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## PROBLEM OF CORRECTION OF THE CHEMICAL OXYGEN DEMAND VALUES DETERMINED IN WASTEWATERS TREATED BY METHODS WITH HYDROGEN PEROXIDE

### ZAGADNIENIE KOREKTY WARTOŚCI CHEMICZNEGO ZAPOTRZEBOWANIA NA TLEN W JEGO OZNACZENIACH W ŚCIEKACH OCZYSZCZANYCH METODAMI Z UDZIAŁEM NADTLENKU WODORU

**Summary:** The use of hydrogen peroxide for pretreatment of wastewaters is connected with the need of introducing the correction factor in order to determine COD (*Chemical Oxygen Demand*) load. The use of this procedure allows us to determine precisely the reduction rate and the changes in COD fractions which take place during the pretreatment with the use of this oxidizer. As a part of this paper the empirical equation correcting the involvement of hydrogen peroxide in COD load in a range from 0.0-7500.0 mg H<sub>2</sub>O<sub>2</sub>/dm<sup>3</sup> was determined. The influence of this compound on the COD = f(t) dependence during aeration time with the use of two techniques and the change of the particular COD fractions during pretreatment were presented on the basis of the selected industrial wastewaters.

**Keywords:** COD determination, hydrogen peroxide, correcting factor, wastewaters treatment

Many types of industrial wastes are subject to pretreatment with the use of systems with strong oxidizers such as: ozone, hydrogen peroxide, mixture using Fenton's reagent, etc. One of the ways of hydrogen peroxide application is using it to enhance flotation processes of the aggregated pollutions carried out with the use of IAF (*Induced Air Flotation*) and DAF (*Dissolved Air Flotation*) techniques [1-3]. In case of using hydrogen peroxide for high concentrations (above 50 mg/dm<sup>3</sup>) which enhance the sewage purification process, the determination of the pollutants reduction effect, ie on the basis of chemical oxygen demand (COD) requires some correction of this parameter value of the amount of load carried by the enhancing oxidizer to the load of total chemical oxygen demand. COD correction is often essential due to the necessity of determination of the precise level of the pollutants load reduction and hydrogen peroxide stability. For a very small group of industrial wastes (from paper production, from textile industry and from plastics processing), this problem has been described in literature by Talini and Anderson, who formulated [4] the empirical correction equation in the form:  $COD_r = COD_p - f \times c$  (where:  $COD_r$  - actual [mg O<sub>2</sub>/dm<sup>3</sup>],  $COD_p$  - determined by a standard method after the use of hydrogen peroxide [mg O<sub>2</sub>/dm<sup>3</sup>],  $c$  - concentration of H<sub>2</sub>O<sub>2</sub> in a sample of wastewater, determined by iodometric method [mg/dm<sup>3</sup>],  $f$  - a correcting factor determined experimentally (acc. to the authors  $f = 0.25$  [4-6])). The above-mentioned equation takes into consideration the correction for the so-called unbounded hydrogen peroxide contained in chemical oxygen demand load in the examined samples. The value of the determined correcting factor comes from the following reactions (1)-(3) [4]: [(1)  $Cr_2O_7^{2-} + 3H_2O_2 + 8H^+ \rightarrow 2Cr^{3+} + 3O_2 + 7H_2O$ ; [(2)  $H_2Cr_2O_7 + 5H_2O_2 \rightarrow H_2Cr_2O_{12} + 5H_2O$ ; [(3)  $H_2Cr_2O_{12} + 8H_2O_2 \rightarrow Cr_2O_3 + 9H_2O + 8O_2$ . The dichromate consumption in reactions (1)-(3) comes to

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the total COD load, in the correcting factor value ( $f \times c$ ). Taking into consideration COD load which results from hydrogen peroxide decomposition is essential especially in case of analytical determination of the COD fraction involvement in pretreated and treated wastes. Detailed elaboration of this problem is also essential in case of slight pollutants reduction and the essential changes in relations of the particular fractions in COD load influenced by hydrogen peroxide. The knowledge of the involvement of the particular fractions is also important as it determines the flotation method and the quantity of hydrogen peroxide used as the factor enhancing the process.

The aim of the research was to determine the application scope of the determined by Talini and Anderson factor correcting the involvement of hydrogen peroxide in COD load and determination of changes in composition of COD fraction influenced by this oxidant in the flotation process.

### Experimental

The research was carried with the use of industrial wastes from fat production of vegetable and animal origin (from the production of lard and gizzard preparation and processing). Two aeration types were used: conventional (IAF) - with the use of dispersed air (with the use of Pfeiderer Water System with membrane ducts of diameter  $d = 120 \mu\text{m}$  and membrane disc diameter  $D = 240 \text{ mm}$ ) and saturation technique (DAF). Hydrogen peroxide concentration was determined iodometrically, chemical oxygen demand (COD) by dichromate method (PN-ISO 15705:2005) and biochemical oxygen demand ( $\text{BOD}_n$ ) by the dilution method (PN-EN 1899-1, 2002). The given fractions were determined and calculated in accordance with the dependence given by Łomotowski and Szpindor's [7]:  $\text{COD-B as } \text{BOD}_5$ ,  $\text{COD-NB} = \text{COD}_x - 1.47 \times \text{BOD}_x$  ( $\text{COD}_x$  and  $\text{BOD}_x - 1.47 \times \text{BOD}_x$  ( $\text{COD}_x$  and  $\text{BOD}_x$  determined in the filtered sample after full biological treatment with the use of the activated sludge method - standard biodegradation test in laboratory conditions),  $\text{COD-DB} = 0.47 \times \text{BOD}_5$ ,  $\text{COD-NBSS} = \text{COD} - (1.47 \times \text{BOD}_5) - [\text{COD-NB} - (\text{COD}_x - 1.47 \times \text{BOD}_x)]$  (where: COD - full load of the determined chemical oxygen demand, COD-B - load for the easily biodegraded substances, COD-DB - load for slowly biodegraded substances, COD-NB - load for non-biodegradable substances, COD-NBSS - load for non-biodegradable suspensions) [7].

### Results and discussion

For the whole tested range of oxidant concentrations the empirical equation in the form  $\text{COD}_{p(r)} = -0.005 \times [\text{H}_2\text{O}_2]^2 + 0.2771 \times [\text{H}_2\text{O}_2] + 9.1322$  was obtained with the correlation coefficient  $R^2 > 0.95$ . The empirically determined relation was used while determining  $\text{COD}_i$  parameter in Figure 1a-c for industrial wastes being subject to aeration with the use of dispersed introduction and enhanced by pressure saturation. On the basis of the carried out tests the systematic decrease in hydrogen peroxide concentration was found in case of aerated industrial wastes samples from vegetable fats' production and in case of wastes from animal fats' production aerated with dispersed system using pressure saturation (Fig. 1a and c). In case of industrial wastes from gizzard preparation and processing, this oxidant loss was small (Fig. 1b). The change in hydrogen peroxide concentration within the aeration time depends on fractional composition in the initial COD load and fatty compounds and suspensions contents.

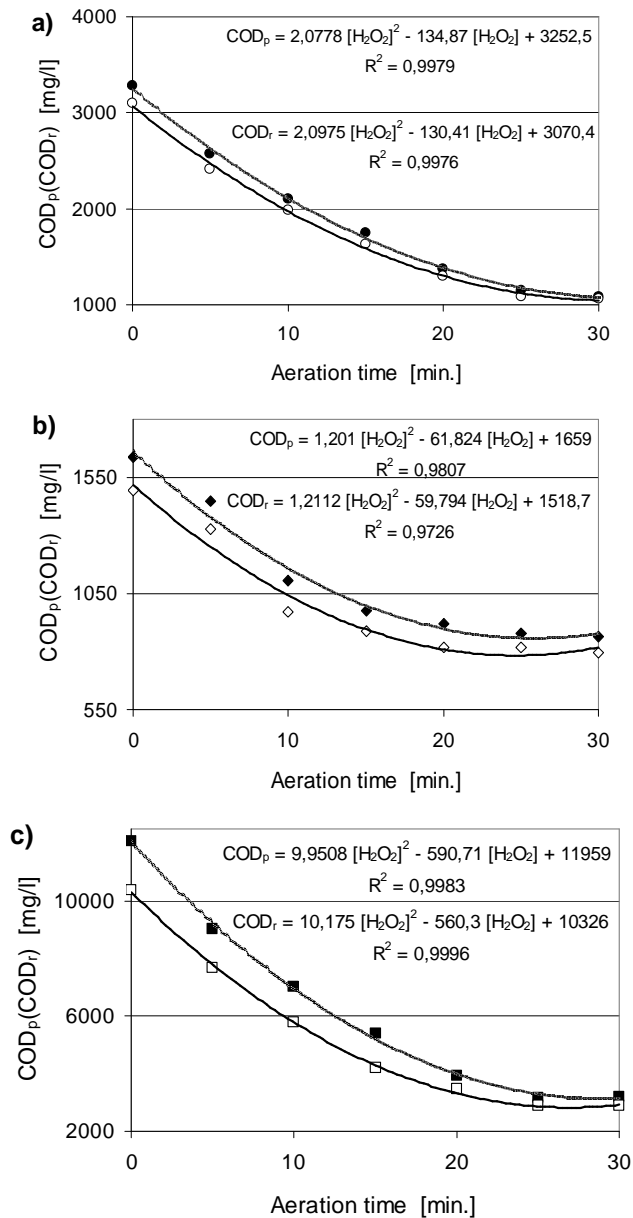


Fig. 1. Change in  $COD_p(COD_r) = f(t_{\text{aeration}})$  as a function of aeration time for the mixture of industrial wastes from: a) vegetable fats' production, b) gizzards preparation and processing, c) animal fats production

Initial parameters in case where: a) enhancing dose  $[H_2O_2]_0 - 750.0 \text{ mg/dm}^3$ ;  $COD_{p0}$  values -  $3277.8 \text{ mg/dm}^3$ ;  $COD_{r0} - 3098.0 \text{ mg/dm}^3$ ; b) enhancing dose  $[H_2O_2]_0 -$

500.0 mg/dm<sup>3</sup>. COD<sub>p0</sub> values - 1638.9 mg/dm<sup>3</sup>; COD<sub>r0</sub> - 1495.7 mg/dm<sup>3</sup>; c) aeration enhanced by pressure saturation - 350 kPa, for the aeration time - 5.0 min, enhancing dose [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub> - 5000.0 mg/dm<sup>3</sup>. COD<sub>p0</sub> values - 12087.9 mg/dm<sup>3</sup>; COD<sub>r0</sub> - 10387.6 mg/dm<sup>3</sup>.

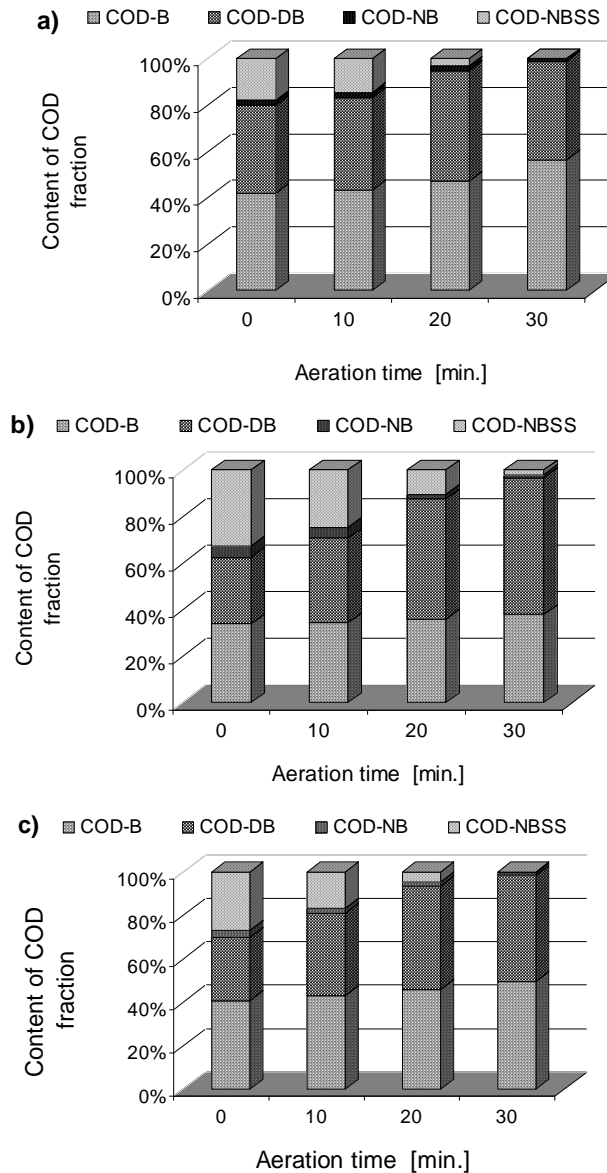


Fig. 2. Change in the COD fractional composition in relation to aeration time for industrial wastes (fractions were determined in wastes after the flotite elimination) from: a) vegetable fats production, b) gizzards' preparation and processing, c) animal fats production. Aeration technique - dispersed air with the use of Pfeiderer Water System

The form in which organic compounds occur in wastes is important for the final selection of the flotation method. This problem is also the subject of the paper. In case of the presence of compounds not susceptible to reactions (ie addition, oxidation, etc) with the use of hydrogen peroxide, the process of enhancing flotation with this compound is considerable and results in the increase in separation efficiency of the floated pollutants. It was found that in case of considerable presence of protein substances there is the essential disturbance in the flotation process which often results in the decrease in the efficiency of floated wastes removal. However, in case of a few wastes, the introduction of hydrogen peroxide to the environment of waste results in the essential change in contents of the given COD fractions in pretreated wastes. In tests for the subject raw wastes and those pretreated with  $H_2O_2$ , the fractions with the equation written below were listed:  $COD = \{[(COD-B + COD-DB)] + [(COD-NB + COD-NBSS)]\}$ .

The aim of the subject tests was determination of fractional composition in the initial raw wastes and pretreated wastes with the use of two flotation techniques. This problem is essential because the influence of this oxidant on the transformations in pollutants load structure at the stage of pretreatment is not known for the subject wastes. Often, due to the complex load composition it is difficult to determine the direction of changes in: COD/BOD, COD/N, BOD/N, COD/P and BOD/P relations which are extremely important for the further purification with the use of biological methods. On the basis of the carried research on the changes in aeration time of the COD load fractional composition (for the different types of wastes), it was found that at the stage of pretreatment with the use of hydrogen peroxide (Fig. 2a-c):

- there is the essential increase in biodegradable fractions in relation to the rest,
- there is the significant decrease in non-biodegradable fractions,
- there are the specific differences in given fractions participation depending on the waste type.

Determination of the given fractions was carried in raw and pretreated wastes after aeration, 10.0, 20.0 or 30.0 minutes after flotation phase elimination.

The determined  $COD_p(COD_r)$  after 0.0, 10.0, 20.0 and 30.0 minutes for the case where:

- a)  $COD_{p0}$ ,  $COD_{p10}$ ,  $COD_{p20}$  and  $COD_{p30}$  - 3277.8, 2108.6, 1375.7 and 1089.7  $mg/dm^3$ ;  
 $COD_{r0}$ ,  $COD_{r10}$ ,  $COD_{r20}$  and  $COD_{r30}$  - 3098.0, 1986.2, 1297.8 and 1059.6  $mg/dm^3$ ;
- b)  $COD_{p0}$ ,  $COD_{p10}$ ,  $COD_{p20}$  and  $COD_{p30}$  - 1638.9, 1107.8, 920.9 and 863.0  $mg/dm^3$ ;  
 $COD_{r0}$ ,  $COD_{r10}$ ,  $COD_{r20}$  and  $COD_{r30}$  - 1495.7, 970.8, 818.9 and 797.0  $mg/dm^3$ ;
- c)  $COD_{p0}$ ,  $COD_{p10}$ ,  $COD_{p20}$  and  $COD_{p30}$  - 12087.9, 7011.3, 3920.0 and 3199.6  $mg/dm^3$ ;  
 $COD_{r0}$ ,  $COD_{r10}$ ,  $COD_{r20}$  and  $COD_{r30}$  - 10387.6, 5780.4, 3480.0 and 2870.0  $mg/dm^3$ .

## Conclusion

Talini and Anderson's equation applies to the range of hydrogen peroxide concentrations  $0.0 \div 1000.0$   $mg H_2O_2/dm^3$  while for the range to  $7500.0$   $mg H_2O_2/dm^3$  we can apply the empirical equation in the form:  $COD_{p(r)} = -0.005 \times [H_2O_2]^2 + 0.2771 \times [H_2O_2] + 9.1322$ . Hydrogen peroxide enhanced flotation results in the increase in the process efficiency and the increase in biodegradable fractions contents in COD load determined for pretreated wastes.

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## ZAGADNIENIE KOREKTY WARTOŚCI CHEMICZNEGO ZAPOTRZEBOWANIA NA TLEN W JEGO OZNACZENIACH W ŚCIEKACH OCZYSZCZANYCH METODAMI Z UDZIAŁEM NADTLENKU WODORU

**Streszczenie:** Zastosowanie nadtlenu wodoru w procesach podczyszczania ścieków wiąże się z koniecznością wprowadzania korekty w oznaczeniu puli ChZT (chemiczne zapotrzebowanie na tlen). Zastosowanie takiej procedury pozwala na dokładne określenie szybkości redukcji i zmian składu frakcji ChZT zachodzących podczas oczyszczania z zastosowaniem tego utleniacza. W ramach niniejszej pracy wyznaczono empiryczne równanie korygujące udział nadtlenu wodoru w puli ChZT w zakresie stężeń 0,0÷7500,0 mgH<sub>2</sub>O<sub>2</sub>/dm<sup>3</sup>. Na wybranych przykładach ścieków przemysłowych przedstawiono wpływ tego związku na zmianę zależności ChZT = f(t) w czasie napowietrzania dwiema technikami oraz na zmianę poszczególnych frakcji ChZT w czasie podczyszczania.

**Słowa kluczowe:** oznaczanie ChZT, nadtlenek wodoru, współczynnik korygujący, oczyszczanie ścieków