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APPLICATION OF ANOLYTE FROM ELECTROLYSIS OF SULFURIC ACID TO OXIDATION OF INDUSTRIAL WASTEWATER ORGANICS

The waste sulfuric acid has been processed to peroxysulfuric acids by electrolysis. The anolyte obtained has been applied to the oxidation of non-ionic detergents in the aqueous solutions and to the treatment the original textile and the dyestuffs production wastewaters. The anolyte appeared to be effective in the treatment of the selected bio-resistant pollutants. The optimum process parameters has been determined. The main disadvantage of the treatment method is the increased concentration of sulfates.

1. INTRODUCTION

In a number of industrial processes considerable amounts of organic and inorganic wastes are formed. One of them is sulfuric acid from sulfonation process. The acid, while undergoing electrolysis at sufficiently high current density, is partly processed to peroxysulfuric acids [3] which can be used for oxidation of waste components resistant to biochemical decomposition [1, 2, 4].

2. CONDITIONS OF SULFURIC ACID ELECTROLYSIS AND COMPOSITION OF ANOLYTE

Electrolysis of sulfuric acid was carried out in a diaphragm cell presented in fig. 1. Sulfuric acid (50%, $d = 1.4$) was introduced to cathode space, whereas the products of electrolysis containing peroxy compounds were temporarily carried away from the water-coil cooled anode space. Concentration of oxidizing agents in anolyte depends on current density, temperature and time of electrolysis.

An increase in current density stimulated the formation of oxidizing agents, but simultaneously the rising temperature accelerated their decomposition.

Formation of peroxy compounds and their decomposition can be presented by the following reactions:

$$2HSO_4^- - 2e = H_2S_2O_8,$$

$$H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4,$$

$$H_2SO_5 + H_2O = H_2SO_4 + H_2O_2,$$

$$H_2O_2 + 2H_2SO_4 = H_2S_2O_8 + 2H_2O,$$

$$H_2O_2 = H_2O + \frac{1}{2}O_2.$$

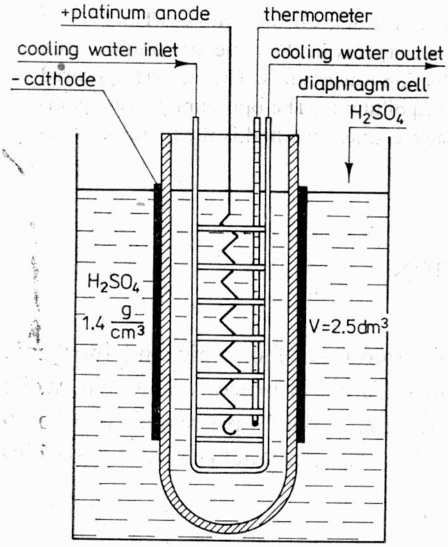

Fig. 1. Scheme of the apparatus for electrolysis of sulfuric acid

Rys. 1. Schemat aparatury do elektrolizy kwasu siarkowego

The increase in concentration of oxidizers, depending on the time of electrolysis at current density of 1.5 A/cm² on the anode and temperature of 25° C, is presented in fig. 2. From the figure it follows that the concentration of oxidizers in an anolyte reaches after some time a constant value. The time and concentration were approximately the same both for the pure acid and for that being a waste product from nitrobenzene sulfonation. The time within which the concentration of peroxysulfuric compounds in an anolyte became constant (880—930 mvql/dm³) was about 90 min. After electrolysis had been finished, the concentration of oxidizers in an anolyte decreased gradually due to their decomposition (fig. 3). That is why the time of wastewater oxidation with anolytes should be performed in the shortest possible time.

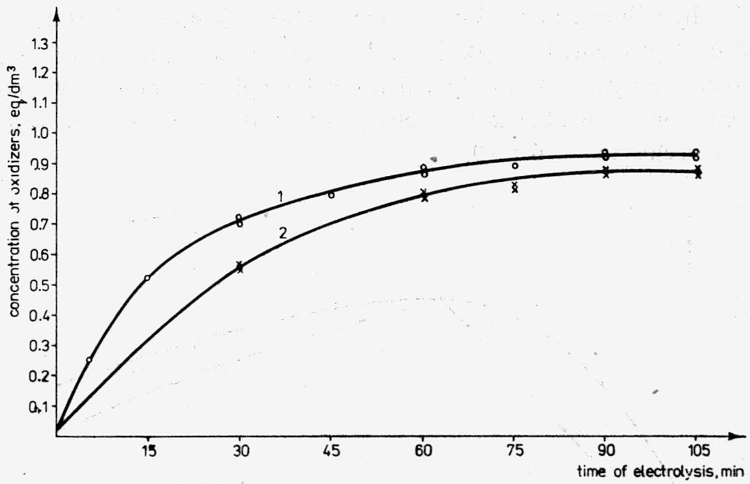

Fig. 2. Concentration of oxidizing agents in an anolyte versus the time of electrolysis

1 — pure sulfuric acid, *2* — waste sulfuric acid

Rys. 2. Zależność stężenia utleniaczy w anolicie od czasu elektrolizy

1 — czysty kwas siarkowy, *2* — odpadowy kwas siarkowy

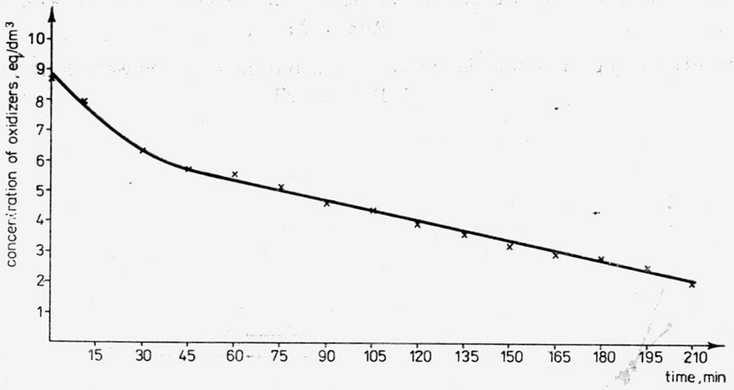

Fig. 3. Concentration of oxidizing agents in an anolyte after electrolysis is completed

Rys. 3. Stężenie utleniacza w anolicie po zakończeniu elektrolizy

3. OXIDATION OF MODEL SOLUTIONS

Optimum oxidation conditions were determined by using model solutions of nonionic detergents of ethoxylated alkylphenols: Rokaphenol N-6 and Roksol JT. Those solutions contained 100 mg of a surfactant in 1 dm^3. The experiments determined the influence of pH and reaction time on the degree of surfactant oxidation. The dose of anolyte was 5% by volume. For pH correction 4 molar solution of NaOH was used. The results obtained are presented in figs. 4—6. As it can be seen in figs. 4 and 5 the highest efficiency of oxidation process is obtained for pH ranging from 4 to 9; but because of the requirements for the wastewaters discharged into the city sewerage system the optimum pH range seems to be 6.5—9.

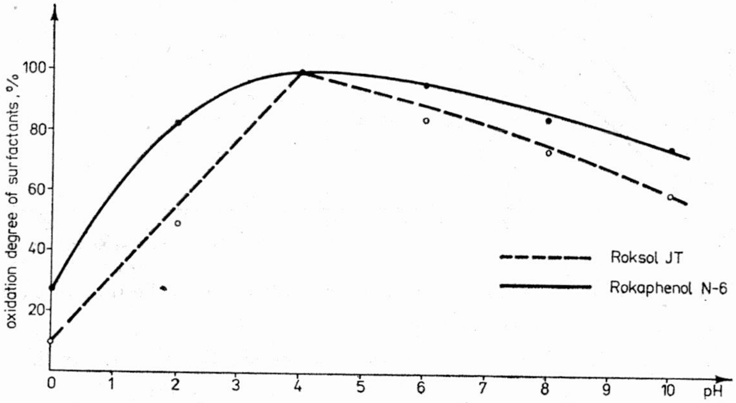

Fig. 4. Influence of pH on oxidation degree of surfactants in model solutions of Rokaphenol N-6 and Roksol JT

Rys. 4. Wpływ pH na stopień utleniania surfaktantu w modelowych roztworach Rokofenolu N-6 i Roksolu JT

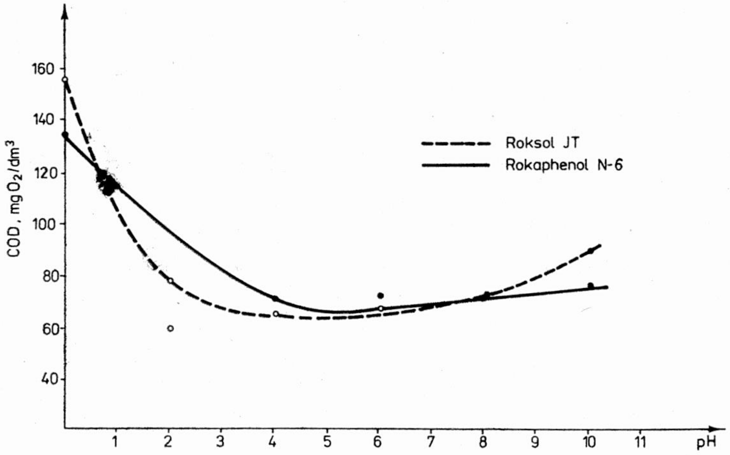

Fig. 5. COD in model solutions after oxidation of detergents with anolyte depending on pH

Rys. 5. Wpływ pH na ChZT roztworu modelowego po utlenieniu detergentów anolitem

The investigations have shown that reaction time slightly affects the oxidation degree (fig. 6), but the process takes longer than about 4 hours to be completed.

It should, however, be noticed that reaction time depends to a considerable degree on the composition of the wastewaters, e.g. on the concentration of iron ions which catalyze decomposition of peroxy compounds.

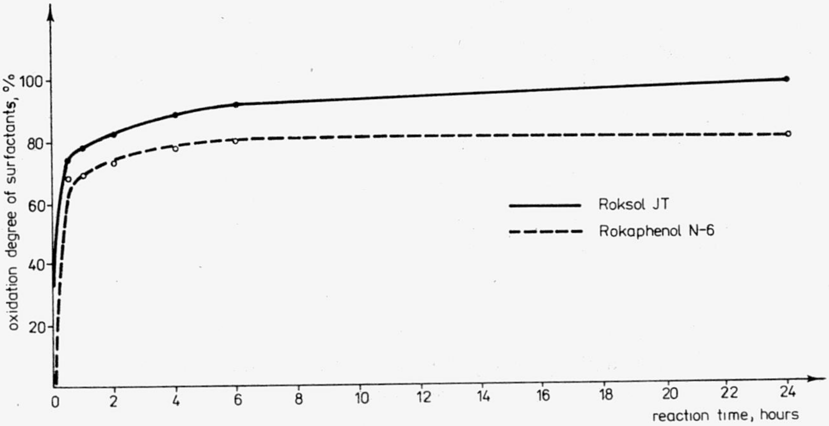

Fig. 6. Oxidation degree of surfactants versus the reaction time for model solutions of Rokaphenol N-6 and Roksol JT

Rys. 6. Zależność stopnia utlenienia surfaktantów od czasu reakcji dla modelowych roztworów Rokafenolu N-6 i Roksolu JT

4. OXIDATION OF ORGANIC COMPONENTS IN WASTEWATERS

Anolyte obtained from the waste sulfuric acid was applied for oxidation of organic components in the wastewaters from textile and dyestuffs industries. The doses of anolyte, equal to 10% and 15% of wastewater volume, were taken from the electrolyser and immediately mixed with wastewater. In order to determine the degree of oxidation of organic compounds the mixture was neutralized to pH = 7 and analysed after 1 hour. From the analysis it follows that the oxidation degree depends on the dose of anolyte and the type of wastewater. In the textile wastewaters (tab. 1) oxidation of anionic detergents and sulfides was complete. Total contents of organics (referred to COD) decreased by 66—97% depending on the initial COD value.

In wastewaters from dyestuffs producing industry (tab. 2) the degree of oxidation of organic pollutants was much lower (from 40 to 79%). It was probably due to their considerably smaller initial concentrations (given in tab. 2 as COD).

It seemed interesting to compare results of oxidation of the same wastewaters from production of dyestuffs using proxysulfuric compounds and ozone produced in an air-supplied laboratory ozonator.

Table 1

Oxidation of textile wastewaters pollutants

Utlenianie zanieczyszczeń ścieków tekstylnych

Type of wastewaters	General wastewater		Dying wastewater			Finishing wastewater	
Dose of anolyte, dm^3/dm^3	0	0.1	0	0.1	0.15	0	0.1
COD, mg O_2/dm^3	1150	390	4200	500	125	750	135
COD removal, %	—	66	—	88	97	—	82
Anionic detergents, mg/dm^3	10	0	5.6	0	0	10.5	0
Anionic detergents removal, %	—	100	—	100	100	—	100
Sulfides, mg/dm^3	12	0	36	0	0	0.5	0
Removal of sulfides, %	—	100	—	100	100	—	100

Table 2

Oxidation of the pollutants of dyestuffs industry wastewaters

Utlenianie zanieczyszczeń ścieków z przemysłu barwnikowego

Dose of anolyte dm^3/dm^3	COD mg/dm^3 O_2	COD removal %
0	840	—
0.05	300	64
0.10	240	71
0.15	180	79
0	130	—
0.05	440	40
0.10	280	62
0.15	240	67

After a 2.5 hour ozonation with 35 mg O_3/hr dm^3 dose of oxidant the COD of wastewaters decreased by 90%. Thus, in the case of ozone, the COD removal was much higher than that achieved with an anolyte, but the ozonation did not decrease the toxicity of wastes, while the addition of anolyte apparently reduced the toxicity of wastewaters which was determined with respect to *Daphnia magna*.

If we assume the toxicity of raw wastewater being equal to 100%, then after ozonation it ranged from 82% to 150%, thus it even increased. For the same wastewaters treated with anolyte the toxicity ranged from 23% to 77% of the initial value, thus it was substantially reduced.

Essential disadvantage of anolyte application for oxidation of wastewater components is the increasing concentration of sulfates.

Thus, in spite of a very good effects of oxidation of waste components with an anolyte, this method may be recommended wherever a waste sulfuric (at least 40%) is available. The acid may be subject to electrolysis at the electric current density of 1.5 A/cm^2 and the resulting anolyte can be applied as an efficient oxidant of wastewater organics which is able to reduce significantly the wastewater toxicity.

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ZASTOSOWANIE ANOLITU Z ELEKTROLIZY KWASU SIARKOWEGO DO UTLENIANIA ŚCIEKÓW PRZEMYSŁOWYCH

Podczas elektrolizy z odpadowego kwasu siarkowego otrzymywano nadtlenowe kwasy siarkowe. Uzyskany anolit stosowano do utleniania niejonowych detergentów w roztworach wodnych i do oczyszczania surowych ścieków z przemysłu tekstylnego i produkcji barwników. Okazało się, że anolit jest efektywnym czynnikiem w oczyszczaniu wybranych zanieczyszczeń opornych na biodegradację. Oznaczono optymalne parametry procesu. Główną wadą tej metody oczyszczania są podwyższone stężenia siarczanów.

VERWENDUNG DER ANODENFLÜSSIGKEIT AUS DER ELEKTROLYSE VON SCHWEFELSÄURE ZUR OXYDATION VON INDUSTRIEABWÄSSERN

Während der Elektrolyse der Abfallschwefelsäure, wurden Peroxoschwefelsäuren erhalten. Die Anodenflüssigkeit wurde zur Oxydation von nichtionogenen Detergentien in wässrigen Lösungen und zur Reinigung von rohen Abwässern der Textilindustrie und aus der Farbstoffherstellung verwendet. Die Anodenflüssigkeit wirkt effektiv auf die Verunreinigungen ein, die sich zur Biodegradation resistent verhalten. Bestimmt wurden optimale Prozeßparameter. Als wichtiger Nachteil dieser Reinigungsmethode ist die höhere Sulfatkonzentration zu nennen.

ПРИМЕНЕНИЕ АНОЛИТА ИЗ ЭЛЕКТРОЛИЗА СЕРНОЙ КИСЛОТЫ ДЛЯ ОКИСЛЕНИЯ ПРОМЫШЛЕННЫХ СТОЧНЫХ ВОД

Во время электролиза из отработанной серной кислоты получали надкислородные серные кислоты. Полученный анолит применялся для окисления неионных детергентов в водных растворах и для очистки сырых сточных вод текстильной промышленности и производства красителей. Оказалось, что анолит является эффективным реагентом в очистке избранных загрязнений, стойких против биодеградации. Определены оптимальные параметры процесса. Главным недостатком этого метода очистки являются повышенные концентрации сульфатов.