Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.909332

54 (2015) 3279–3290
June

Taylor & Francis
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Photocatalytic degradation of poultry wastewater using activated carbon-supported titanium dioxide

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Received 28 October 2013; Accepted 21 March 2014

ABSTRACT

Photocatalytic degradation of real-time poultry wastewater was investigated in a lab-scale batch reactor equipped with low-pressure submergible UV lamp(s). The experiments were conducted using slurry TiO_2 (Slurry-TiO_2) and activated carbon (AC)- supported TiO_2 (granular and powdered), i.e. GAC–TiO_2 and PAC–TiO_2. The TiO_2 coatings on the GAC and PAC surfaces were confirmed by using scanning electron microscopy coupled with energy dispersive spectroscopy.Among the systems investigated, GAC–TiO_2 and PAC–TiO_2 photocatalytic systems produced 100% total solids, total volatile solids and biochemical oxygen demand (BOD) removals under 14 W and 56 W UV irradiation within 180 min of reaction. In contrast, complete destruction of organics was not achieved in the photolytic experiments conducted with 56 W UV irradiation even after 240 min of reaction. The first-order reaction kinetics was adopted to estimate and compare the rate of BOD removal in the systems. A maximum BOD removal rate constant of 0.987 min^{-1} and a maximum BOD removal rate of 320 mg/L/min were observed in 56 W GAC–TiO_2 system. The BOD removal rate observed in 14 W GAC–TiO_2 (227 mg/L/min) and PAC–TiO_2 (247 mg/L/min) systems were comparable; however, GAC–TiO_2 was recovered effectively compared to PAC–TiO_2. At the same time, photocatalytically treated poultry wastewater using both GAC–TiO_2 and PAC–TiO_2 was found to be free from coliforms.

Keywords: Advanced oxidation process; Photocatalysis; Photodegradation; PAC-supported TiO_2; GAC-supported TiO_2; Poultry wastewater; Slurry-TiO_2; Activated carbon

1. Introduction

Poultry industry is one of the major revenue generating industries in India. At the same time, poultry plants use lot of water for their operation and proportionately releases huge amount of wastewater. A typical poultry processing plant releases 1,000–1,500 m^3 of wastewater every day [1]. The poultry processing wastewater contains large amount of dissolved organics (0.8–2.5 kg/ton as biochemical oxygen demand (BOD)), phosphorus (10–100 mg/L), nitrogen (about 6% of the BOD level), fats, proteins, carbohydrates and other residues (i.e. skin and feathers) [2]. Commonly, conventional physicochemical methods (coagulation, sedimentation and filtration) in combination with biological methods are used for the treatment of poultry wastewater. However, fats, proteins and carbohydrates often interfere with the treatment of wastewater and reduce the treatment efficiency. In order to

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increase the treatment efficiency of the poultry wastewater, the conventional physicochemical methods as part of the treatment system are upgraded to advanced oxidation process (AOP). The advantage of upgrading conventional physicochemical method to AOPs such as UV catalysis, Ozone, H_2O_2 and their combination could eliminate the sludge management and disposal problems.

Heterogeneous photocatalysis belongs to the class of AOPs has emerged as an innovative technique for the abatement of hazardous, complex and toxic organic pollutants [3–8]. It offers several advantages including easy operation, high destruction rates and reuse of catalyst. The photocatalytic process has been carried out using several types of semiconductor photocatalysts (TiO_2, ZnO, Fe_2O_3, CdS, GaP and ZnS) for the destruction of many recalcitrant and hazardous pollutants from aqueous and gaseous systems [9,10]. Among the various semiconductors used for photocatalysis, TiO_2 has been recognized as a promising photocatalyst due to its good photoactivity, high chemical stability, low cost, relatively high decomposition activity and non-toxicity [9–11]. However, the post separation of the photocatalyst is found to be difficult, which in turn makes the photocatalysis systems expensive [8–10]. To reduce the cost of photocatalytic operation and to recover the photocatalyst, slurry TiO_2 and immobilized catalysts on various supporting materials such as activated carbon (AC), glass mesh, glass fabric, glass wool, glass beads, microporous cellulosic membranes, alumina clays, ceramic membranes, monoliths, zeolites and stainless steel were used in several pollution abatement studies [12–14]. The porous glass beads supported with TiO_2 nanoparticles were used as the photocatalyst for the discolouration of methyl orange under UV light and exhibited high photocatalytic activity. The high photocatalytic activity of the prepared material was attributed to the large surface area of the highly dispersed TiO_2 nanoparticles offered possibilities to absorb more oxygen and molecular water which react with the photogenerated electrons and eventually decrease the chance of recombination of the photo-induced electron–hole pairs [15]. The clay-supported TiO_2 act as pollution-removing active ingredients in the formulation of paints, coatings, pavement and cement. The benefits of incorporating TiO_2 nanoparticles in the clay matrix include higher durability, slower inactivation and avoiding leaching of nanoparticles to the environment [16]. Therefore, the usage of immobilized catalysts not only reduces the cost of operation but also offers higher degradation efficiency [14,17]. Moreover, coating TiO_2 catalyst on novel and low-cost supporting medium is an emerging area of research in material science and environmental engineering in the recent years.

The catalyst recovery problem has been addressed to a certain extent by coating the catalyst on novel supporting medium but the relative photoactivity restriction owing to the mass transfer limitation of pollutants with TiO_2 surface is still need to be addressed. Among the supporting materials, AC is mostly preferred because of its excellent adsorption property for wide variety of target pollutants. The adsorbed pollutants on the AC concentrate around the deposited TiO_2, which accelerates the pollutant degradation. In addition, AC could adsorb and oxidize the intermediate compounds produced during photodegradation and prevent the formation of secondary pollutant(s). The supported TiO_2 on the surface of AC can be excited resulting in the production of $^{\bullet}OH$ in the aqueous solution under microwave (MW) irradiation, which significantly enhanced the performance of AC/MW process for the degradation of methyl orange. Also, the TiO_2/AC system displayed higher catalytic activity than AC alone under MW irradiation. Therefore, AC-immobilized TiO_2 (AC–TiO_2) was used in several studies taking into account the combined effect of adsorption property of AC and the photocatalytic decomposition by TiO_2 [3–8,12,18–23]. Consequently, AC–TiO_2 has been receiving special attention in the industrial applications. In the recent years, granular AC-immobilized TiO_2 (GAC–TiO_2) photocatalyst has been receiving huge importance in water/wastewater treatment considering easy separation of the catalyst and cheaper cost in their preparation [17,24–26]. On the other hand, the efficiency of powdered AC-immobilized TiO_2 (PAC–TiO_2) was also studied by some researchers [7,12,22,27]. However, GAC–TiO_2 photocatalysis was not applied for real-time poultry wastewater treatment. In addition, the influence of GAC–TiO_2 and PAC–TiO_2 were not studied in detail.

Recent studies reported the self-photoactivity of activated carbon support under UV irradiation, that is greatly inhibited by the immobilization of titania on the composite. In this regard the photochemical behaviour of a series of activated carbons including ash free activated carbon with varied physicochemical features under UV light towards phenol degradation was investigated to differentiate the intrinsic behaviour of certain carbon materials. Photodegradation efficiency was improved when the activated carbons themselves are used as catalysts, pointing out the ability of carbon materials in generating similar or higher quantity of hydroxyl radicals under UV irradiation in the absence of titania. The results suggested the occurrence of carbon–photon interactions which might be propagated through the graphene sheets of the

materials, and could reach the adsorbed molecules inside the pores [18–22].

In the present study, the effect of GAC–TiO_2 and PAC–TiO_2 in the treatment of real time- poultry wastewater in a lab-scale batch photoreactor was investigated. Moreover, the effects of Slurry-TiO_2, catalyst concentration, UV light intensity, reaction time and adsorption property of GAC and PAC were investigated. Based on the experimental data, reaction rate constants were calculated for various photocatalysis systems (Slurry-TiO_2, GAC–TiO_2, PAC–TiO_2, GAC and PAC) and compared.

2. Materials and methodology

2.1. Chemicals and reagents

The commercial anatase type Degussa P25 Titanium dioxide powder (TiO_2, purity ≥ 99%) with 0.044 mm particle size was purchased from Sigma–Aldrich, India. Subsequently, the commercial powder was used for the preparation of Slurry-TiO_2, PAC-immobilized TiO_2 and PAC-immobilized TiO_2 photocatalysts. The precursor titanium(IV) isopropoxide, hydrochloric acid (HCl, 37%) and absolute ethanol were of analytical grade and purchased from Sigma–Aldrich, India. Two different carbon adsorbents of wood-based origin differing in particle size and physicochemical properties were selected for this study. GAC (0.6–2.38 mm particle size) and PAC (0.149 mm particle size) used in the experiments were supplied by Southern Carbon and Chemicals, India and Sigma–Aldrich, India, respectively. The specific surface area (S_{BET}) and total pore volume (V_T) of GAC and PAC are as follows: S_{BET} of GAC ~ 1,012 m^2/g, V_T of GAC ~ 0.596 cm^3/g, S_{BET} of PAC ~ 845 m^2/g and V_T of PAC ~ 0.419 cm^3/g. All other reagents used in the experiment were of analytical grade, purchased from local market and used as received.

2.2. Poultry wastewater

The real-time poultry wastewater before any treatment (i.e. raw wastewater) was collected from Government poultry farm near NITC, Calicut. The sample was collected in plastic containers, transported to the laboratory and stored at 4°C. Subsequently, the initial characteristics of the wastewater such as pH, temperature, BOD, solids (total, suspended, volatile and fixed solids, i.e. TS, SS, TVS and FS) and coliforms were estimated. The characteristics of the raw wastewater are as follows: BOD ~ 1,000 mg/L, TS ~ 1,200 mg/L, SS ~ 200 mg/L, TVS ~ 400 mg/L, FS ~ 800 mg/L and coliform/100 mL is greater than 2,400. The wastewater was found to be slightly in the acidic condition (pH ~ 6.5) and the temperature of the wastewater was 26°C.

2.3. Preparation of photocatalyst

2.3.1. Preparation of slurry-TiO_2

Slurry-TiO_2 was obtained by continuously stirring specified amount of TiO_2 catalyst in 300 mL of double distilled water for 2 h using a magnetic stirrer. Subsequently, the content was ultrasonicated for 30 min (water bath type), vacuum dried at 200°C for 12 h, stored in containers and used for the experiments [14].

2.3.2. Preparation of GAC–TiO_2 and PAC–TiO_2

The GAC/PAC-immobilized TiO_2 catalyst was prepared by simple wet chemical process [3]. Initially, 5 mL titanium(IV)isopropoxide was dissolved in a mixture of 50 mL of absolute ethanol and 1 mL HCl (37%), followed by the addition of 250 mL deionized water and a desired stoichiometric amount of prewashed GAC/PAC. Subsequently, the solution was homogenized using a magnetic stirrer for 30 min and the mixture was kept in a water bath at 80°C for 2 h. After cooling to room temperature, the mixture was centrifuged and washed with deionized water. Following to that the GAC/PAC-immobilized TiO_2 was dried at 100°C and calcined under N_2 atmosphere.

2.4. Experimental set-up

Photolytic (without catalyst) degradation, photocatalytic (with catalyst) degradation and adsorption (without UV) experiments were carried out in a lab-scale cylindrical batch reactor with a working volume of 1.9 L. The reactor was provided with several ports for clamping submergible UV lamps, pH and temperature probes. An electronic overhead stirrer was mounted centrally and the reactor contents were mixed continuously at 200–300 rpm. The schematic diagram of the reactor is shown in Fig. 1. The UV energy was supplied by four numbers of 14 W submergible UV lamps (wavelength of 254 nm and intensity of 40 mW/cm^2).

2.5. Photocatalytic experiments

The photocatalysis experiments were conducted to enumerate the effectiveness of catalyst in poultry wastewater treatment. As a precursor, photolytic experiment was carried out in ambient temperature using 14 and 56 W UV lamps and at pH 6.5. Exactly 1.9 L of raw wastewater was fed into the reactor and

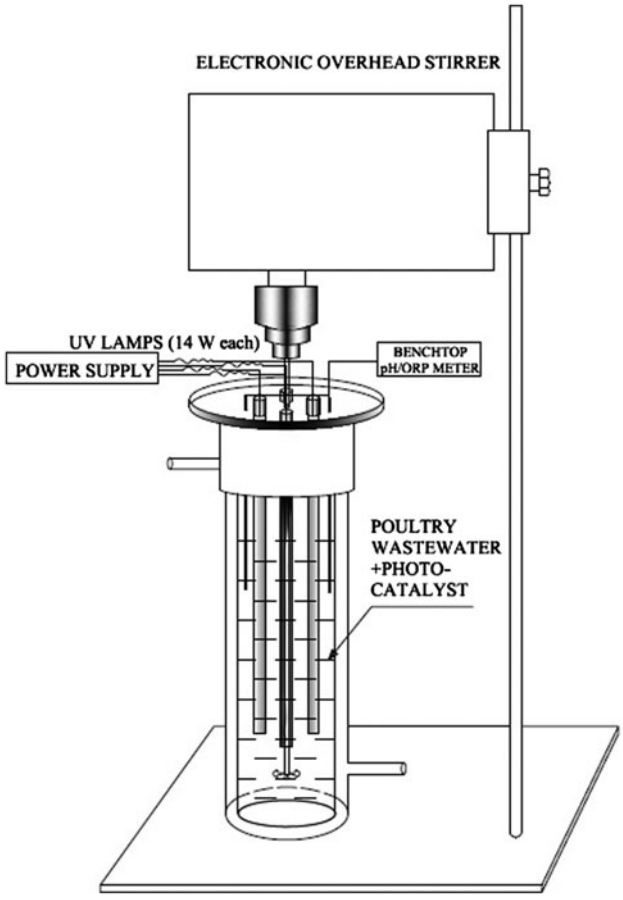

Fig. 1. Schematic diagram of the glass reactor.

the contents were mixed using the overhead stirrer. The UV energy was supplied by using 14 and 56 W UV lamps and the experiment was conducted for 240 min. Subsequently, photocatalyic experiments were conducted under different combinations of UV lamps (14, 28 and 56 W) and in the presence of different catalysts (Slurry-TiO_2, PAC–TiO_2 and GAC–TiO_2) at pH 6.5 for 240 min. The dosage of Slurry-TiO_2, PAC–TiO_2, and GAC–TiO_2 used in the experiments was 4.7, 6 and 6 g/L, respectively. From photolytic and photocatalytic experiments, the samples were collected at 0, 15, 30, 45, 60, 120, 180 and 240 min and analysed for various parameters. Adsorption experiments were carried out using GAC and PAC alone to enumerate the organic pollutant removal ability of GAC and PAC in the absence of UV irradiation and TiO_2. The dosage of both GAC and PAC used in the experiments was 6 g/L. In order to demonstrate the photoactivity of activated carbon support under UV irradiation, a photodegradation experiments was also conducted using GAC alone (6 g/L) at 14 W UV irradiation, i.e. without semiconductor catalyst support.

3. Analytical techniques

The surface morphology of Slurry-TiO_2, GAC-TiO_2 and PAC-TiO_2 was characterized using a field emission scanning electron microscopy (SEM), at an accelerating voltage of 20 kV (HITACHI SU6600, Japan). The elemental composition of the prepared catalysts was quantitatively determined using energy dispersive spectroscopy (EDS, HORIBA EMAX). On the other hand, the protocols mentioned in The Standard Methods [28] were adopted for the determination of BOD, TS, TVS, FS and coliforms. The pH and temperature of the solution were measured using Benchtop pH/ORP Meter (Hanna Instruments, India). In addition, coliform analysis was performed as per The Standard Methods [28] and the the results are expressed in terms of most probable number.

4. Data analysis

From the experimental data, the BOD removal constants were worked out based on the first-order reaction kinetics as shown in Eq. (1).

$$[L] = [L]_0 e^{-kt} \tag{1}$$

where L_0 and L are initial and final concentrations of BOD at time t and k is the reaction rate constant. The proportion of oxidizable organic contents in the poultry wastewater was determined by dividing the concentration of BOD to the respective concentration of VS as shown in Eq. (2).

$$\text{Oxidizable organic content} = \frac{\text{BOD}}{\text{VS}} \tag{2}$$

5. Results and discussion

5.1. Characterization of the prepared catalysts

The SEM images of Slurry-TiO_2, GAC–TiO_2 and PAC–TiO_2 are shown in Fig. 2(a)–(c), respectively. In Fig. 2(b), it can be noticed that TiO_2 particles are dispersed non-uniformly on the GAC surface, which indicate that more adsorption and reactive sites could be offered for the degradation of organic particles present in the poultry wastewater. The heterogeneity in agglomeration of the coated TiO_2 particles on PAC is also evident from Fig. 2(c). The images of the EDS analysis of Slurry-TiO_2, GAC–TiO_2 and PAC–TiO_2 are shown in Fig. 2(d)–(f), respectively. The EDS images along with the elemental composition analysis (Table 1) confirm the absence of contamination in Slurry-TiO_2, GAC–TiO_2 and PAC–TiO_2.

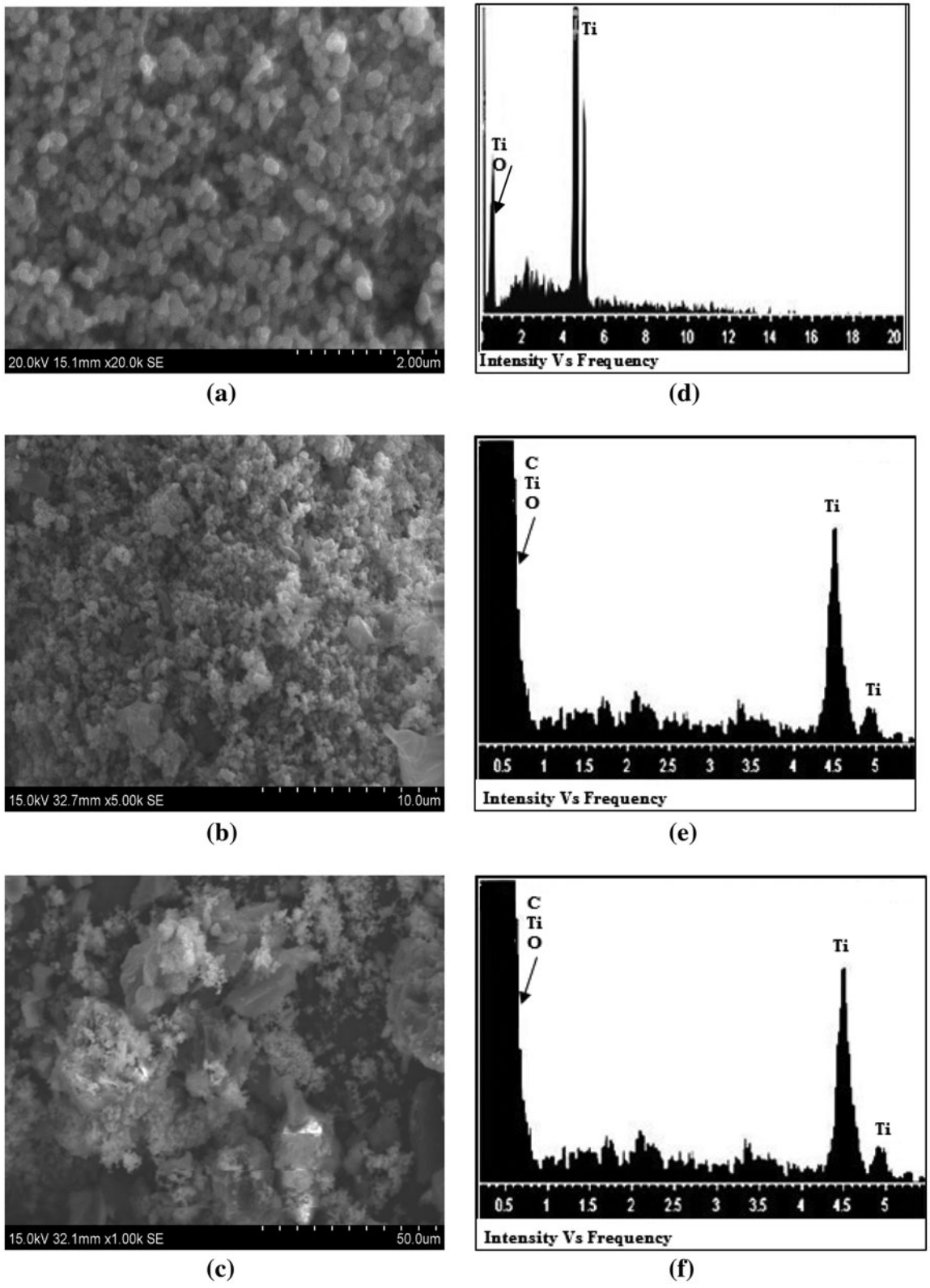

Fig. 2. SEM images of (a) Slurry-TiO_2; (b) GAC–TiO_2 and (c) PAC–TiO_2; and EDS images of (d) Slurry-TiO_2; (e) GAC–TiO_2 and (f) PAC–TiO_2.

Table 1
Characteristics of the prepared catalyst identified using SEM–EDS

Type of prepared catalysts	TiO_2 coverage (%)	Characteristics with EDS		
		Element	Weight (%)	Atomic (%)
Slurry-TiO_2	100	Ti	61.28	34.58
		O	38.72	65.42
GAC–TiO_2	40.52	C	87.30	90.56
		Ti	0.87	0.23
		O	11.83	9.21
PAC–TiO_2	78.5	C	86.16	90.12
		Ti	1.9	0.5
		O	11.94	9.38

5.2. Photodegradation experiments

The samples collected from the photolytic and photocatalytic experiments were analyzed for different parameters. The outcome of the experiments from photolysis and photocatalysis using Slurry-TiO_2, GAC–TiO_2 and PAC–TiO_2 in the degradation of poultry wastewater are shown in Table 2. The results attribute that TS, TVS and BOD removals are appreciably related to the photoenergy supplied by UV lamps. Fig. 3(a) and (b) shows the removal efficiency of TS, TVS and BOD of wastewater under photolysis experiments using 14 and 56 W UV lamp. The TS removal efficiency reached 8.6 and 11.9% after 45 min of 14 and 56 W UV irradiation, respectively. However, the TS removal efficiency reached its maximum (31.6 and 46.8%) at the end of reaction time (i.e. 240 min) at 14 and 56 W. On the other hand, TVS and BOD removal efficiencies reached 7.5 and 30% at 14 W and 14.4 and 34% at 56 W UV irradiation, respectively, after 15 min. The corresponding removal efficiencies increased with the progress of reaction time and showed their maximum (43.8 and 60% at 14 W and 58 and 69.2% at 56 W, respectively) at the end of 240 min. The percentage BOD removal was increasing with reaction time and the maximum BOD removal rate were obtained as 20 and 22.67 mg/L/min after 15 min at 14 and 56 W UV irradiation, respectively. However, the removal rate were decreased to 2.5 and 2.89 mg/L/min, respectively at the end of 240 min (Fig. 3(a) and (b)). On the other hand, the BOD removal rate constant obtained as per the first-order kinetics were 0.112 and 0.147 min^{-1} at 14 and 56 W, respectively. Overall, 56 W photolytic experiments showed highest removal for TS, TVS and BOD as the reaction time increased to 240 min as compared to 14 W, which is attributed to the release of more hydroxyl ions with time that stimulated the degradation of organics. On the other hand, this observation is in good agreement with the previous photocatalysis studies conducted in the absence of catalyst for methylene blue and phenolic syntan degradation [5,17–22].

5.3. Photocatalytic degradation experiments

5.3.1. Photocatalysis using Slurry-TiO_2

The photocatalytic degradation of poultry wastewater using Slurry-TiO_2 were carried out under different combinations of photo energy i.e. 14, 28 and 56 W. The removal efficiency of TS, TVS and BOD are shown in Fig. 4(a)–(c), respectively. The addition of Slurry-TiO_2 under UV illumination triggered more surface active sites for the adsorption of solids on the TiO_2 surface [9], which in turn enhanced the TS removal efficiency from the poultry wastewater. Around 2.5% TS removal was obtained after 15 min of 14 W UV irradiation whereas it has increased to 42.3% after 240 min of reaction time. On the other hand, 11.6 and 88.3% TS removals were observed after 15 min in the Slurry-TiO_2 system with 28 and 56 W of UV irradiation, respectively. However, the removal efficiency was maximized to 93.6 and 100% TS at the end of 240 min of reaction under 28 and 56 W, respectively (Table 2). As the UV intensity increases, organics under UV irradiation is excited due to the release of more hydroxyl ions, resulting in enhanced TS removal. Similar trend was observed in the removals of TVS and BOD. However, it can be noticed that TVS removal was comparatively higher under 28 and 56 W Slurry-TiO_2 systems compared to 14 and 56 W photolysis and 14 W Slurry-TiO_2 systems after 15 min of reaction. Table 2 also infers that 56 W Slurry-TiO_2 system showed highest BOD removal after 15 min of reaction time. The observations of TVS and BOD indicate that the organics present in the wastewater are transformed to their highest oxidizable state within 15 min, i.e. organics into carbon-di-oxide, under the highest UV irradiation used in the present study, i.e. at 56 W. Also, it can be understood from Table 2 that highest degree of organics degradation is possible with the increase in UV energy and also the application of UV catalysts like TiO_2. However, the separation of spent catalyst in the form of slurry is difficult, which requires sophisticated removal/filtration/instrumentation facility.

The oxidation of volatile solids contributed to the considerable decrease in the TS removal of the reactor. Extremely high surface area of the slurry particles allowed the volatile components to get oxidized completely resulting in the enhanced removal rates. The experimental results showed a first-order BOD removal rate constant of 0.928, 0.32 and 0.221 min^{-1} in

Table 2
Performance of various photocatalytic systems in poultry wastewater treatment

Type of experiment	Type of catalyst used	UV energy supplied (W)	Parameter	Removal efficiency (%) at the end of reaction time (min)				Rate constant	
				15	45	180	240	(min^{-1})	(r^2)
Photolysis	–	14	TS	1.6	8.6	25.6	31.6	0.112	0.881
			TVS	7.5	12.5	35.3	43.8		
			BOD	30	48	58	60		
			TS	4.8	11.9	36.1	46.8		
Photolysis	–	56	TVS	12.4	24	49.8	58	0.147	0.936
			BOD	34	51	64.8	69.2		
			TS	8.4	17	38.7	44.2		
	GAC alone	–	TVS	13.2	25.4	36.4	38.25	0.103	0.968
			BOD	18.2	34.8	49.6	52.3		
			TS	9.2	18.2	41.2	46.7		
	PAC alone	–	TVS	15.4	26.6	37.3	40.1	0.118	0.964
			BOD	22	37	51.8	55.7		
			TS	40	54	70	82		
Photolysis	GAC alone	14	TVS	76	84	100	100	0.772	0.748
			BOD	77	83	100	100		
Photocatalysis	Slurry-TiO_2	14	TS	2.5	11	35.6	42.3	0.221	0.945
			TVS	7.5	45.3	100	100		
			BOD	44	66	78	82		
		28	TS	11.6	22.6	44.6	93.6	0.320	0.914
			TVS	12.5	47.3	97.8	100		
			BOD	58	72	86	94		
		56	TS	88.3	100	100	100	0.928	0.976
			TVS	100	100	100	100		
			BOD	84	100	100	100		
	GAC–TiO_2	14	TS	43	51	74	85	0.788	0.788
			TVS	80	86	100	100		
			BOD	80	86	100	100		
			Coliforms	99.6	99.9	100	100		
		56	TS	100	100	100	100	0.987	1.00
			TVS	100	100	100	100		
			BOD	100	100	100	100		
			Coliforms	99.9	100	100	100		
	PAC–TiO_2	14	TS	45	54	78	92	0.865	0.985
			TVS	85	90	100	100		
			BOD	88	92	100	100		
			Coliforms	99.5	99.9	100	100		

the UV/Slurry-TiO_2 system at 56, 28 and 14 W, respectively. The addition of catalyst under UV irradiation resulted in the significant increase in the number of activated sites and enhanced the holes to produce hydroxyl radical ($^{\bullet}OH$) on the surface of TiO_2 in the solution and thus the removal efficiency enhanced. The above results are in agreement with the previous studies [8,13,29]. The highest apparent BOD rate constant obtained for 14, 28 and 56 W were 29.3, 38.7 and 56 mg/L/min, respectively (Fig. 4(d)). Interestingly, complete TS removal was also observed in the Slurry-TiO_2 system operated at 56 W. The reason being the increased UV intensity created significant increase in solid particles to get adsorbed on to the Slurry-TiO_2 surface active sites, which in turn increased the size and specific gravity of the catalyst–solid interface. Subsequently, it produced the settlement of high density catalyst–solid interface at the bottom of the reactor with respect to Stokes law.

5.3.2. Photocatalysis using GAC–TiO_2

The outcome of the photocatalytic degradation of poultry wastewater using GAC–TiO_2 carried out

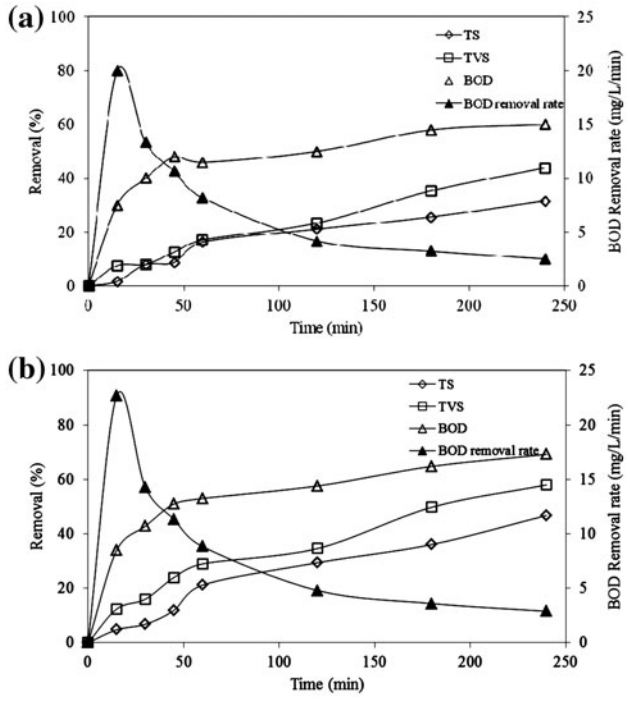

Fig. 3. Effect of photolysis on TS, TVS and BOD removal using (a) 14 W and (b) 56 W.

under different combinations of photo energy, i.e. 14 and 56 W are shown in Table 2 and Fig. 5(a–c). The 14 W GAC–TiO_2 photocatalyic system demonstrated 43 and 85% TS removals in 15 and 240 min, respectively. On the other hand, 100% TS removal was observed after 9 min in the 56 W GAC–TiO_2 photocatalyic system. Both the GAC–TiO_2 systems produced 100% TVS and BOD removals; however, the rate of TVS (Fig. 5(b)) and BOD removals (Fig. 5(c) and (d)) were much higher in the high-energy system, i.e. at 56 W.

The BOD removal rate obtained under the 14 W GAC–TiO_2 system (0.788 min^{-1}) was much higher compared to that obtained under the photolytic systems (0.112 min^{-1} at 14 W and 0.147 min^{-1} at 56 W) and Slurry-TiO_2 systems operated under 14 W (0.221 min^{-1}) and 28 W (0.320 min^{-1}). At the same time, when the intensity increased to 56 W for GAC–TiO_2, the regression coefficients also enhanced to 2.4, 11.9 and 8.53 times as compared to 56 W Slurry-TiO_2 and photolytic systems at 14 and 56 W, respectively (Table 2). The reason for the stimulation in the removal rates in the GAC–TiO_2 system could be GAC–TiO_2 has superior photocatalytic efficiency for pollutant degradation than Slurry-TiO_2 owing to its large adsorption potential. The mechanism underlying TiO_2 degradation on AC can be explained as follows: (i) during the synthesis of GAC–TiO_2, GAC scatters the deposited TiO_2 nanoparticles, preventing their agglomeration and thus improves their excitation under UV irradiation. (ii) During the degradation process, GAC could concentrate the target pollutant molecules adjacent to the TiO_2-loaded sites and subsequently endorse the reaction between pollutant and the hydroxyl radicals produced on the surface of the excited TiO_2 under UV irradiation and result in the improved decomposition rate. Thus, the combined effect of adsorption–photocatalysis phenomena of GAC–TiO_2 has enhanced the target organics [3]. The 56 W GAC–TiO_2 system has showed higher TVS and BOD removals, i.e. 100% within 6 min of reaction, with an overall BOD removal rate of 0.987 min^{-1}. However, the highest apparent BOD rate constant obtained for 14 and 56 W GAC–TiO_2 systems were 226.7 and 320 mg/L/min, respectively (Fig. 5(d)).

In addition, coliforms present in the poultry wastewater before and after treatment was also analysed to check the effectiveness of poultry wastewater treatment under GAC–TiO_2. Nearly 99.6% coliform removal was observed in both the GAC–TiO_2 systems, which indicate that the treated wastewater could be used for agriculture and other gardening purposes (Table 2). Overall, the GAC–TiO_2 photocatalyst with extremely large surface area, macro porosity and high adsorption capacity coupled with the photocatalytic activity by TiO_2 improved the destruction capability of TS, TVS, BOD and coliforms from the poultry wastewater within a very small reaction time [14,17].

5.3.3. Photocatalysis using PAC–TiO_2

The effect of photocatalysis using PAC–TiO_2 on poultry wastewater using 14 W UV irradiation was investigated and compared other photolytic and photocatalytic experiments. The results of PAC–TiO_2 experiments are shown in Table 2 and Fig. 6(a)–(c). The PAC–TiO_2 experiments reflected similar outcomes as that of GAC–TiO_2 system in terms of TS removal. However, TVS and BOD removals in 14 W PAC–TiO_2 system are slightly higher than the 14 W GAC–TiO_2 system from the beginning of the sampling periods (Table 2). As a result, the BOD removal rate (Fig. 6(d)) and the BOD removal rate constant were significantly higher than that observed in other photolytic (Fig. 3) and photocatalytic systems conducted at 14 W UV irradiation (Figs. 4(d) and 5(d)). The BOD removal rate constant obtained for PAC-TiO_2 under 14 W UV irradiation was 0.865 min^{-1} as compared to 0.788 min^{-1} in GAC–TiO_2, 0.221 min^{-1} in Slurry-TiO_2, 0.112 and 0.147 min^{-1} for photolysis at 14 and 56 W under similar conditions. However, the coliforms removal in the 14 W PAC–TiO_2 and GAC–TiO_2 systems was reached nearly 100% at the end of 180 min of reaction (Fig. 7).

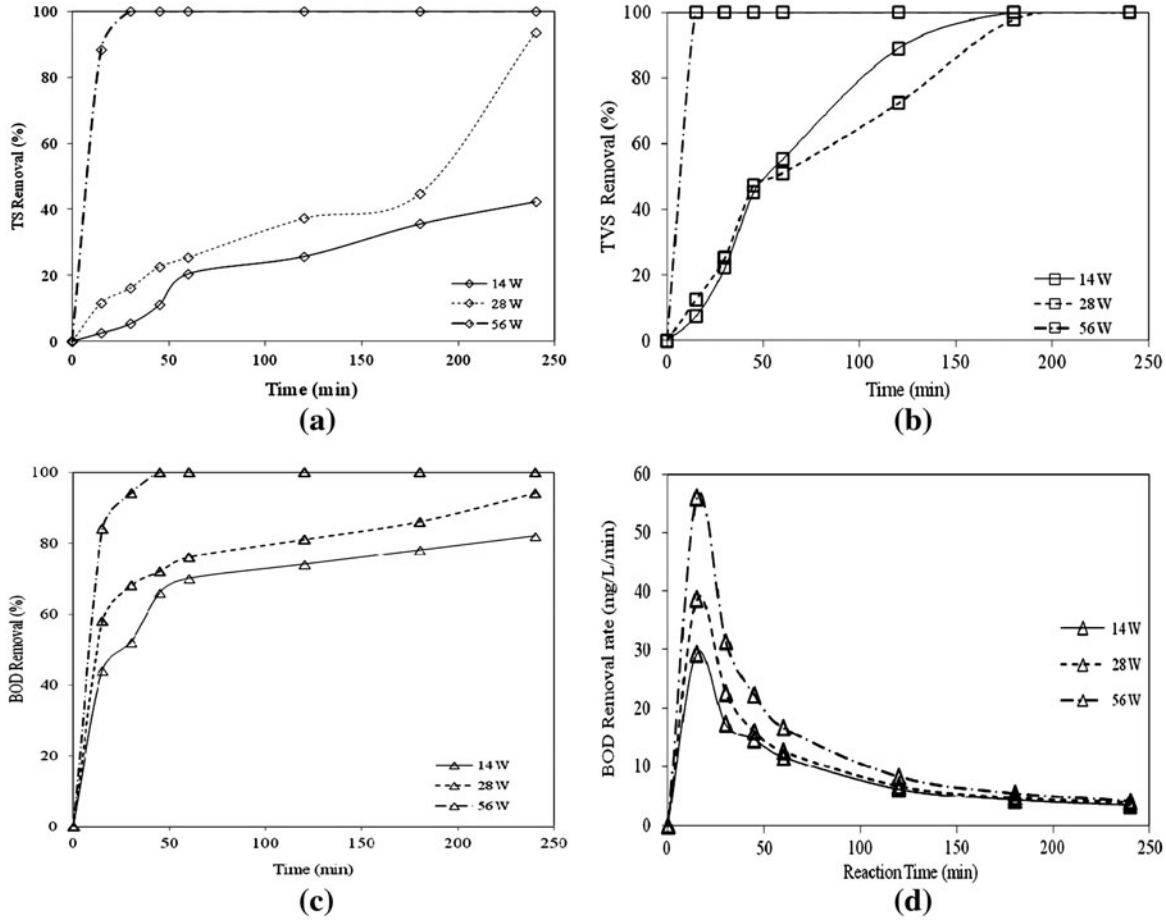

Fig. 4. Effect of Slurry-TiO_2 photocatalysis on (a) TS removal, (b) TVS removal, (c) BOD removal and (d) BOD removal rate.

The reason for higher degradation efficiency in the PAC–TiO_2 system could be basically attributed to the higher surface area available in the PAC as compared to GAC, which substantiating the fact that more finer the particle size, greater the surface area offered. Moreover, the non-homogeneity of the TiO_2 layer coated on PAC has enhanced the deposition of organics on to the TiO_2 surface [17,22]. Photocatalytic activity increased with the increase in TiO_2 loading. In the present study, the TiO_2 deposited on PAC was also higher as compared to GAC (Table 1) because of that there might be increase in the number and rate of electron–hole pair formation. As a result, the PAC–TiO_2 with high porosity and higher dispersion of TiO_2 created the synergistic effect of adsorption and photocatalysis on its surface [22,23,27].

The photocatalytic degradation of poultry wastewater using PAC–TiO_2 exhibited the best catalytic performance compared to all other systems investigated in the study. However, the major concern is about the separation of fine PAC–TiO_2 catalyst particles from the treated effluent, which normally restricts its practical applications. In our previous investigation, it was found that the cost involved in the procurement of catalyst is many folds higher compared to operational cost including the supply of UV energy (data not shown). Therefore, to economically treat the poultry wastewater under photocatalytic conditions it is mandatory to separate the catalyst and reuse it for number of cycles. To minimize the overall cost of treatment without much compromise in the water quality, GAC–TiO_2 can be operated at higher energy levels, which shows comparable performance on par with PAC–TiO_2. It can be argued that PAC–TiO_2 particles can be separated using advanced membrane filtration techniques; however, it would exhibit lots of real-time problems in the form of membrane fouling, reduction in membrane flux, etc. [30]. As a whole, the

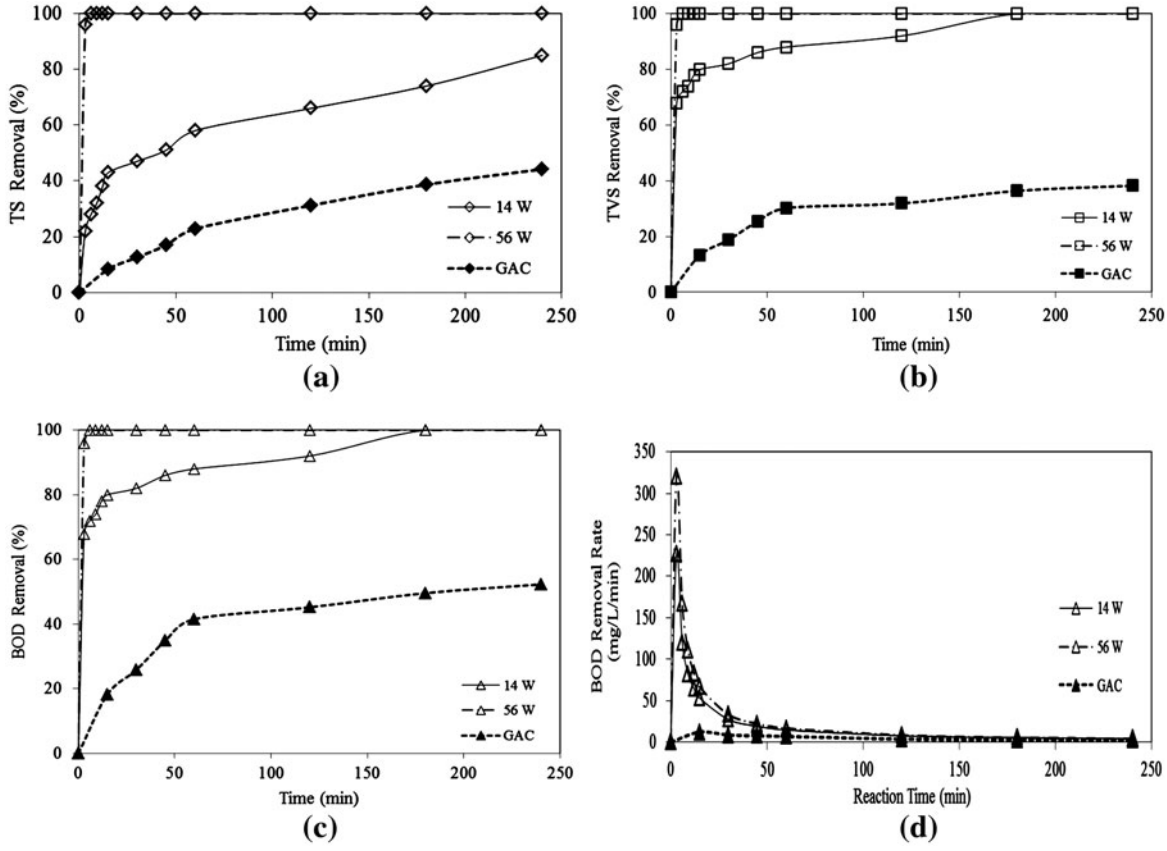

Fig. 5. Effect of GAC–TiO_2 photocatalysis on (a) TS removal, (b) TVS removal, (c) BOD removal and (d) BOD removal rate.

GAC–TiO_2 system could be recommended for poultry wastewater treatment without compromising the treated effluent quality.

5.4. Adsorption experiments using GAC/PAC

The performance of GAC and PAC in TS, TVS and BOD removals were compared with immobilized GAC and PAC systems in Figs. 5 and 6, respectively. The BOD removal efficiency in GAC and PAC adsorption experiments is 52.3 and 55.7%, respectively after 240 min, whereas the removal efficiencies were 60 and 69.2% in photolysis conducted under 14 and 56 W, respectively. However, PAC adsorption system alone showed a slightly better performance for TS, TVS and BOD removals compared to GAC adsorption systems owing to the higher surface area and porous features of the PAC compared to GAC. On the other hand, 100% BOD removal was observed in the case of photocatalysis system operated with TiO_2-immobilized GAC/PAC (Table 2). This remarkable increase in the poultry wastewater degradation is attributed to the simultaneous adsorption and photooxidation process.

5.5. Photodegradation experiments using GAC alone under 14 W UV (without TiO_2)

To demonstrate the large self-photoactivity of activated carbon support under UV irradiation, photodegradation experiment (14 W UV irradiation without TiO_2) was conducted in the presence of GAC alone. The result has shown improved removals in TS, TVS and BOD as compared to photolysis and Slurry-TiO_2 photocatalytic systems operated with 14 W irradiation. After 180 min of UV irradiation, 70, 100 and 100% of TS, TVS and BOD removals were observed. These results were almost similar to that obtained for 14 W GAC–TiO_2. In the absence of semiconductor catalyst, i.e. TiO_2, activated-carbon played the role of catalyst and promoted the photooxidation of organic pollutant. The photolytically broken down organic compounds, i.e. intermediates, might have also adsorbed in the

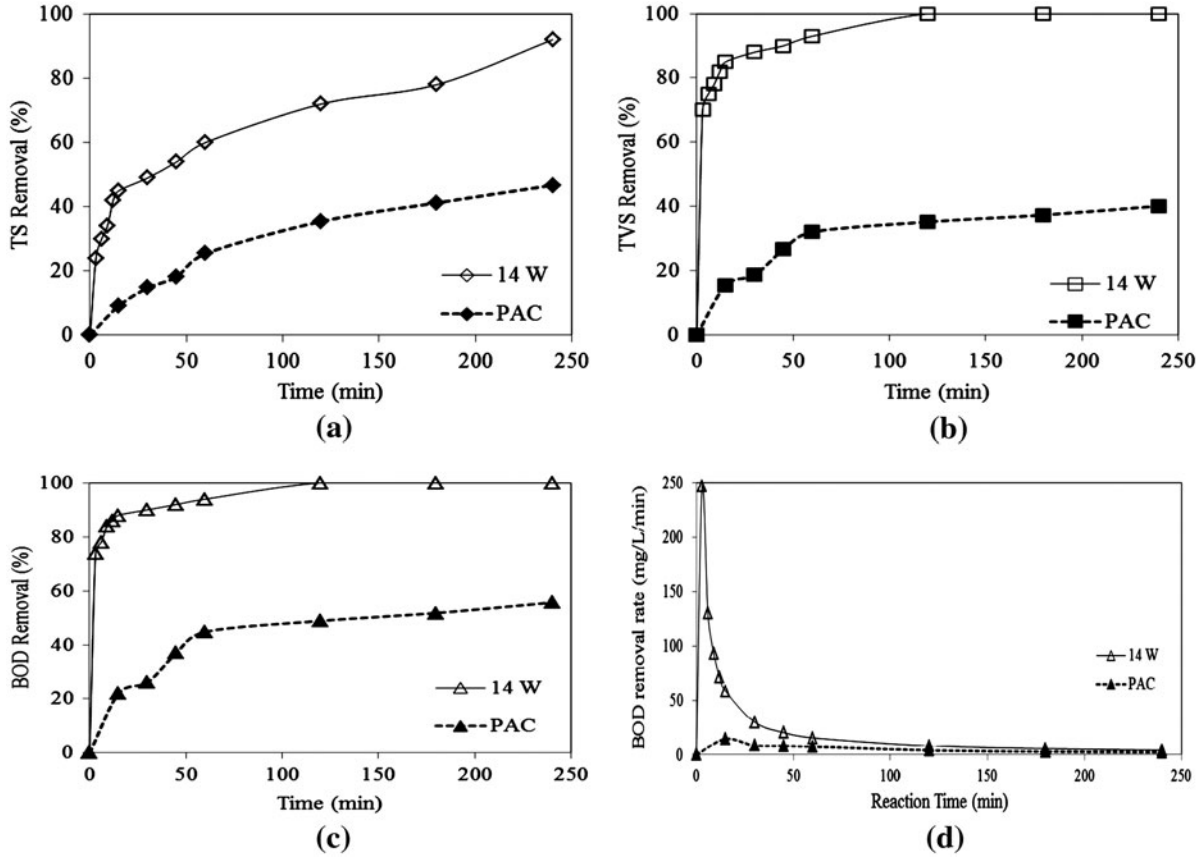

Fig. 6. Effect of PAC–TiO_2 photocatalysis on (a) TS removal, (b) TVS removal, (c) BOD removal and (d) BOD removal rate.

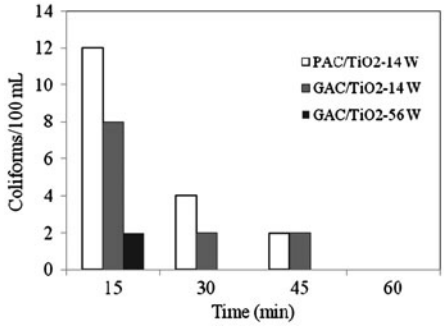

Fig. 7. Effect of photocatalytic process on coliform removal.

porous structure of activated carbon, and subsequently undergone photodegradation–adsorption cycles [18–22]. This could be the reason for the complete removal of BOD in the GAC-Photolysis systems.

6. Conclusions

The extent of photolytic and photocatalytic systems in the treatment of poultry wastewater treatment was investigated. The results showed that photocatalytic systems were highly effective compared to photolytic systems. The addition of photocatalyst triggered the treatment efficiency of poultry wastewater. The photocatalytic systems added with GAC–TiO_2 and PAC–TiO_2 complete degradation of TS, TVS, BOD and coliforms within a short reaction time. The GAC–TiO_2 separation from the effluent is much easier compared to PAC–TiO_2. Since the effluents from GAC–TiO_2 and PAC–TiO_2 systems are free from coliform organisms, it can be used for agricultural and gardening purposes. The results also suggested that in the absence of semiconductor catalyst TiO_2, activated carbons themselves act as catalyst promoting the photooxidation of organic pollutant. As a whole, the GAC–TiO_2 photocatalytic system is recommended for field-scale application with relevance to easy separation of the catalyst, high-rate destruction of the organics and complete coliforms removal in a shorter span of time.

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