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WATER TREATMENT BY FERROUS SULFATE COAGULATION AND DOLOMITE BED FILTRATION

There is described the usefulness of dolomite filter beds when the coagulation process involves iron salts as coagulants. The surface water tested carried either low or high concentrations of organic pollutants. The key findings of the study are as follows: In surface waters, in general, iron compounds form complexes with humic substances. In surface water with high concentration of organic pollutants, iron compounds form complexes with organic compounds as well. The complexes are stabilized either by magnesium (in surface water with low organic pollution) or by calcium (in polluted surface water). The coagulation process (with preoxidized ferrous sulfate as coagulant) was influenced by the colloid system formed by iron compounds with organic substances. When the concentration of iron compounds was low, there might have occurred complexation with humic substances as the coordinating factor. At increased concentration of iron compounds, the coordinating factor for complexation was probably iron hydroxide. The coagulation process involved reactions of the coagulant and its hydrolysis products with complexes, thus inducing magnesium replacement by calcium (in polluted surface water) or calcium replacement by magnesium (in water with low pollution). In transient state, i.e., when iron concentration was high enough to make the system oscillate on the boundary between a humic-substance-coordinated complex and an iron-compound-coordinated complex) there was no calcium or magnesium replacement; the efficiency of organic matter removal was low, whereas that of iron compounds was high. Filtration on partly decarbonized dolomite bed provided co-removal of humic substances and other organics as a result of destabilization, via reaction of the polluting species with the components of the filter bed – calcium or magnesium.

1. INTRODUCTION

Use of dolomite (partly decarbonized dolomite – PDD) is one of the procedures in groundwater treatment. The application of dolomites or PDD to surface water

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treatment seems to be caused by their high chemical activity, providing magnesium enrichment of the treated water. Dolomites have been shown in some studies to act as effective filtering media, and they have also been reported applicable to the treatment of acidic and soft mountain streams with carbon dioxide addition as a prior step [1], [2]. The advantages of using dolomite or PDD beds can be itemized as follows: (a) neutralization and stabilization of the buffering properties of water, (b) magnesium and calcium enrichment, (c) removal of organic compounds, and (d) complexation of organics (predominantly humic substances) with the components of the filter bed [3].

Some complicated treatment trains and high dosage of chemicals decreasing dramatically the cost-effectiveness of the treatment are required to make polluted surface waters fit for drinking purposes. Attempts to overcome this drawback succeeded due to simplification of the treatment train and application of waste salts (e.g., ferrous sulfate) as coagulants. Alum coagulation requires a rigorous technological regime in order to prevent alum from escaping into the effluent. Admissible concentrations of effluent alum are very low, amounting to $0.3 \text{ g} \cdot \text{m}^{-3}$ and $0.2 \text{ g} \cdot \text{m}^{-3}$ in Poland and European Community countries, respectively (the concentration recommended by the European Community being $0.05 \text{ g} \cdot \text{m}^{-3}$) [4]. Taking account of the above, a treatment train consisting of coagulation of treated water with pre-oxidized ferrous sulfate and its further filtration through a PDD bed has advantage over the aforementioned ones.

An inherent drawback of coagulation with iron salts as flocculants is the potentiality for complexation of Fe(III) and Fe(II) cations with the humic substances identified in surface waters. This manifests itself as a substantial increase of colour and iron salt concentration, in spite of its passage through a sand filter [5], [6]. The proneness of Fe(II) to form complexes with humic substances is twice, or even four times as high as that of Fe(III) [7]. The sorbing capacity of humic substances with respect to ferric oxides and hydroxides depends on the quality of raw water. In the absence of calcium and magnesium, the sorption of those species proceeds according to the Langmuir isotherms. When calcium and magnesium are present, the sorbing capacity of humic substances increases [8].

As shown by a previous study [9], active filter beds built of PDD are quite effective when applied to the treatment of slightly polluted surface waters.

2. EXPERIMENTAL METHODS

The study was conducted on three types of water samples: (1) samples from a polluted river (Odra River), (2) samples being a mixture of Oława River water (a

tributary of the Odra) and infiltration water, for the needs of the Na Grobli Waterworks, Wrocław, Poland (proportion 1:3; referred to as mixed-water samples), and (3) samples of infiltration water only (infiltration-water samples). The treatment train consisted of ferrous sulfate coagulation and filtration (water of types (1) and (2)).

The coagulant was preoxidized with an equivalent quantity of chlorine and was added to the solution at the following doses: 50, 60 and 100 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} / \text{m}^3$. As soon as flocs had formed (after 30-minute sedimentation) the water was decanted for a passage through the filter bed. The Odra River samples were filtrated through a PDD bed ($\text{CaCO}_3 \cdot \text{MgO}$) or a mixed-dolomite bed (dolomite, 55 cm, and PDD, 50 cm, marketed under the brand name Decarbonate; grain size, 2–4 mm; referred to as dolomite-decarbonate bed). The bed depth for the Odra River water filtration amounted to 60 cm and 110 cm at a grain size distribution of 0.5–7.0 mm and at three filtration rates: 5, 10 and $15 \text{ m} \cdot \text{h}^{-1}$. For comparison, the effluent after having undergone coagulation was also passed through a sand filter (bed depth, 74 cm; $d_{10} = 1.2 \text{ mm}$; $d_{60} = 1.8 \text{ mm}$). The mixed-water samples and infiltration water samples (both without coagulation) were filtrated through the dolomite-decarbonate bed under the same experimental conditions.

The parameters of raw-water quality are given in the table.

Table

Quality of raw water

Parameter	Unit	Odra River water			Mixed water*			Infiltration water	
		max.	av.	min.	max.	av.	min.	max.	min.
pH	–	7.90	–	6.2	8.2	–	7.15	7.5	7.1
Colour	$\text{g Pt} \cdot \text{m}^{-3}$	70	45	30	60	35	20.0	90	10
Alkalinity	$\text{g CaCO}_3 \cdot \text{m}^{-3}$	120	93	55	155	136	120	150	120
Hardness	deg**	15.8	14.8	12.8	19.4	15.4	12.5	26.9	11.8
Calcium	$\text{g Ca} \cdot \text{m}^{-3}$	81.5	71.5	62.8	115	87.7	66.4	155	65.7
Magnesium	$\text{g Mg} \cdot \text{m}^{-3}$	21.8	19.6	17.6	20.6	13.8	8.8	21.9	11.6
Total iron	$\text{g Fe} \cdot \text{m}^{-3}$	1.15	0.63	0.4	3.4	1.47	0.78	7.4	1.2
BOD ₅	$\text{g O}_2 \cdot \text{m}^{-3}$	16.7	10.1	5.0	4.2	3.0	1.3	–	–
COD _p	$\text{g O}_2 \cdot \text{m}^{-3}$	9.5	8.4	7.4	5.2	3.9	3.1	10	2.5
Humic substances	$\text{g} \cdot \text{m}^{-3}$	7.10	4.4	2.4	5.5	3.24	1.4	–	–
TOC	$\text{g C} \cdot \text{m}^{-3}$	7.3	5.7	2.3	7.54	5.3	3.67	6.7	3.0

*1 portion of Oława River water + 3 portions of infiltration water.

**According to German determination (0.96 deg according to American determination).

3. RESULTS AND DISCUSSION

3.1. TREATMENT EFFICIENCY OF THE COAGULATION-FILTRATION TRAIN

The experiments involved two types of surface water samples – those collected from the Odra River (with a wide spectrum of organic pollutants and an increased salinity level) and those containing a mixture of river water and infiltration water (with much lower organic pollution).

Coagulation with preoxidized ferrous sulfate brought about a removal of the majority of organic pollutants. Thus, the efficiency of BOD₅ removal ranged from 46 to 70% and from 64 to 85%; COD_p removal varied from 44 to 63% and from 23 to 60%, and the efficiency of TOC removal fell in the range of 19 to 46% and amounted to about 36% for the Odra River samples and mixed-water samples, respectively. Filtration through the PDD bed following coagulation accounted for a partial removal of organic species. At the filtration rate of 10 m/h and the bed depth of 110 cm, magnesium concentration increased by 15–60% for the Odra River samples; for mixed-water filtration through the dolomite-decarbonate bed there was even 133% increase. The rise in hardness amounted to 8–21% (the Odra River samples) and 6% (mixed-water samples), and pH approached 8.0. Organic matter removal in the effluent from the PDD bed was as follows: COD_p, up to 27% (the Odra River samples) and 23.3% (mixed-water samples); BOD₅, up to 45% (the Odra River samples) and up to 100% (mixed-water samples); TOC, up to 6% (the Odra River samples) and up to 40% (mixed-water samples). Colour (after having undergone filtration) varied from 5 to 15 g Pt/m³ and from 5 to 10 g Pt/m³, whereas total iron content ranged from 0.04 to 0.5 g Fe/m³ and from 0.04 to 0.2 g Fe/m³ for the Odra River samples and mixed-water samples, respectively.

Coagulation followed by filtration through a sand bed yielded removal efficiencies similar to those for the PDD or for the dolomite-decarbonate bed.

3.2. DISCUSSION

Two major factors affected the removal efficiency of the coagulation-filtration train: (1) proneness of iron compounds to form complexes with humic substances and other pollutants, and (2) chemical properties of the colloids. The treatment effects following coagulation depended strongly on the iron concentration in raw water (and this was associated with the form of the colloidal system). As shown by figure 1, at low initial concentrations of iron its content in the effluent (both from sand filter and PDD bed) decreased with increasing concentration in raw water. Such removal pattern is likely to be associated with the occurrence of colloidal systems which have formed on the basis of humic substance-iron compounds, with humic substances as coordinating factors. At higher initial concentrations of iron,

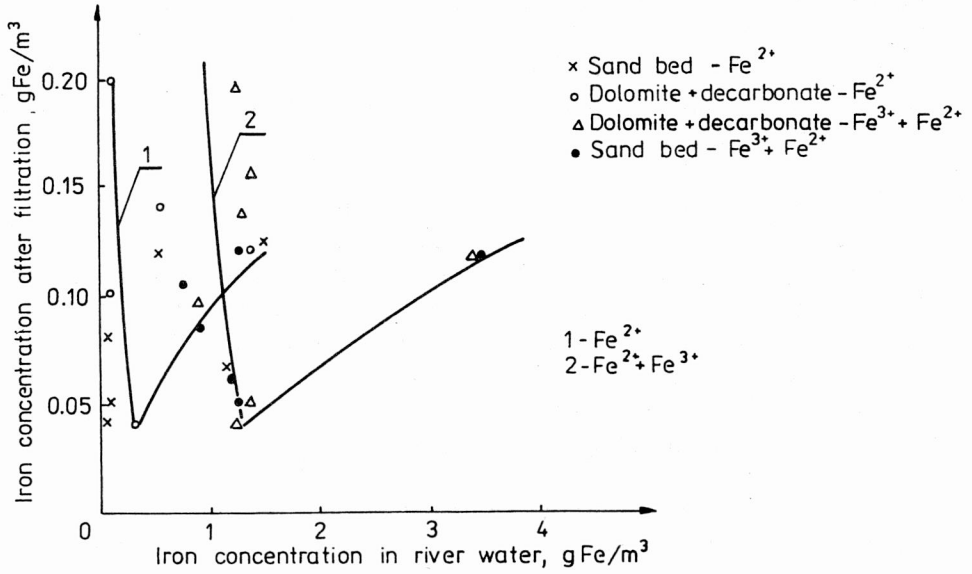


Fig. 1. Effect of iron concentration in raw mixed-water on the iron concentration in the coagulation-filtration effluent

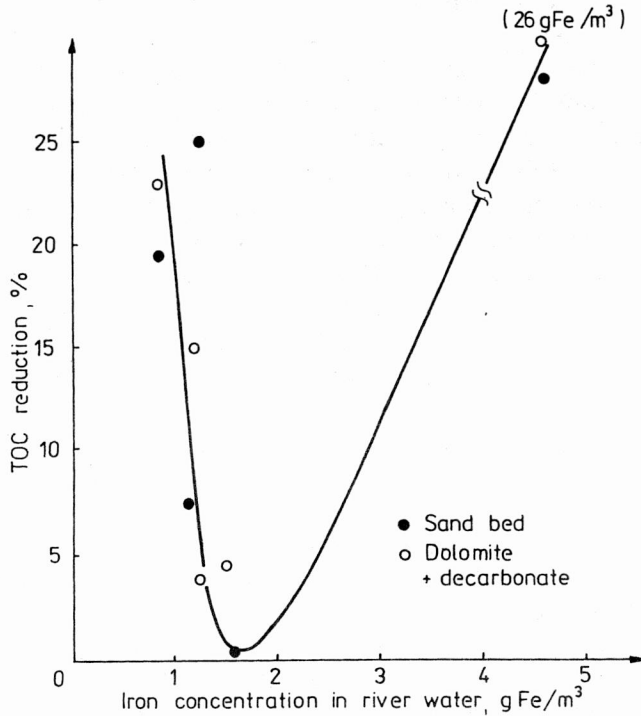


Fig. 2. Effect of iron concentration in raw mixed-water on TOC removal efficiency

its content in the filter effluent increased with increasing concentration in raw water. And this is likely to be due to the occurrence of complexes which formed on the iron compound-humic substances basis, with iron compounds as the coordinating agent.

The efficiency of coagulation was found to be affected by the susceptibility of the polluting species to destabilization, which was high for humic substance-iron compound complexes. The result was the high removal of iron compounds and humic substances for iron concentrations at the minimum point (figure 1), but at the cost of the removal efficiency of other organic pollutants, as shown in figure 2.

Humic substances forming colloidal systems in surface waters contain a certain amount of carboxylic groups which dissociate at $\text{pH} < 7$ as proton donors due to cation exchange. Thus, calcium and magnesium cations were fixed in the absorbing layer of the colloid, whereas monovalent cations, e.g., H^+ or Na^+ , were fixed in the diffusion layer [10]. In the absence of calcium and magnesium cations, iron compounds were bound according to the mechanism of ligand exchange - $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})^{2+}$ are proton donors with respect to humic substances [11]. The presence of calcium and magnesium cations, which are proton donors with respect to humic substances, increased the sorbing capacity of the latter [8]. And this supported formation of protective colloidal systems, e.g., in combination with iron compounds. The electric charge of colloid particles in humic substances (which had been reduced due to the presence of calcium and magnesium) required binding of larger quantities of colloid particles with iron compounds for the neutralization of the potential.

The chemical properties of the colloidal systems varied noticeably with each change of the organic pollution load. In water with low organic pollution, humic substance-iron compound complexes (stabilized by magnesium cations) were dominant, as shown by the analysis of water samples collected in two tributaries of the Odra River (i.e., Oława or Widawa). In polluted water, the complexation occurred on the basis of organic pollutants, iron compounds or, in some cases, calcium carbonate. The complexes were stabilized by calcium cations, as shown by the results from the analysis of the Odra River samples and of one of the Odra River's tributaries (Ślęza). The components of the complexes were in equilibrium. This is indicated by the plots of the iron concentrations versus colour, and humic substance content versus Ca/Mg ratio curves (figure 3). Thus, as the molar ratio of calcium to magnesium increased, iron concentration and colour decreased in the Oława (tributary to the Odra River) and increased in the Odra River (figure 4).

The chemical properties of the complexes identified in the water had a noticeable contribution to the coagulation process. Destabilization of the polluting species resulted from the reaction of the coagulant (preoxidized ferrous sulfate) and its hydrolysis products, i.e., $\text{Fe}(\text{OH})_2^+$ or $\text{Fe}(\text{OH})^{2+}$, with humic substances or iron compounds, replacing calcium by magnesium and magnesium by calcium in magnesium-stabilized systems and calcium-stabilized systems, respectively. Equilibrium was established when calcium or magnesium in the double layer had reached a certain concentration corresponding to the electric charge of the system,

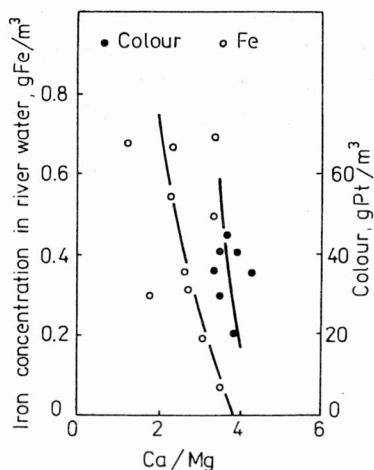


Fig. 3. Effect of Ca/Mg molar ratio on iron concentration and colour (the Oiawa River in the vicinity of aquifer)

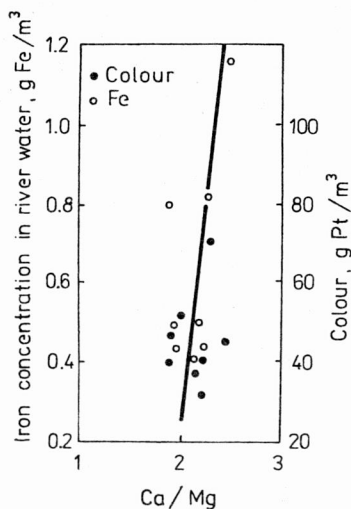


Fig. 4. Effect of Ca/Mg molar ratio on iron concentration and colour (the Odra River)

which is limited by the following factors: the solubility product of CaCO_3 , the stability constant of the complex, or the value of the Ca-to-Mg molar ratio in the water. The concentration of calcium or magnesium increased due to their uptake from the solution.

Such a mechanism governing the reaction of iron compounds with humic acids seemed to be substantiated by the equimolar decrement and increment of calcium or magnesium in the course of the coagulation process. The effect of the Ca-to-Mg ratio on calcium decrement, magnesium increment and Ca^{2+} , Mg^{2+} concentration variations during coagulation of the Odra River and mixed-water samples is shown in figures 5, 6 and 7.

The reactions inhibited the formation of iron-humic substance complexes, thus initiating the reaction of iron compounds with other organic pollutants and contributing to their destabilization. With the increasing iron concentration in the water (figure 1) the reactivity of the complexes with respect to the coagulant increased, and so did the rate at which the destabilized iron-humic agglomerates had been formed. Such a behaviour was

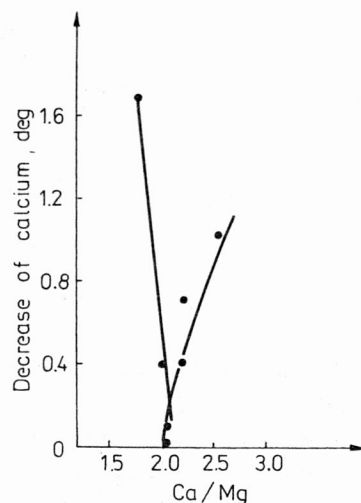


Fig. 5. Effect of Ca/Mg molar ratio on calcium decrement during coagulation of the Odra River water

indicated by the decrease in calcium and magnesium replacement and by the removal efficiencies of organic pollutants (figures 2, 5, 6 and 7). In water with magnesium-stabilized complexes (e.g., in mixed-water samples), the efficiency of organic matter removal decreased, and that of iron compound removal increased with increasing concentration of humic substances. And this is an indication that humic acid-iron compound complexation occurred.

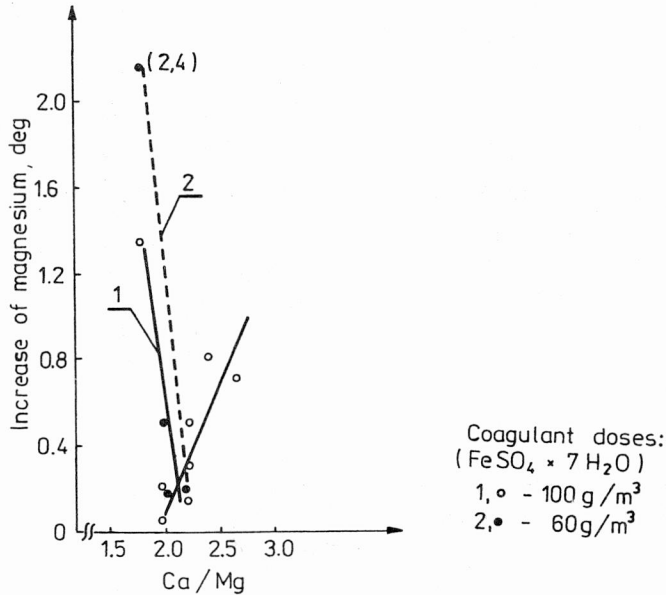


Fig. 6. Effect of Ca/Mg molar ratio on magnesium increment during coagulation of the Odra River water

The opposite was observed in water with calcium-stabilized complexes (e.g., in the Odra River samples): with the increasing humic acid concentration, the removal of organic pollutants increased, whereas that of iron compounds decreased. And this mechanism suggests the potentiality for the occurrence of humic substance-iron compound-organic matter complexation.

Filtration through a PDD bed following the coagulation process accounted for the destabilization of persisting colloids, with preference of humic substance-iron compound complexes. That is why iron concentration in the effluent after treatment train consisting in coagulation with preoxidized ferrous sulfate and filtration through a PDD bed was much lower than when the filtration process involved a sand bed. Thus, iron content varied from 0.04 to 0.5 g Fe/m³ and from 0.1 to 2.8 g Fe/m³ for the PDD filter bed and sand filter bed, respectively; colour intensity ranging from 5 to 15 g Pt/m³ and from 10 to 60 g Pt/m³ for the mixed-water samples and the Odra River samples, respectively.

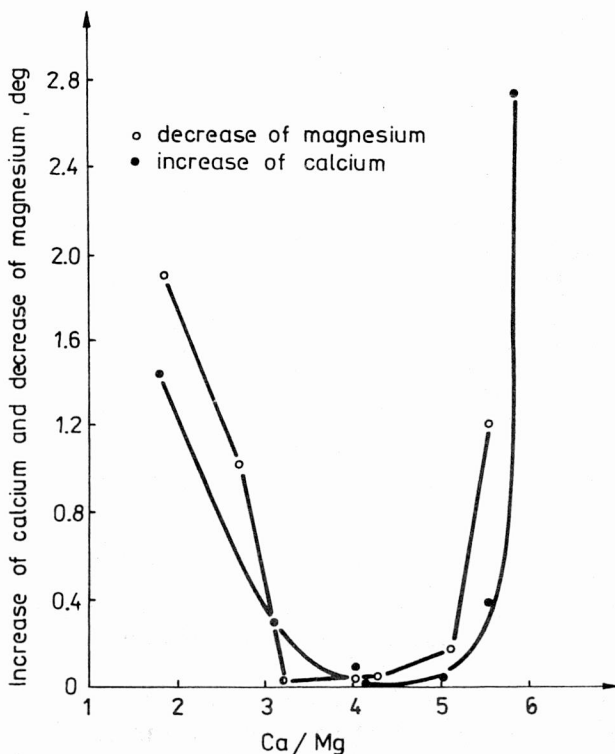


Fig. 7. Effect of Ca/Mg molar ratio on Ca^{2+} and Mg^{2+} concentration during coagulation of mixed-water samples

3.3. EFFICIENCY OF FILTRATION ON DOLOMITE-DECARBONATE BED

Filtration of raw mixed-water (three portions of infiltration water and one portion of the Oława River water) or infiltration water (alone) through the dolomite-decarbonate bed provided removal of organic substances and iron compounds. The efficiency of COD_p and colour removal varied from 11 to 78% and from 40 to 89%, respectively. The concentration of iron in the filter-bed effluent amounted to 0.2 g Fe/m^3 , whereas these of COD_p and colour ranged from 2.0 to $4.1 \text{ g O}_2/\text{m}^3$ and from 10 to 25 g Pt/m^3 , respectively, for both types of water.

Destabilization of the colloidal systems in surface-water streams played an important part in the filtration process. Like in ferrous-sulfate coagulation, the efficiency of destabilization depended on a number of factors which were identical in both processes, and iron concentration in the filter-bed effluent was strongly affected by its concentration in raw water, varying from one type of complexation to another (figure 8). The filter bed provided co-removal of organic substances along with humic

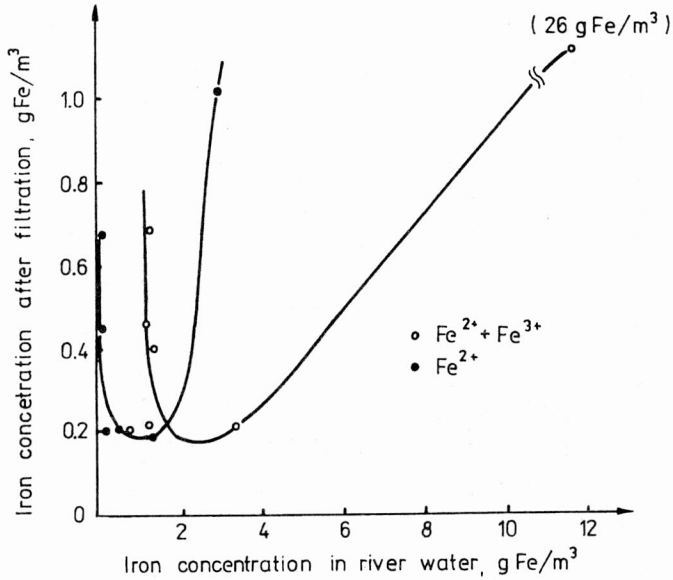


Fig. 8. Effect of initial iron concentration on the concentration of iron in the filtrate from the PDD bed (mixed-water samples)

acid-iron compound complexes. The contribution of iron compounds to organic matter removal is shown in figure 9. The organic pollutants in the water reacted with the components of the bed to become destabilized via this route. When the Ca-to-Mg ratio fell below 4.4 (figure 10), calcium addition to the complexes was found to occur. The complexes identified in the infiltration water sample were stabilized by Ca^{2+} ,

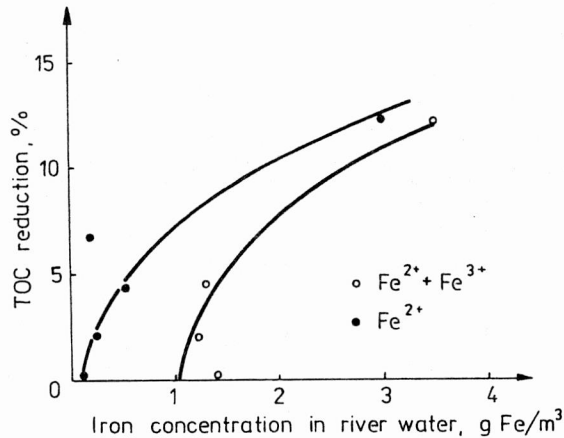


Fig. 9. Effect of initial iron concentration on the removal of organic substances by filtration through the PDD bed (mixed-water samples)

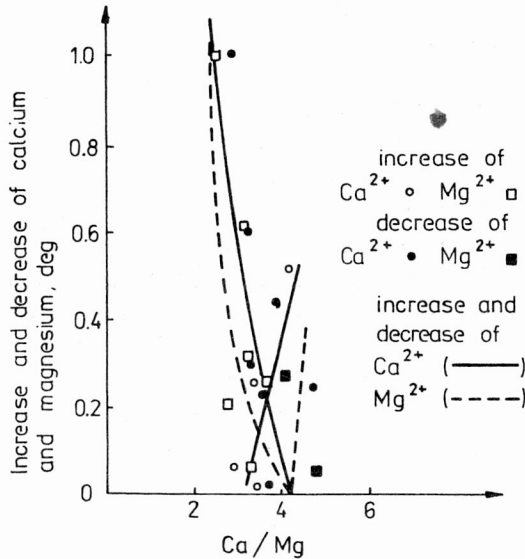


Fig. 10. Effect of Ca/Mg molar ratio on calcium and magnesium concentrations in the effluent from the dolomite-decarbonate bed

and the filtrate showed increased concentration of magnesium. When the Ca-to-Mg ratio exceeded 4.4, there was fixation of magnesium by the complexes, and the filter-bed effluent contained increased calcium concentrations. Such a removal pattern is likely to be associated with an excess concentration of calcium or magnesium in the double-layer zone, which (similarly as during coagulation) corresponds with the electric charge of the system limited by the following factors: the solubility product of CaCO_3 , the stability constant of the complex, or the value of the Ca-to-Mg molar ratio in the water. The concentration of calcium or magnesium increased due to their uptake from the solution. Addition of calcium or magnesium cations made the Ca-to-Mg ratio approach the value of 4.4, at which those cations are not subject to exchange. And such conditions seem to enhance destabilization of the colloid systems identified in the water. This corresponds with the minimum iron concentration in figure 8, as it was in the case when mixed-water samples were treated by filtration or coagulation. The decrease in the removal of organic pollutants with the increasing concentration of humic substances indicates that the infiltration water contained humic acid-iron compound complexes.

4. CONCLUSIONS

The coagulation-filtration train, involving ferrous sulfate (preoxidized with chlorine) as coagulant and partly decarbonized dolomite as a filter medium, provided high treatment efficiency. The system eliminated, or at least reduced, some undesi-

rable phenomena accompanying iron-salt coagulation – secondary colouring of the water and concomitant increase of iron concentration. The treatment effects depended on two major factors – the chemical properties and the proneness of both organic and inorganic pollutants to form complexes. Filtration on the dolomite-decarbonate bed was found to be effective for water of comparatively low organic pollution. The filtration process provided co-removal of colloids and organic pollutants. Both treatment processes, coagulation and filtration through partly decarbonized dolomite bed and the same type of filtration without coagulation, accounted for magnesium-enrichment and for pH adjustment of the water. Magnesium-enrichment is particularly desirable, as the low magnesium content in water is additionally reduced during coagulation.

Another advantage of the treatment train is saving on equipment for lime preparation and dosage which will no longer be needed.

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OCZYSZCZANIE WÓD METODĄ KOAGULACJI SOLAMI ŻELAZOWYMI I FILTRACJI PRZEZ ZŁOŻA DOLOMITOWE

Przedstawiono wyniki badań nad zastosowaniem częściowo zdekarbonizowanych dolomitów jako złóż filtracyjnych wód poddanych koagulacji siarczanem żelazowym, który został wstępnie utleniony chlorem. Badania wykazały, że na proces koagulacji solami żelazowymi mają wpływ właściwości fizyczno-chemiczne układów koloidalnych występujących w wodach powierzchniowych (są to najczęściej kompleksy żelazowo-

humusowe, stabilizowane wapniem w wodach zanieczyszczonych lub magnezem w wodach stosunkowo czystych). W procesie koagulacji produkty hydrolizy soli żelazowych reagują z kompleksami żelazowo-humusowymi, destabilizując je. W czasie tych reakcji następuje wymiana wapnia na magnez w wodach czystych i magnezu na wapń w wodach zanieczyszczonych. Podczas filtracji przez złożę częściowo zdekarbonizowanego dolomitu pozostałe kompleksy reagują z wapniem i magnezem, w wyniku czego następuje ich destabilizacja. Reakcjom tym towarzyszy wyrównanie ubytku wapnia i magnezu powstałego w czasie koagulacji. Ponadto w wyniku reakcji ze składnikami złoża zostaje związany agresywny dwutlenek węgla, dzięki czemu można wyeliminować urządzenia do neutralizacji wody. Zastosowanie omawianego układu umożliwi dobre oczyszczenie wody i zmniejszenie natężenia zjawisk związanych z tworzeniem się w czasie koagulacji solami żelazowymi barwnych kompleksów żelazowo-humusowych, wywołujących często wtórne zabarwienie wody i wzrost stężenia żelaza.

ОЧИСТКА ВОД МЕТОДОМ КОАГУЛЯЦИИ ЖЕЛЕЗНЫМИ СОЛЯМИ И ФИЛЬТРАЦИИ ЧЕРЕЗ ДОЛОМИТОВЫЕ СЛОИ

Представлены результаты исследований частично декарбонизированных доломитов как слоев фильтрационных вод, подверженных коагуляции сульфатом железа, который был предварительно окислен хлором. Исследования обнаружили, что на процесс коагуляции железными солями влияют физико-химические свойства коллоидных систем, выступающих в поверхностных водах (это чаще всего гумусно-ферралитные комплексы, стабилизированные кальцием в водах, загрязненных магнием или в водах относительно чистых). В процессе коагуляции продукты гидролиза железных солей реагируют с гумусно-ферралитными комплексами, дестабилизируя их. Во время этих реакций наступает замена кальция магнием в чистых водах и магния кальцием – в загрязненных водах. Во время фильтрации через слой частично декарбонизированного доломита остальные комплексы реагируют с кальцием и магнием, в результате чего наступает их дестабилизация. Этим реакциям сопутствует выравнивание потерь кальция и магния, возникающих во время коагуляции. Кроме этого, в результате реакции с компонентами слоя агрессивная двуокись серы соединяется, благодаря чему можно исключить устройства для нейтрализации воды. Применение обсуждаемой системы дает возможность хорошей очистки воды и понижения напряжения явлений, связанных с образованием во время коагуляции железными солями цветных гумусно-ферралитных комплексов, вызывающих часто вторичное окрашивание воды и повышение концентрации железа.

