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Formulation And Characterization Of Nanoemulsion Coatings From Azadirachta indica

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Abstract: An attempt has been made to develop nano emulsion coatings based on Azadirachta indica (neem oil) as a replacement of organic solvent based coatings system in surface finishing industry for environmental protection, and for public health and safety. Neem oil nanoemulsion was prepared using neem oil, tween 20 . A mean droplet size ranging from 31.03 - 251.43 nm, was formulated for various concentrations of oil and surfactant. The stable emulsion ratio was taken for the study. Coatings on the steel surface were done using electrophoretic deposition method.
Different combinations of stabilizers were tried and characterized using AFM. The AFM images confirmed the formation of nano emulsified coatings on steel.
Keywords : azadirachta indica ; eco-friendly coatings; nanoemulsion; polymer coatings

1.Introduction

Protection of materials from corrosion is a major deal now a day. Materials like big vessels, water pipes, coolant pipes in nuclear reactors, submerged materials in sea environment face a lot of problems due to corrosion. Antifouling paints are used to protect materials from corrosion. Most of these paints contain trace metals as a component. When metals in water, metal ions leaching are unavoidable. This would finally lead to heavy metal toxicity to aquatic animals [1]. In order to find out solution green chemistry is the only way out. Nanoemulsions is sub-micron oil in water emulsions with droplet diameter in nanoscale. They are thermodynamically stable and translucent dispersions of oil and water having droplet size in the range of 100 – 600 nm [2,3] . Nanoemulsions are prepared by low energy methods such as phase inversion temperature (PIT) emulsification [4] Phase inversion composition [5] or by high shear forces using high pressure homogenizers or ultrasonic generators [6].

Recently nanoemulsions are identified as a promising delivery system. Nanoemulsions preparation of natural oil could be the best technology for protecting materials from corrosion. Neem, (Azadirachta indica) is the traditional plant of India, having many medicinal properties,besides its biocidal nature [7]. This nature of neem protects materials from fouling, when it is coated on to the surface.

The replacement of organic solvent based coatings system by water based systems in surface finishing industry is of recent coating systems for environmental protection, and for public health and safety. However, the coating quality for the water-based system is in general inferior to that of the organic solvent based systems. The nano-sized polymer emulsions developed in recent years provide a breakthrough in this area, because of its superior coating quality with enviable properties has led to promising market potentials, particularly where regulations for the reduction of organic solvent have been imposed on the architectural coating industry. As far as we know, no concrete report is available for the use of neem oil nanoemulsion as electrolyte to produce nanoemulsified poly(ethylene glycol) and TiO2 coatings on mild steel. This is the first indigenous research on coating of nano-emulsion + Poly(ethylene glycol) and nano-emulsion + PEG + TiO2.

2. Experimental methods

2.1 Materials

Azadirachta indica (Neem oil) was procured from medical shop, Vellore, Tamilnadu. Tween 20 (polyoxyethylene (20) sorbitan monolaurate) was supplied by S.D.-Fine Chem. Limited, Mumbai. Deionized water (Milli-Q water, Millipore Corporation) was used for all experiments. All chemicals were of analytical grade.

2.2 Preparation of neem nanoemulsion:

We prepared O/W emulsion using neem oil, tween 20 and water as the continuous phase. Ultrasonication of 1:3 ratios of neem oil and tween 20, we obtained nanoemulsion of size 31.03 nm. Larger emulsion droplets (251.43 nm) shifted to a smaller size of 31.03 nm with an increase in tween 20 concentrations. At this ratio, the nanoemulsion was stable.

2.3 Characterization of Neem nanoemulsion

2.3.1 Droplet Size and Size Distribution

Droplet size and size distribution of neem oil nanoemulsion were determined using Brookhaven Particle Size Analyzer (90S). Nanoemulsions were diluted with water to reduce multiple scattering effects prior to each experiment. Droplet size was described as size in nm and poly dispersity index (PDI) for size distribution. Each measurement was carried out in triplicates.

2.3.2 Atomic force microscope (AFM)

The shape and size of neem oil nanoemulsion was determined using AFM (Nanosurf easy surf 2). Nanoemulsions were diluted with water before it was used for AFM study. AFM studies were carried out by drop coating the diluted nanoemulsion onto a glass slide and dried in oven. It was scanned at of 100 mV/s in the range 50m×50m using Nanosurf easy surf 2 (Switzerland).

2.3.3 Transmission electron microscopy (TEM)

The morphology of the nanoemulsion was determined by transmission electron microscopy (TEM). For TEM studies, a drop of nanoemulsion was placed on copper grid and allowed to dry in vacuum. The transmission electron micrographs were taken using Tecnai G-10, an 80 kV TEM with a W-source and an ultra high resolution pole piece.

2.3.4 Viscosity

Viscosity of nanoemulsion was measured using Thermo Haake Reo Scope at 25ºC. Experiments were performed in triplicates.

2.3.5 pH

The nanoemulsion pH were checked by a pH meter (model HI 8417, Hanna Instruments Inc., Woonsocket, USA), at 20 ± 1 ˚C.

2.3.6 Stability of Nanoemulsion

Stability study was performed by centrifuging the nanoemulsion at 3,500 rpm for 30 min[13]. The stability was also checked at refrigerator temperature (4 ˚C) and room temperature (25 ˚C).

2.3.7 Zeta potential Measurements

Zeta potential of nanoemulsion was determined using Brookhaven 90 plus Zeta Analyzer.

2.4 Preparation of eco friendly nanocoatings on mild steel:

Neem oil based nanoemulsion coatings were prepared to use different combinations of TiO_2, PEG. Mild steel specimens of size 2 x 5 cm^2 were mechanically polished and then decreased with acetone. Then the panels are subjected to electrodeposition both in the nano emulsion as well as nano-emulsion + Poly(ethylene glycol) or PEG and nano-emulsion + PEG + TiO_2. The optimized concentrations of PEG (Molecular weight – 45,000 g $mole^{-1}$) and TiO_2 (particle size 1μm) are 130 ml and 20 g per litre. Anode and cathode were made of mild steel and separated by lugging capillary. The voltage (16V) was passed through the electrolyte for 15 minutes. Then the samples were removed from the plating bath and annealed at 200ºC for 30 minutes.

2.5 Characterization of coatings

AFM is a versatile technique to explore the surface morphology at nano-to micro-scale and has become a new choice to study the influence of inhibitor on the generation and the progress of the corrosion at the metal/solution interface . The two dimensional (2D), AFM morphologies and the AFM cross sectional profile for electrodeposited, nano emulsified panels were analyzed by AFM using Nanosurf easy scan 2 system. The results are presented and discussed.

3.Results and discussions

3.1Physico chemical nature of neem nanoemulsion:

The nanoemulsion formulation of 1:0.30 ratio showed least viscosity (1.67± 0.003) compared to other formulations. This may be due to the increase in surfactant concentration. With the increase in surfactant concentration, the pH of the nanoemulsion formulation increased. Thermo stability of nanoemulsion differentiates it from emulsions with kinetic stability and eventually phases separation. Steric effect plays an important role in stabilization of nanoemulsion. The nanoformulations were found to be physically stable at room temperature. Phase separation was not observed. Our results showed that the formulated nanoemulsions survived the stability tests. Zeta potential of nanoemulsion was between -26.87 mV and -33.94 mV confirming the stability of formulated nanoemulsions.

3.2 Characterization of nanoemulsions

3.2.1 Droplet size and Size distribution

The least droplet size of the nanoemulsion consisting of 1 part oil (6 %) and 3 part surfactant (18 %) was 31.03 ± 1.73 nm. This nanoemulsion was stable at 1:3 ratios. This is in accordance with the data reported by Kale and Allen [8] that the addition of surfactant to nanoemulsion systems caused the interfacial film to condense and stabilize, resulting in small droplet size. Polydispersity of droplet size was found to be 0.211, 0.364 and 0.262 for the nanoemulsion formulations of oil and surfactant 1:0.30, 1:1.5 and 1:3 respectively**.**

3.2.2 Atomic Force Microscope (AFM)

The AFM studies was used to analyze the shape of the nanoemulsion as well as physical properties of nanoemulsified coatings such as root mean-square roughness, average roughness and peak-to-valley value . The shape of the nanoemulsion was approximately spherical in morphology (**Figure 1). The mean diameter was 48.2 nm.**

3.3. Characterization of neem nanoemulsion coatings

The two dimensional AFM morphology for uncoated mild steel, mild steel coated with Nano emulsion, mild steel coated with N.E+PEG, N.E + PEG +TiO_2 were given in figures (2-5) and the results are presented in **table 1.**

3.3.1-Interpretation of Root Mean-Square Roughness, Average Roughness and Peak-to-Valley Value

AFM image analysis was performed to obtain the average roughness, Ra (the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square roughness, Rq (the average of the measured height deviations taken within the evaluation length and measured from the mean line), and the maximum peak-to-valley, P-V, height values (largest single peak-to-valley height in five adjoining sampling heights. Table 1 is a summary of R_q, R_a, P-V values for mild steel surface coated with nano emulsion, PEG, PEG + TiO_2 . Figure 2 displays the surface topography of un-plated metal surface. The value of R_q, R_a and P-V height for the polished carbon steel surface (reference sample) is 101.82 nm, 67.51 nm, and 437.63 nm respectively. Figure 3 indicates the nano emulsion coated surface.The R_q, R_a and P-V height values for the mild steel surface are 204.83 nm, 173.41 nm, and 510 nm, respectively. These data suggest that nano emulsion coated mild steel surface has a greater surface roughness than the un plated metal surface, which indicates the formation of nano emulsion coatings on the steel surface [9-11].

Figure 4 shows the mild steel surface coated with nano emulsion and poly ethylene glycol.The R_q, R_a and P-V height values for the steel surface are 124.82 nm, 106.52 nm, and 327.2 nm, respectively. The Rq, Ra and P-V height values are considerably lower than nano emulsion coated mild steel due to the incorporation polymer in the coating. The parameters in figure 4 confirm that the surface is smoother than nano emulsion coated mild steel because of the existence of poly ethylene glycol into the nano emulsion coatings [12].

The AFM parameters for nanoemulsified coatings with PEG+TiO_2 is given in figure 5. It is evident from figure 5 that, the R_q, R_a and P-V height values are 72.07 nm, 56.22 nm and 238.89 nm respectively. The smoothness of the surface is due to the formation of a compact passive film of TiO_2 embedded in PEG and nano emulsified coatings. Similar observation has been reported earlier for the corrosion inhibition of mild steel in acidic medium [13-15].

Table 1 AFM data for Mild steel coated with nano emulsion, poly ethylene glycol and TiO_2.

Samples	Root mean square roughness, R_q (nm)	Average roughness, R_a (nm)	Mean of maximum Peak-to-Valley Height (nm)
Polished Mild steel	101.82	67.51	437.63
M.S coated with Nano emulsion	204.83	173.41	510
M.S coated with Nano emulsion + PEG	124.82	106.52	327.2
M.S coated with Nano emulsion + PEG+TiO_2	72.07	56.22	238.89

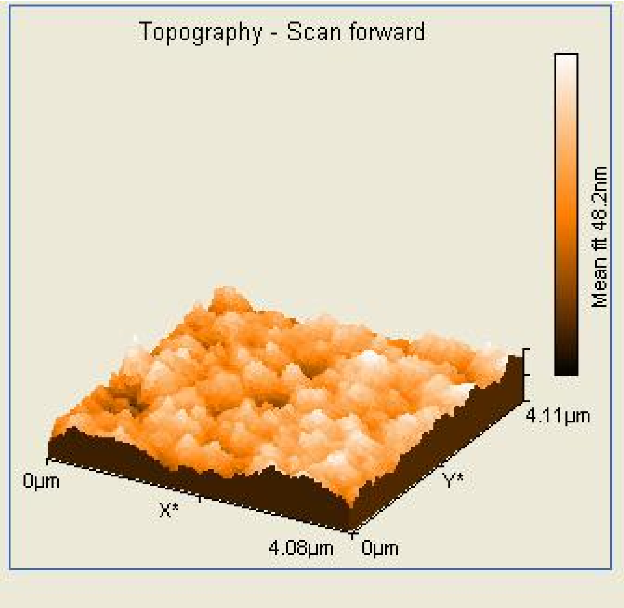

Figure 1- AFM- Surface morphology of nano emulsion

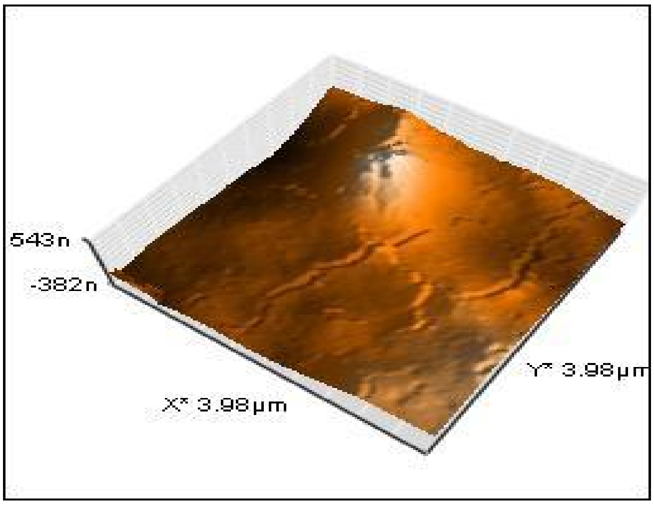

Figure 2- Un plated Mild steel specimen immersed in nano emulsion

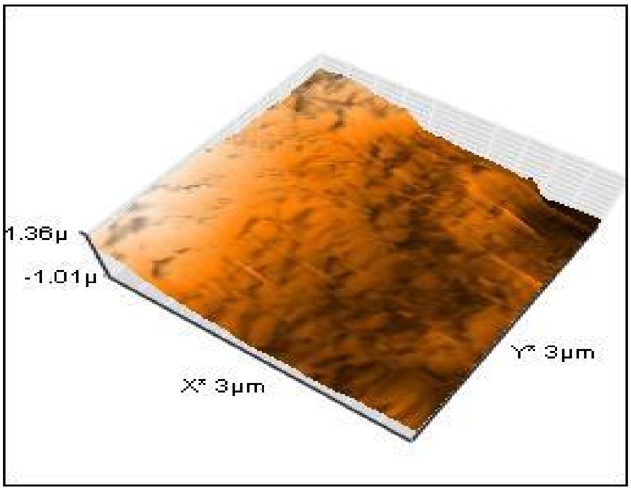

Figure 3- Mild steel specimen coated with nano emulsion

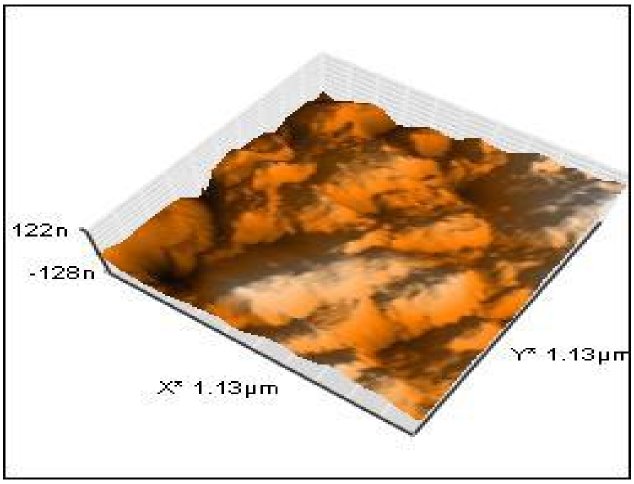

Figure 4- Mild steel specimen coated with nano emulsion and poly ethylene glycol

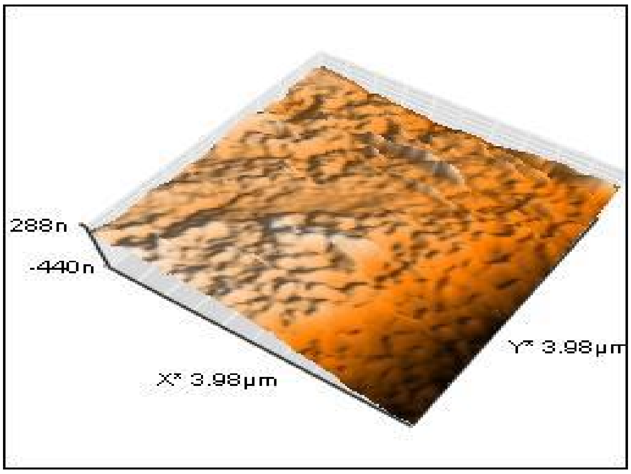

Figure 5- Mild steel specimen coated with nano emulsion + poly ethylene glycol+TiO2

4. Conclusion:

A novel nanoemulsion coatings on mild steel embedded with poly(ethylene glycol) and TiO_2 particles were obtained as a replacement of organic solvent system in plating industries. These coatings deserve much attention on environmental concern with wide applications in surface finishing industry.

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