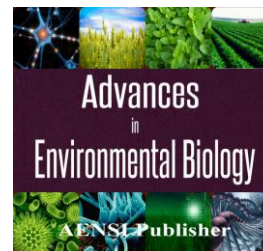




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Preparation Emulsion of PANI - HPC / TiO₂ Nanocomposite Blended with Poly (vinylacetate) Coating for Corrosion Protection and Antibacterial Applications

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ABSTRACT

In this study, Emulsion nanoparticles of polyaniline (PANI) were synthesized in the aqueous media by using Polyvinylpyrrolidone as a stabilizer, ammonium persulfate as an oxidant in the presence of TiO₂ with nanometer size then dedoped with NH₃ (0.5N) solution. Poly (vinylacetate) coating on the carbon steel was prepared by addition of emulsion nanoparticles in different concentrations (10 wt. %, 30 wt. % and 50wt. %) in poly (vinylacetate) as the major matrix. The Tafel plots records used for the definition of potential and corrosion current (I_{corr}). Nanoparticles were characterized and compared by X-ray diffraction (XRD), thermal gravimetric analysis (TGA), Fourier transformation infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). By adding TiO₂ in structure of PANI, thermal stability of nanocomposite increased. Small size of colloidal particles prevent from the precipitation of conducting polymer particles and lead to better dispersion of nanocomposites in matrix of PVAc binder and so the paint is homogeneous and anticorrosion properties of coating increased. According to the results corrosion current of 10 wt.% of HPC-PANI/TiO₂ emulsion nanocomposite in PVAc is much lower than 30 wt. % and 50 wt.% of nanocomposite based paint in 3.5 wt. % NaCl and HCl (1M). The antibacterial properties were also measured by disk diffusion technique against Gram-negative bacteria; E. coli. For disk diffusion technique, 15 mm diameter sterile filter paper disks that were saturated with 50 wt. % PANI-HPC/ TiO₂ emulsion mixed in poly (vinyl acetate) suspension were put on the center of agar plates which had 200 μL inoculums fairly well-distributed. The inhibition zone was measured after 24 h incubation at 37°C. The results clearly showed PANI-HPC/ TiO₂ emulsion mixed in poly (vinyl acetate) inhibit the growth of wild-type E. coli (7 ± 0.5 mm).

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INTRODUCTION

Conducting polymers have become one of the most attractive subjects of investigation [1]. Polymers such as polyaniline, polyacetylene, polythiophene and polypyrrole have unique properties such as electrical conductivity, electrochemical properties, nontoxic and low density make them useful in wide range application such as sensors [2,3], anticorrosive coatings on metals [4], antimicrobial agent [5], removal of heavy metals [6, 7], catalysis [8] and biosensor [9]. The development of non-toxic anticorrosive polyaniline pigments lead to replacement of toxic pigments such as lead and chromium by these materials [10].

Nanocomposites formed by combining conducting polymers and oxides nanoparticles increase mechanical properties and process ability of conducting polymers [11,12]. For example, Titanium dioxide particles lead to enhancement of anti-UV and anti-bacterial properties of paints [13].

The advantages of polymeric antimicrobial agents were nonvolatile, chemically stability, have low permeation through the skin, enhancement of existing antimicrobial agents and minimize the environmental problems attendanting the residual toxicity [14, 15]. Conducting polymers are emerging as antibacterial materials in recent years [16]. The fouling phenomenon has an important effect on the marine shipping industries, where ships are either moved at a low speed or higher fuel consumption due to high frictional resistance [17]. In antifouling paint, toxic compounds such as cuprous oxide (Cu₂O) and tributyl tin (TBT) are distributed from the surface of the paint and barricade microorganisms from attaching to the surface. Though the

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efficiency of these paints was good, they have been found to be detrimental to the marine ecology [18]. Lately, researches have been focused on developing nontoxic paints [19].

The conductive polymers used in Metals deposition by different methods; like electrochemically deposition [20], other method is direct addition of electro- active polymer with epoxy [21] and dissolving these polymers with proper solvent [22]. Electrochemically deposition in large structures was impossible [23]. The PANI is insoluble in organic solvents then the process of it is difficult [24], except for 1-methyl-2-pyrrolidine (NMP) but NMP is not popular in industrial application because of low evaporation rate and high cost [25]. Colloidal preparation of polyaniline was one of the ways for overcoming the processability problems [26]. By using suitable polymeric steric stabilizer can prevent from the precipitation of conducting polymer particles [27]. Colloidal particles could be finely dispersed in a polymer media due to their small size [28].

Different materials used as paint coatings, among of these epoxy resin is one of the most popular choices because of physical, chemical and mechanical properties, safety and low costs [29].

The objective of this article is homogenous dispersion of nanocomposites in matrix of poly (vinyl acetate) binder to increase anticorrosion and antibacterial properties by emulsion polymerization of PANI. In present study emulsion of PANI-TiO₂ nanocomposite has been prepared in the aqueous media using hydroxypropylcellulose as a steric stabilizer and ammonium persulfate as an oxidant then dedoped with NH₃(0.5N) solution to obtain Emeraldine Base (EB).The composite was characterized using SEM ,XRD,TGA and FT-IR. PANI-HPC/TiO₂ emulsion is dispersed in PVAc matrix in various percentages, anticorrosive and antibacterial properties of coating were investigated.

2. Experimental:

2.1. Instrumentation:

A magnetic mixer model MK20, scanning electron microscope (SEM) model XL30, digital scale model FR 200, Fourier transform infrared (FTIR) spectrometer model Shimadzu 4100, X-ray diffraction (XRD), Transmission electron microscopy(TEM) images were collected with a Zeiss - EM10C - 80 KV (Germany) microscope operated at 80 kV , galvanostat/potentiostat SAMA500 (Iran) and three-electrode electrochemical cell system consisted of a St37 sample (coated with nanocomposite) as working electrode, a platinum gauze as counter electrode and an Ag/AgCl as reference electrode were employed for corrosion tests and the thermal gravimetric analysis (TGA) was carried out using a shimadzu TGA-50.

2.2. Reagents and standard solutions:

In this work aniline (extra pure >99%, d=1.02g/cm³, Merck), nanometer size titanium dioxide, sulfuric acid and ammonium per sulfate from Merck, hydroxypropylcellulose (HPC, M_w=10⁶) from Aldrich and Poly (vinyl acetate) (Aldrich grade M_w=500,000) were employed. All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water was used throughout this work. Aniline monomer was purified by simple distillation. The Gram-negative bacteria; *E. coli* (PTCC 1398) provided by the Babol University of Medical Sciences, were used as a test bacterium in the experiments on the antibacterial activity of colloidal polyaniline. Microorganisms were incubated at 37°C for 24 h on a nutrient agar plate before use.

2.3. Pretreatment of St37 samples:

Commercial grade mild steel (St 37) samples were obtained from Khoozestan Steel Company (Ahvaz,Iran) with the following specifications: Iron (99.77 wt. %),Carbon (≤ 0.17 wt. %), Phosphorus and Sulfur (≤ 0.05 wt. %) and Nitrogen (≤ 0.009 wt. %). with 2×2×0.3 cm dimension. The surface of St37 polished by using 100 grade emery papers and finally washed with distilled water and acetone.

2.4. Emulsion polymerization in hydroxypropylcellulose surfactant solution and coating:

In this work PANI-HPC/TiO₂ nanocomposite was synthesized via in situ emulsion polymerization method. In a typical experiment (1 mL) aniline monomer was added to stirred aqueous solution of (100 ml) sulfuric acid (1 M) containing, 0.7 g of ammonium persulfate, 1 g HPC and 0.04 g TiO₂. The reaction was carried out in acidic aqueous media at room temperature for 24 hours.

The colloidal dispersion was dedoped by NH₃ (0.5N) solution for 24 hours and then it was centrifuged (6000 rpm) for thirty five minutes, for the separate the oligomers and impurities, the product was washed several times with deionized water. Different concentrations (10 wt. %, 30 wt. % and 50 wt. %) of PANI-HPC/TiO₂ emulsion mixed in poly (vinyl acetate) binder. It was coated on surface of St37 plates via cast method in corrosion studies. The samples were dried at room temperature for 20 hours and thin layer (65±5µm) of paint was coated on St37 samples.

2.5. Disk diffusion:

The antibacterial properties were also measured by disk diffusion technique against Gram-negative bacteria; *E. coli*. For disk diffusion technique, 15 mm diameter sterile filter paper disks that were saturated with 50 wt. %

PANI-HPC/ TiO₂ emulsion mixed in poly (vinyl acetate) suspension were put on the center of agar plates which had 200 μ L inoculums fairly well-distributed. The inhibition zone was measured after 24 h incubation at 37°C.

Zones of inhibition is an area of media where bacteria are unable to grow, due to presence of antibacterial agent that impedes bacterial growth. The area of the inhibition zone was used as a criterion to ascertain the biocidal activity.

RESULTS AND DISCUSSION

3.1. Structural characterization:

The chemical structure of product was determined by FTIR spectrum. The FTIR spectroscopy has provided valuable information regarding the formation of polyaniline composites. FTIR analysis has been done to identify the characteristic peaks of product. FTIR spectra in the 500-3500 cm^{-1} region, for pure polyaniline and PANI-HPC/TiO₂ are shown in Fig.1. Peak at 1302 cm^{-1} (C-N stretching of the benzenoid ring), 1141 cm^{-1} (C-H in-plane deformation)[30] The main absorption bands of pure polyaniline at 1567 cm^{-1} and 1480 cm^{-1} for the C=C stretching deformation of benzenoid and quinonoid rings[31], Peak at 813 cm^{-1} (C-H out-of-plane deformation in the p-disubstituted benzene ring), peak at 3349 cm^{-1} N-H stretching vibration mode. By using HPC and TiO₂ these peaks little substituted.

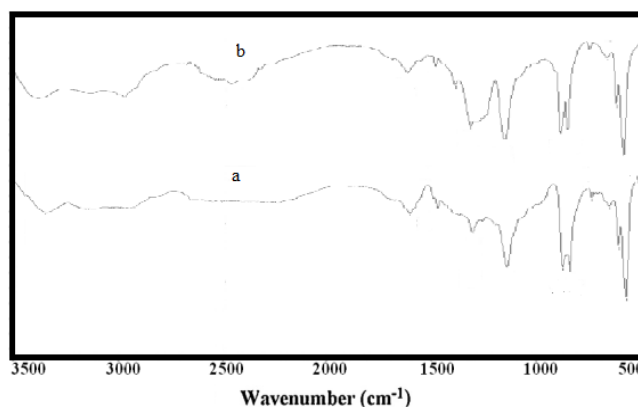


Fig. 1: FTIR spectra of (a) pure polyaniline and (b) PANI-HPC/ TiO₂

Fig. 2 shows the XRD pattern of TiO₂, PANI and PANI-HPC/TiO₂. The main peaks in the XRD pattern of pure PANI are observed at $2\theta = 17.6, 25.2$ and 32.4 . The XRD pattern of PANI-HPC/TiO₂ is partly alike to that of TiO₂, as well as the broad diffraction peak of PANI at $2\theta = 25.2^\circ$ is absent in the PANI-HPC/TiO₂ which display that the presence of TiO₂ in the polymerization system effects the crystalline treatment of PANI and the interplay of PANI and TiO₂ confirm the crystallization of PANI. Absorption of polyaniline on the surface of TiO₂ particles cause molecular chain is limited and the degree of crystallinity decreased. In addition the crystallization treatment of TiO₂ particles not affected by polyaniline deposited on the surface of TiO₂ particles [32].

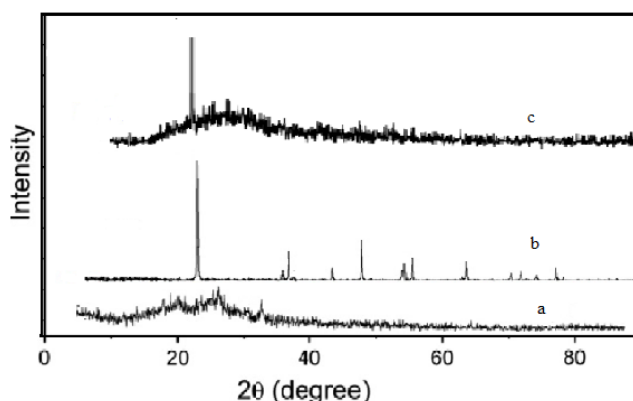


Fig. 2: X-ray diffraction patterns of (a) PANI, (b) TiO₂ and (c) PANI-HPC/ TiO₂

The thermal decomposition behaviors of PANI-HPC and PANI-HPC/ TiO₂ nanocomposites were analyzed by thermal gravimetric analysis (TGA), upon heating in a nitrogen atmosphere at rate of 10°C min⁻¹ with the range of 25-600 °C as shown in Fig .3. As can be seen, by adding TiO₂ in structure of HPC-PANI, thermal stability of nanocomposite increased.

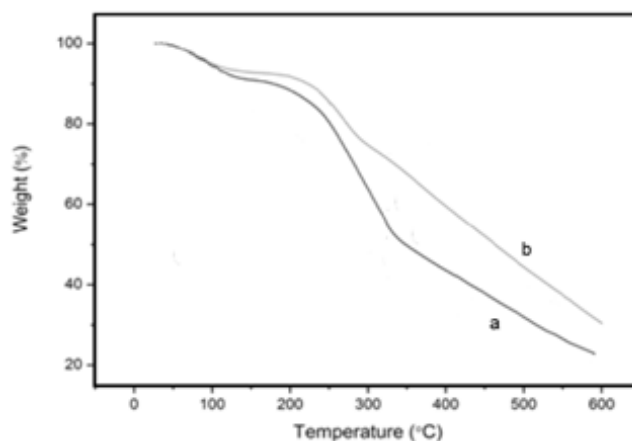


Fig. 3: TGA curves of (a) PANI and (b) PANI-HPC/ TiO₂

3.2. Morphology of nanocomposite:

The morphology of products was analyzed by SEM. The SEM micrograph of 10% (by weight) PANI-HPC-TiO₂/PVAc is shown in Fig 4. The combination of PANI-HPC/TiO₂ and PVAc is compact, homogenous and no pores or pinholes structure. Fig.6 shown the SEM micrograph of PANI-HPC in aqueous media surfactant prevent from gross aggregation of particle, and the average diameter of particle was about 38-48 nm. Fig.5 shown the TEM micrograph of PANI-HPC/TiO₂ nanocomposite prepared in aqueous media. PANI-HPC/TiO₂ nanocomposite in aqueous media exhibits uniform structure, and the average diameter of particles was about 48-65 nm. As can be seen, by adding TiO₂, the average size of nanocomposites increased.

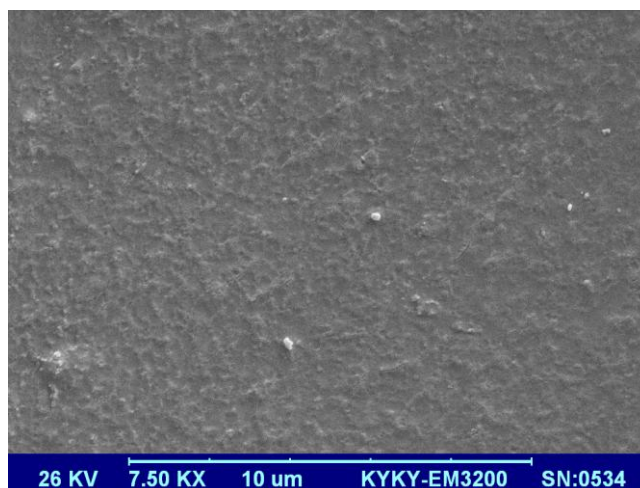


Fig. 4: SEM Micrograph of 10% PANI-TiO₂-HPC/PVAc.

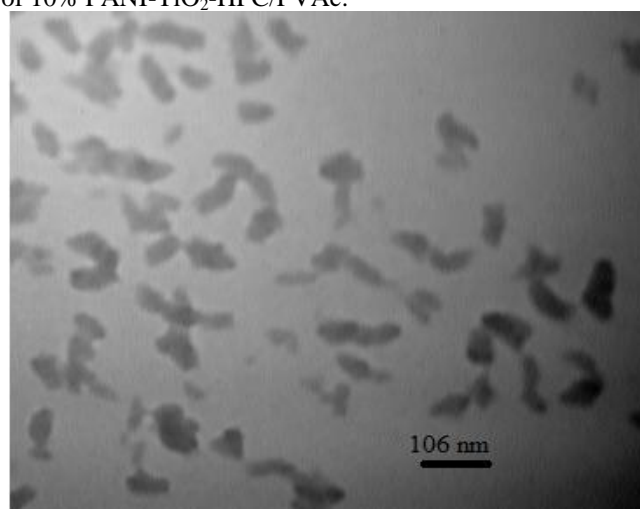


Fig. 5: TEM Micrograph of: PANI-HPC in queues media (HPC 10g/L, aniline 10.75×10^{-2} mol/L, (NH₄)₂S₂O₈=7 g/L, TiO₂=0.04 g/L).

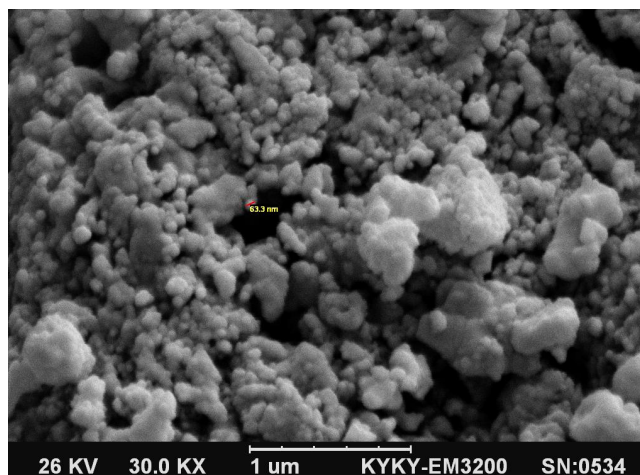


Fig. 6: SEM Micrograph of: PANI-HPC in aqueous media (HPC 10g/L, aniline 10.75×10^{-2} mol/L, $(\text{NH}_4)_2\text{S}_2\text{O}_8=7$ g/L, $\text{TiO}_2=0$ g/L).

3.3. Corrosion studying:

The potentiodynamic polarization technique is used to examine the unpainted St37 carbon steel and polyaniline based painted on St37 samples in aqueous 3.5 wt % NaCl solution and HCl (1M) solution. In (Tables 1–2) the values related to the corrosion potential (E_{corr}), corrosion current (I_{corr}) and corrosion rate (CR) calculated from Tafel plots for uncoated St37 and different concentrations (10 %wt, 30 %wt, and 50 %wt) of HPC-PANI/ TiO_2 emulsion mixed in polyvinyl acetate (PVAc) binder coated St37 samples respectively in HCl (1M) and NaCl (3.5 %, wt) electrolytes have been recorded.

The polarization curves were obtained starting from the open circuit potential. Potential of the working electrode was around, up to 800 mV and down to -800 mV. The potential scan rate was 2 mV s^{-1} . Electrochemical measurement was carried out at room temperature.

Also it can be seen that in acidic environment and in 3.5% NaCl aqueous solution. Comparison of the corrosion current and corrosion potentials of nanocomposite based paints indicate that the corrosion potential of PANI-HPC/ TiO_2 (10 wt. %) nanocomposite based paint sample is more positively shifted and corrosion current reduced than 30% and 50% nanocomposite based paint.

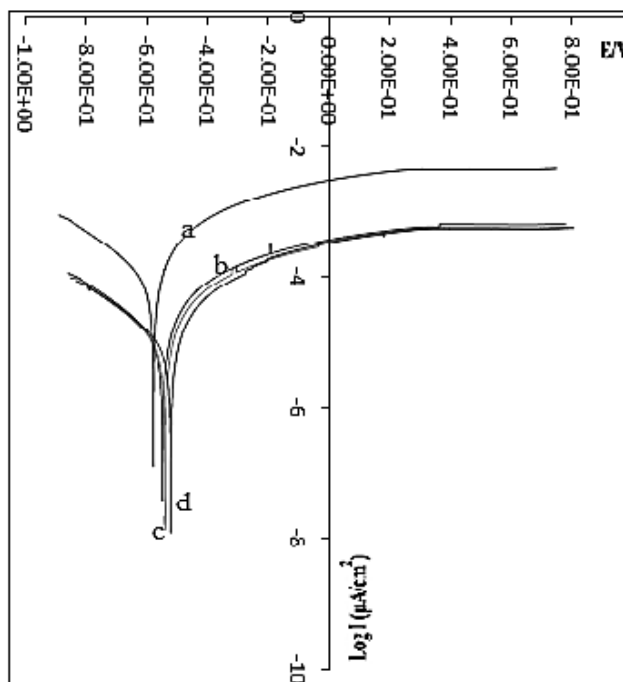


Fig. 7: Tafel plot for (a) St37 (b) 50% PANI- TiO_2 -HPC/PVAc (c) 30% PANI- TiO_2 -HPC/PVAc and (d) 10% PANI- TiO_2 -HPC/PVAc and content coated St37 samples in HCl (1M) solution.

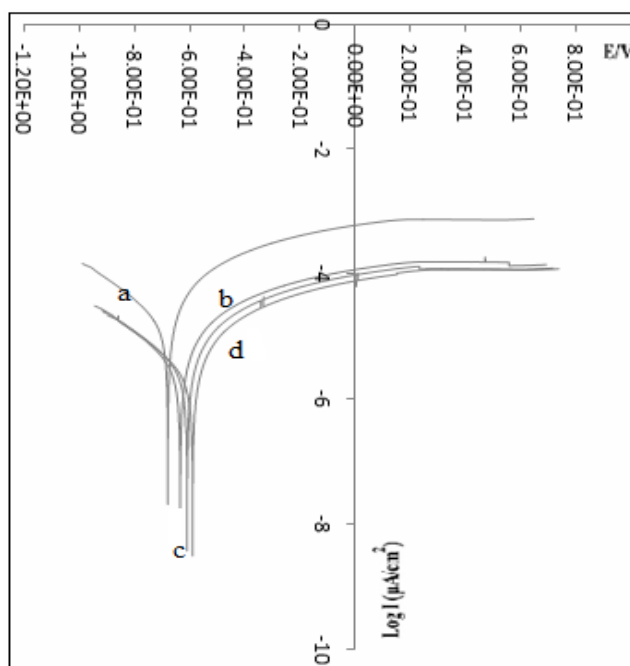


Fig. 8: Tafel plot for (a) St37 (b) 1% PANI-TiO₂-HPC/PVAc (c) 1.5% PANI-TiO₂-HPC/PVAc and (d) 2% PANI-TiO₂-HPC/PVAc and (e) 1% PANI- HPC/PVAc coated St37 samples in NaCl (3.5 wt. %) solution.

Table 1: Corrosion current (I_{corr}), corrosion potential (E_{corr}) and corrosion rate (CR) values calculated from Tafel plots for St37, 10% PANI-TiO₂-HPC/PVAc, 30% PANI-TiO₂-HPC/PVAc, 50% PANI-TiO₂-HPC/PVAc coated St37 samples in HCl (1M) solution.

CR (mm/year)	I_{Corr} (μAcm^{-2})	E_{Corr} (V)	Coating
12.3	105	-0.57	St37
1.2	10.4	-0.52	10% PANI-TiO ₂ -HPC/PVAc
1.3	11.7	-0.53	30% PANI-TiO ₂ -HPC/PVAc
1.6	13.75	-0.54	50% PANI-TiO ₂ -HPC/PVAc

Table 2: Corrosion current (I_{corr}), corrosion potential (E_{corr}) and corrosion rate (CR) values calculated from Tafel plots for St37, 10% PANI-TiO₂-HPC/PVAc, 30% and PANI-TiO₂-HPC/PVAc 50% PANI-TiO₂-HPC/PVAc coated St37 samples in NaCl (3.5 wt. %) solution.

CR (mm/year)	I_{Corr} (μAcm^{-2})	E_{Corr} (V)	Coating
2.1	17.8	-0.67	St37
0.315	2.6	-0.58	10% PANI-TiO ₂ -HPC/PVAc
0.378	3.2	-0.6	30% PANI-TiO ₂ -HPC/PVAc
0.441	3.78	-0.624	50% PANI-TiO ₂ -HPC/PVAc

The small size of colloidal particles prevent from the precipitation of conducting polymer particles and lead to better dispersion of nanocomposites in matrix of poly (vinyl acetate) binder so the paint is homogeneous and anticorrosion properties of coating increased. Anion exchange and porosity properties of polyaniline are disadvantageous and these properties will be intensified in pitting corrosion media [33]. It should be noted that if polyaniline contain a polymer matrix with fibers or small filler particles, corrosion resistance can be improved. It can be seen by adding TiO₂ in polyaniline matrix improve the anticorrosive efficiency. The adhesion of coating could be important factor which control the corrosion rate and addition of polyaniline-TiO₂-HPC in poly (vinyl acetate) matrix reduce corrosion rate. This coating disconnects the metal surface from corrosion environment such as oxygen and acidic ions and also moves metal potential to noble direction.

3.4. Antibacterial activity:

Fig.9 showed 50 wt. % PANI-HPC/ TiO₂ emulsion mixed in poly (vinyl acetate) inhibit the growth of wild-type *E. coli* (7 ± 0.5 mm). White, hazy areas indicate bacterial growth, whereas the more transparent circles surrounding the saturated filter paper, in the agar, indicate bacterial-free regions, i.e. zones of inhibition.

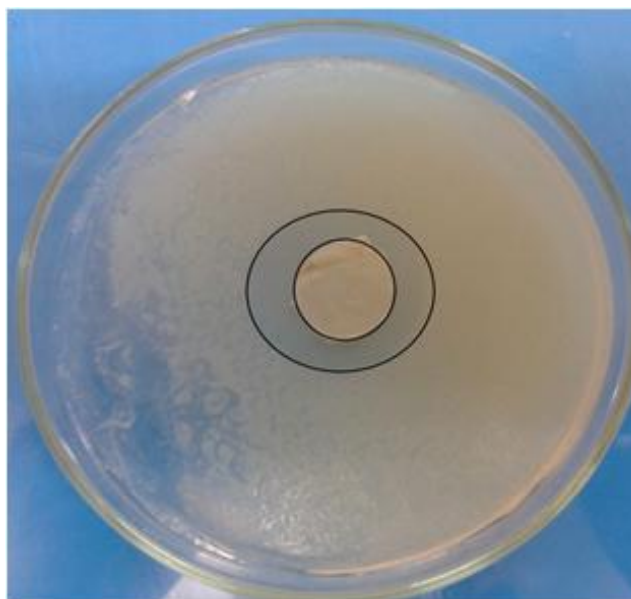


Fig. 9: Inhibition zones of PAN against *E. coli*.

4. Conclusions:

The experimental results have shown in acidic environment and in 3.5% NaCl aqueous solution, Comparison of the corrosion current and corrosion potentials of nanocomposite based paints indicate that the corrosion potential of PANI-HPC/ TiO₂ (10 wt. %) nanocomposite based paint sample is more positively shifted and corrosion current reduced than 30% and 50% nanocomposite based paint. It was found that by increasing PANI-HPC/ TiO₂ nanocomposite concentration in poly (vinyl acetate) matrix corrosion rate increased. The objective of this article is homogenous dispersion of nanocomposites in matrix of poly (vinyl acetate) binder to increase anticorrosion properties by emulsion polymerization of PANI. Colloidal preparation of PANI nanocomposites lead to the better dispersion of nanocomposites in matrix of poly (vinyl acetate) binder and PANI-HPC/ TiO₂ emulsion mixed in poly (vinyl acetate) inhibit the growth of wild-type *E. coli* (7 ± 0.5 mm).

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