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Biomineralization of 2-Chlorophenol in an UASB Reactor with Starch Water as co-substrate

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Abstract: **Chlorophenol compounds are environmental pollutants that are both anthropogenic and xenobiotics. Some of these chemicals are carcinogenic and toxic to a number biochemical processes. The present research aims at 2-CP degradation in a UASB reactor with starch water as co-substrate. Synthetic 2-CP and starch water were given as feed to UASB reactor at an HRT of 24 h. The performance of the reactor was remarkably stable and efficient during 2-CP additions at a range of 5-800 mgL^{-1}. The reduction of 2-CP and COD was found to be 100-67.9 and 98.1-59.3% respectively. The optimum 2-CP and COD removal efficiencies were 97.5 and 90.4%. The VFA concentrations of the reactor were lesser than 250 mgL^{-1}. The biogas production at 600 mgL^{-1} of 2-CP was 20 Ld^{-1}.**

Keywords: 2- Chlorophenol, UASB, Starch, Mixing Ratio, Two-Phase

I. INTRODUCTION

Ecological devastation has been attributed to the presence of resistant synthetic organic compounds in the environment. Some of these compounds are important, such as the organochloride compounds released into the environment in increasing amounts by their application in a variety of activities. Chlorophenols are chloroaromatic and commonly used as biocides, flame retardants, wood treatment agents, solvents and in synthetic chemistry [1]. They are toxic to a wide range of organisms and are common contaminants in water and soil. Misuse, accidental spillage and improper disposal of these toxic compounds have resulted in intensive pollution [2], which has detrimental biological effects, including chronic toxicity, mutagenicity, and carcinogenicity. Among various chlorophenols, 2-chlorophenol (2-CP) is included in the list of priority pollutants [3] because of their toxicity and suspected carcinogenicity and poses a significant impact on water and soil environment. As a result, proper treatment and disposal of this type of waste are required.

Numerous expensive physico-chemical treatment methods are in practice. Conversely, biological treatment methods are relatively inexpensive and result in complete mineralization [4, 5, 6, and 7] or into less resistant or toxic compounds. Among the biological processes, upflow anaerobic sludge blanket (UASB) reactor has been widely used to treat a variety of industrial and domestic wastewaters all over the world. One common feature offered by all the high-rate processes is its ability to provide high solid retention time (SRT) in relation to HRT. The granular sludge with good settling velocities and mechanical strength is suitable for the treatment of wastewater containing xenobiotic and recalcitrant compounds, and also it can be used for the treatment of wastewater previously considered unsuitable for anaerobic treatment [8]. This study aims to degrade 2-Chlorophenol using starch water as co-substrate in a biphasic bench scale UASB reactor.

II. MATERIALS AND METHODS

A. Biomass

The granular sludge with unknown microorganisms used in this experiment was procured from the anaerobic digester treating sago effluent at M/s Sriman Narayana SAGO factory, Namagiripet, Tamilnadu, India. Before loading the reactor, granular sludge was clearly washed, filtered through a fine mesh ASTM 16 to remove all floating and suspended contents. The volatile suspended solids content of the sludge was estimated as per the standard methods and was found to be 45, 000 mgL^{-1} [9].

B. Preparation of 2-cp and tapioca starch water

The synthetic 2-CP wastewater was prepared by dissolving 1 g of 2-CP in one litre of warm distilled water as a stock solution, from this stock solution the required concentration of 2-CP was taken for the experiments. The synthetic starch water was prepared by dissolving tapioca starch powder; 1 g of starch powder was dissolved in 1 L of water to give a COD concentration of about 2200 mgL^{-1}. The dissolved starch water was pre-acidified before being fed into the reactor to avoid the settling of starch particles at the bottom of the influent container. Since the simulated 2-CP and starch water are deficient in available nutrients, ammonium chloride, Ferric chloride, calcium chloride and potassium dihydrogen orthophosphate were added to adjust the C:N:P ratio to 100:5:1. This is a proprietary nutrient mixture available for biological treatment systems [10].

C. Experimental setup

A bench-scale bi-phasic hybrid up-flow anaerobic sludge blanket reactor system (Fig. 1) consisting of 4 L acidogenic and 16 L methanogenic reactors were used in this study. The reactors were installed at different levels to maintain sufficient hydraulic flow, to achieve proper fluidization and mixing of sludge granules inside the reactors. The Gas Liquid Solid Separator (GLSS) was installed at the top of the UASB reactor, which effectively separates the treated effluent, sludge granules, and biogas.

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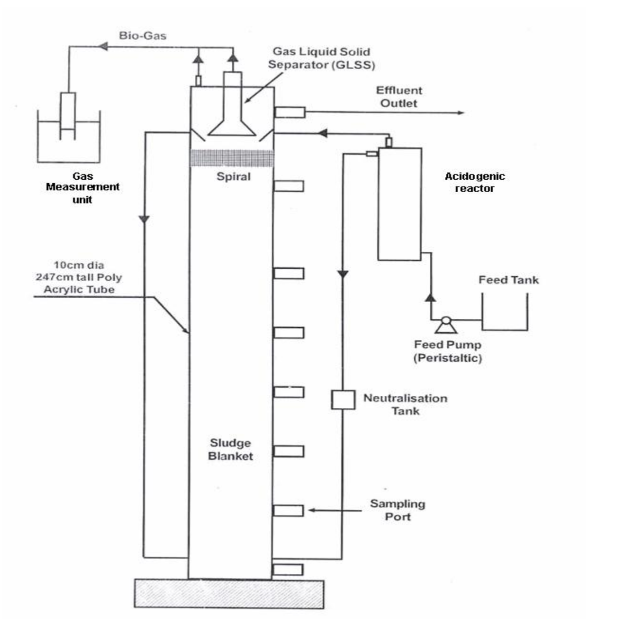

Fig. 1. Schematic representation of experimental setup

In addition to GLSS arrangement, PVC spirals (size 26 mm, surface area 500 m2/m3 and void ratio 87%) were also packed for a height of 15 cm (located in between the reactor height of 1.91–2.06 m level). These spirals will retain the biomass as well as gives a polishing effect to the effluent. The sludge granules trapped in GLSS and the packed media will return to the reactor, as soon as the gas entrapped inside the granules was released. Biogas generated was measured by water displacement method. After stabilizing the reactor, studies were conducted under the steady state conditions. The pH of the acidogenic reactor outlet was adjusted to 6.0 by the addition of sodium bicarbonate, whereas that of the methanogenic phase was set at 7.0. A variable-speed peristaltic pump was used. The reactor was operated at room temperature (28±5°C) at various concentration of 2-Chlorophenol with starch water at various Organic Loading Rate (OLR). Since the two phases of the reactor were designed on the volumetric ratio of 1:4, the acidogenic and methanogenic reactors were operated at a Hydraulic Retention Time (HRT) of 24 h.

D. Analytical methods

All analyses were carried out in accordance with Standard Methods [9]. 2-CP, gas production, COD, pH, VFA, and alkalinity were monitored daily; Suspended solids (SS), Volatile Suspended Solids (VSS) and TSS were recorded weekly. COD was measured using the open reflux method and gas production using water displacement method. 2-CP concentrations were determined using 4-amino antipyrine method and colour intensity was measured by a UV-vis spectrophotometer (Hitachi U-2001). 2-CP and its removal were measured in terms of absorbance at a wavelength of 500 nm, in which the colour intensity absorbed maximally; (λmax) and the absorbance values were proportional to 2-CP concentration.

III. RESULTS AND DISCUSSION

A. Removal of 2-Cp

At the end of 60 d of start-up period, the reactor was fed with a mixing ratio of 20% 2-Chlorophenol and 80% of starch initially, the concentrations of 2-Chlorophenol were increased as 5, 25, 50, 100, 200, 300, 400, 600 and 800 mgL^{-1}. Figure 2 shows the concentration of 2-CP in feed and the outlet of the reactor. Fig. 3 shows the removal of 2-CP at various concentrations throughout the acclimatization period of 110 d. At the initial concentration of 2-Chlorophenol, the removal efficiency was 100% up to concentrations of 300 mgL^{-1}, a further increase in the 2-Chlorophenol concentration viz. 400, 600 and 800 mgL^{-1} the removal efficiency gets decreased viz. 99.5, 97.5 and 67.9 respectively. The optimum removal efficiency of 97.5% 2-CP was achieved at 600 mgL^{-1}. From the Fig. 3, it is apparent that as the concentration of the 2-CP increases the removal efficiencies decreased. This indicates that anaerobic mixed bacterium was able to withstand about 600 mgL^{-1} of 2-CP. Majumder and Gupta (2007) [3] reported that the maximum removal of 96.5% 2-CP was achieved with sodium acetate as co-substrate using 12.1 L UASB reactor.

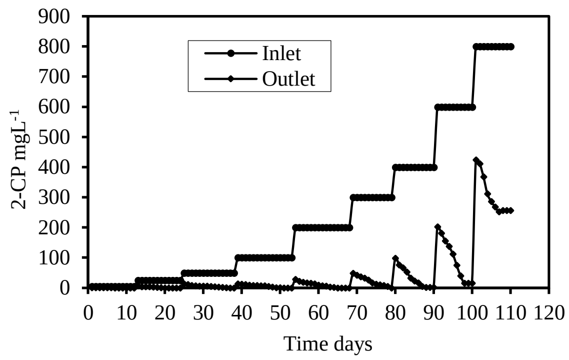

Fig. 2. Concentration of 2-CP at inlet and outlet of the reactor

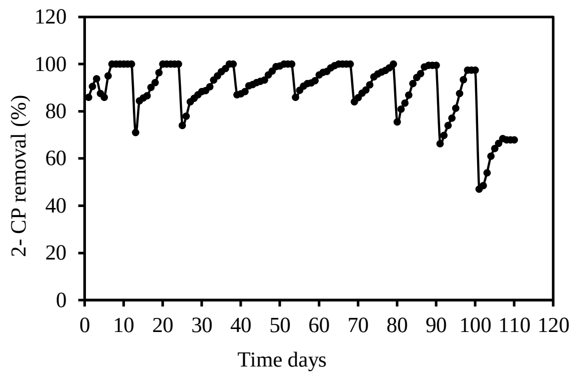

Fig. 3. Removal (%) of 2-CP at various concentrations

B. COD removal

The COD of the inlet and outlet of UASB reactor is shown in figure 4. The inlet contains the combined wastewater of synthetic starch 80 and 20% 2-CP (at various concentrations viz. 5, 25, 50, 100, 200, 300, 400, 600 and 800). The inlet and outlet COD of the reactor was in the range of 2120-2560 and 2000-40 mgL^{-1} respectively, for various concentration of 2-CP. From the Fig. 4, it is clear that the increase in 2 chlorophenol concentration increases the COD of the influent. Fig. 5 shows the COD removal efficiency at a various concentration of 2-CP. From the Figure 5, it is evident that the COD removal efficiency has decreased viz., 98.1, 96.4, 94.7, 93.7, 93.2, 92.0, 91.9, 90.4 and 59.4 as the concentration of 2-CP increased as 5, 25, 50, 100, 200, 300, 400, 600 and 800 mgL^{-1} respectively. Optimum removal of COD (90.4%) was achieved at 600 mgL^{-1}. As the concentration of the 2-CP increases the organic loading rate and the toxicity also increased and this may be the reason for the decrease in the COD removal. Shen et al., (2005) [1] reported that the COD removal was about 90.4% with initial pentachlorophenol concentration of 100 mgL^{-1} using UASB reactor. Pokhrel and Viraraghavan (2004) [11] reported that the optimum removal of COD was 90.4% for chlorophenols found in Kraft bleaching wastewater using UASB reactor.

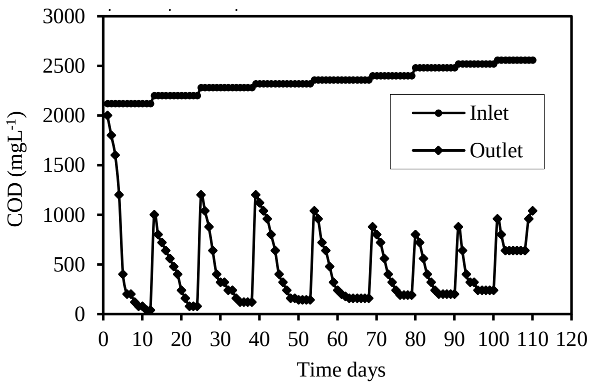

Fig. 4. COD at various concentration of 2-CP

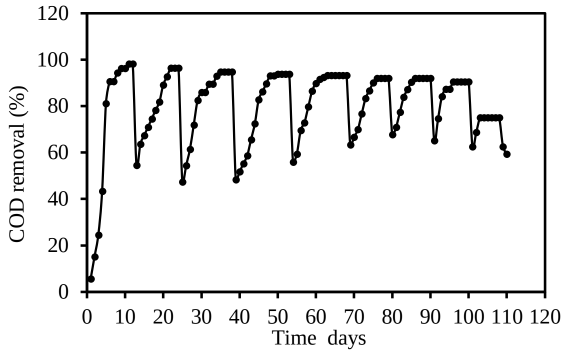

Fig. 5. Removal of COD at various concentration of 2-CP

C. pH

The pH of inlet and outlet for various concentrations of 2-CP with 80% of starch wastewater as co-substrate were shown in Figure 6. Inlet pH was in the range of 6.2-7.6 and the outlet pH the reactor was in the range of 7.4-7.98 for various concentration of 2-CP. When the pH is less than 6.0 consumption of fatty acid is strongly inhibited and when pH is greater than 8.0, bacterial growth will be limited by low concentrations of non-ionised fatty acid [12]. The generally accepted pH range for optimal efficiency was 6.5-7.6 [13]. It should be noted that for an optimum operational performance or optimum anaerobic treatment pH should be in the range of $6.5 < pH < 8.2$ [14, 15]. The pH is the integral expression of the acid based condition of any anaerobic treatment process as well as an intrinsic index of the balance between the two of the important microbial groups [16] Compared to influent pH (5.7-7.4), the outlet pH (7.5-8.2) was higher. The same results were obtained and reported by Venkatamohan et al. (2005) [17].

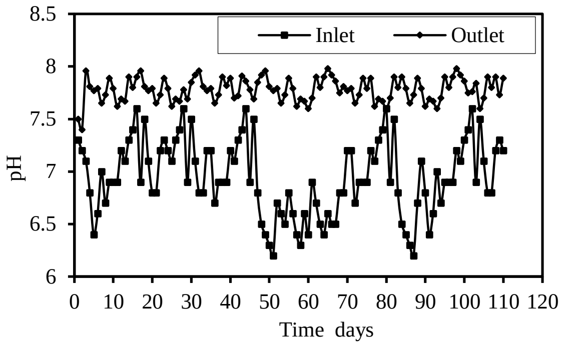

Fig. 6. Variation of pH at various concentration of 2-CP

D. Volatile fatty acid (VFA)

The VFA of the reactor under the various concentration of 2-CP are shown in Fig. 7. The concentration of VFA within UASB reactor was in the range of 12-124 mgL^{-1} at various concentration of 2-CP. Transformation of VFA to CO_2 and methane (CH_4) caused the generation of alkalinity in the anaerobic microbial process. The VFA concentration was low till 600 mgL^{-1} of 2-CP concentration, whereas the VFA increased to the maximum of 124 mgL^{-1} at 800 mgL^{-1} which indicates that the stability of the reactor gets decreased. Speece (1996) [18] also reported that for a stable operation of a reactor the VFA concentration should be less than the critical limits (250 mgL^{-1} as acetic acid).

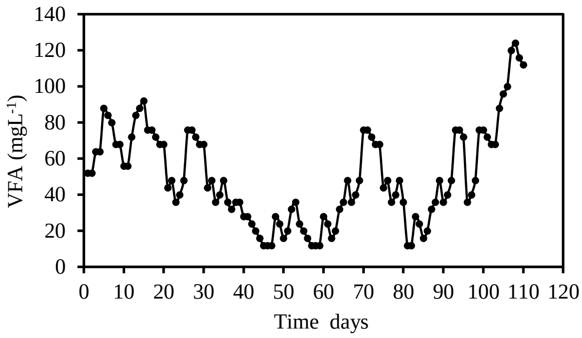

Fig. 7. VFA of the reactor at various concentration of 2-CP

E. Biogas

Fig. 8 shows biogas generation at different concentration of 20% 2-CP and 80% starch wastewater. The biogas production increases as the COD removal efficiencies increases for various concentration of 2-CP and decreased as the concentration of 2-CP increases. The maximum biogas production achieved at various 2-CP concentrations of 5, 25, 50, 100, 200, 300, 400, 600 and 800 mgL^{-1} were 42, 38, 34, 27, 24, 22, 20 and 12 Ld^{-1} respectively. Montenegro et al. (2001) [19] reported the similar type of results as the biogas production decreases with increases in the concentration of chlorophenol.

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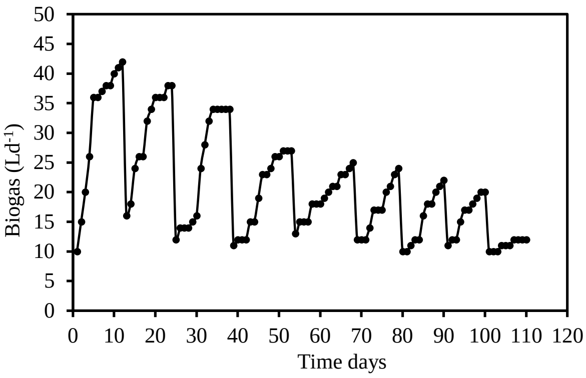

Fig. 8. Biogas production at various concentration of 2-CP

IV. CONCLUSIONS

The principal mechanism of 2-CP removal in this study is biodegradation. The results of this study showed that 2-CP wastewater could be treated effectively by UASB reactor. This study proved that even at higher concentration (600 mgL^{-1}) of 2-CP, the removal efficiencies of 2-CP and COD are about 97.5 and 90.4% respectively. The VFA concentration of the effluent was lesser than 250 mgL^{-1} indicating that the reactor was stable. The maximum biogas production achieved was about 42 Ld^{-1}. This study concludes that biphasic UASB reactor could be a very feasible alternative, eco-friendly and sustainable treatment system for 2-CP wastewater along with starch water as a co-substrate, producing very less organic sludge.

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