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EFFECTIVE USE OF FERRIC SULFATE IN TREATMENT OF DIFFERENT FOOD INDUSTRY WASTEWATER

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Abstract. Plants processing food of animal origin like dairy, meat or fish products need usually large quantities of clean water in production. More than 90% of clean water is converted into wastewater demonstrating very high potential risk of environmental pollution. The present study was undertaken to compare, under the same analytical conditions, the efficiency of ferric sulfate used as coagulant (dose: 450 g/m^3) in chemical treatment of raw technological wastewater collected from three various food industry plants (dairy processing, meat processing and fish processing). Results of visual and physicochemical evaluation of chemically treated wastewater indicated significant improvement of their selected characteristics, however different response to the coagulant treatment was observed within the tested samples. Removal efficiencies for individual parameters varied in the wide range between 20.9 and 97.2%. Since bacterial bioluminescence inhibition used as biotoxicity indicator of effluents collected after treatment with ferric sulfate was less than 20%, they should be considered as non-toxic samples.

Key words: food industry wastewater, coagulation, ferric sulfate, biotoxicity

INTRODUCTION

Industrial food processing is often recognized as unfriendly to natural environment and considered as a source of numerous potential threats connected with possible environment degradation. Meat, poultry, dairy or fish processing plants are places producing "difficult" wastewater with large total load of organic pollutants like proteins or fats and chemicals used for cleaning and sanitizing processing equipment [Konieczny and Uchman 1997, Morgen-Lewińska 1992 a, Ochrona... 1998, Orzeszko 1997, Pezacki 1991].

Food industry generates a considerable quantity of wastewater containing various pollutants. The pollutants in the animal origin raw materials processing wastewater are: biodegradable organic material, nitrogen in several chemical forms, fat and oils, phosphorus and chlorides. Self-evident consequence of resultant activity of factors influencing the quality and quantity of wastewater rising in food processing plants is a high

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variability of different pollutant characteristics like BOD, COD, total solids or fat (ether extract) [Konieczny and Uchman 1997, Ochrona... 1998, Usydus 1999].

Wide range of complex solutions for treatment of wastewater exists in industrial plants. In reference to food industry wastewater, treatment processes have to assure first of all required quality of discharged effluents. Costs analysis, but also possible utilization of substances contained in wastewater are taken into consideration. Plant localization and the water quality impact assessment defining characteristics of wastewater which are led from the processing plant to the municipal sewage system or to surface waters are another important factor while selecting an individual wastewater treatment method [Konieczny and Uchman 1997, Morgen-Lewińska 1992 a].

Experience of many plants which process raw materials of animal origin indicate that the best results of efficient technological wastewater treatment are achieved with combination of physical methods (i.e. screens, sieves, sedimentation tanks or flotation units) with chemical treatment. Fat flotation is often combined with addition of chemicals acting as coagulants and precipitants of pollutants. Selected polymers are usually used as efficient binding agents in such technologies [Bengt 2002, Kubicki and Nowitkiewicz 1993, Poradnik... 1995]. Some of the additional benefits for the application of e.g. ferric or aluminum salts in wastewater treatment are: precipitation of sulfur compounds, easier sludge dewatering, increased efficiency in elimination of pollutants, and reduction in energy consumption in the biological process applied as final stage of treatment. It is also important to understand some disadvantages of this methodology and e.g. the addition of treatment chemicals may increase the total volume of sludge, large amounts of chemicals may need to be transported to the treatment location and polymers used can be expensive [Camacho and Huerta 2002, Pezacki 1991].

Food industry wastewater demonstrates a complicated system containing different components, including pollutants coming from the processed raw materials, chemicals and residues of technological additives used in individual operations. Since chemical precipitation has become a widely used technology for both industrial, as well as municipal wastewater treatment, the principal aim of the investigations presented in this publication was to verify the efficiency of the ferric sulfate applied as coagulant for treatment of three various food industry effluents. Additionally, for all samples treated with the coagulant, the commercially available bioassay based on measurement of *Vibrio fischeri* bacterial bioluminescence as an indicator of wastewater biotoxicity was applied.

MATERIALS AND METHODS

Raw wastewater samples, each of 10 dm^3, were collected at random from three selected food processing plants.

Wastewater sample from meat processing plant came from the modern plant of slaughter capacity of about 1000 hogs/day. Plant wastewater treatment there involves screening and grit removal, adding selected chemicals and removing pollutants by the use of dissolved air flotation (DAF) system. In the secondary treatment with activated sludge process additional organic matter in wastewater is broken down and removed before discharging the treated effluents to the river.

Next sample of wastewater was collected at an industrial dairy plant producing soft cheeses, where technological wastewater is mixed with effluents from plant canteen and laundry before two stages treatment process. Methods based on a physical/chemical pretreatment and the DAF system are the first step of wastewater treatment in this plant, while final pollutant removal by biological methods in so-called BIOBLOK units creates the second stage of this system.

The third sample of wastewater was collected in a small fish processing plant. Wastewater is generated there during primary processes of fish raw material like head removing, evisceration, filleting, salting, smoking etc. An essential part of wastewater entering the local municipal sewage system are effluents collected during processing lines cleaning and sanitizing.

The parameters of raw wastewater samples were determined in accordance to Polish Standards [Hermanowicz et al. 1999] and these were: COD (chemical oxygen demand), BOD_5 (biological oxygen demand), fat (ether extract), total phosphorus, total nitrogen, total suspension concentrations and pH value. The same characteristics were determined for wastewater samples collected after coagulation process.

Standardized jar testing procedure with automated jar test equipment of KEMIRA KEMWATER company were employed in a lab test of coagulation process of examined wastewater [Poradnik... 1995]. The coagulant used was PIX 112 [$Fe_2(SO_4)_3$, d = 1.5 kg/m^3, ~ 12% total Fe], purchased in KEMIPOL S.A., Police.

The general test procedure (Fig. 1) consisted in introducing 1,000 ml of raw wastewater sample in the calibrated jar test beakers, the coagulant was added (dose: 450 g/m^3) and rapidly mixed at 400 rpm during 10 seconds (destabilization). After that paddle rotation was reduced to 30 rpm and samples were slowly mixed for 10 minutes (coagulation). Next, all paddles were switched off so that flocs could settle on the bottom. After sedimentation (10 minutes) clarified wastewater samples (about 200 ml) were collected from each beaker to conduct all chemical analyses.

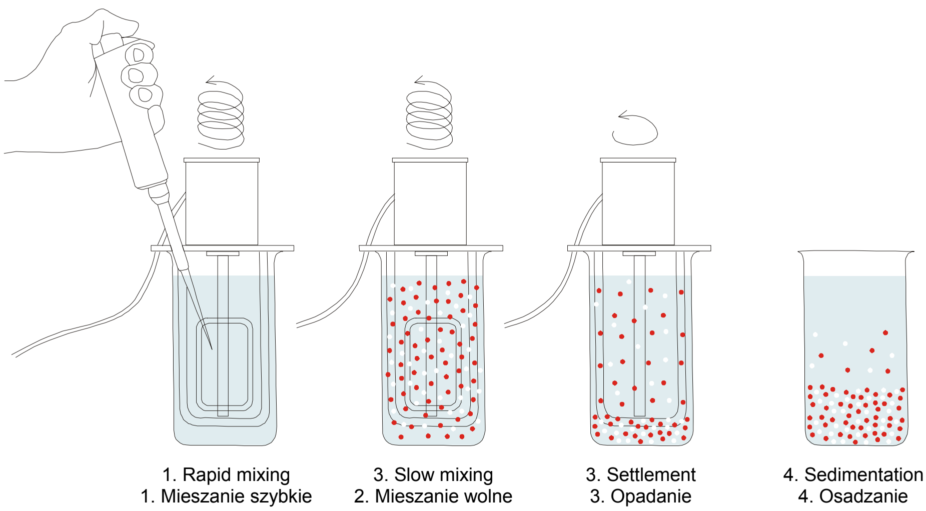

Fig. 1. Steps of wastewater testing by the use of jar testing apparatus (source: Poradnik... 1995)
Rys. 1. Etapy badania ścieków metodą testu naczyniowego (źródło: Poradnik... 1995)

Visual evaluation of coagulation process of examined wastewater samples was focused on flocs formation and sedimentation. Volume of coagulated sediment (ml) was determined. The influence of coagulant both on wastewater colour as well as removal of turbidity was also studied. Flocs sizes were compared using 6 points scale.

The samples of clarified wastewater were tested for toxicity using the ToxAlert® 10 system purchased in Merck, Germany, based upon luminescence inhibition of freeze-dried bacteria strain *Vibrio fischeri* and used as described in the ToxAlert 10 Manual [Manual... 2001]. The percentage of inhibition (% INH) was determined by comparing the response given by a saline control solution to that corresponding to the sample. Therefore, the bioluminescence inhibition was calculated using the following formula:

$$\% \text{ INH} = [1 - (\text{sample solution light}/\text{control solution light})] \times 100$$

RESULTS AND DISCUSSION

Table 1 shows the average values of the determined parameters of the raw wastewater originated from selected food processing plants. The values are typical for food industry effluents and indicated relative high variability between examined samples. High load of organic pollutants resulted in values of BOD_5, COD and other wastewater characteristics and correspond well with literature data [Konieczny et al. 1998, Konieczny and Uchman 1997]. Very high values, however, were found for total phosphorus content in raw effluent of dairy processing plant (77 g/m^3), and total nitrogen content in fish industry wastewater (181 g/m^3). Ether extract contents for samples collected

Table 1. Physico-chemical characteristics of examined raw wastewater
Tabela 1. Właściwości fizykochemiczne badanych ścieków surowych

Determination Oznaczenie	Raw wastewater type Rodzaj ścieków surowych		
	from milk processing mleczarskie	from meat processing mięsne	from fish processing rybne
BOD_5, mg O_2/dm^3 BZT_5, mg O_2/dm^3	1 216	646	914
COD, mg O_2/dm^3 ChZT, mg O_2/dm^3	2 833	2 392	3 017
Total suspension, mg/dm^3 Zawiesina ogólna, mg/dm^3	820	766	866
Total P, mg/dm^3 Fosfor ogółem, mg/dm^3	77	13	43
Total N, mg/dm^3 Azot ogółem, mg/dm^3	70	80	181
Fat (ether extract), mg/dm^3 Ekstrakt eterowy, mg/dm^3	32	28	125
pH value Odczyn pH	7.69	7.08	7.34

from meat processing and dairy processing plants (28 and 32 g/m^3, respectively) were significantly lower than in wastewater samples from fish processing plant (125 g/m^3). It was found, that in the day of sample collection, fish industry wastewater did not contain effluents from fish thawing process, while, an additional amount of fat-rich effluents from smoking chambers and containers cleaning were discharged to raw wastewater tank. It should be emphasized that quantitative and qualitative composition of raw food industry wastewater is characterized by high variability reflecting various and unpredictable technological situations occurring in processing plants [Morgen-Lewińska 1992 b, Pezacki 1991].

The biggest problem in the chemical treatment of wastewater is the selection of the chemicals, which must be added to the wastewater in order to separate the dispersed pollutants. The problem nearly always cumulates in finding a suitable coagulant, as this must be easy to handle, store and prepare. Another key question is always coagulant dose selection ensuring the required degree of the pollutants removal [Camacho and Huerta 2002, Kubicki and Nowitkiewicz 1993, Poradnik... 1995]. Since the main purpose of this study focused on comparison of coagulant response versus various food industry wastewater only, one selected preparation (PIX 112) in the same dose (450 g/m^3) has been proposed here. The selected coagulant works very well in a wide pH range and pH correction was not necessary. Additionally, the PIX 112 preparation does not have the same operational problems as e.g. ferric chloride [Camacho and Huerta 2002]. The results of wastewater susceptibility to treatment with the selected coagulant are presented in Table 2.

Table 2. Visual assessment results of wastewater after coagulation with ferric sulfate (dose 450 g/m^3)
Tabela 2. Wizualna ocena ścieków po koagulacji chemicznej z użyciem siarczanu (VI) żelaza (III) (dawka: 450 g/m^3)

Treated wastewater type Rodzaj oczyszczanych ścieków	Time required for floc formation Czas potrzebny dla utworzenia kłaczków min	Floc size* Wielkość kłaczków*	Volume of sediment, ml/1 dm^3 of sample Ilość wytrąconego osadu, ml/1 dm^3 próby	Turbidity and specific colour Zmętnienie i barwa
From milk processing Mleczarskie	4	4	200	almost clear, bright yellow dość klarowne, jasnożółta
From meat processing Mięsne	2	5	80	clear, bright pink klarowne, jasnoróżowa
From fish processing Rybne	8	2	100	turbidity, bright brown mętne, jasnobrunatna

*6 = fast sedimentation, large flocs, 1 = small flocs, visible and none sedimenting suspension.
*6 = duże kłaczki, szybko opadające, 1 = drobne kłaczki, widoczna nieopadająca zawiesina.

Visual evaluation of tested samples indicates good applicability of ferric sulfate in applied dose to remove pollutants from food industrial wastewaters, however, individual wastewater reveals various susceptibility to coagulation process. Best results were obtained in the case of meat and dairy industries wastewater demonstrating markedly changed desirable colour and low turbidity. Simultaneously, flocs of coagulated pollutants from these samples had large size and rapidly settled on the bottom of the beakers. By the same dose of coagulant (450 g/m^3) time required for floc formation varied in the range between 2 and 8 minutes for meat processing and fish processing wastewater, respectively. In wastewater coming from fish processing, coagulated with PIX 112 in proposed dose, the colour and the turbidity was practically comparable with the control untreated sample. Small size flocs and particles suspended in whole volume of beaker were found in this case.

Under industrial, real conditions of food processing plants, it was observed that ferric sulfate is a very efficient coagulant, particularly, when it was used in combination with the right applied polymer. It should be mentioned that the wastewater clarification efficiency can be much improved by an application of dissolved air flotation units (DAF). Clarified wastewater is next discharged or even recycled at the plant for purposes such as washing crates or trucks [Bengt 2002, Camacho and Huerta 2002, Kubicki and Nowitkiewicz 1993].

In a physical/chemical process for selected food industry wastewater the ferric sulfate acted on almost all characteristics. All tested wastewater samples after treatment with PIX 112 in proposed dose were characterized by lower pH in comparison to initial values achieving values 7.18, 6.37, and 6.58 for dairy, meat and fish processing wastewater, respectively. It is very important that pH of wastewater entering the sewer system be maintained within certain limits. Acceptable pH discharge limits may vary depending on permit limitations imposed by local authority, but are typically range of 6.5 through 9.5 [Konieczny and Uchman 1997].

Application of the PIX 112 resulted in achieving high removal efficiency for almost all wastewater characteristics as can be seen in Figure 2 a-d. The varying concentration of solids in tested wastewater, together with the size of particulate materials and the differences in particle charge are the main factors influencing the parameter. Markedly reduction of individual pollutants concentrations was observed in each analytical variant corresponding well with other literature data. Camacho and Huerta [2002] reported BOD_5, TSS and turbidity removal efficiencies equal to 90%, 95%, 96%, respectively, from chicken processing plant dosing ferric sulfate between 300 and 350 g/m^3 and DAF system. Results obtained in our study indicate however that the discharge of coagulated wastewater to municipal sewage system would not be possible without correction of some parameters. For example the achieved values of phosphorus concentration in coagulated fish and dairy wastewater (25.5 and 34 g/m^3, respectively) still exceeded discharge limit (10 g/m^3). Both results of chemical analyses as well as observations collected during visual evaluation of treated wastewater showed, that under conditions of this study, fish processing wastewater demonstrated significantly lower removal efficiencies in comparison to the other tested wastewater samples. In this case, selection of another PIX 112 dose or even change of coagulant to another one could be suggested.

Ecotoxicological testing of iron and aluminum salts done recently by KEMIRA company using *Daphnia Magna* as a test organism indicated that they represent group of "low concern" chemicals (EC50[*] > 100 mg/dm^3) according hazard ranking [Information... 2003]. It seems very likely that also the determination of so-called "biotoxicity", based on the measurement of bioluminescence emitted by the test bacteria *Vibrio fischeri* will offer an interesting tool in monitoring of various chemicals and hazardous

[*] EC50 = the minimal effective concentration of chemical causing 50% luminescence inhibition.

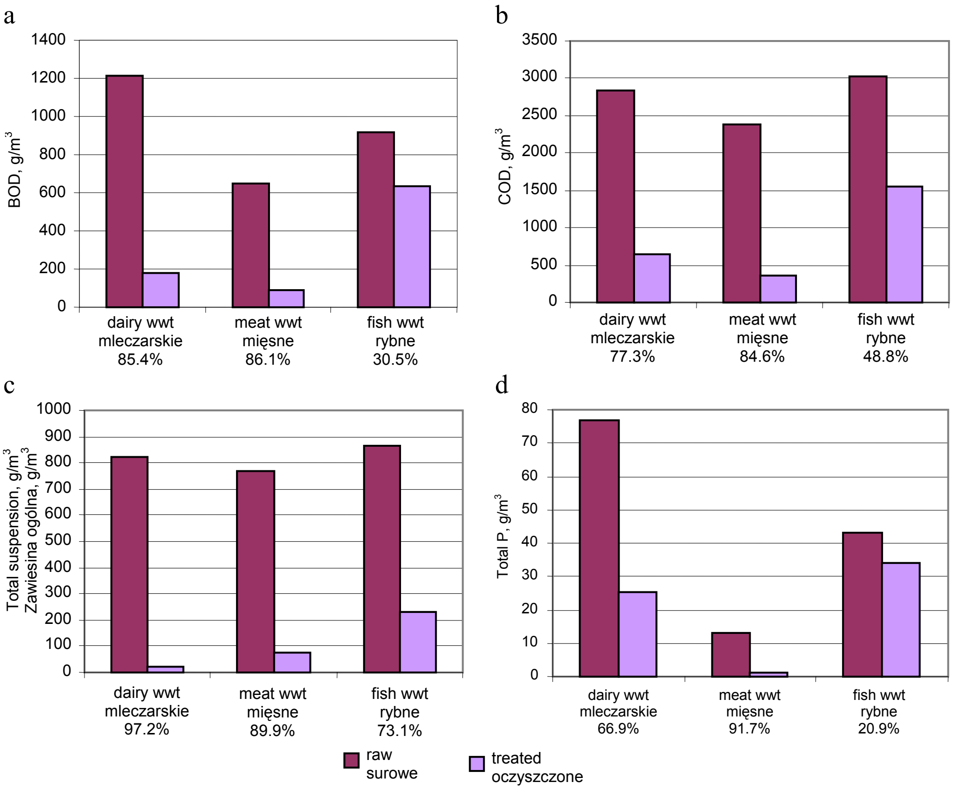

Fig. 2. Removal efficiency of BOD (a) and COD (b) total suspension (c) and total phosphorus (d) from wastewater (wwt) coagulated with ferric sulfate (PIX 112) with a dose 450 g/m^3
Rys. 2. Stopień redukcji BZT (a) i ChZT (b) zawiesiny ogólnej (c) i fosforu ogólnego (d) w ściekach poddanych koagulacji siarczanem (VI) żelaza (III) w dawce 450 g/m^3

media [Kieβling and Rayner-Brandes 1998]. Approaches to the use of bioluminescence technique for determination of biotoxicity of wastewater and sludge from meat processing plant has been already done [Konieczny and Uchman 1997, 1999, Konieczny et al. 1998]. Therefore, determination of biotoxicity was also included to the presented study, and the obtained results are presented in Table 3.

Raw wastewater is a difficult material to test its toxicity because its dark colour and high turbidity can affect the results during bioluminescence toxicity screening. Nevertheless, inhibition values in range between 40 and 60% have been found for raw meat industry wastewater, while non-treated municipal effluents demonstrated even higher values [Konieczny and Uchman 1999].

It was found during this study that all chemically treated wastewaters quenched the intensity of bioluminescence emitted by *Vibrio fischeri*, however inhibition values were always below 20% which is recommended as a limit value between toxic and non-toxic substances [Information... 2003, Manual... 2001]. It confirms that wastewaters treated with ferric sulfate are safe both for further treatment by biological methods i.e. with bacteria of activated sludge, as well as for discharge to lakes or rivers.

Table 3. Bioluminescence inhibition average values* for wastewater after coagulation with ferric sulfate (dose: 450 g/m^3)
Tabela 3. Średnie wartości inhibicji bioluminescencji bakteryjnej* w ściekach po koagulacji siarczanem (VI) żelaza (III) (dawka: 450 g/m^3)

Treated wastewater type Rodzaj oczyszczanych ścieków	INH, %
From milk processing Mleczarskie	18.46 ± 0.21
From meat processing Mięsne	14.62 ± 0.35
From fish processing Rybne	9.14 ± 0.58

*values expressed as mean ± SD (standard deviation).
*wartości średnie ± SD (odchylenie standardowe).

Taking into consideration the average biotoxicity values obtained in this study (Table 3), examined samples should be ranged as follows: dairy processing wastewater > meat processing wastewater > fish processing wastewater. Nevertheless, basing on data shown in Table 2 and Figure 2, this sequence has not been confirmed by results of chemical analyses and removal efficiencies for selected characteristics of tested wastewater treated with ferric sulfate. It is generally supposed, that the bioluminescence emitted by *Vibrio fischeri* reflects the effect influenced by many factors and for this reason the results obtained do not allow simple calculation of relationship between quenching effect of bacterial bioluminescence and the other parameters of wastewater samples [Konieczny et al. 1998]. The further studies and more detailed experiments before industrial application of this interesting analytical technique for such purposes would be still needed.

CONCLUSIONS

1. Samples of food industry wastewaters collected as raw material for this study demonstrated different chemical composition reflecting both complexity of technological situations occurring under industrial conditions, as well as various technical status of wastewater treatment systems working in individual plants.
2. Under the same analytical conditions, all examined wastewater samples coming from dairy, meat and fish processing plants revealed various susceptibility to coagulation process with ferric sulfate added in the same amount of 450 g/m^3 of wastewater.
3. Results of chemical analyses and visual evaluation of coagulation process have confirmed that the ferric sulfate acted principally on colour, turbidity, BOD_5, COD and other wastewater characteristics, however, this effect depended on wastewater origin; significantly higher removal efficiencies for individual characteristics were obtained in the case of dairy and meat processing wastewater than for fish processing wastewater samples.

4. No toxicity measured by the use of commercially available test luminescent bacteria was observed for all examined wastewater treated with ferric sulfate, which is of special importance both for further treatment of wastewater by biological methods, as well as for its discharge to any type of surface water.

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EFEKTYWNE ZASTOSOWANIE SIARCZANU (VI) ŻELAZA (III) W OCZYSZCZANIU ŚCIEKÓW RÓŻNEGO POCHODZENIA

Streszczenie. Zakłady spożywcze, zwłaszcza przetwarzające surowce pochodzenia zwierzęcego (np. mleko, mięso, ryby) zużywają z reguły znaczne ilości wody, a ponad 90% jej ilości zostaje przekształcone w ścieki o wysokim potencjalnym zagrożeniu dla środowiska naturalnego. Proces oczyszczania ścieków zakładów spożywczych można zintensyfikować między innymi przez wprowadzenie do ich strumienia związków nieorganicznych, a jak pokazuje praktyka do najbardziej skutecznych należą sole wielowartościowych metali, zwłaszcza żelaza i glinu. W prezentowanej pracy podjęto próbę porównania, w tych samych warunkach analitycznych, skuteczności działania siarczanu (VI) żelaza Fe (III) jako koagulanta (dawka: 450 g/m^3) w chemicznym oczyszczaniu prób surowych ścieków technologicznych, pobranych w trzech różnych zakładach przemysłu spożywczego (mleczarskich, mięsnych i rybnych). Wyniki oceny wizualnej i oznaczenia chemiczne (BZT, ChZT, zawartość fosforu i zawiesiny ogólnej) w ściekach po koagulacji wykazały znaczącą poprawę wybranych parametrów ścieków, chociaż podatność badanych ścieków na działanie koagulanta była zróżnicowana. Stopień redukcji poszczególnych parametrów ścieków mieścił się w szerokim zakresie 20,9-97,2%. Wykazano jednocześnie, że badane ścieki po koagulacji chemicznej charakteryzowała mała (< 20%) zdolność wygaszania bioluminescencji testowego szczepu bakterii (*Vibrio fischeri*), co pozwala uznać je za próby nietoksyczne dla środowiska naturalnego.

Słowa kluczowe: ścieki przemysłu spożywczego, koagulacja, siarczan żelaza, biotoksyczność

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