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The Significance of Electrokinetic Potential in the Adsorption Process of Humic Substances

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1. Introduction

Humic substances (HS) commonly found in ground waters give the ground waters colour and until recently, have been treated as being totally harmless and having no ill effects on human and animal health. However, research carried out in recent years has shown that those substances when undergoing the chlorination process are precursors of halogen-organic pollutants, including mutagenic and cancerogenous compounds such as trihalomethans (a derivative of short chained aliphatic carbohydrates like chloroform) and 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX). Besides, humic substances, because of their structure which gives them hydrophilic character [1] are good sorbents for both organic and inorganic substances including toxic compounds too, such as pesticides, phthalates and polychlorinated biphenyls. On account of these properties, it is necessary to undertake the total removal of humic substances from water intended for public supply. A commonly used process to get rid of water colour is coagulation together with less effective processes such as sorption or ion-exchange [2]. Coagulation may be supported by substances showing sorption features. Those substances are usually added to water being treated. The amount added is usually between 2 to 15 g/m^3, but this varies and sometimes the maximum amount of 100 g/m^3 is necessary. For both the humic substances and the sorbent particles the reaction mechanism is strongly connected to their surface charge and the structure of the double electric layer. A determinable factor characterizing the double electrical layer is its electrokinetic potential. That potential characterizes moving particles and occurs in the place where shear plane forms. To make it clearer, it is assumed that the electrokinetic potential dominates on the border of the adsorptive layer and the diffuse layer. When we know the value of the electrokinetic potential (called ζ potential) we can explain the phenomena taking place between the phases in the physico-chemical processes [3].

That is why the electrokinetic potential was used to examine and explain the mechanism of humic substances removal in the adsorption process and a hypothetical model of that process was developed for defining the optimum process conditions.

2. Materials and methods

2.1. Preparation of adsorbents

First an investigation into the sorption process of humic substances was carried out using batch experiments. The following sorbents were applied: natural bentonite, activated bentonite, hydrophilic powdered activated carbon Norit CN 1, hydrophilic powdered activated carbon Norit S.A. Super.

Activated bentonite was obtained by the exchange of interpack cations against protons. 100 g of natural bentonite was mixed with 500 mL of 6 n HCl and heated for 2 hours to a temperature of 100°C. After two hours the supernatant was separated from the residue by decanting and then the bentonite was purified. This process was repeated twice. Then, the bentonite was dried at 105°C until its weight stabilised.

Before the investigation began the natural bentonite and the activated carbons were mixed with distilled water until a 20 g/L concentration was achieved. This mixture was thoroughly stirred. After 24 hours the water was decanted. This process was repeated once and then the sorbent was dried at 105°C until its weight stabilised. The suspension of sorbent in distilled water was prepared one day before its use.

2.2. Preparation of stock solution

Water samples from which humic substances were adsorbed were prepared from tap water whose average composition is given in table 1.

In order to give the water turbidity and colour, silica (10 mg/L) and HS were added. The silica was prepared in the following way: 25 g of technical water-glass was dissolved in 500 mL of distilled water and the solution was adjusted to achieve pH 7.0 by using H_2SO_4. This solution was stirred very slowly for 2 hours until a colloidal solution was reached. The solution was diluted until it reached a volume of 1 litre. The final concentration of silica was

10g/L. Before using the silica was homogenised. The water reaction was corrected with NaOH or HCl solution to maintain pH of 5.5 or 7.5.

Table 1. Tap water composition
Tabela 1. Skład wody wodociągowej

Parameter	Unit	Value
Turbidity	mg/L	1.0
Colour	mg Pt/L	5.0
Scent	-	2.0
Reaction	pH	7.5
Total hardness	mval/L	7.0
Alkalinity	mval/L	3.5
Iron	mg/L	0.1
Chlorides	mg/L	35.8
Ammonia nitrogen	mg/L	0.01
Nitrous nitrogen	mg/L	0.05
Oxygen consumption	mg/L O_2	1.6
Manganese	mg/L	mark
Electrolytic conductivity	µS/cm	594

Humic substances were obtained from the bottom of the Dzierżęcinka river on the basis of information given in articles by Ohkubo et al. [4] and Pempkowiak [5]. The recovery of HA, which is presented in figure 1, was described in papers by Anielak et al. [6] and Świderska [7]. In the extraction process used fulvic (FA) and humic acids (HA) were obtained, which were mixed in proportion 3:2. The HS solution was prepared 24 hours before the investigation began.

The HA concentration was determined by using the spectrophotometric method for measuring real water colour. Interfering colloidal substances were removed by rotating the sample in a centrifuge for 10 minutes at a speed of 3000 rpm. Then, colour was determined with spectrophotometer HP 8453 at 455 nm against platinum-cobalt standards.

Identification of the basic functional groups in the FA and HA particles was made using an infrared spectrophotometry. The analysis was made on a Hewlett Packard (IR 15 I) using the KBr compensation pastilles technique. The determination of the heavy metals (Co, Fe, Cu, Cd, Pb, Zn) was made using an Atomic Absorption Spectrometry (AAS) on Video 11 E (Thereno Ierrell Ash).

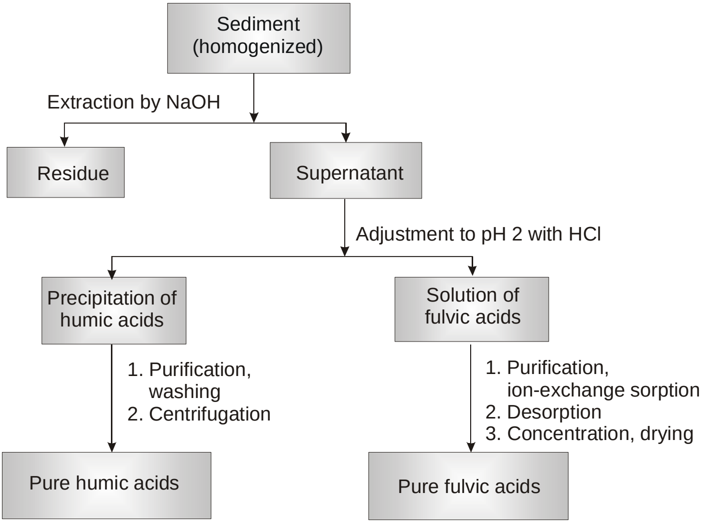

Fig. 1. Diagram of humic substances isolation from sediments
Rys. 1. Schemat otrzymywania substancji humusowych z osadów dennych

In order to determine the iron concentration acid samples were prepared in the following way: 20 mg of acids were digested in 5 mL of a HNO_3 and $HClO_4$ (1:1) mixture for 2 hours at 120°C. Then, the acids were evaporated and dried, the part remaining was once again dissolved in 10 mL of HNO_3 with a concentration 0.1 mol/L.

The concentration of Al was determined spectrophotometrically using a HACH DR/2010. The samples of humic substances were mineralized in a DIGESDAHL system with $H_2SO_4 + H_2O_2$.

2.3. Electrokinetic potential measurement

The electrokinetic potential of sorbent particles was determined by the electrophoresis method measuring the electrophoretic movement at nine depths of the measuring cell and applying the method described in an article by Anielak [8].

The measurements of the electrokinetic potential and the particle size of the humic substances were taken on a Brookhaven zetameter applying the Zeta Pals method, in which Doppler's effect is used, occurring as a result of laser beam dissipation going through the media of dispergated particles moved by electrical pole with specified intensity. Before measuring the adsorbent, silica and fulvic acids particles were classified using a centrifuge in order to obtain a research fraction of a size <3 μm.

2.4. Humic substances adsorption experiment

This investigation into the adsorption process was carried out using the static method. A sample with the adsorbent was closed in a flask, stirred for the first hour of the experiment and then put away for a specified period of time. After given time a well mixed sample was taken and its colour was determined.

3. Results and discussion

3.1. Characteristics of humic substances

The IR spectra of humic substances showed the presence of the carboxyl, alcoholic, phenolic, amido, methyl and methoxyl groups in their structure. In humic acids structure there are more aromatic rings but in fulvic acids there are more aliphatic chains with more carboxyl groups. A detailed analysis of the IR spectra of the investigated humic substances was presented in a paper by Świderska [7]. Chemical analysis showed that trace metals also occurred in the investigated samples of fulvic and humic acids (see table 2).

Table 2. Contents of trace metals in fulvic and humic acids samples
Tabela 2. Zawartość metali śladowych w próbkach kwasów fulwowych i huminowych

Kind of sample	Concentration in μg/g									
	Mn	Fe	Cu	Ni	Co	Cd	Pb	Zn	Cr	Al
FA	34.9	1154	32.5	6.9	1.5	<0.77	4.6	8.6	1.9	0.5
HA	43.7	9623	262.5	77.9	6.5	2.1	30.6	132.9	140.4	2450

On the basis of the results obtained, it is concluded that humic acids contain more trace metals than fulvic acids. In humic acids there are particularly large amounts of iron (approx. 10 mg/g) and copper. The large amounts of aluminum (2450 μg/g), are also remarkable and they probably come from aluminosilicate which could have a mineral-organic connection with humic acids. Hardly any aluminium was found in fulvic acids.

3.2. Electrokinetic potential

Knowing the values of the electrokinetic potential of the adsorbent particles, humic substances and colloidal silica enabled us to analyse the adsorption process. Investigations were carried out at different pH measures. pH-corrections of the suspension were made with 0.1 n NaOH or HCl. Measurements were taken according to the procedure described in an article by Anielak [8] with the current intensity E = 16.46 V/cm and temperature t = 22-26^{o}C.

The results of the investigations are presented in Figure 2. The electrokinetic potential of natural bentonite within the range of pH from 3.5 to 9.3- has the values of –22.19 to –39.38 mV. For activated bentonite those changes are larger, at pH 3.6 it is ζ= –12.78 mV, and at pH 9.0 it is ζ= –56.44 mV. Both kinds of bentonite, natural and activated have negative potential in the whole range of pH changes measured in these experiments. Carbon Norit CN 1 adsorbent has the lowest ζ potential of all the adsorbents that were measured in the experiments. Its pH values decreased during the experiments from -43.04 to -59.88 mV. However, activated hydrophobic carbon Norit SA Super in an acid environment has a positive ζ potential. At pH~5.2, the electrokinetic potential is equal to 0 while at pH > 5.2 it has negative values.

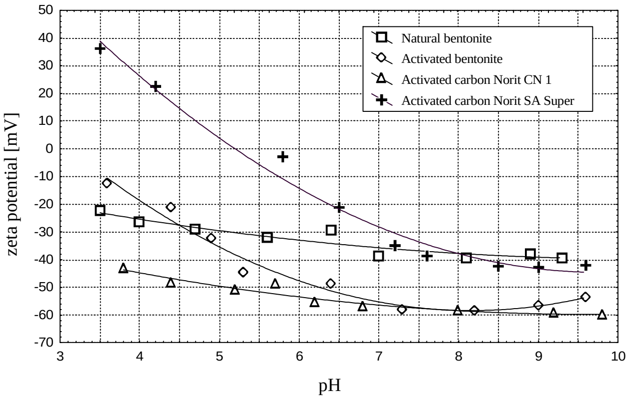

Fig. 2. Influence of pH solution on electrokinetic potential of researched adsorbents
Rys. 2. Wpływ pH roztworu na potencjał elektrokinetyczny badanych adsorbentów

The investigation showed that fulvic acids particles with a diameter of about 403 nm, have a potential ζ= –41.56 mV, at pH=7.55. Humic acids particles with a diameter of about 419 nm have a potential ζ= -39.46 mV, at pH=10. The electrokinetic potential of silica with a diameter of about 409 nm has –31.52 mV, at pH= 6.64. Measurements were taken with samples with a concentration of 0.01 mg/mL and at a temperature of 25°C.

3.3. Humic substances adsorption in the absence of silica

The results of adsorption kinetics of humic substances by chosen adsorbents is presented in Figure 3. The solution of HS with concentration 40 mg/L was prepared on the basis of tap water and adjusted to pH 7.5 by using NaOH. From the shape of the curve it may be concluded that humic substances adsorption by all four examined adsorbents is a long lasting process. The first quick phase is followed by a second phase lasting for many days.

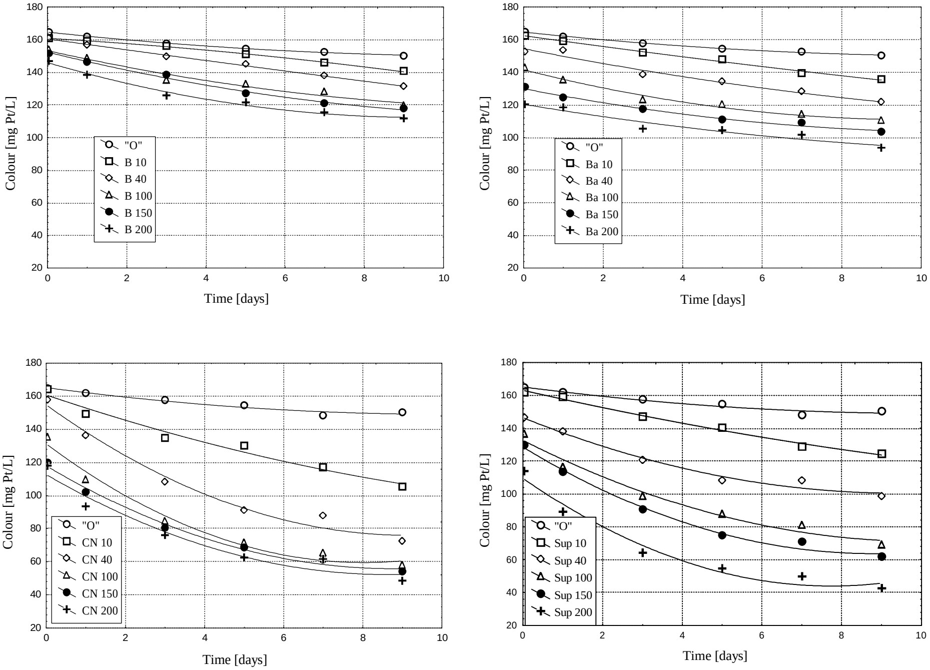

Fig. 3. Kinetics of humic acids adsorption with concentration 40 mg/L dissolved in tap water at pH 7.5 on selected sorbents added to the solution HA in the amount 10, 40, 100, 150 and 200 mg/L. „O” – test without sorbent, B – natural bentonite, Ba – activated bentonite, CN – hydrophilic activated carbon Norit CN 1, Sup – hydrophobic activated carbon Norit SA Super

Rys. 3. Kinetyka adsorpcji kwasów humusowych o stężeniu 40 mg/L rozpuszczonych w wodzie wodociągowej o pH 7,5 na wybranych sorbentach dodawanych do roztworu KH w ilości 10, 40, 100, 150 i 200 mg/L. „O” – próba bez sorbentu, B – bentonit naturalny, Ba – bentonit uaktywniony, CN – węgiel aktywny hydrofilowy Norit CN 1, Sup – węgiel aktywny hydrofobowy Norit SA Super

The results after five days of observation of the adsorption process are presented in Figure 4 and Table 4 as Freundlich isotherms in logarithmic form:

$$\log y = \log k + 1/n \log C$$

where:

$y=x/m$ – the humic substances adsorption ability of the adsorbent is expressed in colour units mg Pt/g,

C - equilibrium concentration of humic substances expressed in colour units mg Pt/L,

k – equilibrium constant characterising sorption capacity.

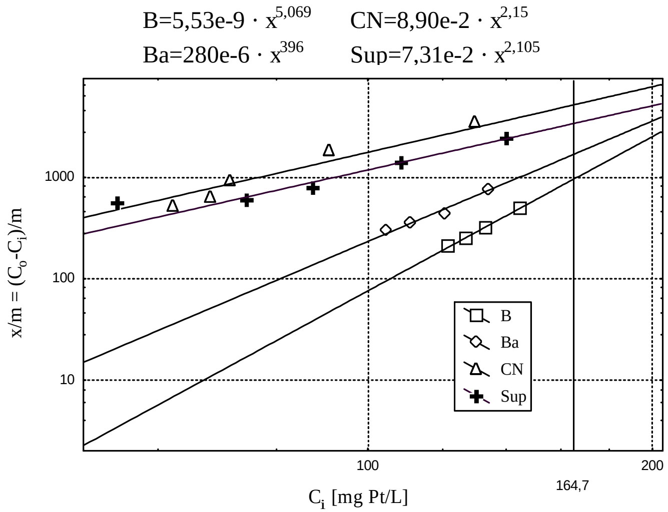

Fig. 4. Determination of sorption capacity and constants of Freundlich adsorption isotherm equation in the process of humic acids adsorption with concentration 40 mg/L dissolved in tap water at pH 7.5 on the following sorbents: B – natural bentonite, Ba – activated bentonite, CN – hydrophilic activated bentonite Norit CN 1, Sup – hydrophobic activated carbon Norit SA Super. Initial concentration of HA C_o=164.7 mg Pt/L, adsorption time – 5 days.

Rys. 4. Wyznaczanie pojemności sorpcyjnej i stałych adsorpcji równania izotermy Freundlicha w procesie adsorpcji kwasów humusowych o stężeniu 40 mg/L rozpuszczonych w wodzie wodociągowej o pH 7,5 na sorbentach: B – bentonit naturalny, Ba – bentonit uaktywniony, CN – węgiel aktywny hydrofilowy Norit CN 1, Sup – węgiel aktywny hydrofobowy Norit SA Super. Stężenie początkowe kwasów humusowych C_o=164,7 mg Pt/L, czas adsorpcji – 5 dób

Table 3. Determination of sorption capacity and constants of Freundlich adsorption isotherm equation in the process of humic acids adsorption with concentration 40 mg/L dissolved in tap water at pH 7.5 on the following sorbents: B – natural bentonite, Ba – activated bentonite, CN – hydrophilic activated bentonite Norit CN 1, Sup – hydrophopbic activated carbon Norit SA Super. Initial concentration of HA C_o=164.7 mg Pt/L, adsorption time – 5 days

Tabela 3. Wyznaczanie pojemności sorpcyjnej i stałych adsorpcji równania izotermy Freundlicha w procesie adsorpcji kwasów humusowych o stężeniu 40 mg/L rozpuszczonych w wodzie wodociągowej o pH 7,5 na sorbentach: B – bentonit naturalny, Ba – bentonit uaktywniony, CN – węgiel aktywny hydrofilowy Norit CN 1, Sup – węgiel aktywny hydrofobowy Norit SA Super. Początkowe stężenie kwasów humusowych C_0 = 164,7 mg Pt/L, czas adsorpcji – 5 dób

Adsorbent	Constants of adsorption		Adsorbed adsorbate with equilibrium concentration C_o on adsorbent mass unit	Theoretical volume of adsorbed adsorbate with equilibrium concentration C_o on adsorbent mass unit [3]
	k	1/n	$(x/m)_{Co}$ [mg Pt/g]	V_{Co} [L/g]
B	5.53 E-9	5.069	950.8	5.77
Ba	2.80 E-6	3.960	1680.6	10.20
CN	8.90 E-2	2.150	5191.4	31.52
Sup	7.31 E-2	2.105	3399.9	20.64

On the basis of the values of constants k and l/n which are found from the isotherms we can make the following affinity series of adsorbents to humic substances:

- according to adsorption intensity (*1/n*):

B > BA > CN > SUP

- according to sorption capacity (*k*):

CN > Sup > Ba > B

- according to theoretical unit capacity of adsorbed adsorbate (V_{Co}) [3]:

CN > Sup > Ba > B

On the basis of the given affinity series it may be concluded that hydrophilic carbon Norit CN 1 and the least natural bentonite have the greatest affinity to humic substances.

3.4. Humic substances adsorption in the presence of silica

The influence of silica with a concentration of 10 mg/L on the adsorption of humic substances was then tested. The adsorption isotherms obtained from this and the research results are presented in Figure 5.

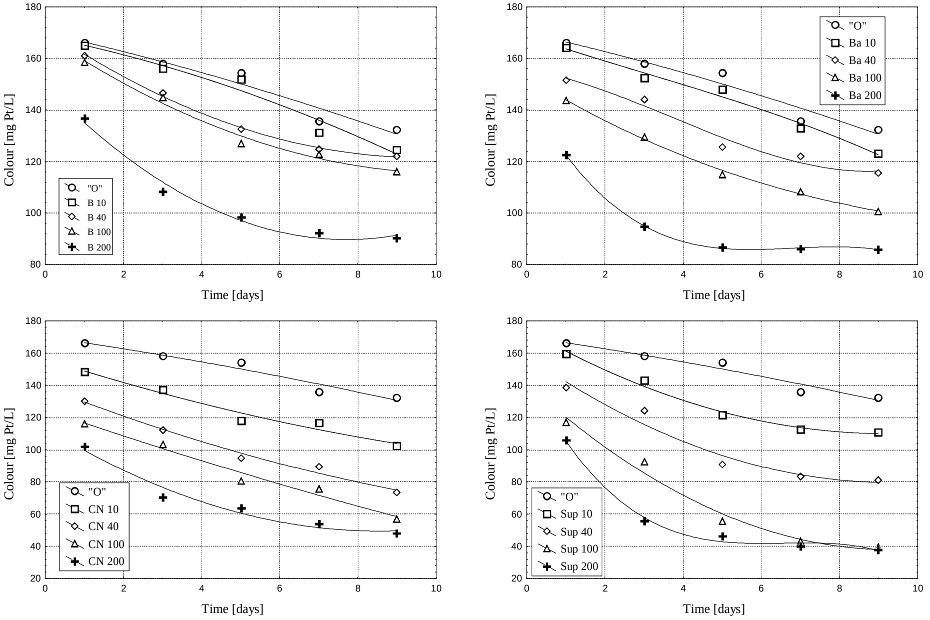

Fig. 5. Kinetic of humic acids adsorption with concentration 40 mg/L solved in tap water with addition of silica (10 mg/L) and pH 7.5 on selected sorbents added to the solution of HA in the amount of 10, 40, 100 and 200 mg/L. „O" – sample without sorbent, B – natural bentonite, Ba – activated bentonite, CN –hydrophilic activated carbon Norit CN 1, Sup – hydrophobic activated carbon Norit SA Super

Rys. 5. Kinetyka adsorpcji kwasów humusowych o stężeniu 40 mg/L rozpuszczonych w wodzie wodociągowej z dodatkiem krzemionki (10 mg/L) i pH 7,5 na wybranych sorbentach dodawanych do roztworu KH w ilości 10, 40, 100 i 200 mg/L. „O" – próba bez sorbentu, B – bentonit naturalny, Ba – bentonit uaktywniony, CN – węgiel aktywny hydrofilowy Norit CN 1, Sup – węgiel aktywny hydrofobowy Norit SA Super

Comparing the colour sample with silica to the colour sample without silica we see that there is a difference between the colour of both samples which increases even after the 7th day and on the 7th day the difference is nearly 20 mg Pt/L. It may be assumed that silica reacting with humic substances gives mineral-organic complexes which when precipitating out of the solution, decrease its colour.

Freundlich isotherms drawn from the results obtained after 5 days of adsorption, and the determined values of constants k and 1/n are presented in Figure 6. The theoretical volume of the adsorbed adsorbate with an equilibrium concentration C_o per the unit of adsorbent mass (V_{co}) is shown in Table 4 along with values of constants k and 1/n.

$B=2{,}05e\text{-}4 \cdot x^{3{,}078}$ $\quad$ $CN=3{,}00e\text{-}3 \cdot x^{2{,}91}$

$Ba=3{,}47e\text{-}4 \cdot x^{3{,}06}$ $\quad$ $Sup=4{,}70e\text{-}1 \cdot x^{1{,}884}$

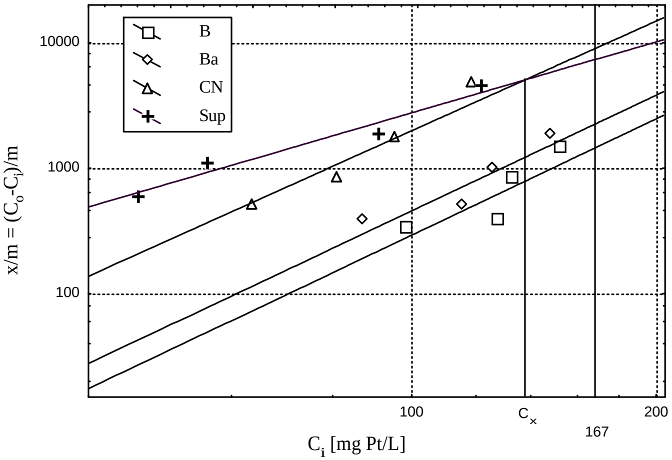

Fig. 6. Fixing of sorption capacity and constants of Freundlich adsorption isotherm equation for humic acids with concentration 40 mg/L dissolved in tap water at pH 7.5 on the following sorbents: B – natural bentonite, Ba – activated bentonite, CN – hydrophilic activated bentonite Norit CN 1, Sup - hydrophobic activated carbon Norit SA Super. Initial concentration of HA C_o=167 mg Pt/L, adsorption time 5 days.

Rys. 6. Wyznaczanie pojemności sorpcyjnej i stałych adsorpcji równania izotermy Freundlicha dla kwasów humusowych o stężeniu 40 mg/L rozpuszczonych w wodzie wodociągowej o pH 7,5 z krzemionką w ilości 10 mg/L na sorbentach: B – bentonit naturalny, Ba – bentonit uaktywniony, CN – węgiel aktywny hydrofilowy Norit CN 1, Sup - węgiel aktywny hydrofobowy Norit SA Super. Stężenie początkowe kwasów humusowych C_0 = 167 mg Pt/L, czas adsorpcji 5 dób

Table 4. Determination of sorption capacity and constants of Freundlich adsorption isotherm equation for humic acids with concentration 40 mg/L dissolved in tap water at pH 7.5 with addition of silica in the amount of 10 mg/L on the following sorbents: B – natural bentonite, Ba – activated bentonite, CN – hydrophilic activated bentonite Norit CN 1, Sup - hydrophobic activated carbon Norit SA Super. Initial concentration of HA C_0 = 167 mg Pt/L, adsorption time 5 days.

Tabela 4. Wyznaczanie pojemności sorpcyjnej i stałych adsorpcji równania izotermy Freundlicha dla kwasów humusowych o stężeniu 40 mg/L rozpuszczonych w wodzie wodociągowej o pH 7,5 z dodatkiem krzemionki w ilości 10 mg/L - na wybranych sorbentach: B – bentonit naturalny, Ba – bentonit uaktywniony, CN – węgiel aktywny hydrofilowy Norit CN 1, Sup - węgiel aktywny hydrofobowy Norit SA Super. Stężenie początkowe kwasów humusowych C_0 = 167 mg Pt/L, czas adsorpcji 5 dób

Adsorbent	Constants of adsorption		Adsorbed adsorbate with equilibrium concentration C_o on one unit of adsorbent mass	Theoretical volume of adsorbed adsorbate with equilibrium concentration C_o on one adsorbent mass
	k	1/n	$(x/m)_{Co}$ [mg Pt/g]	V_{Co} [L/g]
B	2.00 E-4	3.078	1417.6	8.49
Ba	3.47 E-4	3.060	2192.8	13.13
CN	0.003	2.910	8815.1	52.78
Sup	0.470	1.884	7239.3	43.35

The results obtained from this investigation show that silica truly influences the adsorption process. In the presence of silica the affinity series are as follows:

- according to adsorption intensity:

$$B \cong Ba > CN > Sup$$

- according to sorption capacity:

$$\text{for } C_x < 138 \Rightarrow Sup > CN > Ba > B$$
$$\text{for } C_x > 138 \Rightarrow CN > Sup > Ba > B$$

- according to theoretical unit capacity of adsorbed adsorbate (V_{co}):

$$CN > Sup > Ba > B$$

The largest adsorption intensity shows hydrophilic activated carbon and the sorption capacity of hydrophobic activated carbon Norit SA Super. In the presence of silica, after exceeding equilibrium concentration of humic substances $C_x \approx 138$ mg Pt l^{-1} expressed in colour units affinity change occurs and according to sorption capacity the sequence is as follows:

$$CN > Sup > Ba > B\underline{x},$$

Therefore, it complies with the series for V_{Co}. Thus, it may be concluded that silica which has a negative surface charge, decreases the sorption capacity for adsorbing dissolved substances of hydrophilic activated carbon, which also has a negative charged surface. After exceeding equilibrium concentration $C_x \approx 138$ mg Pt/L the reaction of silica decreases and the carbon affinity towards humic substances increases. So, the deciding factor is the humic substances concentration.

Comparing adsorption constants and the theoretical capacities of the adsorbed adsorbate with the equilibrium concentration C_o in the presence of and absence of silica it is possible to say that silica increases the adsorption capacity of the configuration and the theoretical capacity of the adsorbed adsorbate.

The percentage colour decrease, due to the significant influence of silica on the adsorption process of humic substances, was calculated after ten days of adsorption. These results are presented in Figure 7. The dependencies obtained confirm the positive role of silica in the process of humic substances removal from water.

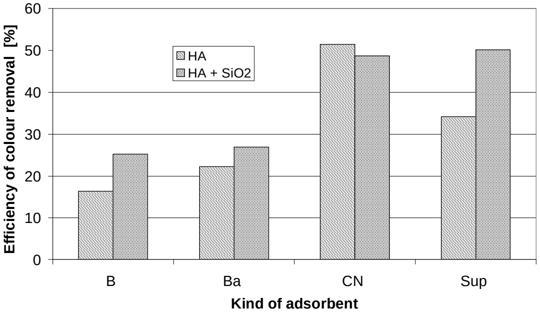

Fig. 7. Influence of silica on adsorption of humic acids with concentration 40 mg/L dissolved in tap water at pH 7.5 – adsorption time 7 days, concentration of adsorbent 40 mg/L

Rys. 7. Wpływ krzemionki na adsorpcję kwasów humusowych o stężeniu 40 mg/L rozpuszczonych w wodzie wodociągowej o pH 7,5 – czas adsorpcji 7 dób, stężenie adsorbentu 40 mg/L

A very important factor in the adsorption process is the pH of the solution. The investigation was carried out at pH 7.5. Considering the humic substances structure, one may expect in an acid environment relationships other than those which occur at pH 7.5. That is why two series of tests were carried out for HS solutions at pH 5.5 both with and without silica (see Figure 8).

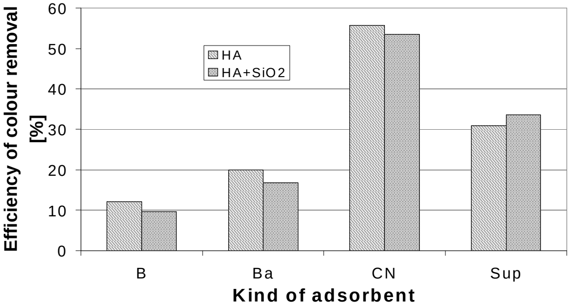

Fig. 8. Influence of silica on adsorption of humic acids with concentration 40 mg/L dissolved in tap water at pH 5.5. Adsorption time 6 days, adsorbent concentration 40 mg/L

Rys. 8. Wpływ krzemionki na adsorpcję kwasów humusowych o stężeniu 40 mg/L rozpuszczonych w wodzie wodociągowej o pH 5,5. Czas adsorpcji 6 dób, stężenie adsorbentu 40 mg/L

The results of the analysis show, that at pH 5.5 silica has a negative influence on the process of humic substances removal from water. Such a phenomenon may be explained in the following way: at low pH values silica occurs as polyacids which have a smaller surface charge. At the same time an increase of the concentration of protons decreases the negative surface charge of the particles. The decrease in the reaction increases the amount of humic substances removed and the amount of colour removed at the same time. For example in the presence of activated carbon Norit CN 1 without silica at pH 7.5 and HS concentration 40 mg l^{-1} the efficiency of colour removal amounted to 46.7%, and at pH 5.5 it is equal to 55.7%. This results from the fact that in an acid environment, humic substances form bigger and less soluble particles, which are then precipitated from the solution or adsorbed on the adsorbent surface. Besides, humic substances show less colour in an acid medium. Attention should also be given to the fact that, the adsorption process took place in a tap water environment, which contains different cations making humic substances adsorption easier on adsorbents particles and silica. In order to confirm this, an investigation of humic substances adsorption was done in an environment containing a minimal amount of cations i.e. in a solution prepared from distilled water at pH 5.5.

The results show the great stability of humic substances dissolved in distilled water. Within a week, the solution did not essentially change its colour. At the same time it was shown that humic substances dissolved in distilled water are hardly adsorbed on the tested adsorbents, excluding hydrophobic activated carbon Norit SA Super. This arises from the chemical structure of humic substances, which create alkyl-aromatic chains. In an acid medium carboxyl groups are still hardly dissociated and amino groups are electropositive. In such a combination, especially, there is the possible reaction between the hydrophobic aromatic rings of the humic substances and the hydrophobic activated carbon and also between the electropositive ionised amino groups and the negatively charged surface of the adsorbent aiding substance. However, at the same time the negative surface charge is compensated by protons whose concentration is increased together with a pH decrease. That is why as a result of humic substances adsorption on activated carbon Norit SA Super, 45% of the acids were removed and the other adsorbents removed a maximum of 10% of the acids (see Figure 9). On the account of the different pH of the water samples after adsorbent had been added (we know that water colour depends on pH), the colour of the sample was calculated into a hypothetical colour of acids solution at pH 5.5, using the given dependency colour = f(pH).

Comparing the results obtained, of adsorption with the electrokinetic potential of adsorbents (see Figure 10), it should be noted, that there are dependencies between the adsorption process and the value of electrokinetic potential of the adsorbent particles [3]. The greater the negative value of the electrokinetic potential of the adsorbent particles the more humic substances are adsorbed by them. However, it is interesting that the electrokinetic potential of adsorbent particles is negative. So, the electrostatic repulsion of negative carboxyl ions should take place. However, the results obtained during the investigation show that the adsorption of humic substances on an electronegative adsorbent surface takes place. The observed dependence may arise as a result of two reasons: which have already been mentioned by the authors [9]. Firstly, humic substances have positive functional groups (amino groups), which occur in an acid environment in ionized form. Secondly, tap water includes cations which willingly adsorb on the adsorbent-adsorbate border changing the electronegative character of the adsorbent surface or the adsorbat into electropositive. Such a surface easily adsorbs anions. The electrokinetic potential of the adsorbent particles at pH 5.5 is presented in Figure 10.

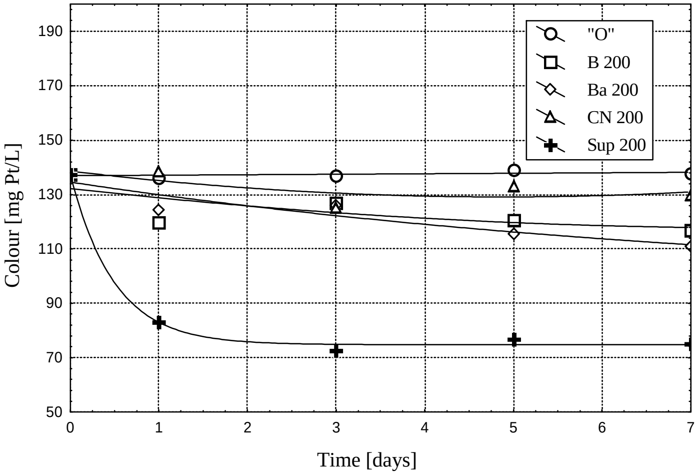

Fig. 9. Kinetics of humic acids adsorption with concentration 40 mg/L dissolved in distilled water at pH 5.5. Dosed adsorbents in the amount of 200 mg/L: B – natural bentonite, Ba – activated bentonite, CN – hydrophilic activated carbon Norit CN 1, Sup - hydrophobic activated carbon Norit SA Super, „O" – test without sorbent

Rys. 9. Kinetyka adsorpcji kwasów humusowych o stężeniu 40 mg/L rozpuszczonych w wodzie destylowanej o pH 5,5. Adsorbenty dozowane w ilości 200 mg/L: B – bentonit naturalny, Ba – bentonit uaktywniony, CN – węgiel aktywny hydrofilowy Norit CN 1, Sup - węgiel aktywny hydrofobowy Norit SA Super, „O" – próba bez sorbentu

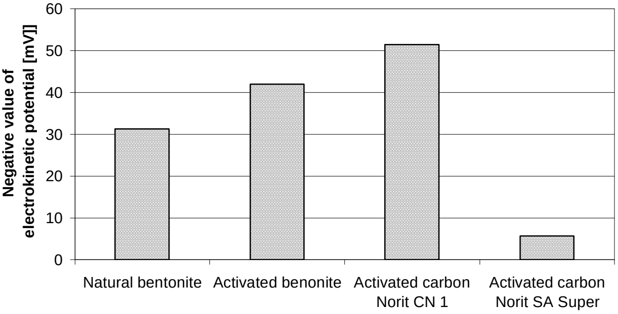

Fig. 10. Electrokinetic potential of researched adsorbents in distilled water with pH 5.5

Rys. 10. Potencjał elektrokinetyczny badanych adsorbentów w wodzie destylowanej o pH 5,5

In investigating the three adsorbents: natural bentonite, activated bentonite and hydrophilic carbon Norit CN 1, proportional dependence was obtained between the value of the electrokinetic potential and the amount of adsorbed humic substances. But in the case of hydrophobic carbon intermolecular forces (van der Waals forces) play the main role in the adsorption and this confirms the physical dependencies presented in an article [3], in which the author describes double electric layer.

4. The hypothetical model of humic substances adsorption on adsorbents

Humic substances (HS) adsorption on sorbent particles may take place in an acid environment as a result of the exchange of ligand between the proton group OH_2^+ coming from sorbent (*S*) and the carboxyl group of humic substances which may be written in a schematic way:

$$S\text{-OH} + \text{H}^+ = S\text{-OH}_2^+$$
$$S\text{-OH}_2^+ + \text{HS-COO}^- = S\text{-OH}_2^{+-}\text{OOC-HS}$$
$$S\text{-OH}_2^{+-}\text{OOC-HS} = S\text{-OOC-HS} + \text{H}_2\text{O}$$

When both the humic substances and the sorbent have a negative charge, binding may take place as a result of bridging by multivalent cations, e.g. Ca^{2+} and Mg^{2+} or Al^{3+}:

$$S\text{-OH} + \text{H}_2\text{O} = S\text{-O}^- + \text{H}_3\text{O}^+$$
$$S\text{-O}^- + \text{Ca}^{2+} + \text{HS-COO}^- = S\text{-O-Ca-OOC-HS}$$
$$S\text{-O}^- + \text{Mg}^{2+} + \text{HS-COO}^- = S\text{-O-Mg-OOC-HS}$$

An important factor in the process of humic substances adsorption on hydrophobic activated carbon Norit SA Super (Sup) is the pH of the water used. Depending on the value of the pH the value of the electrokinetic potential of the carbon changes which in an acid reaction show positive values and at pH ≈ 5.2 changes into a negative. Simplifying its behaviour in water at different pH:

$$\text{Sup-OH} + \text{H}^+ = \text{Sup-OH}_2^+ \qquad \text{acid reaction}$$
$$\text{Sup-OH} + \text{H}_2\text{O} = \text{Sup-OH} + \text{H}_2\text{O} \qquad \text{neutral reaction}$$
$$\text{Sup-OH} + \text{OH}^- = \text{Sup-O}^- + \text{H}_2\text{O} \qquad \text{alkaline reaction.}$$

The above equations explain the observed higher adsorption of humic substances in an acid media when the activated carbon has a positive surface charge and electrostatic reactions with negative humic substances are possible.

5. Conclusions

1. The electrokinetic potential of hydrophobic activated carbon Norit CN 1 has negative or positive values depending on the pH of the solution.
2. The electrokinetic potential of fulvic and humic acids and activated silica is negative.
3. Humic acids adsorption takes place as a result of the electrostatic attraction of functional groups or intermolecular interaction forces between hydrophobic functional groups (aliphatic chains and aromatic rings) and adsorbent – depending on the character of the adsorbent surface and its electrokinetic potential. In the case of the adsorbate and the adsorbent surfaces having the same charge, adsorption takes place by bridging with multivalent cations.
4. Silica influences the adsorption capacity of all the compounds participating in the adsorption.
5. Humic acids adsorption on adsorbents depends on the affinity series (according to sorption ability): CN>Sup>Ba>B, which changes in the presence of silica, with a humic substances concentration < 138 mg Pt/L: Sup>CN>Ba>B.
6. The phenomena occurring on the phase boundary during the process of coagulation and the adsorption of humic substances in the presence and absence of adsorbents can be described with chemical and physicochemical reaction equations.

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Znaczenie potencjału elektrokinetycznego w procesie adsorpcji substancji humusowych

Streszczenie

W pracy przebadano proces adsorpcji substancji humusowych na wybranych sorbentach-obciążnikach stosowanych w procesie koagulacji wód powierzchniowych. Określono szereg powinowactwa danych adsorbentów do substancji humusowych. W oparciu o pomiary potencjału elektrokinetycznego cząstek adsorbentu–obciążnika przedstawiono hipotetyczny proces adsorpcji substancji humusowych na powierzchni ciała stałego.

Zgodnie z tym modelem adsorpcja substancji humusowych zachodzi w wyniku przyciągania elektrostatycznego grup funkcyjnych lub oddziaływania sił międzycząsteczkowych między hydrofobowymi fragmentami (alifatycznymi łańcuchami i aromatycznymi pierścieniami) i adsorbentem – w zależności od charakteru powierzchni adsorbentu i jego potencjału elektrokinetycznego. W przypadku, gdy powierzchnie adsorbatu i adsorbentu mają ładunki jednoimienne adsorpcja zachodzi poprzez mostkowanie wielowartościowymi kationami.

Inne wnioski, które można wyciągnąć na podstawie uzyskanych wyników badań, są następujące:

- potencjał elektrokinetyczny hydrofobowego węgla aktywnego Norit CN 1 posiada wartości dodatnie lub ujemne w zależności od pH roztworu,
- potencjał elektrokinetyczny kwasów fulwowych i huminowych oraz krzemionki jest ujemny,
- krzemionka posiada wpływ na pojemność sorpcyjną wszystkich związków biorących udział w procesie adsorpcji,
- adsorpcja kwasów huminowych na adsorbentach zależy od szeregu powinowactwa (na podstawie zdolności sorpcyjnej): CN>Sup>Ba>B, który zmienia się w obecności krzemionki, przy stężeniu substancji humusowych < 138 mg Pt/L na: Sup>CN>Ba>B,
- zjawiska zachodzące na granicy faz w czasie procesu koagulacji i adsorpcji substancji humusowych w obecności i braku adsorbentów można opisać równaniami rekcji chemicznych i fizykochemicznych.