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TREATMENT OF ACID AND SOFT WATERS ON DOLOMITE BEDS

The method of treatment of acidic and soft waters is presented. The method involves filtration of water saturated with gaseous carbon dioxide through a dolomite or half-burned dolomite bed. Such a method allows neutralization, buffer stabilization, calcium-magnesium enrichment of the effluent and removal of organic pollutants from the water. Contents of Ca^{2+} and Mg^{2+} and the values of pH, alkalinity and hardness depend on the dose of carbon dioxide (50–100 g CO_2/m^3), depth of bed (1–1.5 m) and hydraulic loading (5–15 m^3/m^2h). During filtration of the water through these beds the complex organic compounds with calcium and magnesium are formed on the surface of dolomite. The reduction efficiency of organic pollutants on half-burned dolomite beds (the maximum decrease in permanganate value about 65%) depends on the capability of these pollutants to form complex compounds (maximum reduction at pH = 6.0–7.0 and above 9.0).

1 INTRODUCTION

High concentrations of airborne sulphur oxides and nitrogen oxides are responsible for the occurrence of acid or very soft waters in some parts of Poland. This holds specifically for the Karkonosze and Tatra Mountains [1] and [2]. Mountainous shelters, hostels and many other places providing tourist services make use of very simple sewage treatment systems (predominantly digestion tanks) which are mostly overloaded or inadequately operated. Mountain streams carry waters differing considerably in their physicochemical composition from those of the lowland streams. Composition of a mountain stream varies from one catchment to another, and the variety of components is rather poor. Streams flowing over swampy areas carry large amounts of humic substances, while those coming from a rocky area contain low concentrations of suspended solids or mineral substances. Generally, the temperature of mountain streams ranges from 271.5 to 291 K throughout the year. Mineral matter content (dissolved solids), hardness, alkalinity and pH are low, varying from 35 to 264 g/m^3, from 0.19 to 4.0 deg, from 0 to 52 g $CaCO_3/m^3$ and

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from 3.2 to 7.3, respectively. Concentration of organic compounds varies considerably (permanganate COD, 1.6 to 18.6 g O_2/m^3; BOD_5, 0.4 to 24 g O_2/m^3; dichromate COD, 4.2 to 40 g O_2/m^3), and so does bacteriological contamination (Coli titre, 0.00004 to 50). As a result, mountain streams cannot be used for municipal purposes until after-treatment in a full technological system consisting of coagulation, filtration, sorption and disinfection.

Mountain stream intakes have two inherent disadvantages – a small size and difficult access. It is therefore advisable that those objects were automated in order to eliminate need for involving high-skilled manpower. It is worth noting that a water treatment plant using a full physicochemical system would not only be difficult to operate, but also insufficient to yield the treatment effects desired.

Low alkalinity and low pH are a serious hindrance to the coagulation process [3]. The coagulating agent hydrolyzes, and the evolving acid reacts with the bicarbonates that the present in the water to be treated, thus reducing its alkalinity (e.g., a coagulant dose of 1 g $Al_2(SO_4)_3 \cdot 18H_2O$ decreases alkalinity by 0.45 g $CaCO_3$). For this reason, slightly alkaline water should be pretreated with calcium hydroxide.

The efficiency of the coagulation process is also influenced by the presence of some other anions or cations. For example, concentrations of sulphates that are not sufficiently high [4] may considerably extend the duration of the flocculation process and, consequently, inhibit the formation of flocs. This was so in the case of the Kwisa River water treatment. In spite of pH adjustment by calcium hydroxide addition, no flocs were found to form [5].

In this paper, a new technology of acid and soft water treatment (which is particularly suitable for polluted mountain streams) has been proposed. In the method, carbon dioxide is added to the water to be treated and thereafter filtration is run on a half-burned dolomite bed [6].

2. METHODS

Water samples were treated with an aqueous solution of carbon dioxide in portions of up to 400 g CO_2/m^3 and thereafter passed through a half-burned dolomite or a dolomite bed, which had a depth of 120 cm, a diameter of 4 cm, and a grain size range of 0.5 to 7 mm. Filtration rate varied from 5 to 15 m^3/m^2h. Before passage through the filter bed, the water samples were treated with 1 to 5 g Cl_2/m^3.

The investigations were carried out on water samples collected from the mountain river Kwisa upstream of Świeradów. The following parameters were determined: pH, total hardness, alkalinity, permanganate COD, colour calcium, magnesium and manganese concentrations, as well as bacterial counts. Concentrations of heavy metals (Pb, Cu, Zn, Ni, Cr and Co) were determined in batch samples.

3. EXPERIMENTAL

3.1. CHEMICAL PROCESSES IN THE HALF-BURNED DOLOMITE BED

Filtration through the half-burned dolomite bed involved some physical and chemical phenomena accounting for the rise in alkalinity, hardness and pH [7]. There were also favourable conditions for the sorption of organic pollutants which brought about a decrease of permanganate COD and colour intensity.

The half-burned dolomite bed was produced by partial decarbonization of dolomite at 873 to 1125 K in the presence of carbon dioxide. The reaction runs as follows:

$$n\text{Mg} \cdot m\text{Ca}(\text{CO}_3)_{n+m} \rightarrow n\text{MgO} + m\text{CaCO}_3 + n\text{CO}_2. \tag{1}$$
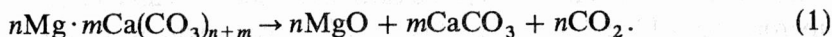
The half-burned dolomite bed involves the following reactions:

$$\text{MgO} + 2\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Mg}(\text{HCO}_3)_2, \tag{2}$$

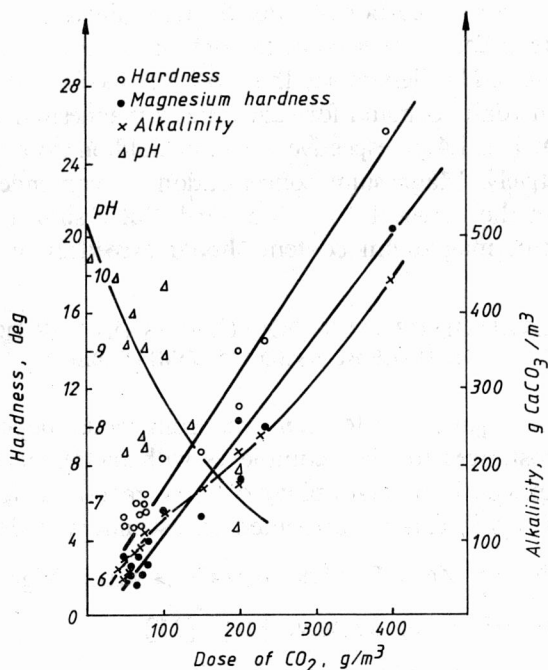$$\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{HCO}_3)_2. \tag{3}$$
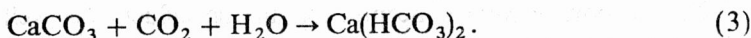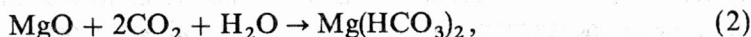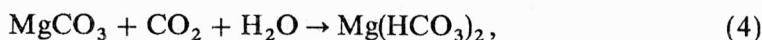

Fig. 1. Effect of carbon dioxide dose on pH, hardness and alkalinity of the effluent passed through the half-burned dolomite bed (filtration rate, 5 m/h)

At low filtration rates or low carbon dioxide doses (effluent pH > 8.3) the reaction proceeds as follows:

$$MgCO_3 + CO_2 + H_2O \rightarrow Mg(HCO_3)_2, \tag{4}$$

$$MgO + Mg(HCO_3)_2 \rightarrow 2MgCO_3 + H_2O. \tag{5}$$

The reaction of carbon dioxide with half-burned dolomite accounted for the increase of hardness and alkalinity (figure 1), which varied according to the carbon dioxide dose and the filtration rate applied. The increment in total hardness decreased with the increasing filtration rate, amounting, e.g., to 0.085 deg/mg CO_2 for $V_f = 5$ m/h, and to 0.057 deg/mg CO_2 for $V_f = 15$ m/h, which proved that the process involved reactions (2) and (5) rather than reaction (3). But it was primarily magnesium hardness that contributed to the degree and increment of total hardness (60 to 80%). The increase of alkalinity depended far more on the carbon dioxide dose than on the filtration rate, and approached 1.13 g $CaCO_3$/g CO_2 (which is consistent with the theoretical value).

Both filtration rate and carbon dioxide dose contributed to the pH level in the effluent which varied between 0.5 and 10.5, according to the filtration rate applied. The increase of the carbon dioxide dose brought about a decrease of pH.

The carbon dioxide concentration in the effluent (as well as its form) was also dose-dependent. At doses ranging between 50 and 100 g CO_2/m^3, there persisted some small amounts of aggressive carbon dioxide in the effluent.

The reactions described here accounted for enrichment of the river water with calcium and magnesium. Needless to say that both the species are of importance to the human organism. The daily demand for calcium and magnesium varies in adults from 0.8 to 1.2 g and from 1 to 1.4 g, respectively, and in children from 0.4 to 0.6 g and from 0.5 to 0.7 g, respectively. Magnesium concentration recommended by the WHO for potable water falls in the range of 30 to 125 g/m^3. But if sulphate concentrations are higher than 250 g/m^3, magnesium content should exceed 30 g /m^3 [8].

3.2. REMOVAL OF ORGANIC POLLUTANTS ON THE DOLOMITE OR HALF-BURNED DOLOMITE BED

The efficiency of organic matter removal from water depends heavily on the ability of humic substances to form complexes with metals, in that particular case with calcium and magnesium. The ability of some metals to form complexes with humic acid (at pH = 5.0) can be presented in ascendent order [9]:

$$Pb, \; Cu, \; Fe^{+3} > Zn > Fe^{+2} > Ni > Co > Mn > Mg > Ca > Ba.$$
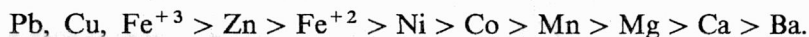
For fulvic acids (at pH = 5.0) we have [10], [11]:

$$Cu > Pb > Fe^{+2} > Ni > Mn \sim Co > Ca > Zn > Mg.$$

Humic acid–metal complexes are formed either by ion exchange (cation H^+ for metal ion) or as a result of formation of coordinate bond by weakly acidic functional groups (COOH and OH, containing oxygen which acts as a ligand atom). Complexees with dominating coordinate bonds are more stable [12].

Many investigators assume that fulvic and humic acids form complexes with Ca^{+2}, Mg^{+2} and Al^{+3} through bridges (and these are predominantly built of the cations mentioned) [13]. Calcium and magnesium cations are collected in the adsorption layer of humic substances. They abate the negative potential of the ligand, thus facilitating sorption of other metals, e.g. iron [14]. The efficiency of organics removal by sorption depends on the biochemical degradability of the species to be removed [15]. Thus, with the increasing degree of biochemical degradability the removal efficiency of easily biodegradable pollutants decreases and that of slowly biodegradable species increases.

3.3. FIXATION OF ORGANIC POLLUTANTS
IN THE DOLOMITE AND HALF-BURNED DOLOMITE BEDS

The reaction of organic substances with the filter bed is influenced by the following factors: pH, biochemical degradability and the ability of organic substance to form complexes with calcium and magnesium. Thus, slightly acidic and alkaline pH (~ 6.0 and 9.5 to 10.5; figure 2) yielded the highest efficiences of organic substances removal which varied from 20 to 30% and from 50 to 60% for dolomite and half-burned dolomite, respectively. There was a simultaneous reduction in colour intensity which varies from 25 g Pt/m^3 to 5 g Pt/m^3. The efficiency of organic matter removal
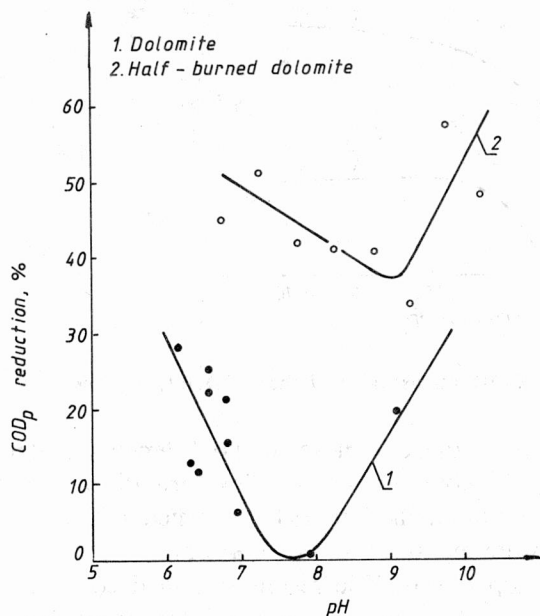

Fig. 2. Effect of pH on the decrease of permanganate COD after filtration through the half-burned dolomite bed
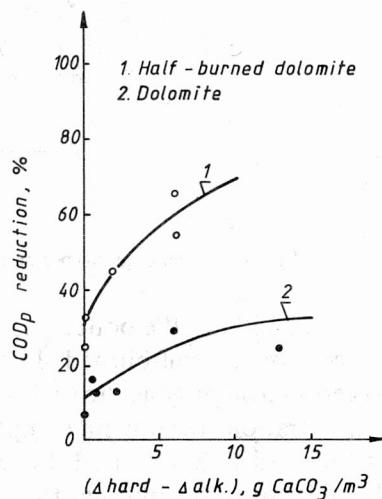
Fig. 3. Percentage of permanganate COD decrease versus ability of pollutants to form organic complexes

was the lowest at pH $= 7.5$, amounting to 0% for dolomite. At pH $= 9.0$, that efficiency amounts to 35% for half-burned dolomite (figure 2). Such a relationship should be attributed both to the ability of organic pollutants to form complexes with the bed components and to the bed pore structure which – as a result of decarbonation – was far better developed in half-burned dolomite.

The content of organic substance–calcium (or magnesium) complexes in the water was determined from the difference in the increment between hardness and alkalinity:

$$c_{\text{org. compl.}} = \Delta_{\text{hard.}} - \Delta_{\text{alk.}}$$

where $c_{\text{org. compl.}}$ is concentration of organic complex (g $CaCO_3/m^3$), $\Delta_{\text{hard.}}$ is increment of water hardness after filtration through half-burned dolomite or dolomite (g $CaCO_3/m^3$) and $\Delta_{\text{alk.}}$ is increment of water alkalinity after filtration through half-burned dolomite or dolomite (g $CaCO_3/m^3$).

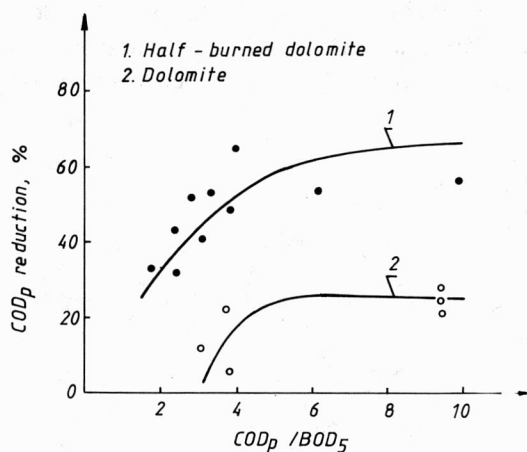The amount of organic complexes (in terms of calcium carbonate) varied from zero to 13 g $CaCO_3/m^3$.

Fig. 4. Percentage of permanganate COD versus value of the COD_p/BOD_5 ratio

The ability of the pollutants to form organic complexes was pH-dependent. Thus, in the case of half-burned dolomite, the efficiency of complex formation was the largest in a slightly acidic (pH $\sim$ 6.5) and in an alkaline (pH $\sim$ 10) media. The lowest concentrations of organic complexes were measured at pH $\sim$ 8–9 and at pH $\sim$ 7 for half-burned dolomite and dolomite, respectively. The results obtained corroborate the relationship between the efficiency of organics removal after their passage through a dolomite or a half-burned dolomite bed and the pH of the water. This relation can be seen from figure 3 where the removal efficiency is related to the effluent concentration of organic complexes (at pH 6 to 7). As shown by the curves,

the decrement of permanganate COD increased with the ability of the pollutants to form organic complexes. The plots in figure 3 are similar to those relating the permanganate COD decrement to the value of the COD_p/BOD_5 ratio (i.e., to the biochemical degradability of organic pollutants), (figure 4). For the water under study, the value of permanganate COD expressed primarily coloured matter concentration, whereas the value of the COD_p/BOD_5 ratio showed the contribution of humic substances to biodegradable pollutants. The efficiency of organic substance removal by half-burned dolomite or dolomite increased with the increasing proportion of coloured matter to the total amount of pollutants. But once a certain value had been reached $((COD_p/BOD_5) > 6$ with a 25% decrease of COD_p for the dolomite bed, and $(COD_p/BOD_5) > 10$ with an almost 65% decrease of COD_p for the half-burned dolomite bed), the removal efficiency for organic substances remained on a constant level (figure 4). Such a behaviour was an indication that the organic complexes involved were formed on the basis of humic substances. This finding was corroborated by the linear relationship between coloured matter concentration and organic complexes concentration [7].

4. CONCLUDING REMARKS

Our investigations have shown that the technology proposed for the treatment of acidic and soft waters from mountain streams provides an effluent of the quality desired. The technological system involves the following steps: addition of carbon dioxide and filtration through a burned-dolomite bed. Such an approach enables neutralization, buffer stabilization, calcium and magnesium enrichment and removal of organic species. The efficiency of organics removal depends on the pH of the water to be treated and on the biochemical degradability of the organic species to be removed. And this is associated with the ability of organic substances to form complexes with the components of the filter bed.

The technology proposed is simple; it enables wide application of containers and full automation of the water treatment plant.

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OCZYSZCZANIE KWAŚNYCH I MIĘKKICH WÓD NA ZŁOŻACH DOLOMITOWYCH

Przedstawiono metodę oczyszczania kwaśnych i miękkich wód. Polega ona na ich filtracii przez częściowo zdekarbonizowane złoże dolomitowe ($CaCO_3 \cdot MgO$) lub dolomitowe ($CaCO_3 \cdot MgCO_3$) po uprzednim dodaniu CO_2 do wody. Badano miękką i zanieczyszczoną wodę rzeki Kwisy. W wyniku reakcji dwutlenku węgla ze złożem wzrasta twardość wody, głównie magnezowa (dolomit częściowo zdekarbonizowany) i wapniowa, i zwiększa się stopień neutralizacji i stabilizacji wody. pH, a także zawartość wapnia i magnezu w wodzie zależą od dawki CO_2 i prędkości filtracji. Na złożu są również usuwane zanieczyszczenia organiczne, które wiążą się z jego składnikami. Powstają kompleksy organiczne substancji humusowych z wapniem i magnezem. Stopień usuwania zanieczyszczeń organicznych zależy od ich podatności na biochemiczny rozkład, łatwość tworzenia kompleksów z wapniem i magnezem oraz od pH wody. Maksymalny stopień usunięcia zanieczyszczeń organicznych (ok. 65%) uzyskano poniżej i powyżej pH = 8,5 (dolomit częściowo zdekarbonizowany) oraz powyżej i poniżej pH = 7,5 (dolomit).

ОЧИСТКА КИСЛЫХ И МЯГКИХ ВОД НА ДОЛОМИТНЫХ СЛОЯХ

Представлен метод очистки кислых и мягких вод. Он заключается в фильтрации через частично декарбонизированный доломитный слой ($CaCO_3 \cdot MgO$) или доломитный ($CaCO_3 \cdot MgCO_3$) после предварительного добавления CO_2 к воде. Исследована мягкая и загрязненная вода реки Квисы. В результате реакции двуокиси углерода с доломитным слоем растет жесткость воды, в основном магниевая (доломит частично декарбонизированный) и кальциевая, и повышается степень нейтрализации и стабилизации воды. pH, а также содержание кальция и магния в воде зависят от дозы CO_2 и скорости фильтрации. На слое удаляются также органические загрязнения, которые связываются с его компонентами. Образуются органические комплексы гуминовых веществ с кальцием и магнием. Степень удаления органических загрязнений зависит от их восприимчивости к биохимическому разложению, легкости образования комплексов с кальцием и магнием, а также от pH воды. Максимальную степень удаления органических загрязнений (ок. 65%) получили ниже и выше pH = 8,5 (доломит частично декарбонизированный), а также выше и ниже pH = 7,5 (доломит).