

SUPERABSORBENTS AS EFFECTIVE MATERIALS FOR ADSORPTION OF METAL COMPLEXES WITH BIODEGRADABLE COMPLEXING AGENT

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Abstract

Superabsorbents can be applied in modern agriculture as materials for preparation of mineral fertilizers of controlled activity. TerraHydrogel[®]Aqua (THA) was used as a sorbent for Cu(II), Zn(II), Mn(II) and Fe(III) ions removal from aqueous solutions in the presence of sodium salt of N-(1,2-dicarboxyethylene)-D,L-aspartic acid (IDS) under static conditions.

Kinetic and adsorption parameters of the removal process at different doses of THA, changing pH, initial concentration of metal complexes with IDS as well as phase contact time were investigated by static method.

The results showed that the increase in the THA dose from 10 to 50 g/dm³ significantly increased the anionic complexes of the [M(II)ids]²⁻ adsorption rates from 46 to 78%. The increase in the pH range 4-10 resulted in decrease in the Cu(II), Zn(II) and Mn(II) complexes adsorption capacity. The adsorption process was fast and it reached equilibrium after 60 min. of the phase contact time. The equilibrium process was well described by the Langmuir isotherm model with the maximum adsorption capacity from 47.17 to 53.76 mg/g for Cu(II) complexes at 293-333 K. THA has proven to be a promising material for the removal of metal complexes with biodegradable IDS from wastewaters.

Not only THA is a cheap adsorbent but it is also highly efficient when metals are sorbed in the form of anionic complexes with the biodegradable agent IDS. It can be applied in modern agriculture as a base for slow-release fertilizers. Additionally, the proposed complexing agent is characterized by the high rate of biodegradability and promising properties.

Keywords: superabsorbents, new complexing agents, IDS, adsorption

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1. Introduction

Polymer superabsorbents (PSA) commonly known as hydrogels are cross-linked highly molecular compounds able to absorb water from physicochemical fluids in the amounts from tenfold to one hundredfold larger than their dry mass. The phenomenon of water absorption is a result of separation of polymer chain network which is manifested by swelling of polymer material assuming the gel form [1, 2].

The most desirable features of hydrogels as regards their application are first of all large adsorption capacity, high rate of reversible fluid absorbing power, mechanical strength, non-toxicity, chemical resistance as well as mechanical resistance (particularly essential in special application of hydrogels) and water absorbing ability in the saline solution. The above mentioned materials are widely applied in many fields of industry. They are used, among others, in medicine, agriculture, pharmacy, cosmetics, electronics, gardening, forestry, architecture as well as in many branches of chemical industry [3-5].

Recently, the preparation of polymer/clay superabsorbent composites has attracted a great attention because of their relative low production cost and high water absorbency [6].

Fertilizers and water are important factors that limit the production of agriculture, so it is very important to improve the utilization of water resources and fertilizer nutrients. On the other hand application of fertilizer is essential to produce food of adequate quality and in sufficient quantity. However, on the other hand, an increasing attention was being directed to reducing the amount of fertilizers and other biologically active agents used in modern agricultural crop management.

The most widely used and commonly considered macro nutrients limiting plant yield are nitrogen (N), phosphorous (P) and potassium (K) or NPK fertilizers. Nitrogen, the most widely applied plant nutrient, has commonly been considered to be the yield limiting one. In most cases urea is a source of nitrogen. However, urea cannot be absorbed easily by the charged soil particles before hydrolyzing, resulting in a great quantity of urea running off and serious environmental hazards as only a fraction is really absorbed by plants. One possible way to improve nutrients efficiency and reducing the environmental hazards is application of slow-release fertilizers.

Compared to the conventional type, slow-release fertilizers have many advantages, such as decreasing fertilizer loss rate, supplying nutrients sustainably. Slow-release fertilizers can be generally classified into 4 types: (i) inorganic materials of low solubility, such as metal ammonium phosphates; (ii) chemically or biologically degradable low solubility materials, such as urea-formaldehyde; (iii) relatively

soluble materials that gradually decompose in soil; and (iv) water soluble fertilizers controlled by physical barrier, such as coated fertilizers. Coated fertilizers, physically prepared by coating fertilizer granules with various materials, are the major categories of slow-release fertilizers. Many materials such as polysulfone, polyvinyl chloride, polystyrene have been reported to be used as coatings. However, after the release of fertilizers, remaining coating materials in the soil are very difficult to degrade and can accumulate over time to become a new type of pollution. Therefore the environmentally safe and biodegradable coating materials are expected to be used [7-11].

Superabsorbents are the three-dimensionally crosslinked hydrophilic polymers that can absorb and retain large volumes of water up to thousands of times their own weight, and the absorbed water is hardly removable even under pressure. Because of their excellent characteristics, superabsorbent polymers have been used extensively in agriculture and horticulture [12]. Many investigations have shown that they can help reduce irrigation water consumption, lower the death rate of plants, improve fertilizer retention in soil, and increase plant growth rate [13]. Besides water absorbing and retention, the superabsorbent polymers have many advantages over conventional ones, such as a sustained supply of nutrition to plants for a longer time, thus increasing the phosphate fertilizer use efficiency and decreasing application frequency. Furthermore, they can be used as soil moisture preservation material [14-16].

The intensive studies on slow-release fertilizers combined with superabsorbents to obtain both slow-release and water-retention properties are well described in the literature. Three classes of superabsorbent polymer are commonly used and are classified as natural, semi-synthetic and synthetic polymers [17, 18]. In general, combining fertilizers with superabsorbents is done by two methods. In the first method, fertilizers are blended with superabsorbents. In the second approach, the fertilizers are added to the reaction mixture and polymerized *in situ* whereby the fertilizers are entrapped in the superabsorbents. These two methods always lead to a "burst effect" and higher release rate [19, 20].

In the presented paper the commercial hydrogel TerraHydrogel®Aqua was used for the adsorption of Cu(II), Zn(II), Mn(II) and Fe(III) complexes with the IDS. It is also available as Baypure CX 100 (Iaxness, Germany). (N-1,2-dicarboxyethyl)-D,L-aspartate acid also known as iminodisuccinic acid belonging to the group of the biodegradable complexing agents of a new generation. It is an environmentally friendly and non-toxic. It is prepared by thermal polymerization of aspartic acid and characterized by extremely rapid biodegradation, which equals approx. 80% after just 7 days [21, 22]. It can solubilize in water in any ratio. Its ability to form soluble complexes with metals ions dissolved in water is in the range from 4 to 10. Formation of IDS complexes with ions of metals can be described as follows:



where: *ids* is the ligand iminodisuccinic, *M* is the metal ion, *n*=0-3.

IDS is a pentadentate complexing agent. It forms chelates of octahedral structure with many metals ions. For example, for Cu(II) ion there are known the following complexes: [Cu(Hids)], [Cu(ids)²⁻], [Cu(OH)(ids)]³⁻. The stability constants of metal complexes with IDS were presented in [23, 24].

The aim of this study is to investigate the influence of chemical conditions on hydrogel, kinetic and adsorption behaviour of TerraHydrogel®Aqua (THA) towards Cu(II), Zn(II), Mn(II) and Fe(III) ions in the presence of the chelating agent of a new generation i.e. IDS. The studies were carried out to investigate the effect of the sorbent dose, pH of the solution, initial concentration as well as phase contact time and temperature on the adsorption efficiency. The kinetic parameters based on the kinetic models i.e. the pseudo first order (PFO), the pseudo second order (PSO) and the intraparticle diffusion (IPD) equations were also determined. From the linear dependence of the Langmuir and Freundlich isotherms the maximal adsorption capacities and the constants of the studied hydrogel in relation to the complexes of Cu(II), Zn(II), Mn(II) and Fe(III) with IDS were determined. After the effective adsorption of metal complexes with a biodegradable complexing agent preparation of slow-release fertilizers of controlled activity of a new generation is possible. It should be mentioned that only a few fertilizer producers offer this type of commercial ones.

2. Materials and Methods

2.1. Materials

The commercial TerraHydrogel®Aqua (THA) (Terra, Poland) was used in the investigations. The physical and chemical properties of the used superabsorbent are listed in Table 1. The characteristic parameters for hydrogels were also determined, among others gel content (*G*%) and moisture retention (*M*%). Moreover, water absorbency was determined in water and NaCl solutions (*Q*_{H₂O}%, *Q*_{NaCl}%) [25]. To acquire a better understanding of mechanism of adsorption of metal complexes with IDS the Fourier transform infrared spectra using the attenuated total reflectance technique (FTIR-ATR) of THA in the dried and wet forms were measured and presented in Fig.1. It shows the characteristic stretching vibrations at 1453 cm⁻¹ connected with the presence of -CH₂ group as well as the symmetric and asymmetric stretching vibrations of the carboxylate ion (COO⁻) at 1399 and 1553 cm⁻¹ [26]. Moreover, it was found that at pH 2, the carboxylate functional groups of the polymer are completely protonated, whereas at pH 11 the groups are fully ionized.

In the investigations there were selected the following metal ions: Cu(II), Zn(II), Mn(II) and Fe(III). The initial concentration of metal ions was 1×10⁻³ M. Aqueous solutions of each metal ion in the presence of IDS

were prepared by dissolving equimolar amounts of metal chlorides in the IDS solution and were left for about 24 h to make sure that appropriate metal complexes were quantitatively formed. The other chemicals e.g. NaOH and HCl were of analytical reagent grade purchased from POCH S.A.(Poland).

2.2. Analytical methods

At the first stage the dried THA was being extracted in distilled water for 24 h at 293 K. The insoluble part corresponding to the gelled one was dried and weighed. The gel content was determined using the equation (2):

$$G\% = (m_d - m_s) \times 100\% \quad (2)$$

where: m_d is the weight of dried THA before extraction and m_s is the swollen weight of the samples, after the extraction of the ungelled parts.

THA particles of 2 mm thickness were allowed to swell in water over night. Then they were placed in a petri dish, at room temperature. The samples were weighed at initial (m_o) and different time intervals (m_t). Moisture retention capability ($M\%$) was measured using the equation (3):

$$M\% = \frac{m_t}{m_o} \times 100\% \quad (3)$$

THA was immersed in distilled water or NaCl solution at room temperature to reach the swelling equilibrium. After appropriate time the samples were separated from the solution by filtration. The water ($Q_{H_2O}\%$) and the NaCl solution ($Q_{NaCl}\%$) absorbency of THA was determined by weighing the swollen samples and the $Q\%$ of the samples was calculated using the following equation (4):

$$Q = \frac{m_s - m_d}{m_d} \times 100\% \quad (4)$$

where: m_d and m_s are the weights of the dry sample and the water-swollen sample, respectively. All the experiments were carried out three times to obtain the average values. Q_{H_2O} was calculated as grams of water per a gram of sample. It was found that $G\%$, $M\%$ as well as $Q_{H_2O}\%$ and $Q_{NaCl}\%$ values were equal to 98%, 89% (after 24 h) as well as 98.4% and 67%, respectively.

Static (batch) tests of adsorption of metal complexes with IDS were made by putting 0.1 g of THA and 50 cm³ of Cu(II), Zn(II), Mn(II) i Fe(III) complexes with IDS solution (in the system M(II)/(III):IDS=1:1) into 100 cm³ conical flask and shaking mechanically using the laboratory shaker for 1-120 min. The stirring speed was 180 rpm. pH values were measured using pH meter. The procedure was repeated three times.

The amount of Cu(II), Zn(II), Mn(III) and Fe(III) complexes with IDS adsorbed on THA was calculated from the difference between the initial concentration and the equilibrium one. The rate of complexes adsorption is expressed as percentage of the amount of metal ions adsorbed after a certain time related to that required for the state of equilibrium. It can be described as follows:

$$S\% = \frac{(c_o - c_e)}{c_o} \times 100\% \quad (5)$$

The adsorption capacity (q_t , mg/g) of THA was calculated from the following equation:

$$q_t = \frac{c_o - c_t}{m_d} \times V \quad (6)$$

where: c_o is the initial concentration of M(II/III) complexes with IDS solution (mg/dm³), c_t the concentration of M(II/III) complexes with IDS in the aqueous phase at time t (mg/dm³), V the volume of the solution (dm³) and m_d the mass of the dried THA (g).

The amounts of the metal complexes sorbed at the equilibrium were calculated analogously, using c_e instead of c_t .

Adsorption capacities were determined for the complexes of Cu(II), Zn(II), Mn(II) and Fe(III) with IDS and plotted vs. the phase contact time, initial concentration and pH.

Adsorption process parameters were determined on the basis of linear equations from the Langmuir and Freundlich adsorption isotherm (Eqs.7 and 8) [27, 28]:

$$\frac{1}{q_e} = \frac{1}{K_L q_o c_e} + \frac{1}{q_o} \quad (7)$$

$$\log q_e = \frac{1}{n} \log c_e + \log K_F \quad (8)$$

where: q_o is the Langmuir monolayer adsorption capacity (mg/g), K_L is the Langmuir constant related to the free energy of the adsorption (dm³/mg), q_e is the amount of M(II) or M(III) sorbed at equilibrium (mg/g), c_e is the equilibrium concentration (mg/dm³), K_F is the Freundlich adsorption capacity (mg/g) and $1/n$ is the Freundlich constant related to the surface heterogeneity.

The kinetic expressions used for the analysis of the obtained results are the pseudo first order (PFO) and the second order kinetic (PSO) models [29, 30], which were also used by Milosavljević et al. [31].

The pseudo first order kinetic equation is represented as (Eq.9):

$$\log(q_{e,t} - q_t) = \log q_{e,t} - \frac{k_1 t}{2.303} \quad (9)$$

where: $q_{e,1}$ and q_t denote the amount of adsorption at equilibrium and at time t (mg/g) respectively; k_1 is the rate constant of the pseudo first order adsorption (1/min). Based on the plot of $\log(q_{e,1}-q_t)$ vs. t the kinetic parameters were calculated.

The pseudo second order model is expressed as (Eq.10):

$$\frac{t}{q_t} = \frac{t}{q_{e,2}} + \frac{1}{k_2 q_{e,2}^2} \quad (10)$$

where: $q_{e,2}$ and q_t denote the amount of adsorption at equilibrium and at time t (mg/g) respectively; k_2 is the rate constant of the pseudo second-order adsorption (g/mg min). The kinetic parameters were calculated based on the plots of t/q_t vs. t .

Furthermore the experimental data were analyzed according to the Weber-Morris kinetic equation, i.e. the intraparticle diffusion model (IPD) given below [32]:

$$q_t = k_i t^{1/2} + C \quad (11)$$

where: k_i is the intraparticle diffusion rate constant (mg/g min^{0.5}), C is the intercept which reflects the boundary layer effect.

To study the effect of pH on adsorption the experiments were carried out at pH 2.0-11.0 at the contact time 120 min. and 293 K. The adsorption isotherms were investigated at various concentrations (from 2.5×10^{-4} mol/dm³ to 2.0×10^{-2} mol/dm³) in the M(II) or M(III):L=1:1 system. The mixtures was shaken at the contact time of 120 min and at temperature 293 K. The concentration of Cu(II), Zn(II), Mn(II) and Fe(III) complexes with IDS in the filtrate was determined using the inductively coupled plasma optical emission spectrometer.

The pH of the point of zero charge pH_{zpc} was measured using the pH drift method [33]. The pH of the sorbent in 0.01 M NaCl solution was adjusted between 2 and 12 by adding 0.1 M NaOH and 0.1 M HCl. 0.2 g of the THA was added to 50 cm³ of the solution and after 24 h the final pH was measured.

2.3. Apparatus

The studies were carried out by the static method. The samples were shaken using the laboratory shaker type 357 (Elpin Plus). The pH was measured using a pH meter CPI-505 (Elmetron, Poland).

The concentration of Cu(II), Zn(II), Mn(II) and Fe(III) complexes with IDS in the filtrate was determined using the inductively coupled plasma optical emission spectrometer ICP-OES of type 720 ES (Varian, Australia). The sample introduction system consisted of a OneNeb® nebulizer and cyclonic spray chamber. Operating parameters and selected analytical lines are listed in Table 2.

Scanning electron microscopy images were obtained Quanta 3D FEG microscope (FEI). Fourier transform infrared spectra of THA were obtained using the attenuated total reflectance technique (FTIR-ATR) and measured with a FTIR Carry 630 spectrometer (Agilent Technologies).

3. Results

3.1. Effect of the hydrogel dose

The effect of the adsorbent amount is an important variable in the adsorption process. However, for a given metal concentration, the lower concentration of adsorbent in solution, the higher is adsorbate-adsorbent ratio and the effectiveness of the adsorption. Different sorbent concentrations (19-50 g/dm³) were used, while volume, initial concentration of the Cu(II)-IDS complexes adsolution at the desired pH value were kept constant (data not presented). The results indicated the loss of sorbent effectiveness at its high concentrations. The removal of IDS complexes increases with sorbent dosage. This may be attributed to increased THA surface area and availability of more adsorption sites resulting from the increased dose of the THA.

3.2. Effect of initial pH

The most important parameter influencing the adsorption capacity is the pH of adsorption medium. The initial pH of an adsorption medium affects the adsorption mechanisms on the adsorbent surface and influences the nature of the physicochemical interactions of the species in solution as well as the adsorptive sites of the adsorbents. As follows from Fig.2 the pH_{zpc} determined for THA was equal to 6.9. At $pH > pH_{PZC}$ the surface charge will be negative while at $pH < pH_{PZC}$ positive.

The percentage removal of Cu(II), Zn(II), Mn(II) and Fe(III) complexes with IDS after 2 h equilibration at various pH values with the THA is plotted in Fig.3. It has been shown that during the adsorption process that pH of the system is altered. In the case of the adsorption of Cu(II) complexes with IDS the adsorption percentage (S%) slightly decreases at pH values from 2 to 11. This effect is evident especially for Fe(III) complexes which may suggest a different mechanism of adsorption or adsorption of complexes of various types, for example $[M(Ids)]^{2-}$ for Cu(II), Zn(II) and Mn(II) or $[M(Ids)]^+$ for Fe(III). It was also shown that the adsorption efficiency for Zn(II) complexes with IDS increased for pH values from 10 to 11.

In the whole pH range of 2-11 THA was the most efficient for the removal of Cu(II)-IDS complexes. Generally, the adsorption was more favourable at the pH values in the range 4-10 and dropped sharply at the pH values of 2 and 13, especially for Fe(III).

3.3. Effect of the phase contact time and kinetic studies

The comparison of the adsorption percentage (S%) of Cu(II), Zn(II), Mn(II) and Fe (III) complexes with IDS in the range of the phase contact time from 1 to 120 min. for THA are presented in Fig.4. It was proved that with the increasing phase contact time, the increase in the efficiency of the process is observed. Analogous results were obtained in the case of the comparison of the adsorption capacities (Fig.5). However, for the Fe(III) complexes with IDS the adsorption equilibrium was not obtained after 120 min. and remarkable changes should be observed for longer the phase contact time. In the initial stage of the adsorption process of Cu(II) and Zn(II) complexes with IDS there was a rapid increase in the adsorption capacity (q_t), which is associated with a large number of active sites available on the amount of sorbed complexes. Complexes undergo rapid adsorption on the surface of the adsorbent and only after saturation of all active sites of diffusion into the pores can be observed. As the reaction proceeds, these values gradually increase and reach almost constant value of q_t at approx. 60 min. In addition, the efficiency also increases with the increasing concentration of the starting solution of metal complexes.

In order to determine the mechanism of Cu(II), Zn(II), Mn(II) and Fe(III) ions adsorption in the presence of IDS based on the kinetic pseudo first order (PFO) and pseudo second order (PSO) models proposed by Lagergren and Ho kinetic parameters were determined [29, 30]. The obtained data are given in Table 3. Because of the linear relationship $t/q_t = f(t)$ and close to unity values of the coefficients of determination (R^2) as well as good agreement with the experimental data, it was proved that the kinetic pseudo second order model is fully suitable for description of the adsorption process. The maximum adsorption capacity with respect to the tested complexes in the case of THA were as follows: 12.39 mg/g for Cu(II), 14.42 mg/g for Zn(II), 12.55 mg/g for Mn(II) and 19.32 mg/g for Fe(III).

The mechanism of adsorption of a sorbate on a sorbent follows a series of steps. The slowest of these steps control the overall rate of the process. Generally, pore and intraparticle diffusion are often rate limiting in a batch system while, for a continuous flow system, the film diffusion is more likely the rate limiting step [34]. In the case of the IPD model, initial part is connected to faster mass transfer through the boundary layer and/or adsorption on the solid surface, followed by slow diffusion inside the particles. The obtained rate constants k_i are shown in Table 3. It was found that this model is not convenient for describing the adsorption process.

3.4. Adsorption isotherm studies

In the next step, based on the Langmuir and Freundlich adsorption models, the adsorption parameters were determined. The examples of adsorption isotherms for the complexes of Cu(II) with IDS are presented in Fig.6.

The Langmuir model is based on the assumption that the surface of the used sorbent is homogeneous, with a specific number of adsorption sites, so-called active centers. The energy states of each of the adsorbed molecules is not dependent on the presence of other atoms or molecules of the adsorbate. All active centers have the same affinity for the adsorbate. In addition, there is no possibility to create multilayer and the adsorption energy is constant. The surface is energetically homogeneous.

In contrast to the Langmuir model, the Freundlich model assumes heterogeneity of the surface of the used sorbent, reflecting the surface energy the heterogeneity.

The Langmuir constants and other parameters determined from the plot c_e/q_e vs. c_e are shown in Table 4. The applicability of the Langmuir isotherm (Eq.7) was examined based on the linear plot.

Adsorption experiments were conducted at three different temperatures (293, 313 and 333 K) in order to study the effect of temperature on the sorption capacity of the THA (Fig.6). The complexes adsorption increases slightly with the increasing temperature. Moreover, it was also found that iminodisuccinic complexes adsorption on THA was shown to follow the Langmuir isotherm but the data did not fit the Freundlich isotherm. The adsorption capacities q_e at 293 K, 313 K and 333 K were for THA in the order: 47.17 mg/g, 50.51 mg/g and 53.76 mg/g, respectively. The effect of temperature according to the Langmuir model was as expected that is the obtained K_L values increase as temperature increases from 293 to 333 K. The increase in the amount of Cu(II) complexes adsorbed to form a monolayer coverage at higher temperature can be due to the increasing mobility of the formed complexes or the reaction of sorbed complexes and surface functional groups of THA.

4. Conclusions

The research on the adsorption of Cu(II), Zn(II), Mn(II) and Fe (III) with IDS onto hydrogel TerraHydrogel®Aqua indicates that this complexing agent has a beneficial effect on the efficiency of the process compared to the adsorption of Cu(II) in the non-complexed form. IDS is a new generation of complexing agent characterized by a higher biodegradability compared with the conventional agents, such as, for example, EDTA. Both complexes of Mn(II) and Zn(II) exhibit high affinity for THA. The process efficiency increases with the increasing phase contact time. The adsorption process of Cu(II), Zn(II), Mn(II) and Fe(III) complexes with IDS onto THA proceeds according to the pseudo second order mechanism reaction, as evidenced by the high values of the determination coefficients. The adsorption mechanism can

be described by the Langmuir equation. The process is also temperature dependent. The preliminary experiments also shown that the presence of chloride ions adversely affects the process efficiency. This effect will be studied in the next paper.

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Table 1. The physicochemical properties of this superabsorbent TerraHydrogel®Aqua (THA).

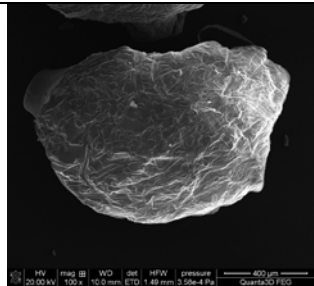
Superabsorbent	TerraHydrogel®Aqua (THA)
Matrix	polyacrylate, cross-linked
Structure	gel
Functional group	carboxylate
Commercial form	Na ⁺
Appearance	white granules
Size	>1.0 mm 2.28% 1.0 mm-0.8mm 19.42% 0.8 mm-0.4mm 55.60% <0.4mm 22.70%
The water absorbency (%)	180-300 g H ₂ O/g
Bead size (mm)	0.177-0.255
Operating pH range	6-8
Humidity,%	6-10
Biodegradability, years	2-3
SEM scan	

Table 2. The instrumental parameters and operating conditions used for determination of the studied elements by the ICP-OES technique.

Spectrometer	Varian 720 ES, Varian
Power (W)	1200
Spray chamber	cyclonic
Nebulizer	OneNeb® (Glass Expansion)
Plasma argon gas flow rate (dm ³ /min)	15.0
Auxiliary argon gas flow rate (dm ³ /min)	2.25
Nebulizer argon gas flow rate (dm ³ /min)	0.70
Pump rate (rpm)	12
Analytical wavelength (nm)	Cu 327.395 Fe 259.940 Zn 213.857 Mn 257.610

Table 3. The kinetic parameters of the Cu(II), Zn(II), Mn(II) and Fe(III) complexes with IDS on THA.

Parameter	Cu(II)-IDS=1:1	Zn(II)-IDS=1:1	Mn(II)-IDS=1:1	Fe(III)-IDS=1:1
PFO				
q_{e1} , mg/g	5.16	8.34	6.32	1.98
k_1 , 1/min	0.017	0.016	0.014	0.034
R^2	0.8867	0.8654	0.7543	0.7651
PSO				
q_{e2} , mg/g	12.22	14.39	12.12	16.24
k_2 , g/mg min	0.001	0.003	0.007	0.119
R^2	0.9998	0.9999	1.0000	0.8765
IPD				
k_i , mg/g min	0.453	0.321	0.654	0.378
R^2	0.7992	0.8971	0.6654	0.7543

Table 4. The adsorption parameters of the Cu(II), Zn(II), Mn(II) and Fe(III) complexes with IDA on THA.

Parameter	293 K	313 K	333K
Langmuir parameters			
q₀	47.17	50.51	53.76
K_L	0.002	0.003	0.006
R_L	0.681	0.609	0.461
R²	0.9823	0.9933	0.9818
Freundlich parameters			
K_F	1.14	1.66	2.51
n	2.13	2.236	2.339
R²	0.9204	0.9241	0.9562

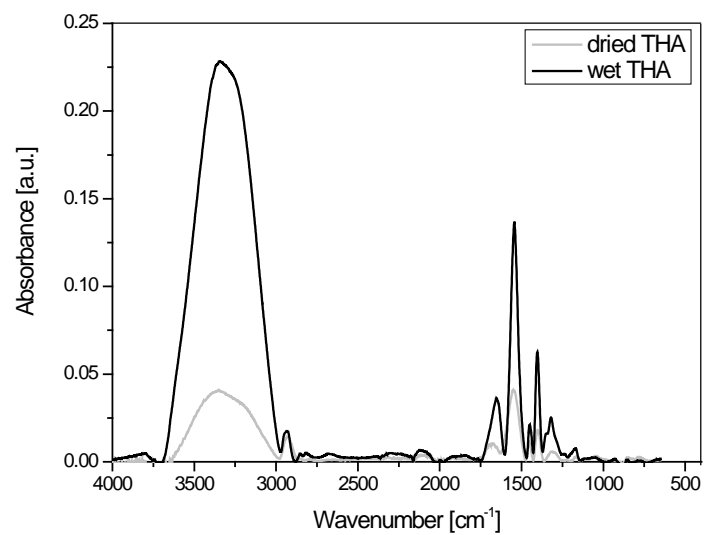


Fig.1. The ATR FT-IR spectra of THA.

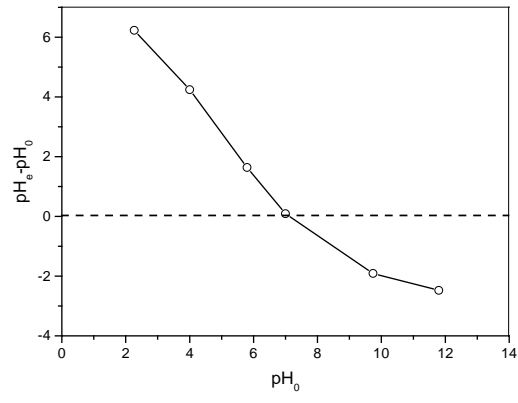


Fig.2. Point of zero charge of THA.

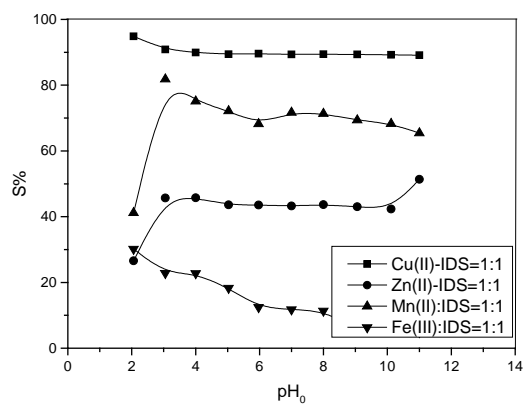


Fig.3. Comparison of the sorption percentage (S%) of Cu(II), Zn(II), Mn(II) and Fe(III) complexes with IDS on THA depending on the pH of the solution.

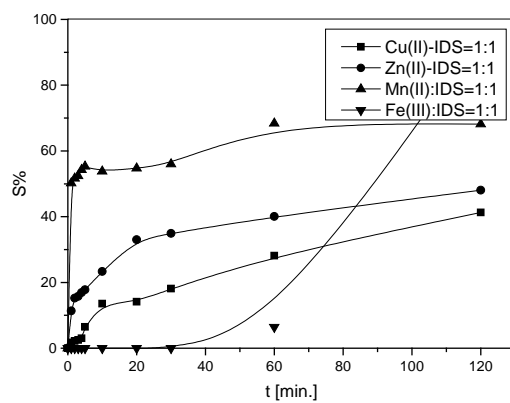


Fig.4. Comparison of the sorption percentage (S%) of Cu(II), Zn(II), Mn(II) and Fe(III) complexes with IDS on THA depending on the phase contact time.

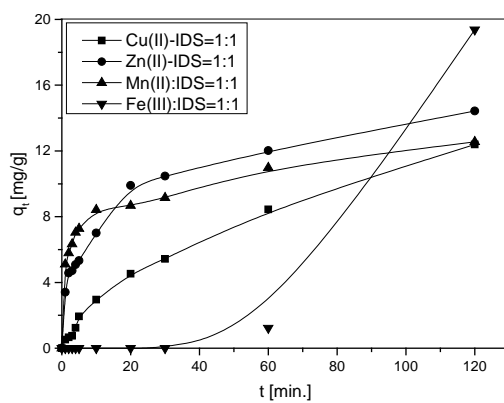


Fig.5. Comparison of the sorption capacities (q_t) of Cu(II), Zn(II), Mn(II) and Fe(III) complexes with IDS on THA depending on the phase contact time.

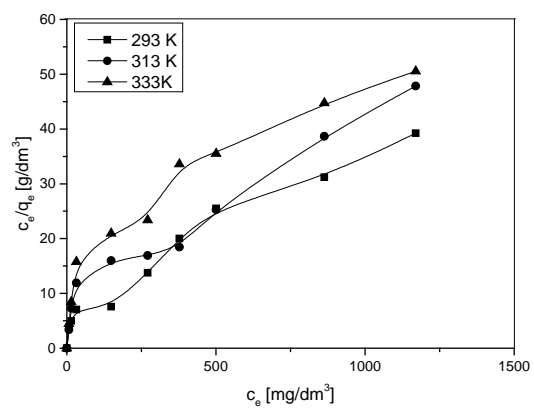


Fig.6. The adsorption isotherm of Cu(II) complexes with IDS on THA on different temperatures.