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Applications of a new type of poly(methyl methacrylate)/TiO_2 nanocomposite as an antibacterial agent and reducing photocatalyst

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Abstract

A new type of poly(methyl methacrylate) (PMMA)/TiO_2 nanocomposite film sensitized by ionic liquid with low dosage of TiO_2 nanoparticles was prepared based on microemulsion method. The photocatalytic activity, via the photoreduction of 4-Nitrophenole (4-NP) to 4-Aminophenole (4-AP) by $NaBH_4$ and the photocatalytic-based antibacterial activity over *Escherichia coli* and *Staphylococcus arouse* destruction of the prepared nanocomposite film were investigated. The conditions for maximum efficiency in the present of visible light irradiation have been evaluated. The rate constant of photoreduction of 4-NP to 4-AP was calculated and the maximum rate constant was found over the 0.01 *wt.*% of TiO_2 content in photocatalyst and solution pH of 7.5. A photocatalytic antibacterial maximum activity against gram negative bacterium was also obtained over the 0.01 *wt.*% of TiO_2 content in photocatalyst. A notable exception of this work is that PMMA/TiO_2 nanocomposite films show efficient photocatalyst activity at very low loading of TiO_2 in contrast of other previous reports.

Keywords: TiO_2; microemulsion; Photoreduction; 4-Nitrophenole; Antibacterial activity

1. Introduction

Titanium dioxide (TiO_2) as a popular photocatalyst has been drawing a lot of attention because of its environmental applications in the decomposition of pollutants and microbial species in water and air.[1-3] Since the past two decades, much scientific attention in the field of polymer-based photocatalyst has been focused owing to its advantages, such as easy post treatment recovery.[2,4] Some of various research works have additionally been reported in the visible light active TiO_2 photocatalyst. Singh *et al.*[2] presented a remarkable review that this comprehensive study covers over a hundred published papers. Until today, as per other literature survey it appears that the polymer-based TiO_2 was fabricated with high loading of TiO_2 and sometimes in presence of different sensitizer additive such as dye and noble metals.[2,5]

It must be noted that the preparation of novel polymer-supported TiO_2 nanocomposite with the above pleasing properties and especially low TiO_2 contents is a utopia. As the best of knowledge, we found that still any research papers have been reported on very low concentration of TiO_2 in polymer composites. This makes a promising research area to be explored and developed further. In order to providing a novel route for fabrication of a buoyant polymer-TiO_2 nanocomposite with very low TiO_2 content and to confirm the necessity of visible light photocatalyst applicability, a very simple process based on ionic liquid-microemulsion system is conducted in this work to emphasis this global concerns.[6] By using the ionic liquid based microemulsion system, a polymer-TiO_2 nanocomposite can be deduced which not only is visible light active photocatalyst without any additive, but also improves the recombination of photogenerated holes and electron as the major limitation of polymer-TiO_2 mediated photocatalysis. An important highlight as per our previous literature study is to prepare an economical PMMA/ionic liquid sensitized TiO_2 with very low dosage of TiO_2. The prepared low dosage of PMMA/ TiO_2 can be an effective photocatalyst in degradation of methylene blue dye to overcome the main drawback of the previous developed polymer/TiO_2 nanocomposite that published by Magalhase *et al.*[7] They prepared low density polyethylene (LDPE)/ TiO_2 photocatalyst using various TiO_2 contents (32, 68, 82 *wt.*%). In progressing of our previous research work in waste water treatment,[6] in this study we considered the photodegradation of a phenolic compound and also photocatalyst antibacterial activity by using a very low TiO_2 contents (0.008-0.014 *wt.*%) immobilized in PMMA.

Phenolic compounds such as 4-Nitrophenol, which is one of the organic pollutants listed by EPA in U.S.A, are carcinogenic and harmful for the environment. These types of compounds are extensively used in plastic industries, petrochemical, agrochemical and so forth.[8] The selective reduction of aromatic nitro compounds to the corresponding aromatic amines which are widely utilized in the dyes, photographic, agricultural, and pharmaceutical industries, is one of the fundamental transformation with reducing agents in organic synthesis.[9] Photodegradation of p-nitrophenol (PNP) has been investigated by Chen at different conditions, in aqueous suspension of P25 TiO_2 nanoparticles and also over immobilized P25 TiO_2 nanoparticles.[10] They reported pseudo firs-order kinetics that it respects for all of parent compounds. Indeed, we underline to the role of TiO_2 as a photocatalytic antibacterial material that has considerable beneficial properties such as bio-compatibility, high potential for self-cleaning and high antibacterial activity[11,12] and is now the basis for a number of commercial antibacterial products.[13-16]

Surprisingly, there is an increasing interest in combining photocatalytic activity of TiO_2 and hydrophobic polymer for preparation of polymer supported TiO_2 in bacteriological study.[3] So, polymeric materials are a good candidate to use in the health care industry and environment materials.[17,18] Ratova *et al.*[3] produced LDPE/ TiO_2 films by an extrusion method and tested photocatalytic antibacterial activity, via the destruction of *Escherichia coli* at the same time as TiO_2 contents was 5 and 30 *wt.*%. They also investigated the photodecomposition of methylene blue dye under UV illumination by the same (LDPE)–TiO_2 films. Hence, in continuation of our research works on microemulsion systems as soft template for nanomaterials synthesis[19,20], the chief object of the present examination is to focus on the some environmental applications of PMMA/TiO_2 nanocomposite, prepared by ionic liquid based microemulsion system. An interesting feature of advanced innovative microemulsion systems is effective and sustainable synthesis route with very low concentration of ionic liquid and TiO_2 nanoparticles in composite. In our previous report, PMMA/TiO_2/IL nanocomposite as a highly efficient visible light photocatalyst was synthesized and characterized.[6] In the current work, the application of the prepared PMMA/TiO_2/IL nanocomposite with very low dosage of TiO_2 for photoreduction of 4-NP has been investigated. The effects of TiO_2 dosage, pH and light intensity of lamp on the rate constant of photoreduction process have been determined. As a second application the antibacterial effect of the nanocomposite was also tested on the destruction of clinical strain of *Escherichia coli* (Gram-negative) and *Staphylococcus arouse* (Gram-positive) in visible light.

2. Experimental

Materials

Hydrophilic ionic liquid, ([bmim][BF_4]),and the nonionic surfactant of Triton X-100 were purchased from Sigma-Aldrich. The titanium dioxide TiO_2 nanoparticles used in this study was Degussa P25 (ca. 80% anatase, 20% rutile, with a BET surface area of 50 m^2/g and particle size of less than 15 nm). Methyl methacrylate (MMA) monomer (AR grade), benzoyl peroxide (BPO), 1-butanol, sodium borohydride and 4-nitrophenol as a pollutant model were prepared from Merck. All aqueous solutions were prepared with deionized water (0.055 μΩ) which was produced in our lab with PKA (Smart two pure) instrument.

Preparation of the modified PMMA/TiO_2 nanocomposite

In order to synthesis modified PMMA/TiO_2 nanocomposite a microemulsion system consisting of hydrophilic ionic liquid [bmim][BF_4] (2.26 *wt.%*), MMA (88.94*wt.%*), TX-100 (6.56 *wt.*%) and1-buthnol (2.24 *wt.*%) was prepared. Then, different amounts of TiO_2 nanoparticles were loaded into this microemulsion system. Benzoyl peroxide (BPO) as an initiator (0.2 *wt.*% based on the weight of MMA) was added to the above stabilized TiO_2 colloidal systems to start polymerization process at 60°C. For labeling purposes, the resultant transparent nanohybrid films of PMMA/TiO_2 were termed as S1, S2, S3, and S4 referring to the amounts of TiO_2 nanoparticles corresponding to 0.008, 0.01, 0.012 and 0.014 *wt.*%. No apparent visible phase separation was observed during polymerization process for all samples. Pure PMMA was also prepared under the same condition and identically formulated microemulsion without TiO_2 loading. The nanocomposite films were obtained using an automatic film applicator (ELCOMETER). The set-up of the automatic film applicator is shown in Fig. S1†. All of the produced transparent films had the uniform thickness with an average central thickness of 100 μm, as measured by a micrometer. Techniques such as UV-Vis diffuse reflectance spectra (DRS), TEM, FT-IR and TGA were used to characterize the resulting modified nanocomposite and reported in our previous paper.[6] The UV-Vis transmittance was also used to claim transparency of the fabricated film.

UV-Vis transmittance

The UV-Vis transmittance spectrum of the prepared nanocomposite for S2 as a typical sample was obtained in air at room temperature in the wavelength range of 200–600 nm by using a UV/Vis/NIR spectrophotometer (JASCO, V-670 (190-2700 nm).

Photocatalytic activity test

Photoreactor and Photoreduction of 4-NP

All the nanocomposites and pure PMMA films were initially assessed for the photoreduction of 4-NP at normal laboratory environmental conditions. The photoreduction experiment was carried out in a glass beaker as the reaction vessel. The assembled photocatalytic activity test system was described elsewhere.[6] In this system there is a sun-light fluorescent lamp attached vertically at the top. The distance between the light and the reactor was fixed at 10 cm. The assembled system was placed inside a wooden box coloured black so that no stray light can inter the reactor. The reduction of 4-nitrophenol to a beneficial compound, 4-aminophenol, by sodium borohydride was chosen as a model reaction. A thin film of the nanocomposite was heterogeneously placed into a 20 mL of total aqueous solution containing 4-nitrophenol (0.144 mM) and excesses amount of 1.2M sodium borohydride solution in the presence of visible light irradiation. During the reduction process the UV−visible spectra of the reaction mixture was recorded at intervals of 60 min. Before analyzing with a double beam UV-vis spectrophotometer (Perkin Elmer lambda 15), the nanocomposite film was removed from all solutions to stop reaction. The temperature of the reaction solution was kept constant at 25°C. Three following control samples were employed: blank (1), a solution of 4-NP without the photocatalyst and sodium borohydride, blank (2), a solution of 4-NP in the presence of the photocatalyst without sodium borohydride, and blank (3), a solution of 4-NP with sodium borohydride and without the photocatalyst. The removal efficiency was measured by applying the following equations:

$$\%\ \text{Photocatalytic efficiency} = \frac{}{} \times 100 \qquad (1)$$

where A_o (at 400 nm) is the initial absorbance of 4-NP at zero time and A_t the absorbance of 4-NP at t time.

Antibacterial activity test (Kirby-Bauer method)

The photocatalytic-based antibacterial activity of each of the produced nanocomposite films and pure PMMA film were evaluated as a series of photocatalytic experiments. A clinical isolates *Escherichia coli* bacterium (from Gram-negative) and Staphylococcus arouse (from Gram-positive) were used for this study. Agar well diffusion method[21] was used for determination of the degree of photocatalytic destruction of *Escherichia coli* and *Staphylococcus arouse.* The pH was fixed at 7.3. Briefly, sterile molten Mueller-Hinton agar (20 ml) was poured into sterile petri dishes and allowed to solidify at room temperature. Pyre cultures of pathogenic bacteria as 0.5 McFarland (10^8 CFU/ml) was swabbed on the Muller-Hinton agar plates. Further 5 mm thin film disk of pure PMMA as a control sample and all of nanocomposite films with different dosage of TiO_2 (samples S1 to S4) were situated onto 5 mm paper disk on the inoculated surface of Mueller-Hinton agar plates. Inoculated plates were incubated for 24 h at 37 °C in a thermostatic light incubator under visible light irradiation (lamp 60 W). The substrates were kept 20 cm away from the light source. The zone of inhibition was measured and the results were expressed as mm compared to control pure PMMA. This procedure was repeated three times.

3. Results and discussion

UV-Vis transmittance

The UV-Vis transmittance spectrum of the prepared PMMA and PMMA/TiO_2 nanocomposite (S2) is illustrated in ESI (Fig. S2†). As expected, the UV-VIS spectrum of PMMA sample exhibit a transmittance of 60% and higher at or above 260 nm. The UV-Vis spectrum of PMMA/TiO2 is also revealed an increase in the transmittance at above 400 nm due to the presence of TiO_2 nanoparticles as can be seen in Fig. S2†.

Effect of TiO_2 contents of nanocomposites on the 4-NP photoreduction

In order to study the kinetic of the photoreduction process by UV-visible method, a time-dependent spectra for 4-NP/sodium borohydride reaction mixture containing nanocomposite (S2) was obtained and shown in Fig.1. As can be seen, the absorption band of the nitrophenolate ions at ca. 400 nm is decreased, while the absorption band at ca. 300 nm increased due to the formation of aminophenolate ions.[22]

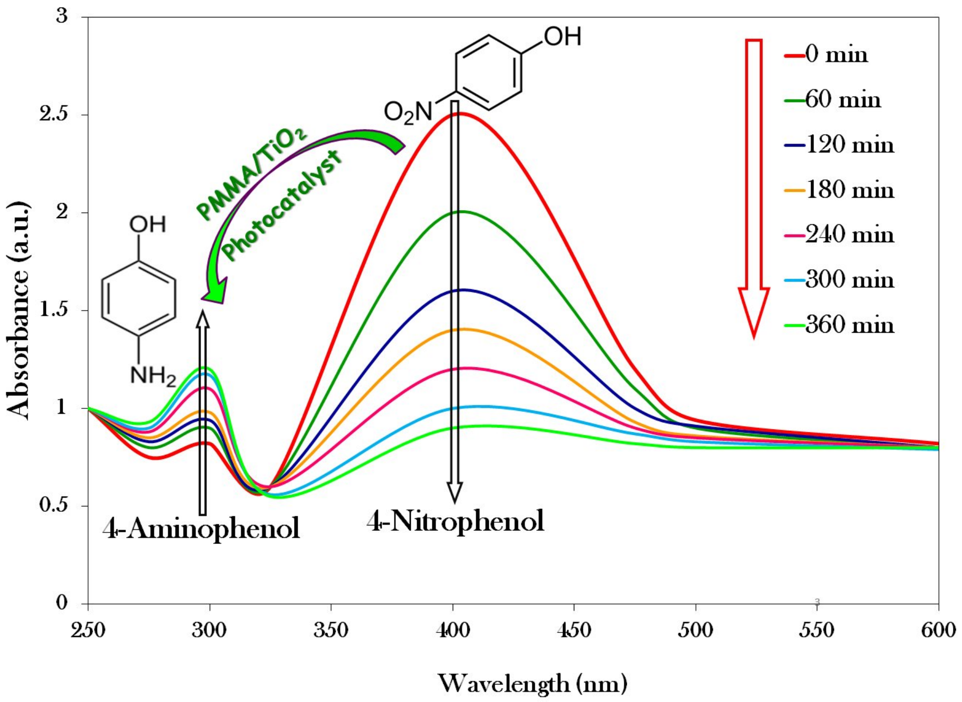


Fig 1. Spectral patterns of 4-NP solution during the photocatalytic reduction process in the presence of S2 nanocomposite sample, under visible-light irradiation for 6 h.

The photocatalytic activity of the prepared nanocomposites was tested in photoreduction of 4-NP by sodium borohydride in aqueous solution. Fig. 2 shows the photoreduction process of 4-NP at different conditions. The nitrophenolate ion as an intermediate forms in the aqueous solution of sodium borohydride from nitrophenol. The nitrophenolate ion can be reduced to aminophenolate ion in the presence of desired PMMA/TiO_2 photocatalyst and the reducing agent by equation (2). Actually, visible light active TiO_2 in this new type of nanocomposite is acted to expedite electron transfer from donor (BH_4^-) to acceptor (4-NP). UV−visible spectrophotometric analysis substantiated that the modified PMMA/TiO_2 served as a photocatalyst for the photoreduction reaction.

$$4-\mathrm{NP}+\mathrm{NaBH} \longrightarrow 4-\mathrm{AP} \qquad (2)$$

A reduction test on 4-NP as a blank (3) (without photocatalyst) shows that, without addition of a photocatalyst, the photoreduction of 4-NP by $NaBH_4$ is slow and the photoreduction efficiency, which was calculated by equation (1), is less than 9%

after 6h of visible light illumination. No remarkable change was also observed for blank (1) and (2) solutions. As can be seen from Fig. 2, the concentration of 4-NP decreased as a function of irradiation time. Pure PMMA as S0 sample was also tested in photoreduction reaction and the obtained result was same as the blank (3). The maximum photoreduction efficiency, calculated by equation (1), was 78.25 %, belonging to sample S2, after 6 h irradiating. As we expressed in our previous work, which was the photocatalytic degradation of MB dye, it is clearly found that the ionic liquid sensitized TiO_2 supported PMMA could be an effective catalyst for the water treatment.[6] For this catalyst a noticeable effect of IL on the catalytic activity under visible light was established and a suitable mechanism was proposed.

Since the sodium borohydride was used in excess, the rate of photoreduction process can be described by the following equation[22]:

$$\frac{[}{} =^{]} - \quad [4 - \mathrm{NP}] \qquad (3)$$

where k is the rate constant of the photoreduction. The concentration of 4-NP was calculated based on the absorbance at 400 nm. The rate constant could be determined from the slope of the plot of $ln(A_0/A_t)$ versus time. A_t and A_0 are the time-dependent absorbance and initial absorbance, respectively. The result of plotting $ln(A_0/A_t)$ versus the reaction time exhibits a good linear correlation. The calculated rate constants of photoreduction and the linear regression values are reported in Table 1. The rate constant toward the S2 sample of the photocatalyst was calculated as 3.3×10^{-3} min^{-1}, which was the maximum value. As shown in the results of Table 1, the rate constant was increased with the increasing dosage of TiO_2 and approaching a limiting value at high loading of nanoparticles. This behaviour may be due to aggregation of nanoparticles in polymer matrix which causing a decrease in the number of surface active sites.

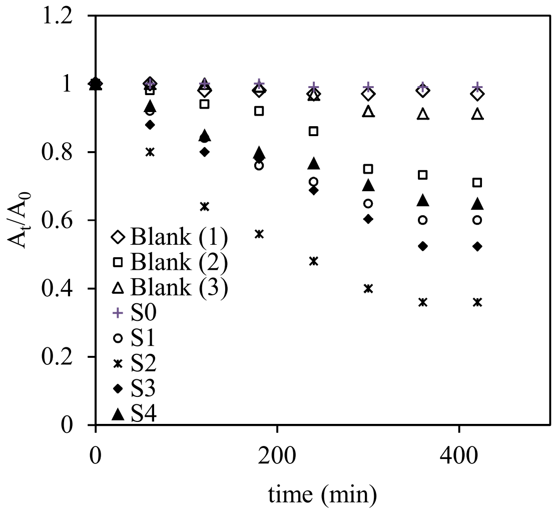


Fig 2. Effect of TiO_2 nanoparticles concentration of PMMA/TiO_2 photocatalyst on 4-NP photoreduction under visible light irradiation.

Table 1 The calculated pseudo first-order rate constants of 4-NP photoreduction and the linear regression values

Sample	$k \times 10^{-3}$(min^{-1})	R^2
Blank (1)	0.0900	0.7319
Blank (2)	0.8000	0.8818
Blank (3)	0.2000	0.9976
S0	0.2000	0.9800
S1	1.4001	0.9984
S2	3.3310	0.9995
S3	1.7000	0.9831
S4	1.2011	0.9926

Effect of pH

The pH value of the reaction medium during photoreduction reactions plays a very significant role in the process design and control photocatalysts.[6,23] To evaluate the photocatalytic activity at different pH, the S2 sample was used. The higher efficiencies were observed at pH value of about 7.5 (Fig. 3). It is clear that the change in the solution pH has a critical effect on the 4-NP photoreduction, which directly affects the surface charge properties of the photocatalyst and the adsorption of pollutants.[6] As can be seen any further decrease or increase of pH less than 7 or more than 8, significantly decrease the photocatalytic reduction efficiency. Therefore, we suggest that a pH of 7.5 is optimum for the reduction of 4-NP with S2 sample nanocomposite. As Islam *et al.* [23] expressed the effect of pH on degradation of 4-NP against TiO_2 at neutral condition, the following reaction is possible for generation of $^{\cdot}OH$:

$$h^+ + H_2O_{(ads)} \rightarrow {}^{\cdot}OH_{(ads)} + H^+ \qquad (4)$$

This reaction would increase the photoreduction of 4-NP by electron and holes mechanism at neutral pH.

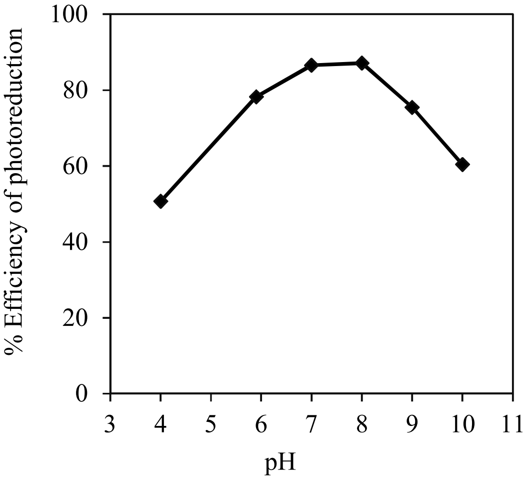


Fig 3. Effect of solution pH on the 4-NP photoreduction over S2 nanocomposite sample under visible light irradiation.

Effect of light intensity

The kinetics of the 4-NP photoreduction by (S2) sample, under three various visible light lamps was studied. Table 2 contains a summary of first order rate constants and linear regression values of kinetic data. The emission spectrum and the total radiation data of the fluorescence lamps (18, 36 and 60 W), obtained using Avaspec 2048 TEC instrument at the same condition of the photocatalysis test, are shown in Fig.S3† and reported in table 2. It can be seen that the rate constant value of 4-NP photoreduction under 60 W irradiating was much higher than the other cases. This result is in good agreement with the excellent generation of electron and holes pairs at the high intensity which causing an increase in the photocatalytic activity. This interesting result confirms that the synthesised nanocomposite capable to absorb visible light with different intensity and acts as an effective photocatalyst. It can be suggested that the photoactivity of the prepared PMMA/TiO_2 nanocomposite can be extrapolated for higher power lamps >60 W.[24]

Table 2 Effect of power and intensity of lamp on the pseudo first-order rate constants of 4-NP photoreduction, for S2 photocatalyst sample

Lamp power (W)	Total radiation (mW/cm^2)	$k \times 10^{-3}$ (min^{-1})	R^2
60	0.141	3.3	0.9995
36	0.069	2.1	0.9967
18	0.035	1.8	0.9977

Recycling and photocatalyst stability of the nanocomposite

Catalyst recycling is a key step in assessing its practical application and developing heterogeneous photocatalysis technology for wastewater treatment. To evaluate the photocatalytic stability of the composite photocatalyst, PMMA/TiO_2 (S2) was used for several photocatalytic runs, and each run lasted 360 min. The results, which shown in Fig. 4, is the ratio of A_t/A_0 vs. number of runs, confirms that the composite photocatalyst is reusable with high activity and stable after several experimental runs.

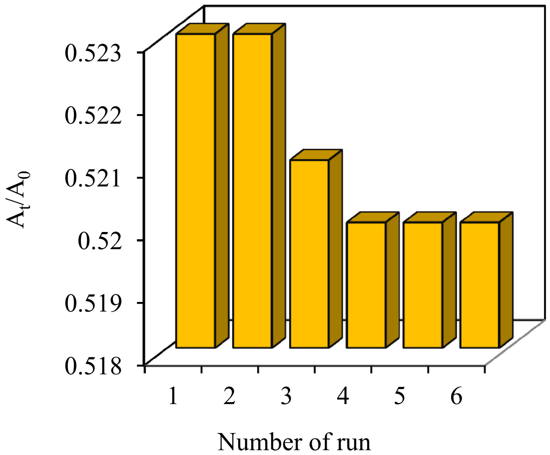
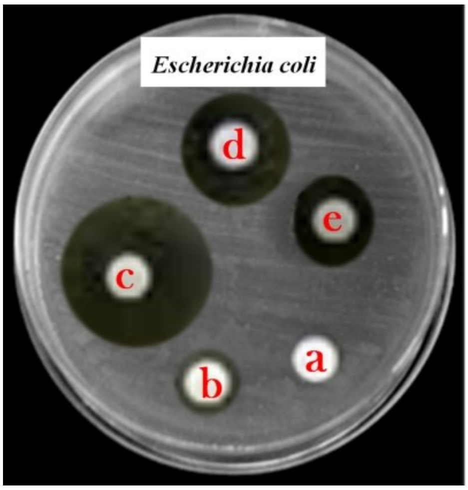


Fig. 4. Reusability of the nanocomposite (S2) for photoreduction of 4-NP solution under visible irradiation.

Antibacterial activity results

The zone of inhibition toward clinical isolate *Escherichia coli and Staphylococcus arouse* with pure PMMA and PMMA/TiO_2 nanocomposites with different loading of TiO_2, was evaluated under visible light. The obtained data showed that PMMA/TiO_2 nanocomposite has the much more antibacterial activity against *Escherichia coli* and *Staphylococcus arouse* than the pure PMMA. For two types of bacteria, with increasing TiO_2 dosage, firstly antibacterial activity increased and with further loading, the antibacterial activity decreased. The maximum antibacterial efficiency was belonging to sample S2 of PMMA/TiO_2 nanocomposite and has broad spectrum antibacterial activity. The determined zones of inhibition with pure PMMA (as control), S1, S2, S3 and S4 samples against *Escherichia coli* and *Staphylococcus arouse* were obtained as 0, 7 ± 0.50, 19 ± 0.72, 14 ± 0.51 and 10 ± 0.28, respectivelyagainst *Escherichia coli*and toward *Staphylococcus arouse* were 0, 7± 0.52, 20± 0.81, 15± 0.23 and 14± 0.26, respectively. Fig.5, presents a photograph of the zone of inhibition against to *Escherichia coli* and *Staphylococcus arouse* obtained by Kirby-bauer method. As expected, the antibacterial activity was found to increase with the increasing dosage of TiO_2 and loss of antibacterial activity can be observed at high loading of TiO_2. As mentioned above this trend may be due to aggregation of nanoparticles in polymer matrix, which causing a decrease in the number of surface active site. As an excellent result, it was found that the prepared nanocomposite has the best antibacterial activity against *Staphylococcus arouse* due to electrostatics interaction between surface of nanocomposite and corresponded Gram positive bacterium. The main killing mechanism for the antimicrobial effect of TiO_2 photocatalysis is attributed to the hydroxyl radicals and oxygen reactive species as part of the photocatalytic mechanism. The creation of electron–hole pairs during visible light irradiation, which, in turn, can lead to the photocatalytic process. The hydroxyl radicals and oxygen reactive species in which the bacterial cell membrane is the primary oxygen reactive species attack site, leading to lipid peroxidation cell membrane.[25-28] However the diffusion length of oxygen reactive species in Agar was not considered, so the aim of this study is comparing of the nanocomposite samples with different TiO_2 dosage. It was found that by increasing of TiO_2 loading up to 0.01 wt.% in nanocomposite the antibacterial activity increased. After that by increasing TiO_2 content the antibacterial effect was decreased due to agglomeration of TiO_2 nanoparticles in polymer matrix. Hebeish *et al.*[29] reported the killing mechanism of the microorganisms originally may be explained as follows: the degradation of the cell wall and cytoplasmic membrane by hydroxyl radicals and hydrogen peroxide that initially leads to leakage of cellular contents. Finally cell lysis followed by complete mineralization of the organism. As can be seen from Fig. 5, no zone of inhibition was observed for PMMA in contrast of the conductive polymer same as polypyrrole. Key factors such as electrostatic adsorption between conductive polymer and bacteria, higher molecular weight, surface hydrophilicity and direct contact between polymer and bacteria cell lead to existence of antibacterial activity of pure conductive polymer.[23]



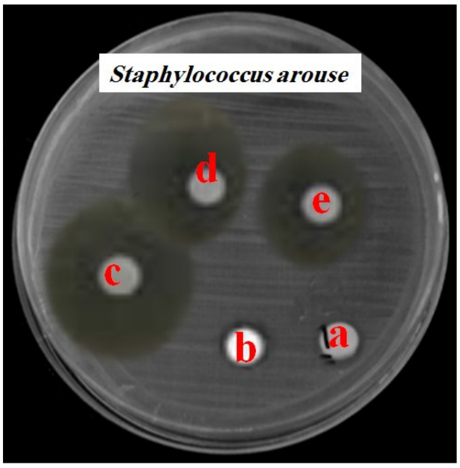


Fig 5. Antibacterial activity of clinical strain of *Escherichia coli* and *Staphylococcus arouse*, with (a) Pure PMMA,(b) S1, (c) S2, (d) S3 and (e) S4, by Kirby-bauer method.

4. Conclusion

In this study, $PMMA/TiO_2$ nanocomposite film sensitized by ionic liquid with very low content of TiO_2 nanoparticles was prepared based on microemulsion technique. It is shown that the as-prepared nanocomposite films exhibit noticeable photocatalytic activity, especially for an optimized value of TiO_2 content in the nanocomposite. The best performance of this special catalyst in photoreduction of 4-NP to 4-AP and bacteriological study was obtained among the sample with 0.01 *wt.*% of TiO_2. It is also verified that using ionic liquid based microemulsion systems for preparation of $PMMA/TiO_2$ causes the high photocatalytic activity under visible light, as was mentioned in our previous work. This could be associated with the role of ionic liquid in enhancing the transportation of photo-induced electrons and hole in the photocatalyst nanocomposite. The highest efficiency in 4-NP photoreduction was also achieved at pH = 7.5 with a 60 W lamp. According to the results, it is clear that, a higher visible light photocatalytic antibacterial activity means a higher antibacterial activity due to positive correlation between the photocatalytic activity and antibacterial activity of the nanocomposite films. It is worthy to note, by virtue of its application of our nanocomposite, it could be promising for possible industrial and medical applications.

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