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Nano CuO incorporated Polyethylene Glycol Hydrogel Coating over Surface Modified Polyethylene Aquaculture Cage Nets to Combat Biofouling

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Abstract

Biofouling on aquaculture cage netting is a major problem and its management costs the quarter of the total budget. The present study aimed to develop an antifouling coating over surface modified polyethylene cage netting. Polyethylene nettings were surface modified with polyaniline and the same surface was coated with nano CuO incorporated polyethylene glycol hydrogel. Strong and uniform coating of polyaniline and hydrogel were formed over the nettings. This was evidenced by FTIR, AFM and SEM studies. The treated cage nets were exposed to the test sites of Cochin estuary for three months and they exhibited a significant reduction in fouling compared to untreated nettings. The nano CuO incorporated hydrogel coating was about 53% more efficient than control. The CuO hydrogel was semi hydrophilic in nature, defect-free and more compact surface. These led to the protein inhibition, thereby biofouling resistance. The coating is a potential candidate for preventing biofouling in the cage nets.

Keywords: biofouling; hydrogel; cage aquaculture; polyaniline

Introduction

Submerged structures in the marine environments are susceptible to the accumulation of undesirable organisms like microbes, algae, plants and fouling organisms, termed as biofouling. Accumulation of fouling organisms in the marine structures, aquaculture cages and ship hulls is a menace and its removal is expensive. Biofouling initiates after the formation of a thin film called biofilm, formed by the adsorption of organic molecules like protein over the surface (Kobayashi & Ikacia, 1991). Thereafter, macroorganisms like barnacles, bryozoans, mollusks, seaweeds and hydroids get attracted to the surfaces. A surface capable to prevent the protein adsorption during submerged condition in the marine or estuarine environment will be free from biofilm formation and hence the attachment of macrofoulers. The major prerequisite for a protein resistant surface is that it must have hydrogen bond acceptors, hydrophilic characteristics and with zero net charge (Rosenhahn et al., 2010).

Much attention was paid in recent years to develop the polymeric antifouling surfaces for application in water treatment, antimicrobial coating, submerged structures and biomedical applications (Chen et al., 2011; Li et al., 2012; Bellotti et al., 2012). The major polymeric derivatives used for the purpose were polyethylene glycol derivatives and zwitterionic polymers or copolymers (Peng et al., 2010; Zhao et al., 2011; Li et al., 2012; Ashraf & Edwin, 2016). Hydrogels are synthesized from natural to synthetic polymers (Annabi et al., 2014). Hydrogels support micro environments which enable anchorage, nutrient support, signaling, structural integrity and homoeostasis similar to extracellular polymeric substances (Annabi et al., 2014; Peppas et al., 2006). General methods to improve hydrogel material characteristics by modifying the polymeric properties and density of cross-linking. These approaches limit the mechanical and electrical properties and nutrient transport of the hydrogel. Incorporation of nano materials into the hydrogel matrix improve the biological, mechanical and electrical properties (Shin et al., 2013; Cha et al., 2014; Xavier et al., 2015; Dvir et al., 2011). Nano material incorporated hydrogels are extensively applied for developing

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multifunctional tissues and other clinical trials (Ramon-Azcon et al., 2013).

Polyethylene glycol hydrogels are inert, resistant to protein adhesion and display soft tissue like character (Hoffman & Benoit, 2013; Hoffman et al., 2013; Vats & Benoit, 2013; Shubin et al., 2015; Van Hove et al., 2015a,b; Ahearne et al., 2005). These properties make it an important molecule to develop antifouling strategies and to study cell – material interactions (Vats et al., 2017). Polyethylene glycol (PEG) and their derivatives exhibited efficient antifouling properties. It has been extensively employed in commercial antifouling operations (Kang et al., 2007; Susanto & Ulbricht, 2007; Sagle et al., 2009). Polyethylene glycol methacrylate hydrogels are having increased swelling in aqueous environments and this will lead to decreased adhesion of proteins (Kulik & Ikada, 1996; Ekblad et al., 2008; Resmi et al., 2017). The properties like mechanical, microstructure and water uptake can be tuned by altering the PEG monomers (Zhang et al., 2011; Knop et al., 2010). Presence of weak basic ether moiety in the molecule and reduced polymer-water interfacial energy made the PEG hydrogel as an effective antifouling polymer (Chen et al., 2008; Krishnan et al., 2008). It was reported that swollen hydrogels are encouraging slight protein adsorption and this will deteriorate the efficiency (Lei et al., 2013). The nano CuO incorporated PEG hydrogels in nylon nettings and their three months exposure in the marine environment exhibited excellent fouling resistance (Ashraf & Edwin, 2016). Here CuO acted synergistically to resist fouling in the nylon nettings.

Polyethylene netting is extensively employed in the construction of aquaculture cages and it is highly susceptible to biofouling under submerged condition. Polyethylene is a nonpolar molecule and hence conventional organic or inorganic coatings against biofouling over polyethylene are unstable. Polyaniline, a conducting polymer, was successfully synthesized in situ over polyethylene webbing (Ashraf et al., 2017). PEG based hydrogels exhibited excellent protein resistance (Gudipati et al., 2005) and these hydrogel acts not only as non-hydrogen bond donors and also have increased interaction with water and neutral charge (Ostuni et al., 2001). Hydrophilic poly (2-hydroxyethylmethacrylate) – biocide - hydrogel was found to be effective antifouling molecule under field conditions (Cowie et al., 2006; Lundberg et al., 2010). The nano CuO incorporated methacrylate hydrogel synthesized over polyamide netting materials showed excellent biofouling resistance under real field condition (Ashraf & Edwin, 2016). Polyethylene is extensively employed as a material for construction of cages in the marine or fresh water aquaculture cages. The in situ synthesis of hydrogel over this non polar polyethylene matrix will not be applicable and hence needed a surface modification with a polar molecule like polyaniline. Polyaniline used for surface modification of polyethylene and was very effective (Ashraf et al., 2017). The paper discussed about the in situ synthesis of nano copper oxide incorporated hydrogel over polyaniline-coated polyethylene and its application for biofouling resistance in the aquaculture cage nets.

Materials and Methods

The polyethylene aquaculture cage nettings were procured from Matsyafed Netting factory (owned by Government of Kerala) and HEMA and PEGMA from Sigma Aldrich. Polyethylene nettings with colour is preferred generally by the fishers and hence blue coloured nets were procured for carrying out the experiment. Nano CuO (40 ± 5 nm size) was purchased from Reinste Nano Ventures New Delhi India. The size of the particle was checked by AFM analysis and it was about 40 to 45 nm. Aniline, ammonium persulphate were obtained from Fischer Chemicals. In situ synthesis of polyaniline over polyethylene was carried out as described elsewhere (Ashraf et al., 2017). Polyethylene netting were immersed in aniline – HCl acid solution overnight. Next day ammonium persulphate was added along the sides of the beaker of acidified aniline and allowed to polymerize. The beaker was kept undisturbed for 24 h. Then the samples were taken out and washed with MilliQ water to remove excess polyaniline attached over the nets. A uniform coating of polyaniline was formed over the polyethylene. The polyethylene nets of size 15×15 meshes coated with polyaniline were immersed overnight in 1:1 mixture of poly(ethyleneglycol) methacrylate (PEGMA) and hydroxyethylmethacrylate (HEMA) containing varied amounts of nano CuO. Next day the materials were taken out, allowed to drain excess solutions. The nettings were spread over 100 ml quartz crucible and subjected to microwave processing using Milestone Ethos Plus Microwave lab station. The heating was programmed to reach room temperature to 60^{o}C in 4 min. 15 min vent time

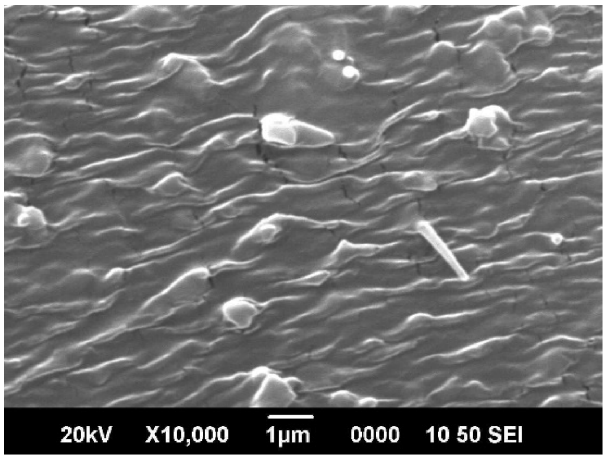
was allowed after attaining the temperature. The materials were taken out and stored in a clean polyethylene pouch. Nano CuO concentration (weight / volume basis) in the hydrogel was 0.01% (P1) and 0.02% (P2), PE-PANI alone (P3) and Untreated polyethylene (P0). The pre-weighed nettings were tied over a square frame made using PVC pipes with proper tagging and the nettings were finally tied over 4×3 PVC rack frame. The sample racks were immersed in the test site in 2 m depth from surface at Cochin estuary for 90 days. Samples were drawn in every month. Retrieved cage nettings were underwent soft cleaning to remove the dirt. The weights were taken to record biomass accumulation and the samples were observed through a Leica MZ16A stereo microscope at 25X magnification.

Infrared spectra of the formed hydrogel were analyzed using Thermo Nicolet iS10 Fourier transform infrared (FTIR) spectrometer fitted with diffuse reflectance accessory. The samples were scanned from 400 to 4000 cm^{-1}. Scanning Electron micrographs of cage nettings were analyzed using JEOL 6390 LV after treating it with low vacuum gold sputtering. Atomic Force Micrographs (AFM) of hydrogel coated PE films were scanned under non-contact mode using Park XE 100 AFM with XEI image processor. The Si probe (<10 nm tip) was used for scanning and the probe was aligned using a CCD camera fitted optical microscope.

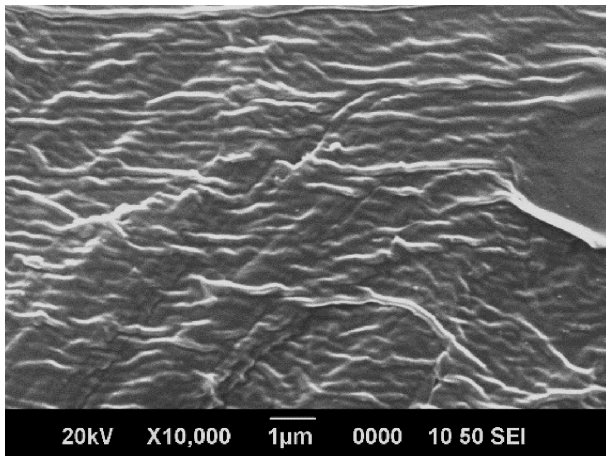
Results and Discussion

Microwave assisted synthesis was considered as faster, mild, energy efficient and greener method of synthesis. Nano CuO incorporated hydrogel was synthesized as per the procedure described above. The hydrogel formed over polyaniline coated polyethylene aquaculture cage nets was having uniform consistency and coating. The polar molecules of reactants selectively absorb microwave radiation directly, undergo core heating which leads to a homogenous temperature gradient and finally form the product (Tran & Nguyen, 2014). The materials were subjected to further evaluation.

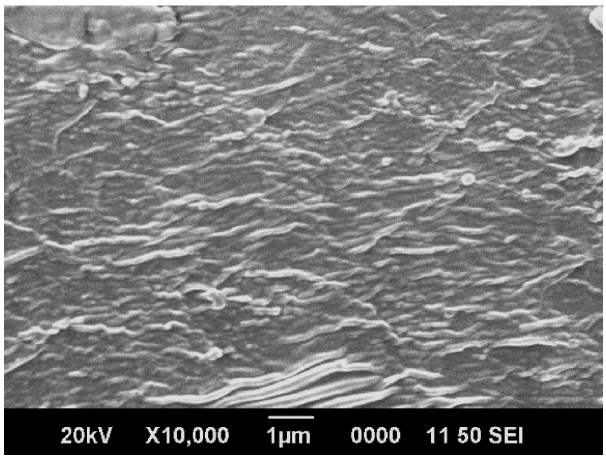
The polyaniline coated polyethylene (PE-PANI), PE-PANI treated with nano CuO incorporated hydrogel (PE-PANI-CuHY) and PE-PANI coated with hydrogel (PE-PANI-HY) over nettings surfaces were analyzed using SEM (Fig. 1). The micrographs showed the hydrogels were formed over the nettings and Cu particles were clearly visible in the



PE-PANI (P0)



PE-PANI-HY (P1)



PE-PANI-CuHY (P2)

Fig. 1. Scanning electron micrographs of polyaniline coated polyethylene (PE-PANI), PE-PANI coated with PEG hydrogel (PE-PANI-HY) and PE-PANI coated with nano CuO incorporated PEG hydrogel (PE-PANI-CuHY) netting materials

PE-PANI-CuHY treatments. The PANI coatings were uniformly covered by the hydrogel molecules and uniformly distributed. The surface structure was improved compared to the PE-PANI. Introduction of nano CuO in the hydrogel, transformed the coating more compact and fine textured one compared to hydrogel alone treated cage nets. Nano CuO was clearly visible in the hydrogel matrix. Surface characteristics like low surface energy and protein resistance plays an important role in the biofouling resistance (Chen et al., 2010).

Surface topography of PE, PE-PANI and PE-PANI-CuHY was presented in Fig. 2. Taking micrographs of twine surface was difficult due to its curved surface and small diameter. Hence the experiment was repeated in a plane PE sheet separately and AFM was recorded. The coarse surface of the polyethylene film was completely covered by PANI and it was further finer and compact after nano CuO incorporated hydrogel. The average roughness (Ra) for PE, PE-PANI and PE-PANI-CuHY was 1.63 nm, 4.20 and 2.00 nm respectively. The increased roughness in PE-PANI was due to the PANI nano fibres / rods over the surface. This was evident from the AFM and earlier studies (Ashraf & Edwin, 2016). Reduced surface roughness in CuO incorporated hydrogel was due to the more compactness of the hydrogel. SEM images clearly show the same.

The treated film was subjected to study the hydrophilic or hydrophobic nature. 5 µl of MilliQ type 1 water was pipetted over the film and examined the droplet through Leica MZ16 stereo microscope (20 X) and it was shown in Fig. 3. The micrographs showed the hydrophobic nature of untreated PE and PANI treated PE. Hydrogel alone coated PE-PANI showed a higher area of coverage and water spread maximum due to the hydrophilic nature of hydrogel. The nano CuO incorporated hydrogel exhibited less spread of water than hydrogel without CuO treated one. This implied that the hydrogel with CuO was less hydrophilic than hydrogel but not hydrophobic. Characterization of the functional groups will enable more details about the structural characteristics.

The coordination number of copper in nano CuO is 4, implies Cu is linked with four neighboring oxygen atoms with square planar geometry (110 plane). Similarly, oxygen coordinated with four Cu atom in a distorted tetrahedral geometry. It has a mixture of ionic and covalent bonding with oxidation state of +2 (Tran & Nguyen 2014). The nano CuO incorporated hydrogel was formed in orderly fashion compared to raw hydrogel. Introduction of nano CuO made closer interaction with PEG hydrogel molecules due to the electron cloud and

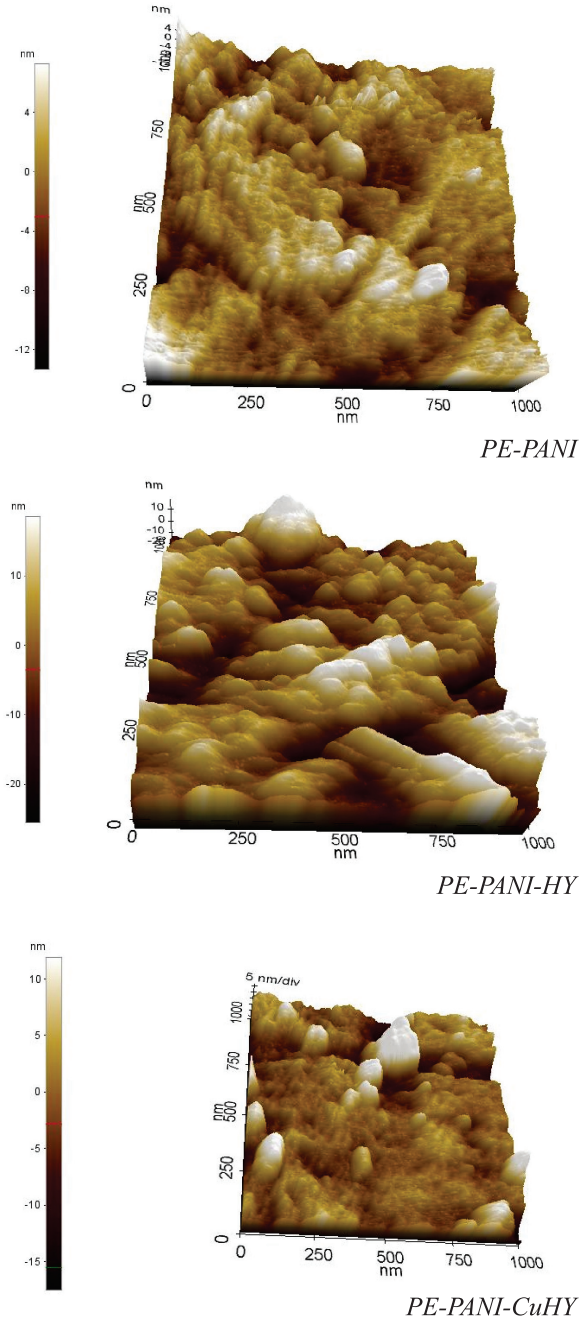


Fig. 2. Atomic force micrographs of polyaniline coated polyethylene (PE-PANI), PE-PANI coated with PEG hydrogel (PE-PANI-HY) and PE-PANI coated with nano CuO incorporated PEG hydrogel (PE-PANI-CuHY) over a polyethylene film

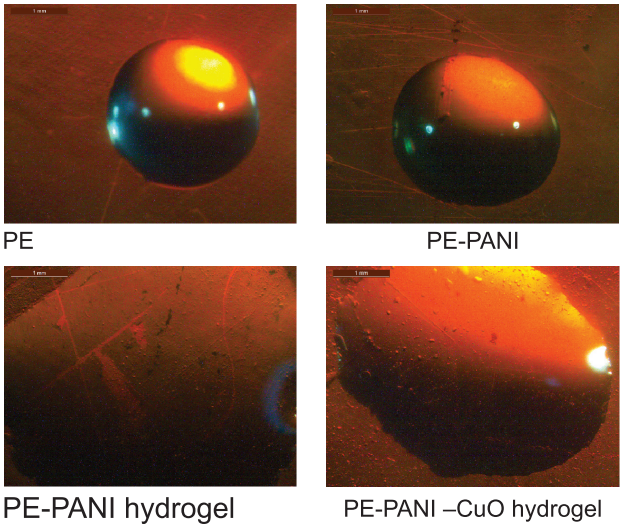


Fig. 3. Stereo microscopic image (20x magnification) of 5 µl water over polyethylene film treated with PANI, Hydrogel and nano CuO incorporated hydrogel

also increased number of particles in the square area (Fig. 4). The increased polymer density, as evidenced from the SEM micrograph, prevented the approach of solute or proteins in swollen hydrogel (Peppas et al., 2000). The protein inhibition characteristic of the hydrogel was showed the earlier studies (Ashraf & Edwin, 2016). The nano CuO also acts as a strong biocide also prevented any bacterial attack.

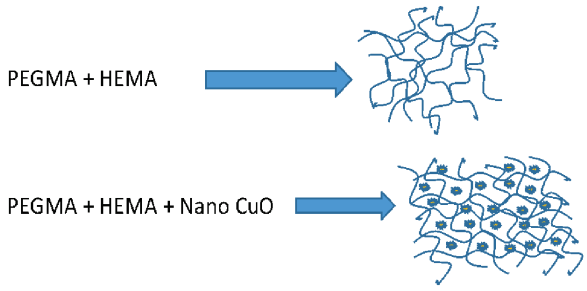


Fig. 4. Graphical representation of the hydrogel formation

The FTIR spectra and absorption of PE, PE-PANI and PE-PANI-CuHY were presented in Fig. 5 and Table 1. The characteristic absorption of polyethylene was exhibited in all the three samples. The characteristic IR absorption of PE was 2923 and 2881, the absorption peak of treated netting was moved respectively in 2977 and 2872 cm^{-1}. This was due to the surface coating of PANI and hydrogel. The PANI Quinoid=NH^{4+} absorption was shifted from 1027 to 1014 cm^{-1} highlighted the influence of polyethylene. This was further evidenced by the absorption peak of the benzenoid ring at 1467 instead of 1500 cm^{-1}. The CuO generally showed at 658 cm^{-1} and in the present case it was shown at 624 cm^{-1}. It was explained due to the influence of hydrogel matrix composite. The reported IR absorption bands of hydrogel were 561, 946, 1122, 1700 and 2977 cm^{-1} designated respectively was C-C def, OH bending, C-C str and CH_2 str (Ashraf & Edwin, 2016). In the present study, we employed microwave synthesis of PEG hydrogel in situ over the PE-PANI treated nets. The microwave energy initiated the free radical polymerization. The polyethylene glycol methacrylate monomer co-polymerized with 2-hydroxyethyl methacrylate (HEMA) onto the polyaniline coated surface. 0.The ester carbonyl was clearly exhibited at 1700 cm^{-1} and asymmetric and symmetric stretches of CH_2 were exhibited at 2943 and 2877 cm^{-1} respectively. The results showed the presence of all the peaks reported with slight decrease or increase. This was due to the bonding between the polyaniline and polyethylene glycol methacrylate hydrogel. To conclude, FTIR absorption analysis revealed that the hydrogel was successfully synthesized in situ over the PE-PANI matrix. The nano CuO incorporated hydrogel expected to prevent the attachment of foulers under submerged marine environment through the synergistic action of protein resistance surface and antimicrobial effect of CuO.

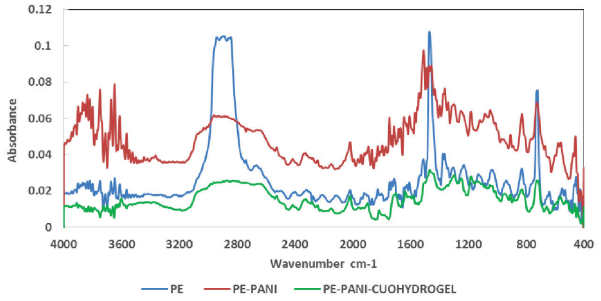


Fig. 5. FTIR spectra of polyethylene nettings, polyaniline coated polyethylene and nano CuO incorporated hydrogel coated over PE-PANI nettings

To evaluate the antifouling characteristics of aquaculture cage nettings under field condition, the treated samples were exposed under estuarine environment. The PE, PE-PANI, PE-PANI- HY and PE-PANI-CuHY aquaculture cage nettings were exposed in the test sites of Cochin estuary for 90

Table 1. FTIR characteristics of plyethylene, PE-PANI and nano CUO incorporated hydrogel coated PE-PANI aquaculture nettings.

FTIR absorption frequencies	PE	PE-PANI	PE-PANI -CuHY	Remarks
PE STANDARD IR PEAKS				
731, 720	721	722	724	CH_2 Rocking deformation
1176		1179	1180	CH_2 Wagging deformation
1306	1304	1304	1297	CH_2 Twisting
1351, 1366	1363	1366		CH_2 Wagging deformation
1377	1396	1397		CH_2 symmetric
1473,1463	1468	1467	1465	CH_2 bending
2851	2889	2871	2872	CH_2 symmetric
2919	2923		2977	CH_2 Assymmetric
PANI STANDARD IR PEAKS				
829		828	828	Quinoid ring out of plane
1027		1014	1014	Quinoid =NH4+
1141		1122	1122	Quinoid =NH+
1300		1304	1297	u (C-N) Sec Aromatic amine
1500		1467	1465	Benzenoid ring
1585		1578	1579	Quinoid ring
COPPER				
624			658	
HYDROGEL STANDARD IR PEAKS				
576			561	C-C def
932			946	OH bending
1126			1122	C-C str (sym)
1175			1180	COC str
1297			1297	CH2 twisting
1464			1465	NH def/CH2 scissoring
1641			1605 /1637	Amide I str
1719			1700	C=O Str
2872			2872	CH2 str
2914			2977	CH2 str
3339			3383	NH I sym str

days. The panels were retrieved from the test site after 1, 2 and 3 months and were shown in Fig. 6. Evaluation of biomass accumulation in the estuarine exposed treated and untreated panels were shown in Fig. 7. There was a steady increase of biomass in all the panels except in the 60 days exposed samples. In the 60th day sample, less biomass was probably the foulers were sloughed off due to adverse field conditions like unexpected rainfall and higher fresh water runoff. Unexpected rainfall is very common since the test site is in tropical region. The biomass accumulated on 60th day sample followed the same trend. The panels treated with 0.02% nano CuO incorporated hydrogel showed lowest biofouling density. This shows the nano CuO incorporated hydrogel treatment was effective in controlling the fouler accumulation. The treatment was 53% more efficient than the control (based on 3 month data).

According to Jion et al. (1991) the protein adsorption was prevented by the PEG hydrogel by steric repulsion due to the compression of polyethylene oxide chains. Protein adsorption resistance depends on the increased surface density and chain length of the material. In PEG hydrogels hydration through hydrogen bonds plays important roles in biofouling resistance. The water molecules were occupied over the ethylene glycol unit of the polymeric chains (Jeon et al., 1991). PEG based materials highly susceptible for bacterial adhesion and the major reason attributed due to the low surface density (Lusse & Arnold, 1996). Probably this was the reason in hydrogel without CuO was fouled within few days of immersion in the estuarine environments. The SEM micrographs have showed that the nano CuO hydrogel coated surface has improved the surface characteristics. This led to the prevention of initial microbial attack in the nano CuO incorporated hydrogel. The phenomenon also explained due to the semi hydrophilic nature of nano CuO incorporated hydrogel. This was not encouraged the adsorption of protein over the matrix and also microbial attack. The process of in situ synthesis of polyethylene glycol hydrogel over the matrix provides defect free surface characteristics than manual coating of the hydrogel. Defect surfaces are highly prone to cell and protein adhesion (Chen et al., 2010).

Polyethylene is non polar and the valence electron moves around the nuclei of the polymer and exhibit temporary imbalances. This implies a brief positive and negative charge over the nuclei makes it

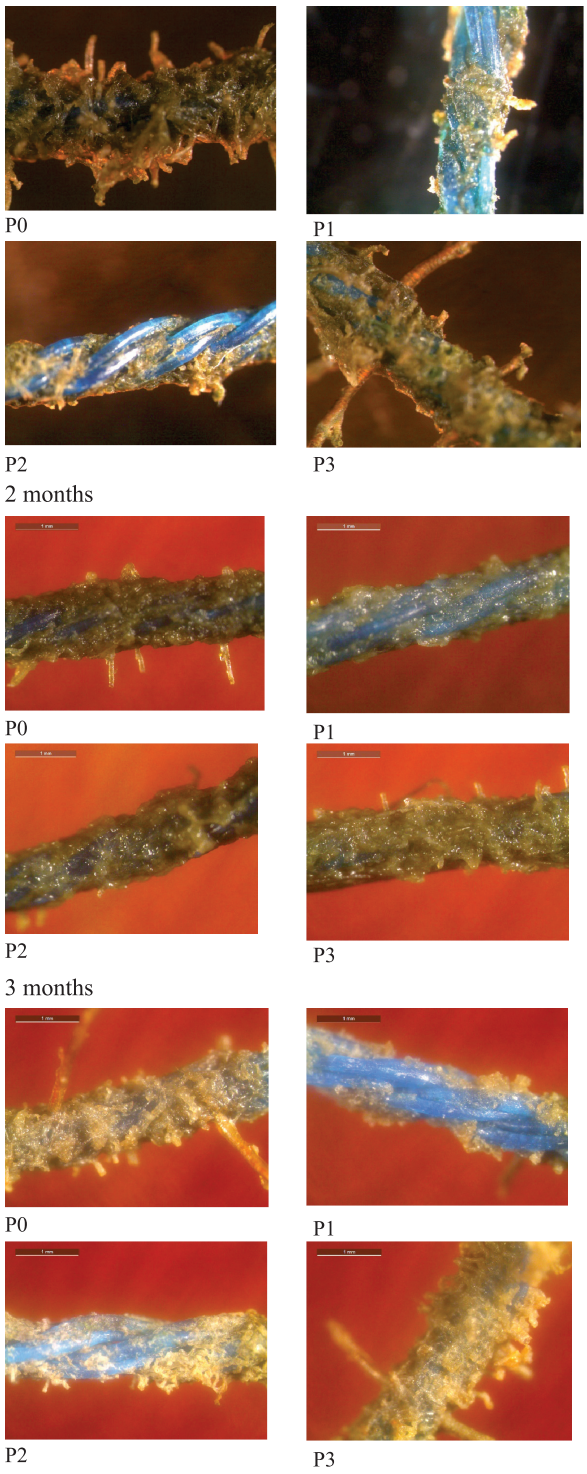


Fig. 6. Microscopic images of estuarine exposed netting material after 1, 2 and 3 months of exposure. The P0 – PE-PANI coated with Hydrogel, P1 - PE-PANI coated with 0.01% nano CuO incorporated Hydrogel, P2 - PE-PANI coated with 0.02% nano CuO incorporated Hydrogel and P3 – Untreated polyethylene netting.

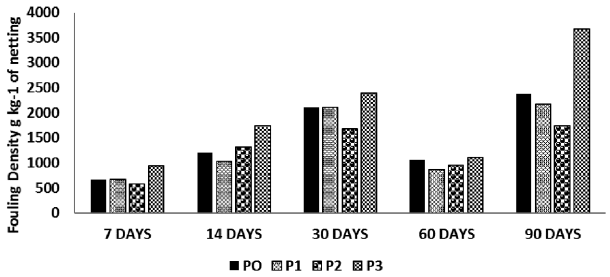


Fig. 7. Fouling biomass accumulation over cage netting material after different days of exposure in the Cochin estuary

temporary weak polar surface. The chromophore responsible for the blue color of the polyethylene may also influence the absorption of polyaniline over the matrix. The benzenoid group interacts with the carbon and the nitrogen with the C-H hydrogen atom. This interaction made the system more compact and stable (Fig. 8). Hydrogels were strongly adhered over the polyaniline molecule through the interaction of lone pair electron over the N present in aniline molecule and oxygen of carbonyl and amines present in the methacrylate moiety through hydrogen bonding. Nano CuO in the hydrogel increased further the oxide concentration over the hydrogel which acts as a point source to prevent the accumulation of microbes and thereby foulers (Ashraf & Edwin 2016). Lansdown (2002) showed the inhibition of microorganisms efficiently by nano copper ions in the presence of functional groups present in the cell membrane.

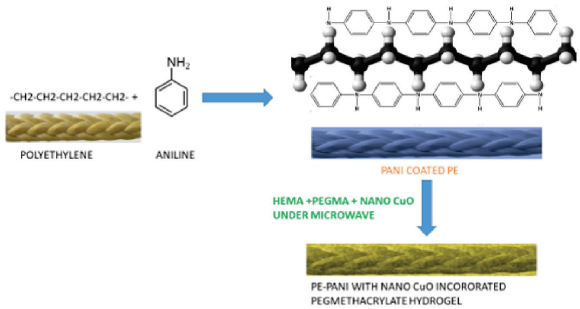


Fig. 8. Mechanism of reaction

The non-polar polyethylene aquaculture cage netting was surface-modified to make polar through in situ synthesized polyaniline. The PANI treated PE was coated with nano CuO - PEG hydrogel through microwave synthesis. The surface evaluation by SEM and AFM exhibited the strong and compact coating of PANI and hydrogel were formed over the polyethylene. FTIR study confirmed the formation of nano CuO - PEG hydrogel. The field evaluation showed excellent fouling resistance and treatment over PE was 53% more efficient than control. Among the treatment, 0.02% nano CuO incorporated hydrogel showed better performance. The nano CuO incorporated hydrogel was semi hydrophilic in nature, defect free and more compact surface. These led to the effective antifouling characteristics over the aquaculture cage net. The techniques can be applied to aquaculture cage nettings to prevent biofouling accumulation.

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