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Photocatalytic Degradation of Benzene and Toluene in Aqueous Medium

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ABSTRACT: The resource intensive human activities (such as mining and extraction of mineral oils for betterment of life and modernization of society) have increased environmental pollution several folds. Products of mining and petrochemical industries are advantageous for the modern society. But waste generated such as BTEX from such industries are carcinogenic, toxic and causes adverse effects on environment and human health. These wastes are classified as hazardous waste which cannot be used further. Pollution of soil-water interface due to the release of hydrocarbons in environment is a major public health concern, and therefore, remediation of these pollutants is needed to reduce risk to human and environment. Various methods such as biological, chemical and physical method are used to degrade these pollutants from wastewater. In the present works photochemical degradation of toluene and benzene in wastewater are studied using activated Carbon−TiO_2 composites as catalysts in the presence of UV irradiation in photochemical reactor. Composites are prepared by sol-gel method and further characterized by X-ray diffractometry (XRD), scanning electron microscope (SEM) and Fourier transformed-Infrared spectroscopy (FT-IR). The Photocatalytic efficiencies of the synthesized composites were determined by the mineralization of toluene and benzene under UV irradiation in photochemical reactor.

Keywords: benzene, nanocomposite, petrochemical pollutants, photochemical degradation, TiO_2, toluene.

INTRODUCTION

Petroleum industry, since its emergence and thence, has entrenched its position in novel trend seeking and fast-track evolving globalized world. What has increased with this trend is the greed of human to exploit the natural resources, which, in turn, has created the serious concern for increasing environmental pollution level. Though Petroleum industry has shown a trend-mark impact in globalized economy (Farzanegan and Markwardt, 2008; Adam and Marquez, 1983), the attenuation of emitting carcinogenic (USEPA, 1996) and polluting volatile organic pollutants (VOCs) has

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been a nightmarish concern among environmentalists and chemical engineers (Sava and Carlsten, 2012).

Oily sludge generated from various petrochemical industries is one of the solid wastes. It is the composition complex and containing various petroleum hydrocarbon such as Benzene toluene xylene ethyl benzene ,water, heavy metals, and other solid particle .These recalcitrant pollutant are released in the environment during refinery processing, transportation and storage. These wastes are considered as the hazardous waste in many countries and pose a serious threat to environment and human being also (Hu *et al.*, 2013; Mrayyan and Battikhi, 2005; liu *et al.*, 2009; Mater *et al.*, 2006; Rocha et al., 2010; Hu et al., 2009). These effluents composes of theses waste are also a major source of aquatic environmental pollution (Wake, 2005; Singh *et al*., 2015).

Recently, many authors have propounded the research based on the BTEX compounds due to their carcinogenic potential and abundance in urban ambient air (Caselli *et al.*, 2010, Scheepers *et al*., 2010, Yujie *et al.*, 2012). BTEX, most commonly found in crude oil (Haroldo, 2006) and its by-products such as gasoline (John, 2003) are main components in surface and ground water which generally originate from leakage of petroleum storage tanks, spills at production wells, refineries, pipelines, and storage and distribution terminals (Bonvicini, 2014).

The degradation of petrochemical waste generally depends upon the type of petroleum hydrocarbon being processed. Various methods for the treatment of petrochemical waste are coagulation, adsorption chemical oxidation, membrane seperation, wet oxidation; microwave processes and biological method are also reported (Udden *et al.*, 2011; Demirci *et al.*, 1997; El-nass *et al.*, 2009, Jou and Huang, 2003; Sun *et al*., 2008). Though microbial degradation methods are highly effective and majorly attenuating process (Schaefar, 2010) along with dispersion, dilution, sorption, and other reactions. However, the importance is the assessment of other effective processes to distinguish the relative importance of all. The problem associated with these methods involved the transfer of pollutant into one to another form. Therefore another step is required for elimination of these compound. The processes have also low efficiency, and low reaction rate. In case of biological processes, they are time consuming processes and need specific microbes for degradation.

Advance Oxidation Processes (AOPs) are evolving techniques for efficient sequestration of chemically stable and less biodegradable organic pollutants (Parilti and Atkin, 2010). These oxidation processes are another alternative for degradation of petrochemical waste and are regarded as the environmental cleanup technologies (Diya, udden *et al*., 2011). Recently, Advanced Oxidation Processes have been studied for treating of petrochemical waste water like Fenton processes (Millioli *et al*., 2003) for the removal of oil spill, electrochemical processes (Santos *et al*., 2006), wet oxidation (Sunetal, 2008). In AOP, heterogeneous photocatalyst is well established oxidation processes and destroy wide range of organic pollutant (Fujishima *et al.*, 2008). Advantages of this technique on the other oxidation processes is complete mineralization, production of less sludge and economically feasible processes (Rajeshwar *et al*., 2008; Akpan and Hamid, 2009; Wang *et al*., 1999). Photocatalytic degradation of various organic pollutants has cynosurally drawn much attention (Karunakaran, 2014; Han *et al*., 2007). Titanium dioxide (TiO_2) powder with its strong oxidizing tendency, acts as a photocatalyst further, low cost and non-toxicity adds to its value and usage (Haque, 2007). However, its applicability and efficiency for practical use is still moderate.

Table 1. Various heterogeneous photocatalysts used for degradation of petrochemical waste

Catalyst	Petrochemical compound	Light source	Reference
Carbon/nitrogen-doped TiO_2	phenol	UV illumination.	(Abdullah et al.)
V2O5/ TiO_2	1,3,5-Trichlorobenzene chlorinated benzenes	UV	(Wang et al. 2015)
TiO2 nanoparticles	gaseous benzene	UV light irradiation	(Wang and Wu 2015)
MnFe2O4	gaseous benzene	visible-light	(Shen et al. 2015)
TiO_2/SiO2/Bi2O3	benzene	UV light irradiation, visible-light	(Ren et al. 2015)
TiO_2modified by transition metals	gaseous benzene	vacuum ultraviolet (VUV) irradiation	(Huang et al. 2015)
TiO_2 nanoparticles doped with CeO2 and supported on SiO2	phenol	Visible light	(Hao et al. 2015)
N-doped mixed TiO2 and ZnO	BTX	Visible light	(Ferrari-Lima et al. 2015)
Carbon-doped TiO2 nanoparticles wrapped with nanographene	phenol	Visible light	(Yu et al. 2014)
Nano-ZnO, TiO_2 and ZnO–TiO2 composite	phenol	UV light irradiation and direct sun light	(Prabha and Lathasree 2014)
N–H– TiO_2 photocatalyst by annealing in NH3 and H2	Benzene	visible light irradiation	(Li et al. 2014)
Pd-deposited TiO2 fil	gaseous toluene	UV254+185 nm	(Kim et al. 2014)
TiO_2/SiC nanocomposite fil	toluene	Uv Led	(Zou et al. 2013)
TiO2/SiO2	benzene	Mercury lamp	(Liu et al. 2013)
Ca2Nb2O7 nanopolyhedra and TiO2	benzene	uv	(Liang et al. 2013)
perlite granules coated with indium doped TiO2	ethyl benzene	Uv	(Hinojosa-Reyes et al. 2013)
N-doped TiO_2	benzene	UV-light irradiation	(He et al. 2013)
Au/ZnO nanocomposites	benzene	UV-light irradiation	(Yu et al. 2012)
Mg-ferrite/hematite/PANI nanospheres	benzene	Visible lighr	(Shen et al. 2012)
CNT/Ce- TiO_2	phenol	UV	(Shaari et al. 2012)
W-doped TiO_2	BTEX	Visible light	(Sangkhun et al. 2012)
Degussa P25 TiO_2	phenol	UV radiation	(Royaee et al. 2012)
Pt-TiO2/Ce-MnOx	benzene		(Ren et al. 2012)
Pt-loaded TiO_2/ZrO2		Thermo photo	(Aarthi et al. 2007)
BiPO4 catalysts	benzene	Uv light	(Long et al. 2012)
CdS-sensitized TiO_2 fil	benzene	UV light	(Liu et al. 2012a)
Fe/ TiO_2	2,4-dichlorophenol	UV	(Liu et al. 2012b)
TiO2-based catalys	BTEX	UV	(Korologos et al. 2012)
TiO_2-based catalysts	benzene, toluene, ethylbenzene and m-xylene	UV	(Korologos et al. 2012)
zirconium-doped TiO_2/SiO_2	Toluene and xylene.	UV	(Kim et al. 2012)
Ag–AgBr–TiO_2	benzene	UV light and visible light irradiation	(Zhang et al. 2011)

Nanocomposites formation, where these nanosized particles are adhered to any porous surface such as activated carbon (Mahmoodi *et al.,* 2011), zeolites (Shao and Pinnavaia, 2010), carbon nanotubes (Koo *et al*., 2014), show a large escalation in their photocatalytic activity in presence of UV radiation. Heterogeneous photocatalytic degradation has been widely explored over the last few decades for the various environmental cleanup applications. Photocatalysts are the class of compound which generate electron hone pair when come in contact or absorption of light quanta and causes chemical trans formation of substrate that come into contact with them (Kuen jo and Tayade, 2008). Many semiconductors have been studies for the degradation of petrochemical compound which some of them are listed in Table 1.

The present work entails the treatment of benzene (B) and toluene (T) compounds in liquid phase, using photocatalytic processes in presence of ultraviolet (UV) radiation. These methods are rapid, energy efficient, and effective for destruction of a wide range of organic pollutants. TiO_2/activated-carbon (C) composites were prepared and its ability to degrade BT was investigated using different combinatorial treatment strategies. Benzene and toluene are associated with the group of widely industrial chemical usage and considered as the most common environmental pollutant. Large amount of benzene and toluene are released in the environment from above mentioned sources (Liu *et al.,* 2015). Several physical and chemical properties of Benzene and toluene are tabulated in Table 2 (Van Agteren *et al.,* 1998) and chemical structure is shown in Figure 1. The results obtained, showed noteworthy increase in degradation.

MATERIALS AND METHODS

1. Chemicals and materials

Activated carbon (<20 μm) used for the preparation of TiO_2/Activated-C (TiO_2/AC) nanocomposite was purchased from Rankem chemicals, India. Titanium tetra-isopropoxide (TTIP) and hydrogen peroxide (H_2O_2) were procured from Sigma Aldrich, India. Toluene (99.5%) and benzene (99.5%) of analytical grade were purchased from Merck, India.

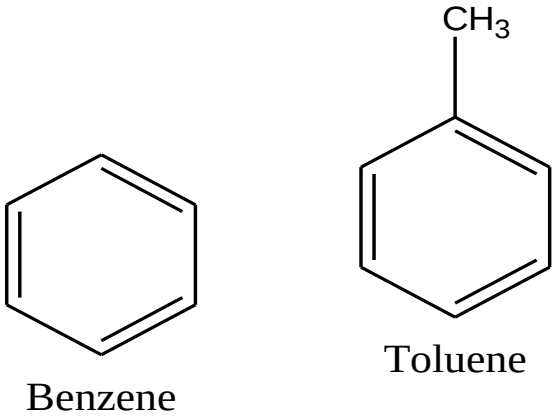

Fig. 1. Structure of benzene and toluene

2. Catalyst synthesis

TiO_2/AC nanocomposite was synthesized using the hydrothermal processes method as describe elsewhere using tetra-isopropoxide as a binder and commercial available activated carbon (Inoue *et al.,* 1994; Horiea *et al.,* 1998; Kubo *et al.,* 2007). During the preparation process, 35.8 gm of TTIP was dissolved in 180 ml of 99.9% propanol and 20 ml of 34% HCl (*w/v*) and sonicated for 1 hour (h) for homogenization. The resulting solution was diluted to 1000 ml by adjusting pH (pH=3) by adding NaOH. 10 grams of activated carbon and 8-20 g of P25 TiO_2 particles were mixed together and stirred for 3 h. Obtained gel solution was then filtered through membrane filter and oven-dried at 80^{o}C for 24 h. The dried samples were crushed and calcinated at different temperature of 350^{o}C for 3 h (Singh *et al*., 2015).

3. Characterization

The prepared catalysts were characterized by X-ray diffraction (XRD) pattern for the crystal structure and its dimensions were

procured with a diffractometer, using Cu-K_a radiation. Assays of average particle size and its morphology were studied using Scanning Electron Microscopy (SEM). Fourier-Transform Infrared (FT-IR) spectra were measured at room temperature, using a spectrometer and the KBr pellets technique.

Photocatalytic reactivity of TiO_2/AC nanocomposite was assayed by benzene and toluene degradation by exercising different process combinations and by varying their concentrations. Initial concentration of benzene and toluene was maintained at 200 ppm. 0.5 g of photocatalysts was added to 1000 ml of BT solution and stirred for 30 minutes in dark for efficient adsorption of BT on photocatalyst. Samples were collected with a time interval of 5 minutes and were further centrifuged at 4000 rpm for 10 minutes to check the amount of BT degraded after undergoing the processes, degraded BT and its by-product concentration were measured using gas chromatography (GC) (Ines *et al.,* 2008).

4. Sample preparation for degradation experiment

Benzene and toluene were added in the ratio of 1:1 in 50 ml water. An aqueous solution of BT was placed in the quartz reactor, surrounded by the impact-full UV radiation. Water bath proved to be effective for constant temperature maintenance by nullifying the effect of heat liberated and temperature variation. Various effects of UV were exercised profoundly in presence of TiO_2/AC nanocomposite.

5. Degradation analysis

Gas chromatography (GC) was used to measure BT concentrations directly in the liquid phase. Accurate kinetic measurements without being mass transfer limited can be achieved using this indirect method of determining the aqueous phase concentration. Samples were analyzed on a Nucon Gas Chromatograph (5765), consisted of a Flame Ionizing Detector (FID) along with a fused silica capillary column (DB-5, 0.53 mm I.D., 30 m length, 1 μm film thickness) that was designed to be well suited for the analysis of volatile components, particularly BTEX compounds. Hydrogen (flow rate ~15 ml/min) was used as the carrier gas and the injector and detector temperatures were set to 140°C and 290°C, respectively. The initial temperature of the column was 75°C and the final temperature was 140°C at a temperature increase rate of 25°C/min. Gas chromatograph was recorded on a personal computer equipped with Thermo Scientific Dionex Chromeleon Chromatography Data System (CDS, version 7.2) software to perform peak integration and analysis.

6. Photocatalytic testing

Photodegradation of given organic compound using TiO_2/AC (photocatalyst) was evaluated in photochemical reactor. The experimental setup consisted of a biogas analyzer for monitoring of CO_2 released during the oxidation process. The reactor design was as shown in Figure 2. Initial and final concentration of toluene and benzene were measured at the time intervals of 5 minutes.

RESULT AND DISCUSSION

Photo-degradation study for two important BTEX (*viz.,* benzene and toluene) was performed using TiO_2/AC nanocpmposite as catalyst. The catalyst was prepared and following characterizations were carried out.

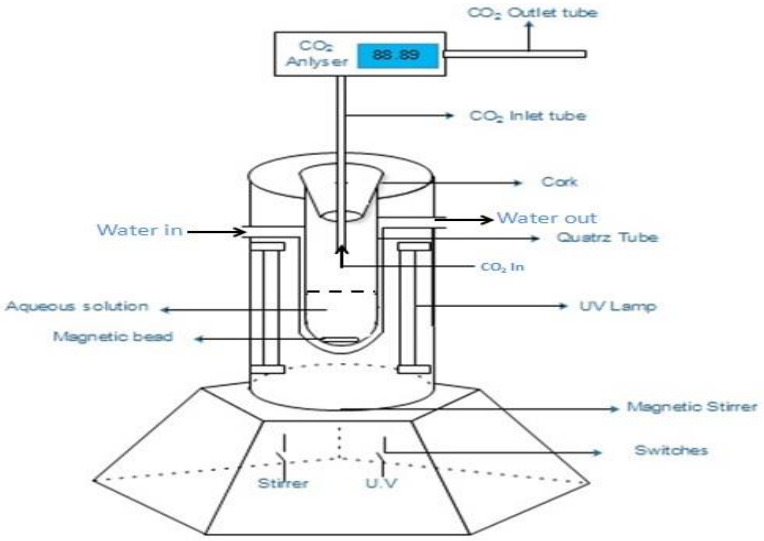

Fig. 2. Line diagram of photochemical reactor

1. X-ray diffractometer (XRD) analysis

X-ray diffraction analysis was performed to assay the phase composition and crystalline nature and size of prepared A.C/TiO_2 nanocomposites. JCPDS 894921 was used to identify the peaks as shown in Figure 3 of the sample by comparing with the standard data. Various Diffraction peaks at 2θ=25.4°, 48.02°, 54.19°, 62.72°, were given by A.C/TiO_2 nanocomposite which were assigned to (101), (200), (105), (103) reflections of anatase phase and peaks at 2θ=27.475°, 36.066°, 37.80°, 69.00° being assigned to (001), (021), (210), (220) reflects the rutile phase of TiO_2. The average intensity of rutile phase is considerably less as compared to that of anatase phase. Average crystalline size can be determined using Scherer's equation as:

$$D = K\lambda/\beta\cos\theta \quad (1)$$

where K= Scherer constant
λ= X-ray wavelength
β= the peak width of half maximum and
θ= Bragg diffraction angle

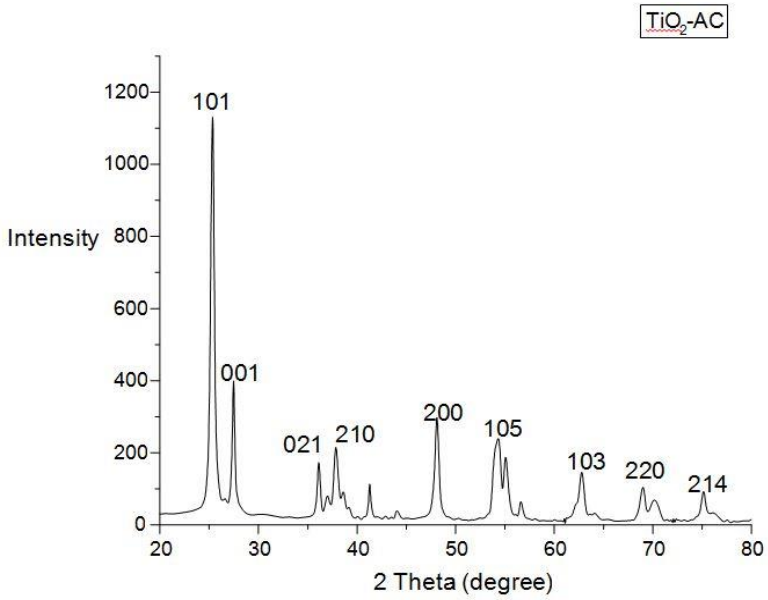

Fig. 3. XRD patterns of TiO_2/Activated carbon nanocomposite

2. Scanning Electron Microscope (SEM) Analysis

The TiO_2/AC nanocomposite was observed in scanning electron microscope (SEM) for investigating its surface characterization and structure. TiO_2 particle were clearly observed as well dispersed and intertwined on activated carbon. The surface morphology of TiO_2/AC nanocomposites were obtained as shown in Figure 4. The TiO_2 particles with the assessed diameter of about 25 nm enlaced and draped over the relatively large number of TiO_2 particles-A.C (Fig. 4) was in order.

3. FTIR Analysis

FTIR analysis of TiO_2/A.C nanocomposites was performed to study the variation on the functional groups of nanocomposites formed. The FTIR spectra (Fig. 5) show absorbance peaks at 3120.3, 2344.1, 1539.4 and 507.1 cm^{-1} in the spectrum. The bands below 1000 cm^{-1} represent Ti–O–C, indicating a weak conjugation between Ti–O bonds and A.C.

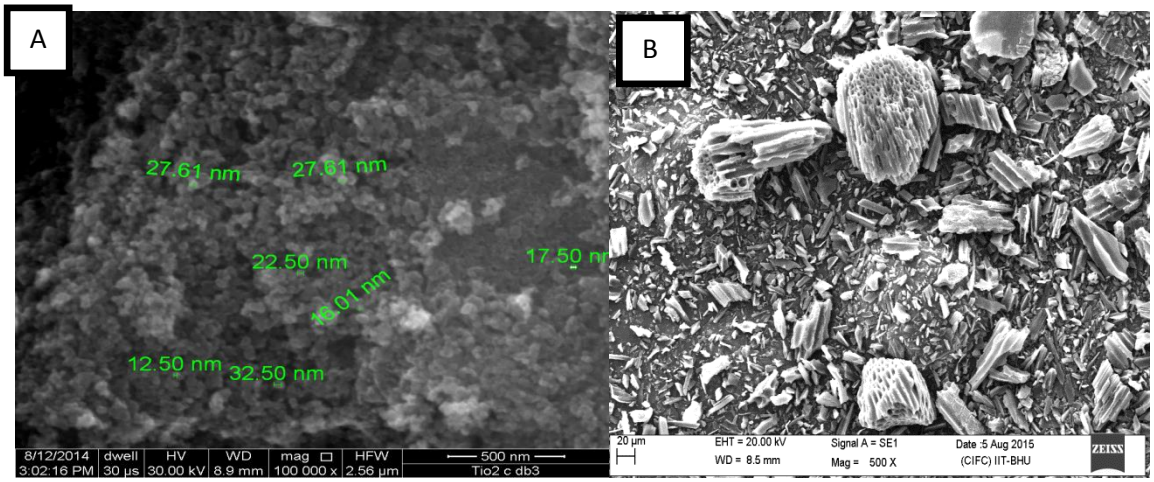

Fig. 4. Scanning electron micrograph (A) TiO_2/Activated carbon nanocomposite (B) activated Carbon

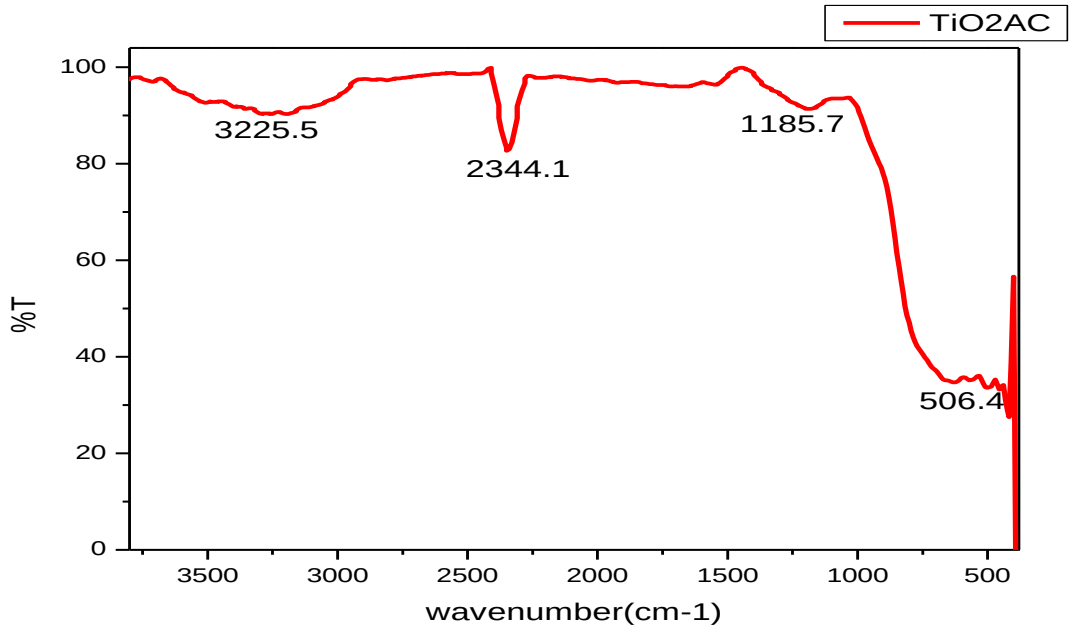

Fig. 5. FT-IR spectra of TiO_2/Activated carbon nanocomposite

4. Degradation of benzene and toluene

The degradation of benzene and toluene were conducted in the photochemical reactor as shown in Figure 1. Toluene and benzene in the ratio of 1:1 (concentration= 200 ppm) were irradiated in the quartz tube with 0.5g/L of TiO_2/AC nanocomposite catalyst. Removal efficiency of toluene and benzene in different time intervals were taken as shown in Figure 6. The intensity of the lamp used in the photo reactor was 10 W/m^2. Very high percentages of degradation were observed in each case, however in case of toluene the amount of degradation was slightly higher. The photocatalyst (TiO_2/AC) has proved to be effective for both benzene and toluene.

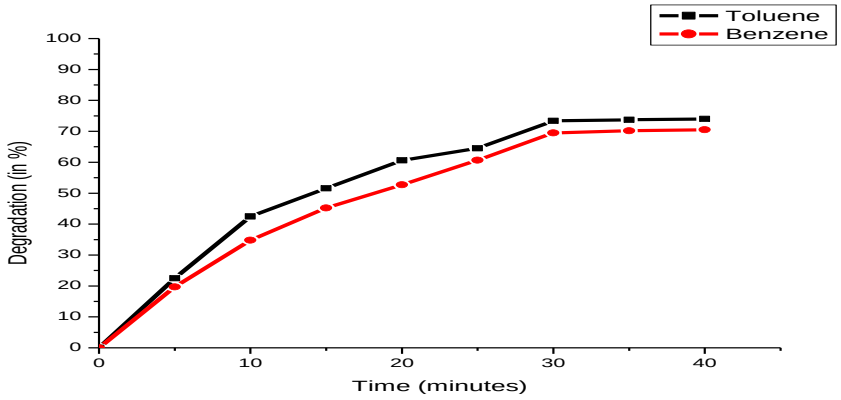

Fig. 6. Degradation of benzene and toluene with respect to time in presence of TiO_2/Activated carbon nanocomposite

CONCLUSION

A series of TiO_2/AC photocatalysts with different TiO_2/AC ratio were prepared by the sol–gel method. The doping of AC increases the surface area significantly. Degradation rate of TiO_2/AC nanocomposite was higher as compared to TiO_2. The photocatalytic degradation of benzene and toluene contaminated wastewater in the presence of TiO_2/AC nanocomposite has advantages. In this process very low sludge is produced. Higher degradation of benzene and toluene are achieved in this process. Catalyst which is used, can be regenerated and reused further. Hence, this is sustainable method for degradation of organic pollutant and can be used for mineralization of other pollutant. In addition, the photocatalytic degradation can be a useful method for the degradation of recalcitrant organic pollutants.

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