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## CONTRIBUTION OF HYDROGEN ION CONCENTRATION TO THE REMOVAL OF HUMIC SUBSTANCES AND SOME HEAVY METALS FROM AQUEOUS SOLUTIONS

The contribution of pH value to the removal of copper, zinc, lead, nickel, and humic acids (HA) was determined. Being responsible for the solubility of the pollutants removed, the pH level is the main contributing factor. It is also the interaction between organic ligands and heavy metals that influences the removal of lead and copper as well as HA. Each of the four heavy metals under study is effectively removed at alkaline pH. In the presence of HA, lead and copper are also removed in the form of metal-organic complexes, particularly at acid reaction. In solutions with and without heavy metals, high efficiencies of HA removal are achieved by alum coagulation at  $\text{pH} \leq 6.0$  and by pH adjustment to about 10. Both processes were followed by 2-hour sedimentation, which appeared to be a necessary condition.

### 1. INTRODUCTION

Removal of heavy metals and humic acids (HA) from aqueous solutions is a self-evident and a unquestionable necessity. The presence of heavy metals in natural waters creates serious hazards to aquatic organisms. It is a well-known fact that HA are precursors of trihalomethanes (THMs) which dangerously affect human health [1]. HA are also found to interact with other components, thus producing new compounds which may, in some instances, have an unfavourable influence on living organisms. The results presented substantiate the possibility of removing heavy metals and HA by conventional treatment processes. The study also confirms the contribution of hydrogen ion concentration to the removal efficiency.

### 2. REMOVAL OF HA AND SOME HEAVY METALS

The experiments were run on three types of model solution samples, which contained HA, heavy metals (copper, zinc, nickel, lead) and both the pollutants,

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respectively. The contribution of hydrogen ion concentration to the efficiency of removal was estimated for the following processes: sedimentation, filtration through filter paper, sorption, and coagulation.

### 3. HA REMOVAL EFFICIENCY

Experiments involving the efficiency of HA removal from aqueous solution samples have shown that, irrespective of whether heavy metal ions were present or not, the efficiency of the investigated processes is pH-dependent which means that it depends far more on the solubility of HA than on any other technological parameter of the treatment processes involved.

#### 3.1. SOLUTIONS WITH NO HEAVY METAL IONS

Filtration (through filter paper), sorption, and coagulation at a natural pH (i.e., that of HA stability) were far less effective than at an acid or alkaline reactions (i.e., that of decreased HA solubility). Sedimentation failed to be effective in the pH ranging within 6–9 (fig. 1). HA persisted in the aqueous solution in the form of dissolved, colloidal and fine-dispersed, poorly settleable particles which were resistant even to a 2-hour sedimentation. To make the sedimentation process effective, it was necessary to adjust pH to a level higher than 9.0. In this medium HA were co-precipitated with  $\text{CaCO}_3$  and (with increasing pH) with  $\text{Mg}(\text{OH})_2$  to yield good removal efficiencies. Removal of HA at pH adjusted to a level below 6.0 was less effective than that in the alkaline medium, because coloured fractions alone (i.e., humic and hyalomelanic acids) were subject to aggregation and, consequently, to precipitation.

Similar relations were found to occur during the other treatment processes. In the pH-range of HA stabilization, some part of the poorly settleable fraction was removed. Nevertheless, each of the treatment processes failed to yield satisfactory removal efficiencies in the range of  $6 < \text{pH} < 9$  (10); they were much lower than in the medium of high  $\text{OH}^-$  or  $\text{H}^+$  concentrations. The sorbents applied in this study (pulverized activated carbons (Carbopol Z-4 and Norit) and bentonite) accounted primarily for the removal of slightly soluble fractions and were particularly effective at the pH level of co-precipitation with  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$  (fig. 2).

Of the processes under study coagulation (which is strongly pH-dependent) was found to be the most effective. The highest efficiencies of HA removal were achieved at  $\text{pH} \leq 6.0$  both with alum and ferric sulfate. Coagulation conducted at an optimum pH yielded a decrease in permanganate COD, colour intensity, and HA

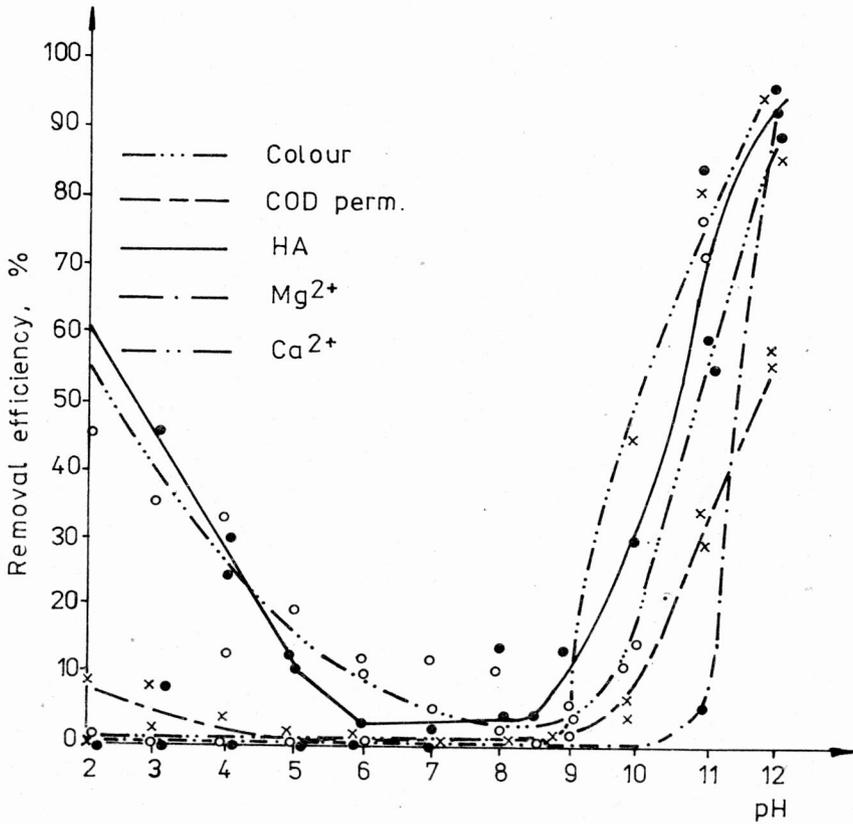


Fig. 1. Relationship between pH and removal of some pollutants during 2-hour sedimentation

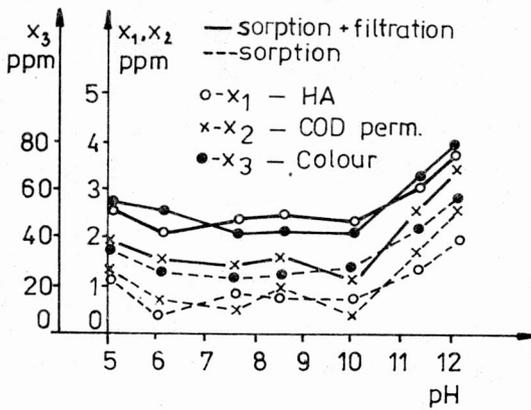


Fig. 2. Relationship between pH of aqueous solutions and sorption efficiency on pulverized activated carbon Carbopol Z-4

content to the level of  $< 3.0 \text{ g O}_2/\text{m}^3$ ,  $\leq 20 \text{ g Pt}/\text{m}^3$ , and  $0.5 \text{ g HA}/\text{m}^3$ , respectively, with coagulant doses lower than those required for other pH levels. The high efficiency of HA removal ( $> 90\%$ ) at  $\text{pH} \leq 6.0$  should be attributed to the following factors: the presence of  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and positively charged Fe and Al hydroxy complexes which have a neutralizing effect on organic colloids, the minimal solubility of  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$ , as well as the low solubility of HA, which is evidently lower than at natural pH (yielding a decreased efficiency of the coagulation process).

The effectiveness of the coagulation process under alkaline conditions is high. But it is not so much the coagulating effect as the co-precipitation of the pollutants with  $\text{CaCO}_3$  and particularly with  $\text{Mg}(\text{OH})_2$  that contributes to the high removal efficiencies. Measured values of coagulant consumption coefficients indicate that the utilization of  $\text{Al}^{3+}$  ions is greater than that of  $\text{Fe}^{3+}$  ions, especially during coloured matter removal.  $\text{Fe}^{3+}$  ions had a great ease to form coloured, non-settleable complexes with HA (primarily fulvic acids), which were not removed, irrespective of the treatment process applied. This behaviour is an indication that iron salts as coagulants fail to be fit for HA removal.

### 3.2. SOLUTIONS CONTAINING HEAVY METALS

The efficiency of HA removal depended on  $\text{H}^+$  ion concentration and on the type of heavy metal ion. The interaction between heavy metals and HA (determined by the author of this paper) and the susceptibility of heavy metal series to form metal-organic complexes with HA ( $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} \geq \text{Ni}^{2+}$ ) [2] had a distinct influence on the removal of both pollutants. Depending on the pH involved, the presence of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  either increased or slightly decreased the quantity of HA removed. The favourable contribution of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions to HA removal was particularly distinct at pH between 5 and 7. This is the range of pH in which the  $\text{HA-Cu}^{2+}$ ,  $\text{HA-Pb}^{2+}$  interactions reached their maximal efficiencies. A similar contribution of the two ions could be observed when the pH of the solution was the same as the one at which inorganic slightly soluble copper and lead compounds (specifically hydroxides) are precipitated. These compounds are likely to act as co-precipitators of HA, in the same way as  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ .

A slight decrease in the efficiency of HA removal due to the presence of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  occurred at  $\text{pH} > 10$ . In this pH range, some part of readily soluble  $\text{Cu}^{2+}$ -HA or  $\text{Pb}^{2+}$ -HA complexes persisted in the solution. Nickel ions and zinc ions had only a slight effect (if at all) on HA removal which should be attributed to their poor readiness to form complexes with HA.

The interaction of HA with  $\text{Cu}^{2+}$  or  $\text{Pb}^{2+}$  ions accounts for the co-removal of the two pollutants, the efficiencies of removal being linearly correlated.

## 4. REMOVAL OF HEAVY METALS

Removal efficiency depends both on the concentration of  $H^+$  and the presence of HA.

### 4.1. SOLUTIONS WITH NO HUMIC ACIDS

Each of the four heavy metals was removed in the form of an inorganic slightly soluble compound, and removal efficiency increased with the increasing pH. The optimum pH for  $Pb^{2+}$  and  $Zn^{2+}$  removal amounted to 10.0. At higher  $OH^-$  concentrations there was no increment at all, or a slight decrease, in the removal efficiency. And this is to be attributed to the formation of water-soluble plumbites and zincates. Since no hydroxy complexes of copper and nickel were found to form in the pH range up to 12.0, we may assume that the pH of copper hydroxide and nickel hydroxide precipitation is higher ( $pH > 10.0$ ) than the pH of lead hydroxide and zinc hydroxide precipitation.

### 4.2. SOLUTIONS CONTAINING HUMIC ACIDS

Nickel and zinc removal followed the same pattern as that for the solution with no HA, the removal efficiency increased with the increasing pH (up to 10.0 and 12.0 for zinc and nickel, respectively). Both metals were removed predominantly in the form of inorganic slightly soluble compounds. The presence of HA had a distinct contribution to the efficiency of copper ion and lead ion removal. The contribution was pH-dependent and was equally pronounced in each of the treatment processes under study.  $Cu^{2+}$  and  $Pb^{2+}$  were removed in the form of inorganic compounds or metal-organic complexes. The removal efficiency of  $Cu^{2+}$  and  $Pb^{2+}$  depended on the pH of the solution and on the efficiency of HA removal (fig. 3). Thus, both ions were effectively removed in acidic medium. At increased pH level, there was an evident drop in the increment of the removal efficiency. The favourable conditions for increased removal efficiency at pH lower than neutral are due to the neutralizing interaction of negative organic colloids and  $Pb^{2+}$ ,  $Cu^{2+}$  cations. As a result, the destabilized complexes were easier to remove than the two metal ions. The inhibition in the increment of  $Cu^{2+}$  and  $Pb^{2+}$  ion removal at natural or higher pH is to be attributed to the stability and dissociation of HA, which leads to the persistence of colloidal and dissolved humic fractions (along with the fixed heavy metals) in the solution. The presence of HA had an adverse effect on the removal of  $Cu^{2+}$  and  $Pb^{2+}$  at  $pH > 10.0$ , which created advantageous conditions for the formation of water-soluble metal-organic complexes.

A similar pH-dependence was established for the sorption process. The sorbents

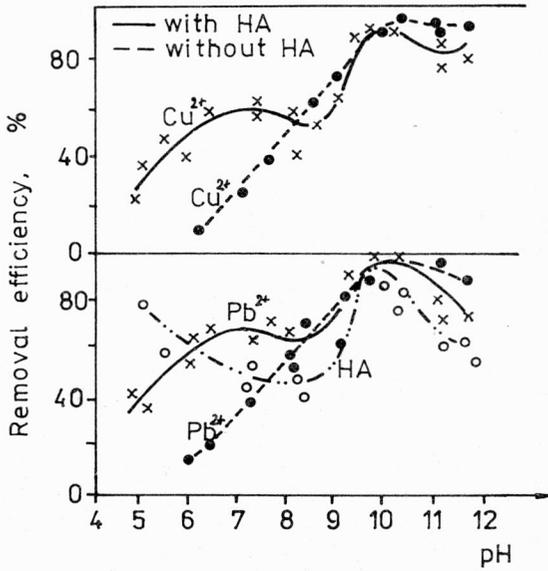


Fig. 3. Effect of pH value and humic acids on lead and copper removal in the following processes: pH adjustment and filtration through a filter paper

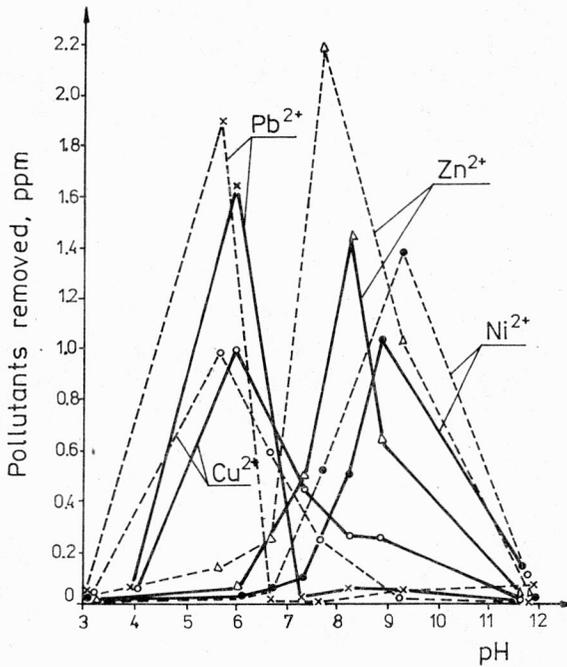


Fig. 4. Effect of pH on the increment of heavy metals removal in alum (————— 90 ppm) or ferric sulfate (----- 90 ppm) coagulation and 2-hour sedimentation

applied enabled only the removal of slightly soluble heavy metal compounds. The best removal efficiencies were obtained at the optimal pH for the precipitation of metal hydroxides.

At alkaline pH, each of the processes studied yielded satisfactory and comparable removal efficiencies. Under acidic conditions, only coagulation gave very high removal of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions. Optimum pH approached 6.0 (fig. 4), enabling effective coagulation of HA and fixed  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions (1 g of HA removed accounts for the removal of 1.176 g  $\text{Pb}^{2+}$  and 1.002 g  $\text{Cu}^{2+}$ , the removal of  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  being close to zero). Compared to the other treatment processes, coagulation is particularly effective. This effectiveness can be attributed to the following phenomena involved: 1) the products of hydrolysis of the coagulant act as destabilizers of negative organic colloids and unsaturated metal-organic complexes, 2) there is a sorption of pollutants on the flocs of  $\text{Al}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_3$ . Of the two coagulants, alum is far more effective, especially in colour removal. The iron coagulant has the inherent disadvantage of being prone to form chelates and increase colour intensity, when applied at a non-optimal pH.

## 5. SUMMARY

Analysis of the data sets for the efficiencies of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and HA removal enables the following generalizations to be made:

1. The chemism and removal of the pollutants are strongly influenced by the concentration of  $\text{H}^+$  ions as the main contributing factor.
2. HA are effectively removed by alum coagulation (at  $\text{pH} \leq 6.0$ ) or by pH adjustment to a level higher than 10.0 and 2-hour sedimentation.
3. The interaction between the pollutants influences their removal efficiency, which depends on the pH level and the type of heavy metal ion.
4. At alkaline pH, when HA are absent, each of the four heavy metals is removed in the form of inorganic slightly soluble compound. In the presence of HA, copper and lead are also removed in the form of metal-organic complexes, particularly at acid reaction.
5. High efficiencies of HA removal in a combination with copper and lead may be achieved by alum coagulation at  $\text{pH} \leq 6.0$ , and by pH adjustment to about 10.0. The optimum pH for zinc and nickel removal corresponded to  $\text{pH} = 10.0$  and  $\text{pH} > 10.0$ , respectively. Both processes were followed by 2-hour sedimentation, which appeared to be a necessary condition.
6. The formation of copper-humic acid or lead-humic acid complexes accounts for the increase of HA removal, particularly at  $\text{pH} = 5$  to 7 and at the pH of precipitation for inorganic slightly soluble compounds of the heavy metals investigated.

## REFERENCES

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### WPLYW JONÓW WODOROWYCH NA USUWANIE SUBSTANCJI HUMUSOWYCH I NIEKTÓRYCH METALI CIĘŻKICH Z ROZTWORÓW WODNYCH

Określono znaczenie stężenia jonów  $H^+$  w usuwaniu miedzi, cynku, ołowiu i niklu oraz kwasów humusowych. Wykazano, iż głównym parametrem decydującym o usuwaniu tych zanieczyszczeń była wartość pH, determinująca formę występowania domieszek. Ponadto interakcja badanych ligandów organicznych z metalami zmieniała usuwanie miedzi, ołowiu, oraz kwasów humusowych, tj. zanieczyszczeń tworzących połączenie metaloorganiczne. Wszystkie badane metale usuwane były w środowisku alkalicznym, a miedź i ołów dodatkowo w środowisku kwaśnym, łącznie z kwasami humusowymi. W roztworach zawierających metale ciężkie i w roztworach ich pozbawionych efektywne usuwanie kwasów humusowych zapewniły koagulacja (siarczanem glinowym) przy  $pH \leq 6,0$ , a także alkalizacja do  $pH$  ca 10,0. Po wspomnianych procesach niezbędna była 2 h sedymentacja.

### ВЛИЯНИЕ ИОНОВ ВОДОРОДА НА УДАЛЕНИЕ ГУМИНОВЫХ ВЕЩЕСТВ И НЕКОТОРЫХ ТЯЖЕЛЫХ МЕТАЛЛОВ ИЗ ВОДНЫХ РАСТВОРОВ

Определено значение концентрации ионов  $H^+$  в удалении меди, цинка, свинца и никеля, а также гуминовых кислот. Было обнаружено, что главным параметром, решающим об удалении этих загрязнений, было значение pH, детерминирующая форма выступления примесей. Кроме этого, интеракция исследуемых органических лигандов с металлами меняла удаление меди, свинца, а также гуминовых кислот, т.е. загрязнений, образующих металлоорганические соединения. Все исследуемые металлы удалялись в щелочной среде, а медь и свинец — добавочно в кислой среде, вместе с гуминовыми кислотами. В растворах, содержащих тяжелые металлы и в растворах, в которых они отсутствуют, эффективное удаление гуминовых кислот обеспечила коагуляция (сульфатом алюминия) при  $pH \leq 6,0$ , а также alkalizация до  $pH = \text{ок. } 10,0$ . После упомянутых процессов необходима была седиментация в течение 2 часов.