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Treatment of Pharmaceutical Effluent by Photochemical Oxidation on Titanium Dioxide

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Abstract: The waste effluent from Gonoshasthaya Antibiotic Ltd. (GAL) was treated by photochemical (sunlight) degradation on TiO_2 prepared from ilmenite ($FeTiO_3$). Results showed that after 18 hours of irradiation, 94% of dissolved organic compounds were degraded to environmentally acceptable products such as CO_2, H_2O and other mineral acids or their salts. The GAL effluent had the initial chlorine content (CC) of 7024 ppm and this increased to 7842 ppm in solar water purifier after 18 hours of irradiation. The concentration of total dissolved solid (TDS) in GAL effluent had 46,000 ppm which was reduced to 2600 ppm after 18 hours of irradiation. The concentration of total suspended solid (TSS) in the GAL effluent was 455 ppm and after 18 hours of irradiation no change in concentration was observed. Furthermore, the relative distribution of the number of compounds decreased with increasing irradiation time.

Key words: Waste effluents, land degradation, pollution, oxidation.

Introduction

The wastewater discharged from industrial operations is the worst source of water pollution and can affect rain, the rivers, the lakes, the oceans and ground water (Laws, 1981). Most of the industrial units, which are situated along the bank of rivers drain out their effluents directly into the nearby rivers or agricultural land without any treatment. Such draining of effluents and wastes are also responsible for land degradation as well as pollution of ground water. The situation is worst during dry season when the pollutants are concentrated in a specific area near the industrial activity.

In Bangladesh, majority of chemical industries have no wastewater or effluent treatment plant. They generally discharge the effluents into the nearby agricultural crop fields or nearest water bodies. In this study, we have chosen M/s Gonoshasthaya Antibiotic Ltd., which manufactures four bulk chemicals used by the pharmaceutical industries for the production of capsules and dry syrups of amoxycillin trihydrate BP/USP, ampicillin trihydrate BP/USP, cephalexin monohydrate BP/USP and coxacillin–Na BP/USP. Similar raw materials are also manufactured by Square Pharma, Beximco Pharma, Drug International and Globe Research. They use methylene chloride, isopropyl alcohol, pivaloic acid, triethyl amine, trimethylchlorosilane, ethanol, acetone, ethyl acetate, sodium hydroxide, methyl iso-butylketone, etc., as raw materials.

Industrial effluent discharged into the environment is one of the major problems in recent days in Bangladesh and this has become a national concern. To solve the problems of increasing use of water and its pollution and to save the environment, it is singularly important to develop sustainable low-cost water purification system, wastewater recycling and effluent treatment techniques.

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To meet that need, this research was undertaken to characterize the wastewater effluents discharged from Gonoshasthaya Antibiotic Ltd., and to study the removal efficiency of organic wastes from effluents discharged at the above pharmaceutical industry by photochemical degradation on TiO_2.

Materials and Methods

A mixture of 100 g of ilmenite and 200 g of 89% sulphuric acid was refluxed (at 195–200 ºC) taking in a 500 mL round bottom flask with air condenser for 20 hours on an oil bath. After heating, the mother liquor was allowed to cool down at room temperature and 600 mL of distilled water was added to it with gentle stirring. The resulting solution was then boiled at around 70–80 ºC for one hour with constant stirring. The hydrated TiO_2 thus generated was allowed to settle down. The precipitate was washed with distilled water to make it free of sulphate ion and then wash it with dilute ammonia to adjust the pH. The precipitate obtained thus was dried at 200 ºC for an hour and then calcined in a furnace at 800 to 900 ºC for an hour to obtain the desired TiO_2.

Intensified sunlight achieved by collimated beam was produced by placing the reactor containing effluent of Gonoshasthaya Antibiotics Ltd. (GAL) at the focus of a parabolic reflector (Figure 1). The concentration of TiO_2 was 6.0 g per litre of the effluent.

Sunlight irradiation was performed for 6, 12, 18 and 24 hours respectively and at the end of each time required quantity of sample was collected for both HPLC (Waters-510, Water's Millipore) and GLC (GC-14B, Simadzu, Japan) analysis. COD and DOC were also determined using standard methods at the same time. The other effluent quality parameters were analysed using standard methods before and after the 24 hours of irradiation.

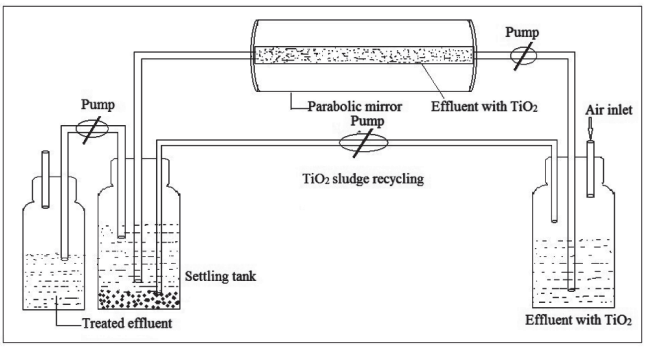

Figure 1: Instrumentation of solar water purifier.

A reference effluent was produced for the determination of concentration of GAL effluent at different irradiation time.

Results and Discussion

For the determination of the concentrations of the effluent of the GAL, a reference effluent was prepared with the probable organic materials discharged during manufacturing processes of different antibiotics such as amoxycillin trihydrate, ampicillin trihydrate, cephalexin monohydrate, cloxacillin sodium, etc. The composition of the reference effluent is presented in Table 1.

Table 1: Composition of 100 ml reference effluent

Particulars	*Amount taken (g)*	*Volume of reference effluent (mL)*	*Concentration (ppm)*
Amoxycillin	0.1	100	1000
Ampicillin	0.1		1000
Cloxacillin	0.1		1000
Cephalexin	0.1		1000
Isopropyl alcohol	10		100000
Methylene dichloride	0.2		2000
Triethylamine	0.9		9000
Total	11.5		115000

The reference and GAL effluents were analysed by HPLC and GLC and the observed value of peak area and peak height from both the chromatograms are presented in Tables 2 and 3, respectively.

GAL effluent containing a specified amount of TiO_2 was exposed to concentrated sunlight for 0, 6, 12, 18 and 24 hours and data of HPLC and GLC analysis have been given in Tables 4 and 5, respectively.

Values of pH, DOC and COD of GAL effluent were determined after above mentioned each irradiation time (Table 6).

And the CC, TDS and TSS concentrations were measured only before and after 18 hours of irradiation (Table 7).

The application of illuminated semiconductor for the remediation of the contaminants has been used successively for a wide variety of compounds (Safiullah et al., 1998; Safiullah and Khan, 1998; Mills and Hoffman, 1991; Pelizzetti et al., 1993), such as, phenols, alkanes, aliphatic alcohol, aliphatic carboxylic acids, alkenes, phenols, aromatic carboxylic acids, halogenated alkanes and alkenes, surfactants and pesticides as well as for the reductive deposition of heavy metals from aqueous solution to surfaces (Albert et al., 1992).

Table 2: HPLC data of reference and GAL effluent

Reference effluent				*GAL effluent*			
Retention time (min)	*Height (cm)*	*Peak area*	*Area percent*	*Retention time (min)*	*Height (cm)*	*Peak area*	*Area percent*
2.53	469504	469.504	22.79	2.41	1.754	1754	0.10
2.77	270464	270.464	13.13	2.76	478.645	478645	26.21
3.25	271924	271.924	13.20	3.06	315.905	315905	17.30
3.8	382304	382.304	18.56	3.51	277.749	277749	15.21
4.08	357564	357.564	17.36	4.20	261.696	261696	14.33
4.23	129997	129.997	6.31	4.45	170.082	170082	9.32
5.44	16814	16.814	0.82	4.58	166.770	166770	9.13
7.11	86356	86.356	4.19	6.03	17.950	17950	0.98
9.16	9720	9.720	0.47	7.15	3.707	3707	0.20
13.01	21888	21.888	1.06	7.97	57.492	57492	3.15
14.86	1823	1.823	0.09	10.13	8.349	8349	0.46
15.96	441	0.441	0.02	11.15	0.341	341	0.02
19.38	20299	20.299	0.99	12.85	0.897	897	0.05
21.85	21101	21.101	1.02	13.60	0.538	538	0.03
Total	2060199	2060.199	100.00	14.63	20.757	20757	1.14
				16.60	1.318	1318	0.07
				18.06	0.454	454	0.02
				19.46	0.577	577	0.03
				21.63	22.921	22921	1.26
				25.23	17.980	17980	0.98
				Total	1825.882	1825882	100.00

Table 3: GLC data of reference and GAL effluent

Reference effluent				*GAL effluent*			
Retention time (min)	*Area*	*Height (cm)*	*Area %*	*Retention time (min)*	*Peak area*	*Height (cm)*	*Area %*
1.249	1561	314	0.080	1.315	3664	547	0.194
1.717	13106	352	0.674	1.675	17100	388	0.909
6.175	4010	152	0.206	6.283	8653	300	0.457
7.280	1925523	31880	99.039	7.392	1832322	29773	98.445
Total	1944200	32698	100	Total	1861739	31008	100

Table 4: HPLC data of GAL effluent after sunlight irradiation in presence of TiO_2 at different time in solar water purifier

Irradiation time (hour)	*Retention time (min)*	*Peak area*	*Height (cm)*	*Area %*	*Irradiation time (hour)*	*Retention time (min)*	*Peak area*	*Height (cm)*	*Area %*
	2.41	1.754	1754	0.10		2.65	241.213	241213	38.86
	2.76	478.645	478645	26.21		3.08	83.593	83593	13.47
	3.06	315.905	315905	17.30		3.48	182.945	182945	29.47
	3.51	277.749	277749	15.21		4.22	4.739	4739	0.76
	4.20	261.696	261696	14.33		4.46	21.144	21144	3.41
	4.45	170.082	170082	9.32		5.79	4.519	4519	0.73
	4.58	166.770	166770	9.13		6.15	1.887	1887	0.30
	6.03	17.950	17950	0.98		7.05	2.924	2924	0.47
	7.15	3.707	3707	0.20	6	7.49	3.460	3460	0.56
0	7.97	57.492	57492	3.15		7.92	62.506	62506	10.07
	10.13	8.349	8349	0.46		11.47	0.356	356	0.06
	11.15	0.341	341	0.02		21.78	11.431	11431	1.84
	12.85	0.897	897	0.05		Total	620.717	620717	100.00
	13.60	0.538	538	0.03	12	2.75	276.050	276050	64.37
	14.63	20.757	20757	1.14		3.53	144.836	144836	33.77
	16.60	1.318	1318	0.07		4.40	4.210	4210	0.98
	18.06	0.454	454	0.02		5.94	3.748	3748	0.87
	19.46	0.577	577	0.03		Total	428.844	428844	100.00
	21.63	22.921	22921	1.26	18	2.75	225.522	225522	100.00
	25.23	17.980	17980	0.98		Total	225.522	225522	100.00
	Total	1825.882	1825882	100.00					

Table 5: GLC data of GAL effluent after irradiation (sunlight) with TiO_2 at different times in solar water purifier

Irradiation time (hour)	*Retention time (min)*	*Peak area*	*Height (cm)*	*Area %*	*Irradiation time (hour)*	*Retention time (min)*	*Peak area*	*Height (cm)*	*Area %*
	1.315	3664	547	0.194		1.218	3194	522	0.605
	1.675	17100	388	0.909		1.603	15229	361	2.882
0	6.283	8653	300	0.457	12	7.722	509945	8494	96.513
	7.392	1832322	29773	98.445		Total	528368	9377	100
	Total	1861739	31008	100		1.325	3128	509	1.487
	1.436	3123	465	0.469		1.712	15910	374	7.563
	1.817	16616	369	2.497	18	7.846	191312	3220	90.950
6	7.733	645324	10341	97.033		Total	210350	4103	100
	Total	665063	11175	100		1.214	2876	499	1.697
	1.608	14867	345	8.773	24	7.892	151722	2571	89.530
						Total	169465	3415	100

Table 6: The value of pH, DOC, COD and observed colour change of GAL effluent at the end of each irradiation time

Sl No.	*Particulars*	*Irradiation time (hour)*	*pH*	*DOC (ppm)*	*COD (ppm)*	*Observed colour*
1	Effluent of GAL	0	7.1	9540	59900	Brown
2	Status of effluent	6	7.0	3910	29950	Yellow
3	Status of effluent	12	7.0	2547	26200	Light yellow
4	Status of effluent	18	6.9	592	6550	Light yellow

Table 7: The value of CC, TDS and TSS of GAL of raw and treated effluent

Parameters	*Untreated effluent (ppm)*	*Treated effluent (ppm)*
CC	7024	7842
TDS	46000	2600
TSS	455	455

Table 8: Concentration of GAL effluent at different irradiation time obtained from HPLC and GLC analysis

HPLC area			*GLC area*		
Irradiation time (hour)	*Total peak area*	*Concentration of effluent (ppm)*	*Irradiation time (hour)*	*Total peak area*	*Concentration of effluent (ppm)*
0	1825.882	101920.46	0	1861739	110122.41
6	620.717	34648.33	6	665063	39338.67
12	428.844	23938.01	12	528368	31253.12
18	225.522	12588.60	18	210350	12442.26
			24	169465	10023.90

In the present study photocatalytic degradation of organic wastes present in the effluents takes place on suspended TiO_2 when exposed to sunlight and continuous aeration. Upon irradiation with UV radiation present in sunlight, a semiconductor photocatalyst produces electron/hole pairs when free electrons are in empty conduction band while the positive holes remain in the valence band (Bard, 1979; Schiavello, 1987). The holes acting as strong oxidizing agents that migrate to the semiconductor surfaces and react with organic compounds and degrade them. Depending upon the ambient conditions, the lifetime of an electron/hole separation process can be from a few nano seconds to a few hours. The recombination of the electron/hole pairs can take place either in the energy bands or on the surface. As a result of the electron/hole recombination, the photocatalytic efficiency is reduced. When certain conducting materials are incorporated into the semiconductor it facilitates the electron transfer and prolongs the lifetime of the recombination process (Izumi et al., 1980). Since the source of TiO_2 in the present study was ilmenite, it is possible that iron is present as an impurity and the presence of iron may have increased the photochemical efficiency of TiO_2. It was observed that the waste of effluent was degraded, when they are subjected to intensified sunlight achieved by the parabolic reflector. This was confirmed by carrying out HPLC and GLC analysis and it is found that the concentrations of the waste of effluent decreases are decreasing with the increase of irradiation time (Table 8 and Figures 2 and 3).

Concentrations of wastes in GAL effluent at different irradiation time was calculated from the total peak area of the reference effluent and the total peak area of the

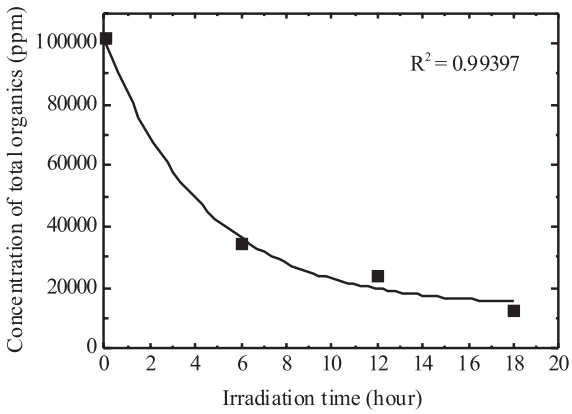

Figure 2: Change of concentration of total organics with irradiation time.

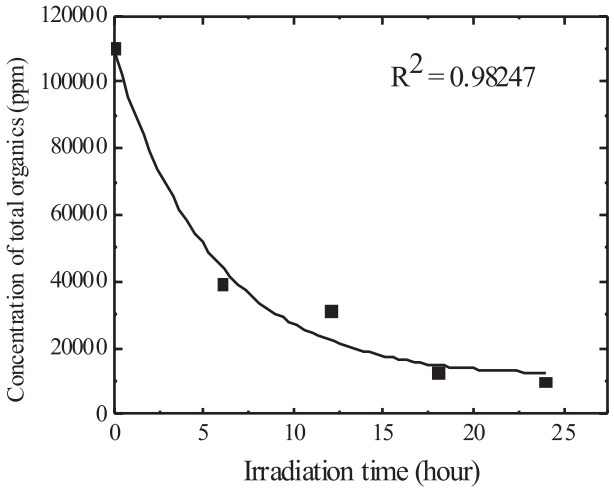

Figure 3: Change of concentration of total organics with irradiation time.

GAL effluent at the end of each irradiation time. The photo-oxidation of many organic substances is dominated by OH radical (Izumi et al., 1980; Izumi et al., 1981; Fuzihira et al., 1981; Matthews, 1984; Brickley and Stone, 1973). In the present study, generation of CO_2 was observed. So it is assumed that hydroxylated intermediate products corresponding to similar species are produced (Al-Eakabi and Serpone, 1988; Okamoto et al., 1985).

The irradiation of TiO_2 with the light energy 3.2 eV generates conduction band electrons (e^-) and valence band positive holes (h^+). Excited state conduction band electrons and valence band holes may recombine and dissipate input energy as heat and get trapped in meta-stable surface states or react with electron donors and electron acceptors adsorbed on the semiconductor surface. In the presence of molecular oxygen (air), an essential ingredient in this photo-oxidation, the e^- is scavenged to form the super-oxide radical (O_2^-), thereby permitting excess h^+ to conduct oxidative reaction. Thus by studying photo-adsorption of oxygen at the surface of TiO_2, it was proposed that a dissociation chemisorption takes place at the surface of $Ti^{4+}O^{2-}$ pair, thereby holes with the formation hydroxyl radical. This TiO_2 constitutes the major paths to the formation of hydroxyl radicals. Another source of OH radical originates from the super oxide radical to form H_2O_2, and this ultimately yields OH radical species through interaction of the peroxide with e^- or O_2^-. This route appears to play a minor role in the formation of OH radical (Matthews, 1986). In the present study OH radical in presence of light source and TiO_2 suspension is responsible for photocatalytic oxidation of organic compound according to the following scheme.

Organic compounds (by products) → Intermediate organics

Intermediate organics + OH• → Other intermediates

Other intermediates → $CO_2 + H_2O$ or other mineral acids

The principal effluents discharged during the manufacturing process from GAL mainly contained the organic constituents. Results of HPLC and GLC analysis showed that the total concentrations of waste of these effluents were decreasing at different irradiation time.

The same trend is observed with the organic carbon concentration. Results showed that the initial concentration of DOC in the effluent was found 9540 ppm and after 18 hours of irradiation the concentration of DOC was found to be 592 ppm, indicative of 94% of degradation of dissolved organic carbon. These organic carbons are ultimately decomposed to environmentally acceptable products such as CO_2, H_2O and other mineral acids or their salts (Block and Bickley, 1992). The concentration of DOC with respect to irradiation time is shown in Figure 4.

The chemical oxygen demand (COD) measures the pollution strength of wastewater. Most of the organic compounds are oxidized to carbon dioxide and water by the action of oxidizing agents regardless of biological assimilability of the substances. The COD concentration at different irradiation time is shown in Figure 5. The decreasing trend of COD value indicated that significant amounts of organic waste were degraded and most of them were removed or degraded after 18 hours of irradiation.

The chlorine content, total suspended solids and total dissolved solids of the effluent were also analysed and they are presented in Figure 6. The result showed that

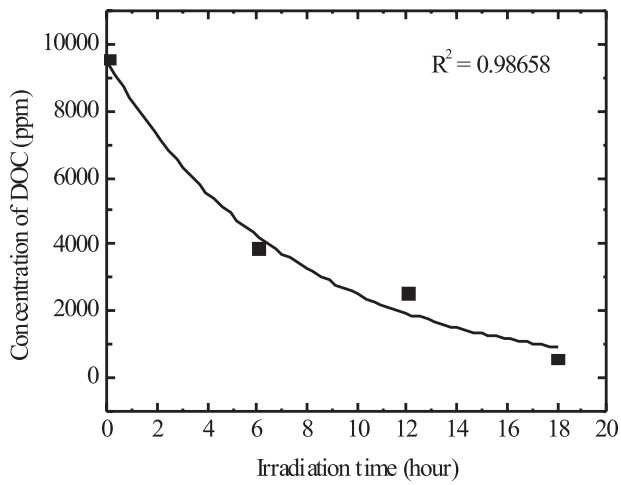

Figure 4: Change of DOC with irradiation time.

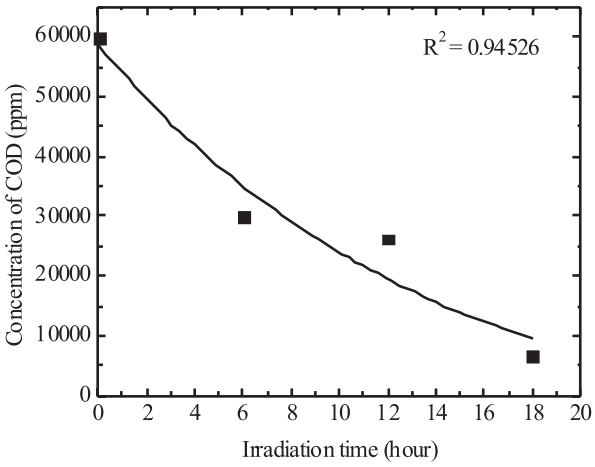

Figure 5: Change of COD with irradiation time.

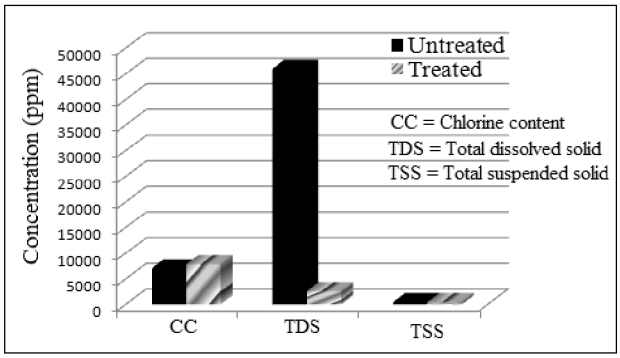

Figure 6: Concentration of some effluent quality parameters before and after treatment.

the value of total dissolved solids was reduced to 2600 ppm from 4600 ppm. However, the value of total suspended solids remains constant and there is some increase in the value of chlorine content. The initial value of chlorine content was 7024 ppm and after 18 hours of irradiation, its value increases to 7842 ppm. The increase of chlorine concentration and lowering of pH indicate that methylene chloride present in the original effluent has been photochemically degraded to CO_2 and HCl.

Furthermore, number of compounds decreases with increasing irradiation time as indicated by the decrease of the number of peaks surmised from both HPLC and GLC data. Physical examination showed that the odour (especially for isopropyl alcohol) very quickly decreased and the colour of the effluent became light yellow from deep brown after 18 hours of irradiation. This indicates that the concentration of different compounds gradually decrease with the increase of irradiation time, presumably by photo degradation.

Limitations of This Method

High intensity light is required for the system to enhance its activity of degradation or mineralization. There are six seasons in Bangladesh. Intense UV light from sun can be achieved in the months of summer and winter. But in the other seasons, especially rainy season, there is a little possibility of getting intense UV light from the sun. During these seasons, this process of wastewater treatment based on TiO_2 is difficult. Some extra source of intense light should be arranged during these seasons to make the system effective. Photochemical process may thus be used in combination with other processes such as adsorption filtration and precipitation coagulation.

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