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OXIDATION OF SULPHITES IN AQUEOUS SOLUTIONS

The paper presents the way of sulphites removal from aqueous solutions by means of aeration and chemical oxidation. The effects of catalyst concentration and the time and intensity of aeration on the removal efficiency have been investigated. The required dose of the catalyst (ferric chloride) depends on the concentrations of sulphites: being 1 g/m³ for low concentrations (up to 200 g/m³) and 2 g/m³ for the higher ones. The application of the above mentioned doses may bring about the oxidation of sulphites even higher than 95% during at most 3 hours, at the aeration intensity of 1.5–2.0 m³ air/m³·h.

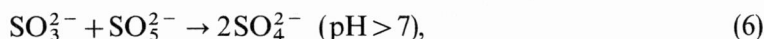
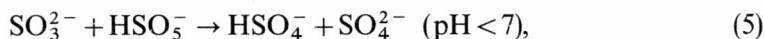
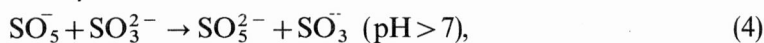
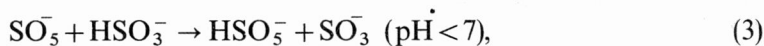
In order to oxidize sulphites with chlorine its dose introduced to the solution should amount to (0.8–0.85) D_t , where D_t is a theoretical dosage of chlorine ($D_t = 0.88 \text{ g Cl}_2/\text{g SO}_3^{2-}$). The above dosage assures a 97–100% oxidation of sulphites during 5 minutes at the concentration of residual chlorine close to 0.

1. INTRODUCTION

The process of sulphites oxidation in water is usually realized by means of atmospheric oxygen in the presence of a catalyst. In this process the role of the catalyst is performed by the ion of a suitable metal, i.e. manganese, cobalt, iron or copper. As yet the process of sulphite oxidation with oxygen has not been sufficiently explained. It is known that its course depends on the kind and concentration of the catalyst as well as on the pH of solution. According to HEGG and HOBBS [1] the most probable course of oxidation is the following:



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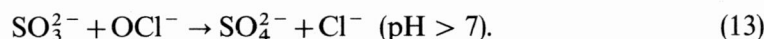
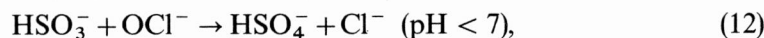


On the other hand, the mechanism given by GOMÓŁKA and SZAYNOK [2] takes into account solely the ion of HSO_3^- , thus it refers to the acid reaction of the medium:



In the above reactions M^+ denotes the cation of a transient metal which initiates the chain reaction. According to TRZEPIERCZYŃSKA [3] the particularly useful cation is Fe^{3+} — the higher is its concentration, the higher is the degree of sulphites oxidation.

The oxidation of sulphites may also be realized with the help of an oxidizing agent. In the case of chlorine this process runs as follows:



From the reactions (12) and (13) it follows that the oxidation of sulphites by means of a strong oxidizer requires no catalyst.

2. EXPERIMENTAL

2.1. OXIDATION OF MODEL SOLUTIONS OF SULPHITES BY AERATION

The experiment has been performed according to the scheme presented in fig. 1. Air pump (1) forces the air through a rotameter (2) to a porous diffuser (3) placed on the bottom of a 2 dm^3 vessel (4) filled with the solution. The diffuser is a pipe with

porous walls made of sintered poly(methyl methacrylate). The valve (5) allows a smooth regulation of the air flow rate. The experiment has been performed for 3 air flow rates (3, 4, and 6 dm³/h), the corresponding aeration intensities (I) being 1.5, 2 and 3 m³ air/m³ · h. The presented intensities are included within the range used for a fine-bubble aeration of wastewater [4].

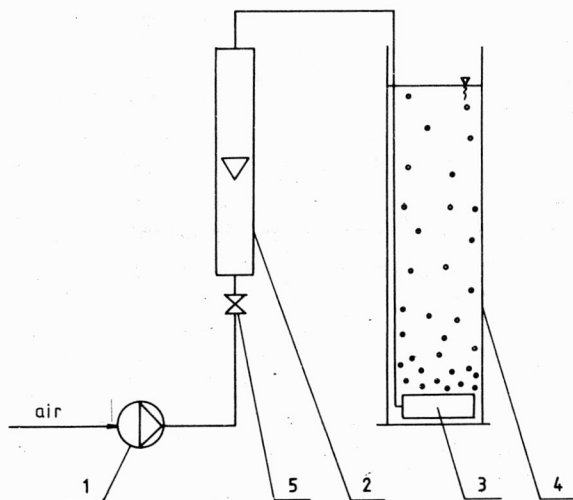


Fig. 1. Experimental set-up

1 - aeration pump, 2 - rotameter, 3 - porous diffuser, 4 - vessel with solution, 5 - control valve

The concentrations of sulphites (C_0) used in the experiment ranged from 10 to 400 g SO₃²⁻/m³ with ferric chloride (FeCl₃ · 6H₂O) as a catalyst. Its concentration in water (C_k) (calculated for ferric ion) varied from 0.1 to 2 mg Fe³⁺/m³, depending on the concentration of sulphites.

2.2. OXIDATION OF MODEL SOLUTIONS OF SULPHITES BY MEANS OF SODIUM HYPOCHLORITE

The experimental concentrations of sulphites ranged from 10 to 400 g SO₃²⁻/m³. The theoretical dose of chlorine (D_t) indispensable to the oxidation of sulphites has been calculated from the equation (13). It amounts to: $D_t = 0.88$ g Cl₂/g SO₃²⁻. The doses of the oxidizing agent introduced to the solutions of sulphites ranged from 0.5 to 1.05 D_t . After the solutions were mixed the changes in concentrations of sulphites

and residual chlorine (Cl_{2p}) occurring in time [5] have been investigated.

3. RESULTS AND DISCUSSION

3.1. THE EFFECTS OF THE CATALYST CONCENTRATION AND OF THE TIME AND INTENSITY OF AERATION ON THE EFFICIENCY OF SULPHITES REMOVAL

In the first phase of investigations the concentration of the catalyst necessary to obtain the maximal degree of sulphite removal has been determined during the aeration time not exceeding 3 h, i.e., typical time of wastewater aeration. Initial concentration of the solution subject to aeration amounted to $50 \text{ g SO}_3^{2-}/\text{m}^3$, while the concentration of the catalyst ranged from 0 to $1.0 \text{ g Fe}^{3+}/\text{m}^3$. The obtained results are presented in fig. 2.

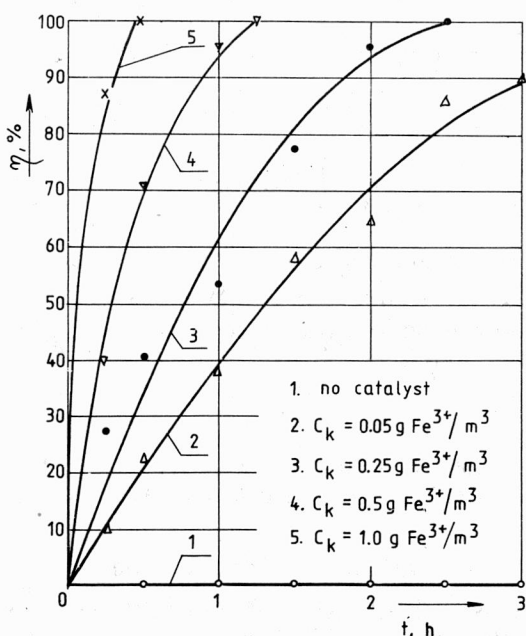


Fig. 2. Degree of sulphite removal (η) vs aeration time (t) at various concentrations of catalyst (C_k) (acid solutions)

$$C_0 = 50 \text{ g SO}_3^{2-}/\text{m}^3, I = 2 \text{ m}^3 \text{ air}/\text{m}^3 \cdot \text{h}$$

From the performed analysis it follows that sulphites cannot be removed if the solution does not contain iron ions, whereas a small addition of the catalyst (0.05 g

$\text{Fe}^{3+}/\text{m}^3$) makes possible the oxidation of about 90% of sulphites in the required time. The time of aeration decreases with the increasing concentration of the catalyst and for $1.0 \text{ g Fe}^{3+}/\text{m}^3$ it amounts scarcely to 0.5 h. It should be emphasized that the investigations were performed in acid reaction (pH 4–4.5) which was reduced to about pH 3.5 during aeration. Since the processes of biological treatment which can be applied to wastes containing sulphites require that the pH of solution be close to the neutral one, the further analyses were performed at pH = 7.

Solutions subject to aeration had the same initial concentrations of sulphites ($50 \text{ g SO}_3^{2-}/\text{m}^3$); the concentrations of the catalyst being 0.5 and $1.0 \text{ g Fe}^{3+}/\text{m}^3$. During aeration the reaction of solution was corrected to pH 7.0. Results of analyses presented in fig. 3 show univocally that in neutral solution the time required for a full oxidation of sulphites is much longer than in the case of acid solutions. Thus, at the concentration of catalyst equal to $0.5 \text{ g Fe}^{3+}/\text{m}^3$ the aeration time grows from 1.25 h to more than 2 h. Since an almost 100% removal of sulphites has been obtained for the concentration of Fe ions equal to $1 \text{ g Fe}^{3+}/\text{m}^3$ (in time not exceeding 3 h), this concentration was taken as the optimal one and applied in further experiments.

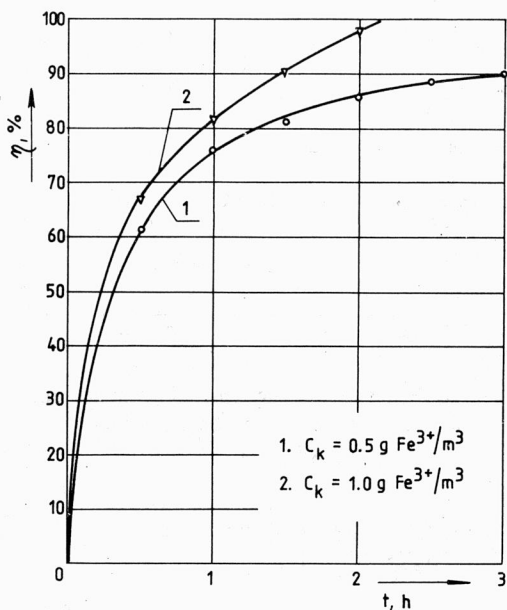


Fig. 3. Degree of sulphite removal (η) vs aeration time (t) at various concentrations of catalyst (C_k) (neutral solutions)

$$C_0 = 50 \text{ g SO}_3^{2-}/\text{m}^3, I = 2 \text{ m}^3 \text{ air}/\text{m}^3 \cdot \text{h}$$

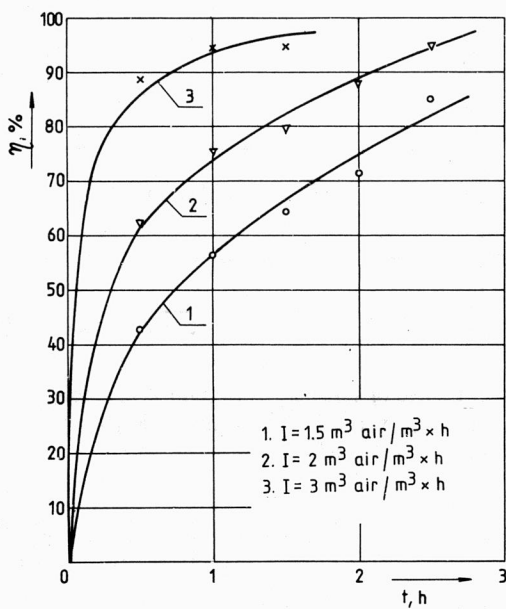


Fig. 4. Degree of sulphite removal (η) vs aeration time (t) at various aeration intensities (I)

$$C_0 = 10 \text{ g SO}_3^{2-}/\text{m}^3, C_k = 1 \text{ g Fe}^{3+}/\text{m}^3$$

These experiments were intended to determine the required aeration intensity for different initial concentrations of sulphites. Some selected results of analyses are presented in figs 4–6. It has been stated that in concentrations ranging from 10

to $200 \text{ g SO}_3^{2-}/\text{m}^3$ the efficiency of sulphites removal exceeds 95% at the catalyst dose of $1 \text{ g Fe}^{3+}/\text{m}^3$ and the aeration intensity of $1.5 \text{ m}^3 \text{ air}/\text{m}^3 \cdot \text{h}$. Under the above conditions the required aeration time does not exceed 2.5 h. In the highest concentrations of sulphites (300 and $400 \text{ g SO}_3^{2-}/\text{m}^3$) the addition of $1 \text{ g Fe}^{3+}/\text{m}^3$ appeared to be insufficient even at the highest aeration intensity. The required dose of the catalyst for the above concentrations is $2 \text{ g Fe}^{3+}/\text{m}^3$. The recommended aeration intensity ranges then from 1.5 to $2.0 \text{ m}^3 \text{ air}/\text{m}^3 \cdot \text{h}$, and the aeration time does not exceed 2.5 h. It may be reduced to 1.5 – 2 h when the intensity of aeration is higher ($3 \text{ m}^3 \text{ air}/\text{m}^3 \cdot \text{h}$).

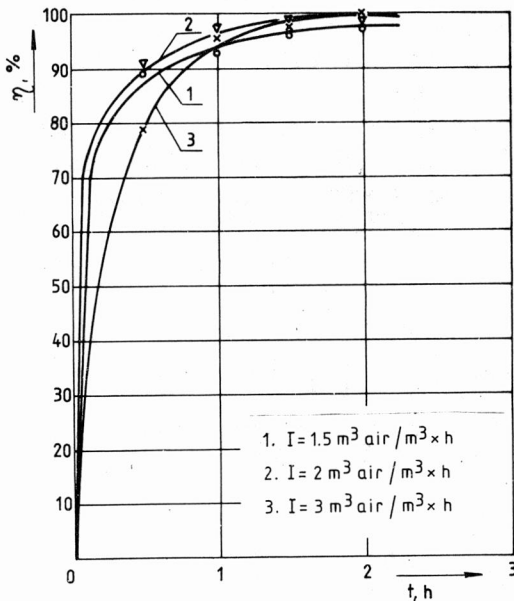


Fig. 5. Degree of sulphite removal (η) vs aeration time (t) at various aeration intensities (I)
 $C_0 = 200 \text{ g SO}_3^{2-}/\text{m}^3$, $C_k = 1 \text{ g Fe}^{3+}/\text{m}^3$

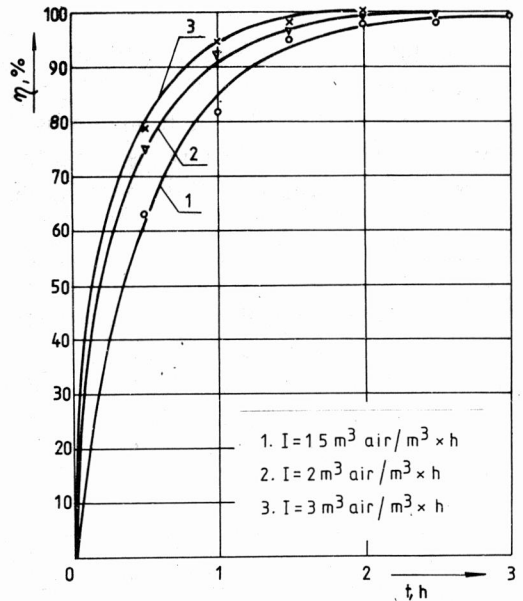


Fig. 6. Degree of sulphite removal (η) vs aeration time (t) at various aeration intensities (I)
 $C_0 = 400 \text{ g SO}_3^{2-}/\text{m}^3$, $C_k = 2 \text{ g Fe}^{3+}/\text{m}^3$

3.2. THE EFFECT OF SODIUM HYPOCHLORITE DOSE ON THE EFFICIENCY OF SULPHITES REMOVAL

It has been stated the reaction of sodium hypochlorite with sulphites runs very fast. For $D_{\text{Cl}_2} \geq 0.8 D_t$ (D_t is a theoretical dose) the reaction time does not exceed 5 min. Only for small doses of chlorine ($D_{\text{Cl}_2} < 0.8 D_t$) the degree of sulphite removal slightly increases during the next 10 minutes. Some selected results of analyses are presented in figs 7–9.

From the above presented data it follows that in the investigated range of sulphites concentrations a satisfactory degree of their removal is assured by chlorine dose

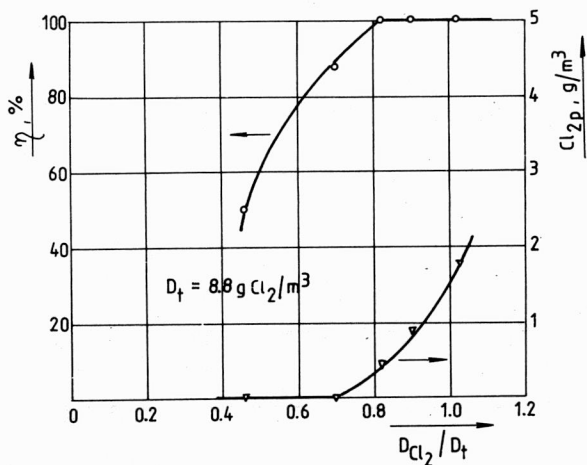


Fig. 7. Degree of sulphites removal (η) and concentration of residual chlorine (Cl_{2p}) vs chlorine dose referred to the theoretical one (D_{Cl_2}/D_t)
 $C_0 = 10 \text{ g SO}_3^{2-}/\text{m}^3$

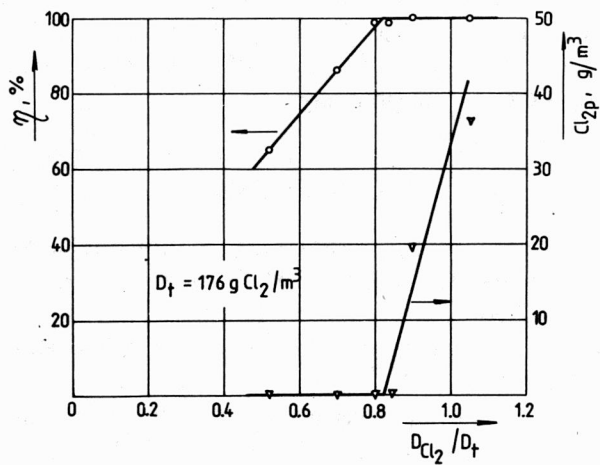


Fig. 8. Degree of sulphites removal (η) and concentration of residual chlorine (Cl_{2p}) vs chlorine dose referred to the theoretical one (D_{Cl_2}/D_t)
 $C_0 = 200 \text{ g SO}_3^{2-}/\text{m}^3$

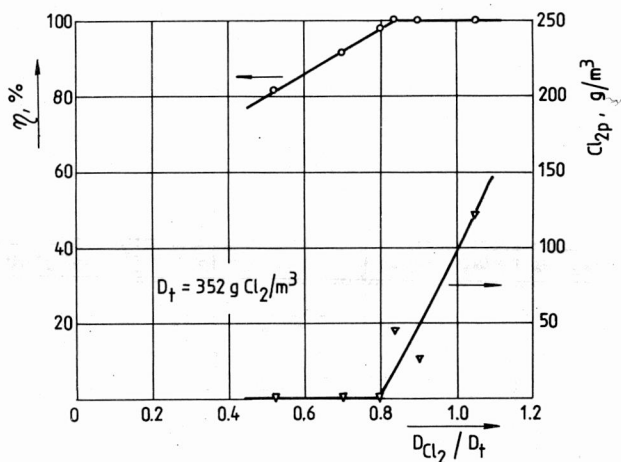


Fig. 9. Degree of sulphites removal (η) and concentration of residual chlorine (Cl_{2p}) vs chlorine dose referred to the theoretical one (D_{Cl_2}/D_t)

$$C_0 = 400 \text{ g SO}_3^{2-}/\text{m}^3$$

equal to $(0.8-0.85) D_t$. Under the above conditions this degree reaches 97–100%, and the concentration of chlorine residual is close to zero. It should be emphasized that for the solutions of higher sulphites concentrations the dose of the oxidizing agent should not exceed $0.8 D_t$, because of the high concentration of the residual chlorine (figs. 8 and 9). Hence, for high concentrations of sulphites in water theoretical dose of chlorine should be determined precisely.

4. CONCLUSIONS

1. Sulphites can be removed from aqueous solutions by aeration in the presence of ferric chloride as a catalyst ($FeCl_3 \cdot 6H_2O$). Its dose depends on the sulphite concentration: for the concentrations up to $200 \text{ g SO}_3^{2-}/\text{m}^3$ — it amounts to $1 \text{ g Fe}^{3+}/\text{m}^3$ and for the concentrations ranging from 200 to $400 \text{ g SO}_3^{2-}/\text{m}^3$ — it is equal to $2 \text{ g Fe}^{3+}/\text{m}^3$.

2. The efficiency of sulphites removal depends also on the aeration intensity. In order that the degree of sulphites removal exceeds 95% during 2.5–3 h, the required aeration intensity should amount to $1.5-2 \text{ m}^3 \text{ air}/\text{m}^3 \cdot \text{h}$.

3. Oxidation of sulphites with sodium hypochlorite is a fast and efficient process. If D_t is the dose of chlorine determined theoretically ($D_t = 0.88 \text{ g Cl}_2/\text{g SO}_3^{2-}$) then the introduction of $(0.8-0.85) D_t$ into the solution assures 97–100% of sulphites removal during 5 minutes. The concentration of residual chlorine is then close to zero.

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UTLENIANIE SIARCZYNÓW W ROZTWORACH WODNYCH

Przedstawiono sposób usuwania siarczynów z roztworów wodnych przez napowietrzanie oraz chemiczne utlenianie. Zbadano wpływ stężenia katalizatora oraz czasu i intensywności napowietrzania na skuteczność usunięcia siarczynów. Wymagana dawka katalizatora (chlorek żelazowy) zależy od stężenia siarczynów: dla stężeń do $200 \text{ g SO}_3^{2-}/\text{m}^3$ wynosi $1 \text{ g Fe}^{3+}/\text{m}^3$, a dla stężeń większych — $2 \text{ g Fe}^{3+}/\text{m}^3$. Stosując wymienione dawki katalizatora, można uzyskać ponad 95% utlenienia siarczynów w czasie do 3 h, przy intensywności napowietrzania $1,5\text{--}2,0 \text{ m}^3 \text{ powietrza}/\text{m}^3 \times \text{h}$.

W celu utlenienia siarczynów chlorem należy do roztworu wprowadzić dawkę chloru równą $(0,8\text{--}0,85) D_i$, gdzie D_i jest teoretyczną dawką chloru ($D_i = 0,88 \text{ g Cl}_2/\text{g SO}_3^{2-}$). Wymieniona dawka utleniacza zapewnia 97–100% utlenienia siarczynów w czasie 5 min przy stężeniu chloru pozostałego bliskim 0.

ОКИСЛЕНИЕ СУЛЬФИТОВ В ВОДНЫХ РАСТВОРАХ

Представлен способ удаления сульфитов из водных растворов путем аэрации, а также химического окисления. Исследовано влияние концентрации катализатора, а также времени и интенсивности аэрации на эффективность удаления сульфитов. Требуемая доза катализатора (хлорное железо) зависит от концентрации сульфитов: для концентраций до $200 \text{ г SO}_3^{2-}/\text{м}^3$ составляет $1 \text{ г Fe}^{3+}/\text{м}^3$, а для концентраций выше $200 \text{ г} - 2 \text{ г Fe}^{3+}/\text{м}^3$. Применяя вышеуказанные дозы катализатора, можно получить свыше 95% окисление сульфитов в течение до 3 ч при интенсивности аэрации $1,5\text{--}2,0 \text{ м}^3 \text{ воздуха}/\text{м}^3 \cdot \text{ч}$.

С целью окисления сульфитов хлором необходимо к раствору добавить дозу хлора равную $(0,8\text{--}0,85) D_i$, где D_i является теоретической дозой хлора ($D_i = 0,88 \text{ г Cl}_2/\text{г SO}_3^{2-}$). Данная выше доза окислителя обеспечивает 97–100% окисление сульфитов в течение 5 мин при концентрации хлора близкой 0.