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BIODEGRADATION OF AROMATIC AMINE COMPOUNDS USING MOVING BED BIOFILM REACTORS

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ABSTRACT

Three moving bed biofilm reactors were used to treat synthesized wastewater of aromatic amine compounds including aniline, para-diaminobenzene and para-aminophenol that are found in many industrial wastewaters. The reactors with cylindrical shape had an internal diameter and an effective depth of 10 and 60 cm, respectively. The reactors were filled with light expanded clay aggregate as carriers and operated in an aerobic batch and continuous conditions. Evaluation of the reactors' efficiency was done at different retention time of 8, 24, 48 and 72 h with an influent COD from 100 to 3500 mg/L (filling ratio of 50%). The maximum obtained removal efficiencies were 90% (influent COD=2000 mg/L), 87% (influent COD=1000 mg/L) and 75% (influent COD=750 mg/L) for aniline, para-diaminobenzene and para-aminophenol, respectively. In the study of decrease in filling ratio from 50 to 30 percent, 6% decrease for both para-diaminobenzene and para-aminophenol and 7% increase for aniline degradation were obtained. The removal efficiency was decreased to about 10% after 15 days of continuous loading for each of the above three substrates. In the shock loading test, initially the COD removal rate was decreased in all reactors, but after about 10 days, it has been approached to the previous values. Finally, biodegradability of aromatic amines has been proved by nuclear magnetic resonance system.

Key words: Light expanded clay aggregate, biodegradation, moving bed, biofilm, nuclear magnetic resonance

INTRODUCTION

In most industries such as chemical ones, discharge of wastewater containing organic solutes such as aniline, para-diaminobenzene and para-aminophenol is a serious problem and the wastewater should be treated before entering the environment.

Aniline is commonly used in a number of industrial processes such as dyes, plastic, paint, pigments, herbicides, pharmaceutical preparation and rubber accelerator production (Datta *et al*., 2003; Qi *et al*., 2002; O'Neill *et al*., 2000; Brillas and Casado, 2002). It is a hazardous substance that readily dissolves in water up to 3.5 percent. Therefore, due to its high solubility in water the risk of possible pollution in wastewater and drinking water sources especially in case of a chemical spill is increased (Selcuk and Teresa, 2007).

Para-diaminobenzene as a low toxic diamine is used as a component of polymers and composites, aramid fibers, hair dyes, rubber chemicals, textile dyes and pigments. It is selected for the outstanding properties, including high temperature stability, high strength, and chemical and electrical resistance (Afzal Khan *et al*., 2006).

Para-aminophenol is the hydrolytic product of acetaminophen and is reported to have significant nephrotoxicity and teratogenic effects, and has been detected as synthetic intermediate (Afzal Khan *et al*., 2006). It is toxic, irritable to eyes, skin, kidney and respiratory system. It is used in the manufacturing of acid wool, azo and leather dyes. It also has an application as photograph developer, rubber autoxidation agent and petroleum additives.

Wastewater containing aromatic amines such as aniline has been shown to be treated by photodecomposition, electrolysis, resin adsorption, ozone oxidation, and biodegradation methods. They are not completely decomposed by activated sludge process and also inhibit biodegradation of other

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chemicals because of their hard biodegradability. Therefore, further studies on advanced biological processes were and still are necessary for these compounds.

The researches done by Afzal Khan on para-diaminobenzene degradation using *Pseudomonas sp. strain ST-4* have shown 84 percent removal efficiency with an influent COD of 470 mg/L (Afzal Khan *et al.*, 2006). In another research (Wang *et al.*, 2006) the bacterial strain has been isolated from Northeastern China petrochemical wastewater treatment plant activated sludge which was rich in pentyl amine and aniline. The optimal conditions for degradation of pentyl amine and aniline mixture were concentration ranging between 150 and 200 mg/L, reaction time of 24 h and a maximum solution dissolved oxygen level of 6 mgO_2/L at 30^oC and pH of 7.0. The results have shown 91 percent removal of aniline with an influent concentration of 770 mg/L. Selcuk and Teresa have obtained 75% removal efficiency in anaerobic treatment of p-nitrophenol (p-NP) with an influent COD of 350 mg/L during 186 days study (Selcuk and Teresa, 2007).

Moving Bed Biofilm Reactor (MBBR) which was introduced about 14 years ago and now is popular in Europe, has been successfully operated in urban and some industrial wastewaters treatment systemes (Rusten *et al.*, 2006; Maurer *et al.*, 2000). MBBR is designed to offer the advantages of the biofilm process (compact, stable removal efficiency and simplicity of operation) without its drawbacks (channeling and clogging of medium). The idea behind the development of MBBR process was to adopt the best features of activated sludge as well as those of fixed-bed biofilter processes (Maurer *et al.*, 2000; Jahrena *et al.*, 2002). Contrary to the most biofilm reactors, the whole tank volume of MBBR is utilized for biomass growth. It also has very low head-loss. Relatively large volume of carriers with sizes from 0.1 to 5 cm is performed in MBBR. Due to enough turbulence in the reactor they are always in suspended form and proper contact with the wastewater.

MBBR has been found to be a commercial successful process. There are presently several hundred small and on-site treatment units in Germany and more than 400 full scale wastewater treatment plants in operation in 22 different countries all over the world (Maurer *et al.*, 2000).

The purpose of this research was to investigate the inhibitory effect of three aromatic amines including aniline, para-diaminobenzene and para-aminophenol on the efficiency of wastewater treatment in three aerobic MBBRs. Effect of different parameters on the degree of aromatic amines biodegradation was also studied.

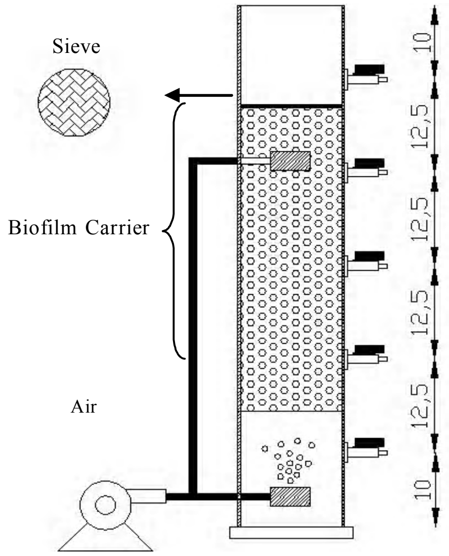
MATERIALS AND METHODS

Three cylindrical MBBRs were used in this study as shown in Fig. 1. Internal diameter, height and wall thickness of each reactor was 10, 70 and 0.4 cm, respectively. The effective depth of wastewater in each reactor was 60 cm filled with up to 50% floating biofilm carrier elements made of Light Expanded Clay Aggregate (LECA) with a density of 0.55 g/cm^3 lower than the density of water (Fig. 2). LECA is a kind of aggregate that has been used in many structural projects in Iran such as light weight concrete. This material has also been used for agricultural purposes. High surface area of this material has made it more suitable as carrier in the biofilm reactors.

The synthetic wastewater has been prepared using aniline, para-diaminobenzene and para-aminophenol which were supplied by Merck Company. In order to have C/N/P=100/5/1 and enough alkalinity, necessary nutrients (urea, KH_2PO_4, K_2HPO_4) were used as supplement feed to the reactors.

The parameters of pH, soluble chemical oxygen demand (COD) filtered through Vattman paper No.42 and dissolved oxygen (DO) were daily measured. Total suspended solids (TSS), mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were examined on alternative days. Microscopic investigation was done regularly. All laboratory experiments were conducted at room temperature close to mesophilic condition. Dissolved oxygen concentration was always controlled above 3 mg/L. All analytical tests were done as outlined in the Standard Method Handbook (APHA, 2005).

During the start up the reactors (30 days) with the sludge seed obtained from Ekbatan



a) Schematic diagram

b) Pilot plant

Fig. 1: Schematic diagram the three aerobic cylindrical MBBR pilot plants used in this study with internal diameter of 10, height of 70 and wall thickness of 0.4 cm and 5 sampling ports

Fig. 2: Carrier Light Expanded Clay Aggregate (LECA) with a density of 0.55 g/cm^3

wastewater treatment plant, microbial acclimation has been done with a solution of glucose and synthetic wastewater. In this stage, the removal efficiency was reached to 80% for $COD_{aromatic}/COD_{glucose}= 0.5$. After that, the amount of Organic Loading Rate (OLR) was increased stepwise within 60 days. The efficiency of the reactors was evaluated at different retention times of 8, 24, 48 and 72 h and influent COD from 100 to 3500 mg/L for para-diaminobenzene and para-aminophenol and 4000 mg/L for aniline. Loading stages of aniline, para-diaminobenzene and para-aminophenol are shown in Figs. 3 and 4, respectively. The effect of carrier filling ratio, toxic shock and continuous loading were investigated. Biodegradation of influent wastewater by MBBR systems was also checked using Nuclear Magnetic Resonance (NMR) system and the results were compared by CHEM OFFICE 2006 program.

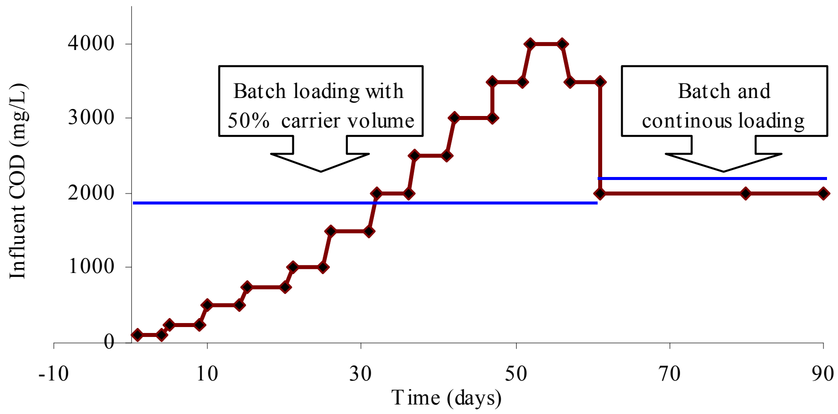


Fig. 3: Variation of aniline influent organic loading rate (batch loading with filling ratio of 50 % for 60 days and batch and continuous loading with filling ratio of 30% for 30 days)

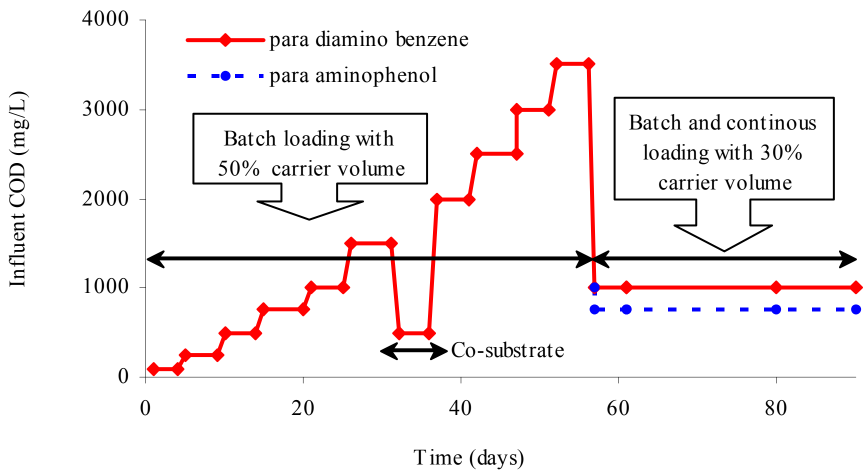


Fig. 4: Variation of diaminobenzene and para-aminophenol influent organic loading rate (batch loading with filling ratio of 50 % for 60 days and batch and continuous loading with filling ratio of 30% for 30 days)

RESULTS

Retention time effect

The effect of different retention time (8, 24, 48 and 72 h) on COD removal rate for each reactor was studied after every step increase in COD (Figs. 5 to 7).

As shown in the figures, at low concentration of para-diaminobenzene and para-aminophenol (from 750 to 1000 mg/L) the maximum efficiencies were obtained (87% in COD=1000 mg/L for para-diaminobenzene and 75% in COD=750 mg/L for para-aminophenol) after 3 days.

A decrease in the removal efficiencies were observed for influent COD of 1500 and 2000 mg/L for para-diaminobenzene and para-aminophenol, respectively. The removal rate for aniline was better than the others whereas the most efficiency was observed (90%) for COD of 2000 mg/L.

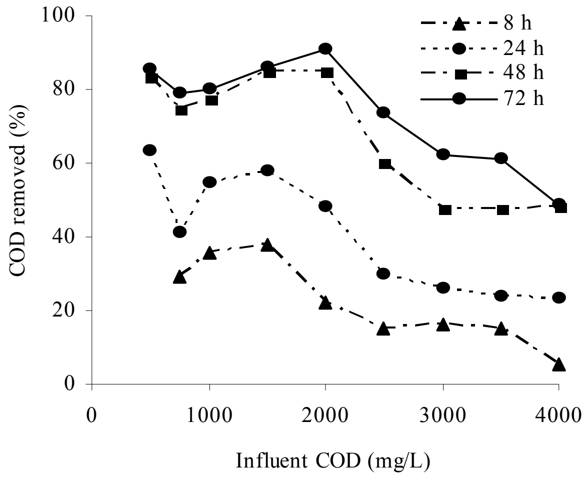


Fig. 5: Variation of aniline wastewater loading rate on COD removal in different retention time of 8, 24, 48 and 72

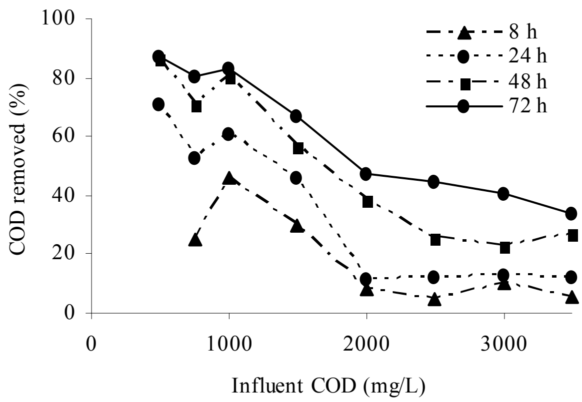


Fig. 6: Variation of para-diaminobenzene wastewater loading rate on COD removal in different retention time of 8, 24, 48 and 72 h

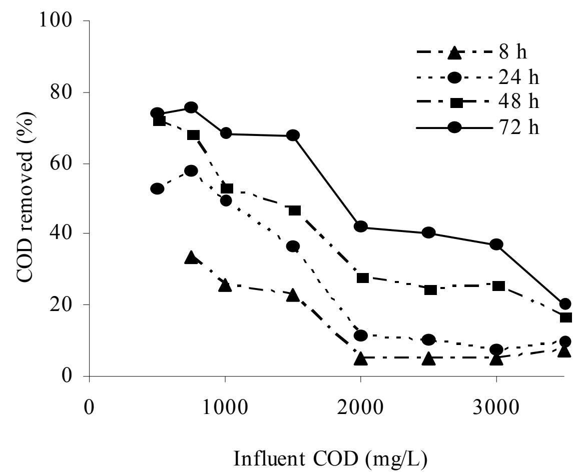


Fig. 7: Variation of para-aminophenol wastewater loading rate on COD removal in different retention times of 8, 24, 48 and 72 h

Comparing three aromatic amine compounds COD removal

The COD removal versus influent concentration for aromatic amine compounds after three days retention time is shown in Fig. 8. It can be seen that the COD removal of aniline wastewater had better efficiency as compared to the other two compounds which were approximately the same.

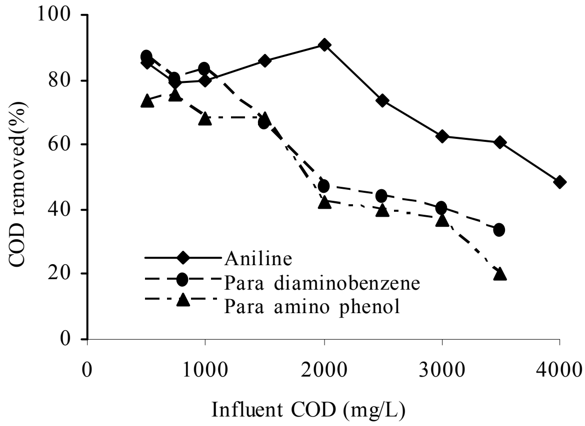


Fig. 8: Comparison of COD removal efficiency between aniline, para-diaminobenzene and para-aminophenol compounds for influent COD from 500 to 3500 mg/L after 72 h retention time

It has also been observed that for the reactor containing aniline, the removal efficiency decreases slightly whereas it is quite different for the other two reactors.

Carriers filling ratio effect

From the results it could be seen that by decreasing filling ratio to 30 percent, 6% decrease for both para-diaminobenzene and para-aminophenol and 7% increase for aniline degradation were obtained. The comparison between COD removal rate in 30 and 50% filling ratio are shown in Figs. 9 to 11.

Continuous study

In the continuous study with the maximum influent COD as compared to the batch studies, the removal efficiency for aniline, para-diaminobenzene and para-aminophenol was decreased to about 10% after 15 days loading (82, 72 and 68 percent, respectively).

Shock loading effect

In order to examine the effect of shock loading on the reactors, 4 times of the obtained optimum COD loading rate in this study were added to the systems. Removal

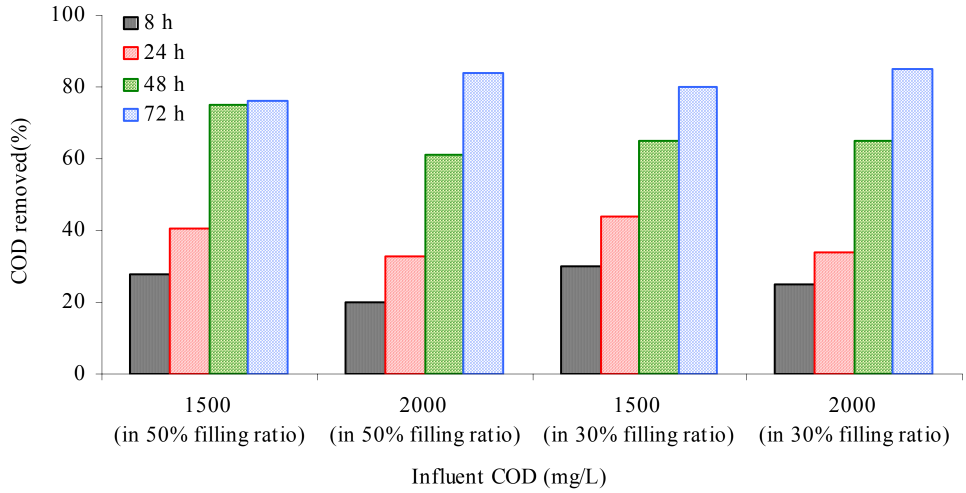


Fig. 9: COD removal efficiency in filling ratio of 30 and 50 percent for two aniline loading rates of 1500 and 2000 mg/L after 8, 24, 48 and 72 h

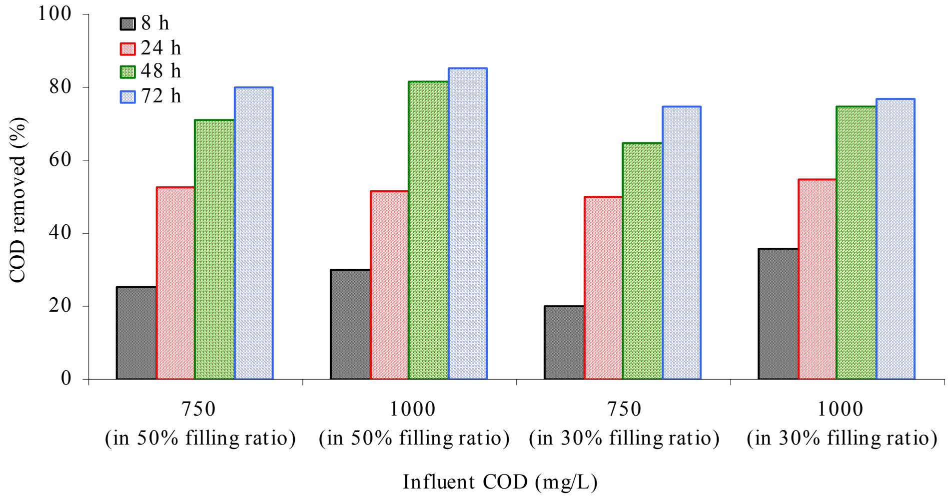


Fig. 10: COD removal efficiency in filling ratio of 30 and 50 percent for two para-diaminobenzene loading rates of 1500 and 2000 mg/L after 8, 24, 48 and 72 h

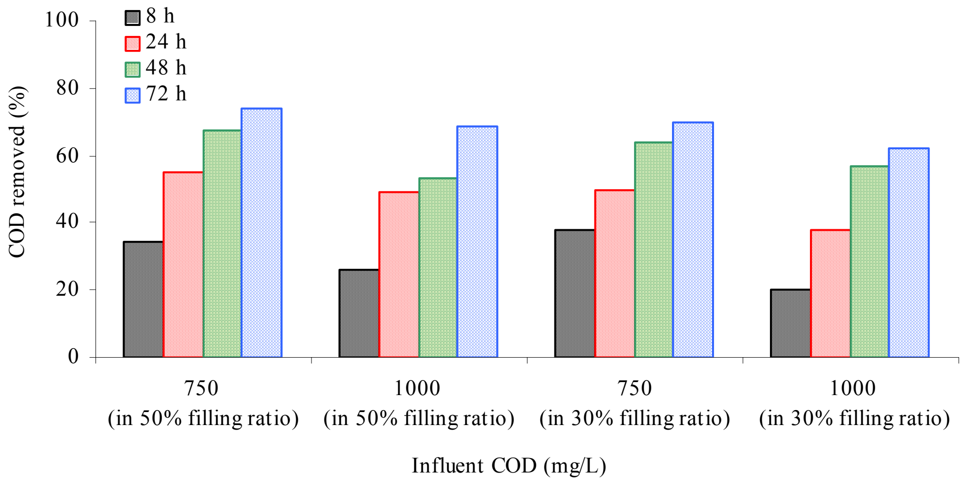


Fig. 11: COD removal efficiency in filling ratio of 30 and 50 percent for two para-aminophenol loading rate of 1500 and 2000 mg/L after 8, 24, 48 and 72 h

efficiency for the reactors was measured every day. Initially the removal rate was decreased in all reactors, but they were gradually increased until reached (after about 10 days) to the acceptable limit of 82, 72 and 68 percent for aniline, para-diaminobenzene and para-aminophenol, respectively (Fig. 12).

NMR analyses

In order to investigate the degree of biodegradation of organic compounds, both influent and effluent solutions were examined by NMR. The results as shown in Figs. 13 to 15 indicated that all compounds were degraded to the simple molecules.

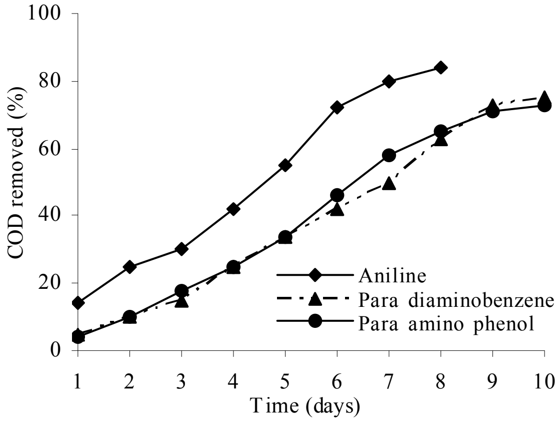
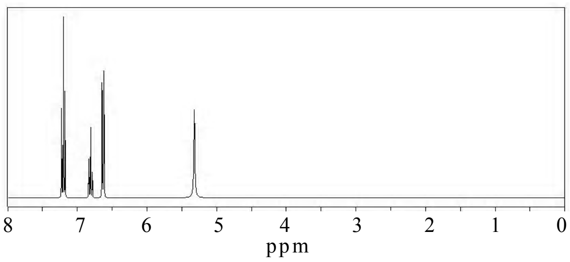
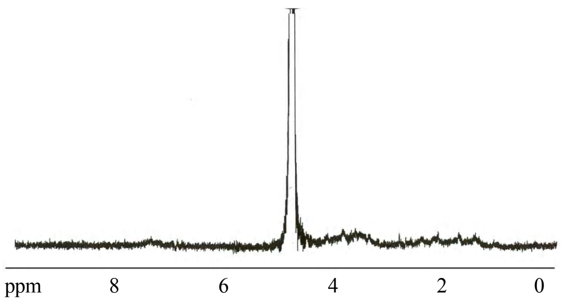


Fig. 12: Removal efficiency rate during shock loading study for COD influent equal to four times of the optimum one

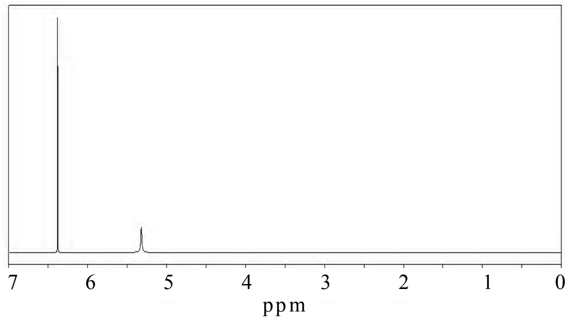


a) influent

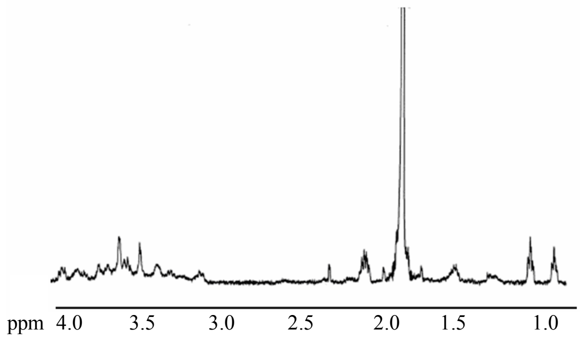


b) effluent

Fig. 13: NMR results for biodegradation of a) influent and b) effluent organic solution for aniline reactor

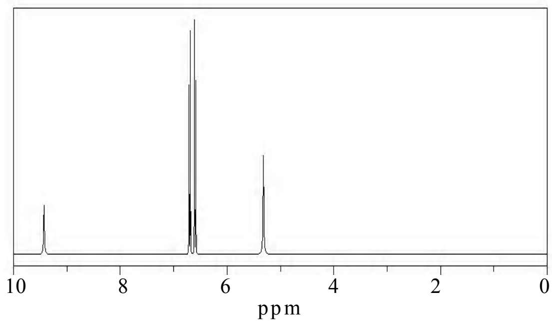


a) influent

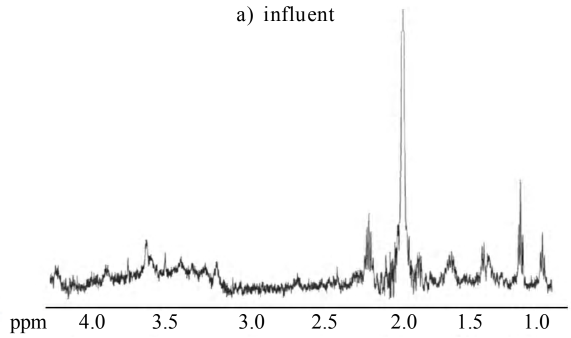


b) effluent

Fig. 14: NMR results for biodegradation of a) influent and b) and effluent organic solution for para-diaminobenzene reactor



a) influent



b) effluent

Fig. 15: NMR results for biodegradation of a) influent and b) and effluent organic solution for para-aminophenol reactor

DISCUSSION

As mentioned in the introduction part, the removal efficiency of three aromatic amine compounds including aniline, para-diaminobenzene and para-aminophenol from industrial wastewater using chemical treatment such as photodecomposition, electrolysis, resin adsorption, ozone oxidation have been done by many investigators. But not much work has been reported for biological removal of these chemicals.

In this study, the maximum efficiencies were obtained after 3 days (87% in COD=1000 mg/L for para-diaminobenzene and 75% in COD=750 mg/L for para-aminophenol). As compared to these compounds, aniline had the highest COD removal efficiency (90%) for COD of 2000 mg/L.

The results of this study are comparable with similar researches in recent years. For example 91 percent of aniline has been removed using an isolate bacterial strain (*Pseudomonas sp.*) with an influent concentration of 770 mg/L (Wang *et al.*, 2006). But the same removal efficiency was obtained using mixed culture with more than two times higher influent COD in this study. 84 percent of para-diaminobenzene was degraded with influent COD of 470 mg/L using *Pseudomonas sp. strain ST-4* (Afzal Khan *et al.*, 2006), whereas in this study the maximum removal efficiency was 83 percent for an influent COD of 1000 mg/L.75 percent removal efficiency of para-aminophenol has been obtained with an influent COD of 350 mg/L (Selcuk and Teresa, 2007) which was the same for this study but using higher influent COD (750 mg/L). Therefore, MBBR as an advanced biological process had a proper COD removal efficiency for the treatment of aromatic amine wastewater.

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