Degradation of 2, 4 DCP by sequential biological–advanced oxidation process using UASB and UV/TiO$_2$/H$_2$O$_2$

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A B S T R A C T

Sequential biological–advanced oxidation process (AOP) was taken up in the present work for the degradation of 2, 4 dichlorophenol (2, 4 DCP). Up-flow anaerobic sludge blanket (UASB) reactor and UV/H$_2$O$_2$/TiO$_2$ system were used to carry out degradation of 2, 4 DCP. Anaerobic pretreatment dehalogenated the parent compound thereby producing lighter and less toxic compounds. UASB system was able to achieve 52.27% substrate removal and 73.35% COD removal at an HRT of 6 h. Though complete mineralization was not achieved in the UASB reactor but the end products of biodegradation were such that in AOP post treatment which was carried out for 1.5 h, the reaction preceded towards complete mineralization achieving 83.5% substrate removal and 90% COD removal. Results suggested to apply anaerobic treatment especially by UASB reactor for the treatment of recalcitrant substrate such as 2, 4 DCP prior to advanced oxidation for reducing the overall time of mineralization and also the overall cost.

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1. Introduction

Among the various organic wastes, chlorophenols are significantly harmful environmental pollutants due to their high toxicity, recalcitrance, bioaccumulation, and persistence in the environment. Chlorophenols have been widely used as bactericides, insecticides, herbicides, fungicides and wood preservative as well as intermediates of dyes [1]. The paper and pesticides industries are the main sources of wastewater with chlorophenols [2,3]. Chlorophenolic compounds are recalcitrant to biodegradation and therefore persistent in the environment. They are considered harmful for human health due to their potential carcinogenic, mutagenic activity and toxicity. Unfortunately, chlorophenols are highly toxic and tend to persist in the environment that is why they have been listed as priority pollutants by the US EPA and the EU [4].

Conventional processes to remove these pollutants involve physical, chemical and biological methods. Nevertheless, these techniques applied individually are generally limited and cannot degrade such recalcitrant organic matter completely [5,6]. Biological degradation can take place aerobically and/or anaerobically. The anaerobic mechanism offers advantage of less energy requirement, less biological sludge production, fewer nutrients required and methane production over aerobic mechanism [7]. For this reason, anaerobic treatment presently is accepted as a potential technology. One of the most notable developments in anaerobic treatment process technology was the up flow sludge blanket (UASB) reactor developed by Lettinga and his coworkers [7]. Atuanya et al. [8] showed the degradation of 2, 4 DCP by UASB reactor with aerobic sludge granules (ASG) reactor as a post treatment which gave a maximum of 95% COD removal after the post treatment step. Sponza and Ulukoy [9] showed the treatment of 2, 4 DCP in a sequential UASB and aerobic continuous stirred tank reactor at increasing organic loading rates which gave a maximum of 90% COD removal efficiency. Biological treatment methods are generally cheaper than physical or chemical treatment methods [10,11]. However, sometimes, the inherent toxicity of chlorophenols or of the intermediates produced during their degradation compromises the ability of these methods to completely mineralize in the wastewater. Therefore, biological treatment techniques, if used alone, have a serious limitation in treating non-biodegradable/toxic chemicals.

In recent years, several advanced oxidation processes (AOPs) such as electrochemical anodic oxidation [12,13], electro-Fenton oxidation [14,15], Fenton oxidation [16] and photochemical oxidation [17] have been proposed for the degradation of chlorophenols. There are many advantages of destructive technologies for the treatment of non-biodegradable pollutants. The AOPs generate free radicals, which act as strong oxidants to destroy the organic pollutants. In AOP, oxidant agents such as H$_2$O$_2$, O$_3$, TiO$_2$, UV and ultrasound, are used alone or in a combination [18–20].

Latest investigations on the degradation of organic pollutants are focused on the combination of biological and physical–chemical treatments. This saves a considerable amount of energy in comparison with what is needed to achieve the full mineralization of the pollutants by chemical oxidation [21]. Pedroza et al. [22] reported

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the degradation of generated chlorophenol from bleaching process during paper production by sequential biological–AOP using T. versicolor and UV/TiO$_2$/Ru$_x$Se$_y$ obtaining a 99% chlorophenol removal after 96 h and 20 min with a 97% reduction in chemical oxygen demand. On the other hand, Essam et al. [23,24] evaluated the degradation of a mixture of chlorophenols by sequential AOP–biological process using activated sludge and either UV, UV/TiO$_2$/H$_2$O$_2$, UV/TiO$_2$ or UV/H$_2$O$_2$ as oxidant agent.

Literature review revealed that though the sequential biological and advanced oxidation techniques have been studied, there is no available literature on using UASB as the pretreatment step followed by AOP (UV/H$_2$O$_2$/TiO$_2$) process. In this work the sequential biological degradation–advanced oxidation process for 2, 4-dichlorophenol (2, 4 DCP) was evaluated. Biological degradation was carried out using laboratory scale UASB process and AOP in a batch recycle photochemical reactor.

2. Material and methods

2, 4 Dichlorophenol was purchased from Merck, India. Hydrogen peroxide solution (30% w/v) in stable form was purchased from Finar Reagents. Photocatalyst (TiO$_2$, anatase grade) and all other chemicals obtained were of reagent grade quality and were used as received. Solutions were prepared using doubly distilled, deionized water.

2.1. Experimental setup

The schematic diagram of the experimental setup of UASB reactor for carrying out biodegradation is shown in Fig. 1. A 34.7 L bench scale UASB reactor was operated to investigate the performance of sequential biological and advanced oxidation process. The total length, height and breadth of the reactor were 17 cm, 120 cm, and 17 cm respectively. Gas was collected from the headspace on the top of the reactor and measured by the liquid displacement method.

In the UASB reactor, the influent is distributed uniformly over the bottom of the reactor and then following an up flow path; it rises through a thick layer of anaerobic sludge, from where it is withdrawn at the top of the reactor. Thus, the contact between the influent organic material and the sludge mass in the reactor is automatically guaranteed. In order to maintain a large sludge mass, the UASB reactor has a built-in phase separator, where the dispersed solids are retained by settling, so that an effluent virtually free from suspended solids can be discharged. The retained sludge particles will end up sliding back from the settler compartment into the digester compartment and accumulate there, thus contributing to the maintenance of a large sludge mass in the reactor. Excess sludge is withdrawn in a periodic manner by ports. High-rate UASB reactors are becoming increasingly popular for the treatment of various types of wastewaters because of their low initial and operational costs, smaller space requirements, high organic removal efficiency and low sludge production, combined with a net energy benefit through the production of biogas.

Fig. 2 shows the experimental setup used for carrying out the advanced oxidation process. The reactor was cylindrical with 250 mL volume and was made from quartz glass. Irradiation was achieved by using UV lamp of 125 W which was immersed in the glass tube. The UV lamp was equipped with a cooling water space which was placed in the reactor vessel. The reaction chamber was filled with the reaction mixture, which was placed between the reactor walls and UV lamp system. Mixing was accomplished using air bubbler to keep the photocatalyst in suspension.

2.2. Biodegradation procedure

Biological degradation of 2, 4 DCP was carried out in a laboratory scale UASB reactor which was operated almost five months continuously with and without co-substrate. The synthetic wastewater was prepared as per Sheldon et al. [25] (COD 0.25 ± 0.5 g/L, glucose 0.25 ± 0.5 g/L, 2, 4DCP 0.05–0.1 g/L, (NH$_4$)$_2$SO$_4$, 0.3 g/L, NaHCO$_3$ 1.5 g/L, K$_2$HPO$_4$ 0.2 g/L, KH$_2$PO$_4$ 0.2 g/L, and yeast extract 0.5 g/L, pH 7.0 ± 7.6). Synthetic wastewater was prepared daily and used immediately to avoid decomposition of the feed. 2, 4 DCP was dissolved in 5 mL of 0.2 M NaOH before adding into the influent container. UASB effluent was fed into AOP setup for further degradation. Samples were taken daily and analyzed immediately to avoid further reaction. Concentration changes of 2, 4 DCP were determined by a UV–Vis spectrophotometer [26]. Samples at different time intervals were also analyzed to determine dechlorination efficiencies [26]. COD analysis was carried out by a UV–Vis spectrophotometer (DR 5000 HACH Co., USA) as per APHA [26].
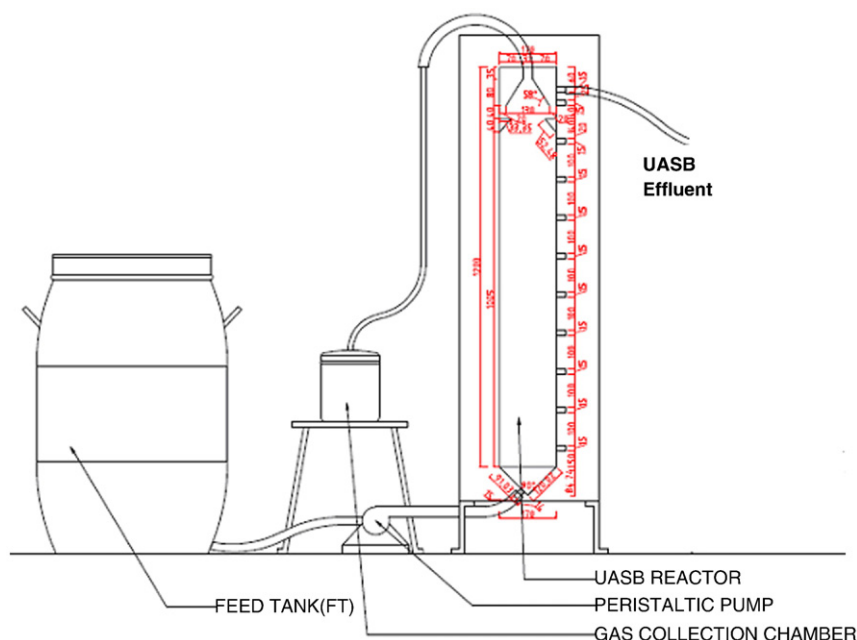

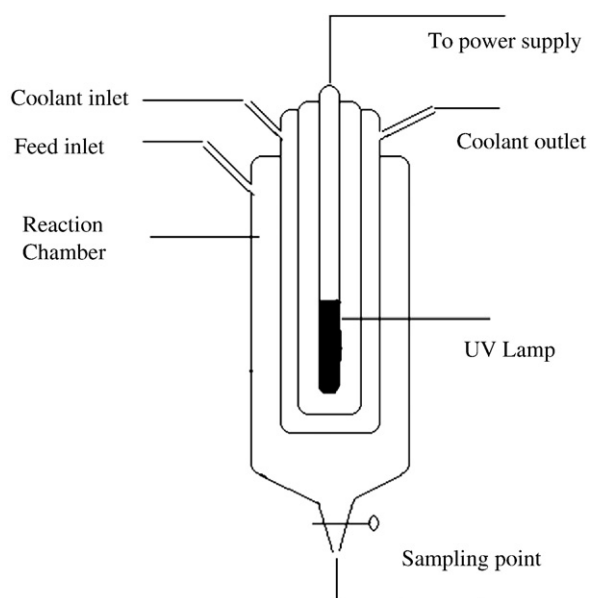**Fig. 1.** UASB reactor setup used in the experimentation.

Fig. 2. AOP unit used in the experimentation.

2.3. Advanced oxidation process procedure

Advanced oxidation process ($UV/H_2O_2/TiO_2$) was utilized for further treatment of anaerobically pretreated waste by taking optimum values of parameters i.e.100 mL/L H_2O_2, 1 g/L TiO_2, pH 4 and 90 min of irradiation time. For each experiment, TiO_2 was added to the effluent from UASB and was kept for stirring for 30 min so that equilibrium adsorption is achieved. Hydrogen peroxide was added to the reaction mixture just before starting the reactor. 250 mL of the feed mixture was fed into the reactor. Air was bubbled into the solution throughout the experiment to keep the photocatalyst in suspension and also as a source of oxygen for effective degradation.

3. Results

3.1. 2, 4 DCP degradation by UASB reactor

The degradation of 2, 4 DCP was carried out in UASB reactor. Phase 1 to phase 5 were carried out to check the performance of UASB reactor with and without glucose as a co-substrate. Final values were taken considering stable conditions of the reactor at different days for different phases. In phase 1 (HRT = 24 h), 100% (1000 mg/L) glucose was used in the feed, considering primary phase (start-up) of the reactor for which easily biodegradable substrate was provided to the anaerobic microorganisms, OLR of the system was 1.003 kg COD/m^3 day. 45.2% COD removal was found in this phase. During phase 2, 10 mg/L of 2, 4 DCP was added with 90% of initial glucose concentration (OLR = 1.023 kg COD/m^3 day) for slowly acclimatizing the reactor, COD reduction was found 43.1%. Minor change was found in the performance of the reactor after applying 2, 4 DCP concentration. This shows the adoption of 2, 4 DCP by the microorganisms in the presence of co-substrate. After reaching steady state, HRT was further changed to 8 h from 24 h (OLR = 3.06 kg COD/m^3 day). On increasing OLR, COD removal increases (47.7%) because of increasing concentration of glucose in the system.

Further, 30 mg/L 2, 4 DCP was added with 70% of glucose in the feed (OLR = 2.25 kg COD/m^3 day). Due to reduction of OLR, COD removal was also decreased up to 43.4%. Again in phase 4, 70 mg/L of 2, 4 DCP was further added with 30% of glucose in the feed (OLR = 1.18 kg COD/m^3 day). Sudden increase in the concentration of 2, 4 DCP caused poor COD removal efficiency (only 16.1%) of the reactor, showed negative effects and impaired the functioning of the

microorganisms. Due to the poor performance of UASB reactor, its OLR was further increased (1.57 kg COD/m^3 day) by changing HRT of 6 h from 8 h without waiting its stable condition. Reactor was monitored up to its stable conditions. Its percentage removal was found increased (from 16.1% to 75.3%), again showing the adoption of 2, 4, DCP by microorganism for long time with co-substrate. Finally, reactor was operated with 100 mg/L of 2, 4 DCP (without glucose) with OLR of 0.482 kg COD/m^3 day. Sudden decrease in COD removal was found and finally it was stabilized at 30.8 mg/L (74.4% removal) concentration. UASB reactors are considered to be high rate reactors; finally reactor was set at HRT of 6 h and its effluent was used for advanced oxidation process. A summary of all the phases is given in Table 1. In all phases reactor performance was also monitored by dissolved oxygen, pH and sludge characteristic which was found satisfactory.

3.2. 2, 4 DCP removal by combined UASB–AOP process

Anaerobically pretreated wastewater was further sent to advanced oxidation process ($UV/H_2O_2/TiO_2$) in order to check the efficiency of the combined process. At this stage concentration of 2, 4 DCP was also analyzed along with COD and chloride ion concentrations in the effluents. Within 90 min of the treatment of $UV/H_2O_2/TiO_2$ system, COD of the anaerobic effluent was further reduced up to 11.5 mg/L from 30.8 mg/L with the corresponding concentration of 2,4 DCP from 47.23 mg/L to 16.3 mg/L. It is observed that the combined system had higher efficiency than UASB and AOP alone. Fig. 3 is plotted for showing the performance and comparison among UASB, AOP, and combined system for the percentage removal of 2, 4 DCP and COD. Only AOP data ($UV/H_2O_2/TiO_2$) is taken from Essam et al. [24] for comparing individual systems. When 2,4 DCP removal is compared among the different systems under consideration, it is observed that for 100% removal of 50 mg/L substrate concentration, 40 h was needed when only AOP was employed [24]. While in the combined process in the present case, only 7.5 h (6 h + 1.5 h) was required for about 83.5% removal for 100 mg/L substrate concentration which is twice that used in AOP system. When COD removal is compared, it is seen that the combined process gave about 90% removal which is much higher than the individual systems under consideration. Comparing all the systems, it can be observed that the combined process in the present work, gives more efficient results in terms of both DCP and COD removals; it is also an efficient process from power consumption point of view.

Fig. 4 represents the chloride ion generation from the combined system. It is clear that the effluent from UASB already contained loose chloride ions which indicate that dechlorination had already started in the anaerobic system prior to the advanced oxidation. Further dechlorination continues in the advanced system which reaches to its maximum of about 100 mg/L in 90 min of irradiation time.

4. Discussion

Anaerobic treatment method scores over the aerobic due to the fact that when the latter is put into use for the treatment of chlorophenol,

Table 1
Operating conditions for UASB reactor during the stabilizing phases.

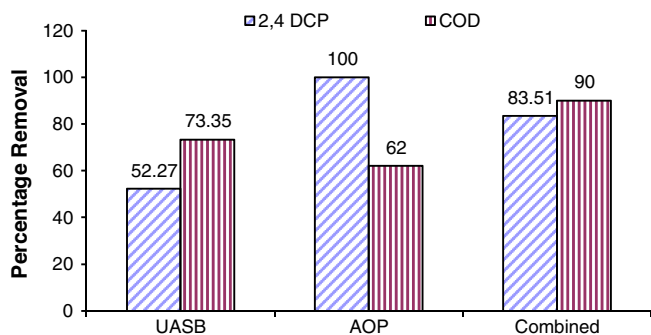| HRT (h)	Phases	OLR (kg COD/m^3 day)	COD (mg/L) Feed	COD (mg/L) UASB effluent	% COD removal in UASBR
24	Phase 1	1.003	963.8	528.5	45.20
	Phase 2	1.023	1006.7	572.4	43.14
8	Phase 2	3.06	1008.4	527.8	47.66
	Phase 3	2.25	735.7	416.4	43.40
	Phase 4	1.18	392.8	329.5	16.12
6	Phase 4	1.57	394.6	97.3	75.34
	Phase 5	0.482	120.2	30.76	74.41

Fig. 3. Percentage removal of 2, 4 DCP and COD in UASB, AOP [24] and in combined system.

Table 2
Comparison of present work with previously published works.

System	Substrate	AOP irradiation time	Degree of degradation (%)	Reference
O_3 — AS Non acclimated sludge	2, 4 DCP (100 mg/L)	–	68 (TOC)	[38]
Acclimated to phenol sludge			82 (TOC)	
UV — AS	4 CP (50 mg/L)	40 h	84 (COD)	[23]
	2, 4 DCP (50 mg/L)		82 (COD)	
	2, 4, 6-TCP (50 mg/L)		81 (COD)	
	PCP (50 mg/L)		76 (COD)	
$UV/H_2O_2/TiO_2$ — AS	2, 4 DCP (50 mg/L)	40 h	87 (COD)	[24]
	4 CP + 2, 4 DCP + 2, 4, 6-TCP + PCP (50 mg/L each)		88 (COD)	
UV/TiO_2 — AS	POH (100 mg/L)	60 h	81 (COD)	[24]
	PNP (50 mg/L)		83 (COD)	
UV/TiO_2 — AS	4 CP (400 mg/L)	5 h	100 (Substrate)	[39]
White rot fungus — UV/TiO_2	PCP (15 mg/L)	3 h	94.5 (Substrate)	[37]
	2CP (15 mg/L)		91.1 (Substrate)	
	DCP (15 mg/L)		82.8 (Substrate)	
	TCP (15 mg/L)		79.3 (Substrate)	
UASB — $UV/H_2O_2/TiO_2$	2, 4 DCP (100 mg/L)	90 min	83.5 (Substrate) 90 (COD)	Present work

ring cleavage does not essentially occur after dechlorination. This means that dechlorination is not the first step and thus the products formed after aerobic treatment are mostly chlorinated diverse intermediates of varying toxicity [27]. In aerobic conditions incomplete oxidation of chlorophenol results in the formation of substituted catechols and other refractory intermediates [28].

The purpose of employing UASB treatment for carrying out biological degradation was that under anaerobic conditions, the degradation of chlorophenol compounds is initiated by reductive dechlorination steps. The aromatic ring is thus totally dechlorinated prior to ring cleavage [29,30]. Boyd and Shelton [31] stated that the first two steps in the degradation of 2, 4 DCP involve reductive dechlorination of phenol. The toxicity of dechlorinated products is usually lesser [32]. Krumme and Boyd [33] showed that an anaerobic up-flow bioreactor alone was able to reductively dehalogenate and partially mineralize monochlorophenols and to a lesser extent, more highly substituted chlorophenols. Atuanya and Chakrabarti [34,35] while studying the 2, 4 DCP removal in UASB reactor observed that COD removals were relatively less than the corresponding 2, 4 DCP removal and concluded that this indicated incomplete metabolization of substrate.

Anaerobic biodegradation of 2, 4 DCP takes place via formation of 4-chlorophenol, phenol, benzoate, acetate, carbon dioxide and methane [36]. The higher COD removal in the sequential system can be attributed to the fact that lighter and less toxic compounds are formed in the UASB reactor which when fed to the AOP system proceeds towards complete mineralization thereby giving COD removal of 90%.

Table 2 presents the comparison between the present work and previously done works on the sequential systems of different combinations of biological and AOP process. It can be seen from the data that AOP as a pretreatment to biological is less efficient in terms of substrate removal, COD removal and energy efficiency. Gonzalez
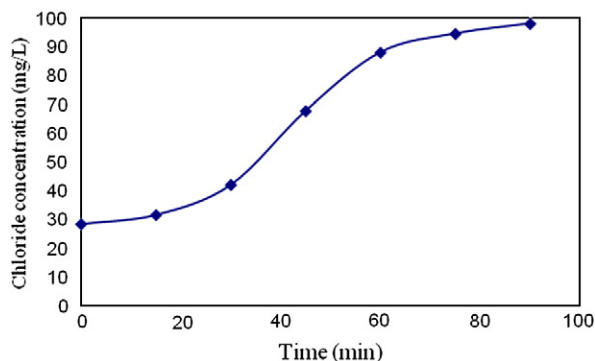
et al. [37] employed sequential system with biological (white rot fungus) as a pretreatment to UV/TiO_2 for 15 mg/L 2, 4 DCP and obtained 82.8% substrate removal. In the present work also biological (UASB) was employed as a pretreatment to $UV/H_2O_2/TiO_2$ system and very effective results are obtained in terms of percent substrate removal. It can be seen from Table 2 that in all the stated previous works the time period of irradiation is much higher than that in the present case. Also, in none of the cases COD removal of 90% was achieved with such higher substrate concentration of 100 mg/L as in the present work.

Essam et al. [24] performed AOP via $UV/H_2O_2/TiO_2$ for 40 h prior to biological treatment at 2, 4 DCP concentration of 50 mg/L and achieved 87% COD removal. When the aforementioned work is compared with the present work, it is seen that a higher 2, 4 DCP concentration (100 mg/L) using UASB as pre-treatment to AOP reduces the time duration of running AOP significantly (only 90 min) which in turn lowers the power consumption by the system. Also a COD removal of 90% is achieved in the present work which is higher than the previously performed work.

Overall, the UASB–AOP emerges out to be the most efficient one if compared with other reported combinations for phenolic substrates. In most of the works the time period of AOP is quite high (3 h–60 h) as compared to present system where the illumination was done only for 90 min. Also, if 100% substrate removal is to be considered in the present work, the time period of AOP run comes to about 1.8 h thereby making the UASB–AOP run time of 7.8 h only which is much lesser than the other systems.

5. Conclusions

The high cost of advanced processes and low efficiency of biological processes make the use of combination of both the processes a viable option available. The first step of dechlorination initiated in the UASB system is the key factor for the efficient performance of the sequential UASB–AOP process. The sequential process scores over the individual UASB and AOP in terms of both substrate and COD removal. The present sequential system gives much higher substrate and COD removal for higher substrate concentration in lesser time as compared to the AOP when employed

Fig. 4. Chloride ion generation from the combined system.

alone. Also, the sequential system emerges out to be an energy efficient process.

Acknowledgement

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