

Investigation of Structural, Morphological Properties and Antibacterial Activities of Polypyrrole-Gold Nanocomposites

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Abstract- We describe the successful synthesis of Polypyrrole-Gold nanocomposites (PPy-Au NCs) by the chemical oxidative polymerization of pyrrole with ferric chloride as an oxidizing agent, in the presence of a colloidal suspension of gold nanoparticles. Gold nanoparticles (Au NPs) were synthesized by standard citrate reduction method. Au NPs and PPy-Au NCs were characterized by Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD) techniques for morphological and structural confirmations. Further, the antibacterial activity of synthesized PPy-Au NCs showed effective inhibitory activity against Gram negative bacteria viz. *Escherichia coli*, *Klebsiella pneumonia* and Gram positive bacteria viz. *Staphylococcus aureus* and *Sarcina lutea*. All the polymer composites showed significant anti-bacterial activity. The more prominent effect was observed against Gram positive organisms as compared to the Gram negative organisms.

Keywords- Gold nanoparticles colloid, Polypyrrole-Gold Nanocomposite, antibacterial activity.

I. INTRODUCTION

In recent years, conducting polymer-based nanocomposites loaded with metallic nanoparticles have attracted great interest since they often exhibit improved physical and chemical properties as well as wide range of applications like chemical sensors, electrocatalysis and microelectronic devices [1-4]. Embedding of metal particles inside the core of conducting polymers such as polypyrrole (PPy), polythiophene (PTh) and polyaniline (PANI) has become one of the evoking aspects of nanocomposite synthesis [5-7]. Metallic nanoparticles, particularly silver, gold, platinum, zinc and copper, have been the focus of great interest because of their unique properties such as optical, thermal, electronic, catalytic, antibacterial, photoresponsivity and many applications in various fields [8-12]. Polymers are basically insulators, but a new class of polymers was synthesized three decades ago that can conduct electric

current, known as conducting polymers. Among various types of conducting polymers, PPy is extensively studied because it is a highly conducting p-type polymer. It has a high mobility of charge carriers along and across the polymer chains with highly delocalized π -bond structure [13, 14]. PPy is the most promising conducting polymer among the known conducting polymers. It has received attention due to its special properties such as high conductivity, atmospheric stability and excellent mechanical properties. PPy has applications in sensors and biosensors, corrosion protection, microactuators, electronic devices, electrochromic devices, and many other [15-18, 19]. Several reports have also been published for the synthesis of polymer-gold nanocomposites. For example, J. Vorzobova et al. reported synthesis of gold nanoparticles into the acrylic polymer matrices by the direct physical method to produce gold-polymer nanocomposite [20]. K. Xue et al. reported the successful one-step synthesis of 3D dendritic gold/polypyrrole nanocomposites via a simple self-assembly method, the synthesis was carried out in the presence of poly (sodium 4-styrenesulfonate), which acts as both dopant and surfactant [21]. Single-step surfactant-free synthesis of gold nanoparticle and polypyrrole nanocomposites were reported by L. Mikoliūnaitė et al. employing in-situ polymerization of pyrrole using tetrachloroauric acid as an oxidant in the presence of gold seeds, at room temperature [22]. Electrochemical Methods in Aqueous Solutions for the synthesis of Gold/Polypyrrole Core-Shell Nanocomposites and Elemental Gold Nanoparticles Based on the Gold-Containing Nanocomplexes was adopted by Y. Liu et al. [23].

In this communication, we report a novel synthesis of PPy-Au NCs. Au NPs were synthesized by chemical reduction method. The PPy-Au NCs were successfully synthesized by in-situ chemical oxidative polymerization of pyrrole in the presence of a colloidal suspension of Au NPs. The synthesized Au NPs and PPy-Au NCs were characterized by TEM, AFM, FEM, SEM, FTIR and XRD. Anti-microbial activity of the polymer composites was investigated against Gram negative and Gram positive test microorganisms, namely *Escherichia coli*, *Klebsiella pneumonia*, *Staphylococcus aureus* and

Sarcina lutea. Anti-bacterial activity was tested using agar cup method.

II. EXPERIMENTAL

A. Materials and Reagents

Pyrrole (Spectrochem, Mumbai) was double distilled and stored in a refrigerator before use. Ferric Chloride (anhydrous) and trisodium citrate were procured from S. D. Fine Chem. Ltd., Mumbai. Chloroauric Acid was procured from Molychem, Mumbai. These chemicals were of AR grade and were used as received. All solutions of reacting materials were prepared using double distilled water, in this investigation. PPy-Au NCs were prepared by a two-step method. In the first step, we have prepared gold nanoparticles by citrate reduction method. In the second step, in situ chemical oxidative polymerization of pyrrole is performed in presence of citrate stabilized gold nanoparticles.

B. Synthesis of Polypyrrole (PPy)

PPy was synthesized by chemical oxidative polymerization using monomer pyrrole and ferric chloride as an oxidizing agent. 1M pyrrole solution was prepared using distilled water and cooled in an ice bath ($\sim 0^\circ\text{C}$) with continuous stirring for 30 minutes. The precooled aqueous solution of FeCl_3 (1M) was added dropwise to the pyrrole solution. The oxidant to monomer ratio was 1:1. The polymerization was carried out for 3h under constant stirring at $\sim 0^\circ\text{C}$. This mixture was allowed to settle for 24h to ensure complete polymerization. The solution was filtered under reduced pressure. The obtained product was washed with distilled water successively to remove the unreacted monomer, oxidant and dried under vacuum at room temperature to a constant weight.

C. Synthesis of gold nanoparticles (Au NPs)

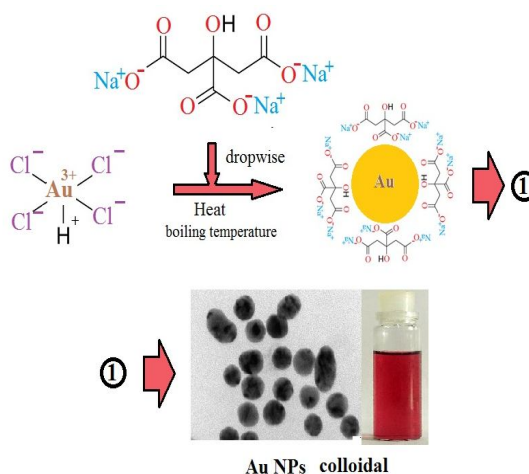


Figure 1. Schematic representing a process of gold nanoparticles formation.

Synthesis of citrate stabilized gold nanoparticles colloid was carried out using Turkevich method [24]. In a typical experiment, 100 ml chloroauric acid (0.5 mM) was heated up to boiling temperature. 10 mL trisodium citrate (38 mM) was added dropwise to initiate the reduction of chloroauric acid in the above solution. During this process, the solutions were mixed vigorously and the boiling temperature was maintained. Immediately after addition of trisodium citrate, the solution turned colourless from translucent yellow. After 5-6 minutes, the colour slowly changes to violet and then finally to ruby red after ~ 9 minutes, indicating the formation of Au NPs [25]. Trisodium citrate here acts both as a stabilizing and a reducing agent. Figure 1 presents schematic of preparation of Au NPs.

D. Synthesis of PPy-Au Nanocomposite (PPy-Au NCs)

The PPy-Au NCs was synthesized by in situ chemical oxidative polymerization. In a typical synthesis experiment, 40 ml, Au NPs colloidal solution was cooled in an ice bath ($\sim 0^\circ\text{C}$) and stirred by a magnetic stirrer. 1M solution of pyrrole was then added via syringe to this solution. Precooled 1M ferric chloride solution was added dropwise to the above solution under constant magnetic stirring for 3h. The colour of the solution changed from ruby red to grey and then finally to black. The solution was kept in a refrigerator at rest for 24h to complete the polymerization process. The product was filtered under reduced pressure, washed with distilled water until the filtrate became colourless and dried under vacuum at room temperature to a constant weight. Figure 2 presents schematic of preparation of PPy-Au NCs. Another two different samples were prepared by the same procedure using two different concentrations of Au NPs (80mL and 120mL). Samples were

labeled as S0(pure PPy), S1(PPy + 40mL Au NPs), S2(PPy + 80mL Au NPs), S3(PPy + 120mL Au NPs).

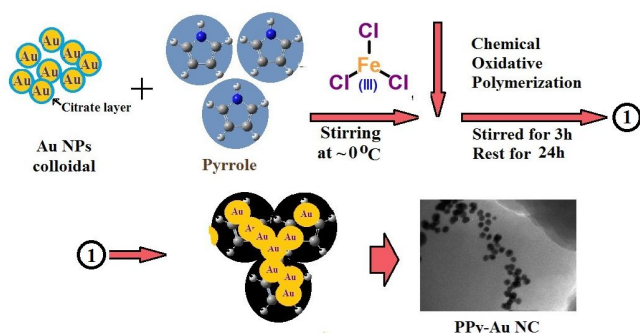


Figure 2. Schematic representing a process of polypyrrole-gold nanocomposite formation.

E. Instruments and Analysis

The UV-Vis absorption spectrum of Au NPs was recorded by Equiptronics make UV-EQ-825. The morphological examination of PPy and PPy-Au NCs was carried out using scanning electron microscope (FEI Quanta 250) at an accelerating voltage of 10 kV. The surface morphology was also examined by Atomic Force Microscopy (AFM) on BRUKER Innova. The TEM images were recorded with a Philips CM 200 transmission electron microscope, operating at a voltage of 200 kV. The chemical structure was examined by FTIR spectroscopy (Perkin-Elmer, Frontier) in the range of 400-4000 cm^{-1} . The X-ray diffraction measurements were carried out using BRUKER D8 Discover with Cu $K\alpha$ radiation ($\lambda = 0.154056 \text{ nm}$) in the range of $2\theta = 200$ to 800.

Anti-microbial activity of the polymer composites was investigated against Gram negative and Gram positive test microorganisms, namely *E. coli*, *K. pneumoniae*, *S. aureus* and *S. lutea*. Anti-bacterial activity was tested using agar cup method. In this method, saline suspension of the test organism was bulk seeded in sterile Muller Hinton Agar at a concentration matching to McFarland turbidity of 0.4-0.5 ($1.5 \times 10^8 \text{ CFU}$). Muller Hinton Agar used was from the authentic source i.e. Himedia Laboratories, which was reconstituted and sterilized by autoclaving. Agar cups were made using sterile cork borer of diameter size of 10mm. 100 microlitre of the test samples of polymer composites were added in the well. The plates were then incubated in the incubator at 37°C for 24 hours for allowing growth of the test microorganisms. The test substances diffuse in the medium and produce a clear zone of inhibition if it has anti-bacterial activity. The zone of inhibition is produced due to bacteriostatic or bactericidal effect of the test substance filled the wells as it diffuses in the radial manner. The size of diameter of zone of

inhibition indicates the antimicrobial efficacy of the test substance against the sensitive test organism.

III. RESULTS AND DISCUSSION

A. UV-Vis Spectroscopy

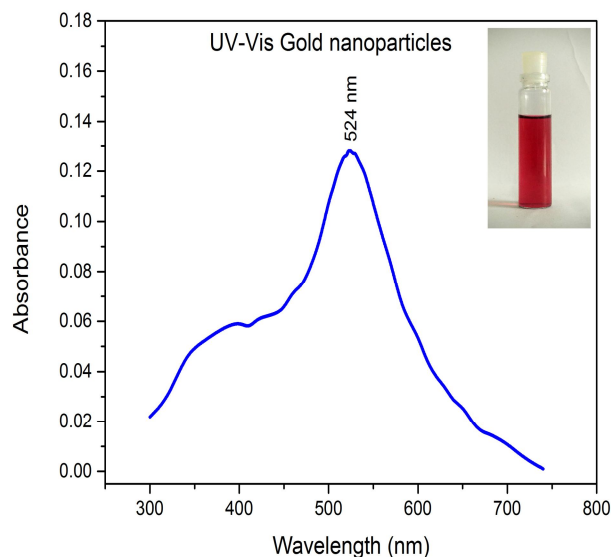


Figure 3. UV-Vis absorption spectra of colloidal solution of Au NPs.

The UV-Vis absorption spectrum of the colloidal solution of Au NPs is shown in Figure 3. The distinctive ruby red colour of colloidal gold is due to the surface plasmon resonance phenomena of the electrons in the conduction bands of gold, indicated the formation of gold colloids having nanometer-sized dimensions. The appearance of a plasmon peak at 524 nm confirms the formation of Au NPs [24, 26]. The nanoparticles formation and the particle size (20-26 nm diameter) were confirmed by the TEM and SEM images.

B. TEM analysis

Transmission Electron Microscopic (TEM) analysis of the Au NPs and PPy-Au NCs was conducted. It can be observed from Figure 4(a) that Au NPs were nanospheres in size distribution from 20 to 26 nm indicating monodispersity. Large particles of different sizes in the range of 32-40 nm were also seen, which may be due to clustering of nanoparticles.

Figure 4(b), (c) and (d) show the TEM images of PPy-Au NCs of S1, S2, and S3 respectively. Au NPs are completely embedded inside the polymeric layer during the polymerization procedure. Moreover, these Au NPs have a little aggregation in the PPy particles. The size of Au particles

in PPy-Au NC, calculated from TEM and XRD was in good agreement with each other.

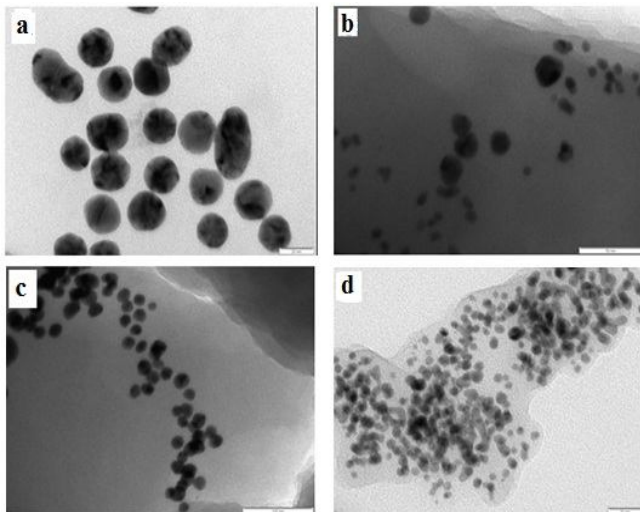


Figure 4. TEM images of Au NPs (S0) and PPy-Au NCs (S1,S2,S3)

Figure. 5 shows the Selected Area Electron Diffraction (SAED) pattern of the Au NP (S0) and PPy-Au NC (S3). The electron diffraction pattern showed characteristic concentric ring-like diffraction pattern associated with crystalline nature of gold. The diffraction rings could be indexed on the basis of the FCC structure of gold. Four strong diffraction rings arise due to reflections from (1 1 1), (2 0 0), (2 2 0) and (3 1 1) lattice planes of gold, as mentioned in previous reports [27].

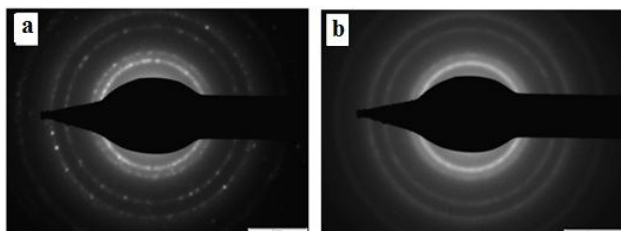


Figure 5. SAED pattern of the (a) Au NPs (S0), (b) PPy-Au NC (S3)

C. SEM analysis

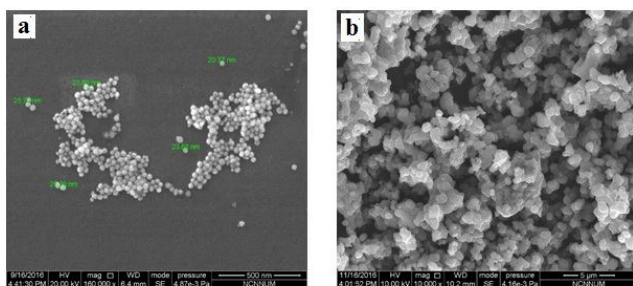


Figure 6. SEM images of (a) Au NPs (S0), (b) PPy-Au NC (S3)

The surface morphology study of Au NPs and PPy Au NCs was conducted by Scanning Electron Microscopy (SEM) and is shown in Figure 6. From figure 6(a), the size of Au NPs is about 20 to 26 nm, which is well in agreement with TEM results. Figure 6(b) shows the surface morphology of PPy-Au NCs. It revealed that the growth is mostly in the globular form, and the average size of globules was found to be about 180 nm to 400 nm. It also shows that the Au NPs are dispersed in the PPy matrix.

D. AFM analysis

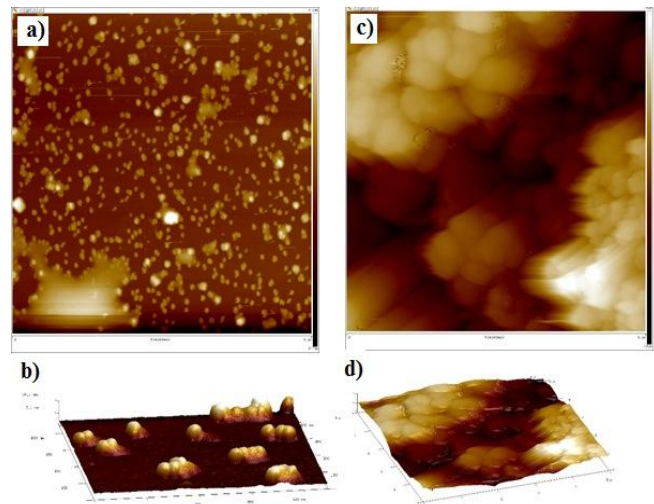


Figure 7. Morphological features of AFM image of (a) Planar surface of Au NPs (S0), (b) 3-D view of Au NPs (c) Planar surface of PPy-Au NC and (d) 3-D view of PPy-Au NC (S3)

The two-dimensional (2D) and three-dimensional (3D) nature and the morphological features of Au NPs and PPy-Au NCs were studied using AFM images. Figures 7(a) - (d) shows the AFM surface topographic images of Au NPs and PPy-Au NCs. It reveals that gold nanoparticles of a spherical structure with a diameter about 20-30 nm protrude out of the surface. For the composite PPy-Au NCs, it can be noted that the crystalline structure vanishes and now a large number of globules appear. We can find that the Au NPs are inside the PPy particles, this structure is certainly much different than that of Au NPs.

E. FTIR Result

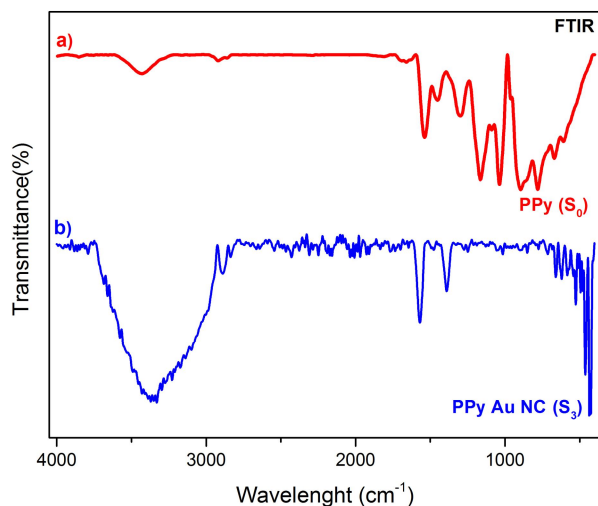


Figure 8. FTIR spectra of PPy (S0) and PPy-Au NC (S3)

FTIR identifies the chemical bonds and the type of functional group present. The FTIR spectra of PPy and PPy-Au NC are shown in Figure 8. For pure PPy as shown in Figure 8(a), the band appears in the region 3300 - 3450 cm^{-1} due to N-H stretching of pyrrole ring. The characteristic peaks for PPy observed at 1451 cm^{-1} and 1538 cm^{-1} are attributed to the vibration of the pyrrole ring. The peak at 1293 cm^{-1} corresponds to C-H deformation. Peaks around 725–1110 cm^{-1} represent the C-H in-plane and C-H out-plane deformation in PPy. The assignment of peaks reveals that the synthesized product is PPy [28-31]. In the case of PPy-Au NC, a shift in the position of the peak at 1451 cm^{-1} to 1472 cm^{-1} and 1538 cm^{-1} to 1569 cm^{-1} indicates an effective charge transfer between the Au and PPy. Incorporation of Au NPs in PPy matrix leads to a small shift of the peak's wavelength and also decreases the intensity of the peaks, which indicates that the structural change of polymer occurs due to doping [32,33]. Similar to that of pure PPy, all the other characteristic bands are observed for PPy-Au NC, as seen in Figure 8(b). Thus the structure of PPy backbone in PPy-Au NC is similar to that of conventional PPy. This analysis confirms that the Au NPs are dispersed in the PPy matrix.

F. XRD Result

To confirm the presence of stable Au NPs in the final nanocomposite, the XRD spectra of PPy as well as of PPy-Au NC was taken. XRD pattern of pure PPy and PPy-Au NC is presented in Figure 9. The XRD pattern of pure PPy shows a broad peak at $2\theta = 26^\circ$, which supports amorphous structure of the PPy. This broad peak in PPy may arise due to the scattering of X-rays caused by short-range arrangement chains of PPy [34-36]. The XRD pattern of PPy-Au NC shows the characteristic peaks at $2\theta = 38.5^\circ$, 44.6° , 65.1° , 77.8° representing Bragg's reflections from (1 1 1), (2 0 0), (2 2 0), (3 1 1) planes of the face centred cubic (FCC) structure of Au.

These values are well in agreement with the reported ones. All the four characteristic peaks are due to the crystalline structure of Gold. In addition to these four peaks, a broad peak is observed at 26° due to the amorphous structure of PPy. This confirms the existence of metallic Au in the PPy black [33, 37-38].

The average crystallite size from an intense peak at 38.5° , Au (1 1 1) diffraction line for PPy-Au NC is estimated by using Scherer's equation $D = \frac{K\lambda}{\beta \cos \theta}$, where D is the mean

dimension of the crystallites, K is the shape factor (equals 0.89), λ is the wavelength of the Cu K α radiation (1.5414 nm), β is the peak FWHM in radian and θ is the diffraction peak position [39]. The average crystallite size of the Au NP is found to be about 26.37 nm which is consistent with the result of TEM.

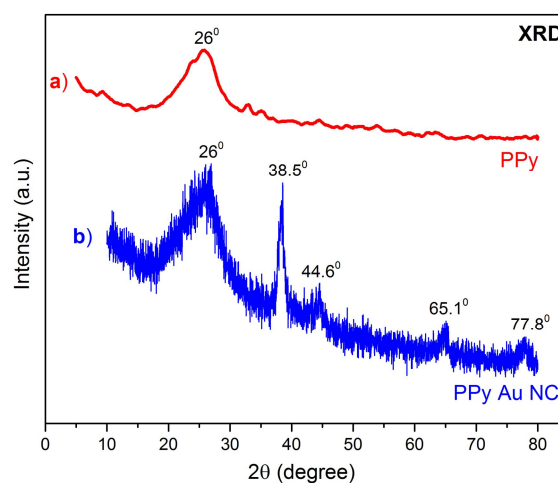


Figure 9. XRD pattern of PPy (S0) and PPy-Au NC (S3)

G. Antibacterial properties of synthesized PPy-Au nanocomposites

The polymer composites showed anti-bacterial activity against all the test microorganisms, namely Escherichia coli, Klebsiella pneumonia, Staphylococcus aureus and Sarcina lutea. The test substances diffuse in the medium and produce a clear zone of inhibition if it has anti-bacterial activity. The zone of inhibition as shown in Figure 10 is produced due to bacteristatic or bactericidal effect of the test substance filled the wells as it diffuses in the radial manner. The size of diameter of zone of inhibition indicates the antimicrobial efficacy of the test substance against the sensitive test organism. The anti-bacterial activity of the polymer composites.

Table 1. Anti-bacterial activity of the polymer composites

Sample	Anti-bacterial zone size (mm)			
	<i>Escherichia coli</i>	<i>Klebsiella pneumoniae</i>	<i>Staphylococcus aureus</i>	<i>Sarcina lutea</i>
A	25.5	21	32	34.5
B	24.5	23.5	31.5	30.5
C	22.5	22	27.5	30
D	23.5	21	28	28

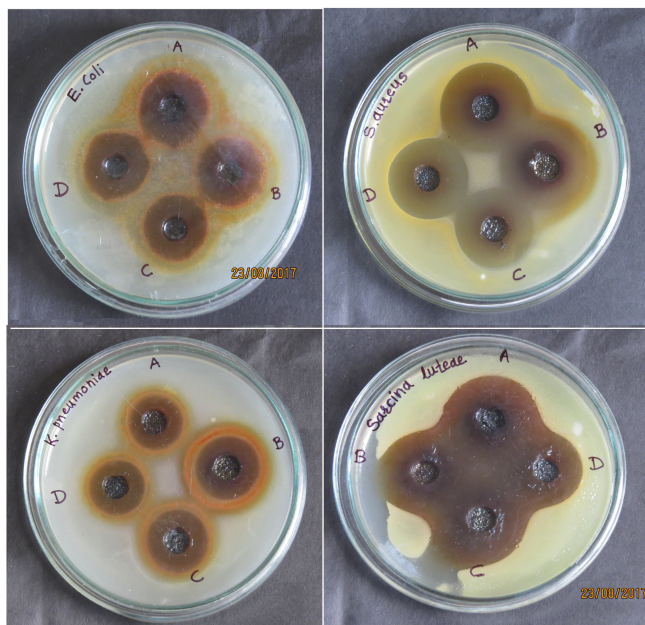


Figure 10. Photograph of anti-bacterial activity of the polymer composites

IV. CONCLUSION

Polypyrrole-Gold nanocomposites have been successfully synthesized by in-situ chemical oxidative polymerization of pyrrole in the presence of a colloidal suspension of Au NPs. The presence of gold nanoparticles in PPy is confirmed by the characterization techniques viz. TEM, SEM, AFM, XRD, and FTIR analysis. More significantly, in-situ chemical oxidative polymerization synthesis method might be a facile but effective route and could be readily used for mass production of the PPy-Au NCs. All the polymer composites showed significant anti-bacterial activity. More prominent effect was observed against Gram positive organisms as compared to the Gram negative organisms.

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