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## REMOVAL OF HUMIC ACIDS AND SOME HEVAY METALS FROM WATER

The interaction between humic acids (HA) and some heavy metals (HM) in water and its contribution to the removal of these pollutants was investigated. The presence of HA influenced the efficiency of  $Pb^{2+}$  and  $Cu^{2+}$  ions removal but had no effect on the removal of  $Zn^{2+}$  and  $Ni^{2+}$  ions. This was in agreement with the proneness of these HM to form metal-organic complexes with HA. The main contributing factor in the processes being tested was pH level. The efficiencies of HA and HM removal in precipitation, sorption, sedimentation and coagulation were determined.

### 1. INTRODUCTION

The presence of heavy metals (HM) and humic acids (HA) in waters can cause some problems during their purification. Taking account of this statement, the interactions of HA with lead, copper, zinc and nickel and the effect of this phenomenon on heavy metal removal were studied. Investigations were carried out to explain the following problems: the behaviour of HA in aqueous solutions and in the course of the treatment process; the formation of metal-organic complexes; the mechanism and efficiency of heavy metal removal from solutions with or without humic acids.

### 2. RESULTS OF INVESTIGATIONS

The experiments were carried out on two types of water samples: polluted model solutions enriched with HA (analytically pure or isolated from peat or black-earth) and HM, and the Odra River water enriched with HM.

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## 2.1. REMOVAL OF HUMIC ACIDS

The results showed that the solubility of HA was pH-dependent and influenced by the presence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. In solutions with no  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, at  $\text{pH} > 4.0$ , the solubility of HA was found to increase. When  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were present there was a distinct decrease in the solubility of HA at pH of  $\text{CaCO}_3$  precipitation and particularly of  $\text{Mg}(\text{OH})_2$  precipitation. These compounds acted as co-precipitating factors for organic pollutants. The solubility of HA was found to decrease at pH ranging from 2.0 to 4.0, irrespective of the presence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. This can be attributed to the increasing aggregation of slightly soluble humus fractions, which leads to the precipitation of humic and hylatomelanic acids. The experiments also showed that humic and hylatomelanic acids were responsible for an increase in colour intensity, while fulvic acids contributed to an increase of permanganate COD ( $\text{COD}_p$ ).

The efficiency of HA removal depended primarily on pH, i.e., on the solubility of these acids. Thus, pH adjustment combined with 2-hour sedimentation brought about a decrease of their content in the environment of high  $\text{H}^+$  or  $\text{OH}^-$  ion concentration. The high efficiency of HA removal obtained in an alkaline medium substantiates the usability of precipitation methods for water softening during the treatment of aqueous solutions which contain humic acids.

The decrease of HA content in an acidic medium was slighter than that in an alkaline medium. At pH up to about 4.0, coloured fractions alone were precipitated, whereas a strongly alkaline medium enabled partial removal of fulvic acids. At  $4.0 < \text{pH} < 9.0$ , humic substances persisted in the solution in a dissolved or colloidal form, or in the form of dispersed non-settleable particles which had not been removed during the 2-hour sedimentation. Filtration through a hard filter paper enabled the removal of a significant part of the humus fractions (predominantly slightly soluble and coloured fractions). It may be assumed that during filtering the particles of the substances to be removed are prone to form aggregates and that the sediment retained on the filter paper acts as an aid to removing these organics.

The efficiency of HA sorption on PAC (Carbopol Z-4 or Norit) and bentonite depended not so much on the sorbent dose and duration of the process as on pH. Carbopol Z-4 and Norit yielded primarily the removal of slightly soluble humus fractions. High efficiencies were obtained at  $\text{pH} > 11.0$ . In the range  $6.0 < \text{pH} < 10.0$ , the efficiencies achieved were very low. Of the unit processes studied, coagulation was the most effective. But coagulation was also pH-dependent. Thus, the best effects were obtained at  $\text{pH} \leq 6.0$  and  $\text{pH} > 10.0$ , irrespective of whether alum or iron salts ( $\text{Fe}^{3+}$ ) had been used as coagulants. The high efficiency achieved at  $\text{pH} \leq 6.0$  may have been contributed to the following factors: the presence of iron and aluminium ions and their hydroxocomplexes (having positive charges), which exert a neutralizing effect on the negatively charged organic colloids; extremely slight solubility of  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  and slight solubility of HA.

The high efficiency of the process in an alkaline medium should be attributed to the co-precipitation of organics with the particles of  $\text{Mg}(\text{OH})_2$  and  $\text{CaCO}_3$ . A decrease of the coagulation efficiency at  $6.0 < \text{pH} < 10.0$  resulted from the increased dissociation of humic acids and from the decreased quantity of agents destabilizing these acids. At this  $\text{H}^+$  ion concentration, ferric sulphate appeared to be less efficient than alum, especially in removing a colour intensity.  $\text{Fe}^{3+}$  ions were prone to form nonsetttable coloured complexes with HA, in general, and more commonly with fulvic acids. This is an important reason why iron salts should be eliminated as coagulants in the treatment of water when humic substances are present. The value of the coagulant consumption efficiency (CCE) was an indication that  $\text{Al}^{3+}$  ions were more efficiently utilized than  $\text{Fe}^{3+}$  ions. Thus, application of identical doses of alum and ferric sulphates yielded CCE values that were 2.5 times higher for  $\text{Al}^{3+}$  than for  $\text{Fe}^{3+}$  ions.  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  cations acted as coagulants and coordination ions for humic substances. The residual concentrations of the cations in the effluent ( $\text{Fe}_r^{3+}$  or  $\text{Al}_r^{3+}$ ) were linearly correlated with the remaining concentrations of humic acids ( $\text{HA}_r$ ):

$$\text{Fe}_r^{3+} = 1.794 \text{ HA}_r - 1.89 \quad [\%],$$

$$\text{Al}_r^{3+} = 0.996 \text{ HA}_r + 6.94 \quad [\%].$$

## 2.2. FORMATION OF METAL-ORGANIC COMPLEXES

Investigations of the formation of metal-organic complexes showed that this process efficiency depended on pH as well as on the type and concentration of metal ions and HA. In aqueous solutions of a constant  $\text{H}^+$  concentration, the proneness of metals and humic acids to form complexes increased with the increasing concentrations of these acids. The values of unit coefficients of metal bounding indicated that utilization of organic substances at pH 7.0–8.0 was not complete. The proneness of the HM tested to form metal-organic complexes with HA can be arranged in the following descending order:



The formation of lead-humic acids and copper-humic acids complexes was most efficient at  $5.0 < \text{pH} < 7.0$  (8.0). Both metals combined easily with organic ligands.

At pH lower than 5.0 and higher than 7.0 (8.0), the efficiency of copper and lead bounded to HA was smaller. This might be associated with a concurrent inorganic bounding in an alkaline medium and with the instability of these complexes in an acidic medium.

The efficiency of metal-organic complex formation was also influenced by the type of the humus substance. A slightly better efficiency was achieved with sodium salts of HA than with analytically pure HA. This is likely to be due to the

dissociation of salts which is greater than that of acids. Furthermore, analytically pure HAs were able to bound greater amounts of metals than peat-isolated acids. Of the extracts tested, alkaline extracts of HA were the most efficient; alkaline solutions of humatomelanic acids and aqueous extracts of HA rank second and third, respectively. This can indicate that the HM under study were primarily bounded to slightly soluble humic and humatomelanic acids, as well as to colloidal humic substances. The contribution of water-dissolved humus fractions was less significant. Metal-organic complexes formed at pH approaching 7.0 were unstable at high concentrations of  $H^+$  ions. Lowering pH to a level of 4.0 brought about a release of HM from the complex to the aqueous solution and the removal of some portions of humic and humatomelanic acids together with the  $Cu^{2+}$  and  $Pb^{2+}$  ions bounded to them. The metal ions, which have left the complex, were substituted by competitive  $H^+$  ions which showed a greater electronegativity and, moreover, occurred in larger amounts than the metal ions of interest.

### 2.3. THE INFLUENCE OF HUMIC ACIDS ON THE REMOVAL OF HEAVY METALS

The influence of HA on the removal of HM was investigated in the following processes: precipitation of slightly soluble metal compounds, sorption and coagulation. The results obtained substantiated this contribution. The influence of HA fits with the order of HM readiness to form metal-organic complexes. Thus, zinc and nickel ions (which combine with HA to a small extent only) were removed in the form of slightly soluble hydroxide irrespective of the degree of humus removal.

Lead and copper ions forming metal-organic complexes were removed in conjunction with HA. The contribution of organic ligands to the removal of copper and lead was the following: they increased the removal efficiency when pH was lower than 7.0, and decreased the degree of removal when pH was higher than 7.0. At the latter pH, HAs are stable and dissociate, specifically in samples with no  $Ca^{2+}$  and  $Mg^{2+}$  ions.

The favourable effect of HA on the removal of  $Pb^{2+}$  and  $Cu^{2+}$  ions at  $pH < 6.0$  (7.0) should be attributed to the neutralizing interaction of negatively charged organic colloids with copper and lead cations. The decreasing efficiency of  $Pb^{2+}$  and  $Cu^{2+}$  ion removal in the presence of HA at natural or alkaline pH is associated with the stability and dissociation of humic substances, i.e., with the persistence of colloidal and dissolved humus fractions (and the HM bounded) in the aqueous solution. At  $pH > 10$ , irrespective of whether or not humic substances were present, no increase (or decrease) in the efficiency of zinc and lead ion removal was observed. This is due to the formation of zinc and lead hydroxocomplexes in the water. Such a phenomenon was not observed for nickel or copper up to a pH level of 12.0.

The neutralizing interaction of negatively charged organic colloids with metal ions also accounted for the removal of humic substances which could be filtered through a hard filter paper, particularly at pH ranging from 5.0 to 6.0. At higher

concentration of  $\text{OH}^-$  ions, this effect was less pronounced, and the required quantity of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions was significantly greater than in the medium where the formation of metal-organic complex occurred.

The sorbents applied in this study accounted for the removal of slightly soluble organic and inorganic metal compounds only. The efficiency of sorption depended both on pH and removal of sorbent together with the metal compounds retained on them. Coagulation (irrespective of the coagulant involved) yielded very good removal of the metal ions and humic substances. Both copper and lead were bounded to HA and therefore their concentrations decreased in the course of coagulation and 2-hour sedimentation. This indicates that those metals were removed from the aqueous solutions in the form of metal-organic complexes. The optimum pH for the coagulation process was about 6.0.

The contribution of humic substances to the removal of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions was particularly distinct at pH ranging from 5.0 to 6.0 and  $\text{pH} > 10.0$ . At  $\text{pH} > 10$ , HA brought about a slight decrease in the efficiency of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  removal, which was associated with the persistence of dissolved metal-humic acid complexes. At pH approaching 6.0, the presence of HA accounted for an increased removal of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions. The effect of these organic ligands on  $\text{Pb}^{2+}$  ion removal was greater than that on  $\text{Cu}^{2+}$  ion removal. This was due to the closer affinity of lead for the HA tested.

At pH equal to or less than 6.0,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions were removed in a combination with humic substances. At higher pH, the effective removal of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions was strongly influenced by the removal of the inorganic compounds of copper and lead as well as by the removal of metal-organic complexes.

The decrease in the efficiency of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and HA removal at pH higher than 7.0 and lower than 9.0 was on the one hand caused by the increased solubility of humic substances,  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$ , and on the other hand by bounding of these metals to inorganic ligands. The maximum increment in the removal of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions obtained in the coagulation process at pH ranging from 5.7 to 6.0 was contributed to the following factors: neutralization of organic anions by  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and cations of the coagulants applied as well as sorption of destabilized organics together with the metal ions bounded to them on the  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$  flocs. Of the two coagulants used, alum was more efficient in removing coloured matter (especially from the Odra River water). This fact was in agreement with the CCE values determined for 1 g of  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$ . Ferric coagulants exhibited certain disadvantages. Applied at a non-optimum pH, they accounted for an increase in colour intensity, forming coloured chelates with HA. Comparable efficiencies of alum and ferric sulphate coagulants were achieved at  $\text{pH} \geq 11.0$ . At this pH, the contribution of the coagulation process to the treatment of the aqueous solutions was less distinct than at a lower pH because of the increased solubility of both  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$ . The high treatment efficiency was the result of co-precipitation of humic substances and metal-organic complexes mainly with  $\text{Mg}(\text{OH})_2$  and  $\text{CaCO}_3$ .

Analyses showed that the relationship between the remaining concentrations of HA and the cations of the coagulants applied was linear in nature and that the presence of these organics accounted for the greater utilization of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  ions, particularly in an alkaline medium.

### 3. CONCLUSIONS

1. The chemism and removal of the pollutants tested depended on pH value.
2. Heavy metals formed with humic acids metal-organic complexes. The proneness of the metals tested to form these complexes can be arranged in the following descending order:  $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$ .
3. The interaction between humic acids and the heavy metal ions tested influenced the removal efficiency of these pollutants. Humic acids were removed together with heavy metals ( $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ ) bounded to them.
4. The high efficiency of humic acid removal was achieved by alum coagulation at  $\text{pH} \leq 6.0$  or by pH adjustment to  $\text{pH} > 10$  and 2-hour sedimentation.
5. The presence of humic acids improved the efficiency of lead and copper removal, particularly in an acidic medium. Zinc and nickel were removed predominantly in the form of inorganic, slightly soluble compounds.
6. The best results of  $\text{Pb}^{2+}$ -HA and  $\text{Cu}^{2+}$ -HA complex removal were achieved also by alum coagulation at  $\text{pH} \leq 6.0$ .

#### USUWANIE KWASÓW HUMUSOWYCH I NIEKTÓRYCH METALI Z WODY

Omówiono interakcję ołowiu, miedzi, cynku i niklu z kwasami humusowymi oraz jej wpływ na usuwanie tych zanieczyszczeń z wody. Przedstawiono skuteczność procesu sorpcji, koagulacji i strącania chemicznego. Wykazano, iż parametrem decydującym o chemizmie i usuwaniu badanych zanieczyszczeń była wartość pH.

Stwierdzono, że obecność kwasów humusowych zmieniała przebieg i skuteczność usuwania miedzi i ołowiu tworzących z tymi ligandami organicznymi połączenia, a pozostawała bez wpływu na usuwanie cynku i niklu – metali tylko w minimalnym stopniu wiążących się z kwasami humusowymi. Ołów i miedź były usuwane jako połączenia metalo-organiczne i nieorganiczne, cynk i nikiel zaś przede wszystkim jako trudno rozpuszczalne związki nieorganiczne.

#### УДАЛЕНИЕ ГУМИННЫХ КИСЛОТ И НЕКОТОРЫХ МЕТАЛЛОВ ИЗ ВОДЫ

Обсуждена интеракция свинца, цинка и никеля с гуминовыми кислотами, а также ее влияние на удаление этих загрязнений из воды. Представлена эффективность процесса сорбции, коагуляции и химического осаждения. Было обнаружено, что параметром, решающим о химизме и удалении исследуемых загрязнений было значение pH.

Было установлено, что наличие гуминовых кислот изменяло протекание и эффективность удаления меди и свинца, образующих соединения с этими органическими лигандами, а не влияло на удаление цинка и никеля – металлов лишь в незначительной степени соединяющихся с гуминовыми кислотами. Свинец и медь удалялись как металлоорганические и неорганические соединения, зато цинк и никель – прежде всего как трудно растворимые неорганические соединения.