A Descriptive Study On The Use Of Nanomaterials As Corrosion Inhibitors In Oil And Gas Industry

Parijat Burhagohain, Gitalee Sharma

Abstract: In oil and gas industry, corrosion is electrochemical caused by the presence of some highly corrosive medium like CO₂, SO₂ and free water. It has become one of the most challenging problems leading to the loss of billions of money every year. Use of Corrosion inhibitors is the most popular corrosion mitigation technique. Organic corrosion inhibitors containing N, S and O atoms offer excellent inhibition efficiency, but may be toxic either in their synthesis or in application. However, nanomaterials, a new emerging alternative for corrosion inhibitors with excellent biocompatibility and inhibition efficiencies has arisen as a solution to the problem of toxicity. Nanoparticles with large surface area are expected to form a uniform film on the metal surface, thereby making them advantageous over other organic inhibitors. This paper presents an evocative account of nanomaterials used as corrosion inhibitors in the field of oil and gas industry.

Index Terms: Corrosion, Nanomaterials, Corrosion Inhibitors, Oil and Gas Industry,

1. INTRODUCTION

In oil and gas industry, corrosion of the steel pipelines is due to the occurrence of various electrochemical reactions on coming in contact with corrosive environment like CO₂, SO₂ and free water [1]. CO₂ corrosion is recognized to be the main potent corrosive agent in oil and gas industry [2]. API5L grade carbon steel, the most commonly used material for oil and gas transportation possessing excellent mechanical properties has however, inefficient corrosion resistance [3]. Various corrosion mitigation techniques are used in oil and gas industry, which includes material selection, proper designing, internal and external coatings, cathodic and anodic protection and inhibitors, the most popular one. Inhibitors are chemicals used to protect surface of the materials in pipelines for corrosion prevention. These chemicals either merge with the material or react with the impurities present in a corrosive environment [4]. They restrict the rate of anodic or cathodic process by blocking the active site on the metal surface. Alternately, they can increase the potential of the surface for the metal to enter the passivation region with the formation of a natural oxide film [5]. Inhibitors are mainly of two types, anodic inhibitors and cathodic inhibitors. Organic compounds like mercaptans, amines, substituted urea, heavy metal soaps and heterocyclic O, N and S containing molecules such as imidazolines, amines, amides, quaternary ammonium salts etc are being extensively used as cathodic corrosion inhibitors [6]. However, the toxicity of these inhibitors either in the process of synthesis or in application has slacked off their utility. To remove toxicity, some natural plant extracts and natural biodegradable polymers also have been synthesized [7]. But short shelf life period has made their study a stag. As an elucidation to this problem, the study of nanomaterials as corrosion inhibitor is significant.

Nanomaterials are advantageous due to their low toxicity, cost effectiveness and easy production with high inhibition efficiencies. They possess some unique properties in terms of physical, chemical, mechanical and physicochemical due their large surface area. This causes increase of active centers thereby facilitating adsorption phenomena [8]. They can positively adsorb on the metal surface that undergoes corrosion either through physisorption or chemisorption, and thus inhibits corrosion of material. Further, incorporation of nanomaterials with plant extracts and natural polymers satisfactorily enhance inhibition efficiency. [8]. This paper presents the spectrum of applications of nanomaterials as corrosion inhibitors for mild steel used mainly in oil and gas industry.

2 TYPES OF NANOMATERIALS AS CORROSION INHIBITORS

2.1 Metal/ Metal Oxide Nanoparticles

Metal nanoparticles are good anticorrosion agent. Various reports have been found in literature for application of metal nanoparticles as corrosion inhibitor. Obot et.al studied the inhibitive properties of synthesized Ag nanoparticles for mild steel in HCl solution. They synthesized Ag nanoparticles using natural honey as both reducing and capping agent with irradiation to sunlight. The inhibition efficiency was found to be 91.5% with a very low inhibition concentration with addition of AgNps [9]. L.M. Rivera-Grau et.al worked on the effect of hydroxyethyl imidazoline inhibitor in conjunction with Ag nanoparticles against CO₂ corrosion for mild steel in NaCl and diesel solution. Incorporation of Ag nanoparticles increased inhibition efficiency close to 99% at a very low inhibition concentration [10]. M. M. Solomon et.al formulated a green corrosion inhibitor with natural polymer and nanoparticles for mild steel against acid corrosion. They synthesized gum arabic which was used in conjunction with Ag nanoparticles (GA-AgNPs) as anti-corrosive agent from natural honey but its inhibition efficiencies were found to be very less (44%) when studied for mild steel against acid corrosion. Incorporation of Ag nanoparticles to GA matrix significantly increased the inhibitor performance up to 92.93% in HCl solution and 90.99% in H₂SO₄ solution [11]. Migahed et.al investigated the

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* Parijat Burhagohain is currently pursuing PhD program in Chemistry in Dibrugarh University, Assam, India.

* Gitalee Sharma is currently an Assistant Professor in the Department of Engineering Chemistry, DUET, Dibrugarh University, Assam, India, E-mail: gitaleesharma@dibru.ac.in
inhibition action of dodecyl cysteine hydrochloride, incorporated with gold nanoparticles and found that gold nanoparticles had synergistic effect on the inhibition performance of dodecyl cystine hydrochloride. Incorporation of gold nanoparticles raised the inhibition efficiency from 76.8% to 90.8% at 175 ppm inhibitor concentration [12]. K.L. Palanisami et.al synthesized a green corrosion inhibitor from vegetable oil, viz. linseed oil and olive oil, which was incorporated with iron oxide nanoparticles. With linseed oil stabilized nanoparticles the inhibition efficiency was 69.11% and with olive oil stabilized nanoparticles it was 80.88% [13]. Atta et.al modified magnetite nanoparticles with rose amidoxin as corrosion inhibitor for mild steel. The inhibition efficiency was found to reach 96.8% at an inhibitor concentration of 150 ppm [14]. Zubillaga et.al studied anticorrosion properties for titanium oxide nanoparticles for carbon steel and stainless steel [15]. Nickel zinc ferrite nanoparticles was synthesized by Chaudhary et.al whose inhibition effect was studied for API 5L X80 carbon steel against H$_2$SO$_4$ as corrosion medium. It was observed that a very small concentration of this nanoparticle offered excellent anticorrosive activity [16].

2.2 Nanocomposites and Nanogels

Polymer composites as coatings inhibit corrosion process for carbon steel. However, the limitation is that they have a poor adhering capacity to the metal surface. Modifications are done by incorporating nanomaterials to polymer composites to serve as excellent corrosion inhibitor. Metal oxide nanoparticles may agglomerate causing decrease in their inhibitive properties. Hence, for better dispersion of metal oxide nanoparticles in solutions and in coatings nanocomposite are used [17]. El-Mahdy et.al. synthesized TiO$_2$ nanoparticles in PNa-AMPS composite, which was found to be effective corrosion inhibitor for carbon steel against acid corrosion with an inhibition efficiency of 91% at 250 ppm concentration [18]. Graphene/polyetherimide (PEI) nanocomposites are employed by R V Dennis et.al as a replacement for hexavalent chromium in anticorrosive coatings [19]. Atta et.al studied poly sodium acrylic acid modified magnetite nanocomposite as corrosion inhibitor for carbon steel with 99% inhibition efficiency at 50 ppm inhibitor concentration [20]. Further, polyacrylamide (PAM) super paramagnetic magnetite core-shell nanogels were synthesized by A. M. Atta et.al with controllable particle size from 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylic acid (AA) and acrylamide (AM) through solution polymerization at room temperatures in an initiator free aqueous system. The synthesized nanogels proved to be efficient corrosion inhibitor for carbon steel against acid corrosion [21]. Plant extracts, being rich source of various phytochemicals are also used to form nanoparticles. They moreover, possess multiple adsorption sites on metal surfaces to provide corrosion inhibition. E. A. Essien et.al. experimented for the first time olive-Ti nanocomposite from ethanolic extract of olive leaves in presence of TiCl$_4$ solution. The prepared nanocomposite successfully inhibited acid corrosion of mild steel with an inhibition efficiency that increased from 83.5% to 93.4% after incorporation of Ti nanoparticles at a very low inhibitor concentration [22].

2.3 Nanocontainers as Inhibitor Storage

For uniform dispersion of corrosion inhibitors, nanocontainers encapsulation is crucial, provided nanocontainers have a good compatibility to the passive coating matrix. It also allows corrosion inhibitors to release in quick response to the change in pH of surroundings. They can accommodate the corrosion inhibitor without effluence and release it after the rapture of the coating [17]. T. Chen et.al investigated some hollow mesoporous nanoparticles as nanocontainers for corrosion inhibition which proved to be promising [23]. A comparative study on the use of polyelectrolyte modified halloysite nanotubes (PHN), polyelectrolyte modified silica nanoparticles (PSN) and polyelectrolyte modified nanocapsules (PNC) was carried out by Zafari et.al for encapsulating benzo triazole corrosion inhibitor [24]. J. M. Falcona et.al studied the use of silica nanoparticles for encapsulation of dodecylamine corrosion inhibitor [25]. A smart polymer coating consisting of alkyl paint with silica nanoparticles was developed as nanocontainers for corrosion inhibition by C. Avila-Gonzalez et.al. [26]. K. Kamburova et.al. encapsulated hametite nanoparticles with polyacrylic acid (PAA) and polydiallyldimethylammonium chloride (PDMAAAC) as nanocontainers for release of benzo triazole corrosion inhibitor [27]. Thus the nanocontainers studied till date have proved to be promising anticorrosive agents.

2.4 Carbon dots

Carbon dots (CDs) are fluorescent nanomaterials with stable chemical properties, low toxicity and biocompatibility. They are effectively used as environmentally safe corrosion inhibitors. M. Cui et.al prepared N-doped carbon dots and evaluated its action as corrosion inhibitor for carbon steel in 1M HCl for the first time. The inhibition efficiency was found to be 90.9% at 10 mg/L concentration [28]. H. Cen et.al synthesized N and S co-doped carbon dots and studied their corrosion inhibition efficiency for carbon steel in CO$_2$ saturated NaCl solution. Doping of CDs with highly electronegative N and S atoms effectively improved inhibition properties of CDs upto 93% at 50 mg/L concentration [29].

3. Results and Discussion

The comparison of the different nanomaterials detailed in this paper was made based on their inhibition concentration (IC) and % inhibition efficiency (IE) which is highlighted in table 1.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Inhibitor Name</th>
<th>Item Code</th>
<th>IC (ppm)</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/16</td>
<td>Ni-Zn-Ferrite Nps</td>
<td>CI1</td>
<td>8.4</td>
<td>72.64</td>
</tr>
<tr>
<td>2/28</td>
<td>N-doped CDs</td>
<td>CI2</td>
<td>10</td>
<td>90.9</td>
</tr>
<tr>
<td>3/9</td>
<td>Ag NPs</td>
<td>CI3</td>
<td>6</td>
<td>91.5</td>
</tr>
<tr>
<td>4/10</td>
<td>HEI and Ag NPs</td>
<td>CI4</td>
<td>20</td>
<td>99</td>
</tr>
<tr>
<td>5/29</td>
<td>N.S co-doped CDs</td>
<td>CI5</td>
<td>50</td>
<td>93.5</td>
</tr>
<tr>
<td>6/20</td>
<td>PNa-AA &amp; Magnetite NPs</td>
<td>CI6</td>
<td>50</td>
<td>99</td>
</tr>
<tr>
<td>7/13</td>
<td>Linseed oil-IONPs</td>
<td>CI7</td>
<td>-</td>
<td>69.11</td>
</tr>
<tr>
<td>8/13</td>
<td>Olive oil-IONPs</td>
<td>CI8</td>
<td>-</td>
<td>80.33</td>
</tr>
<tr>
<td>9/14</td>
<td>Rose amidoxin&amp; magnetite</td>
<td>CI9</td>
<td>150</td>
<td>96.8</td>
</tr>
<tr>
<td>10/12</td>
<td>DCHS+Au nanoparticles</td>
<td>CI10</td>
<td>175</td>
<td>90.8</td>
</tr>
<tr>
<td>11/18</td>
<td>PNa-AMPS&amp; TiO2 NPs</td>
<td>CI11</td>
<td>250</td>
<td>91</td>
</tr>
<tr>
<td>12/21</td>
<td>PAMPS-Na magnetite</td>
<td>CI12</td>
<td>250</td>
<td>81.9</td>
</tr>
<tr>
<td>13/21</td>
<td>AMPS/AA magnetite</td>
<td>CI13</td>
<td>250</td>
<td>89.9</td>
</tr>
</tbody>
</table>
The studies revealed that the nanomaterial corrosion inhibitor CI4 proved to be the most potent as it shows a very high corrosion efficiency of 99% with a low concentration of 20 ppm in a blended solution of NaCl and diesel. CI4, a metal oxide nanoparticulate inhibitor, prepared with hydroxyethyl imidazoline inhibitor in conjunction with Ag nanoparticles have great adsorption properties because of N atom in its structural framework. Hence the result is the high % inhibition efficiency even at a very low inhibition concentration. Next in the list is CI6 with an identical efficiency of 99% but at a little higher inhibition concentration of 50 ppm. The poly sodium acrylate modified magnetite nanocomposite in CI6 also facilitate efficient adsorption of it on the corroded metal, because of the presence of high binding O atom in it, thereby resulting in high % inhibition efficiency. The other corrosion inhibitors CI5, CI9, CI10, CI11, CI14, CI15 and CI16, though have a relatively high % IE, but at the cost of gradually increasing inhibition concentration. CI2 and CI3, shows the maximum inhibition efficiency at low concentration of 10 ppm and 6 ppm but its %IE is far behind the benchmark CI4. The corrosion inhibitors CI7 and CI8 prepared from plant extracts however, showed low %IE at some unknown concentration. The comparative evaluation of the nanomaterials studied in this paper can also be represented graphically as scatter plot as shown in figure 1 below.

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Fig 1: Scatter Plot Representation of the Comparative Evaluation of a Few Nanomaterials.

The plot shows that the corrosion inhibitors CI4 and CI6 are at the highest position in the graph and at a very low concentration compared to the other inhibitors. Hence they behave as benchmark for the others.

4 CONCLUSION

Nanomaterials, because of their low toxicity and large surface area for efficient adsorption has occupied a prime place as corrosion inhibitor of mild steel. Although in its nascent state, researchers all over the globe has synthesized different categories of nanomaterials and evaluated their % corrosion efficiency with efficiency concentration. On comparing the % IE for the nanomaterial corrosion inhibitors discussed in this paper, it was observed that CI4 overreached the other inhibitors and hence can be considered as a benchmark for the other inhibitors noted here. CI6 listed second in position having the inhibition concentration higher than CI4. Thus, from the study detailed in this paper, it can be inferred that nanomaterials with modifications and keeping CI4 as benchmark has great potential to behave as efficient corrosion inhibitor to mild steel.

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