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ARTICLE



Solid-phase photocatalytic degradation of polyaniline under UVA and UVC light irradiation

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ABSTRACT

In this study, pure polyaniline (PANI0) and polyaniline/titanium dioxide composites, including 15 wt.% TiO₂ (PANI15) and 25 wt.% TiO₂ (PANI25), respectively, were synthesised using an in-situ polymerisation technique in the absence and in the presence of titanium dioxide nanoparticles, respectively. The solid-phase photocatalytic degradation of polyaniline/titanium dioxide (TiO₂) composites was compared with that of the pure polyaniline with the aid of weight loss measurements. The structural and morphological properties of the prepared samples were studied by Fourier transform infrared spectroscopy, field emission scanning electron microscopy, energy dispersive X-ray analysis, thermogravimetric analysis and X-ray diffraction analysis. The loading of TiO₂ nanoparticles in polyaniline enhanced the solid-phase photocatalytic degradation of the pure polymer both under UVA light and under UVC light, respectively. Fourier transform infrared spectroscopy illustrated that Pani was synthesised successfully in the presence of TiO₂ nanoparticles. Field emission scanning electron microscopy revealed homogeneous TiO₂ dispersion within Pani matrix. Thermogravimetric analysis supported the idea that the thermal property of the pure polymer was improved with the photocatalyst contribution. The crystalline structure of TiO₂ did not change with Pani.

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Photocatalytic degradation; polyaniline; titanium dioxide; UV light

1. Introduction

Although polymeric materials have various applications, having eased the human life to a great extent, continued rise in the use of polymeric materials has led to serious environmental problems. Polymeric materials reveal a major disposal and treatment problems in urban solid waste management since they are chemically and biologically inert materials, remaining stable in the environment for hundreds of years. Limited disposal and treatment methods have been applied to eliminate the plastic problem. Incineration method, which is the easiest technique among applied methods, creates harmful and toxic gases accompanied by air pollution [1]. The recycling of polymeric materials does not solve the problem too much since very few plastics can be recycled by using expensive and time-consuming methods. The biodegradation method suffers from the drawback of low degradation rate. As an alternative to the specified techniques, the

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solid-phase photocatalytic degradation method has become popular due to its low cost and moderate process conditions [2]. Titanium dioxide (TiO_2) is one of the most studied photocatalyst for photocatalytic degradation of the plastics since it is highly active, photostable, inexpensive and reusable. TiO_2 has a wide band gap in the ultra-violet (UV) range (3.0 eV – 3.2 eV). Thus, UV light irradiation is required to activate TiO_2 photocatalyst for the photocatalytic plastic degradation [3].

The photocatalytic degradation feature of TiO_2 comes from the formation of photo-generated charge carriers, which are electrons and holes. These photogenerated charge carriers occur upon the absorption of the UV light corresponding to the band gap of TiO_2 . With the absorption of the UV light, electrons from the valence band excite to the conduction band of the photocatalyst, which leads to the formation of the photogenerated charge carriers. The photogenerated electrons and holes diffuse to the photocatalyst surface and react with surface adsorbed oxygen and water molecules, forming highly active radicals like hydroxyl and superoxide anions. These active radicals can decompose any kind of organic-based plastic materials in contact with TiO_2 through the chain scission reactions into small molecules [4]. The solid-phase photocatalytic degradation of plastic materials with TiO_2 immobilisation has recently attracted considerable attention and many polymeric materials, such as polyethylene [2], polypropylene [5], polyvinyl chloride [2], polystyrene [6], polyvinyl borate [7], and polyvinyl alcohol [8], was investigated in the presence of TiO_2 nanoparticles.

Polyaniline (Pani), with excellent properties including low production costs, high conductivity, good environmental and thermal stability, has gained comprehensive attentions among conductive polymers for different applications like membrane [9], electrical and electronic industrial applications [10]. Therefore, the polyaniline waste has become intense in our environment and the disposal of this plastic waste has gained importance. In literature, the disposal of polyaniline through the solid-phase photocatalytic degradation has not been studied much. Zhang and co-workers [11] studied the photocatalytic degradation polyaniline with the TiO_2 photocatalyst under UVA light irradiation. Polyaniline composites with different TiO_2 compositions were prepared using the in-situ polymerisation technique. The highest weight loss of about 6.8 wt.% was obtained with the composite, including 75 wt.% TiO_2 nanoparticles after 60 h of UVA light irradiation [11]. In this study, polyaniline composites, containing 15 wt.% and 25 wt.% of TiO_2 nanoparticles, respectively, were synthesised and the solid-phase photocatalytic degradation characteristic of polyaniline was investigated in the presence and absence of the photocatalyst, respectively, under UVA and UVC light irradiations. The novelty of this study was to evaluate the solid-phase photocatalytic degradation of polyaniline in the presence of low content of the photocatalyst with two different UV light sources, respectively.

2. Experimental

Aniline hydrochloride, ammonium peroxydisulfate, acetone and hydrochloric acid, provided from Sigma-Aldrich Chemie GmbH, Germany, were used to synthesise polyaniline. TiO_2 nanoparticles (anatase, <25 nm, 99.7% trace metals basis), supplied by Sigma-Aldrich Chemie GmbH, Germany, were used as photocatalyst. Polyaniline was synthesised in the presence of the photocatalyst nanoparticles via the in situ polymerisation method to prepare the composite, including 15 wt.% TiO_2 (PANI15) and 25 wt.% TiO_2 (PANI25),

respectively. Aniline hydrochloride ($\geq 99\%$) was introduced into the reaction vessel with 100 ml of distilled water and it was stirred to provide 0.04 M aniline solution. Certain amount of TiO_2 nanoparticles were introduced into the same reaction vessel and the solution was kept under stirring for 1 h to obtain a uniform suspension. At the same time, ammonium peroxydisulfate ($\geq 98.0\%$) was added into another reaction vessel with 100 ml of distilled water and it was stirred to obtain 0.05 M oxidant solution. Then, the oxidant solution was added dropwise to the aniline solution, containing the photocatalyst nanoparticles. The final mixture was kept under stirring for 24 h to complete the polymerisation reaction. After the precipitated slurry was filtered and rinsed with hydrochloric acid solution and acetone, respectively, the resulting product (PANI15 and PANI25) was dried at 60°C for 24 h. For comparison purposes, pure polyaniline (PANI0) was also synthesised in the absence of the photocatalyst nanoparticles in accordance with the procedure, followed during PANI15 and PANI25 synthesis [12].

The chemical structure of the composite was studied on Fourier transform infrared (FTIR) spectra of PANI0, PANI15 and TiO_2 , recorded with Thermo Scientific-Nicolet 380 model spectrophotometer in the region of $4000\text{--}400\text{ cm}^{-1}$. The morphology of TiO_2 nanoparticles and the composites was studied with a field emission scanning electron microscope at 30,000 kV (FESEM, QUANTA 400F, Thermo Fisher Scientific, Inc., UK) equipped with an EDX (Energy dispersive X-ray) analyzer (JXA-8230 EDX Microanalysis Instrument, Thermo Fisher Scientific, Inc., UK). FESEM images were also used to obtain the particle size distribution. Prior to SEM analyses, the samples were coated with Au-Pd against charging effects of polymer and TiO_2 under electron beam irradiation. The thermogravimetric analyses (TGA) of PANI0, TiO_2 PANI15 and PANI25 were characterised using a thermogravimetric analyser (Setaram Labsys TGA/DTA). X-ray diffraction (XRD) characterisation of TiO_2 and PANI25 was conducted on a X-ray diffractometer (Rigaku Ultima IV) over a 2θ range from 20° to 50° with $\text{Cu K}\alpha$ radiation.

The solid-phase photocatalytic degradation of PANI0 and the composite samples (1.0 g) was conducted in the ambient air by using a 12 W UVA lamp and 30 W UVC lamp, respectively. The samples were placed 10 cm away from the lamp. The solid-phase photocatalytic degradation of all samples was evaluated directly by their weight loss.

3. Results and discussion

Figure 1 illustrates the FTIR spectra of PANI0, PANI15 and TiO_2 . For the spectrum of PANI0 (Figure 1(a)), the peaks at 1585 cm^{-1} , 1498 cm^{-1} , 1301 cm^{-1} , 1143 cm^{-1} and 817 cm^{-1} were related to C = C stretching of the quinoid rings, C = C stretching of the benzenoid rings, C-N stretching of tertiary aromatic amine, C-N stretching of the quinine units and C-H stretching of the benzenoid units, respectively. The wide transmission peak observed at around 3450 cm^{-1} was corroborated to N-H stretching of secondary amine units. Most peaks of the pure polymer were also appeared on the FTIR spectrum of the composite (Figure 1(b)). However, a little shift was observed in the FTIR spectrum of PANI15 compared to the FTIR spectrum of PANI0, which might be due to hydrogen bonding between N-H groups of polyaniline and TiO_2 nanoparticles. The transmission peak at 1585 cm^{-1} became stronger and the peaks at 1498 cm^{-1} , 1143 cm^{-1} , 817 cm^{-1} became weaker in intensity. The transmission band between 400 cm^{-1} and 750 cm^{-1} was assigned to Ti-O stretching of TiO_2 nanoparticles within the composite structure [13,14]. For the spectrum of TiO_2 (Figure 1(c)), the

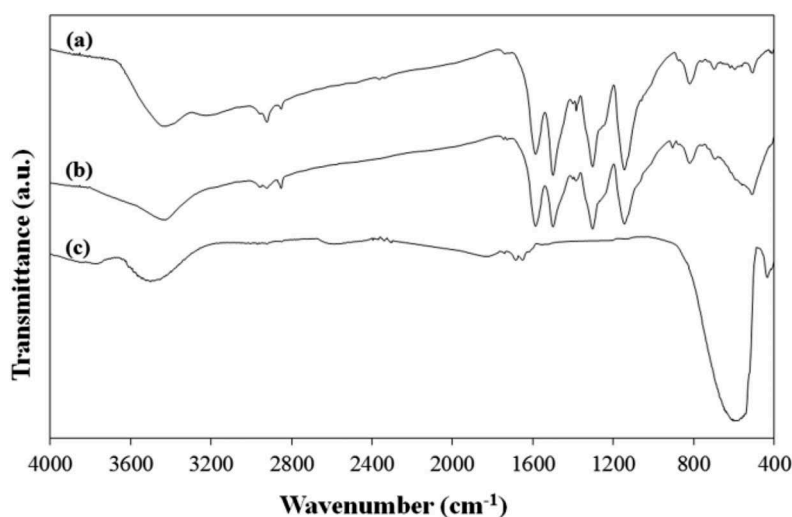


Figure 1. FTIR spectra of (a) PANI0, (b) PANI15 and (c) TiO₂ nanoparticles.

peaks at 3477 cm⁻¹, 1641 cm⁻¹ and 555 cm⁻¹ were assigned to – OH stretching, Ti-OH stretching and Ti-O stretching of TiO₂ nanoparticles [15].

FESEM images for TiO₂ nanoparticles and the composites are illustrated in Figure 2. Figure 2 (a) displays TiO₂ nanoparticles in agglomerate structure, ranging from 100 nm to 500 nm. Figure 2(b,c) display also spherical shaped nanoparticles in agglomerate form, which ranges from 250 nm to 1000 nm. It revealed that the conductive polymer encapsulated TiO₂ nanoparticles quite uniformly, which might lead to the uniform dispersion of the photocatalyst nanoparticles in the polymer matrix. Figure 3 shows the particle size distribution of TiO₂ and the composite nanoparticles. When compared with PANI0, the average particle size of the composites increased slightly. Homogeneous arrangement of TiO₂ nanoparticles within the conducting polymer is also important in terms of the photocatalytic degradation efficiency. It is expected that intimate contact between the photocatalyst and the polymer provides enhancement in the reaction rate of the photocatalytic degradation. To reveal the possible effect of the solid-phase photocatalytic degradation on the morphology of the samples, FESEM was also applied to TiO₂ nanoparticles, PANI15 and PANI25, exposed to 120 h of UVC light irradiation. According to Figure 2S, there was no significant difference in terms of the morphology between the images of the samples, which were exposed to UV light irradiation and not exposed to UV light irradiation. The quantitative elemental composition of the samples is given in Table 1. EDX spectrum of PANI15 revealed that most of TiO₂ nanoparticles preferred to disperse on the surface of the composite rather than the interior of the matrix since Ti weight ratio (15.7 wt.%) of PANI15, obtained by EDX analysis, was higher than the experimental ratio (9 wt.%). According to EDX spectrum of PANI25, most of the nanoparticles preferred to disperse both in the interior and on the surface of the conducting polymer. Ti weight ratio (16.3 wt.%) of PANI25 was comparable to the experimental ratio (15 wt.%) (Table 1).

The thermal behaviour of PANI0, TiO₂ and the composites are illustrated in TGA graph (Figure 4). Polyaniline and the composites displayed three stage degradation (Figure 4(a–c)). The first stage, observed up to 200°C, was corroborated to the removal of moisture and volatile

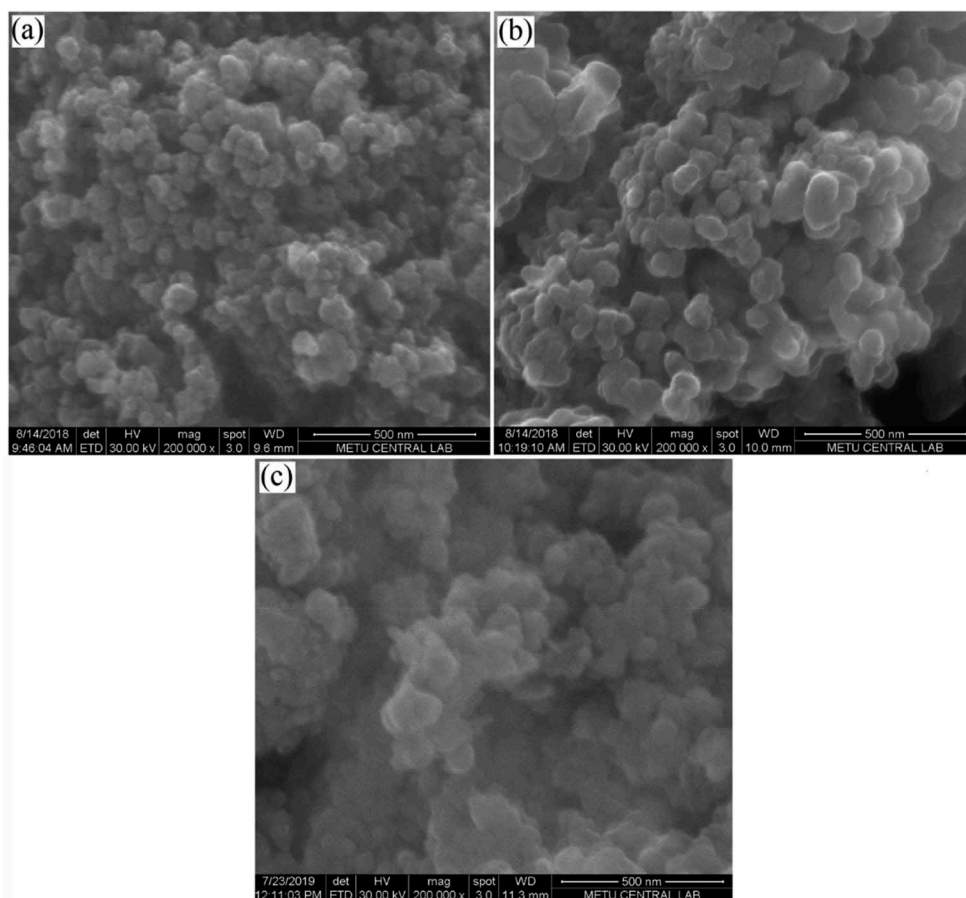


Figure 2. FESEM images (a) TiO₂ nanoparticles, (b) PANI15 and (c) PANI25.

units [16,17]. The second stage, occurred in the range from 300°C to 400°C, was ascribed to the thermal decomposition of the low molecular weight oligomers of the conducting polymer [17]. The last stage was observed between 400°C and 520°C with a weight loss of almost 30 wt. %. This decomposition step was related to the degradation of polyaniline itself [16,17]. The thermal degradation behaviour of PANI15 and PANI25 resembled to the thermal degradation behaviour of PANI0. In addition, the introduction of the photocatalyst nanoparticles improved the thermal stability of the matrix. On the other hand, TiO₂ nanoparticles exhibited approximately 15 wt.% weight loss up to 600°C (Figure 4(d)), which was related to the removal of surface adsorbed water molecules [16]. To reveal the possible effect of the solid-phase photocatalytic degradation on the thermal behaviour of the samples, TGA was also applied to PANI0, exposed to 120 h of UVC light irradiation. The thermal degradation behaviour of this sample resembled to that of PANI0, which was not exposed to UVC light irradiation. After 120 h of UV light irradiation, PANI0 exhibited insignificant weight loss, which might be the reason for this similarity in the thermal behaviour (Figure 1S).

XRD patterns of TiO₂ and PANI25 are illustrated in Figure 5. Figure 5(a) presents the major diffraction peaks of TiO₂ nanoparticles at the angles 25.30°, 37.76° and 47.94°,

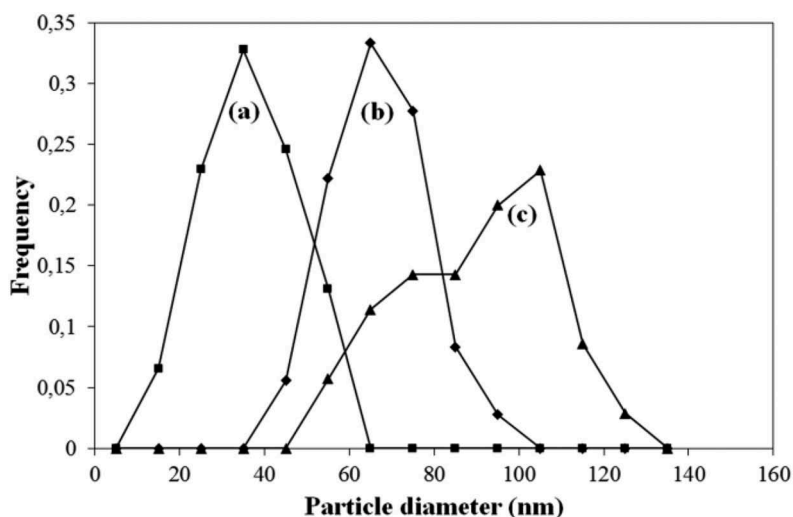


Figure 3. Particle size distribution of (a) TiO₂, (b) PANI15 and (c) PANI25.

Table 1. The quantitative element composition (wt.%) of TiO₂ and the composites.

Sample	Carbon (wt.%)	Nitrogen (wt.%)	Oxygen (wt.%)	Sulphur (wt.%)	Titanium (wt.%)
TiO ₂	-	-	37.7	-	62.3
PANI0	65.4	12.4	12.1	10.1	-
PANI15	48.3	9.2	19.4	7.5	15.7
PANI25	40.2	12.5	27.7	3.4	16.3

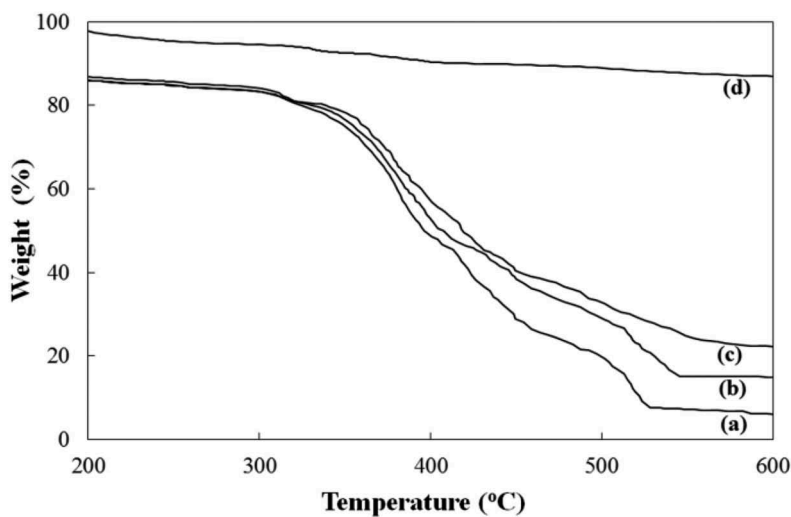


Figure 4. TGA curves of (a) PANI0, (b) PANI15, (c) PANI25 and (d) TiO₂ nanoparticles.

corresponding to anatase TiO₂. XRD pattern of PANI25 shows mostly the characteristic diffraction peaks of TiO₂ and a weak diffraction peak between 20° and 25° (Figure 5(b)), suggesting the suppression of the crystalline nature of polyaniline with TiO₂ contribution.

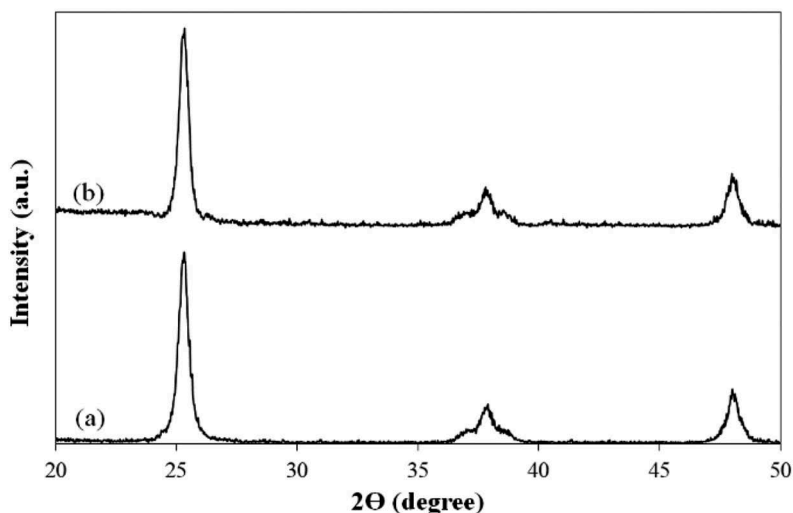


Figure 5. XRD pattern of (a) TiO_2 nanoparticles and (b) PANI25.

In addition, XRD pattern of PANI25 did not exhibit any change in the tetragonal lattice structure of TiO_2 [18].

The solid-phase photocatalytic degradation behaviour of polyaniline and the composites under UVA lamp and UVC lamp are illustrated in Figures 6,7, respectively. The weight loss increased with an increase in irradiation time and the weight loss amount of the composites was much higher than that of PANI0 for both UV lamps. Pure polymer resulted in insignificant weight loss, 0.2 wt.% and 0.4 wt.%, after 120 h of UVA and UVC irradiation, respectively. The resulting weight loss was related to the degradation stability of the conducting polymer,

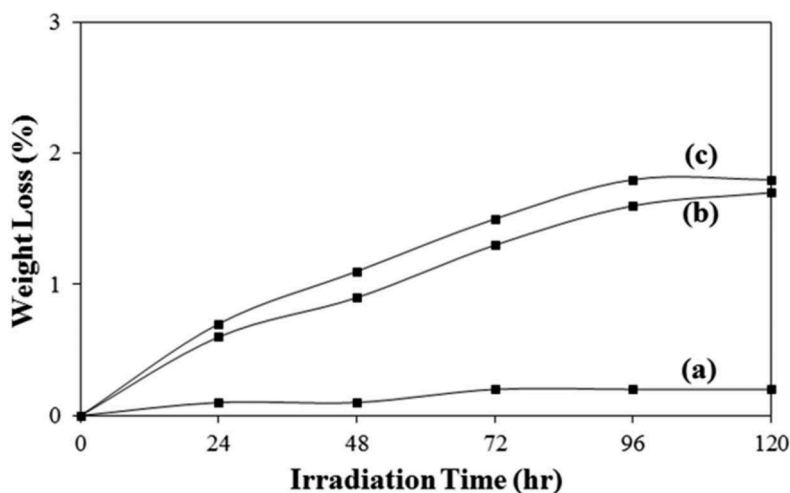


Figure 6. Solid-phase photocatalytic degradation behaviour of (a) PANI0, (b) PANI15 and (c) PANI25 under UVA lamp.

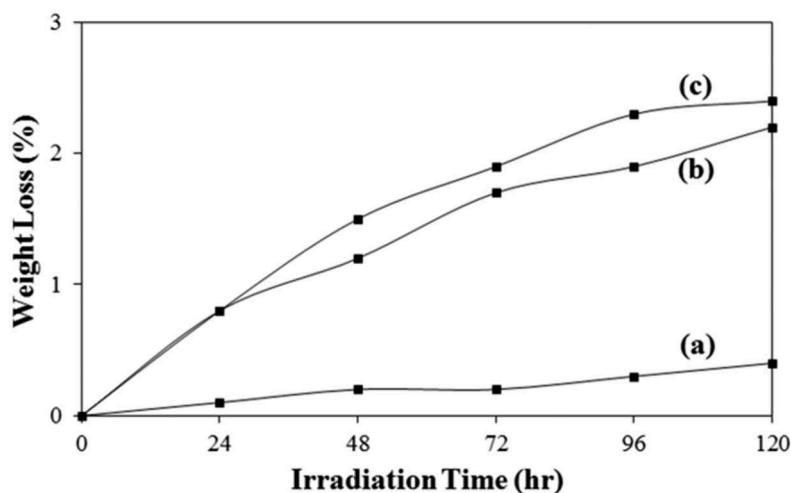


Figure 7. Solid-phase photocatalytic degradation behaviour of (a) PANI0, (b) PANI15 and (c) PANI25 under UVC lamp.

which was also illustrated with TGA curves. On the other hand, PANI15 exhibited the weight loss values of 1.7 wt.% and 2.2 wt.% after 120 h of UVA and UVC irradiation, respectively. PANI25 exhibited the weight loss values of 1.8 wt.% and 2.4 wt.% after 120 h of UVA and UVC irradiation, respectively. As expected, the weight loss amount of the composite increased parallel to the TiO_2 composition. The strong chain structure of the conducting polymer and low content of the photocatalyst might lead to the insignificant weight loss values for both UV lamps. Both lamps radiate UV light, which have necessary energy to activate TiO_2 photocatalyst within the polymer matrix [3]. When photons of UV light are absorbed by TiO_2 nanoparticles, photogenerated charge carriers are generated, which transfer to the photocatalyst surface and react with oxygen to form active radicals. The resulting active species attacked to neighbouring polymer chains, breaking up the C-N bonds of the benzenoid units along polyaniline chains. Hence, the polymer chains can be cut up into small pieces, which might be the fundamental mechanism of the solid-phase photocatalytic degradation of polyaniline [11].

4. Conclusion

Pure polyaniline and the composites were successfully synthesised and FTIR analysis confirmed the success of polyaniline synthesis in the absence and the presence of TiO_2 nanoparticles. The thermal stability of the conducting polymer was improved at a certain extent with the addition of TiO_2 nanoparticles, which was revealed with the thermogravimetric analysis. According to FESEM analysis, TiO_2 nanoparticles in agglomerate form were dispersed homogeneously within the polyaniline matrix. The introduction of the photocatalyst nanoparticles into polyaniline matrix improved the solid-phase photocatalytic degradation behaviour of the polymer under both UVA and UVC light irradiation, respectively. As a conclusion, a green composite product was tried to develop. According to the low weight loss values, the photocatalytic degradation potential of polyaniline is

low and it needs to be improved using different composite and photocatalyst applications. The as-prepared composites with promising photocatalytic performance may find useful application in the polymer industry.

Disclosure statement

No potential conflict of interest was reported by the authors.

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