenges associated with corrosion are enormous, thus, corrosion control is a necessity to prevent damage to infrastructures and assets, prevent environment pollution, and the resulting possible fatalities. To achieve efficient and timely corrosion management, predictive corrosion management techniques are essential. In recent times Artificial Intelligence has been explored in the predictive maintenance of oil and gas facilities with the potential of directing professional asset management practices and driving efficiency, reliability, and sustainability across the oil and gas value chain (Chuka et al., 2024a). So, integrating artificial intelligence into corrosion control in the oil and gas industry using Advanced Analytics, Predictive Modeling, and Machine Learning Algorithms coupled with continued research into advanced analytics techniques, has further enhanced the accuracy and reliability of corrosion control options (Chuka et al., 2024b). While the option of artificial intelligence is being explored to ensure the integrity, safety, and reliability of infrastructure, equipment, and assets, the traditional method of corrosion control such as the application of coatings, corrosion-resistant materials, and the use of corrosion inhibitors, are essential.

Corrosion inhibitors form a protective barrier on metal surfaces, preventing corrosive substances from coming into contact with the metal thereby slowing down the corrosion process. Corrosion inhibitors help extend the service life of assets and reduce maintenance costs (Thakur and Kuma 2021, Nik et al., 2023). Inhibitors provide safe operation and lower the danger of accidents, leaks, and failures by preventing corrosion. They help maintain the integrity and performance of machinery, pipes, and structures. By lessening the possibility of leaks, spills, and releases, inhibitors contribute to the prevention of environmental pollution, safeguarding ecosystems, and limiting harm to the environment. Businesses may increase asset longevity, decrease downtime, and lower the frequency and scope of maintenance tasks by utilizing corrosion inhibitors. Long-term cost reductions are achieved, and overall operational profitability and efficiency are raised. Corrosion inhibitors come in many forms—liquids, powders, and additives, so they can be used in various settings and purposes. They offer adaptable corrosion protection in several contexts and industries for a broad spectrum of surfaces and materials, including metals, alloys, concrete, and composites. They are an adjunct to other corrosion management strategies such as material selection, cathodic protection, and coatings. When combined with these techniques, they can increase their efficacy and provide further layers of corrosion protection, particularly in demanding or hostile settings (Desai et al., 2023).

Different materials have been explored as corrosion inhibitors including protective coats like painting of metal, electroplating, use of grease or oil in the least, use of oxygen scavengers, and inhibitors. The list of inhibitors includes film-forming inhibitors, H₂S scavengers, oxidizing agents, plant extracts, surfactants, polymers, and inorganic substances like - phosphates, nitrates, and chromates (Abdolreza, et al., 2021). However, there are health and environmental challenges associated with the use of some of these inhibitors (such as phosphates, nitrates, and chromates) leading to the discontinuation of their usage. On the other hand, polymers have been used as environmentally friendly corrosion inhibitors even though they have been used as sensors, actuators, and x-ray dosimetry (Romero et al., 2020), in body or personal armor systems manufacture (Benzait & Trabzon, 2018), and electrical, electronics and optoelectronic fields (Namsheer and Rout 2021, Umoren and Solomom, 2019), in the oil and gas as drilling fluid thickeners and filtrate reducer of completion fluids (Carbohydrate Polymers, 2017). Polymers have also been used for oral medication administration systems - as excipients that is, stabilizing, protecting, and taste-masking agents (Rajeswari et al., 2017), polymer concretes (Onuegbu, 2015), and many more applications. Amongst all these applications, polymers stand out as corrosion inhibitors.

The use of polymers as inhibitors has been encouraged because of their high thermal and chemical stability, and their large and broad molecular weight that gives them leverage for wide surface area coverage. These attributes are essential for inhibitors to control corrosion. Researchers and engineers have increasingly recognized these and other advantages of polymers in providing effective corrosion protection for a wide range of metal substrates (Namsheer and Rout 2021). So, to tap these inherent benefits, several polymers are used as corrosion inhibitors. These include natural polymers like dextrin, cyclodextrin, alginate, pectin, and chitosan. Starch and cellulose have also been used as well. These biopolymers show outstanding properties with their molecular weight, coupled with their distinct molecular and electronic structures. Another contributory factor to natural polymers' inhibition of substrate corrosion is their amine

and hydroxyl functional groups. Natural polymers use these functional groups to form complexes that provide large substrate surface area coverage (Verma et al., 2022; Abdolreza, et al., 2021). Inorganic water-soluble polymers like – Polyvinyl alcohol-o-methoxyl aniline (PVAMOA), 1, 4-bis (benzimidazolyl) benzene (BBMB), acrylics, and ionic groups and/or non-ionic hydrophilic modified polyurethanes have also been used (Honarkar, 2018; Beach, et al., 2023). Water-soluble polymers like Polyethylene glycol (PEG) and Hydroxyethyl cellulose (HEC) have also been used (Arukalam et al., 2012, 2014a, 2014b; Izionworu et al., 2020; 2021).

In 2014, Arukalam et al., examined the corrosion inhibition effect of HEC for mild steel and aluminum in 0.5 M H₂SO₄ solution using weight loss and electrochemical techniques. They also investigated the inhibition of copper corrosion using hydroxyethyl cellulose (Arukalam et al., 2014b). Earlier, Arukalam et al., (2012) studied HEC as a corrosion inhibitor for mild steel in HCl solution. He recorded a maximum inhibition efficiency of 69.9% for HEC concentration of 2.5×10^{-3} M in 1 M HCl. Mobin and Rizvi (2017) investigated the efficacy of Hydroxyethyl cellulose and synergistic surfactant additives for carbon steel in 1M HCl. While Farhadian et al., (2012) modified hydroxyethyl cellulose as an inhibitor of mild steel corrosion in a 15% HCl solution at elevated temperatures. These researchers identified HEC as a polymer with great potential as an inhibitor. However, in these studies involving the use of HEC as an inhibitor, the use of aqueous solution of HEC as the inhibitor was not practiced. The focus of this research therefore, is to explore the innovative use of the aqueous solution of HEC as a corrosion inhibitor for mild steel industrial cleaning, acid descaling, and acid pickling action. Another reason for this investigation is to examine the effectiveness of using HEC directly in acid pickling of Well tubing since the common practice is to mix acid (HCl), water, inhibitor, and other additives as stabilizers to make up the pickling solution (Finšgar and Jackson, 2014). Consequently, in this study exploration into the use of aqueous solution of HEC as a corrosion inhibitor in the pickling action of mild steel is conducted, and the mechanisms by which HEC acts as a corrosion inhibitor in aqueous solution, its advantages over other traditional inhibitors, and applications across diverse industries are highlighted.

2. Materials and Method

The materials used in this investigation are 37% analytical grade HCl, Acetone, and absolute 99% ethanol. The 37% analytical grade HCl was serially diluted to 1 M HCl solution as discussed in previous research (Izionworu et al., 2021). 1×10^{-2} M aqueous solution of HEC (Figure 1) was used. To determine the best concentration of HEC for the experiment, four different concentrations of HEC (1 M, 0.1 M, 0.01 M, and 0.001 M) were experimentally subjected to initial weight loss measurement for 72 hours. 1 M HEC in 1L aqueous solution formed a solid mass. 0.01 M HEC which gave a good inhibition in distilled water and HCl was selected for this study. The 1 M HCl and 0.01 M HEC solutions were used to prepare the pickling solution following the ratios presented in Table 1.

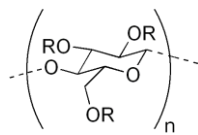


Figure 1 Structure of Hydroxyethyl cellulose (HEC)

Mild steel coupons composed of C = 0.05, Mn = 0.6, Ph = 0.36, Si = 0.03, Cr. = 0.05, and balance Fe, were used for the gravimetric analysis. A mild steel sheet measuring 0.14cm in thickness was mechanically cut into coupons 3 cm x 3 cm. The coupons were polished using emery paper as previously described in various research (Nik et al., 2023). They were then degreased in absolute ethanol, dried in acetone, weighed, and stored in a moisture-free desiccator to prevent corrosion before use. In the gravimetric experiment, previously weighed metal (mild steel) coupons were immersed in 300 ml of the test solution in an open beaker. The mild steel coupons were suspended using polyethylene twines and plastic cross bars. The solution temperature was maintained at ambient temperature. The coupons were withdrawn from the test solution at 24h intervals progressively for 120h and washed after each withdrawal, weighed, and returned to the corrodent solution as described in other research (Izionworu, et al., 2021; Onuegbu et al., 2020 and Khadraoui et al., 2016). Two coupons were immersed in each test solution for reproducibility. The values of weight loss in the absence and presence of the inhibitor were used to calculate the Corrosion rate (C_r), surface coverage (θ) and inhibition efficiency (IE%) using expression 1,2,3 respectively:

$$C_r = \frac{87600 \times \Delta W}{\rho A T} \quad (1)$$

$$\theta = \left(1 - \frac{C_{r1}}{C_{r2}}\right) \quad (2)$$

$$IE\% = \left(1 - \frac{C_{r1}}{C_{r2}}\right) \times 100 \quad (3)$$

With C_{r1} and C_{r2} representing corrosion rates in the inhibited and uninhibited corrodent solution, respectively.

Table 1 Proposed Pickling Solution Inhibitor Blend Ratio

ACID (1 M HCl)	HEC (0.1 M)	% HCl	% HEC
300	0	100	0
285	15	95	5
270	30	90	10
255	45	85	15
240	60	80	20

3. Results and Discussion

The results of the gravimetric experiment measurement are presented in Table 2, Figures 2,3,4 and 5. In the following discussion, the terms pickling solution, cleaning solution and descaling solution will be used interchangeably as the solutions being investigated essentially do the same work on the exposed substrate

3.1. Effect of the Presence and Absence of HEC Over the Immersion Time

The result presented in Table 2 and the plots of Figure 2 reveal that for a Blank acidic solution without the inhibitor (HEC), the corrosion rate ranged from 48.95 mmpy after 24 hours to 32.68 mmpy after 120 hours of immersion. However, in the presence of HEC as an inhibitor in the pickling solution, the corrosion rate of the mild steel was reduced continuously. The reduction in corrosion rate over the immersion time after the initial high value of 48.95 mmpy at 24 hours can be associated with the deposition of corrosion product on the surface of the substrate. This understanding agrees with the report of Singh and Mukherjee (2010). The corrosion product only reduced the contact between the aggressive acid ions and the metal surface but, did not stop the ongoing corrosion. This explains why the corrosion rate of 32.68 mmpy was reported after 120 hours. The implication of the effect of immersion time in the absence of HEC is that extended exposure to the metal substrate in a cleaning solution of this strength without an inhibitor (HEC) will gradually damage the metal substrate. The difference between the corrosion rate for the Blank solution and an inhibited cleaning solution presented in Table 2 indicates that with 20 % HEC composition of a 1 M HCl solution, a good descaling solution that will remove scales and rusts on the substrates is achieved. In this case, the longer immersion time favors HEC's adsorption on the metal surface.

Table 2 Calculated Values of Corrosion Rates (mmpy) and Surface Coverage of Mild Steel in the Presence and Absence of different concentrations of Hydroxyethyl cellulose in 1 M HCl for different Immersion Time

Inh. Conc. (Vol %)	Corrosion rate (mmpy)					Surface Coverage				
	Immersion Time (Hours)					Immersion Time (Hours)				
	24	48	72	96	120	24	48	72	96	120
Blank	48.95	44.36	40.73	35.52	32.68					
5	13.62	11.91	11.57	12.50	11.23	0.72	0.73	0.72	0.65	0.66
10	10.56	9.33	8.76	7.74	7.88	0.78	0.79	0.78	0.78	0.76
15	9.92	8.09	7.43	7.09	6.71	0.80	0.82	0.82	0.80	0.79
20	8.51	7.10	6.33	5.01	4.27	0.83	0.84	0.84	0.86	0.87

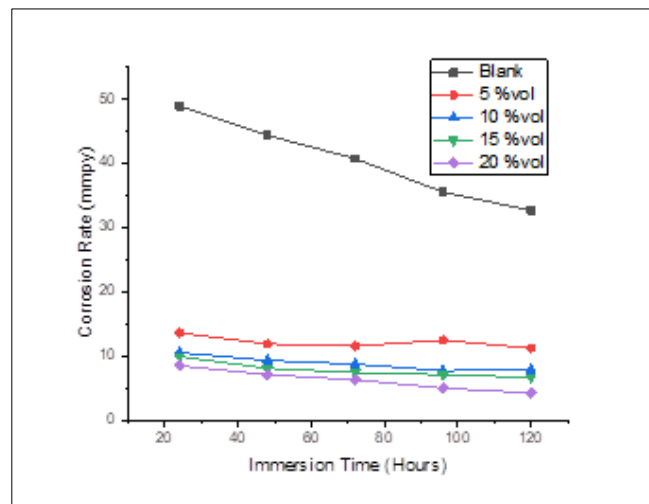


Figure 2 Corrosion rate of Mild Steel in the Absence and Presence of different concentrations of HEC in 1 M HCl for Different Immersion Time

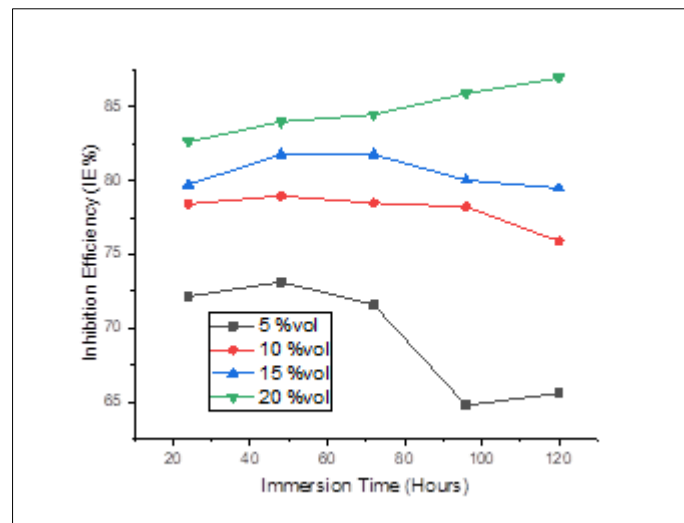


Figure 3 Inhibition Efficiency of HEC on mild steel corrosion in 1 M HCl for different Immersion Time

3.2. Influence of Concentration of HEC

The different concentrations of HEC used in the pickling solution resulted in a reduced corrosion rate as plotted in Figure 2 compared to pickling solutions without HEC. As discussed in the last section and as presented in the plots of Figure 4, cleaning solution with 20% HEC as an inhibitor reduced the corrosion rate appreciatively. This phenomenon could be explained by the inhibitor adsorbing on the mild steel surface and increasing the surface coverage (θ). This is observed in other reports (Arukalam et al., 2014). Arukalam et al. suggested the nature of polymers to gradually solvate as the reason for a gradual increase in surface coverage (Figure 4). Also, it can be attributed to the reduction in dissolution of mild steel in HCl due to the reduced attack of Cl ion. Comparing the corrosion rates for each concentration across the 120 hours of the test reveals that HEC remains relatively consistent as every 5% increase in HEC content further decreases the corrosion rate over time. This indicates stability in the inhibitor's performance indicating a chemisorption as previously reported.

However, further evaluation of Table 2 and Figure 3, shows the values of surface coverage and plots of the Inhibition efficiency of HEC respectively. The values indicate a loss of inhibition effect for 5, 10, and 15 % volume concentrations of HEC in the cleaning solution after 48 hours. This shows a loss of bonding strength likely due to the desorption of the molecules of HEC on the mild steel surface. The desorption may have resulted from a few Hydroxyl (-OH) functional

groups donated by a low concentration of HEC to the surface of the mild steel. This behavior suggests an unsteady Inhibition Efficiency for HEC at lower concentrations. Figures 3 and 5 show a noticeable increase in IE% as the concentration of HEC increased to 20 % vol suggesting a stable inhibitor at a higher concentration. Also the corrosion rate of the mild steel reduced at higher concentrations of HEC as seen in Figure 4. The observed increase can be attributed to more –OH groups donated to the metal surface. It can also be attributed to the ability of HEC to encapsulate chloride ions in the solution.

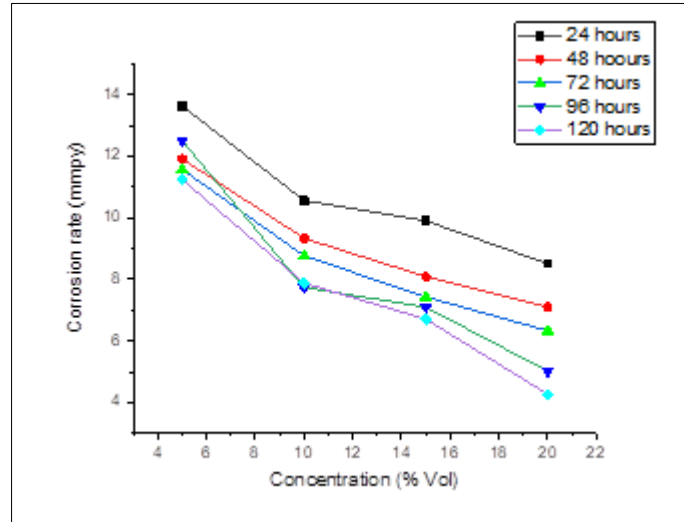


Figure 4 Influence of different concentrations of HEC on the Corrosion rate of Mild Steel in 1 M HCl for different Immersion Time

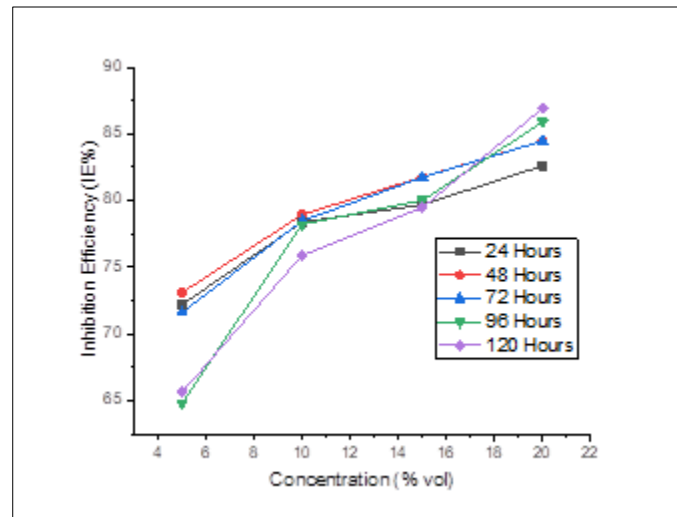


Figure 5 Influence of different concentration of HEC on HEC Inhibition Efficiency of Mild Steel corrosion in 1 M HCl for different Immersion Time

3.3. Mechanism of HEC Inhibition Behavior

The presence of the -OH functional group in HEC as an electron-donating moiety facilitates heavy bonding that enables the adsorption of HEC molecules on the surface of the substrate. This is in agreement with the report of Assad and Kumar (2021), Mobin and Rizvi (2017), and the previous report by Arukalam et al., (2014). Arukalam and coauthors described the adsorption as chemisorption, chemical adsorption resulting from the presence of the polar functional group –OH. Also, it is worthy of note that HEC acts as a microsphere to entrap Cl ion in an acidic solution of HCl since it is incompatible with strong oxidizing agents, acid chlorides, and acid anhydrides (National Center for Biotechnology Information, 2024; Chemicalbook, 2024). This is possible as HEC tends to engage with chlorides in partial hydrophobization although this happens with higher fatty acids (C12 and C18) (Heinze and Liebert, 2012), in this case, HEC encapsulates Cl ions as illustrated in Figure 6 denying the Cl ions access to the metal surface. Also, the molecules of

HEC in the presence of Cl ions can reduce the surface tension of water, hence reducing the cohesive force of water on the metal surface, when that happens HEC blocks out the active corrosion sites since it can get adsorbed on the metal via the $-OH$ ion linkage.

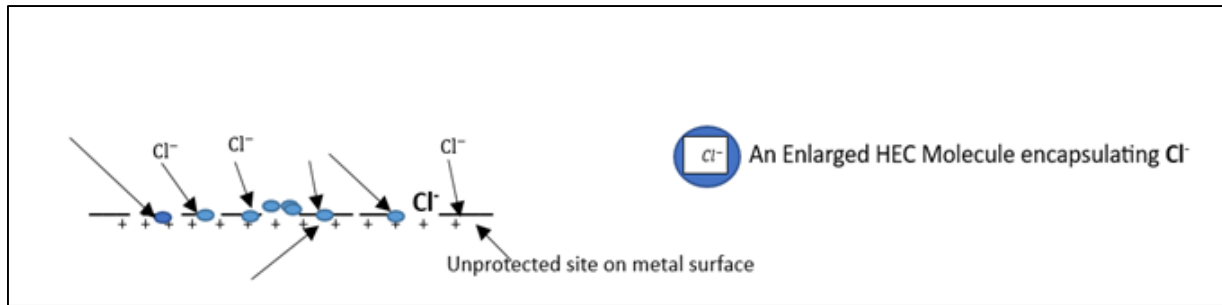


Figure 6 Schematic of the protective action of HEC

4. Conclusion

The study suggests that the Hydroxyethyl Cellulose inhibitor effectively reduces the corrosion rate of mild steel in 1 M HCl solution, and its effectiveness increases with higher inhibitor concentration. The inhibition efficiency and surface coverage increased with an increase in the concentration of HEC. The adsorption of HEC on the surface of mild steel is spontaneous due to the presence of the hydroxyl ($-OH$) functional group in HEC that is donated to the bond at the corrosion active sites. So, the higher the concentration of HEC the more the $-OH$ functional groups are available for bonding and hence mild steel surface coverage. Also, HEC can reduce surface water contact resulting in reduced opportunity for Cl ion attack. The natural properties of HEC as modified cellulose make it a readily available inhibitor that can be used during Oil Well tubing acid pickling action.

Potentiodynamic polarization test, surface morphology, and theoretical analysis are recommended to further elucidate the capability of Aqueous HEC for acid-cleaning actions. Gravimetric Analysis at higher temperatures will confirm the suggested chemisorption adsorption of HEC on mild steel substrate in an HCl environment.

Compliance with ethical standards

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Disclosure of conflict of interest

No conflict of interest to be disclosed.

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