

TADEUSZ KOWALSKI*

TREATMENT OF POLLUTED WATERS ON DOLOMITE BEDS

River water samples were treated by coagulation with chlorinated ferrous sulphate as flocculant and by filtration on a partly decarbonized dolomite bed. For comparison, the filtration process was also run on a sand bed. The application of the dolomite bed was found to be preferable, as dolomite has a noticeably destabilizing effect on the iron complexes formed in the course of the coagulation process. The advantages of the coagulation-filtration process can be itemized as follows: complete removal of turbidity and colour; 60% removal of permanganate COD; residual iron concentration below the admissible level (after sand filtration, iron concentration approached 1.0 ppm); slightly increased calcium and magnesium concentrations; and non-corrosive effluent from dolomite filtration. Coagulant doses varied between 50 and 100 g $\text{FeSO}_4 \times 7\text{H}_2\text{O}/\text{m}^3$.

1. INTRODUCTION

As the pollution load received by surface waters increases continually, their treatment for municipal water supply requires complicated technological systems and very high doses of chemicals. The result is that the treatment costs also continue to increase. To eliminate those drawbacks, attempts are made to use less complex technologies which permit application of waste salts, e.g. ferrous sulphate, as coagulants. It should be noted that alum coagulation involves high technological regimes in order to prevent penetration of aluminium into the effluent. The admissible concentration of aluminium in drinking water is 0.2 g Al/m^3 (the recommended level being as low as 0.05 g Al/m^3) [1].

To meet the quality demands for drinking water, the following technological system has been proposed – coagulation with pre-oxidized ferrous sulphate and filtration on a partly decarbonized dolomite bed [2]. The dolomite bed prepared according to this method has two major advantages – it enables pH adjustment and

* Institute of Environment Protection Engineering, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

provides sorption of organics, especially of humic substances. Carbon dioxide, which is formed in the course of the coagulation process, reacts with the dolomite bed, thus increasing the pH level as well as the concentration of magnesium and calcium [3]. The removal of organics during filtration is governed by the following mechanism – organic compounds have the power to form complexes with calcium and magnesium and are removed via this route [4]. The efficiency of removal depends on the biochemical degradability of the organic pollutants and on their power to form complexes with the components of the filter bed (this power being the highest at $\text{pH} < 7$) [4], [5]. Ferrous salt coagulation, however, has the disadvantage of creating favourable conditions for Fe (III) and Fe(II) cations to form stable complexes with the humic substances which are found in the surface water. This leads to considerable rise in the concentrations of coloured matter and iron compounds, even if filtration is run on a sand bed [6]. It is interesting to note that the power of Fe(II) cations to form complexes with humic substances is twice to four times as high as that of Fe(III) cations [7]. The sorbing capacity of humic substances with respect to iron oxides and iron hydroxides depends on the composition of the influent. In surface water, where calcium and magnesium are absent, sorption is described by the Langmuir isotherm. In the presence of calcium and magnesium, humic substances display an increased sorbing capacity [8].

2. METHODS OF INVESTIGATIONS

Surface water samples for the experiments were collected from the Odra River. The samples were coagulated by ferrous sulphate, which had been oxidized with an equimolar quantity of chlorine water prior to application. The coagulant doses applied amounted to $50 \text{ g FeSO}_4 \times 7\text{H}_2\text{O}/\text{m}^3$ and $100 \text{ g FeSO}_4 \times 7\text{H}_2\text{O}/\text{m}^3$. After sedimentation of flocs, the water samples were passed through a filter bed made of partly decarbonized dolomite ($\text{CaCO}_3 \times \text{MgO}$). Grain size and bed depth varied from 0.5 to 7.0 mm and from 60 to 110 cm, respectively. Three filtration rates were applied: 5, 10 and 15 m/h. For the purpose of comparison, the river water samples were also passed through a sand filter ($h = 74 \text{ cm}$).

3. RESULTS

The river water samples were turbid and showed high concentrations of organic pollutants (BOD_5 , 5 to $16.7 \text{ g O}_2/\text{m}^3$; TOC, 2.3 to $7.3 \text{ g C}/\text{m}^3$ and coloured matter, 30 to $70 \text{ g Pt}/\text{m}^3$). Table 1 includes data on the physicochemical composition of the samples investigated. In the technological system used for the purpose of this study, the majority of organic pollutants were removed by coagulation with oxidized ferrous sulphate. As shown by the data in tables 2 and 3, the removal efficiencies

Table 1

Physicochemical composition of the Odra River water

Parameter	Unit	Value		
		max	mean	min
pH		7.95	—	6.2
Colour	g Pt/m ³	70	45	30
Alkalinity	g CaCO ₃ /m ³	120	93.0	55
Hardness	deg.	15.8	14.8	12.8
Calcium	g Ca/m ³	81.5	71.5	62.8
Magnesium	g Mg/m ³	21.85	19.6	17.6
Iron	g Fe/m ³	1.15	0.63	0.4
BOD ₅	g O ₂ /m ³	16.7	10.1	5.0
COD _p	g O ₂ /m ³	9.5	8.43	7.4
Humic substances	g/m ³	7.14	4.44	2.45
TOC	g C/m ³	7.31	5.74	2.3
Ammonia nitrogen	g N/m ³	2.9	2.08	0.4

Table 2

Physicochemical composition of water after iron coagulation and filtration through partly decarbonized dolomite bed

Parameter	Unit	River water	Water after coagulation by 100 g FeSO ₄ × 7H ₂ O/m ³	Water after filtration				
				V _f				
				10 m/h	15 m/h	5 m/h		
				Bed depth (cm)				
				110	60	110	60	60
pH		7.55	6.5	8.45	7.0	7.2	6.0	7.2
Colour	g Pt/m ³	45.0	15	10.0	10.0	10.0	10.0	10.0
Alkalinity	g CaCO ₃ /m ³	90.0	60	120.0	85.0	90	80	80
COD _p	g O ₂ /m ³	9.0	4.4	4.1	3.7	4.2	3.9	4.1
BOD ₅	g O ₂ /m ³	5.6	5.6	4.3	4.25	4.25	4.25	4.1
Fe ³⁺	g/m ³	0.65	0.5	0.26	0.14	0.2	0.2	0.13
Fe ²⁺	g/m ³	0.5	0.8	0.0	0.08	0.0	0.0	0.0
Hardness	deg.	15.3	15.55	18.5	17.0	17.6	16.75	17.05
Calcium	g Ca/m ³	81.5	74.3	72.1	74.6	75.35	76.0	72.5
Magnesium	g Mg/m ³	18.4	17.07	20.6	16.3	18.5	18.0	21.5
Humic substances	g/m ³	6.12	0.34	0.408	0.408	0.34	—	0.408
TOC	g C/m ³	6.73	3.99	4.82	3.81	4.32	4.22	5.03

varied from 5 to 98.7% (av. 46 to 70%), from 44 to 63%, from 19 to 46% and from 55 to 80% for BOD₅, permanganate COD, TOC and humic substances, respectively. The effluent after coagulation showed only increased coloured matter concentration, which was caused by formation of iron hydroxide and Fe(III)-humic substance complexes. The possibility of treatment by oxidized ferrous sulphate coagulation was indicated by total concentration of iron in the effluent, which ranged from 0.5 to 8.0 g Fe/m³. This pattern is associated with the power of the organic pollutants to form complexes with iron compounds.

Table 3

Physicochemical composition of water after its coagulation by iron and filtration through partly decarbonized dolomite bed or sand bed

Parameter	Unit	River water	Water after coagulation by 100 g FeSO ₄ × 7H ₂ O/m ³	Water after filtration through partly decarbonized dolomite bed			
				V _r		Sand bed	
				10 m/h	15 m/h	10 m/h	
				Bed depth (cm)			
				110	60	110	74
pH		7.95	6.7	7.7	7.1	7.15	6.70
Colour	g Pt/m ³	70	100	10.0	15.0	15	60
Alkalinity	g CaCO ₃ /m ³	115	85.0	110.0	95.0	100	75
COD _p	g O ₂ /m ³	8.8	5.5	4.8	4.8	4.7	5.0
BOD ₅	g O ₂ /m ³	5.44	2.90	2.2	2.0	2.5	1.6
Fe ³⁺	g/m ³	0.32	3.0	0.32	0.6	0.6	2.84
Fe ²⁺	g/m ³	0.52	0.0	0	0.0	0.24	0.0
Hardness	deg.	15.8	15.55	17.8	17.0	17.8	15.0
Calcium	g Ca/m ³	71.4	764	81.4	77.11	75.7	74.5
Magnesium	g Mg/m ³	17.5	17.8	27.4	22.3	24.4	18.2
TOC	g C/m ³	6.92	5.6	5.7	4.8	5.5	4.8
Humic substances	g/m ³	3.5	1.36	0.68	1.15	1.15	1.22

Filtration on the dolomite bed brought about a rise in pH, magnesium concentration and hardness and provided a partial removal of organic pollutants (tables 2 and 3). The increase in magnesium concentration and pH depended on the filtration rate, bed depth [3] and coagulant dose. Thus, at a filtration rate of 10 m/h and a bed depth of about 110 cm, magnesium concentration increased from 15 to 60%, a hardness between 8 and 21%; pH approached 8, and in some instances was even higher (tables 2 and 3). According to the efficiency of the coagulation process,

the removal of permanganate COD, BOD₅, TOC and humic substances varied from 0 to 21%, from 0 to 45%, from 0 to 6% and from 0 to 50%, respectively. Coloured matter concentration and total iron content in the effluent from the filter bed ranged from 5 to 15 g Pt/m³ and from 0.04 to 0.5 Fe/m³, respectively, depending on the bed depth and the filtration rate applied.

When the river water samples were treated^o by coagulation and filtration on a sand bed, the efficiency of organic matter removal fell in the same range as when filtration was run on the dolomite bed. However, colour concentration and iron content in the effluent from the sand bed were noticeably higher, ranging from 10 to 60 g Pt/m³ and from 0.1 to 2.8 g Fe/m³, respectively (table 3).

4. DISCUSSION

The efficiency of filtration on the partly decarbonized dolomite bed depended on the complex-forming power of the organic pollutants present in the river water. This relationship was confirmed by the finding that the concentration of iron compounds in the effluent from the dolomite bed increased with the increasing content of humic substances after coagulation or in the raw water samples (fig. 1). But the complex-forming power also depended on the biochemical degradability of organic pollutants. This mechanism manifested itself in the increase of iron compound concentration and colour intensity in the effluent with the decreasing BOD₅ (fig. 2).

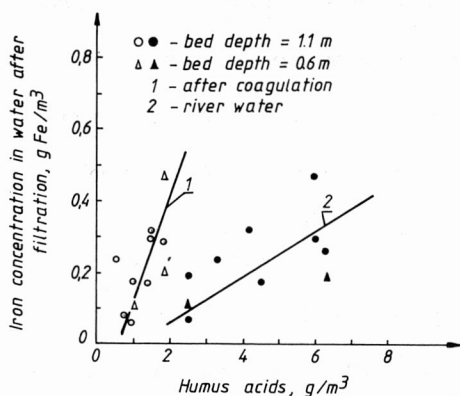


Fig. 1. Effect on humic substance concentrations on removal efficiency

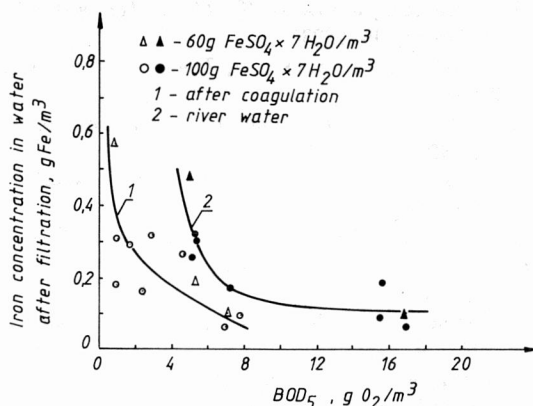


Fig. 2. Effect of BOD₅ on removal efficiency

In the course of the biochemical degradation process, there was a decrease in BOD₅ and an increase in the concentration of humic and protohumic substances, which were resistant to biodegradation [5]. The low reduction concentration of

organic substances during filtration on the dolomite bed proved that the complex-forming power of iron compounds had been exhausted. It should be noted that when the complex-forming power of various compounds is put in order, ferrous compounds are noticeably ahead of these of calcium and magnesium [9].

The low concentration of iron compounds in the effluent from the dolomite bed (as compared to the sand filter) indicates that partly decarbonized dolomite results in destabilization of iron-humic substance complexes.

5. CONCLUSIONS

The technological system involves coagulation with oxidized ferrous sulphate and filtration on a partly decarbonized dolomite bed. The system provides high removal efficiencies, pH adjustment and enrichment of the water with magnesium (magnesium concentration varied from 15 to 60%). It also allows us to eliminate some undesirable phenomena associated with the formation of iron-humic substance complexes.

Another major advantage of using the technological system is the elimination of some additional equipment which becomes necessary when pH is adjusted by lime treatment.

REFERENCES

- [1] CARNEY M., *European drinking water standards*, Journal AWWA, No. 6 (1991), 48-54.
- [2] KOWAL A.L., KOWALSKI T., *The method of treating polluted surface and underground waters*, Patent application P-292237.
- [3] KOWAL A.L., KOWALSKI T., *Treatment of soft water from creeks and torrents*, Ochrona Środowiska, 2 (1991), 43, 11-14.
- [4] KOWALSKI T., *Application of active dolomite beds to surface water treatment*, Ochrona Środowiska, 1 (1992), 45, 21-24.
- [5] KOWALSKI T., *Degree of biochemical decomposition of pollutants in water sewage*, Acta Hydrobiologica, 3/4 (1990), 279-292.
- [6] KOWAL A.L., *Technologia wody (Water treatment technology, in Polish)*, Arkady, Warszawa 1977.
- [7] FRIMMEL F.H., *Untersuchungen zur Komplexbildung des Eisens mit Huminstoffen eines Gewässers, Vom Wasser*, Vol. 53 (1979), 243-247.
- [8] TIPPING E., *The adsorption of aquatic humic substances by iron oxides*, Geochim. Cosmochim. Acta, 49 (1981), 91-199.
- [9] SCHNITZER M., SKINNER S.I.M., *Organometallic interactions in soils: Stability constants of Cu^{+2} , Fe^{+2} and Zn^{+2} fulvic acids complexes*, Soil Science, Vol. 102/6, 361.

OCZYSZCZANIE WÓD POWIERZCHNIOWYCH NA ZŁOŻACH DOLOMITOWYCH

Badano układ oczyszczania wód, w którym koagulowano je wstępnie utlenionym chlorem siarczanym żelazawym ($FeSO_4 \cdot 7H_2O$) i filtrowano przez złożę z dolomitu częściowo prażonego ($CaCO_3 \cdot MgO$). Stwierdzono, że w testowanym układzie następowało całkowite usunięcie mętności i barwy, eliminacja

lub zmniejszenie niekorzystnych zjawisk związanych z tworzeniem się barwnych kompleksów związków żelaza z substancjami humusowymi oraz 60% obniżenie utlenialności. Woda oczyszczona charakteryzuje się zawartością żelaza poniżej wartości dopuszczalnej (po filtracji przez złożę piaskowe stężenie żelaza było często większe od $1,0 \text{ g Fe/m}^3$), jest nieagresywna i wzbogacona w magnez i wapń.

ОЧИСТКА ПОВЕРХНОСТНЫХ ВОД НА ДОЛОМИТНЫХ ФИЛЬТРАХ

Исследована система очистки вод, в которой они подвергались коагуляции предварительно окисленным хлором сульфатом железа(III) ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) и фильтрации через фильтр из частично кальцинированного доломита ($\text{CaCO}_3 \cdot \text{MgO}$). Для сравнения воду одновременно фильтровали через песчаный фильтр. Было установлено, что в тестируемой системе наступали полное удаление мутности и цвета, элиминация или уменьшение отрицательных явлений, связанных с образованием цветных комплексов соединений железа с гуминовыми веществами, а также 60-процентное уменьшение окисляемости. Очищенная вода характеризуется содержанием железа ниже допустимого значения (после фильтрации через песчаный фильтр концентрация железа была больше $1,0 \text{ g Fe/m}^3$), является безвредной и богатой магнием и кальцием.