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CHARACTERIZATION OF A BIOLOGICALLY TREATED WASTEWATER FROM OIL RECLAIMING: RECORDING OF LOW MOLECULAR WEIGHT ORGANICS AND ESTIMATION OF HUMIC SUBSTANCES

H. Gulyas*, M. Reich** and I. Sekoulov*

** Technical University of Hamburg-Harburg, Arbeitsbereich Gewässerreinigungstechnik, Eißendorfer Str. 42, D-21071 Hamburg 90, Germany*
*** Technical University of Hamburg-Harburg, Zentrallabor, Eißendorfer Str. 38, D-21071 Hamburg 90, Germany*

ABSTRACT

Wastewater originating from oil reclaiming (COD about 300 mg/l, TOC about 70 mg/l) which was pretreated by equalization, neutralization, adsorption to activated sludge from a publicly owned treatment work, flocculation, and flotation and finally oxidized in an activated sludge process was analyzed for humic acids and gas chromatographically detectable organic compounds. The humic acid concentration was estimated to represent about 15% of the COD. Hydrocarbons were detected in activated sludge, but no hydrocarbons were identified gas chromatographically. In the two analyzed wastewater samples ethers (mainly containing polyethoxy structures), carboxylic acids and carboxylic acid esters were found. In one sample several nitrogen compounds (amines and amides) were detected. Except for 1,1'-oxybis-(2-methoxy)-ethane, which was a constituent of both samples, the organic gas chromatographically detectable compounds differed completely from sample to sample. This is obviously due to changing composition of the processed spent oils.

KEYWORDS

Oil reclaiming wastewater; organic constituents; residual COD.

INTRODUCTION

Many publications deal with refractory COD, but little is known about the organic compounds which represent the refractory COD. However, knowledge about these compounds is important for judging their potential adverse ecological effects and for the decision on further treatment stages. It is known that some refractory organics are formed during aerobic biological treatment (Hejzlar and Chudoba, 1986), among them considerable amounts of humic substances (Klopp and Koppe, 1991).

Certain refractory organics in the effluents of publicly owned treatment works are originating from industrial plants. As an example we investigated the biologically treated wastewater of an oil reclaiming plant which is discharged to the sewer.

EXPERIMENTAL PROCEDURES

Pretreatment of analyzed wastewater and sampling of wastewater and sludge. The effluent of a biological wastewater treatment plant for purifying aqueous phases resulting from oil reclaiming was investigated. Pre-treatment prior to aerobic biological oxidation (four parallel aeration tanks of 1011 m^3, retention time 5 to 7 days) includes equalization, neutralization, adsorption to activated sludge from a publicly owned treatment work, flocculation, and flotation. The COD of the pre-treated wastewater is about 10,000 to 25,000 mg/l, which is reduced to 300 to 500 mg/l by aerobic biological treatment. At two different times (March 1992 and September 1992) effluent of the secondary clarifier was sampled and analyzed for organic constituents. During a period with enhanced generation of bulking sludge (October 1992) samples of bulking sludge as well as settled sludge were taken from the secondary clarifier in order to determine their hydrocarbon content.

Determination of biological oxygen consumption. Oxygen demand was tested in an electrochemical respirometer. 250 ml of the wastewater samples were inoculated with 1 ml activated sludge of a pilot scale domestic wastewater treatment plant and with allyl thiourea to inhibit nitrification.

Analysis of humic acids. The amount of humic substances was estimated by solid-liquid extraction of the original wastewater with the highly alkaline anion exchange resin "Lewatit MP 500 A", subsequent elution of the resin with NaCl/NaOH and photometric analysis of the eluate. A commercially available humic acid derived from lignite was used as standard.

Analysis of low molecular weight compounds. Small organic molecules were analyzed qualitatively by dichloromethane extraction of the treated wastewater at different pH values (neutral, alkaline and acidified samples) according to the method of Clark *et al.* (1991) and subsequent gas chromatographic analysis of the extracts (mass-selective detector, identification of substances by a computerized library). The sample of March 1992 was concentrated fivefold by reverse osmosis while the wastewater sampled in September 1992 was not concentrated prior to dichloromethane extraction.

Determination of hydrocarbons in activated sludge. Samples of bulking and settled sludge were centrifuged and the pellets were resuspended in distilled water and agitated for 10 min with ultrasound. The resulting suspensions were extracted with 1,1,2-trichloro-trifluoroethane and the hydrocarbon content was determined according to the German standard method DIN 38409 H 18 (Normenausschuβ Wasserwesen, 1981).

RESULTS AND DISCUSSION

TOC values of the biologically treated wastewater samples were 67 mg/l (March 1992) and 73 mg/l (September 1992), resp. About 30 mg/l of humic substances were found in the biologically treated wastewater sampled in September 1992 which exhibited a COD of 333 mg/l. If a constitution of the humic matter of 54% C, 33% O, 4.5% H and 2.7% N is assumed (Ziechmann, 1980), which is equivalent to a formula of about $(C_{70}O_{32}H_{70}N_3)_x$, a concentration of 30 mg humic acids/l represents a theoretical COD of about 50 mg/l (15% of total COD). Some sources of error may lead to an over- or under-estimation of the humic acid concentration and its contribution to COD: As there was used a commercially available humic acid originating from lignite as standard for photometric determination of the humic acids in the wastewater, the absorption coefficients of the humic acids of the different sources may rather differ. It is also uncertain if the element compositions of the humic acids originating from wastewater are similar to the composition presented by Ziechmann (1980). So the estimation of a theoretical COD may not be appropriate. However, it is assumed that the order of magnitude of humic acids content of the biologically treated oil reclaiming wastewater is realistic as similar humic acid concentrations were found in biologically treated domestic wastewater (Rebhun and Manka, 1971).

Recent experiments with a wastewater from another oil reclaiming plant showed that only small amounts of hydrocarbons were dissolved in the aqueous phase. The pretreated wastewater exhibited a hydrocarbon concentration of about 5 mg/l which was decreased to values below 1 mg/l immediately after contact of the

wastewater with activated sludge (Gulyas *et al.*, 1991). This indicates that hydrocarbons are adsorbed very fast and it can be supposed that the pretreatment of the concentrated wastewater with activated sludge from a publicly owned treatment work causes the low hydrocarbon contents. The sample of settled activated sludge from the aerobic biological stage investigated in this study exhibited a hydrocarbon content of 3.2 mg/g sludge. The hydrocarbon content of the bulking sludge was even lower (about 0.2 mg/g). It can be concluded from these data and from recent studies that hydrocarbons are not a major part of COD of biologically treated oil reclaiming wastewater.

TABLE 1. Organic Compounds Identified by GC/MS in Two Samples of Biologically Treated Oil Reclaiming Wastewater. Substances That Were Not Exactly Identified are Given in Parentheses.

compounds	time of sampling:	March 1992	September 1992
Ethers:			
1,1'-oxybis-(2-methoxy)-ethane		X	X
2,5,8,11-tetraoxanonane		X	
2,5,8,11,14-pentaoxapentadecane		X	
2,5,8,11,14,17-hexaoxaoctadecane		X	
[oxaalkane, not identified]			X
1,1,3,3-tetramethoxypropane		X	
2-methyl-1,3,6-trioxocane		X	
2,5-dimethyl-1,4-dioxane			X
Ketones:			
3-ethyl-2-pentanone			X
3,4-dihydro-6,8-dimethyl-1(2H)-naphthalenone			X
Carboxylic acids:			
decanoic acid		X	
3,3-dimethyl-butyric acid			X
trimethyl-hexanoic acid			X
Carboxylic acid esters:			
[heptanoic acid ester, not identified]			X
phthalic acid butyl-*iso*-butylester		X	
[phthalic ester, not identified]			X
Heterocycles:			
1-methyl-piperazine		X	
4-nitroso-morpholine			X
[derivative of benzopyrane]		X	
thiophenethiol			X
[alkylethoxy derivative of thiophene]			X
Nonheterocyclic nitrogen, sulphur and phosphorous compounds:			
3-amino-hexane		X	
N-propyl-3-amino-hexane		X	
[2 amines, not identified]		X	
N,N-dibutylformamide		X	
acetic acid 3-methylheptyl-3-amide		X	
[acetic acid amide, not identified]		X	
[derivative of aniline]		X	
benzothiol			X
phosphoric acid tributyl ester		X	

In the dichloromethane extracts of the sample "March 1992" 19 substances were identified or at least related to classes of organic compounds (table 1): mainly amines, amides, and long chain ethers (polyethers) were found. Also some plasticizers were detected (phosphoric acid tributyl ester and phthalic esters). No hydrocarbons were among the identified compounds which is in good accordance with low hydrocarbon contents of sludge samples. In the sample "September 1992" fewer ethers and nitrogen compounds, but more carboxylic acids and carboxylic acid esters were detected than in the sample "March 1993" (Table 1). The results show that there is a high variance of gas chromatographically detectable organics in wastewaters sampled at different times. This is obviously due to changing composition of processed oils.

There is evidence from previous experiments that most of the organic constituents of biologically treated oil reclaiming wastewater are refractory (Gulyas *et al.*, 1991). This is confirmed by oxygen demand experiments with the two wastewater samples of March and September 1992: Both samples exhibited low BOD_5 values of about 10 mg/l which is equivalent to about 3% of the COD. As the humic acid content is estimated to represent only about 15% of the COD, there are considerable amounts of other refractory organics. A part of them may be oxa-alkanes which are known to be recalcitrant. They were not quantified in this study, however. By the analytical methods used here a couple of classes of organic compounds could not be recorded as e.g. carbohydrates and proteins. It is known that certain biopolymers formed during aerobic biological wastewater treatment which contain sugars, amino sugars, uronic acids and amino acids are recalcitrant (Hejzlar and Chudoba, 1986).

CONCLUSION

Humic acids represent a considerable amount of the refractory organic compounds of biologically treated oil reclaiming wastewater. Further compounds which are an important part of the refractory COD are ethers (mainly polyethoxy compounds), nitrogen compounds and carboxylic acid esters. However, the composition of organic wastewater constituents varies greatly and depends on the processed oil-water mixtures.

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