Pol. J. Environ. Stud. Vol. 20, No. 6 (2011), 1381-1386

Original Research

Significance of Zeta Potential in the Adsorption of Fulvic Acid on Aluminum Oxide and Activated Carbon

Anna M. Anielak[1]*, **Milena Grzegorczuk-Nowacka**[2]

[1]Institute of Water Supply and Environmental Protection, Faculty of Environmental Engineering,
Kraków University of Technology, Warszawska 24, 31-155 Kraków, Poland
[2]Department of Water and Wastewater Technology, Technical University of Koszalin,
Śniadeckich 2, 75-453 Koszalin, Poland

Received: 23 November 2010
Accepted: 7 June 2011

Abstract

Studies on the adsorption of fulvic acid (FA) on activated carbon Norit GAC 1240 and activated aluminium oxide as adsorbents has been conducted. The adsorbents differed in their chemical composition, chemical properties, surface charge, and related zeta potential. The FA used was obtained from mud sampled at Kołobrzeg. The electrokinetic potential of the adsorbents and adsorbate over a wide range of pH was determined. The electrokinetic potential of FA depends not only on the pH of the solution but also on the charge of cations of the substance used to adjust it. A model of the surface of aluminium oxide is presented. The sorption process was conducted in a static environment. In order to determine the amount of adsorbed FA, the concentration of total organic carbon (TOC) before (TOC_i – initial TOC concentration) and after adsorption (TOC_e – equilibrium TOC concentration) was measured. After the adsorption process, the zeta potential of activated aluminium oxide was measured. The TOC removed per adsorbent surface unit was higher for aluminium oxide. The specific surface area and the electrokinetic potential may be useful indicators in selecting an adsorbent for particles of known ionic characteristics.

Keywords: fulvic acid, adsorption, electrokinetic potential, activated carbon, aluminium oxide

Introduction

Humic substances are naturally occurring macromolecular substances widely present in surface waters and characterized by a strong coloration ranging from brown to black. Their concentration in river and lake water can reach about 6 mg/L, and in swamp water may even exceed 30 mg/L. They comprise 60-80% of the entire mass of organic substances occurring in the bottom water of rivers, lakes, and seas. Humic substances form as a result of humification, that is the transformation of organic compounds contained in remains of plants and animals such as lignins, proteins, pectins, and polysaccharides. Their structure varies widely, and their structural model has not been conclusively defined. Fulvic acid (FA) is the soluble fraction of humic substances. The size and structure of FA particles depends on many factors such as the type of material from which they are formed, the environment in which the decomposition takes place, the microorganisms taking part in the decomposition, and the duration of the humification.

Fulvic acid has an elementary composition consisting of between 44% and 50% oxygen, 40% and 50% carbon, and 1% to 3% nitrogen. Most authors believe that humic

---

*e-mail: aanielak@pk.edu.pl

substances are particles with long chains, forming coils with aliphatic and aromatic elements. In aqueous solutions the particles organize into spherical forms. The aliphatic elements are subject to hydration, creating extended, outward-pointing chains with polar functional groups. These groups include hydroxyl (-OH), carboxyl (-COOH), methoxyl (-OCH_3), methyl (-CH_3), and methylene (-CH_2). The water-repelling hydrophobic fragments become condensed and directed toward the centre. They are formed from aromatic and heterocyclic rings such as benzene, furan, pyridine, and also naphthalene, anthracene, indole, and quinoline. There are many models of fulvic acid [1-4]. The model presented by Gonet was tested and confirmed using magnetic resonance [5, 6].

Humic substances are able to complex with metal ions and absorb some organic compounds such as pesticides, which have surfactant properties. It has been shown that humic substances reduce the surface tension of water, which increases the solubility of organic compounds. Studies conducted in 1980 by US researchers show that chlorinating fulvic acid and algae with a dosage of 10 ppm chlorine creates carcinogenic chloroorganic substances, whose amount depends on the reaction time and reaction pH with a constant concentration of FA and algae equal to 1 ppm TOC [7]. Since that time, there has been much research confirming the role of humic substances (including fulvic acid) in the genesis of chloroorganic substances and other carcinogenic and mutagenic substances [8-14]. These are substances such as trihalomethanes, halo-acetic acids (e.g. monochloroacetic, bromoacetic, dichloroacetic acid, trichloroacetic acid), acetonitrile, chloral hydrate, MX, and COHC. To date, several hundred by-products of oxidation and disinfection have been identified. For this reason, the removal of humic substances during water purification is crucial.

One of the processes used to remove fulvic acid from water (besides coagulation, flotation, oxidation, precipitation and ion exchange) is sorption. The chemical affinity of the adsorbate to the adsorbent is an important part of this process. Most often it is the result of the correlation between electrostatic, ion exchanging, and intermolecular (van der Waals) interactions or those interactions caused by chemical reaction (chemisorption). The type of interaction in the interphase layer depends on the surface structure of the adsorbent: the type of surface ion exchanging groups, the presence of unsaturated charges generated by decomposition of the molecular network, surface porosity, the type and concentration of the adsorbate, temperature, pH of the solution, and so on. A very important factor characterizing the surface of the adsorbent is its potential. As it is impossible to measure it, the potential between interfacial double layer (electrokinetic potential, ζ potential) is widely used. Knowledge of the ζ potential over a wide range of pH, if properly interpreted, permits assessment of the chemical affinity of the adsorbate to the adsorbent. For this reason, the goal of the study was to show the correlation between the process of sorption of the difficult-to-remove fulvic acid and the ζ potential of this acid and the sorbent.

Experimental Procedures

The fulvic acid was obtained by extraction from mud sampled at Kołobrzeg (Parsęta River on the southern coast of the Baltic Sea) using the method described by Pempkowiak [15].

Norit GAC 1240 from Norit B.V. (Amersfoort, The Netherlands) and the aluminium oxide from Merck KGaA (Darmstad, Germany) were used as adsorbents. GAC 1240 is produced by steam activation of selected grades of coal. It was selected because, according to the supplier, it offers superior adsorption of organics. Moreover, the GAC 1240 offers a high purity level. According to the supplier specifications, it has alkaline pH and an effective size of D10 0.6-0.7 mm. The total surface area (B.E.T.) of the activated carbon is 1,117 m^2/g [17].

Aluminium oxide as a mineral adsorbent has been chosen due to its high purity (<0.2 % substances extractable by water) and neutral pH (6.8-7.8). The specific surface area of the Al_2O_3, according to the supplier, is 200 m^2/g.

For the tested materials (activated carbon, aluminum oxide, and fulvic acid) we determined the electrokinetic potential over a wide range of pH values. Measurement of the zeta potential was conducted using a zeta analyzer (Zeta PALS; Brookhaven Instruments Corporation, Holtsville, NY) using the frontal electrophoretic light scattering method. The ζ potential was calculated with Smoluchovsky's method used in Brookhaven software. To prepare the solutions we used deionized water with a maximum conductivity of 1.5 μS/cm. The concentration of fulvic acid was maintained at 50 mg/L, and the dosage of the sorbent was 5 g/100 mL FA (5g sorbent/5mg FA). The pH of the solution was adjusted with 0.1 mol/L HCl and NaOH. The sorption was carried out in a static environment. The samples with the sorbent and solution were shaken in flasks at 180 rpm with t = 60 min. Following this, they were allowed to sediment (5 min). The supernatant liquid was filtered (Nutsche filter) through filter paper (pore size 22 μm).

The concentration of fulvic acid was determined directly by spectrophotometry and indirectly by measuring total organic carbon (TOC) in a solution using a SZIMADZU TOC V-CPH analyzer.

Results and Discussion

Fulvic Acid Research

The sampled fulvic acid (FA) was first converted into protonated form by ion exchange. The elemental analysis of their ash-free mass was as follows: N 2.55%, C 45.90%, H 4.97%, S 0.39%, O 46.19%. The elemental characteristics and the infrared spectrum (Fig. 1) were typical of fulvic acid found in surface waters. The zeta potential of the fulvic acid (50 mg/L) solution as a function of solution pH is shown in Fig. 2. The acidity of the solution was altered using various bases. To show that the zeta potential depends not only on the pH of the solution, but also on the charge of

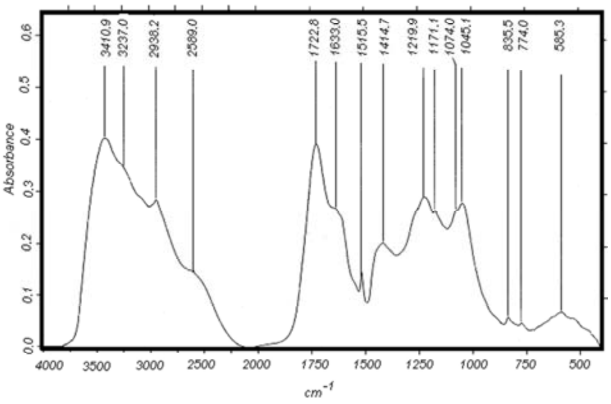

Fig. 1. Infrared spectrum of fulvic acid extracted from Kołobrzeg mud.

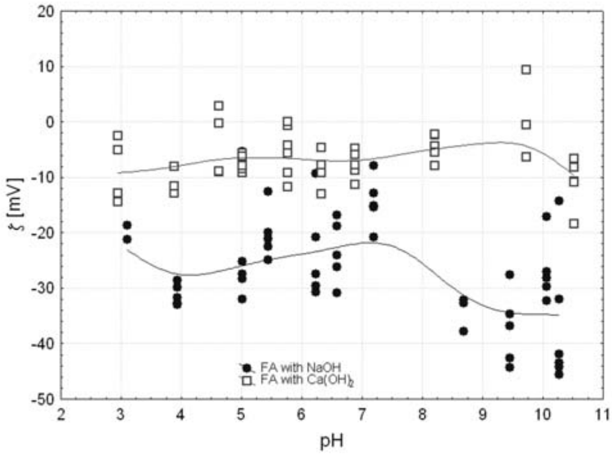

Fig. 2. Electrokinetic potential of the fulvic acid particles in solution. pH regulated with NaOH or $Ca(OH)_2$; [FA] 50 mg/L.

the cation of the substance used to adjust it, the study was conducted on two separate series of samples, dosing with sodium base (Na^+) in the first series and calcium base (Ca^{2+}) in the second. The initial acidity of the aqueous solution of the fulvic acid was acidic with a pH of 3.0.

The size of the FA particles was large, in the nm range (about 500 nm). This size was related to the purity of the FA extracted from the mud. The particles contained various admixtures of impurities, including trace metals, which formed from the FA by bridging complex compounds contributing to their perikinetic coagulation [16]. The results in Fig. 2 demonstrate that fulvic acid has a negative electrokinetic potential over the entire pH range. The absolute value of the electrokinetic potential in the presence of calcium ions is smaller than in the presence of sodium cations. This results from the greater compensation of the negative surface charge of the FA using bipositive cations. The electrokinetic potential in the tested pH range assumed values considerably divergent and in the presence of Ca^{2+} cations it averaged -9 mV, while with Na^+ it was -30 mV.

Sorbent Research

In order to determine the zeta potential, the samples with the adsorbent suspension were suitably prepared. Before the measurement, the dry samples of carbon or aluminium oxide were ground in a mortar, and then, after wetting well with deionized water, subjected to 10 minutes of sedimentation to separate the large and easily sedimenting particles. After decanting, the supernatant was analyzed. The concentration of the carbon and aluminium oxide suspension was of the order of 0.1 mg/mL.

The tests showed that the effective diameter of the aluminium oxide particles was 1028 nm, and for the activated carbon 2,400-2,500 nm. The tests were conducted with the electrical field voltage in the range of 8.63 to 10.63 V/cm for the carbon suspension and between 8.84 and 10.48 V/cm for the aluminium oxide. The electrolytic conductivity for the carbon was between 2.65 and 203 μS/cm, and between 6.36 and 59.89 μS/cm for the aluminium oxide, depending on the pH of the solution.

The analysis of the test results shown in Fig. 3 indicates that the zeta potential of the aluminium oxide in the tested pH range was between +39 and -36 mV and, based on test results, the isoelectric point can be interpolated to be about 7.5 pH. The electrokinetic potential of the GAC 1240 activated carbon changes in the research conditions from +17 to -47 mV and the isoelectric point interpolated based on the plots corresponds to a pH of 4. This means that the surface of the aluminium oxide in an alkaline environment (pH>7.5) has an excess of negative charge, and in an acidic environment (pH<7.5) an excess of positive charge.

This distribution of electrical charge is characteristic of hydrophobic surfaces or of surfaces having both negative and positive centres. The surface of the aluminium oxide according to Peri's model contains so-called defects that act as electron donor and electron acceptor centres. According to this model, three-quarters of the electron donor sites (aluminium oxides with an unsaturated charge) are occupied by OH^- ions, giving the occupied area a net negative surface charge. The model of the activated aluminium oxide can

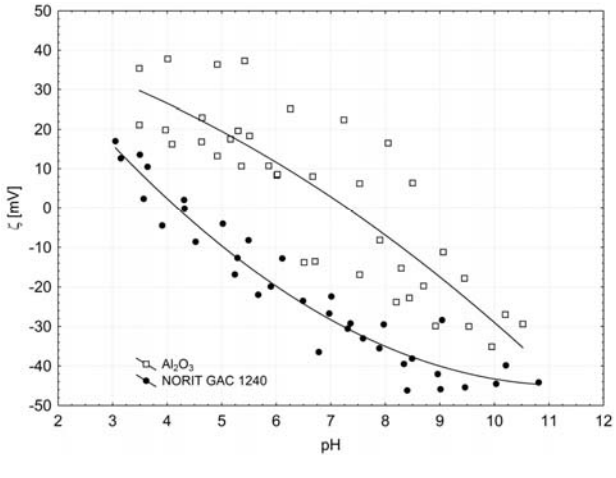

Fig. 3. The potential of GAC 1240 and Al_2O_3 in relation to solution pH.

also be demonstrated in a simple two-dimensional scheme (Fig. 4). This explains why, in an alkaline environment, the aluminium oxide has an electronegative charge (excess of hydroxide ions), and an electropositive charge in an acidic environment (excess of protons). This model is also consistent with the zeta potential measurements and the pH of the isoelectric point.

The model shown in Fig. 4 explains why the surface of the aluminium oxide exhibits electron donor and electron acceptor characteristics, and why it is not hydrophobic. This surface easily undergoes hydration. It is dominated by unstable hydrogen bonds, which in time become stable bonds =Al-OH, and the surface becomes neutral or, as a result of proton dissociation, electronegative (=Al-O-).

The zeta potential values of the activated carbon demonstrate that it contains negative dissociative groups at pH>4. These may be carboxyl groups, which are often present on the surface of activated carbon.

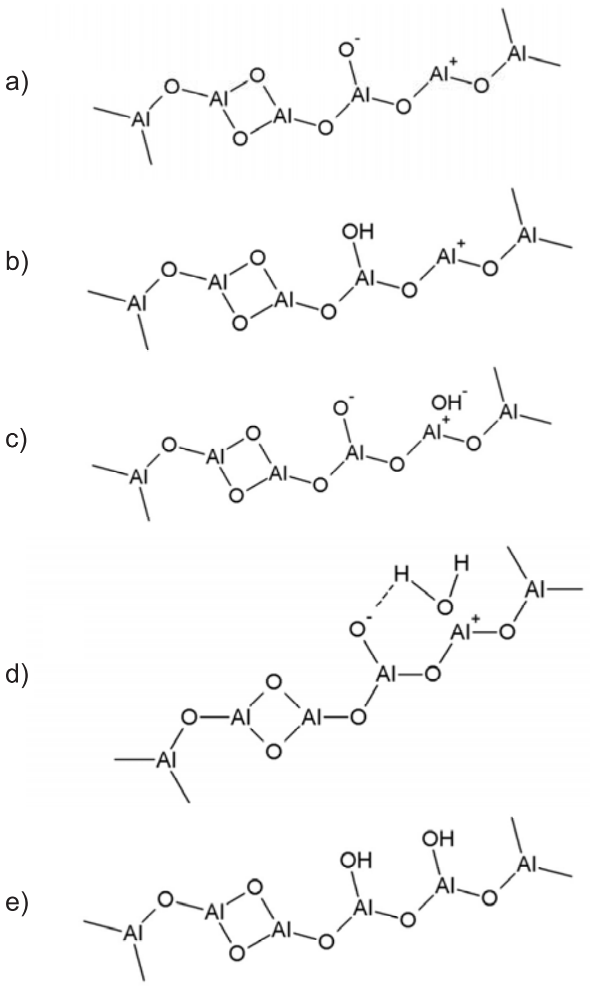

Fig. 4. Activated aluminum oxide surface model.
a) Donor-acceptor centres on aluminum oxide,
b) The model of the activated aluminum oxide surface in acid solution (pH<7),
c) Model of the activated aluminum oxide surface in alkaline solution (pH>7),
d) Model of the neutral activated aluminum oxide surface (isoelectric point pH 7.0-7.5),
e) Model of the changes in the activated aluminum oxide surface resulting from extended hydratation.

FA Adsorption on Sorbents

In order to analyze the effect of the electrokinetic potential and, simultaneously, the nature and size of surface charge of the adsorbent on the process of sorption of fulvic acid, we studied the pH dependency of adsorption. The pH in the sorption process determines the dissociation state of the functional groups and surface character. Because the activated carbon has a considerably larger specific surface (by 5-10 times), the amount of adsorbed fulvic acid (described as $TOC = TOC_i$-TOC_e) was converted to units of the specific surface (A) of the adsorbent. The calculations used 1,117 m^2/g for the activated carbon, and 200 m^2/g for the aluminium oxide. The obtained results have been presented in Fig. 5.

On examining the amount of fulvic acid removed from the solution per surface unit of the sorbent, it is readily apparent that it is considerably larger for aluminium oxide. Only at pH=10 is the amount of adsorbed fulvic acid on aluminium oxide smaller than for the activated carbon. The amount of adsorbed FA particles on the surface of the activated carbon was almost constant at about $0.4 \cdot 10^{-3}$ mg/m^2. Notable for the aluminium oxide was the rapid decrease of FA adsorption for pH>7, that is, in the range in which the aluminium oxide has a negative electrokinetic potential and consistent with the model in Fig. 4c in which only the negative surface centres are active. We conclude, therefore, that electrostatic forces repulse the adsorbate and adsorbent particles, which largely depend on the number of electropositive centres occupied by hydroxide ions.

Adsorption of fulvic acid on the GAC 1240 depends on pH. In low pH the compensation of negative charge of activated carbon and fulvic acid occurs. The FA removal takes place due to adsorption of hydrophobic surfaces of adsorbent and adsorbate. In higher pH, with the increase of the OH^- ion concentration, adsorption decreases. This is a result of exclusion of the hydrophobic surfaces of carbon and FA by hydroxyl ions. Then, the electrostatic repulsion of GAC and FA occurs and effectiveness of the process decreases.

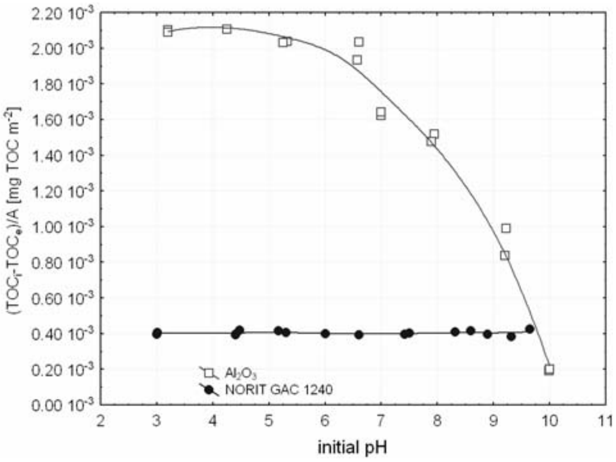

Fig. 5. Fulvic acid adsorption normalized to unit surface area of adsorbent.

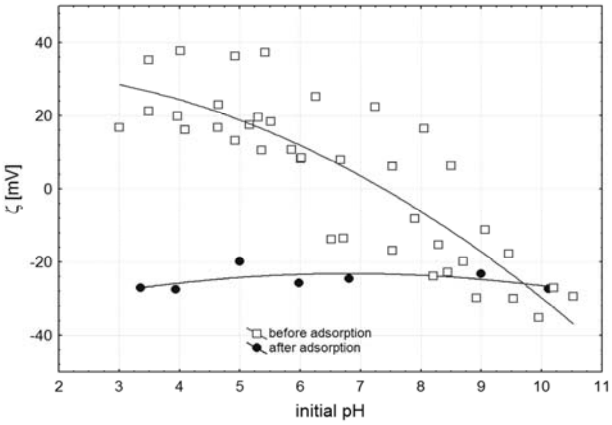

Fig. 6. Electrokinetic potential of aluminum oxide before and after adsorption of fulvic acid.1384

Fig. 6 depicts the electrokinetic potential of the aluminium oxide before and after the adsorption process. The change in the charge potential of the Al_2O_3 after the adsorption of FA is clearly visible. With an initial pH value of about 3.5, the zeta potential before FA adsorption was more than 25 mV. After adsorption, the zeta potential was negative and for any given pH was below -25 mV – a difference of about 50 mV. With increased pH the difference decreased and, in an alkaline environment, the potentials converged. The negative electrokinetic potential of the aluminium oxide particles in the entire pH range confirms earlier results that showed intensive FA adsorption on the Al_2O_3 surface.

Conclusions

- The electrokinetic potential of fulvic acid is negative in a wide range of pH.
- The electrokinetic potential of aluminium oxide in the pH range 3.5-10.4 was between +39 and -36 mV, and the isoelectric point was achieved at a pH of ca. 7.0-7.5.
- The electrokinetic potential of activated carbon NORIT GAC 1240 in the pH range 3-10.8 changed from +17 to -47 mV, and the isoelectric point corresponds to a pH of about 4.
- The adsorbed fulvic acid changes the electrokinetic potential of aluminium oxide from positive to negative. The absolute value of the difference in zeta potential depends on the pH of the solution. For example, at a pH of 4 it is about 50 mV.
- The pH of the solution does not significantly affect the amount of fulvic acid adsorbed by the activated carbon NORIT GAC 1240.
- For the activated carbon, the adsorption of fulvic acid takes place via the van der Waals force occurring between the hydrophobic parts of the adsorbate and the adsorbent.
- The electrokinetic potential may be used to predict the extent of the adsorption process.
- Cations occurring in the solution can change the zeta potential of fulvic acid. The electrokinetic potential may depend on the cation charge.
- The type and value of surface charge for the specific surface unit are crucial in the adsorption process. Research showed that aluminium oxide is a very good adsorbent, but due to the small specific surface its adsorptive properties are weakened.
- The best adsorbent to FA removal is a solid phase with a large specific surface area and electropositive charge.
- The search for such a adsorbent should be continued.

Acknowledgements

This research was fully sponsored by the Polish Ministry of Science and Higher Education, Koszalin University of Technology Statutory Research No. 504.01.14.

References

1. GONET S. S. Structure of humic substances, Zeszyty Problemów Podstawowych Nauk Rolniczych. **411**, 189, **1993** [In Polish].
2. LEENHEER J.A., WERSHAW R.L., BROWN G.K., REDDY M.M. Characterization and diagenesis of strong-acid carboxyl groups in humic substances. Appl. Geochem. **18**, 471, **2003**.
3. SCHNITZER M., KHAN S.U. Humus Chemistry. Marcel Dekker, New York, **1972**.
4. WOLLARD C. D., LINDER P.W. Modelling of the cation binding properties of fulvic acids: an extension of the RANDOM algorithm to include nitrogen and sulphur donor sites. Sci. Total Environ. **226**, 35, **1999**.
5. AOCHI Y.O., FARMERT W.J. Role of Microstructural Properties by the Time-Dependent Sorption/Desorption Behavior of 1,2-Dichloroethane on Humic Substances, Environ. Sci. Technol. **31**, 2520, **1997**.
6. CHIEN Y.Y., BLEAM W.F. Two-Dimensional NOESY Nuclear Magnetic Resonance Study of pH-Dependent Changes in Humic Acid Conformation in Aqueous Solution, Environ. Sci. Technol. **32**, 3653, **1998**.
7. FAUST S.D., ALY O.M. Chemistry of Water Treatment, second edn. Lewis Publishers, Boca Raton, London, New York, Washington D.C., **1998**.
8. ANIELAK A. M., GRZEGORCZUK M., SCHMIDT R. Products of fulvic acid oxidation with sodium hypochloride and dioxidane, Przem. Chem. **6**, 702, **2008** [In Polish].
9. ANIELAK A. M., GRZEGORCZUK M., SCHMIDT R. Effect of chloride ions on formation chloroorganic substances during oxidation of fulvic acid, Przem. Chem. **5**, 404, **2008** [In Polish].
10. FABBRICINO M., KORSHIN G.V. Formation of disinfection by-products and applicability of differential absorbance spectroscopy to monitor halogenation in chlorinated coastal and deep ocean seawater. Desalination. **170**, 57, **2005**.
11. GALLARD H., Von GUTEN U. Chlorination of natural organic matter: kinetics of chlorination and of THM formation. Water Res. **36**, 65, **2002**.
12. RODRIGUEZ M.J., SERODES J-B. Spatial and temporal evolution of trihalomathanes in three water distribution systems, Water Res. **35**, 1572, **2001**.
13. TOROZ I., UYAK V. Seasonal variations of trihalomethanes (THMs) in water distribution networks of Istanbul City. Desalination. **176**, 127, **2005**.

14. LI X., ZHAO H.-B. Development of model for predicting trihalomethanes propagation in water distribution systems. Chemosphere. **62**, 1026, **2006**.
15. PEMPKOWIAK J. Distribution, origin, and properties of humic substances in the Baltic Sea. Ossolineum, Wrocław, **1989** [In Polish].
16. ANIELAK A. M. Examples of the Application of Electronic Potential in Environmental Engineering, in: L. Pawłowski et al. (Eds.) Environmental Engineering Studies. Polish research on the way to the EU, Kluwer Academic/Plenum Publisher, New York, pp. 215-224, **2000**.
17. Norit Datasheet. No. 1240, 16.10, **2006**.