IMPACT OF HYDRAULIC RETENTION TIME IN 2-CHLOROPHENOL DEGRADATION WITH STARCH AS CO-SUBSTRATE IN AN UASB REACTOR

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Abstract: The effect of hydraulic retention time in 2- chlorophenol (2-CP) degradation in a UASB reactor with starch water as co-substrate was explored. The degradation extent of 2-CP at various hydraulic retention time (HRT) viz. 36, 30, 24, 18 and 12 h was monitored at optimized concentration of 600 mg/L.The 2-CP removal efficiency in the reactor was ranging from 80.8 to 97.7 % for various HRT and maximum removal efficiency of 97.7 % was achieved at HRT of 18 h. COD removal efficiency was in the range of 77.8 to 93.6 % in the reactor and maximum COD removal efficiency of 93.6 % was achieved at 18 h HRT. Maximum biogas production of 28 L/d was achieved at 12 h of HRT.

Index Terms - 2-Chlorophenol degradation, HRT, Co-substrate, UASBR

1. Introduction

Chlorophenols (CP) has been widely utilized as wood preservative, antifungal agent, pesticide, and herbicide. (Haggblom and Young, 1990), found in discharges of many industries including petrochemical, oil refinery, plastics, coke oven, pesticides, dyes, pulp and insulating materials (Sponza and Cigal, 2009). The toxic properties of CP are environmentally significant and acts on variety of organisms as a potent inhibitor of oxidative phosphorylation. Based on the toxicological effects of chlorophenolic compounds and carcinogenic responses in various organisms, it has become the target of several investigations to be focused on possible treatment methods (Ye and Shen, 2004; Kaoaet al., 2004). Various treatment such as physio-chemical and biological methods are available. Physio-chemical treatment methods are costlier and require further treatment. Biological treatment can be affected by aerobic and anaerobic microorganisms. Anaerobic processes are reported to be more suitable for the treatment of phenolic wastes (Neilson, 1990; Sivarajan et al., 2017), among which upflow anaerobic sludge blanket (UASB) reactor is more resistant to toxic compounds. Advancement in anaerobic process is dependent on various factors of which HRT affect the rate of methanogenesis in anaerobic microbial conversion processes, as it establishes the extent of time available for biomass contact and subsequent conversion of the organic material to gas and it has a high influence on the chemical oxygen demand (COD) removal (Senthilkumar et al. 2010). Very long HRT may allow dispersed bacterial growth, maintain high bio-solids content (Shen et al., 2005) and very short HRT could cause wash out of dispersed bacterial matter and promote granulation (Lettinga et al., 1983).Numerous studies have been carried out to investigate the influence of various factors such as carbon source, OLR, pH and shock loadings in degradation of 2-CP but very few have reported on the influence of HRT on degradation of 2-chlorophenols with starch as co-substrate in an UASB reactor. The main objective of the present study is to study the fate and effect of HRT on 2-chlorophenol degradation with starch as co substrate in a bi-phasic UASB reactor.

2. Methods

Experimental system

To study the effect of HRT in 2- chlorophenol degradation, a hybrid UASB reactor was fabricated using plexi-glass with inlet/outlet ports made of brass. Figure1 shows the experimental setup of UASB reactor system. The process contained a raw feed storage tank, feed pump, acidogenic reactor, methanogenic reactor, and gas measurement assembly. The acidogenic and methanogenic reactors were made with 1:4 volume ratios. The Gas Liquid Solid Separator (GLSS) effectively separates the treated effluent, sludge granules, biogas and enables the separated sludge to slide back into the digester compartment. The gas was collected in the outer inverted cone and measured by water displacement method. Anaerobic sludge with VSS concentration of 45000mg/L obtained from a digester treating sago effluent was used as seed for the reactor.

Experimental procedure

The reactor was fed with synthetic starch water at an OLR of 2.2 kg COD/m³d at 24 h HRT and pH of 7.2 with up flow velocity of 0.08 m/h during the start-up period. After stabilization, the reactor was operated with synthetic starch and 2-CP at an optimized mixing ratio of 80:20. In this ratio, the substrate concentrations (2-CP) was increased gradually as 5, 25, 50, 100, 200, 300, 400, 600 and 800 mg/L. To study the effect of varying HRT, 2-CP concentration of feed was maintained at optimized concentration of 600 mg/L. The degradation extent of 2-CP at various hydraulic retention time (HRT) *viz.* 36, 30, 24, 18 and 12 h was monitored. The parameters like COD, 2-CP, pH, VFA and biogas were measured and estimated according to Standard Methods (APHA, 2005). Chlorophenols (2-CP) content was estimated by spectro photometric method.



Figure 1 Experimental setup of UASB reactor system

3. Results and Discussion

Effect of HRT on 2-CP removal

The 2-CP concentration of feed was maintained at 600 mg/L and the effect of varying HRT was studied. Figure 2 shows the concentration of 2-CP in feed and outlet of the reactor. The concentration of 2-CP in feed was 600 mg/L and in the outlet, it ranged from 115.2 to 13.6mg/L. The 2-CP removal efficiency in the reactor was ranging from 80.8 to 97.7 % for various HRT and maximum removal efficiency of 97.7 % was achieved at HRT of 18 h. **Ramakrishnan** and **Gupta**, (2008) reported a maximum of 96 % phenolics mixture removal using hybrid UASB reactor treating simulated coal wastewater at 24 h HRT. **Sponza** and **Ulukoy** (2008) reported a maximum removal efficiency of 83 – 99 % at HRT of 2–20 h of an UASB reactor treating synthetic 2, 4-DCP wastewater.



Effect of HRT on COD removal

The COD obtained during the process of varying HRT was plotted in figure 3. The COD concentration of the feed was 2520 mg/L and in the outlet it ranged between 560 to 160 mg/L, respectively. COD removal efficiency was in the range of 77.8 to 93.6 % in the reactor and maximum COD removal efficiency of 93.6 % was achieved at 18 h HRT. The percentage COD removal for various HRT *viz.* 36, 30, 24, 12 was 77.8, 84.1, 90.5, 80.9 % respectively. As the HRT decreased from 36 to 18 h the removal of COD increased from 77.8 to 93.6 %. **Sponza and Ulukoy (2008)** reported a maximum COD removal efficiency of 65–83 % at HRT of 2 - 20 h in an UASB reactor treating 2, 4-DCP.



Figure 3 COD concentrations at various HRT

Effect of HRT on pH concentration

The pH of the inlet and outlet of UASB reactor at various hydraulic retention time is shown in figure 4. The pH in the inlet and outlet of the reactor was ranging from 7.1 to 7.4 and 7.92 to 7.98 respectively. The sensitiveness of methanogens to pH coupled with VFA, which are intermediates of the anaerobic stabilization of chlorophenolic compounds, resulted in a negative response by the anaerobic system. **Sponza** and **Ulkoy (2008)** specified that as the HRT decreased from 20 to 2 h, pH decreased from 7.41 to 6.79 in a UASB reactor treating carbonaceous substrate with working volume of 2.5 L. The acidifying bacteria are more tolerant to pH fluctuations, whereas the methanogenic are sensitive. **Sen** and **Demirer (2003)** reported that the optimum pH condition for anaerobic reactor operation was 6.5 to 7.2. The optimal pH could be explained by the neutralization of hydrogen ions released from volatile fatty acid together with carbonates dissociated from the carbonic acid with the bicarbonate alkalinity inside the UASB reactor.



Effect of HRT on Volatile fatty acid (VFA) concentration

The VFA concentration at reactor outlet is presented in figure 5. Acetic and propionic acids make up the bulk of volatile acids accumulated inside the reactor. From the figure it is clear that the VFA in the reactor was ranging between 56 and 32 mg/L for various HRT. The optimum VFA should be less than 250 mg/L for better operation of anaerobic system (**Speece**, **1996**).

Effect of HRT on Biogas production

The biogas production of the reactor at various HRT is shown in figure 6. Biogas production at different hydraulic retention time *viz.* 36, 30, 24, 18 and 12 h for methanogenic reactor was 12, 14, 19, 24 and 28 L/d respectively. The maximum biogas production of 28 L/d was achieved at 12 h of HRT. Biogas production is directly related to COD stabilization. For example, minimal COD

removal occurs without biogas production and it is associated with the formation and release of H_2 (**Grady** *et al.*, **1972**). **Silva** *et al.* (**1999**) reported that the biogas production rate was influenced significantly by the HRT decrease, in opposite of the COD removal that decreased.



4. Conclusion

The degradation extent of 2-CP at various hydraulic retention time (HRT) viz. 36, 30, 24, 18 and 12 h was monitored at optimized concentration of 600 mg/L. By varying the HRT from 36 to 12 h, it was concluded that the biphasic UASB reactor can treat even higher concentration of substrate effectively. At 18 h HRT 2-chlorophenol degradation was 97.7 % with COD removal efficiency of 93.6 %. The efficiency of the reactor reduced with decrease of HRT below 18 h and increase of HRT above 24 h.

5. References

- APHA–AWWA., 2005. Standard methods for water and wastewater. 20th ed. American Public Health Assoc/American Water Works Assoc. Washington DC, USA.
- Grady, C.P.L., Harlow, L.J., Riesing, R.R., 1972. Effects of growth rate and influent substrate concentration on effluent quality from chemostats containing bacteria in pure and mixed culture. Biotechnology and Bioengineering 14, 391–410.
- Haggblom, M. M., Young, L. Y., 1990. Chlorophenol degradation coupled to sulfate reduction Appl. Environ. Micro biol. 56, 3255-3260.
- 4. Kao, C. M., Chai, C. T., Liu, J. K., Yeh, T. Y., Chen, K. F., Chen, S. C., 2004. Evaluation of natural and enhanced PCP

biodegradation at a former pesticide manufacturing plant. Water Res. 38 (3), 663-672.

- 5. Lettinga, G., Hobma, S.W., Pol, L.W., De Zeeuw, W.j., Jong, Grin, P.C., Roersma, R.S., 1983.
- 6. Design, operation and economy of anaerobic treatment. Water Science and Technology 15(8/9), 177-195.
- 7. Neilson, A.H., 1990. Biodegradation of halogenated organic compounds. J. Appl. Bact. 69, 445–470.
- 8. Ramakrishnan, A., Gupta, S. K., 2008. Effect of hydraulic retention time on the biodegradation of complex phenolic mixture from simulated coal wastewater in hybrid UASB reactors. Journal of Hazardous Materials 153, 843–851.
- 9. Sen, S., Demirer, G.N., 2003. Anaerobic treatment of real textile wastewater with a fluidized bed reactor. Water Research 37, 1868-1878.
- Senthilkumar, M., Gnanapragasam, G., Arutchelvan, V., Nagarajan, S., 2010 Influence of hydraulic retention time in two-phase upflow anaerobic sludge blanket reactor treating textile dyeing effluent with sago effluent as co-substrate. Environmental Science and Pollution Research.
- 11. Shen, D.S., Liu, X.W., Feng, H.J., 2005. Effect of easily degradable substrate on anaerobic degradation of pentachlorophenol in an upflow anaerobic sludge blanket (UASB) reactor, Journal of Hazardous Material 119, 239–243.
- Silva, F.M., Tavares, C.R.G., Bonifico, A.L.E., Costa, R.T., Bergamasco, R., 1999. Hydraulic retention time influence in two-phase anaerobic digestion. II Congresso de Engenharia de Processos do mercosul, Florianopolis, Santa Catarina, Brasil.
- Sivarajan, P., Arutchelvan, V., Nagarajan, S., 2017. Biomineralization of 2-chlorophenol in an UASB reactor with starch water as co-substrate. International Journal of Engineering Research & Technology Vol.6 Issue 9, 43-46.
- 14. Speece, R.E., 1996. Anaerobic Biotechnology for industrial wastewater. Archae press, Nashville, Tennessee, USA.
- 15. Sponza, D. T., Cıgal, C., 2009. Relationships between anaerobic consortia and removal efficiencies in an UASB reactor degrading 2,4 DCP. Desalination 245, 1–18.
- Sponza, D.T., Ulukoy, A., 2008. Kinetics of carbonaceous substrate in an up flow anaerobic sludge blanket (UASB) reactor treating 2,4 dichlorophenol (2,4 DCP). Journal of Environmental Management 86, 121-131.
- 17. Ye, F., Shen, D., Feng, X., 2004. Anaerobic granule development for removal of pentachlorophenol in an up flow anaerobic sludge blanket (UASB) reactor. Process. Biochem. 39 (10), 1249–1256.