

INFLUENCE OF COPPER (II) IONS ON STABILITY OF DISSOLVED HUMIC ACIDS – COAGULATION STUDIES*

Patrycja Boguta, Zofia Sokołowska

Institute of Agrophysics PAS, Doświadczalna 4, 20-290 Lublin, Poland
e-mail: p.warchulska@ipan.lublin.pl

Abstract. The main aim of the paper was to study the effect of coagulation of copper ions on dissolved form of humic acids. Research material was isolated from four peaty muck soils (Teric Histosols). The soils were described by means of the Springer humification number, secondary transformation index, ash content and pH in H₂O and in KCl. For the studied humic acids, surface charge was determined, E4/E6 which described the degree of concentration of the chain of aromatic carbons of the humic acids and could be used as their humification number, and the elemental composition and atomic ratios were determined as well. Systems composed of humic acids and increasing concentrations of copper ions were investigated at pH 5 and in the copper concentration range of 0-40 mg dm⁻³, at constant concentration of humic acids. Coagulation of solutions was studied by measurement of changes of organic carbon and copper ions concentration in liquid phase at pH 5 as well as by observation of absorbance changes at wavelength 465 nm in series of prepared solutions. The results showed that coagulation of experimental systems consisted mainly in humic acid coagulation. In a certain range of concentration of copper added to solutions, metal also partly precipitated and went to the solid phase together with humic carbon, which indicated coagulation of complexed compound of humic acids with copper. At high copper concentration, ionic strength had a dominant influence on coagulation of humic acids. Copper ions stayed all in liquid phase, whereas almost total organic carbon passed to precipitate, which resulted from interactions with electrolyte ions.

Keywords: dissolved humic acids, coagulation, copper ions

INTRODUCTION

The peatlands of Polesie Lubelskie Region as well as those situated in the region of River Biebrza belong to one of the most valuable natural resources of Poland. Apart from their high tourism values, these areas are also the habitat of

*This work was partly realized within the framework of a research project. The project was financed by the National Science Centre in Poland, on the base of decision number DEC-2011/03/N/NZ9/04239.

unique fauna and flora. Peatlands are also a large reservoir of organic matter that is responsible for the sorption and buffering properties, structure, and microbial activity of soils (Boguta and Sokołowska 2012, Sokołowska *et al.* 2011; Piccolo 2002). However, peats still undergo various continuing transformations related both to natural processes and, in particular, to inappropriate water economy (off-hand land reclamation treatments) (Gawlik and Harkot, 2000). Most of the peatlands in Poland have been drained and subjected to agricultural use. Processes of such kind cause acceleration of peat mass transformation to mucks (Inisheva and Dement'eva 1998, Matyka-Sarzyńska and Sokołowska 2004). Changes in peat evolution under melioration processes are mostly characterised by mineralisation and secondary humification. The above processes lead to changes in the morphological, chemical, biological and physical properties of peat soils and can be well described by such parameters as, for example, water holding capacity index proposed by Gawlik (1992, 2000), humification number, specific surface area, surface charge or amount of amino acids (Matyka-Sarzyńska and Sokołowska 2004, Sokołowska *et al.* 2011). Especially important in transformation processes are mineral components of peat-muck soils because in the course of soil transformation their mineral composition is also dynamically changed. That is related with chemical and physical changes of organic matter, especially humic substances (Kyzioł 2002). Humic and fulvic acids and their functional acidic groups, such as the carboxylic and phenolic, are the main factors responsible for binding metal cations and, consequently, for their state and concentration in soils (Lux 1993). In soil environment, soluble combinations of humic acids with metal ions are most significant (Antoniadis and Alloway 2002, Tipping 2002, Sokołowska and Warchulska 2009). According to some theories, metals from such compounds can be better available by plants than insoluble forms or simple ionic forms (Clemens *et al.* 1990, Havlin *et al.* 1999, Brady and Weil 1999). Simultaneously, humic acids have limited sorption capacity and too big a dose of metal or other mineral component which can be sorbed on humic acids can cause saturation of negative, surface charge of humic acids leading to coagulation of soluble compounds. Thereby, there is a risk of higher accumulation of metals, including also heavy metals precipitated as humus insoluble salts. Such processes can lead to soil degradation as well as cause micronutrient deficiency for plants. For organic soils, copper is an especially important metal. This element is a valuable micronutrient necessary for plant growth, however, in too big an amount it behaves like a toxic substance, so the status of this metal in soils rich in organic matter is very important and worth to investigate. Of course, it is obvious that the research subject of interactions between metals and humus substances was brought up earlier, but in the light of peatlands area reducing as well as possibility of mucking peats usage such studies are still

valuable, especially in relation to investigations for soils with different humification stage and for humic acids with various abilities for metal sorption.

For these reasons, the main aim of this paper was to study the interaction between copper ions and dissolved forms of selected humic acids coming from organic soils. It should be stressed that the studies were focused mainly on coagulation processes in the above system, especially on investigation of critical concentration of copper at which coagulation was observed. Apart from finding coagulation points of humic acids by measurements of absorbance and carbon concentration in liquid, these studies also paid attention to copper ions behaviour during coagulation of humic acids. The goal was realized at pH 5 to approximate natural conditions present in such kind of soils. Another aim of these studies was to check different instrumental methods for finding an objective tool for the investigation of interactions between humic substances and metal cations.

MATERIALS AND METHODS

The initial materials in the studies were four peaty-muck soils (Terrie Histosols) formed from proper peats. Above soil samples were selected from a larger group of samples (11 samples: data not shown in this paper) in respect of humification degree (expressed in this paper as Springer humification number, H_2) and in respect of secondary transformation degree (expressed in this paper as water absorption index, W_1). The soil samples were collected from the depth of 5-10 cm (first stage of mucking – MtI: soil designed as S1) and from 5-20 cm (soils with a weak degree of mucking – MtII: soils designed as S2-S4), from 4 sites used as meadows. The sites were located in the low moor area of the Wieprz-Krzna canal (Polesie Lubelskie) and in the Biebrza river valley on peat bogs in Poland. According to Okruszko classification (1976), among 4 studied soils, S1 belonged to peaty muck (Z_1), and S2-S4 belonged to proper mucks (Z_3). Mucking processes of these materials had taken place in the same climatic zone, in similar humidity conditions and land forming, so that it could be assumed that studied samples were mostly varied by secondary transformation index. In this paper, secondary transformation was expressed by the water absorption index, W_1 , determined with the Gawlik method (1992). This index expresses the ratio of water capacity of a sample that had been previously dried at 105°C to water capacity of this sample in the natural state. The stage of advancement of humification processes was displayed by means of the Springer humification number, H_2 (Schlichting et al., 1995). pH of the soils was measured in KCl and H₂O solutions using a digital pH-meter (Radiometer Copenhagen). Ash content was determined by combustion at 550°C in Muffle Furnace FCF 12 SP (Czylok) and weighting the residue (Sapek and Sapek, 1997).

Extraction of humic acids (HAs) from four soils was carried out according to the procedure recommended by the International Humic Substances Society (Swift 1996). Obtained humic acids were highly clear, in hydrogen form. Ash content was below 2%.

Isolated humic acids were described by surface charge of functional groups at pH 5 using potentiometric titration method (Garcia-Gil *et al.* 2004, Prado *et al.* 2006). Potentiometric titration curves were recorded by automatic titrator Titrino 702 SM (Metrohm AG) and on their basis the surface charge was calculated (Matyka-Sarzyńska *et al.* 2000). Chemical composition was investigated by elemental analysis. Determination of nitrogen, carbon and hydrogen was performed for humic acids using Perkin-Elmer CHN 2400 analyser. Oxygen content was calculated from the difference: 100%-H%-C%-N%. Data were presented as weight percentages. From the obtained results, atomic ratios were calculated: H/C, O/H, O/C, C/N. For the chemical nature characterisation of humic acids, the E4/E6 index was determined using the spectrophotometric method, measuring the absorbance ratio at wavelengths 465 and 665 nm (Kononova, 1968). All UV-VIS measurements were carried out using spectrometer JASCO V-530 (Jasco Inc.).

Stability of dissolved humic acids under copper (II) addition was studied in series of solutions containing humic acid at constant concentration (40 mg/dm³), and increasing concentration of copper (0-40 mg dm⁻³). All experiments were conducted at pH adjusted to 5. Metal ions were added to humic acids solutions in the form of concentrated standard of copper (II) chloride (1000 mg dm⁻³). pH of the system was adjusted with solution of HCl or NaOH. Ionic strength was stabilised in 0.5M NaCl. Final volume of sample was 50 cm³. pH was controlled by digital pH-meter (Radiometer Copenhagen). All solutions were first stirred quickly on a magnetic stirrer (5 minutes), and then slowly (2 hours). After this step, solutions were left for 24 hours. Next day, the solutions were centrifuged at 8000rpm and analysed in terms of copper and organic carbon content as well as absorbance at wavelength 465 nm. Copper content was determined in 3 replications using atomic absorption spectrometer (AAS contr AA 300, Analytik Jena). Concentration was calculated automatically on the basis of 10-points calibration curve. Calibration solutions were prepared from certified standard (1000 mg dm⁻³). Results of replications were averaged. Measurements of humic carbon remaining after 24 hours in liquid phase were made in 3 replicates on carbon analyser Multi NC2000 (Analytik Jena, module for liquid samples, platinum catalyser, furnace temperature 800°C). Concentrations were calculated automatically on the basis of 8-point calibration curve. Results were averaged. Calibration standards were prepared from concentrated solution of potassium hydrogen phthalate. Changes of absorbance in studied solutions were performed at 465 nm using UV-VIS spectrophotometer V-530 (Jasco INC.). Choice of wavelength was based on the fact that 4th derivatives of humic acids UV-VIS

spectra show in this area a significant change and it relates to the content of humus substance in initial phases of humification process. In consequence, this wavelength is often used in determination of humic acids concentration.

RESULTS AND DISCUSSION

All parameters describing the four studied soils are collected in Table 1. Data placed in the Table were averaged from 3 replications. Standard deviation did not exceed 5%.

Table 1. Selected physicochemical characteristics of studied soils.

Soil sample No.	W_1	H_z	pH KCl	pH H ₂ O	A (%)	Kind of soil	Mt
S1	0.44	11	4.85	5.22	25.8	Z ₁	Mt I
S2	0.60	14	4.93	5.42	25.3	Z ₃	Mt II
S3	0.72	21	4.85	5.25	20.0	Z ₃	Mt II
S4	0.74	19	5.55	6.01	25.1	Z ₃	Mt II

S – soil, W_1 – water absorption index, H_z – humification number, A – ash, Mt – mucking degree, Z₁ – peaty muck, Z₃ – proper muck.

Studied soils differed in terms of water absorption index (table 1). This parameter expresses the secondary transformation stage. Determination of above index was based on the assumption that peats being transformed into muck lose their water sorption abilities. The range of these changes is related with the secondary transformation degree. In this paper, the range of differences of water absorption index was wide and covered almost the whole scale proposed by Gawlik for assessment of secondary transformation of mucking peats (Gawlik 1992). Studied soils belong to a group formed from proper peats, weakly silted. So that, according to this classification, class I – soils in initial stage of secondary transformation with W_1 : 0.36-0.45, was represented by one sample (S1). Class II – soils weakly secondary transformed with W_1 : 0.46-0.60, was represented by sample S2. Soils S1 and S4 belonged to class III, with medium stage of secondary transformation and W_1 between 0.61 and 0.75.

Values of humification number showed that the highest humification number in studied material was for sample S3 ($H_z = 21$), and the lowest one for sample S1 ($H_z = 11$). In contrast to water absorption index, humification number is a parameter describing chemical changes in soil, especially transformation of organic matter into humus substances. Results of present study showed that values of W_1 and H_z parameters increased in linear manner from S1 to S4 (exception H_z of S3 and S4),

which was an evidence on increasing decomposition of peat mass. According to Ilnicki (Ilnicki 2002), in the case of low-bog peats these phenomena should be accompanied by increasing sorption capacity. According to this statement, results of measurement of surface charge of humic acids at pH 5 (discussed in greater detail in later part of the paper) confirmed that the value of surface charge was the lowest for HA1 and the highest for HA3 of which the soil (S3) had a high W_1 and the highest H_z (Tab. 1). Results of pH indicated that samples No. 1, 2 and 3 belonged to strongly acidic soils, whereas sample No. 4 to weakly acidic. Slightly higher values of pH for S4 could be a result of higher content of alkaline elements. Ash content ranged from 20 to 25.8%. In general, for low-bog peats ash ranges from 5 to 20%, however progressing humification and especially mineralisation processes could be a factor contributing to an increase of ash content (Ilnicki 2002). The smallest participation in these transformations was for sample S3. Other 3 samples showed similar ash content despite different values of W_1 and H_z . That could result not only from mineralisation, but also from silting up by particles of sand, clay and silt.

Table 2. Surface charge (Q), E4/E6 parameter, elemental composition and atomic ratios of humic acids isolated from studied soils

Humic acids No.	Q(pH5) (meq/100 g)	E4/E6	C%	N%	H%	O%	H/C	O/H	O/C	C/N
HA1	308	5.7	47.91	3.38	5.16	43.56	1.29	0.53	0.68	16.56
HA2	439	5.1	47.87	3.86	4.92	43.35	1.23	0.55	0.68	14.46
HA3	475	3.4	46.18	3.83	4.42	45.57	1.15	0.64	0.74	14.08
HA4	439	5.3	47.28	3.89	4.80	44.03	1.22	0.57	0.70	14.19

HA – humic acid samples, Q(pH5) – surface charge of humic acids acidic functional groups at pH 5, E4/E6 – absorbance ratio measured at wavelength 465 and 665 nm, related to degree of aromatic cores concentrations of HAs

Results of surface charge of humic acids at pH 5, E4/E6 parameter calculated from UV-VIS, elemental composition as well as atomic ratios are placed in Table 2. Data presented in Table 2 were averaged from 3 replications (E4/E6 four replications). Coefficients of variation did not exceed 4%. Surface charge ranged from 308 (HA1) to 457 meq/100 g (HA3). This parameter, measured at pH 5, could be an evidence of the highest amount of acidic functional groups, like carboxylic, in the structure of HA3 and the smallest one for HA1. Admittedly, typical pK range for carboxylic functional groups dissociation is in humic acids case from 3 to 7. So that, surface charge measured at pH 5 could be typical for natural conditions in organic soils but these values did not represent charge from total amount of carbox-

ylic groups in humic acids (some part was still protonated). However, stronger carboxylic groups dissociate in lower pH than weaker ones. In connection with the above, higher surface charge in HA3 in comparison with other HAs could indicate stronger sorption abilities and, in consequence, higher affinity to metal bonding. Parameter E4/E6 was the lowest for humic acid HA3 (3.4) and the highest for humic acid HA1 (5.7). All of these values were typical for humic acids fraction according to Kononowa (Kononowa 1968). Value of E4/E6 was related to the degree of aromatic C network. Low values of E4/E6 parameter indicated higher degree of concentration of aromatic humic constituents. So that, this could be connected with high degree of structure humification. Conversely, high E4/E6 ratio was an evidence of low degree of aromatic cores concentration and of structures which were richer in side aliphatic chains. Carbon content in studied humic acids was similar and ranged from 46.18 to 47.91%. This content was simultaneously equal to the content of humic carbon. In general, all values were low in comparison to the typical ones. Oxygen content was also similar (calculated from $100\% - C - H - N$) and ranged from 43.35 to 45.57%. Such low amount of carbon and high amount of oxygen could be a result of superiority of so-called young humic acids fractions, rich in oxygenic functional groups, and thus poorer in carbon. Also important could be the fact that humic acids were isolated from soils originated from low-bog peats, in which carbon content of humic acid is in general lower than carbon content in humic acids extracted from soils formed from high-bog peats (Ilnicki, 2002). Nitrogen content varied from 3.38 to 3.89% and hydrogen from 4.42 to 5.16%. These values were typical for this kind of soils. Calculated atomic ratios H/C (1.15-1.35) according to Van Krevelen (1950), corresponded to aromatic systems coupled with aliphatic chains (up to 10 C atoms). HA3 had the lowest values of H/C (1.15), which could be evidence of high content of aromatic structures. High content of aromatic rings indicated high stability of humic acids. Opposite tendency was noted for sample HA1 with the highest values of H/C parameter (1.29). Thus, it indicated the lowest content of cycling structures. These conclusions were confirmed by E4/E6 values. HA3 had the lowest E4/E6 parameter (3.4) indicating the strongest humification, including high aromaticity and concentration of aromatic cores. In contrary, HA1 had $E4/E6 = 5.7$, which indicated higher content of aliphatic chains. O/H ratio changed in the range of 0.53 (HA1) – 0.64 (HA3). High values of this ratio indicated a high content of oxygen functional groups, like for example carboxylic phenolic or enolic, in comparison to other samples. These conclusions were supported by values of negative surface charge of studied humic acids. The highest surface charge was for HA3 and the lowest one for HA1, which was probably connected with the highest and the lowest content of above functional groups, respectively. O/C atomic ratio had values from 0.68 (HA1 and HA2) to 0.74 (HA3). Higher values indicated structure rich in oxygen functional groups and strong participation of

oxidation processes. Parameter C/N ranged from 14.08 to 16.56. In general, the higher C/N ratio the higher the maturity of HAs.

Influence of copper (II) addition to the solution series of studied humic acids was investigated by using three instrumental methods: measurements of carbon remaining in the liquid phase, measurements of liquid phase absorbance at 465 nm, and measurements of copper content in liquid phase. Coagulation of dissolved humic acids was observed at a certain concentration of copper ions addition. This process was visible as humic acids flocculation and sedimentation of the precipitate. For these reasons, coagulation of dissolved humic acids under copper influence could be investigated by measurements of changes of organic carbon, copper ions and absorbance at 465 nm in liquid phase of studied systems. Measurements of carbon concentration in series of solutions are presented in Figure 1 as a function of organic carbon in liquid phase vs. amount of copper concentration in each solution in series.

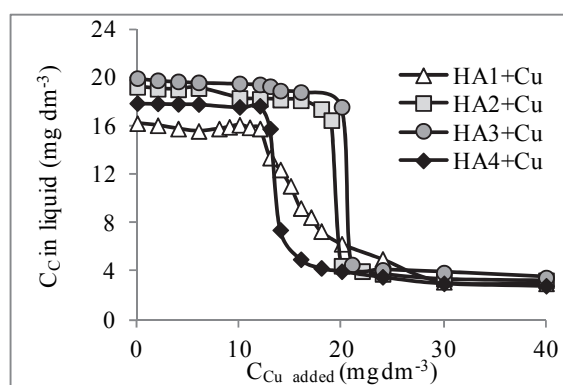


Fig. 1. Humic carbon content (mg dm^{-3}) in the liquid phase in function of copper amount introduced initially (mg dm^{-3}) for the systems HA-Cu at pH 5

From Figure 1 it can be seen that the start of coagulation was different for different humic acids. So, on the basis of these characteristics, two threshold concentrations of copper (C_{CrI} -point of coagulation start, C_{CrII} -point of coagulation end) and distance between the thresholds (ΔC_{Cr}) were determined in graphic way according to Khil'ko *et al.* (2001). Scheme of above parameters determination is depicted in Figure 2. Calculated parameters C_{CrI} , C_{CrII} and ΔC_{Cr} are given in Table 3.

For comparison with carbon measurements, the process of the coagulation of humic acids under copper (II) ions was also investigated by measurements of absorbance at 465 nm in liquid phase after 24 hours from copper addition. These results are presented in Figure 3 as a graph of copper concentration left in the liquid phase in the function of copper amount introduced at start.

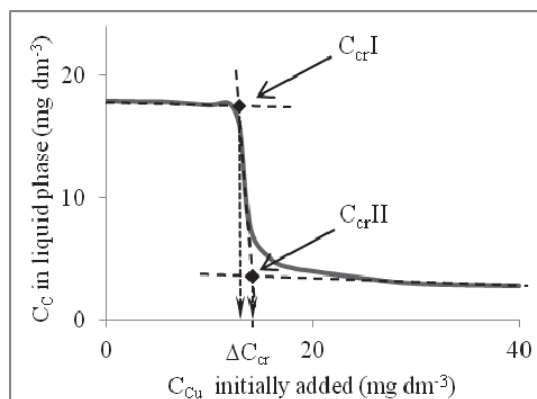


Fig. 2. Scheme of determination of critical copper concentration at which coagulation was observed: C_{crI} – point of coagulation start, C_{crII} – point of coagulation end, ΔC_{cr} – difference between C_{crII} and C_{crI}

Table 3. Critical copper concentrations C_{crI} , C_{crII} and ΔC_{cr} for which start and end of humic carbon coagulation was observed.

Humic acid No.	C_{crI}	C_{crII}	ΔC_{cr}
HA1	12.2	20.7	8.5
HA2	19.3	20.0	0.7
HA3	20.3	21.2	0.9
HA4	12.8	14.5	1.7

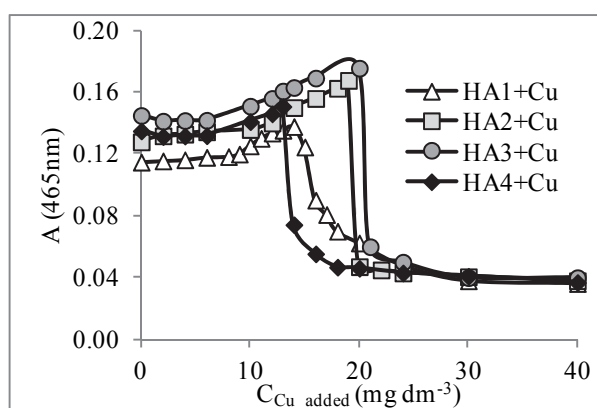
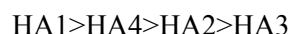


Fig. 3. Absorbance values of the solutions of humic acids at pH 5 with increasing copper concentrations in function of copper amount (mg dm^{-3}) added to the solution at start of experiment

Characteristics presented in Figures 1 and 3 indicate that solutions of all humic acids with copper ions addition at pH 5 were stable in the range of added copper 0-10 mg dm⁻³ (and even slightly more). At these conditions humic acids precipitation (see Figures 1 and 3) was not observed. Carbon concentration in liquid phase (Fig. 1) was constant in this range of copper amount addition (acceptable deviations), and absorbance of the solutions measured at wavelength 465 nm was almost constant or slightly increased close to 10 mg dm⁻³ of copper, which resulted probably from change of the solution colour under copper addition (Fig. 3). So that, it could be supposed that in these circumstances, copper ions complexed particles of humic acids forming soluble complexing compounds or some part of copper was also present in the solution in the form of redundant, not bonded ions. However, it should be noted that high surface charge of humic acids measured at pH 5 (Tab. 2) indicated the presence of acidic functional groups, like for example carboxylic. Such groups have good features for complexing metals with d-electron structure, so this process was highly probable. Simultaneously in these circumstances, the surface of humic acids still had to have some part of not neutralised negative charge coming from not complexed functional groups of humic acids. Due to these reasons, humic acids did not coagulate at low copper concentration.

Loss of humic acids carbon from the liquid phase was clearly observed above copper concentration of ~10 mg dm⁻³ (Fig. 1). From Figure 1 it can be seen that the start of coagulation was different for different humic acids, which resulted from their various surface charge and, in consequence, from the amount of copper needed to neutralise the negative charge of humic acids. Points of start of humic carbon coagulation were designated as C_{cr}I (Tab. 3). Values of this parameter showed that humic acids precipitated at copper concentration range of 12.2-20.3 mg dm⁻³ and in the following order (starting from coagulating the earliest):



End point of carbon coagulation (marked as C_{cr}II) also took place at various amount of copper additions and oscillated from 14.5 to 21.2 mg/dm³. Ending points (C_{cr}II) – where carbon concentration did not change, were observed first for HA4 and then in the order: HA2≈HA1≈HA3, respectively, at copper concentrations: 14.5, 20.0, 20.7, 21.2 mg/dm³. Distance between C_{cr}II and C_{cr}I, designated as ΔC_{cr}, showed total range of coagulation and it expressed speed of flocculation. This parameter, for the studied HA-Cu systems, ranged from 0.7 to 8.5. This high difference could be evidence of some differences in the mechanism of humic acids coagulation.

Coagulation of dissolved humic acids at pH 5 under copper influence was also confirmed, with similar tendencies, by changes of absorbance at 465 nm. Measurement signal dropped off first for the HA4 and then, at subtly higher copper concen-

tration, for HA1. Absorbances for humic acid HA2 and HA3 decreased at the highest copper concentration of, respectively, 20 and 22 mg dm⁻³. So, the order of absorbance dropping of, starting from one at the lowest metal addition, was as follows:

$$\text{HA4} > \text{HA1} > \text{HA2} > \text{HA3}$$

It can be noted that this sequence is slightly different from the one obtained from investigation of carbon concentration in liquid phase. This could be connected with the fact that measurements of copper and carbon are direct indicators and are more precise. Changes of absorbance are commonly applied, but this technique can be influenced by different factors like for example colour or turbidity. Graphically determined coagulation points C_{crI} showed weak positive correlation ($R = 0.71$) with surface charge Q (pH5). C_{crI} had also positive signs of correlations with O%, O/H and O/C. In general, directions of above correlations were quite logical because higher start of humic acids coagulation could be connected both with higher content of their functional groups which had oxygen (carboxylic, phenolic, etc.) and with higher surface charge coming from dissociation of these groups. However it should be stressed that those relationships were still statistically insignificant at $\alpha = 0.05$. So that, studied material should be extended for obtaining more detailed conclusions. Points marked as C_{crII} (describing end of coagulation) did not show any interesting tendencies in relation to properties of humic acids. ΔC_{cr} showed negative correlations with Q (pH5), N% and C/N ratio of humic acids, however the values of C_{crII} were very low so correlations with ΔC_{cr} were not considered as statistically significant. Weak relationships of coagulation points and humic acids properties could derive from dominating role of electrolyte ions in coagulation processes. Charge neutralisation by copper complexation could be weaker in this situation. It is also worth noting that in the case of measurements of humic carbon and absorbance at 465 nm, humic acids did not coagulate in full in each case. After 24 hours, always some low concentration of carbon remained in the solutions. The reason could be small amount of complex HA-Cu remaining in the state of equilibrium with the precipitate, or humic acids particles not taking part in interactions with copper.

For enriching information about coagulation of humic acids, measurements of residual copper content in solution after 24 hours were performed. Copper concentration left in the liquid phase in the function of copper amount introduced to humic acids at the start is presented in Figure 4.

Measurements of copper content in the liquid phase showed that metal concentration started to decrease at a similar point as carbon of humic acids. The order was as follows (starting from the earliest precipitation):

$$\text{HA1} > \text{HA4} > \text{HA2} \approx \text{HA3}$$

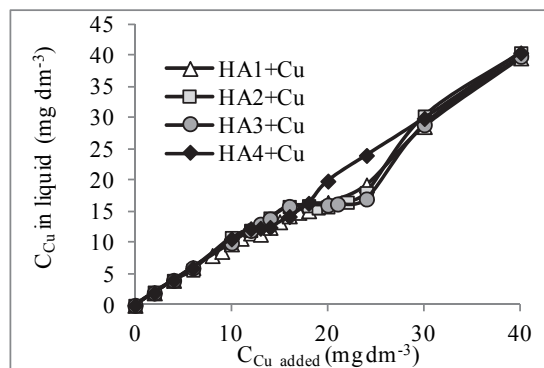


Fig. 4. Content of copper ions remaining in liquid phase (mg dm^{-3}) in function of copper concentration added at start of experiment (mg dm^{-3}) for the systems HA-Cu at pH 5

Copper migration to the solid phase at the same points as humic carbon could be evidence of precipitation of HA-Cu complex. Mechanism of coagulation could be explained by saturation of negative surface charge of humic acids by bonding metal cations. As a result of this, coagulation of systems occurred and, in consequence, loss of copper and carbon was observed in liquid phase. Conclusion about neutralisation of surface charge of humic acids by copper ions is in accordance with values of surface charge of humic acids at pH 5 (see Table 2). Copper and carbon precipitated the earliest for humic acids with the lowest charge value. However, interesting is the fact of almost total humic carbon removal and only small part of copper precipitation. Moreover, decrease in copper concentration was measured only for the middle part of copper which was introduced initially. In the solutions of humic acids at pH 5, containing the highest doses of copper (above 30 mg dm^{-3}), decrease in metal concentration in liquid phase was not observed. Even the drop of copper concentration present in $13\text{--}30 \text{ mg dm}^{-3}$ was also not observed and all copper stayed in the liquid, whereas almost all humic carbon transferred to the precipitate. That could be connected with increasing ionic strength of the solution simultaneously with increasing addition of copper ions, which lead in consequence to precipitation of humic acids without copper. Forming of HA-Cu complex is probably difficult in these circumstances, so almost all copper stayed in liquid as cationic copper or, maybe, in a smaller part as soluble complex with humic acids (small part of organic carbon did not go to solid phase).

CONCLUSIONS

1. Simultaneous measurements of copper and humic acid carbon remaining in the liquid phase are objective methods for the study of coagulation mechanisms.

Changes of absorbance can be influenced by changes of colour, especially when d-electron cations are introduced.

2. Part of coagulation mechanism of studied humic acids at pH 5 takes place as a result of neutralisation of negative charge of humic acids by bonding copper cations.

3. Besides copper ions, interactions with electrolyte play a significant part in coagulation of humic acids particles. Complexation with copper in those conditions could be more difficult because cations from electrolyte compete for active sites on the negative charged surface of humic acids.

4. Humic acids do not precipitate totally. In all cases, some small part of humic carbon stayed in the liquid. It indicates the presence of equilibrium between precipitated humic acids and soluble complex staying in liquid.

5. Points of coagulation can be dependent on some physicochemical properties of humic acids, however these relationships can be disturbed by interactions of humic acids with electrolyte. The observed weak correlation of coagulation points and surface charge, oxygen and atomic ratios with oxygen need to be extended on the basis of wider research material and under various ionic strength.

REFERENCES

- Antoniadis V., Alloway B.J., 2002. Leaching of cadmium, nickel and zinc down the profile of sewage sludge-treated soil. *Communications in Soil Science and Plant Analysis*, 33, 273-286.
- Boguta P., Sokołowska Z., 2012. Influence of phosphate ions on buffer capacity of soil humic acids. *Int. Agrophysics*, 26, 1, 7-14.
- Brady N.C., Weil R.R., 1999. *The Nature and Properties of Soils*. 12th Edition, Upper Saddle River, NJ: Prentice-Hall, Inc. 881.
- Clemens D.F., Whitehurst B.M., Whitehurst G.B., 1990. Chelates in agriculture. *Fertilizer Research*, 25, 127-131.
- Garcia-Gil J.C., Ceppi S.B., Velasco M.I., Polo A., Senesi N., 2004. Long-term effects of amendment with municipal solid waste compost on the elemental and acidic functional group composition and pH-buffer capacity of soil humic acids. *Geoderma*, 121, 135-142.
- Gawlik J., 1992. Water holding capacity of peat formations as an index of the state of their secondary transformation. *Polish J. Soil Sci.*, 25, 121-126.
- Gawlik J., 2000. Division of differently silted peat formation into classes according to their state of secondary transformations. *Acta Agrophysica*, 26, 17-24.
- Gawlik J., Harkot W., 2000. Influence of the kind of moorsh and the state of its transformation on the germination and growth of *Lolium perenne* in the pot plant experiment during spring-summer cycle. *Acta Agrophysica*, 26, 25-40.
- Havlin J.L., Beaton J.D., Tisdale S.L., Nelson W.L., 1999. *Soil Fertility and Fertilizers*. 6th Edition, Upper Saddle River, N.J: Prentice-Hall, Inc., 499.
- Ilnicki P., 2002. *Peatlands and peat* (in Polish). Wydawnictwo AR w Poznaniu, Poznań.
- Inisheva L.I., Dement'eva T.V., 1998. Mineralization rate of organic matter in peats. *Eurasian Soil Sci.*, 33(2), 170-176.
- Khil'ko S.L., Titov E.V., Fedoseeva A.A., 2001. The Effect of Strong Electrolytes on Aqueous Solutions of Sodium Salts of Native and Sulfonated Humic Acids. *Colloid Journal*, 63, 5, 645-648.

- Kononowa M.M., 1968. Soil organic substances: structure, properties and investigation methods (in polish). PWRiL, Warszawa, 281-285.
- Kyziół J., 2002. Effect of physical properties and cation exchange capacity on sorption of heavy metals onto peats. Polish Journal of Environmental Studies, 11, 6, 713-718.
- Lux W., 1993. Long-term heavy metal and As pollution of soils. Applied Geochemistry, 8, 2, 135-143.
- Matyka-Sarzyńska D., Sokołowska Z. and Józefaciuk G., 2000. Variable surface charge of selected peat materials as determined from back titration. Acta Agrophysica, 26, 51-58.
- Matyka-Sarzyńska D., Sokołowska Z., 2004. Usefulness of humification number in studies on the state of secondary transformation in comparison to water holding capacity of mucks (in Polish). Acta Agrophysica, 3(3), 553-563.
- Okruszko H., 1976. Discernment and division of hydrogenic soils in relations to reclamation necessity (in Polish). Bibl. Wiad. IMUZ, 52, 7-54.
- Piccolo A., 2002. The supramolecular structure of humic substances. A novel understanding of humus chemistry and application in soil science. Advances in Agronomy, 75, 57-133.
- Prado A.G.S., Torres J.D., Martins P.C., Pertusatti J., Bolzon L.B. and Faria E.A., 2006. Studies on copper(II)- and zinc(II)-mixed ligand complexes of humic acid. J. Hazard. Mater., 136, 585.
- Sapek A., Sapek B., 1997. Methods of chemical analyses of organic soils (in Polish), Publisher IMUZ, Falenty. 10.
- Schlichting E., Blume H.P., Stahr K., 1995. Bodenkundliches Praktikum, 2 Auflage. Blackwell Wissenschafts Verlag, Berlin, Wien, 167.
- Sokołowska Z., Szajdak L., Boguta P., 2011. Effect of phosphates on dissolved organic matter release from peat-muck soils. Int. Agrophys., 25, 173-180.
- Sokołowska Z., Warchulska P., 2009. Mobilization of humic acids originated from muck soils as a result of sodium, calcium and phosphate ions interaction. Teka Kom. Ochr. Kszt. Środ. Przynr. – OL PAN, 6, 328-334.
- Swift R.S., 1996. Organic matter characterization. In D.L. Sparks et al. (eds) Methods of soil analysis. Part 3. Chemical methods. Soil Sci. Soc. Am. Book Series: 5. Soil Sci. Soc. Am. Madison, WI. 35, 1018-1020.
- Tipping E., 2002. Cation binding by humic substances. Cambridge University Press: Cambridge, UK, 434.
- Van Krevelen D.W., 1950. Graphical-statistical method for investigation of the structure of coal. Fuel, 26, 269-284.

WPŁYW JONÓW MIEDZI (II) NA STABILNOŚĆ ZDYSOCJOWANYCH KWASÓW HUMINOWYCH – PROCES KOAGULACJI

Patrycja Boguta, Zofia Sokołowska

Instytut Agrofizyki im. Bohdana Dobrzańskiego PAN,
ul. Doświadczalna 4, 20-290 Lublin
e-mail: p.warchulska@ipan.lublin.pl

Streszczenie. Głównym celem pracy było zbadanie koagulacyjnego wpływu jonów miedzi na zdysocjowaną formę kwasów huminowych. Materiał badawczy wyizolowano z czterech gleb murszowo torfowych. Gleby scharakteryzowano pod kątem stopnia humifikacji, przeobrażenia, popielności i pH. Dla badanych kwasów huminowych wyznaczono ładunek powierzchniowy i iloraz E4/E6 opisujący stopień humifikacji i aromatyczność struktury. Układy kwasów huminowych z miedzią badano

w pH 5 w zakresie stężeń Cu: 0-40 mg·dm⁻³, przy stałym stężeniu kwasów huminowych. Koagulację roztworów badano poprzez pomiar zmian zawartości węgla organicznego i miedzi w fazie ciekłej po 24 godzinach, a także poprzez obserwację zmian absorbancji serii roztworów przy długości fali 465 nm. Wyniki badań pokazały, że koagulacja badanych układów w głównej mierze polegała na koagulacji kwasu huminowego. W pewnym zakresie stężeń dodawanej miedzi, do osadu przechodził również metal, co wskazywało na koagulację kompleksowego połączenia kwas huminowy – miedź. Przy wysokich stężeniach jonów miedzi, dominujący wpływ miała prawdopodobnie moc jonowa. Jony miedzi pozostawały w całości w roztworze, natomiast niemal cały węgiel organiczny przechodził do osadu, co było rezultatem oddziaływania z jonami elektrolitu.

Słowa kluczowe: zdysocjowana materia organiczna, koagulacja, wpływ jonów miedzi