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Chemical and Process Engineering 2016, 37 (3), 373-382
DOI: 10.1515/cpe-2016-0030

CARBONACEOUS MATERIALS IN PETROCHEMICAL WASTEWATER BEFORE AND AFTER TREATMENT IN AN AERATED SUBMERGED FIXED-BED BIOFILM REACTOR

Karol Trojanowicz, Wlodzimierz Wojcik*

St. Pigon Krosno State College, Department of Environmental Engineering, Rynek 1, 38-400 Krosno, Poland

Results of the studies for determining fractions of organic contaminants in a pretreated petrochemical wastewater flowing into a pilot Aerated Submerged Fixed-Bed Biofilm Reactor (ASFBBR) are presented and discussed. The method of chemical oxygen demand (*COD*) fractionation consisted of physical tests and biological assays. It was found that the main part of the total *COD* in the petrochemical, pretreated wastewater was soluble organic substance with average value of 57.6%. The fractions of particulate and colloidal organic matter were found to be 31.8% and 10.6%, respectively. About 40% of *COD* in the influent was determined as readily biodegradable *COD*. The inert fraction of the soluble organic matter in the petrochemical wastewater constituted about 60% of the influent colloidal and soluble *COD*. Determination of degree of hydrolysis (D_H) of the colloidal fraction of *COD* was also included in the paper. The estimated value of D_H was about 62%. Values of the assayed *COD* fractions were compared with the same parameters obtained for municipal wastewater by other authors.

Keywords: Chemical Oxygen Demand fractions**,** petrochemical wastewater; biofilm reactor

1. INTRODUCTION

Presence of biodegradable organic compounds in wastewater is a condition for application of biological processes in wastewater treatment. Implementation of kinetic mathematical models in dimensioning and process simulation of bioreactors (for example: aerated submerged fixed-bed biofilm reactors - ASFBBR), requires knowledge of the carbonaceous material fractions in wastewater influent. In the available literature, there are examples indicating susceptibility of petrochemical wastewater to biological degradation (Acuna-Askar et al., 2000; Johnson et al., 2000; Lazarova et al., 2000; Park et al. 1996; Schlegel and Teichgraber 2000; Trojanowicz and Dusza, 2003; Yang et al., 2000). However, the content of the biodegradable fraction of organic contaminants in petrochemical wastewater can depend on the technological outline of the particular oil-refinery and also whether it is analyzed as raw wastewater or wastewater pretreated with physical and chemical unit processes. Authors such as Almeida and Butler (2002), Park et al., (1997), Trela (2000), Wentzel et al., (2000) and others (Dulekgurgen et al., 2006; Ferrai et al., 2010; Garcia-Mesa et al., 2010; Hu et al., 2002; Karahan et al., 2008; Lagarde et al., 2005) describe methods for the determination of fractions of organic carbon materials (determined as chemical oxygen demand - *COD*), that utilize physical tests and biological assays. There is a lack of data in the reference materials on *COD* fractions in a pretreated petrochemical wastewater.

*Corresponding author, e-mail: wwojcikg@gmail.com

This article presents the results of experimental studies conducted in order to determine fractions of organic contaminants in mechanically and chemically pretreated petrochemical wastewater flowing into a pilot ASFBBR bioreactor.

2. AIM OF THE PAPER

The aim of the presented research was a quantitative determination of carbonaceous material fractions in mechanically and chemically treated petrochemical wastewater which could be utilized in practice for bioreactor up-scaling and process modelling. During the planning of the experiments it was assumed that:

- it is possible to conduct a determination of *COD* fractions in a petrochemical wastewater utilizing a pilot-scale ASFBBR bioreactor,
- for a steady-state in an ASFBBR reactor working under mechanically and chemically pretreated petrochemical effluent conditions, most of the readily-biodegradable fraction of *COD* in the wastewater is consumed by biomass,
- constraints of biological organic carbon removal kinetics due to the shortage of nitrogen and phosphorous concentration in relation to organic carbon concentration in petrochemical wastewater could be eliminated by adding nitrates and phosphates to the wastewater solution.

3. MATERIALS AND METHODS

Fractions of particulate, colloidal, soluble and readily biodegradable *COD* in a petrochemical wastewater were determined utilizing the combination of a physical-chemical method and bioassay. The method was based on a physical separation of different fractions of carbonaceous material of different particle/ molecule size in a series of dedicated experiments conducted in a pilot-scale ASFBBR. The bioreactor was installed and operated in the real-scale oil-refinery wastewater treatment plant after oil-water separation, coagulation-flocculation and dissolved air flotation units. During those experiments wastewater samples were taken from the inlet and outlet of the continuous flow-through ASFBBR reactor for analysis. Results of *COD* colloidal fraction determination in the petrochemical wastewater before and after biological treatment also allowed an estimate of the degree of hydrolysis (D_H).

3.1. Wastewater sampling program

The grab-samples of wastewater were taken with frequency of one hour at the ASFBBR bioreactor inlet and outlet, then "1-hour" samples were mixed together (inlet and outlet samples separately) in order to prepare "24-hour" representative samples utilized for further analysis. The wastewater samples were being collected for 18 days.

3.2. Method for determination of COD fractions

3.2.1. Determination of particulate, colloidal and soluble fractions of COD

Fractions of organic carbon materials in wastewater inflowing to the ASFBBR reactor (pretreated mechanically and chemically) were estimated utilizing a physical method. The method principle is physical separation (filtration) of the wastewater contaminants' fractions that differ in particle/

molecule size. The *COD* value was assayed in the wastewater samples: (1) before filtration (COD_T); (2) after filtration through 0.45 µm pore size membrane filters ($COD_{0.45}$); (3) upon coagulation with aluminium chlorohydrate $Al_n(OH)_mCl_{(3n-m)}$ and subsequent filtration through 0.45 µm filters ($COD_{0.45,C}$). *COD* analysis for every tested sample was conducted in triplicate and the final *COD* value was the mean of those three measurements. The value of particulate *COD* fraction in the wastewater (COD_P) was calculated as the difference between mean values of COD_T and $COD_{0.45}$. Similarly, the value of a colloidal *COD* fraction in the wastewater (COD_C) was calculated by subtracting value of $COD_{0.45,C}$ from $COD_{0.45}$. The value of soluble *COD* fraction in the wastewater (COD_S) was equal to the determined value of $COD_{0.45,C}$.

The same analysis was conducted for wastewater samples taken at the ASFBBR bioreactor outlet that allowed an estimate of the readily biodegradable soluble fraction of *COD* ($COD_{B,CS}$ *and* $COD_{B,S}$) and degree of hydrolysis of colloidal matter (D_H).

Determinations of chemical oxygen demand (*COD*) were conducted in accordance with Polish Standards (PN).

3.2.2. Determination of a readily biodegradable fraction of COD

The readily biodegradable soluble fraction of *COD* ($COD_{B,S}$) was estimated by means of a bioassay type test that required analysis of wastewater samples taken from the outlet of the continuous flow-through ASFBBR pilot bioreactor. The value of $COD_{B,S}$ was calculated by subtracting the $COD_{0.45,C}$ values determined in the samples taken at the bioreactor outlet from the $COD_{0.45,C}$ values determined in the samples taken at the bioreactor inlet. Simultaneously, a biodegradable fraction of soluble organic matter and small colloids with particle size of less than 0.45 µm ($COD_{B,CS}$) was estimated. It was calculated as the difference between the $COD_{0.45}$values determined in the samples taken at the bioreactor outlet from the $COD_{0.45}$ values determined in the samples taken at the bioreactor inlet.

It was assumed that for a given steady-state in the ASFBBR reactor adapted to petrochemical wastewater with heterotrophic biofilm, operated with a surface organic loading rate (SOL) that did not exceed 10 g*COD*/(m^2·d), almost all soluble biodegradable *COD* fraction is removed from the wastewater. Correctness of the above assumption is justified by the methodology and results of similar studies for municipal wastewater published by other authors (Bortone et al., 1994; Dold et al., 1986; Mamais et al., 1993; Mbewe et al., 1995; Wentzel et al., 1999). This was also proved during respirometric tests and conducted simulations of the ASFBBR reactor's organic carbon removal kinetics (Trojanowicz and Wojcik, 2011; Trojanowicz et al., 2009).

3.2.3. Determination of degree of hydrolysis (D_H) for the colloidal COD

The D_H value of the colloidal *COD* present in the petrochemical wastewater during treatment in the ASFBBR reactor was estimated by comparing the mean values of COD_C determined in the wastewater before and after biological treatment.

4. RESULTS AND DISCUSSION

Results of *COD* fractions' determination in a petrochemical wastewater pretreated with mechanical and chemical processes are shown in Tables 1 - 4. Figures 1 and 2 illustrate the variability of the COD fractions determined at the inlet and outlet from ASFBBR, in the course of the studies.

Table 1. *COD* values determined in "24-hour" samples of petrochemical wastewater taken at the inlet and outlet of ASFBBR reactor (mean-range)

Parameter	Inlet [g*COD*/m^3]	Outlet [g*COD*/m^3]
COD_T	95.5 (34.8-170.9)	56.1 (27.7-126.5)
$COD_{0.45}$	65.2 (31.3-126.2)	37.9 (20.8-103.1)
$COD_{0.45,C}$	55.0 (26.8-121.5)	34.7 (20.3-101.6)

Table 2. COD fractions estimated in "24-hour" samples of petrochemical wastewater taken at the inlet and outlet of ASFBBR reactor (mean-range)

Parameter	Inlet [gCOD/m^3]	Fraction %	Outlet [gCOD/m^3]	Fraction %
COD_T	95.5 (34.8-170.9)	---	56.1 (27.7-126.5)	---
COD_P	30.3 (3.5-85.7)	31.8	18.2 (4.0-56.8)	32.4
COD_C	10.2 (1.3-38.8)	10.6	3.3 (0.0-7.7)	5.8
COD_S	55.0 (26.8-121.5)	57.6	34.7 (20.3-101.6)	61.8

Table 3. Value of the colloidal and soluble biodegradable fraction of COD ($f_{B,CS}$) estimated in petrochemical wastewater pretreated with mechanical and chemical methods as a part of *COD* colloidal and soluble fraction present in the influent

	Mean	Standard deviation	Relative standard deviation [%]
Inlet [gCOD/m^3]	65.2		
Outlet [gCOD/m^3]	37.9		
Fraction $f_{B,CS}$ [%]	41	15	38

Table 4. Value of readily biodegradable soluble *COD* fraction ($f_{B,S}$) estimated for petrochemical wastewater pretreated with mechanical and chemical methods as a part of influent's *COD* soluble fraction

	Mean	Standard deviation	Relative standard deviation [%]
Inlet [gCOD/m^3]	55.0		
Outlet [gCOD/m^3]	34.7		
Fraction $f_{B,S}$ [%]	36	15	41

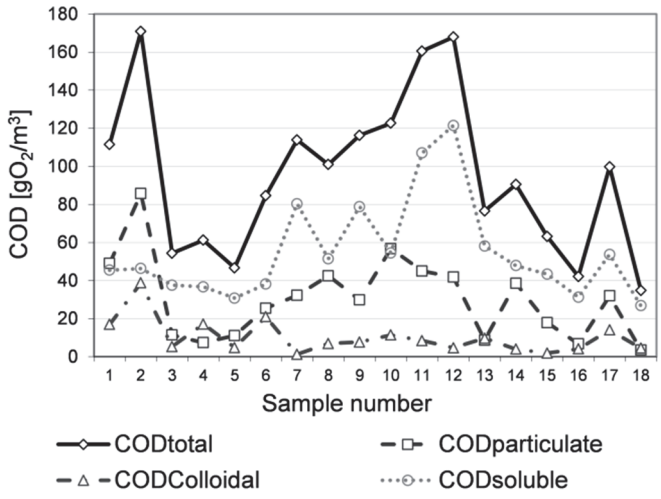

Fig. 1. Values of COD fractions at the inlet to the pilot bioreactor

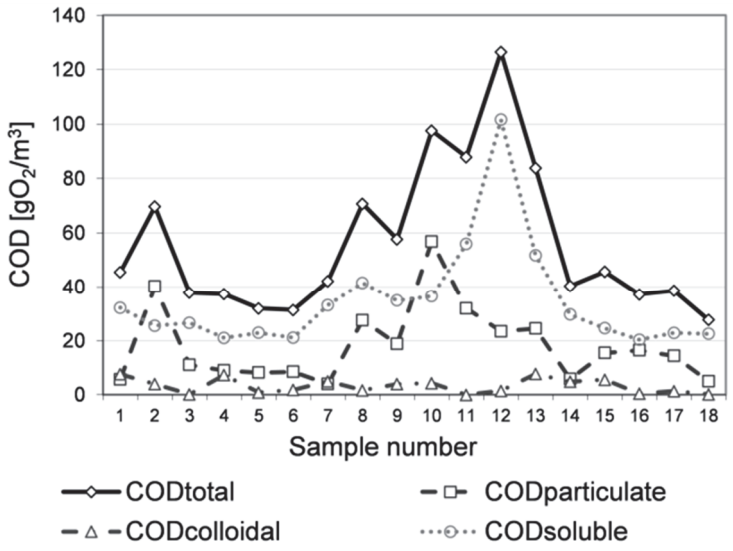

Fig. 2. Values of COD fractions at the outlet from the pilot bioreactor

Results of estimation of the degree of hydrolysis (D_H) of colloidal *COD* in petrochemical wastewater during biological treatment in ASFBBR bioreactor are shown in Table 5.

Table 5. Degree of hydrolysis (D_H) values determined for colloidal *COD* during treatment of petrochemical wastewater in ASFBBR reactor

	Mean	Standard deviation	Relative standard deviation [%]
Inlet [gCOD/m^3]	10.2		
Outlet [gCOD/m^3]	3.3		
Fraction $f_{B,S}$ [%]	62.2	35.1	56.4

The presented results confirm that the main part of the total *COD* in the petrochemical wastewater pretreated with mechanical and chemical processes are soluble organic substances, comprising 57.6% of total *COD*. The fractions of particulate and colloidal organic matter were found to be 31.8% and 10.6%, respectively, of total *COD* in the wastewater inflowing to the ASFBBR reactor. Such results seems to be logical (and could be anticipated) taking into account the source of the wastewater analyzed, which was the buffer tank of the petrochemical wastewater treated with gravity and coalescent oil-water separators, coagulation-flocculation and dissolved air flotation (DAF) unit processes. These processes are designed to remove particulate and colloidal materials from raw wastewater. The source of particulates in the analyzed samples of the wastewater was the residue of the froth from the DAF system. The obtained results of *COD* fraction values in petrochemical wastewater have been applied during calibration and verification of biofilm mathematical models (Trojanowicz and Wojcik, 2011). As organic carbon removal kinetics relates to soluble carbonaceous materials in those models, special attention was paid to the extent to which this part of organic matter could be biologically removed from petrochemical wastewater. As mentioned earlier, the method applied to this end comprised of physical tests and bioassay, based on the same assumptions as those presented by other authors (Bortone et al., 1994; Dold et al., 1986; Mamais et al., 1993; Mbewe et al., 1995; Trela, 2000; Vanhooren, 2002; Wentzel et al., 1999). The main assumption of this method is that, for a steady-state ASFBBR bioreactor, most of the readily-biodegradable fraction of *COD* in the wastewater is consumed by biomass. The risk that such an assumption may be false is related to the fact that the kinetics of a process of a readily biodegradable organic matter removal from wastewater in a biofilm-bioreactor, under a defined surface organic loading rate (*SOL*), is too low for fully removing this *COD* fraction (as the effect that *COD* loading rate (*SOL*) is too high). Furthermore, toxic substances that

inhibit oxidation processes of organic compounds in a biofilm may be present in a petrochemical wastewater. The first argument can be rejected on the basis of the calculated results of the value of an organic carbon removal rate in biofilm. The calculation of this parameter was conducted with a mathematical biofilm model which was calibrated and verified for a petrochemical wastewater (Trojanowicz and Wojcik, 2011). Moreover, constraints for biological organic carbon removal kinetics due to the nitrogen and phosphorous concentration shortage in relation to organic carbon concentration in petrochemical wastewater were eliminated by continuous injection of nitrate and phosphate solution into the inflowing wastewater. Another way to prove that the determined readily biodegradable fraction of *COD* ($f_{B,S}$) is correct is to conduct a complementary biological assay. Described in a separate article (Trojanowicz et al., 2009), the respirometric method for simultaneous determination of maximum growth rate (μ_{max}) and half saturation coefficient of organic carbon (K_S) for heterotrophs forming biofilm under petrochemical effluent is an example of such a test. On its basis, the value of the *COD* removed from a wastewater in the phase of high oxygen uptake rate (*OUR*) may be estimated. It reflects the utilization of a readily biodegradable carbonaceous material in wastewater. If this value is related to the measured value of the total *COD* in the batch reactor at the beginning of the respirometric test, we will obtain the value of the biodegradable fraction of *COD* (f_{BS}). During the respirometric tests mentioned above, the value of f_{BS} of about 0.4 was used for calculating the initial value of readily biodegradable soluble *COD* in the batch reactor. Estimated values of soluble biodegradable *COD* at the moment of OUR sudden decline (see Fig. 1), corresponding to expiration of a readily biodegradable organic substrate in the batch reactor, were near zero. This supports the thesis that the estimated value of the readily soluble biodegradable fraction of *COD* in petrochemical wastewater ($f_{B,S}$) is correct. Obtained results during those tests also indicate that there were no inhibitors present in the petrochemical wastewater, since the determined values of heterotrophic maximum growth rate did not differ significantly regardless of the initial value of the biomass organic loading rate (S_S/X_H) (Trojanowicz et al., 2009). In the case of heterotrophic growth rate inhibition, the higher the values of S_S/X_H had been set in the batch reactor the lower the values of estimated μ_{max} would have been (Kumaran and Paruchuri, 1997).

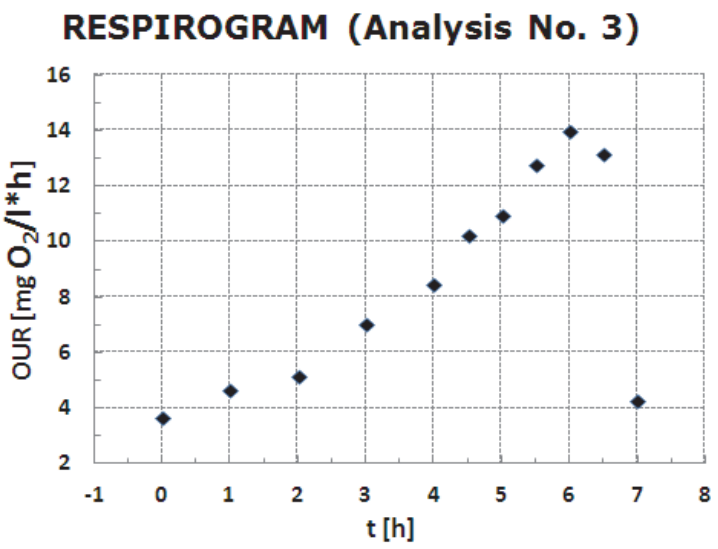

Fig. 3. Representative respirogram obtained during estimation of half saturation coefficient for organic substrate (*Ks*) and maximum specific growth rate of heterotrophic biomass (μ_{max}). The decline in OUR value (at about seventh hour of the test) corresponds to expiration of a readily biodegradable soluble organic matter in the batch reactor (Trojanowicz et al., 2009)

The obtained results presented in Table 2 indicate that the readily biodegradable fraction of organic matter in a pretreated petrochemical wastewater makes up about 36% of the total soluble *COD* and about 40% of the sum of small size colloids and soluble *COD* in the effluent, respectively. The other

part of the soluble contaminants may be considered as the inert soluble COD fraction that cannot be removed from wastewater through biochemical processes in the biofilm. The calculated mean values of the $f_{B,S}$ and $f_{B,CS}$ have a high standard deviation (SD). Consequently, they should be considered as estimations biased with significant uncertainty. We dare say that this uncertainty did not result from methodological errors of the conducted experiments but rather it is a feature of the system and variability of the parameters for the petrochemical wastewater. The variability of the readily biodegradable part of *COD* has been also shown by Trela (2000) during studies at the pilot stations of the municipal wastewater treatment plants of Uppsala and Stockholm and Lagarde et al. (2005). On the other hand, Henze (1992) proves that for a municipal wastewater and given temperature and oxygen concentration conditions, values of *COD* fractions do not vary significantly and major differences are observed rather between different wastewater treatment plants. At this point it is worthwhile to mention the results of *COD* fractionation in the highly polluted petrochemical wastewater originating from the worked-oil recycling plant of Oil Refinery "Glimar" S.A., Gorlice, Poland. This highly polluted wastewater was also pretreated with chemical processes (coagulation and flocculation processes following with sedimentation of precipitated particulates). The results were obtained utilizing biological assay – batch test with respirometric measurements utilizing bio-augmented and acclimated activated sludge (Trojanowicz and Dusza, 2001). On the basis of *COD* determinations and the OUR analysis over 6 days, the value of readily biodegradable *COD* fraction was about 36%. The fraction of about 4% was determined as a hardly biodegradable organic matter. The other part of *COD* – 60% was the inert fraction. So the results were similar as presented in this paper although they were obtained with petrochemical wastewater from a different source and utilizing a different methodology. Values of the *COD* fractions determined for a municipal and a petrochemical wastewater were compared in Table 6.

The results obtained in the course of experiments presented in this paper allowed also to determine the degree of hydrolysis of the colloidal fraction of *COD*. The determined value of the degree of hydrolysis D_H was 62%. Ongoing hydrolysis process in the ASFBBR bioreactor was reflected also in the value of determined $f_{B,SC}$, whose average value was slightly higher in comparison to the sole soluble, biodegradable fraction $f_{B,S.}$ The $f_{B,SC}$ parameter has even higher practical significance because in every day engineering practice we recognize COD value assayed in the wastewater samples upon filtration through 0.45 μm pore size membrane filters as soluble organic matter concentration.

Table 6. Comparison of determined *COD* fractions in municipal and petrochemical wastewater

Wastewater after chemical precipitation and sedimentation	COD_I %	COD_S %	COD_P %	Author
Denmark, Lundtofte	6	56	33	Henze (1992)
Sweden, Kungsgängen	15	27	58	Shulan and Hultman (1996)
Poland, Gorlice, R.N. „Glimar"S.A.*	60	40	---	Trojanowicz and Dusza (2001)
Poland, Gorlice, R.N. „Glimar"S.A.	41	27	32	This study

* Results for the petrochemical wastewater chemically pretreated, respirometric method

5. CONCLUSIONS

Upon analysis of the results of the carbonaceous material of petrochemical wastewater fractionation it can be concluded that:

- the presented method of *COD* fractionation comprising physical tests and biological assay is suitable for this purpose,

- in the physically and chemically pretreated petrochemical wastewater there is a fraction of biodegradable *COD* of about 40% that could be readily removed biologically,
- determined degree of hydrolysis of colloidal residues in the chemically pretreated petrochemical wastewater is about 62%,
- the inert fraction of the soluble organic matter in the petrochemical wastewater makes up 60% of the total influent soluble *COD*,
- in order to broaden the biodegradable *COD* fraction special biotechnological endeavours such as bioaugmentation could be applied.

The authors would like to thank the Management Boards of Oil Refinery "Glimar" S.A., Gorlice, Poland for their partial funding the work presented in this paper.

SYMBOLS

COD	Chemical Oxygen Demand, gCOD/m^3
COD_T	total COD value in unfiltrated wastewater samples, g/m^3
$COD_{0.45}$	COD value in wastewater samples filtrated through 0.45 μm pore size membrane filters, g/m^3
$COD_{0.45,C}$	COD value in wastewater samples coagulated and subsequently filtrated through 0.45 μm pore size membrane filters, g/m^3
COD_T	the value of total COD in the wastewater, g/m^3
COD_P	the value of particulate COD in the wastewater, g/m^3
COD_C	the value of colloidal COD in the wastewater, g/m^3
COD_S	the value of soluble COD in the wastewater, g/m^3
COD_I	the value of inert COD fraction in the wastewater, %
COD_S	the value of soluble COD fraction in the wastewater [%]
COD_P	the value of particulate COD fraction in the wastewater, %
D_H	degree of hydrolysis, %
$f_{B,S}$	soluble readily biodegradable fraction of COD, %
$f_{B,CS}$	colloidal and soluble biodegradable fraction of COD, %
K_S	half saturation coefficient for organic carbon
t	time in hours, h
μ_{max}	maximum specific growth rate

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Received 06 April 2015
Received in revised form 24 May 2016
Accepted 27 May 2016