POLISH JOURNAL OF SOIL SCIENCE
VOL. XLVIII/2 2015 PL ISSN 0079-2985

DOI: 10.17951/pjss/2015.48.2.161

Soil Chemistry

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IMPORTANCE OF HUMIC SUBSTANCES FOR METHODS OF GROUNDWATER TREATMENT

Abstract. Humic substances (HS) constitute a large part of organic matter found in aquatic environment. The HS strongly interact with both inorganic and organic pollutants. Occurrence of the HS in groundwater accounts for many problems with treatment procedures. These natural components cause an increased intensity of water colour, affect its taste and odour, hinder removal of iron, manganese and other metals, organic substances such as, e.g. pesticides from water. The HS are precursors of toxic trihalomethanes during chlorination. For treating groundwater contaminated with humic substances and iron compounds it is not enough to apply solely a conventional groundwater treatment system. Therefore, searching for new methods of removing humic substances from groundwater is a common practice and the existing methods undergo regular improvement. This paper, based on the review of published materials, deals with problems related to the existence of humic substances in groundwater and further discusses possibilities of their removal in order to obtain water that would meet requirements of water intended for human consumption.

IMPACT OF HUMUS SUBSTANCES ON GROUNDWATER QUALITY

Elements that disqualify drawn groundwater are first of all iron, manganese, aggressive carbon dioxide, and in many other cases also organic substances, out of which the most frequent are humus substances (HS) that are leached from soils rich in humus and from brown-coal and coal deposits [24, 37, 44, 49, 55, 57, 60]. The proportion of humic substances in the total organic carbon content of groundwater may even reach 71.4% [37]. Many researchers claim

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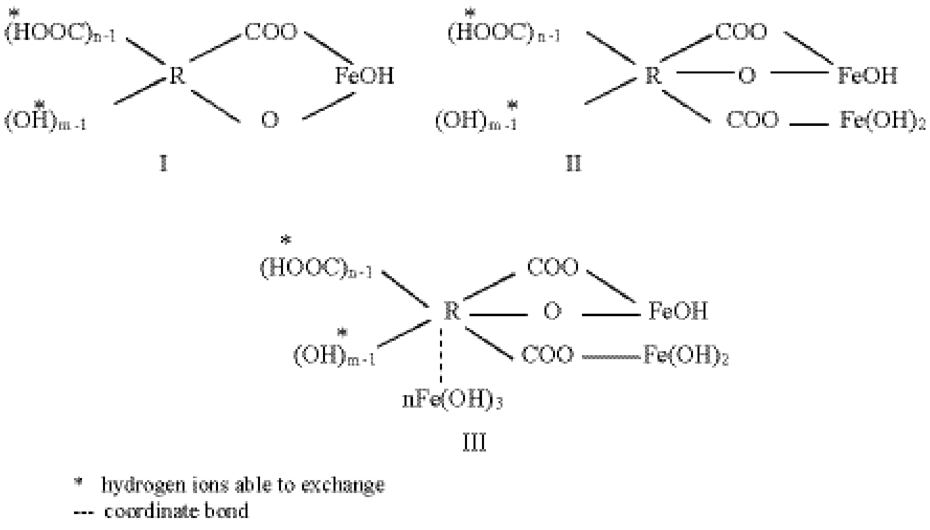
[7, 36, 49, 53, 63] that humic acids and their salts add to groundwater yellow, brown and brownish colour. Most frequently such water is referred to as brownish water, brown or black water [9, 16, 52]. According to Stevenson [27, 49, 51, 52], water colour is caused by the so called chromophoric groups contained in particles of the HS whereas colour intensity of water grows along with the increase in molecular weight, a molecular carbon content, a degree of polymerisation and pH value. In groundwater humic acids are most frequently dominating and decide about water colour intensity whereas in the case of surface water the dominating are fulvic acids [25]. The humic substances in groundwater may occur as dissolved, in a form of colloids and as undissolved impurities. In alkaline environment the humic substances exist as dissociated forms whereas in an acidic or neutral environment they take a form of negative colloids. The compositional and structural characteristics as well as chemical properties of the HS are dependent mainly on their origin, i.e. the environment, from which they have been isolated [37]. According to Cudowski et al. [12] aquatic fungi are widespread biotic components of aquatic ecosystems. These organisms, along with bacteria and protozoa, play essential roles in the functioning of reservoirs ecosystems. Aquatic fungi may be of autochthonic or allochthonous origin. The role of fungi in aquatic ecosystems mainly involves their participation in the decomposition of organic matter, particularly of plant origin such as the humic substances. Moreover, fungi inhabiting water ecosystems actively participate in the synthesis of autochthonic humic substances and decide on the structure of the humic acids and their chemical properties [56]. Electrokinetic potential tests carried out by Anielak [3, 4, 61] show that the fulvic and humic acids have a negative electrokinetic potential, and its absolute value decreases along with the increase in pH and the amount of metal cations absorbed by them. The increase in metal content in organometallic complexes brings about the decrease in the degree of their dispersion together with a growth of absorption coefficient UV (A_{254}) being an evaluation index of the amount of organic substances dissolved in water. One of the methods to determine organic matter could be ultraviolet absorption of water. According to Albertkiene et al. [2], the coefficient of determination between the TOC and UV_{254} equals to 0.94 and between the COD_{Mn} and UV_{254} -it equals to 0.88, while according to Brandstetter [71], the coefficient of determination between the DOC and UV_{254} equals to 0.99, therefore, the UV_{254} method may be successfully applied for determination of natural organic matter. Absorbance at 254 nm is typical for measurements of aromatic compounds [2]. According to Górniak [71], the coefficient of determination between the DOC and UV_{330} equals to 0.92. In natural groundwater, the humic substances most frequently possess an excess of groups with negative electric charge and take a form of colloids, the electrokinetic potential of which approximates to -20 mV [31]. The increase in pH value results in the increase in the stability of the humic substances in water, which is caused by the increase in the degree of dissociation of function groups. At pH ≥8.0 H^+ ions dissociate from hydroxyl groups whereas at pH=4.6-4.9 dissociation of H^+ ions starts from carboxyl groups. Lowering a pH value leads to decreasing a degree of the humic substances dissociation and particle aggregation [62]. A change of concentration of H^+ ions is also a cause of transformations in the structure of chromophoric groups resulting in the colour of humic substances. It is likely that owing to this, along with a decreasing concentration of H^+ ions, the increase in the colour of groundwater containing the humic acids may be observed [31]. Presence of the humic substances in groundwater drawn for human consumption is unfavourable because it brings along bad organoleptic characteristics affecting the groundwater taste, odour and colour. The humic substances, as clean forms are not harmful to human and animal health, however due to their abilities to absorb others, often toxic impurities, their presence in water intended for human consumption is inadvisable and causes technological problems during a treatment process [25, 37].

FORMATION OF IRON COMPLEXES WITH HUMIC SUBSTANCES

In groundwater containing the HS, iron may occur in a form of relatively stable/durable complexes of various solubility and in a form of colloids, and the profile of the combinations formed depends on the type of the humic substances, pH value and a degree of oxidation of iron ions [20, 43, 44, 63]. The analysis of the series of metal susceptibility to forming combinations with the HS leads to the conclusion that both Fe^{2+} as well as Fe^{3+} are relatively durable complexes. Manganese occurs in natural waters in the form of mineral compounds and, to a lesser extent, organic compounds. Its forms particularly depend on the intensity of the microbiological processes which occur in water ecosystems. The microorganisms influencing its form are inter alia aquatic fungi which participate in the process of organic matter decomposition. By producing manganese peroxidase, mycoplankton catalyse the oxidation of manganese (II) ions to manganese(III), which is stabilised by organic acids [11]. Several authors [20, 62], however, refer to divergent information on binding Fe^{2+} or Fe^{3+} ions by the humic acids. According to Van Dijk, Raschid and Trojanowski, the binding ability of the humic acids is bigger in relation to Fe^{2+} ions whereas Schnitzer and Hansen state that Fe^{3+} ions are bound more strongly than Fe^{2+} [37, 62]. Pandey et al [50] are of the opinion that the difference in susceptibility of iron to forming combinations with the HS may result from Fe^{2+} and Fe^{3+}oxidation during formation of the complex. Furthermore, there is no an explicit theory explaining the mechanism of ferro-organic combinations. Hering and Kraemer [29] claim that binding iron ions by the humic acids is a result of an electrostatic reaction of metal cations with negative charged function groups, especially carboxyl groups. Several researchers [13, 19, 23, 50] suggest various mechanisms of binding iron by the humic acids. Frimmel [19] pointed out that for binding purposes, a certain number of Fe^{3+} ions 2-4 times more organic ligands are required than for binding the same number of Fe^{2+} ions. At neutral reaction of 1 g of fulvic acid can bind over 850 mg of Fe^{2+} and 250 mg of Fe^{3+}, at most [25]. It has also been found that the stability constant of the complex grows along with the increase in pH, which is likely to be caused by an increasing dissociation of the functional groups –COOH and -OH as well as a smaller competitiveness of H^+ ions towards metals, which occurs in acidic environment. The theory of a growing stability constant of the organometallic complex along with the increase in pH value was supported by the results of the research carried out by Schnitzer and Hansen, that showed that stability constants of the same organometallic complexes were higher at pH=5 than at pH=3.5. According to Pandey et al. [50] it is a result of the increase in the dissociation of functional groups, especially of carboxyl groups. As Ratajczak and Witczak claim, the most stable water dissolved iron-humic acid complexes are formed at pH=7 [47]. A degree of dispersion of iron-humic substances bonds depends on the value of an organic ligand to metal concentration ratio in a complex compound. Fulvic iron complexes dissolved in water form as a result of the reaction between fulvic acids and microquantities of iron. An increase of iron concentration in water leads to formation of less stable bonds, the degree of dispersion of which may reach the values characteristic for colloids. As Gonczarow et al as well as Pandey et al. point out [20, 50], formation of chelate complexes with the humic acids in natural waters occurs as a result of an exchange reaction between hydrogen ions of carboxyl and phenol groups of the humic acids and iron cations existing under such conditions mainly in a form of hydroxo-complexes $[Fe(OH)]^{2+}$, $[Fe(OH)_2]^+$, such chelate iron complexes are regarded as the most stable [Fig. 1]. Under natural conditions, the HS react not only with metal ions, but also with hydroxides. The ability possessed by the humic substances to transfer poorly soluble metal salts, oxides and hydroxides into a well soluble form is called a chelating activity [34]. According to numerous researchers [23, 40, 51], one of the reasons for iron stabilisation by organic substances in groundwater may also be formation of the so called protective colloids of hydrophilic character as a result of adsorption of organic substances on iron(III) hydroxide surface. Organic stabilisation of iron colloids results from forming an external coating that contains ionised carboxyl groups. The fact that in natural waters iron may form mixed complexes with organic and non-organic ligands has not been ruled out, either.

Stability of such complexes, similarly to mixed ligand complexes of heavy metals, may be bigger than in the case of monoligand complexes. Thus, the effect of iron reaction with the humic substances depends on microbial activity that determine the structure of the humic acids and their chemical properties, concentration of the HS, concentration and a degree of iron oxidation and conditions of environment such as: concentration of other ions, ionic strength of the solution, pH and temperature.



* hydrogen ions able to exchange
--- coordinate bond

Fig.1. Structure of iron-humic complexes [20].

TREATMENT OF GROUNDWATER CONTAINING HUMIC SUBSTANCES

In oxygen saturated water deprived of organic substances a quick oxidation of Fe^{2+} to Fe^{3+} takes place. The necessary time for Fe^{2+} ions oxidation extends mainly along with the concentration of Fe^{2+} and H^+ in water, and to a smaller degree, with the increase in water temperature [37]. Gonczarow et al. [20] proved, that half times of oxidation reaction of Fe^{2+} to Fe^{3+}, at oxygen partial pressure equalled to 21,3 kPa, extended greatly along with an increasing concentration of hydrogen ions in treated water and for pH=7, pH=6 and pH=5 amounted to approximately 4 minutes, 6 hours and one month. In natural waters where organic substances are present, at the same pH values, $p0_2$, concentration of Fe^{2+}, the speed of iron oxidation is several times slower, which, according to some researchers [20, 43, 44, 47, 59, 63] is caused by stabilisation of $Fe^{2+}$by organic compounds. In the presence of organic substances, especially the humic acids, the reaction of forming complexes with Fe^{2+} ions competes with oxidation of Fe^{2+} to Fe^{3+} and precipitation in a form of $Fe(OH)_3$. Many researchers claim [20, 50] that the amount of complex bonded or oxidised Fe^{2+} depends on water pH and qualitative and quantitative composition of dissolved organic substances. Oxidation of the complexed Fe^{2+}goes very slowly along with formation of relevant Fe^{3+} complexes. Iron (III) formed as a result of this reaction may be reduced by organic compounds, which depends on the stability of bindings in complex combinations. The speed of Fe^{2+} oxidation in the presence of organic substances is affected by the concentration of organic ligands and water pH and is the slowest with a high concentration of organic substances and H^+ ions in water. According to Nernst equation, it is likely to be linked with the increased oxidation-reduction potential of Fe^{3+}/Fe^{2+} system [20]. As a result of aeration the easily sedimenting agglomerates of iron (III) hydroxide do not precipitate, instead, colloidal and water dissolved colour iron bonds with organic compounds are forming, for the removal of which conventional groundwater treatment systems such as aeration, sedimentation and filtration are not sufficient [24, 37, 55, 60, 63]. This has been the same finding as in the research carried out for the water treatment plant (WTP) "Zawada" near Zielona Góra. Although the organic substances present in the treated water did not decrease significantly the efficiency of Fe^{2+} to Fe^{3+} oxidation, the oxidation products were colour, difficult to agglomerate and sedimenting Fe^{3+} bonds [42, 65, 66]. Summing up, the conclusion may be clear that the presence of organic substances, and especially the humic substances in ground water significantly impedes removal of iron. Therefore, several various attempts have been made in order to intensify removal of iron present in combinations with organic ligands. One of the recommended methods here is the application of strong oxidisers. For this purpose, however, it is not advisable to use chlorine compounds due to the risk of forming chlorinated organic compounds, including THM. Furthermore, as Sawiniak found [60], using chlorine leads to formation of iron compounds of colloidal character which are not retained on deposits of rapid filters. The advisability of applying other oxidisers such as ozone, hydrogen peroxide is also questionable. According to Graham [55], the mechanism of ozone oxidation is based on transforming the structure of the HS as a result of breaking big particles into smaller ones, which causes a damage of the conjugated system affecting the colour, but also causes formation of side-products of the oszonation process, such as aldehydes, ketones and carboxyl acids [30]. Thus, oxidation efficiency is apparent because colour reduction is not always in line with the release of iron ions from complexes and their oxidation as well as lowering of the DOC concentration in treated water. Results of the research carried out by numerous researchers [10, 17, 33, 34, 38, 40, 41] showed that for oxidation of Fe^{2+} occurring in combinations with organic substances it is beneficial to apply potassium permanganate (VII) because the oxidation process is supported additionally by sorption and catalytic properties of manganese (IV) oxide [47, 48]. Analysis of the results of the tests carried out on infiltration water of the Oława River showed that the efficiency of removing the HS increased along with the dose of potassium permanganate (VII) as well as along with the increase in iron concentration in untreated water [39, 41]. The same finding was reported by Knocke who thinks that the resulted $Mn0_2$ acting as a weight and adsorbent improves sedimentation properties of $Fe(OH)_3$ and the related humic substances [35]. An advantage of potassium permanganate (VII) as an oxidiser is also that it does not generate formation of oxidation side products having negative effects on human health [55]. As Mouchet and Michalakos et al claim [45, 46], very good effects of treating groundwater containing chelate iron complexes with the HS in the USA, Western Europe and especially in France were ensured by aeration followed by filtration through sediments inhabited by microorganisms such as: *Gallionella sp, Gallionella ferrugine, Leptothrix ochracea, Leptothrix lopholea, Leptothrix discophora, Leptothrix cholodnii, Crenothrix polyspora, Toxotrix trichogenes, Clonothrix fusca, Sphaerotilus natans, Sphaerotilus Dichotoma, Lieskeella sp., Siderocapsa treubii, Siderocapsa Major, Sideromonas confervarum, Siderobacter sp., Naumaniella sp., Metallogenium sp*. Currently the research on applying microorganisms to treatment of water containing chelate iron complexes with the humic substances is carried out in Belgium, Bulgaria, Finland, Austria, Australia, Scandinavian countries and Poland. Research results have proven that a significant role in treatment of groundwater containing iron combinations with the HS is played by microbiological transformations taking place in filtration sediments inhabited by microorganisms. If the filtration material is granulated activated carbon, it also functions as an adsorbent of organic substances and a growth medium for microorganisms participating in oxidation of organic substances, iron and manganese. Insoluble oxides and hydroxides formed as a result of Fe^{2+}oxidation are retained on cell organelles of microorganisms as well as on activated carbon [22, 23, 24, 26, 28, 54]. There are several attempts currently being made in order to use other compounds other than active carbon as an adsorbent for the humic substances. The research concerns adsorption of fulvic acids on goethyt [18], zeolite [5] vermiculite [1], xenolith [32] hematite [8] and bentonite [68]. Investigations have also been carried out into treatment of the groundwater containing humic substances by membrane processes. It has been shown that out of all membrane processes used for removing the humic compounds from groundwater best, approximately 90% efficiency is ensured by nanofiltration. Ultrafiltration processes remove colloidal compounds from water, however they do not retain medium and small molecular humic substances, as it is in the case of nanofiltration. A smaller diameter of the membrane pores guarantees a more efficient removal of the humic substances, on the other hand, however, it causes more frequent drops of the stream flow as a result of clogging the pores up with the humic acids removed from water [69]. Another method suggested for treating colour waters contaminated with organic substances and iron compounds is destabilisation of iron agglomerates with the humic substances obtained through a dramatic increase in concentration of H^+ ions to reach the pH of approximately 2. Under such conditions H^+ ions as competitive cations in ferro organic combinations take place of Fe^{2+}, which after alkalinisation may be oxidised to Fe^{3+} [37]. Application of the above-referred to method under technical conditions is practically impossible. Therefore, a technological system of treatment of such groundwater should incorporate another process efficient in removing iron occurring together with organic compounds. This requirement may satisfactorily be met by a properly run coagulation process [57]. The best results of removing the humic substances are obtained by combining the process of coagulation with activated carbon filtration. This may lead even to 80% efficiency of removing the HS. Apart from adding aiding substances, such as polyelectrolytes to water, efficiency of coagulation process may be improved by correction of the reaction or oxidation of organic substances which form protective layers and stabilise colloids. Depending on the type of pollutants present in water, chemical oxidation may improve or deteriorate effects of removing such pollutants due to a risk of producing side effects of oxidation products which are usually more difficult to remove that oxidation substrates [6]. The basic mechanisms of removing the humic substances in a coagulation process are: complexation, charge neutralisation, co-precipitation and adsorption. It has also been shown that there is the dependence between the initial concentration of the humic substances and an optimum dose of a coagulant. The size of removed particles is also important. A coagulant dose in the case of treatment of groundwater containing the humic substances should be determined on the basis of the content of organic compounds rather than on turbidity. Apart from that, researchers indicated that aluminium coagulants are more efficient in treatment of such waters than iron salts because the products of aluminium hydrolysis do not form colour combinations with organic substances, which is contrary to iron [37]. Although in water intended for human consumption the allowable content of organic substances, measured as chemical oxygen demand (COD_{Mn}), is 5 $mg0_2/dm^3$ [58], so a more efficient removal of those impurities should be pursued [64]. As it is illustrated by results of many research works [28, 67], an allowable content of biodegradable dissolved organic carbon in water drawn into water intake system should not exceed 150-200 (300) mgC/m^3. The organic matter dissolved in the water being purified needs to be removed in order to prevent not only the formation of disinfection by-products, but also the secondary pollution of the water in the distribution system. The main cause of the worsening of water quality during transport from the water treatment plant (WTP) to the consumer is a lack of biological and chemical stability at the point of entry into the water distribution network. Water is considered to be biologically stable if it is not only free of microorganisms or their dormant forms, but if it also does not contain nutrient substrates necessary for heterotrophic organism development, i.e. biodegradable dissolved organic carbon (BDOC), non-organic nitrogen compounds and phosphates. Unfortunately, commonly used unit processes that aim to eliminate organic substances do not always allow for a reduction in concentration sufficient for limiting health hazards. Effective removal of biodegradable organic fractions is possible with a treatment train involving biologically active filtration (BAF) through a granular carbon bed. Bio-filtration is preceded by ozonation, where non-biodegradable organic substances are rendered biodegradable, thus providing nutrient supply for the microorganisms that colonise the BAF bed [37, 70].

CONCLUSIONS

The humic substances, due to a specific structure of their macromolecules may be characteristic of a high chemical activity and biological availability in natural waters where they react with both organic as well as inorganic admixtures. Due to the above, in water environment they may be carriers of often very toxic micro-pollutants. Another risk related to the presence of the humic substances in waters is that during water treatment carcinogenic and mutagenic side products of the humic substance oxidation are likely to be formed, and the lack of biological stability of water [20, 24, 50, 66]. The need to remove the HS from water intended for human consumption is out of question. In case of the presence of the humic substances in groundwater, those compounds greatly confuse technology of water treatment forming Fe^{2+} and Fe^{3+} -colour and stable ferro-organic combinations difficult to remove in conventional technological systems of groundwater treatment such as: aeration, sedimentation and filtration. Owing to this, treatment of such water requires application of advanced technological systems comprising numerous single processes such as: coagulation, filtration, activated carbon sorption together with biodegradation on biologically activated carbon filters, chemical oxidation, ion exchange and membrane processes. The best results of removing the HS are obtained by combining coagulation process, the best with aluminium coagulant with activated carbon filtration [15, 25]. Those methods have been classified by the US Environmental Protection Agency as the best available techniques (BAT) for the control of disinfection by-products in drinking water [37]. Analyses of problem the possibility of removing KH from groundwater are of interest to engineers in Poland and in the world. Published materials report that coexistence of organic substances and iron and coexistence of organic substances and manganese in groundwater causes that a particular part of iron and manganese occurs in a form of iron-organic and manganese-organic compounds as colloids or dissolved complexes. Successful treatment of such water generates technological problems. The research conducted by the author [42] on the groundwater from Quaternary formations with high concentration of total iron amounting to 7.0 mgFe/dm^3 and also an increased amount of organic substances (TOC from 4.00 to 7.20 mgC/dm^3) and manganese up to 1.80 mgMn/dm^3 has shown that the effectiveness of pollutant removal from the underground water in the coagulation process was decreased together with the increase in the value of the values of the coefficients of the co-occurrence of organic pollutants and total iron ($D = TOC/Fe_{tot}$) has proven that, irrespective of the type of the coagulant, the effectiveness of decreasing the concentration of total iron, reducing the colour and the turbidity and removing the organic substances is lower for the greater values of coefficient $D= TOC/Fe_{tot}$. Further research into the purification of groundwater with the increased content of organic substances should explain what is the effect of the type and concentration of organic substances on the effectiveness of the removal of iron and manganese during the use of various technological systems water treatment.

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ZNACZENIE SUBSTANCJI HUMUSOWYCH W KSZTAŁTOWANIU SPOSOBU OCZYSZCZANIA WÓD PODZIEMNYCH

Substancje humusowe (HS) stanowią dużą część materii organicznej występującej w środowisku wodnym. Ich obecność w wodach podziemnych powoduje wiele problemów związanych z jej uzdatnianiem. HS są źródłem podwyższonej intensywności barwy wody, wpływają na jej smak i zapach, utrudniają usuwanie żelaza, manganu oraz innych metali, a także substancji organicznych w tym pestycydów. Ponadto HS obecne w oczyszczanej wodzie mogą być prekursorami toksycznych trihalometanów. Do oczyszczania wód podziemnych, w których występują substancje humusowe oraz związki żelaza nie wystarcza zastosowanie konwencjonalnego układu oczyszczania wód podziemnych. W związku z tym poszukuje się ciągle nowych metod usuwania substancji humusowych z wód podziemnych oraz optymalizuje się już istniejące. W prezentowanej pracy na podstawie przeglądu literatury przedstawiono problemy związane z występowaniem substancji humusowych w wodach podziemnych oraz omówiono możliwości ich usuwania w celu uzyskania wody spełniającej wymagania stawiane wodzie przeznaczonej do spożycia przez ludzi.