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Research Note

Combined Chemical and Biological Processes for the Treatment of Industrial Wastewater Containing Formaldehyde

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Combination of chemical and biological processes can be considered as a cheaper option for the treatment of toxic wastewater. Each process is influenced by its own parameters. Chemical treatment is affected by the reaction rate between the chemical agent and organic compounds as well as by environmental factors such as temperature. Biological processes are affected by pH, organic load and sludge concentration. In this study, the treatment of formaldehyde by chemical and biological methods is investigated. The removal efficiency of formaldehyde in the chemical treatment reached 85% when temperature exceeded 60°C and the concentration of lime was 2000 mg/l. In the biological process, after acclimatization, the biodegradation of formaldehyde was well accomplished under both batch and continuous flow conditions. The maximum formaldehyde elimination was about 70%. Biomass and initial formaldehyde concentration have a significant influence on the degradation of formaldehyde.

INTRODUCTION

Formaldehyde is an industrial and chemical substance that due to its high activity is used in various industrial processes. The most significant application of formaldehyde is in the manufacture of urea and phenolic resins. About 80% of the slow-release fertilizer market is based on urea-formaldehyde containing products. Formaldehyde is also used in the manufacture of acetal resins and permanent-press finishes of cellulosic fabrics [1].

Furthermore, formaldehyde is a widely used disinfectant. Process wastewater derived from the production of urea-formaldehyde resins, dimethylterephthalate (DMT) and formaldehyde production itself may contain formaldehyde concentration ranging from 1 to 10 g/l [2-4].

Even at concentrations as low as 5 mg/l, formaldehyde is highly toxic to a diverse type of organisms. Compared with phenol (another commonly used disinfectant), formaldehyde toxicity in most of the organisms tested is more severe [5,6]. Since it has been shown that formaldehyde is a mutagenic and carcinogenic agent [7,8], direct discharge of chemical effluents containing formaldehyde threatens life in the receiving water and implies the need for efficient treatment systems. Treatment of such industrial wastewater containing formaldehyde may be accomplished by either biological or chemical oxidation systems to fulfill legal requirements. A number of potentially useful chemical treatment technologies for the removal of formaldehyde from wastewater have been investigated, including treatment with chemicals such as lime, ammonia, sodium cyanide, hydrogen peroxide and potassium [9]. In chemical oxidation processes, reaction mechanisms change structure and chemical properties of the organic substances. Molecules break into smaller fragments and a higher percentage of oxygen appears in these molecules in the form of alcohols, carboxylic acid etc. Oxidation of organic compounds with oxidants such as ozone or $OH^{\bullet}$ radicals usually yields to more oxidized compounds that, in most cases, are more easily biodegradable than the former ones [9]. This is the general idea that makes some investigators consider the combination of a chemical process followed by a biological process [10].

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Wastewater from a Chemical Industries Company which produces formaldehyde-urea adhesive and industrial resins (melamine and hexamine), containing relatively high organic matter (formaldehyde), has been chosen in this study and treated by combined chemical and biological processes. Biological reactors have shown to be economic and reliable systems for the treatment of wastewater. Nevertheless, there are situations in which these treatments are not recommended, especially if toxic and recalcitrant compounds for the microorganisms are present in the effluents. Formaldehyde is considered as toxic for a biological system [11]; however, there exists research about its treatment by biological systems [12,13].

The main objective of this study is to evaluate the efficiency of a biological system for treating wastewater which was pretreated with a chemical substance and contains relatively high concentration of formaldehyde.

MATERIALS AND METHODS

Wastewater Composition

Wastewater from a Chemical Industries Company producing formaldehyde-urea adhesive and industrial resins was used in this research.

The wastewater had a high COD, 1000-10,000 mg/l, and low TSS, less than 350 mg/l. The organic matter included methanol, formic acid, hexamine, melamine and formaldehyde. Formaldehyde was the main toxic organic compound at the concentration of 500-8000 mg/l. Wastewater pH was between 6.4-7.

Experimental Procedures

The studies were carried out in two different stages: chemical treatment of wastewater with lime (using $Ca(OH)_2$) and biological treatment by activated sludge system.

For the chemical treatment, 1000 ml of the influents and a special amount of $Ca(OH)_2$ were mixed and transferred to glass flasks, sealed to avoid evaporation and shaked at 150 rpm at variable temperature between 30°-80°C. At different times, COD, temperature, pH and formaldehyde concentration were measured in this experiment.

During the biological stage, a lab-scale activated sludge reactor made out of pelexiglass with a volume of 6 l was used. Two seeds were used to inoculate the bench-scale bioreactor; one from a municipal activated sludge plant and the other from the lagoon of the Chemical Industries Company which produced resins.

The influent medium was made up of effluent from the chemical treatment stage which was mixed with ammonium phosphate, urea and diluted molasses (as carbon source); the COD/N/P ratio was adjusted to 100/5/1. The system was allowed to restabilize at slightly below the maximum capacity and operated under a continuous regime, using wastewater with different COD and various combinations of organic loads. The process was monitored and controlled by measuring the pH, temperature, MLSS, COD and formaldehyde concentrations.

Formaldehyde determination was conducted using colorimetric methods by means of Hantzsch reaction [14], other analytical measurements were done in accordance with Standard Methods for the Examination of Water and Wastewater [15].

RESULTS AND DISCUSSION

Chemical Treatment

Results of batch chemical treatment with lime are shown in Figures 1 to 3. The removal efficiency of formaldehyde in chemical treatment reached 85% when the initial formaldehyde concentration was 1200 mg/l. Also, the amount of COD did not undergo considerable variation. In the presence of lime, formaldehyde converts to pentose, which is a relatively biodegradable carbohydrate with 5 carbon atoms. However,

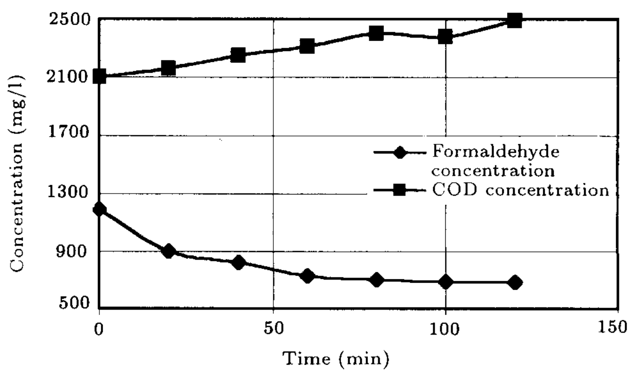

Figure 1. Formaldehyde and COD concentrations during the chemical treatment (T= 30°C, lime conc. = 1000 mg/l).

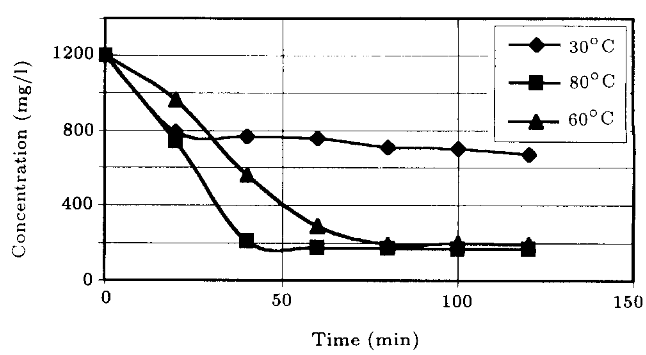

Figure 2. Variation of formaldehyde concentration at different temperatures (initial lime conc. = 2050 mg/l).

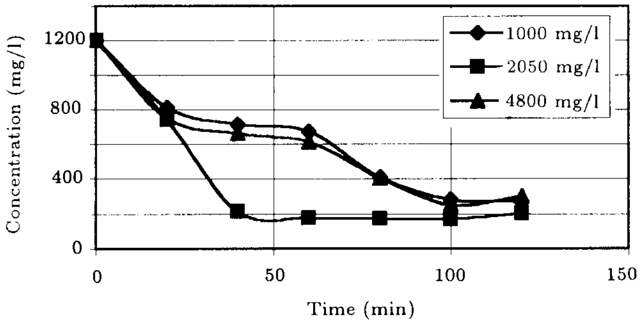

Figure 3. Variation of formaldehyde concentration during chemical treatment with different concentrations of lime (T = 60°C).

significant COD was present when the temperature was below 40°C. Formaldehyde removal was more rapid at higher temperatures.

In Figure 1, the evolution of COD and formaldehyde in the effluent during batch experiment is shown. Formaldehyde removal took place when the initial concentration was near 1200 mg/l, but COD concentration increased from 2100 to 2500 mg/l after 2 h, this concentration remained constant till the end of the experiment. It seems that formaldehyde reacts with lime, thereby, producing aldose and ketose, which are not toxic to microorganisms, but increase the COD concentration. In fact, lime acts as a catalyst and its consumption is low; therefore, the amount of produced sludge is not significant.

Figures 2 and 3 illustrate the concentration of formaldehyde verses operation time during batch experiments, at different temperatures and various lime concentrations, respectively.

As can be seen in Figure 2, removal efficiency is about 85% when temperature is above 60°C and decreases slightly below this value. It seems that the reaction temperature appears as the primary variable that controls the chemical process. Results obtained in experiments with variable concentration of lime are shown in Figure 3. The optimum concentration of lime was about 2000 mg/l, for which the removal efficiency of formaldehyde was close to 82%.

Biological Treatment Stage

To achieve better COD and formaldehyde removal close to the level required by legislation, effluents from the chemical treatment stage were treated in a biological activated sludge unit.

Mixed microorganisms were fed to the bioreactor. Seeding sludge was obtained from a municipal activated sludge and the lagoon of the Chemical Industries Company. It was cultured in the batch regime by being initially fed with molasses and, then, gradually acclimatized to formaldehyde that served as a source of carbon. After acclimatization, the microorganisms were used in the continuous activated sludge plant. The reactor was inoculated with acclimated sludge suspension to a final concentration ranging from 2500-3600 mg MLSS/l.

Acclimation and growth of the biomass in the continuous bioreactor was obtained by applying organic loads between 0.1 and 0.86 gCOD/gMLSS/d to the reactor.

In 35 days, the MLSS reached concentrations between 2500-4000 mg/l, after which, through purges, the MLSS remained nearly constant between 2000-2500 mg/l. After acclimation, the degradation capacity was evaluated for successively larger organic loads (Figure 4). Under continuous feed conditions, efficiencies near 85% were obtained at organic loads below 0.32 gCOD/gMLSS/d. Temperature was around 30°C and pH range was maintained between 7.2 and 7.8.

The efficiency of the system was near 70% in terms of formaldehyde removal, when the initial concentration of formaldehyde was 250 mg/l. However, a significant COD fraction of the raw wastewater (20-30% of COD in the influent) was present in the effluent, indicating the possible existence of non-biodegradable organic matter fraction (formaldehyde) in the influent. In addition, the percentage of COD removal decreased as a fraction of formaldehyde increased in the influent (Figure 5). COD removal percentage was between 52-90% and the maximum formaldehyde elimination was about 70%. No inhibition effects occurred when the

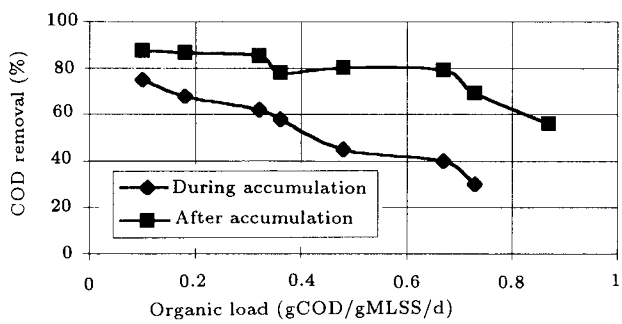

Figure 4. Removal efficiency at different organic loads in the bioreactor.

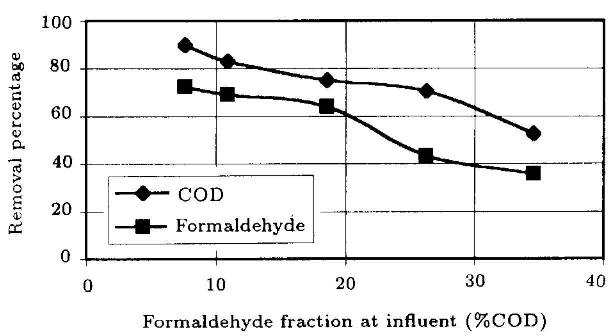

Figure 5. Effect of formaldehyde, as a fraction of total COD, on the COD and formaldehyde removal.

formaldehyde fraction was below 26%. This result also indicates that a fraction of formaldehyde as high as 34% COD causes a 50% inhibition of its biodegradation.

Effect of Sludge Concentration

Biodegradation of formaldehyde and COD removal were proportionally related to the sludge concentration (MLSS). The results of this experiment are shown in Figure 6.

Significant COD and formaldehyde reductions were achieved when the biomass concentration reached near 2500 mg/l, after which the percentage of COD and formaldehyde removal remained nearly constant. During this period (70 days), the activated sludge unit operated at a hydraulic retention time (HRT) of 0.5 day. Figure 7 illustrates the schematic diagram of the combined chemical-biological system that was suggested to the factory and constructed in pilot scale according to the data and results which have been achieved during the lab experiments. This system was installed in the factory for research studies.

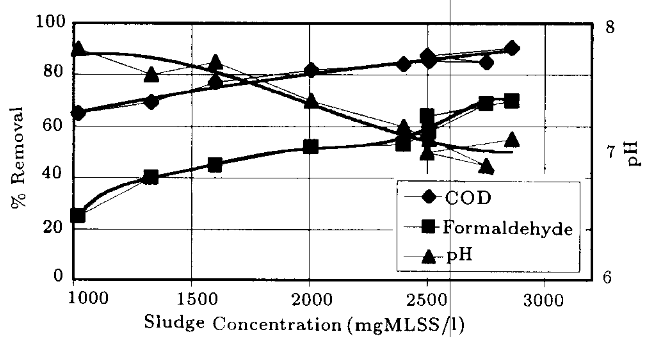

Figure 6. Variation of COD and formaldehyde removal efficiency at different sludge concentrations.

CONCLUSION

Wastewater from a formaldehyde-urea adhesive factory with high organic matter (COD between 1000-10,000 mg/l, mostly due to formaldehyde 500-8000 mg/l) has been treated by combined chemical and biological processes. The removal efficiency of formaldehyde in chemical treatment reached 85% when the initial formaldehyde concentration was 1200 mg/l. The highest removal efficiency was observed when the temperature exceeded 60°C and the concentration of lime was about 2000 mg/l. The results obtained from the biological treatment demonstrate that it is indeed possible to treat toxic wastewater by an aerobic bioreactor. After acclimation, the biodegradation of formaldehyde was well accomplished under both batch and continuous flow conditions. The maximum efficiency of 85% was obtained at organic loads below 0.32 g COD/gMLSS/d. Results demonstrate that both biomass and formaldehyde concentration have significant influence on the degradation rate of formaldehyde.

ACKNOWLEDGMENTS

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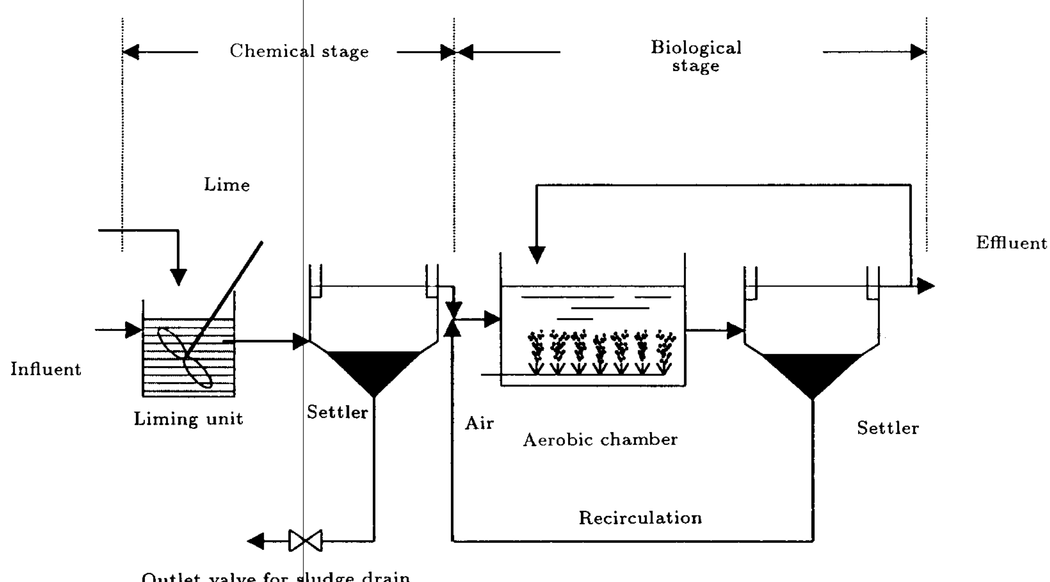

Figure 7. Schematic of the combined chemical-biological system for treating wastewater from the urea-formaldehde adhesive factory.

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