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OXIDATION OF SULPHITES IN WASTEWATER WITH CITRIC ACID

The results of the investigations on the sulphites removal from the vegetable processing wastes are presented. The wastes contained citric acid and sulphites (55–273 g SO_3^{2-}/m^3). It has been stated that an efficient removal of sulphite from aerated wastes occurs at pH 6.5. At the aeration intensity of 2 m^3 air/m^3 h and in the presence of catalyst (1g Fe^{3+}/m^3), the efficiency of sulphite removal exceeds 90% during 3 h at most.

A fast and efficient removal of sulphites from wastewater is assured by chlorination process. The chlorine dose required is 0.9 D_t, where D_t is the theoretical dose equal to 0.88 g Cl_2/g SO_3^{2-}. It guarantees a complete oxidation of sulphites in time not exceeding 15 minutes, the concentration of residual chlorine being close to zero.

1. INTRODUCTION

The concentration of sulphites in surface water is not limited, their presence is, however, not indifferent to aquatic organisms. According to MEINCK [1] sodium sulphite in concentration of 100 g/m^3 is harmful to fish. Sulphites are also noxious for anaerobic microorganisms: in concentration of 100 g/m^3 the fermentation process is significantly limited. The noxious effect of sulphite is first of all due to the fact that under favourable conditions they may be oxidized to sulphates by utilizing oxygen dissolved in water. Taking into account the course of sulphite oxidation presented in the former paper [2], it may be easily calculated that the oxidation of 60 g of sulphites/m^3 requires 8 g of oxygen/m^3, thus the whole amount of oxygen dissolved in water. Moreover, it should be noticed that the concentration of sulphates, the product of sulphites oxidation, in surface water is limited, e.g. for the water of the 1st class of purity it amounts to 150 g/m^3. From the equations presented in [2] it may be stated that such an amount of sulphates results from the oxidation of 168 g of sulphites/m^3.

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Hence, it follows that noxious effect of sulphites on aquatic organisms occurs at their concentrations lower than 60 g/m^3 at which under favourable conditions there occurs deoxidation of the receiving water.

2. EXPERIMENTAL

2.1. AERATION OF WASTEWATER

The aeration process was conducted in the set-up described in details in [2]. The aeration is performed by means of a porous diffuser placed at the bottom of a cylinder filled with wastewater.

The investigations of wastes from vegetable processing plant were carried out. The wastes contained sodium bisulphite and citric acid. Due to the fact that the concentrations of wastes from the separate sections of the plants differed considerably, the wastes from blanching and final bath of mushrooms were mixed and appropriately diluted with tap water, therefore their composition was similar to this of total wastes. For this reason the aeration process involved 3 kinds of wastes of various sulphite concentrations (C_o), i.e. diluted wastes from blanching (55 g SO_3^{2-}/m^3), diluted mixture of wastes from blanching and final bath (83 g SO_3^{2-}/m^3) and the mixture of wastes from blanching and final bath (136 g SO_3^{2-}/m^3). The process of aeration was conducted in the presence of $FeCl_3 \cdot 6H_2O$ as a catalyst which is particularly advantageous for the oxidation of sulphites [3]. The concentration of the catalyst (C_k) based on the previous investigations [2] was equal to 1 g Fe^{3+}/m^3. The aeration process was conducted at a constant intensity (I) of 2 m^3 air/m^3h which is included within the range applied to fine-bubble aeration of wastewater [4] and results from the previous investigations performed with model solutions [2].

2.2. CHLORINATION OF WASTES

Chlorination process involved 2 kinds of wastes, i.e. from blanching (273 g SO_3^{2-}/m^3) and final bath (136 g SO_3^{2-}/m^3) of mushrooms. Theoretical dose of chlorine indispensable to oxidation of sulphites was determined from the equation

$$SO_3^{2-} + OCl^- \rightarrow SO_4^{2-} + Cl^-.$$
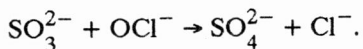
Theoretical dose (D_t) amounts to 0.88 g Cl_2/g SO_3^{2-}. Chlorination was conducted with sodium hypochlorite. After the wastes were neutralized (pH 6.5–7.0), the oxidizing agent was added in the following doses: 0.8, 0.9 and 1.0 D_t. Thereupon the changes in concentrations of residual chlorine (Cl_{2r}) and sulphites occurring in time were determined.
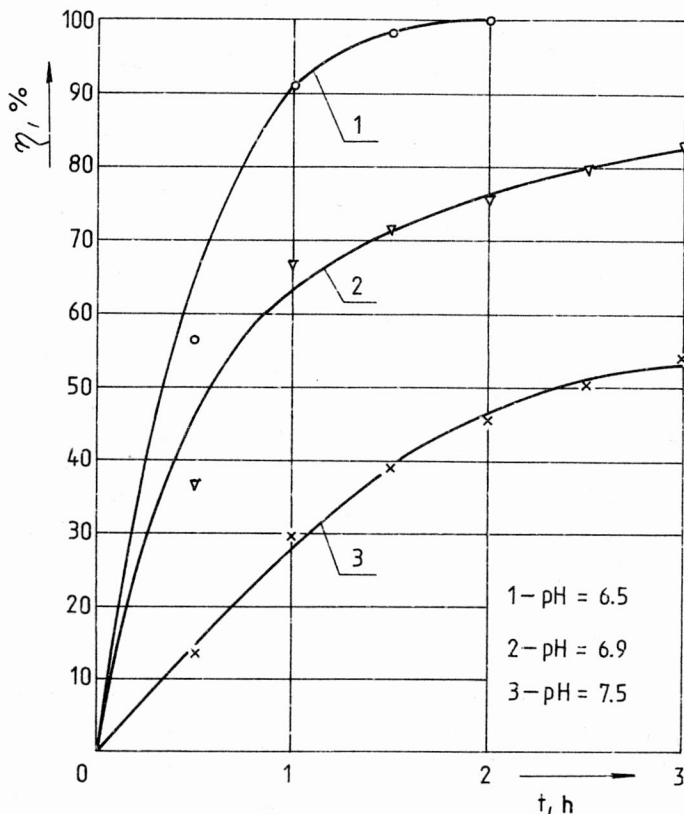
Fig. 1. Degree of sulphite removal (η) vs. aeration time (t) of diluted wastes of various pH from blanching.
$C_0 = 55$ g of SO_3^{2-}/m^3, $C_k = 1$ g of Fe^{3+}/m^3, $I = 2$ m^3 of air/m^{3}h

3. RESULTS AND DISCUSSION

3.1. SULPHITE REMOVAL FROM WASTEWATER IN AERATION PROCESS

It has been stated that citric acid present in wastes makes impossible the oxidation of sulphites even at high doses of the catalyst; it does not show inhibitory effect solely in a very narrow range of pH (6.1–6.7). It may be presumed that within this range there appear in solution positive colloidal particles of ferric hydroxide resulting from hydrolysis of ferric chloride, which coagulate citric acid radicals. In this way citric acid may be removed from the medium in which sulphites are oxidized catalytically.

The data concerning the effect of pH of wastes on the efficiency of sulphite removal are presented in fig. 1. The investigations involved diluted wastes from blanching (pH 6.5, 6.9 and 7.5). From the data presented it follows that at pH 6.5 the oxidation of wastes is the quickest, as a complete oxidation of sulphites occurs within 2 h of aeration. At the same time the sulphite removal from wastes of pH 6.9 and 7.5 amounts to 76 and 46%, respectively.
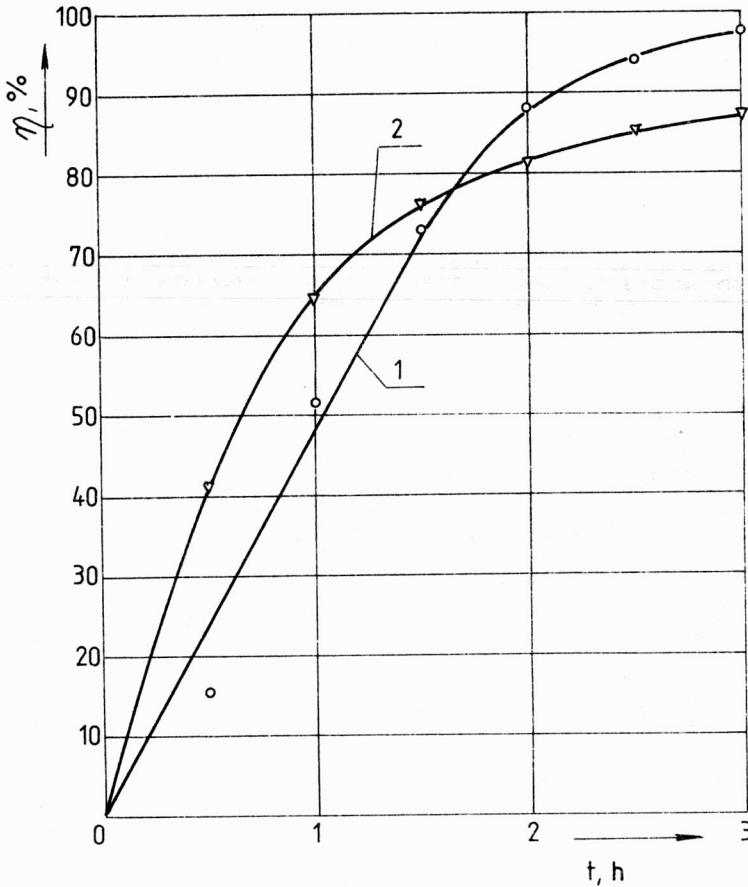
Fig. 2. Degree of sulphite removal (η) vs. aeration time (t) of diluted mixture of wastes from blanching and final bath (1) and mixture of wastes from blanching and final bath (2), pH = 6.5, C_k = 1g of Fe^{3+}/m^3, I = 2 m^3 of air/m^3h

The next analyses were made with diluted mixture of wastes from blanching and final bath, neutralized to pH 6.5. The results obtained are presented in fig. 2 (curve 1). It has been noticed that the admixture of wastes from final bath makes the catalytic oxidation of sulphites considerably slower. The aeration time required increases from 2 h (diluted wastes from blanching) to 3 h (diluted mixture of wastes). This phenomenon is due to a considerable concentration of citric acid in wastes from final bath (pH 5.2).

The above observation has been confirmed by final results of aeration of the mixture of wastes from blanching and final bath. From the shape of curve 2 shown in fig. 2, it may be induced that the process of sulphite oxidation is less efficient if the percentage of wastes from final bath is high. This efficiency is not improved significantly even when the aeration lasts longer than 3 h. Hence, it follows that the wastes from final bath must be about 10 times diluted with other wastes of a low concentration of citric acid.
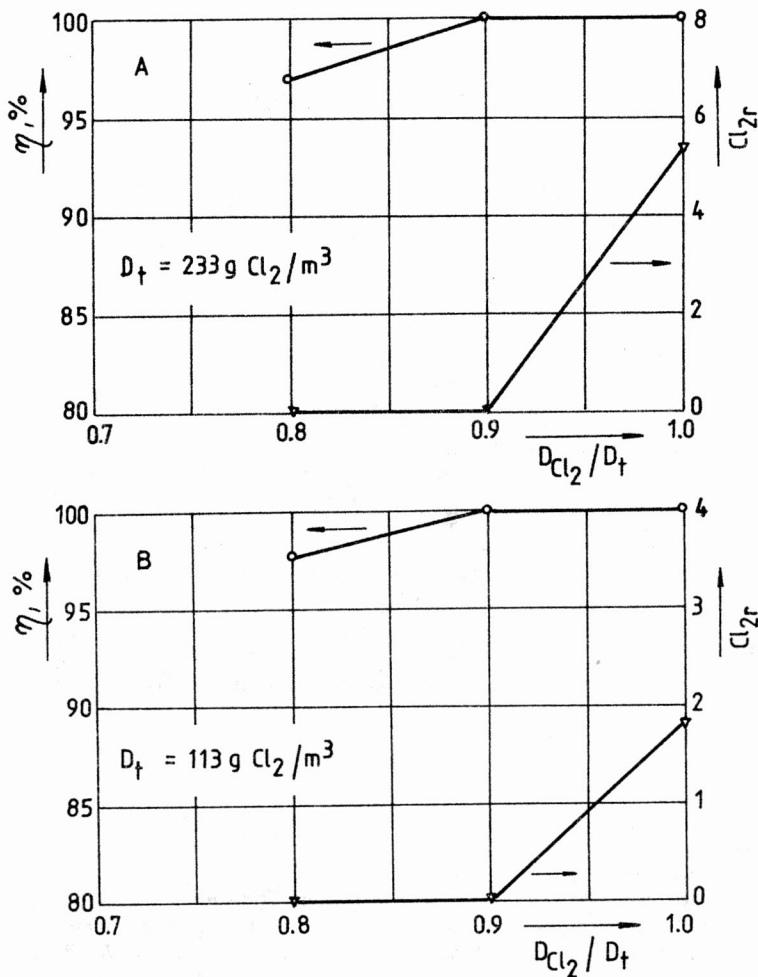
Fig. 3. Degree of sulphite removal (η) and concentration of residual chlorine (Cl_{2p}) vs. chlorine dose referred to the theoretical one (D_{Cl_2}/D_t) for wastes from blanching (A) and mixture of wastes from blanching and

final bath (B)

3.2. SULPHITE REMOVAL FROM WASTEWATER IN CHLORINATION PROCESS

Taking into consideration the fact that sulphites are not completely oxidized in aeration process, the efficiency of their removal by chlorination has been examined. Results of analyses are presented in fig. 3.

It has been noticed that chlorination of wastes runs in the way similar to that of model solutions of sulphites. For $D_{Cl_2} \leq 0.9 D_t$ the maximum oxidation degree is achieved in 15

min, whereas for $D_{Cl_2} = 0.9\,D_t$ a complete oxidation occurs as soon as in 5 min. This dose, however, should be considered too high because of the presence of free chlorine in solution. The optimal doses of chlorine for wastes from blanching and their mixture with final bath are 210 g Cl_2/m^3 and 102 g Cl_2/m^3, respectively.

It should be noticed that for the wastes the optimal doses of chlorine are somewhat higher than those for model sulphite solutions (0.8–0.85 D_t). This due to easily oxidizing organic compounds present in wastes. For the same reason the concentration of residual chlorine (at its highest dose) is relatively low.

4. CONCLUSIONS

1. Oxidation of sulphites by aeration in wastewater in the presence of citric acid must be conducted at pH~ 6.5. The removal efficiency of sulphites higher than 90% and in time not exceeding 3 h is possible when the aeration intensity is 2 m^3 air/m^3h, and the concentration of $FeCl_3 \cdot 6H_2O$ catalyst is 1g Fe^{3+}/m^3.

2. Oxidation of sulphites in wastewater by means of sodium hypochlorite is a very fast and undisturbed process. If D_t denotes a theoretical dose of chlorine ($D_t = 0.88$ g Cl_2/g SO_3^{2-}), then the application of a dose equal to 0.9 D_t makes possible a complete oxidation of sulphites during 15 minutes at most, the concentration of residual chlorine being close to zero.

REFERENCES

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UTLENIANIE SIARCZYNÓW W ŚCIEKACH ZAWIERAJĄCYCH KWAS CYTRYNOWY

Przedstawiono wyniki badań nad usuwaniem siarczynów ze ścieków pochodzących z zakładu przetwórstwa warzyw. Ścieki zawierały kwas cytrynowy oraz siarczyny w ilości 55–273 g SO_3^{2-} /m^3. Stwierdzono, że skuteczne usunięcie siarczynów w procesie napowietrzania ścieków zachodzi przy pH~6,5. Prowadząc proces napowietrzania z intensywnością 2 m^3 powietrza/m^3h w obecności katalizatora o stężeniu 1 g Fe^{3+}/m^3, uzyskuje się ponad 90% usunięcie siarczynów w czasie do 3 godzin.

Szybkie i skuteczne usunięcie siarczynów ze ścieków zapewnia proces chlorowania. Wymagana dawka chloru wynosi 0.9 D_t; D_t jest dawką teoretyczną równą 0,88 g Cl_2/g SO_3^{2-}. Wymieniona dawka zapewnia pełne utlenienie siarczynów w czasie do 15 min, a stężenie chloru pozostałego jest bliskie zeru.

ОКИСЛЕНИЕ СУЛЬФИТОВ В СТОЧНЫХ ВОДАХ, СОДЕРЖАЩИХ ЛИМОННУЮ КИСЛОТУ

Представлены результаты исследований удаления сульфитов из сточных вод, происходящих из овощеперерабатывающих заводов. Сточные воды содержали лимонную кислоту и сульфиты количеством в 55–273 г SO_3^{2-} / m^3. Было установлено, что эффективное удаление сульфитов в процессе аэрации сточных вод имеет место при pH 6,5. Проводя процесс аэрации с интенсивностью 2 $м^3$ воздуха/$м^3$ч в присутствии катализатора концентрацией в 1 г Fe^{3+}/$м^3$ получается свыше 90-процентное удаление сульфитов в течение до 3 часов.

Быстрое и эффективное удаление сульфитов из сточных вод обеспечивает процесс хлорирования. Требуемая доза хлора составляет 0,9 D_t; D_t является теоретической дозой равной 0,88 г Cl_2/г SO_3^{2-}. Приведенная выше доза обеспечивает полное окисление сульфитов в течение до 15 минут, а концентрация оставшегося хлора близко нулю.