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Two Stage Treatment of Pharmaceutical Compounds by Biological and Advanced Oxidation Process

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Abstract—*The present study was performed to assess the removal efficiencies of micro pollutants, namely Metronidazole and Barbituric acid, commonly found in sewage through sequential anaerobic - aerobic biological treatment. Studies were also performed to assess the efficacy of photo - degradation of Barbituric acid. Anaerobic treatment was carried out in anaerobic hybrid reactor (AHR) consisting of suspended growth in the bottom and attached growth in the top portion of the reactor. Aerobic reactor used in the present investigation was a submerged aerobic fixed film (SAFF) reactor. Photodegradation of Barbituric acid was carried out using a photo reactor and a photo - catalyst titanium dioxide. The removal efficiency of drugs was more through anaerobic reactor as compared to aerobic reactor and was 80% and 60% respectively. The overall removal efficiencies of metronidazole and barbituric acid through sequential anaerobic - aerobic system were found to be 92% and 91% respectively. Moreover, the presence of drugs did not decrease the COD removal efficiency of sewage. The photo - degradation of barbituric acid was attempted using three types of titanium dioxide and the removal efficiency of 94% was obtained using TiO_2 nanoparticles Degussa P25 catalyst. GC MS analysis showed the complete mineralization of drugs through both biological as well as photo - degradation processes.*

1. INTRODUCTION

Sewage treatment plants are constructed for the reduction of organic matter and nutrients, the removal of micro pollutants is not incorporated in the design. Due to this fact, a vast number of micro pollutants are not completely removed and a significant fraction of them continuously discharged to the environment. Organic micro pollutants refer to a wide group of carbon containing chemical compounds, mainly of xenobiotic nature including pharmaceutical compounds, personal care products, harmones, pesticides, brominated flame retarders, plasticisers. Some of these compounds are persistent organic pollutants capable of long range transport and result in bioaccumulation in human and animal tissues. Micro pollutants based on Pharmaceutical and Personal Care Products (PPCPs) constitute a wide group of chemicals comprising human and veterinary medicines, hormones and cosmetic ingredients. Special attention should be paid to these biologically active substances, due to the possibility of some adverse effects which these compounds could exert on aquatic organisms living in rivers, lakes, etc.

Micro-pollutants have been detected in surface waters in most of the countries [1,2] and they are of increasing importance in water pollution control. In particular, the role of chemicals that are suspected of having an impact on the hormonal systems of humans and wildlife, i.e. endocrine-disrupting compounds (EDC) and other micro-pollutants such as pharmaceutical compounds has to be emphasised. It is thought that endocrine-disrupting compounds and pharmaceutical residues enter rivers, streams and surface waters through the effluents and residual sludge from wastewater treatment plants (WWTPs).

The common organic pollutants usually detectable in wastewater sludges are adsorbable organic halogens (AOX), linear alkylbenzene sulfonates (LAS), hydrocarbons (HC), nonylphenols/ nonylphenol ethoxylates (NPE) and di-ethyl-hexyl-phthalate (DEHP). Other chemicals that are toxic to human beings and threaten potentially chronic long-term effects are polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDF).

Human pharmaceuticals are consumed in high quantities worldwide. The expectations are that these amounts will only keep increasing because of improving health care system and longer life expectations of people.

Pharmaceuticals administered to (consumed by) humans after required action in the body get excreted with urine and faeces as a parent (original) compound and usually as a number of metabolites. It is generally accepted that the principal source of human pharmaceuticals detected in the aquatic environment is patient excretion. The most important is on-house consumption.

The 'typical' wastewater from a residential area contains, pain killers, beta-blockers, cholesterol lowering agents and anti-epileptics in concentrations up to tens of µg/L. Sedatives, tranquilizers, depressants, anxiolytics, soporifics, sleeping pills, downers, or sedative hypnotics these are different names for substances, which depress the central nervous system (CNS), resulting in calmness, relaxation, reduction of anxiety, sleepiness, slowed breathing, slurred speech, staggering gait, poor judgment, and slow, uncertain reflexes. Barbiturates are

drugs that act as central nervous system (CNS) depressants, and by virtue of this they produce a wide spectrum of effects, from mild sedation to anesthesia.

Disposition of Metronidazole in the body is similar for both oral and intravenous dosage forms, with an average elimination half-life in healthy humans of eight hours. The major route of elimination of Metronidazole and its metabolites is via the urine (60 to 80% of the dose), with fecal excretion accounting for 6 to 15% of the dose

Furthermore, it has been observed that the level of these xenobiotics (LAS, PAH, NPE, DEHP) is much higher in anaerobically digested sludge than in aerobically stabilized sludge [3]. This indicates that they can be partly or fully degraded under aerobic conditions, but not under anaerobic conditions [4]. However, recent findings indicate that degradation of LAS is possibly initiated by desulfonation under anaerobic conditions [5].

The aerobic post-treatment of anaerobically digested sludge represents an established solution for the elimination of organic sludge pollutants. However, for certain organic, xenobiotic substances its efficiency is limited. Blika et al. [6] have reported on the limited removal of 4-NP techn., phenanthrene, fluoranthrene and pyrene even after extended aerobic treatment.

Grossberger A et. al. studied the biodegradation of pharmaceutical compounds in agricultural soils irrigated with treated wastewater and concluded that pharmaceutical compounds are degraded through soils via co metabolism [7]. Vieno N and Sillanpaa M reviewed the fate of diclofenac in municipal wastewater treatment plant and concluded that diclofenac are poorly biodegradable and further research was required for the same [8]. Schroder H.F. et. al. worked on the treatment of wastewater containing non-steroidal anti-inflammatory drugs and antibiotics using MBRs with HRT of 15and 30 days and concluded that non-steroidal anti-inflammatory drugs were removed with a higher efficiency than the antibiotics [9]. Langenhoff A., et. al. Worked on the microbial removal of Ibuprufen and Diclofenac from wastewater and concluded that Ibuprufen was completely removed and there was partial removal of diclofenc necessitating the need for post treatment [10].

Kawabata K et al. [11] worked on the photodegradation of nine pharmaceutical compounds using sunlight and UV irradiation. They concluded that UV and sunlight degraded few compounds completely. However, in some drugs the intermediate compounds formed were more toxic than the parent compounds. Giri R.R. et al. [12] worked on the degradation of sixteen pharmaceutical compounds and personal care products using advanced oxidation process. They concluded that ozone based techniques rather than ultraviolet based techniques were powerful in the simultaneous degradation of the compounds. They further concluded that ozonation combined with ultraviolet radiations was the most appropriate technique for the simultaneous degradation of pharmaceutical compounds. Farzadkia M et. al. [13] worked on the photodegradation of metronidazole (MNZ) with illuminated TiO_2 nanoparticles at different catalyst dosage, contact time, pH, initial MNZ concentration and lamp intensity. Maximum removal of MNZ was observed at near neutral pH. Removal efficiency was decreased by increasing dosage and initial MNZ concentration. Haq et. al.[14] worked on the photocatalytic activity of TiO_2 for the degradation/mineralization of Barbituric acid and Matrinidazole and were successful in achieving the results. The knowledge on the fate of pharmaceuticals during a variety of treatment technologies is, despite significant scientific efforts, limited. To design an optimal treatment system that is able to eliminate the majority, if not all, of entering pharmaceutical micro-pollutants has not been possible yet.

The objective of the study was to evaluate the performance of sequential anaerobic –aerobic treatment for the biodegradation of pharmaceutical based micropollutants, namely Barbituric acid and Metronidazole present in sewage. Experiments were also carried out to assess the efficacy of photo oxidation process for the degradation of one of the pharmaceutical compounds, namely, barbituric acid.

2. MATERIAL AND METHODS

Materials

Barbituric acid and Metronidazole were purchased from Merck for the study purpose. Stock solutions were prepared using double distilled water.

Biodegradation Studies

Biodegradation studies were carried out in a reactor system comprising of anaerobic hybrid reactor (AHR) and submerged aerobic fixed film (SAFF) reactor connected in series. The AHR was fabricated with Perspex material having an internal diameter of 0.05 m, total height of the reactor was 1.450 m. The effective volume of the reactor was 2.50 litres. It consisted of Upflow Anaerobic Sludge Blanket (UASB) at the bottom and an anaerobic filter at the top. The media used for anaerobic filter was PVC pipe of inner diameter of 0.025 m which was cut into pieces of nearly 0.025 m in length. The SAFF reactor consisted of two identical compartments, in series, each containing the PVC media for support of the biofilm. The lower portion of the reactor contained microorganisms under suspension and it acted as a suspended growth system. Diffused aeration was provided in the lower portion of the reactor. The reactor set up is shown in Fig. 1.

Both the reactors were seeded with appropriate sludge obtained from a working sewage treatment plant at Okhla. Initially both aerobic as well as anaerobic reactors were fed with sewage obtained from the campus and were operated for 15 days to activate the microorganisms. The drugs with concentration 1 mgL^{-1} of Metronidazole and 2 mgL^{-1} of

Barbituric acid were introduced in the reactor. The effluent samples were analysed on alternate days using spectrophotometer to find the removal efficiency of drugs. The concentration of the drugs in feed was increased to 1.5 mgL^{-1} of Metronidazole and 2.5 mgL^{-1} of barbituric acid and 2.0 mgL^{-1} of metronidazole and 3.0 mgL^{-1} of barbituric acid after 40^{th} and 60^{th} day of reactor operation, respectively. The reactors were operated for nearly three months.

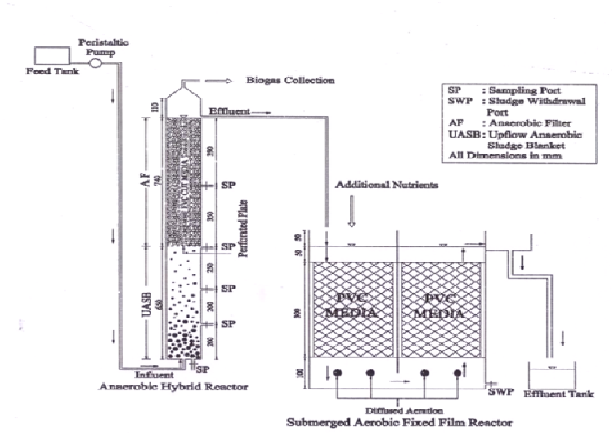

Fig. 1: Sequential Anaerobic - Aerobic Biological Reactor System

Photo - degradation Studies

An immersion well photochemical reactor made of Pyrex glass equipped with a magnetic stirring bar, water circulating jacket and an opening for supply of molecular oxygen was used for photodegradation studies. Fig. 2 shows the set up of the photo-reactor. The aqueous solution of the drug with desired concentration was taken into the photo-reactor and required amount of photo-catalyst was added for irradiation experiment. The solution was stirred and bubbled with molecular oxygen for at least 15 minutes in the dark to allow equilibration of the system so that the loss of compound due to adsorption can be taken into

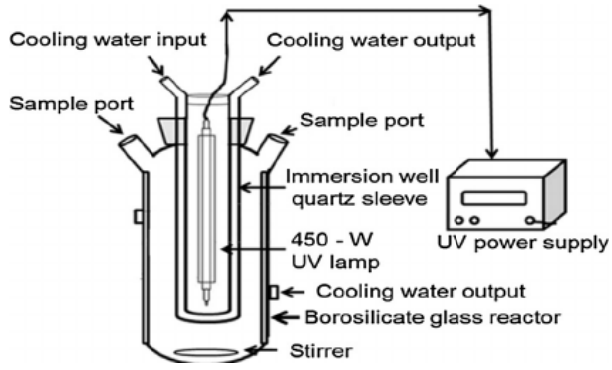

Fig. 2: Experimental Set up of Photo-reactor

account. The zero-time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with molecular oxygen throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp (Philips). IR-radiation and short-wavelength UV-radiation were eliminated by water circulating Pyrex glass jacket. Samples (10 mL) were collected before and at regular intervals during irradiation and analysed after centrifugation.

GC – MS Analysis

For GC-MS analysis, the supernatant was initially extracted three times using chloroform in 1:2 ratio in a separating funnel by intermittent shaking and it is kept for complete vaporisation of other compounds. 1µL of blank and reactor effluent was injected in GC-MS equipped with a split/split less injector. The MS was operated in the EI mode (70eV). Helium was employed as carrier gas and its flow rate was adjusted to 1 mL/min. The analytical column connected to the system was a PE-5MS capillary column (length 30 m, diameter i.d.250µm).

The GC column temperature was programmed at 105ºC.A solvent delay of 3.5 minute was selected. The injector temperature was set at 200ºC, and all injections were carried out on the split less mode. The GC-MS interface was maintained at 250ºC.The oven programme was 50ºChold 5min /@10ºC/min to 285ºChold 10 min. The MS was operated in the total ion current (TIC) mode, scanning from m/z 30 to 500.

3. RESULTS AND DISCUSSION

Biological Treatment

The overall performance of the reactor system was evaluated by monitoring the COD of the influent and effluent through both aerobic as well as anaerobic reactor. Initially sewage (COD ¬ 200 mg/L) alone was fed to the reactors for activating the microorganisms. As explained earlier, the drugs at concentration of 1.0 mg/L metronidazole and 2.0 mg/L barbituric acid were introduced in the reactor after 15days of operation. The COD removal efficiency decreased after introduction of the drugs in the sewage. However, over a period of time the microorganisms have become acclimatised and were able to degrade pharmaceutical compounds. There was a drop in the COD removal efficiency when the concentration of drugs was increased. However, again with time the microorganisms were able to produce enzymes that were capable of degrading the higher concentration of drugs. The same pattern was observed in aerobic reactor system. The COD removal efficiencies through aerobic treatment were found lesser as compared to anaerobic treatment. This may be attributed to better resistance of anaerobic microorganisms for the pharmaceutical compounds. The drug removal efficiency was monitored after regular intervals. Table 1 gives the maximum removal efficiency of drugs under aerobic as well as anaerobic treatment.

Table 1: Removal efficiencies of drugs at different concentration

Name of Drug	Concentration	Removal Efficiency		Overall Efficiency
	mgL-1	Anaerobic	Aerobic	%
Metronidazole	1.0	71	45	84
	1.5	85	55	93
	2.0	80	60	92
Barbituric Acid	2.0	65	50	82
	2.5	78	57	90
	3.0	80	58	92

It is seen that the maximum metronidazole removal efficiency of 85 was achieved at concentration of 1.5 mg/L under anaerobic conditions. However, the maximum removal efficiency was only 60% under aerobic conditions. The maximum barbituric acid removal efficiency of 80% was obtained at concentration of 3.0 mg/L under anaerobic conditions. The trend under aerobic conditions was similar as was in the case of metronidazole and maximum removal efficiency of 58% was achieved. However, the overall efficiency of sequential treatment was excellent and complete mineralization of drugs took place. The overall COD removal efficiency was 92% through sequential anaerobic - aerobic treatment. The pH and alkalinity in the effluent of both the reactors were in the permissible limits. Qualitative GC MS analysis was also carried out to find the formation of intermediate compounds of biodegradation. Following intermediate compounds were detected in the effluent from anaerobic reactor. However, these compounds were absent in the effluent of aerobic reactor thereby indicating complete mineralization of drugs through sequential anaerobic - aerobic biological treatment.

Photo-degradation Studies

Photolysis of Aqueous Suspensions of Barbituric acid in the presence of TiO_2 nanoparticles

Irradiation of aqueous suspensions of Barbituric acid in the presence of TiO_2 nanoparticles with constant bubbling of air lead to decrease in substrate concentration and depletion in Total Organic Carbon (TOC) content as a function of time. Fig. 3 depicts the change in concentration and depletion in TOC content as a function of time on irradiation of aqueous suspensions of Barbituric acid in the presence of TiO_2 nanoparticles.

Comparison of Different TiO_2 nanoparticles Photo – catalysts

The photo catalytic degradation of Barbituric acid was tested with three different commercially available TiO_2 nanoparticles powders (namely Degussa P25, Hombikat UV100 and Millennium Inorganic PC500) in order to determine the best photo - catalyst. The rate obtained for the degradation of Barbituric acid in presence of three different types of TiO_2 nanoparticles samples is shown in Fig. 4.

For better photocatalytic activity, the catalysts having smaller particle size with large surface area would result in better adsorption of compounds followed by interaction of light. Degussa P25 consists of 80% anatase and 20% rutile with a specific BET surface area of 50 m^2g^{-1} and primary particle size of 20 nm .Hombikat UV100 consist of 100% anatase with a specific BET-surface area >250 m^2g^{-1} and primary particle size of 5 nm.

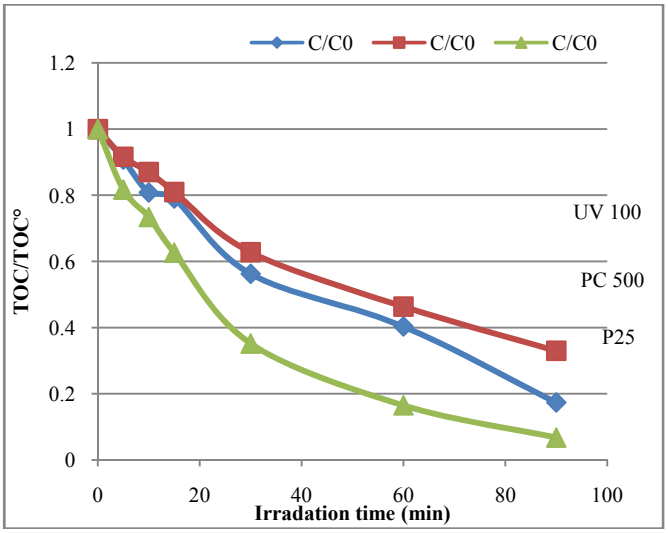

Fig. 3: Variation of TOC with Irradiation Time

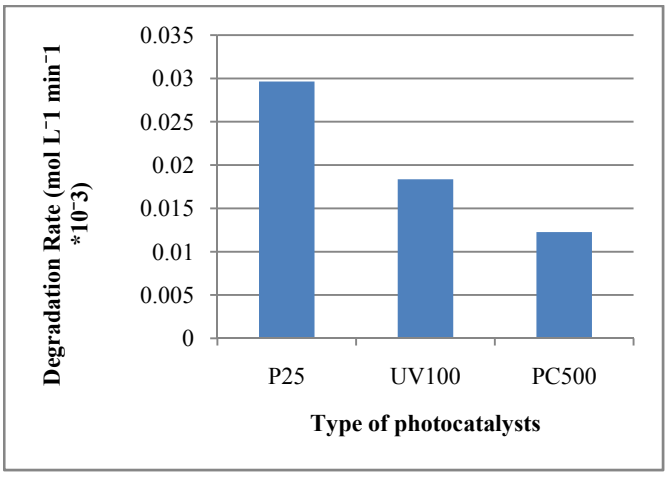

Fig. 4: Degradation rate of Barbituric acid in the presence of different photo -catalysts .

Experimental conditions : 1.0 m M Barbituric acid, V=250mL, photo-catalyst TiO_2 nano particiles Degussa P25 (1 g L^{-1}), Sachtleben Hombikat UV100 (1 g L^{-1}), Millennium Inorganic PC500 (1 g L^{-1}), ,Irradiation time =90 minutes

The photocatalyst PC500 has a BET-surface area of 287 m^2g-1 with 100% anatase and primary particle size of 5-10 nm . Hence according to particle size and BET surface area, the photocatalytic activity should be in the order of Hombikat

UV100> PC500 >Degussa P25. But the result of these studies indicates that the rate of degradation for Barbituric acid was found to be better in presence of Degussa P25 as compared with other two TiO_2 nanoparticles samples. The better photocatalytic activity of Degussa P25 for the degradation of large number of compounds has been reported earlier [14] which could be attributed on the basis of the fact that P25 being composed of small nano-crystallites of rutile being dispersed within an anatase matrix. The smaller band gap of rutile "catches" the photons, generating electron-hole pairs. The electron transfer, from the rutile conduction band to electron traps in anatase phase takes place. Recombination is thus inhibited allowing the hole to move to the surface of the particle and react.

Effect of Catalyst Dosage

For any practical application, the optimum catalyst concentration [$(TiO_2$ nanoparticles$)_{OPT}$] has to be found in order to avoid excess catalyst and ensure total absorption of efficient photons. The effect of catalyst concentration on the degradation kinetics of Barbituric acid was investigated employing different concentration of Degussa P25 varying from 0.5 – 3gL^{-1}. The degradation rate for Barbituric acid at different catalyst loadings are shown in Fig. 5

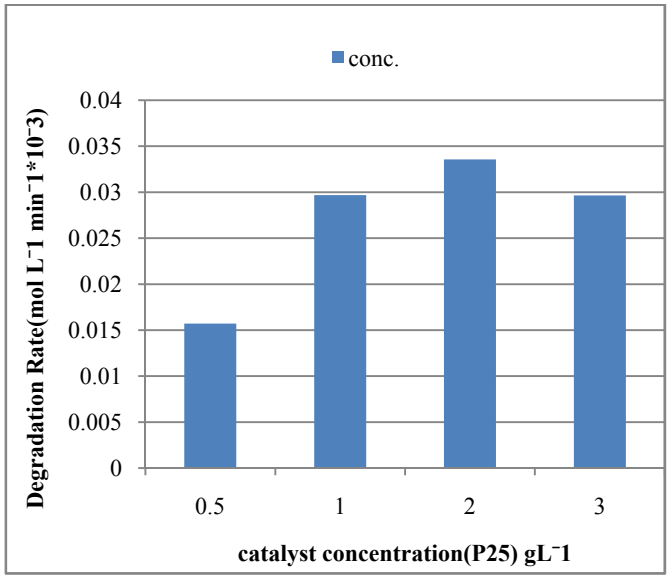

Fig. 5: Degradation rate of Barbituric acid in the presence of Degussa P25 at varying catalyst dosage

Experimental conditions : Drug solution concentration and volume (0.5,1,2and 3 $gL^{-}1$) ,Irradiation time =90 minutes

As expected, the rate of degradation for Barbituric acid in the presence of Degussa P25 was found to increase with increase in catalyst loading from 0.5 to 2gL^{-1} and further increase in catalyst loading lead to slight decrease in the degradation rate.

It is believed that both the number of solute molecules adsorbed as well as photons absorbed increases with increase in catalyst particles upto the optimum value. Beyond the optimum value, the increase in catalyst concentration may cause scattering and screening effects which reduces the specific activity of the catalyst. The reaction rate diminishes due to the excessive opacity of the solution, which prevents the catalyst farthest from being illuminated. At higher concentration, the catalyst particles may aggregate which leads to decrease in catalytic activity The degradation efficiency of this compound was found to be 94% with photocatalyst P25 having concentration of 2g L^{-1}.

Intermediate Products

An attempt was made to identify the intermediate products formed during the photo catalytic degradation of Barbituric acid in the presence of titanium dioxide using GC/MS analysis technique. Fig. 6 and 7 shows the results.

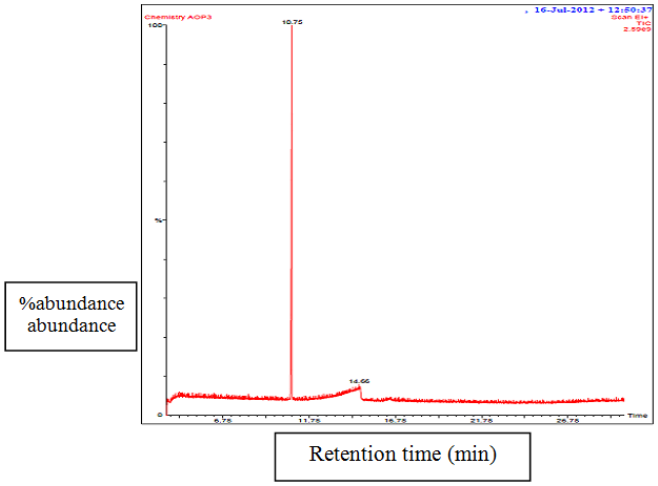

Fig. 6: Gas chromatogram of Barbituric acid of irradiated mixture (60 min)

Analysis of the irradiated mixture of Barbituric acid for 60 min indicate the formation of several products as shown The formation of products during the photo catalytic degradation of Barbituric acid can be 1,3 hydroxy-pyrimidine-2,4,6-trione,benzothiazole, 2,6-dimethyl,2,4(1h,3h)-pyrimidinedione, 5-hydroxy which can be compared with the mass fragmentation of NIST library.

From the above formation of the products it can be concluded that the parent compound was degraded.

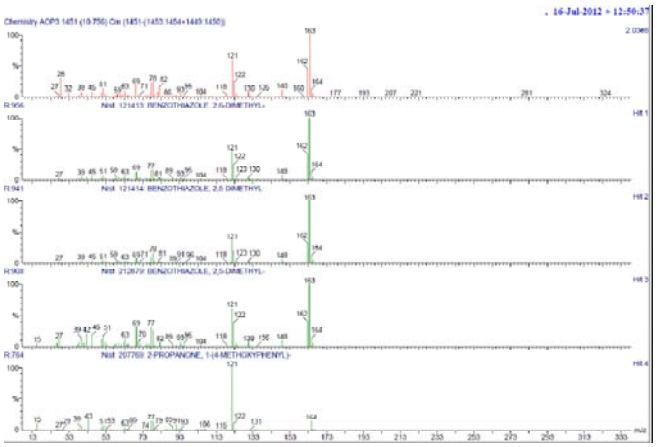

Fig. 7: Gas Chromotagraph showing the formation of Intermediate compounds

4. CONCLUSIONS

The sequential anaerobic - aerobic treatment of pharmaceutical based micropollutants namely, metronidazole and barbituric acid was found effective and the overall removal efficiencies were found as 92% and 91% respectively

The results of GC-MS analysis effluent showed the absence of the parental compounds and formation of intermediate products in the effluent of anaerobic reactor. However, they were absent in the effluent of aerobic reactor thereby indicating complete mineralization of micropollutants.

Photodegradation of barbituric acid was found effective The results of photodegradation studies indicate that TiO_2 nanoparticiles can efficiently catalyze the photo-degradation of Barbituric acid in the presence of light and oxygen. The photo - catalyst, TiO_2 nanoparticles Degussa P25 was found to be more efficient for the degradation as compared to other TiO_2 nanoparticles powders. GC MS results showed the absence of parental compounds.

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