

Biological Removal of Chloroorganics from Water and Wastewater

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Phenolic compounds are a group of organic pollutants present in the environment as a result of various industrial and agricultural activities, e.g. their usage as additives and as pesticides. Phenolic compounds such as chlorophenols are known for their toxicity and persistence in the environment. Thus, some of them have been included in the list of priority pollutants of several countries and are subject to legislation. Toxicity and bioaccumulative potential of chlorophenols increase with the degree of chlorination or the number of chlorine substituents on the phenolic ring and chlorophenol lipophilicity. Lipophilicity or affinity to fat leads to its accumulation up the food chain.

The toxic effects of chlorophenols seem to be linked to a chain reaction of their gradual dechlorination in body fluids and the formation of free radicals interfering with subcellular structures. The formation of peroxides and other products of lipid oxidation may result in enzyme deactivation and liver dystrophy. Chronic toxicity studies on the carcinogenic properties of some chlorophenols showed that higher chlorophenols have immunosuppressive effects, are nephrotoxic and interfere with blood formation. Chlorophenols are excreted from an organism mainly in urine, partially free and partially in the form of their sulphate and glucuronide conjugates. Chlorophenols are known for their pronounced organoleptic characteristics, with a taste threshold ranging between 0.040-30 mg/L and smell threshold between 30-1600 mg/L.

Chloroorganics Removal

Being present in water and wastewater at trace concentrations, and being recalcitrant means that chloroorganics would not be generally removed by conventional wastewater treatment processes. Analysis of treated effluents from several treatment plants, even those meeting the Standard A of the Malaysian Environmental Quality (Sewage and Industrial Effluent) Regulation 1979, or the EQ(SIE)R 1979, showed

presence of several types of chloroorganics, which are often termed as *adsorbable organohalides* (AOX) [1]. Studies on biofilm water and wastewater treatment processes have shown these to be effective in the removal of trace organics and nutrients, mainly due to adsorption as well as the presence of both reductive and oxidative processes in the biofilms [2]. The biofilm processes that have undergone various trials for treatment of water and wastewaters are available as "Sequencing Batch Biofilm Reactor" (SBBR) or "Expanded Bed Biofilm Column" (EBBC). Both reactor types possess characteristics which render them effective for removal of trace recalcitrant organics, namely:

1. Adsorptive porous media with very high surface to volume ratio, due to its large number of internal pores, and rough surface texture, which also acts as an excellent bacterial immobilisation matrix to form biofilms.
2. Mobile beds which keep bacterial films in active state and enhances pollutant removal. Recalcitrant organics would be adsorbed and then slowly degraded by microorganisms through both reductive and oxidative environments. This biodegradation in turn regenerates active adsorption sites.
3. The systems operate at high biomass concentrations, thus are able to overcome toxic effects due to manmade organics.

The removal of AOX from the treated effluent of a papermill is shown as an example here.

Example of treatment to remove chloroorganics

Effluent from the wastewater treatment plant, with secondary level treatment, of a paper mill processing recycled paper, was treated in an SBBR reactor. Prior to treatment the effluent was analysed for AOX using *High Performance Liquid Chromatography* (HPLC). The SBBR was then operated with the effluent as feed

over several months. This is to achieve steady state after each change made so as to enable acquisition of kinetic and other operational parameters.

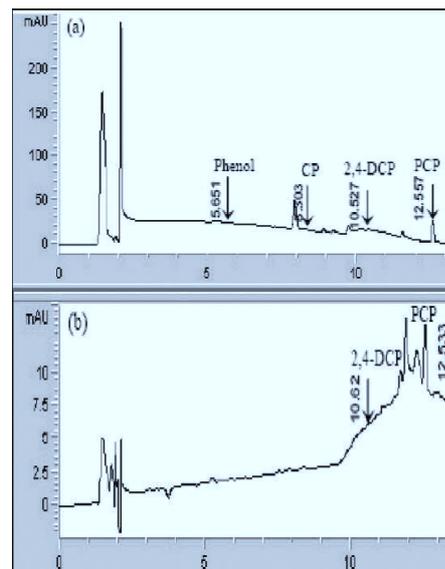


Figure 1: HPLC chromatograms for SBBR's (a) influent and (b) effluent

Table 1: Percent removal of chlorophenol compounds via SBBR bioreactor

Chlorophenol Compounds	% Removal
PCP	70.05
2, 4-DCP	86.47
CP	100
Phenol	100

Figure 1 shows the HPLC chromatograms for the SBBR's influent and effluent, with the numbers indicating the HPLC residence times of the species, while the percentage removal of the major AOX is listed in Table 1.

PCP appears to be very resistant to microbial degradation due to its highly chlorinated organic nature; nevertheless the process was still able to remove about 70% of it.

Was this removal permanent, i.e. via biodegradation, or temporary, i.e. via adsorption? To answer these questions, biodegradation pathway studies have to be carried out. This involves, among other things, analysis of metabolites or the

intermediate compounds, if any. From there, a possible biodegradation mechanism may be postulated, based on the identified chemical species.

In a parallel study, the acclimatised biomass (bacterial culture) was fed with wastewater containing *pentachlorophenols* (PCP), this being the highest substitute of the chlorophenols. Results of this study indicated that biodegradation had indeed occurred and that reductive dechlorination had been carried out by the acclimatised mixed culture in the reactor. Via this mechanism, the PCP was dechlorinated to lesser and lesser chlorinated compounds (CP, DCP and Phenol) and eventually mineralisation to CO₂ would occur. Reductive dechlorination, or removal of Cl atoms directly from the ring of aromatic compounds is a very significant process because the dechlorinated products are usually less toxic and are more readily degraded either

anaerobically or aerobically. The unique reductive and oxidative states present in this process has enabled such reduction for dechlorination and oxidation for phenol cleavage [3] to occur, resulting in mineralisation of the recalcitrant and toxic organic.

Conclusion

The conventional water and wastewater treatment process can no longer be relied on to remove dangerous man-made organics discharged by human activities; this may result in negative human health and aquatic biodiversity consequences. Adsorptive-reductive-oxidative biofilm processes have been developed and tried on several industrial wastewaters and river waters and have been found capable of removing recalcitrant organics, especially those of the AOX family due to the states present in the process which would not be available in conventional activated sludge type of processes

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REFERENCES

- [1] Rakmi A.R. 2005. *AOX in Wastewater: Analysis and Treatment*. Presented at SIDA-ARRPET Combined Regional Workshop on Wastewater and Hazardous Wastes, Kanpur, India, 11-12 March 2005.
- [2] Abdul-Rahman Rakmi, Ozaki Hiraoka and Zainol Norazwina. 2003. *Expanded Bed Column Bioreactor Performance and Hydrodynamics*. Canadian J. Chem Eng, 81(3-4) 867-874.
- [3] Rakmi A.R., Y. Terashima and H. Ozaki. 1990. Biodegradation of Azo Dye by an Acclimated Culture in a Continuous Process. In "Effluent Treatment and Waste Disposal," IChE, Rugby, UK.