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SOME PROBLEMS OF PRECHLORINATION OF WATERS CONTAINING HUMIC ACIDS

In water treatment, coagulation or sorption is used very often for the removal of humic acids. To increase the efficiency of these processes, prechlorination is applied. The investigations revealed that chlorine causes only a degradation of macromolecular humic acids, which thereafter are still present in water. During subsequent treatment stages, removal of small molecules, fulvic acids mainly, is limited. Therefore, after prechlorination the efficiencies of both coagulation with aluminium salts and sorption on powdered active carbon decrease.

1. INTRODUCTION

Humic acids are natural pollutants of ground waters. These substances penetrate to natural waters from soil where they are formed in natural processes of biological and chemical degradation of vegetable matter. If humic acids are present in water, an increase of colour intensity and COD is observed. These substances can easily react with other pollutants existing in water, giving rise to new harmful substances. In addition, humic acids can adsorb mineral and organic substances on their surfaces and they also can form complexes with heavy metals (e.g. lead, copper). During their reaction with chlorine, trihalomethans (THMs) are formed [1].

In water treatment, different methods are used to remove humic acids from water and thus to obtain a permissible level of drinking water purity.

2. EFFICIENCY OF UNIT PROCESSES USED IN WATER TREATMENT DURING REMOVAL OF HUMIC SUBSTANCES

BLACK [2] reported that natural waters contain 15-50 g/m³ of natural organic substances (humic substances) which are composed of fulvic acids (87%), hymetamelanic acids (11%) and humic acids (2%). It is assumed that humic acids having the highest mo-

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lecular weight (up to 200,000 [3]) are responsible for colour intensity. On the other hand, COD is mainly due to fulvic acids (molecular weight up to 1,000).

Coagulation, sorption and oxidation are processes most frequently used in removal of humic acids. The efficiency of these processes differs considerably and depends on the reagents used as well as on chemical composition of the water being purified.

In water treatment, humic acids, because of their colloidal character and a negative electric charge, are frequently coagulated by polyelectrolytes and hydrolyzing iron and aluminium salts. During coagulation of humic acids, a decrease of colour intensity was more substantial (up to 100%) than the decrease of COD (up to 80%) [4].

Humic acids can also be removed as a result of their coagulation by lime. SEMMENS and STAPLES [5] found that this method enables 52% removal of the fraction of molecules having a molecular weight between 1,000 and 10,000. Simultaneously there is observed a 40% increase in the concentration of the fraction having a molecular weight < 1,000, being the result of desintegration of long organic chains. This is a risk, because just from these fractions, to a great extent, THMs are formed (in a chlorination reaction).

Sorption efficiency on active carbon depends considerably on the molecular weight of impurities, their polarity and pH of water [6]. It was found that during sorption the fractions with a molecular weight between 100 and 1,000 are removed efficiently. Use of powdered active carbon allows a 90–95% decrease of BOD [7].

3. PRECHLORINATION OF WATERS CONTAINING HUMIC ACIDS

Attempts to remove humic acids by their oxidation with chlorocompounds or ozone revealed [8] that an intense decrease of colour intensity was a result of degradation of humic substances to fulvic acids which are characterized by a lower colour intensity. Therefore, the efficiency of humic acids removal is only apparent. In addition, due to the application of chlorine in presence of humic acids, THMs are formed. THMs are compounds of general formula CH_3X (where X denotes Cl, Br, I and F) and because of their cancerogenity their concentration in drinking water has to be kept as low as possible.

TRUSSELL and UMPRESS [9] reported that formation of THMs is affected by many parameters. They also found that THM formation is the slowest reaction in water treatment which can proceed even longer than 24 h. According to these authors, a pH decrease from 9 to 7 (fig. 1) causes a decrease in concentration of halogenated organic compounds to about 50%. Also the presence of bromides in water is essential, because in presence of chlorine they participate in formation of THMs (fig. 2).

In many Water Plant Units, prechlorination is commonly used as the step in water treatment. The aim of this operation is the improvement of the subsequent technological processes. However, very recent investigations indicate that prechlorination improves only apparently the efficiency of other processes. On the other hand, it can even cause secondary water pollution, among others, with cancerogenic THMs.

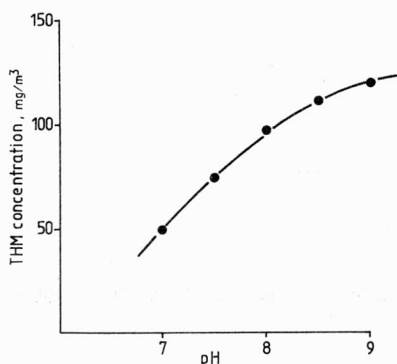


Fig. 1. Influence of water pH on the concentration of THMs [9]

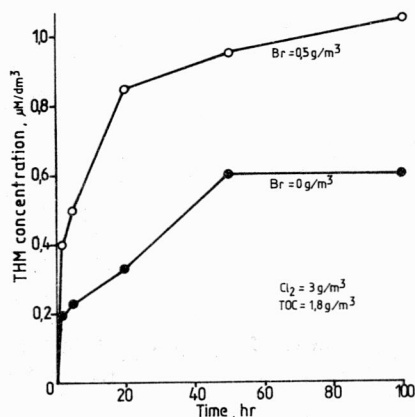


Fig. 2. Influence of bromide concentrations on the concentration allowing formation of THMs [9]

4. EXPERIMENTAL

The investigations carried out proved that prechlorination of water containing humic acids affects the efficiency of their removal from natural waters as well as the decrease in COD and colour intensity in volume coagulation processes using $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and during batch sorption on powdered active carbon, Carbopol Z-4 (ZEW Racibórz, Pl).

5. MATERIALS

Model water solutions were prepared from synthetic humic acids (Fluka, Switzerland) as well as ground waters strongly polluted with humic substances. 1% $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ water solution was added to the water samples investigated and the suspensions obtained were rapidly mixed (3 min) followed by slow-mixing period (25 min) and sedimentation (1.5 h). Sorption occurs in 1% suspension of powdered active carbon (grain fraction of $0.038\text{--}1.41 \times 10^{-3}\text{m}$). After 0.5 h the samples were filtered. Diluted chlorine water ($1\text{ g Cl}_2/\text{m}^3$) was used for prechlorination. The prechlorinated samples were analyzed after 0.5 h at room temperature.

6. EXPERIMENTAL DATA AND THEIR ANALYSIS

6.1. CHLORINATION OF WATER CONTAINING HUMIC ACIDS

The effect of chlorine dose on the efficiency of colour intensity and COD removal and humic acids concentration was estimated. It has been stated that a distinct removal of colour intensity observed depends directly on the chlorine dose and the contact time between coloured impurities and chlorine. Simultaneously (fig. 3), only a small decrease in humic acid concentration is observed. Probably at chlorine doses of $5\text{ g}/\text{m}^3$ the macromo-

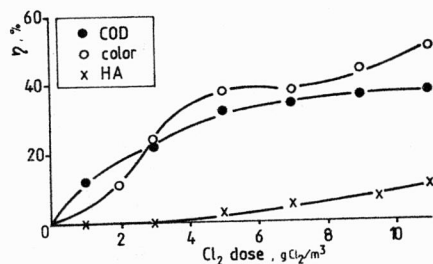


Fig. 3. Influence of chlorine dose on decrease in colour intensity, COD and humic acids concentration ($HA_0 = 5 \text{ g/m}^3$, contact time = 1 h)

lecular humic acids are degraded only to smaller molecules of fulvic acids which still remain in the solution. Only at doses of $11 \text{ g Cl}_2/\text{m}^3$ an inconsiderable decrease in concentration of humic substances is observed, which confirms the thesis on formation of volatile THMs. Simultaneously with the increase of the chlorine dose, a decrease in COD of the solution was observed.

Taking into account the change of colour intensity, COD and humic acid concentration, it can be assumed that during chlorination mainly large, coloured molecules of humic acids are degraded to smaller molecules of fulvic acids with a lower colour intensity. It can also be assumed that in water solutions simultaneously with the increase in chlorine dose, there are formed organic substances resistant to oxidation by $KMnO_4$ (especially at Cl_2 dose $> 5 \text{ g/m}^3$). Probably that is the reason why COD decreases (about 34%) with a simultaneous slight removal of humic acids (about 8%).

6.2. PRECHLORINATION AND COAGULATION OF HUMIC ACIDS WITH ALUMINIUM SULPHATE

Aluminium sulphate was used to coagulate humic acids. Its optimal dose determined in preliminary experiments was $40 \text{ g of Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}/\text{m}^3$. Influence of prechlorination on treatment efficiency of water containing humic acids is given in fig. 4.

It was found that during coagulation with aluminium salts, the removal efficiency of coloured organic compounds is unfavourably influenced by prechlorination. It was observed that chlorine doses higher than 9 g/m^3 reduced (by about 40%) the colour removal. This is the result of degradation of the large molecules of humic acids to smaller ones, which are less prone to be removed with $\text{Al}(\text{OH})_3$ flocks. It was also observed that a chlorine dose of 2 g/m^3 decreases the efficiency of COD removal by about 20%. If the chlorine dose was increased up to 11 g/m^3 , the effect obtained was close to that obtained in experiments without prechlorination ($\eta_{\text{COD}} = 50\%$). Simultaneously, this dose efficiently decreased removal of humic acids (by about 30%) in the coagulation process. A further increase in the chlorine dose has no influence on the process efficiency. The results obtained confirm the view on the formation, in water, of halogenated organic compounds resistant to oxidation which are also unremovable during coagulation process.

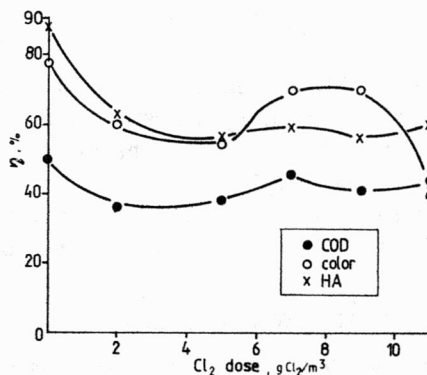


Fig. 4. Influence of prechlorination on the coagulation efficiency of water containing humic acids ($D_{\text{coag}} = 40 \text{ g Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$)

6.3. PRECHLORINATION AND SORPTION ON POWDERED ACTIVE CARBON

The influence of chlorination on sorption efficiency of humic acids on powdered active carbon was established at the optimal dose (70 g/m^3) of active carbon added after sample prechlorination.

Analysis of the influence of chlorine dose on the decrease of colour intensity, COD, and concentration of humic acids (fig. 5) allows the statement that the increase of chlorine dose introduced into the water slightly decreases the sorption efficiency of coloured pollutants (from $\eta_c = 92\%$ to $\eta_c = 86\%$ at $D_{\text{Cl}_2} = 13 \text{ g/m}^3$). The data obtained can indicate that small molecules of fulvic acids as well as the halogenated organic compounds formed are weakly sorbed on powdered active carbon. Comparing the results obtained with those reported by other authors, we may also assume that some pollutants are desorbed due to the presence of chlorine as well as that formation of compounds not existing in untreated water is catalyzed by carbon.

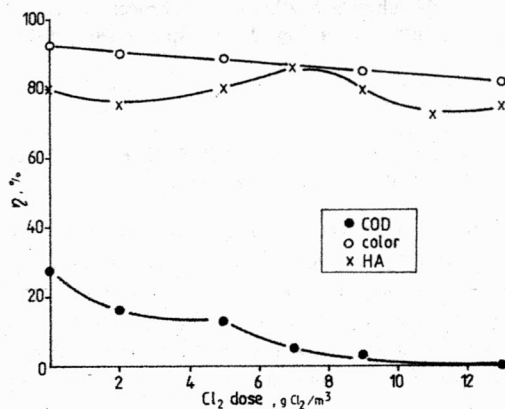


Fig. 5. Influence of prechlorination on sorption efficiency of water containing humic acids ($D_{\text{p.a.c.}} = 70 \text{ g/m}^3$)

7. CONCLUSIONS

From the experimental results obtained the following conclusions can be drawn:

1. Chlorination of humic acids considerably decreases colour intensity of solution, and only slightly COD and concentration of these acids. This means that only degradation of macromolecular humic acids is caused by chlorine.

2. In the coagulation process with aluminium salts and the sorption on powdered active carbon, prechlorination affects unfavourably the removal efficiency of humic acids.

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WYBRANE ASPEKTY WSTĘPNEGO CHLOROWANIA WÓD ZAWIERAJĄCYCH KWASY HUMUSOWE

Koagulacja i sorpcja w technologii wody są często stosowane do usuwania substancji humusowych. Aby zwiększyć efektywność tych procesów, stosowane jest także wstępne chlorowanie wód. Badania wykazały, że chlor powodował jedynie degradację makromolekuł, których pochodne nadal pozostawały w wodzie. Efektywność usuwania małych cząsteczek, głównie kwasów fulwowych, w klasycznych procesach oczyszczania wody jest ograniczona. Stąd też zastosowanie wstępnego chlorowania powodowało spadek sprawności zarówno koagulacji, jak i sorpcji kwasów humusowych.

ИЗБРАННЫЕ АСПЕКТЫ ПРЕДВАРИТЕЛЬНОГО ХЛОРИРОВАНИЯ ВОД, СОДЕРЖАЩИХ ГУМИНОВЫЕ КИСЛОТЫ

Коагуляцию и сорбцию в технологии воды часто применяется для удаления гуминовых веществ. Чтобы увеличить эффективность этих процессов, применяют также предварительное хлорирование вод. Исследования обнаружили, что хлор вызывал лишь деградацию макромолекул, которых производные в дальнейшем оставались в воде. Эффективность удаления малых частиц, в основном фульвокислот, в классических процессах очистки воды является ограниченной. Отсюда также применение предварительного хлорирования вызывало понижение производительности как коагуляции, так и сорбции гуминовых кислот.