

MARIA ŚWIDERSKA-BRÓŹ*

CONTRIBUTION OF HUMIC ACIDS TO THE REMOVAL OF SOME HEAVY METALS BY CHEMICAL PRECIPITATION

The objective of the study reported was to determine the effect of humic acids on the removal of lead, copper, zinc, and nickel ions from aqueous solutions either by pH adjustment and sedimentation or by pH adjustment and filtration through a filter paper. When analysing the data sets obtained, it becomes obvious that the presence of humic acids influences the efficiency of lead and copper ions removal, but is without any effect on the removal of zinc and nickel ions. This fact is in agreement with the series of proneness of these metals to form metal-organic complexes with humic acids ($Pb^{++} > Cu^{++} > Zn^{++} \geq Ni^{++}$). Zinc and nickel ions are removed from aqueous solutions predominantly in the form of slightly soluble inorganic compounds, irrespective of the efficiency of humic acid removal. The opposite holds for lead and copper ions which are removed together with humic acids.

The presence of humic acids brings about an increment in lead and copper ions removal at acid reaction, which creates favourable conditions for the formation of metal-organic complexes. At pH greater than 7.0, the presence of humic acids accounts for a distinctly poorer increment in the removal efficiency of lead and copper ions because in this range of pH the stability of humic acids is high, the efficiency of metal-organic complex formation has a tendency to decrease and there exists a competitive fixation of lead and copper ions to inorganic ligands.

Owing to the interaction of humic acids with lead and copper ions, both the heavy metals contribute to the increase in the efficiency of humic acid removal (particularly under acidic conditions) by destabilization of negative organic colloids.

1. INTRODUCTION

The mechanism governing heavy metal (HM) removal from and aquatic environment with no organic ligands by means of chemical precipitation is well understood — pH should be adjusted to an optimal value for the precipitation of slightly soluble heavy metal compounds, and the sediments thus obtained should be removed as

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

effectively as possible. But the problem of heavy metal removal becomes sophisticated when the aqueous solution contains organic ligands which are ready to form metal-organic complexes. Of the various organics present in natural surface waters, humic substances (naturally occurring organic ligands) play a certain role in the removal of heavy metals. The interaction between humic acids (HA) and heavy metals may create favourable conditions for the formation of organo-metallic complexes. There is a competitive fixation of heavy metals to organic and inorganic ligands.

The literature contains several references ([1]–[7]) on the formation of metal-humic acid complexes in aquatic systems and soils. Attempts are also made to explain the mechanisms involved, but the explanation is still far from being satisfactory. Different conclusions are reported on the contribution of humic acids to the efficiency of heavy metal removal. While some investigators [8]–[10] believe that the presence of organic compounds has an unfavourable effect on the removal efficiency, others [2], [6], [11] claim to have observed the opposite. In general, the problem calls for further study.

In this paper, the contribution of humic substances to the removal of lead, copper, zinc and nickel ions by pH adjustment and sedimentation or filtration is described.

2. EXPERIMENTS AND DISCUSSION OF RESULTS

2.1. METHODS AND PROCEDURES

The experimental solutions were polluted with humic acids and lead, copper, zinc and nickel ions. The treatment process involved either pH adjustment followed by 2-hour sedimentation or pH adjustment and filtration on a filter paper, pH was adjusted, using aqueous solutions of sodium hydroxide and nitric acid.

To determine the influence of organic ligands on the removal efficiency of the four metal ions, concurrent experiments were run on aqueous solutions with no humic acid content. In one of her earlier studies [12], the writer found that the coexistence of the said metal ions with humic acids in the aqueous solutions created favourable conditions for the formation of metal-humic acid complexes (colloids, readily and slightly soluble compounds). The volume of the agglomerates produced depended on the heavy metal, as well as on the ligand and pH involved.

Taking into account the proneness to form complexes, the heavy metals of interest may be arranged in the following series: $Pb^{++} > Cu^{++} > Zn^{++} \geq Ni^{++}$, which is in agreement with the series reported by Van DIJK [13]. The pH value at which the formation of lead-humic acid and copper-humic acid complexes was the most intensive varied from 5.0 to 7.0 or 8.0, the metal-stabilizing fractions being primarily humic acids and hylatomelanic acids (which display a slight water solubility).

2.2. AQUEOUS SOLUTIONS WITH NO ORGANIC LIGANDS

The effect of pH adjustment and 2-hour sedimentation on the removal efficiency is plotted in fig. 1. As shown by these plots, the metal ions of interest are removed predominantly in the form of slightly soluble hydroxides. pH values in the case of precipitation of slightly soluble lead and zinc hydroxides should not exceed 10.0

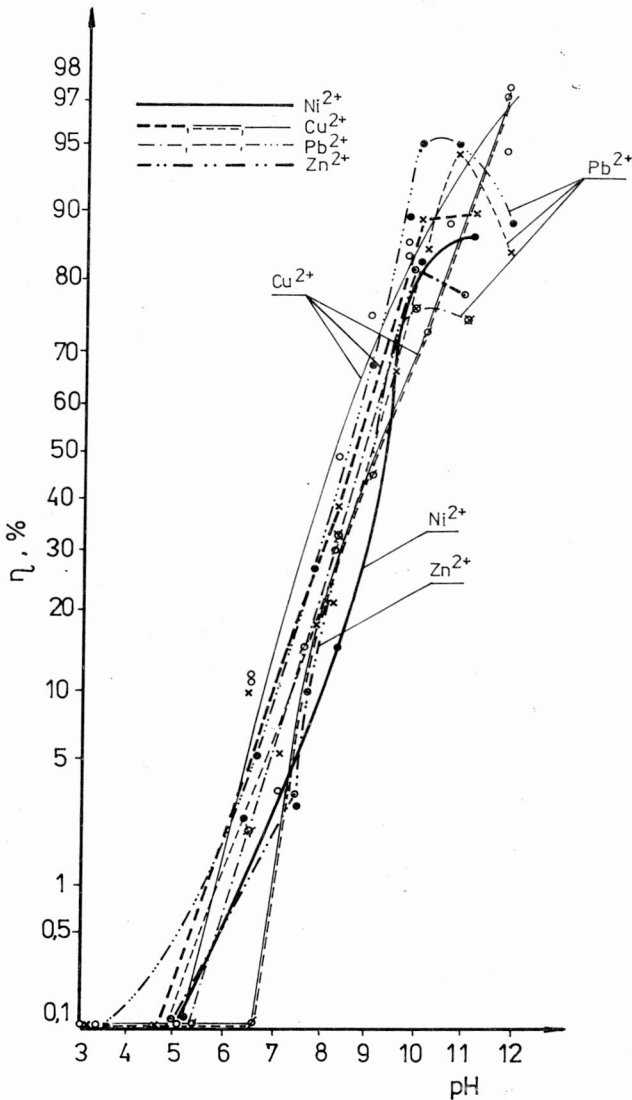


Fig. 1. Effect of pH on the precipitation of slightly soluble inorganic lead, copper, zinc, and nickel compounds

because pH greater than 10.0 accounts for the origin of water-soluble plumbites and zincates. Copper ion and nickel ion removal efficiencies increase with the increasing pH until the value of 12.0 is achieved.

2.3. AQUEOUS SOLUTIONS CONTAINING ORGANIC LIGANDS

Experiments involving water samples polluted with humic acids have shown that the presence of organic ligands influences the efficiency of heavy metal removal. Thus, the contribution of humic acids was very high in the case of lead and copper removal. There was no such contribution when zinc ions or nickel ions were involved. This behaviour is in agreement with the established series of readiness to form complexes ($Pb^{++} > Cu^{++} > Zn^{++} \geq Ni^{++}$). The effect of humic acids (peat extracts in a concentration amounting to 2.465 g m^{-3}) on the removal of lead ions and copper ions during pH adjustment and filtration is plotted in fig. 2. As shown by

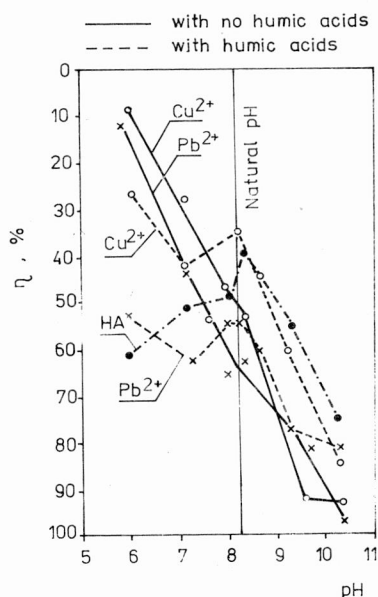


Fig. 2. Effect of humic acids on copper and lead removal during pH adjustment and filtration

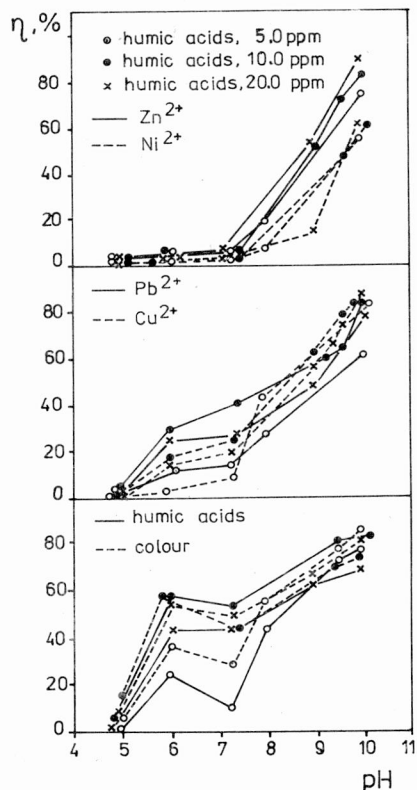


Fig. 3. Effect of initial humic acid concentration on lead, copper, zinc, and nickel removal from solutions with adjusted pH

these curves, the presence of humic acids brings about an increase of the removal efficiency (especially of lead ions) in an acidic medium, and a decrease at $\text{pH} > 7.0$. The removal efficiency curve also shows that the heavy metal ions under study are removed in the form of metal-organic complexes and that the stability of these agglomerates at a natural pH is high. Similar relations have been obtained in aqueous solutions containing chemical preparations of humic acids (fig. 3). The contribution of these ligands fails to occur in the case of nickel ions and zinc ions which are resistant to form metal-organic complexes.

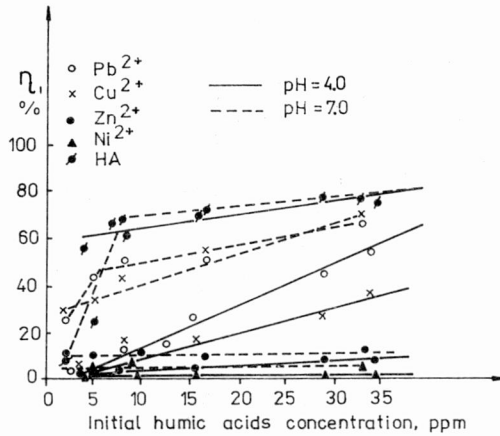


Fig. 4. Influence of initial humic acids concentration on the efficiency of 2-hour sedimentation

The experiments have also revealed that at $\text{pH} = 4.0$ and $\text{pH} \sim 7.0$ (fig. 4), as well as at an adjusted pH (fig. 3), lead ions and copper ions are removed in the form of metal-humic acid complexes, while zinc ions and nickel ions are not; the removal efficiency of copper-humic acid and lead-humic acid complexes increases with the increasing initial concentration of humic acids. The decreased concentrations of lead ions and copper ions at $\text{pH} = 4.0$ are to be attributed to the precipitation of humic and humatmelanic acids, along with the heavy metal ions included in them. At $\text{pH} = 4.0$ lead, copper, zinc and nickel in aqueous solutions with no humic acids occur in ionic forms and their concentrations should not decrease. This, however, was not so. Hence, the decrease of lead ion and copper ion concentrations observed at $\text{pH} = 4.0$ is an indication that the two heavy metals form complexes with humic acids and are removed via this route.

Most of the lead-humic acid and copper-humic acid complexes which are formed in the aquatic environment display a low settleability. They may be removed either by filtration or by co-precipitation with other slightly soluble compounds, at high concentrations of hydroxyl ions (fig. 5). The plots in fig. 5 (especially those for the water samples treated by filtration) illustrate the contribution of humic acids to

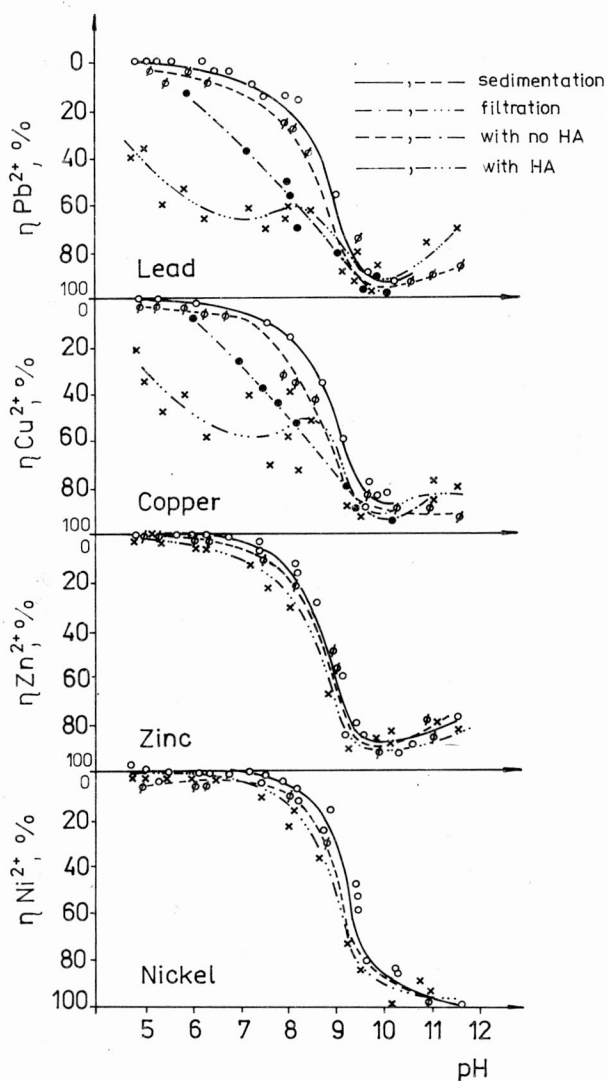


Fig. 5. Metal-ion removal as a function of pH

the efficiency of copper ion and lead ion removals. They also show that this contribution fails to exist when zinc ions and nickel ions are involved. The favourable contribution of humic acids is particularly pronounced to pH 8.0 (which creates the most advantageous conditions for the formation of metal-organic complexes). At natural and alkaline pH (~ 8.0 and ≥ 10.0 , respectively) humic acids persisted in the solution, thus decreasing the increment in copper ion and lead ion removal efficiency. The concurrent drop in the increment of the humic acid removal

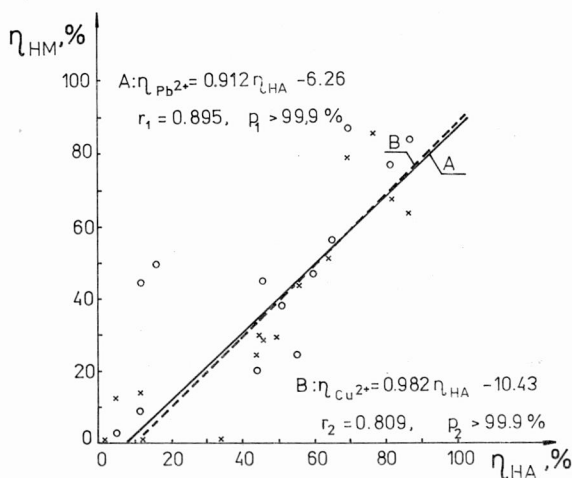


Fig. 6. Correlations between humic acid removal and lead ion removal (A), and humic acid removal and copper ion removal (B), respectively

efficiency (specifically at $pH > 10.0$) is, again, an indication that lead ions and copper ions are removed in the form of metal-humic acid complexes.

To support the correlation between heavy metal removal and humic acid removal, equations of linear correlation, probability values and correlation coefficients for the investigated water samples were established. The results are given in fig. 6.

2.4. EFFECT OF LEAD IONS AND COPPER IONS ON HUMIC ACID REMOVAL

Experiments were run in order to determine the effect of lead ions and copper ions (occurring in concentrations of about 2.0 g m^{-3}) on humic acid removal from aqueous solutions after pH adjustment and filtration on a filter paper. The results show that the contribution of lead ions and copper ions to the removal of humic acids (peat extracts) becomes particularly pronounced at $pH = 5.5$. And this should be attributed to the destabilization of negative organic colloids, as well as to the formation of metal-organic complexes. The contribution of lead ions and copper ions becomes less distinct (and directly proportional to their initial concentrations) in natural pH (~ 8.0).

Two fundamental processes may be regarded as governing such a behaviour: 1) fixation of lead ions and copper ions to inorganic ligands (and this process gives a decrease in the concentration of free lead and copper ions which account for the destabilization and aggregation of humic acids), and 2) dissociation of humic acids. Under alkaline conditions ($pH = 11.0$), specifically at increased humic acid concen-

tration, the treatment effects were poor due to presence of water-soluble metal-organic complexes which persist in the aqueous solution. But when the concentration of humic acids was lower than the total concentration of heavy metals, the presence of copper ions and lead ions had only a slight influence on the removal efficiency, if at all.

3. SUMMARY

Analysis of results allows the following generalizations:

1. The presence of humic acids contributes to the efficiency of removal when lead ions and copper ions are involved. There is practically no contribution in the case of zinc ion and nickel ion involvement. The influence of organic ligands on the removal of the four heavy metals is in agreement with the ease to form metal-organic complexes ($Pb^{++} > Cu^{++} > Zn^{++} \geq Ni^{++}$).

2. Lead ions and copper ions are removed together with humic acids in the form of metal-organic complexes. Increasing the initial concentration of humic acids brings about an increase in the removal of lead ions and copper ions.

3. Zinc ions and nickel ions are separated predominantly in the form of slightly soluble inorganic compounds (mostly hydroxides). Their removal efficiency fails to depend on the efficiency of humic acid removal.

4. Metal-organic agglomerates display a poor settleability. At pH equal to, or smaller than, 9.0, they are amenable to filtration and can be removed via this route. When pH is greater than 9.0, 2-hour sedimentation will suffice.

5. The presence of humic acids increases the efficiency of lead ion and copper ion removal at pH lower than neutral. The opposite holds when pH exceeds the range of 7.0 to 8.0.

6. The presence of lead and copper ions brings about an increment in the removal efficiency of humic acids, particularly at acid reaction.

7. Creating favourable conditions for the interaction and co-precipitation of organic and inorganic complexes and, furthermore, applying sedimentation or filtration, enable high removal efficiencies to be achieved both for humic acids and heavy metal ions.

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WPLYW KWASÓW HUMUSOWYCH NA USUWANIE NIEKTÓRYCH METALI CIĘŻKICH W PROCESIE ICH CHEMICZNEGO STRĄCANIA

Określono wpływ kwasów humusowych na usuwanie jonów Pb^{+2} , Cu^{+2} , Zn^{+2} i Ni^{+2} z roztworów wodnych w procesach korekty odczynu i sedymentacji lub filtracji przez twardy sącdek. Badania wykazały, iż obecność kwasów humusowych wpływała na skuteczność usuwania jonów Pb^{+2} i Cu^{+2} i pozostawała praktycznie bez wpływu na usuwanie jonów Zn^{+2} i Ni^{+2} . Oddziaływanie to było zgodne z ustalonym szeregiem podatności badanych metali do tworzenia połączeń z kwasami humusowymi. Jony Zn^{+2} i Ni^{+2} były usuwane głównie w postaci trudno rozpuszczalnych połączeń nieorganicznych niezależnie od stopnia usuwania ligandów organicznych.

Obecność kwasów humusowych zwiększała usuwanie jonów Pb^{+2} i Cu^{+2} w środowisku kwaśnym, w którym były warunki powstawania połączeń tych metali z kwasami. Przy $pH > 7,0$ obserwowano obniżone usuwanie miedzi i ołowiu w obecności kwasów humusowych. W wyniku interakcji powyższych zanieczyszczeń, szczególnie w środowisku kwaśnym, stwierdzono zwiększenie efektywności usuwania kwasów humusowych jako wynik destabilizacji ujemnych anionów organicznych przez jony Pb^{+2} i Cu^{+2} .

ВЛИЯНИЕ ГУМИНОВЫХ КИСЛОТ НА УДАЛЕНИЕ НЕКОТОРЫХ ТЯЖЁЛЫХ МЕТАЛЛОВ В ПРОЦЕССЕ ИХ ХИМИЧЕСКОГО ОСАЖДЕНИЯ

Определено влияние гуминовых кислот на удаление ионов Pb^{+2} , Cu^{+2} , Zn^{+2} и Ni^{+2} из водных растворов в процессах выравнивания реакции и седиментации или фильтрации через твёрдый фильтр. Исследования обнаружили, что присутствие гуминовых кислот влияло на эффективность удаления ионов Pb^{+2} и Cu^{+2} и практически не влияло на удаление ионов Zn^{+2} и

Ni^{+2} . Это воздействие было согласно с установленным рядом податливости исследуемых металлов к образованию соединений с гуминовыми кислотами. Ионы Zn^{+2} и Ni^{+2} удалялись, главным образом, в виде труднорастворимых неорганических соединений, независимо от степени удаления органических комплексов.

Присутствие гуминовых кислот повышало удаление ионов Pb^{+2} и Cu^{+2} в кислой среде, в которой были условия для образования соединений этих металлов с кислотами. При $\text{pH} > 7,0$ наблюдалось пониженное удаление меди и свинца в присутствии гуминовых кислот. В результате интеракции вышеупомянутых загрязнений, особенно в кислой среде, установили повышение эффективности удаления гуминовых кислот, как результат дестабилизации отрицательных органических анионов ионами Pb^{+2} и Cu^{+2} .