Biopolymers - Carbon Sources for Composite Materials Used as Adsorbents for As (V)

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Large areas of S-E of Asia (Bangladesh), East of Europe (Hungary, West of Romania, Serbia), Nord and South America contain deep ground waters contaminated with arsenic. In these areas the quantity of arsenic in deep aquifers exceeds maximum allowed concentration of 10 µg/L. In order to use these water sources new adsorbent materials are required for their treatment. A composite material based on carbon and iron-oxide (used as surface modifier) present many advantages such as: chemical stability, higher removal efficiency, possibility of regeneration and very good selectivity for As(V) ions due to presence of iron-oxide particles onto the surface. The purpose of this study was to develop a new method to obtain a composite material using cellulose and soluble starch as carbon sources for the adsorbent material and iron chloride as precursor for the surface modifier. Produced composite material was characterized using several methods: TG-DTG, SEM, EDX, RDX and FT-IR. During experimental test obtained adsorbent material was used as adsorbent for As(V) removal form aqueous solutions. Arsenic residual concentration was measured using ICP-MS method. Maximum adsorption capacity obtained for adsorption experiments was 280 µg As (V)/g of adsorbent material.

Keywords: bio-polymer, composite, iron-oxide, starch, cellulose, arsenic, adsorption

Pollution of the surface water sources has lead at increased use of the groundwater as a drinking water source. In extended areas of the world, like S-E of Asia (Bangladesh), East of Europe (Hungary, West of Romania, Serbia), Nord of America(SUA), South America, the ground waters are contaminated with arsenic. Arsenic is a semi metallic element known since antiquity for its toxicity. Arsenic is present in water in two forms, trivalent (arsenite) or pentavalent (arsenate) form, the most toxic form is considered to be the arsenite one [1-3]. Long-term exposure to arsenic-contaminated water can primarily cause kidney and liver dysfunctions, and then affect internal organs such as lungs and gallbladder [4-6]. The way, the disease develops depends on water quality and especially onto the arsenic concentration, iron and manganese water content, correlated with water consumption and nutrition. High concentrations of arsenic accelerate the progression of disease, while the presence of iron and manganese reduce the effects of arsenic contamination by adsorption and precipitation as iron and manganese compounds before the water is consumed. Factors influencing the water transformation processes are the oxidation-reduction potential (Eh) and the *p*H [7].

The removal of arsenic compounds from water represent a major concern, in this regard a number of conventional techniques were developed, such as coagulation-flocculation, precipitation, adsorption and ion exchange, membrane filtration; or alternative methods such as ozone oxidation, bioremediation and electro-chemical treatment [3]. The classical methods present advantages and in same time some disadvantages. Most common disadvantages are: (i) lack of selectivity because of the competitiveness between different ions into the adsorption and into the ion exchange processes, (ii) production of large amounts of waste when the flocculation – coagulation and precipitation processes are used, (iii) and the high cost for implementation of membrane filtration, ozone oxidation, bioremediation, or electrochemical treatment processes.

Another way of removing arsenic is represented by the production of some composite adsorbent materials, with a chemical resistant matrix and a specific adsorbent substance obtained by using a surface modifier. Graphitic structures having a very good chemical resistance are suitable for matrix production on which specific adsorbents are grafted as surface modifiers.

Iron oxide nanoparticles, magnetite, are known to be very good arsenic absorbers [8] being ideal candidates for use as surface modifiers of the composite adsorbent materials.

In this paper was studied the possibility of obtaining a composite material containing magnetite nanoparticles grafted on surface of a graphitic structure. Cellulose and soluble starch were used as precursors for the graphitic structure and ferric chloride was used as the precursor of the iron oxide nanoparticles.

Obtained material was characterized by electronic scanning microscopy (SEM) and X-Ray energy dispersion (EDX - QUANTA FEG 250), X-ray dispersion (XRD - Rigaku Ultima IV), thermogravimetric analysis (TG-DTG - NETZCH STA 449C) and Fourier transform infrared spectroscopy (FT-IR - Bruker Platinum ATR-QL Diamond). Arsenic concentration in all solutions was measured by mass spectrometry coupled with inductive plasma using the ICP-MS Bruker Aurora M90. The mechanism of the adsorption process was determined by kinetic and equilibrium studies.

Experimental part

For the synthesis of the compound it was used soluble starch (Merck), cellulose Avicel PH-101 (Fluka Analytical) and anhydrous ferric chloride (Merck).

In order to obtain the composite material 0.5 g of soluble starch were dissolved in 80 mL of bi-distilled water, resulted

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solution was heated at 55°C after which there were added under continuous stirring 4g of anhydrous $FeCl_3$ dissolved in 20 mL bi distilled water. Obtained mixture was maintained at 55°C under continuous stirring for another 6 h. After 6 h of mixing, 20 g of crystalline cellulose (Avicel PH-101) were added under continuous mixing until a paste was obtained. After that, obtained paste was dried in oven for 24 h at 50°C.

After drying, the material is subjected to a heat treatment in N_2 atmosphere at 400°C for several hours, obtaining a material designed as CeAmFe which was characterized using characterization methods described above.

Adsorption process mechanism was studied by performing kinetic and equilibrium studies.

To study the effect of contact time onto the adsorption capacity of the obtained material were accurately weighed 0.1 g of material over which were added 25 mL solution of As(V) with a concentration of 1 mg/L. The samples were stirred at various times (5, 15, 30, 45, 60, 90, 120 and 180 minutes) in a shaker at 200 rpm.

To establish the effect of the initial concentration of As(V) on the adsorption capacity of the material were used solutions of As(V) of different concentrations (0.1, 1, 3, 5, 6, 7, 10, 12 mg/L), which were obtained by appropriate dilution of a stock solution (1000 mg/L As(V) in 2% nitric acid, prepared with high purity As_2O_3 and water, Merck, Darmstadt, Germany).

Analysis of the residual arsenic content of the solutions following the adsorption process was performed by inductively coupled plasma mass spectrometry using ICP-MS (Aurora M90 BRUKER). For the preparation of solutions bi-distilled water was used.

Results and discussions

Characterization of the material

Thermogravimetric analysis

The thermogravimetric analysis of synthesized material in nitrogen controlled atmosphere is shown in figure 1.

From data depicted in figure 1 it can be seen that during thermal treatment cellulose and starch suffers a thermal decomposition process. Three mass loss are observed up to a temperature of 673 K, these losses corresponding to the following phenomena: first loss corresponds to the water loss and appears until the temperature reach 393K, second loss appears into the temperature interval of 393 - 453 K and corresponds to the loss of water contained into the iron aqua cations, and the last loss appears into the temperature range of 473 - 653 K were the polysaccharides decomposition takes places, as result of the rupture of glycoside bond along with the formation of a carbon structure and the release of volatile substances (CO, CO_2, aldehydes, furans) [9].

In temperature range of 523 - 633 K along with cellulose and starch thermal decomposition is taking place the reduction of ferric oxy-hydroxide particles leading at a mixture of Fe(II) and Fe(III) oxides, which are the precursors of the magnetite (Fe_3O_4). Considering these transformations, it has been established that the thermal treatment of the precursors mass must be made at 673K for several hours with a slow heating rate.

Analysis by scanning electronic microscopy

The scanning electronic microscopy- SEM images of the material obtained are shown in figure 2.

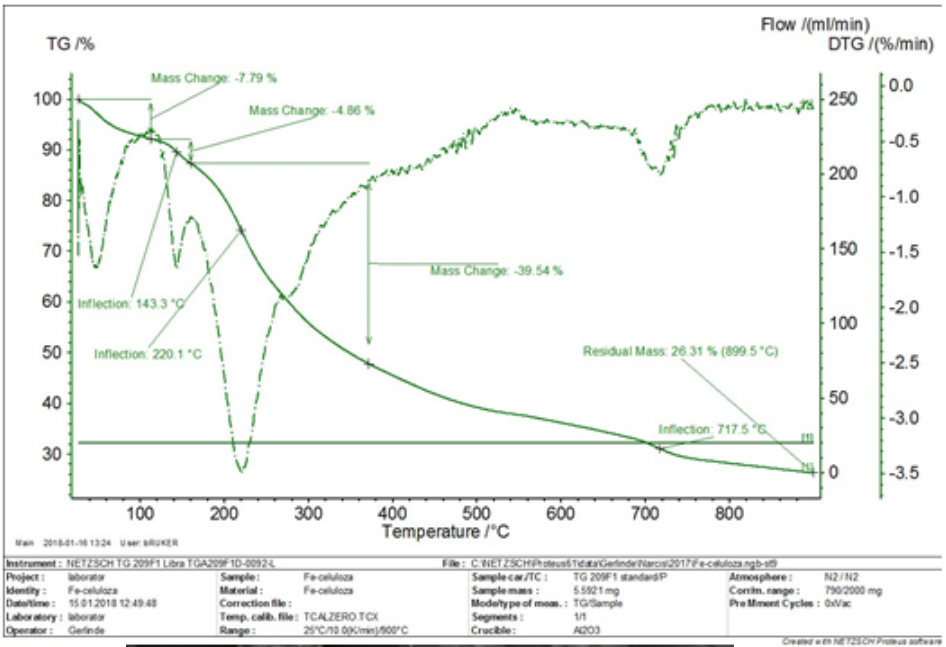

Fig. 1. TG and DTG analysis of starch – cellulose mass

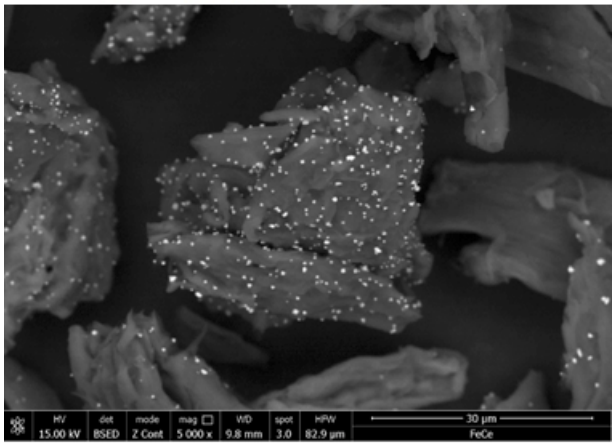

Fig. 2a. Scanning electronic microscopy- SEM images of CeAmFe material

a.The morphology of the particles of the CeAmFe

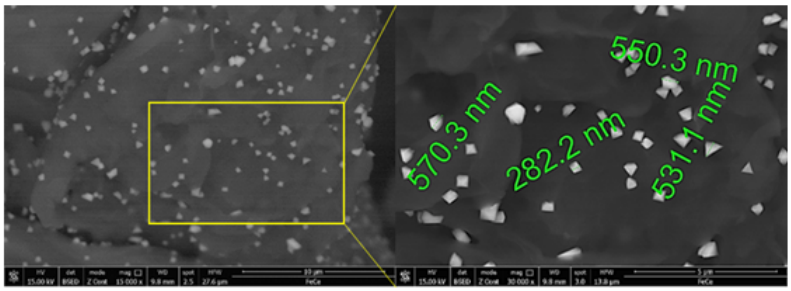

Fig. 2b. Scanning electronic microscopy- SEM images of CeAmFe material

b.Distribution and size of particles of Fe_XO_Y on the C support

Analyzing the images shown in figure 2 it can be noticed the presence of two different phases, one of them being the support material with a carbon structure (with dimension of the particles in range of tens of μm) on which are grafted the second phase represented by the magnetite particles with dimensions into the range of hundreds of nanometers. Most Fe_XO_Y particles having the size between 200 and 500 nm.

These dimensions of the iron oxide particles provide a high capacity for arsenic adsorption onto the obtained material.

Production of magnetite particles grafted onto the carbon structure can be explained by taking into account the phenomena that take place during the material preparation.

Thus, during the dissolution of the anhydrous ferric chloride a process of hydrolysis occurs with the formation of complexes of iron with water, iron hydroxyl-oxide and HCl. During this process, the formation of iron water complexes is followed by their deprotonation. Simultaneously are formed iron hydroxyl aqua complexes which represent the intermediates which may participate at condensation reactions leading at Fe - O - Fe bonds [10].

Production of HCl during iron chloride hydrolysis leads at starch acidic hydrolysis, when glucose molecules are released form starch molecule. Resulted glucose molecules replace water molecules into the structure of iron aqua complexes, therefore forming iron complexes with glucose, thus preventing further condensation reactions between iron aqua complex particles, stabilizing it and limiting their size [12-14].

The mixing time of 6 h allows the stabilization of most iron particles, leading at relative uniform size of the iron oxide particles in the synthesized material.

When cellulose is added, the stabilized particles of iron complexes are attached by cellulose free OH groups, involving some hydrogen bonds.

X-ray energy dispersive spectroscopy, EDX

Obtained material was characterized by X-ray energy dispersive spectroscopy-EDX; recorded spectra is depicted in figure 3. Analyzing this spectra can observe the presence of peaks specific for C and O (elements specific for starch and cellulose) and iron-specific peak.

X-ray diffraction, XRD

The X-ray diffraction spectrum of the obtained material is shown in figure 4.

From the depicted X-ray diffraction spectrum can observe that the produced material is an amorphous one. Also in this spectra are observed two main phases, respectively: carbon and magnetite. Aim of present study was not to obtain a crystalline material, but to produce a material with high adsorbent performance.

FT-IR Infrared spectroscopy analysis with Fourier transformed

The FT-IR spectrum of the composite material obtained is shown in figure 5.

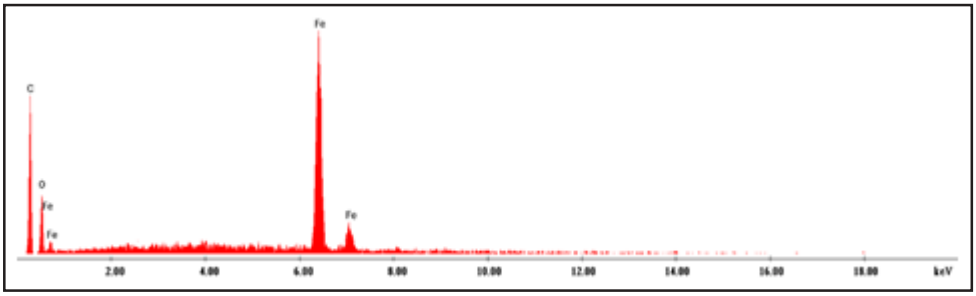

Fig. 3. Spectrum EDX of CeAmFe material

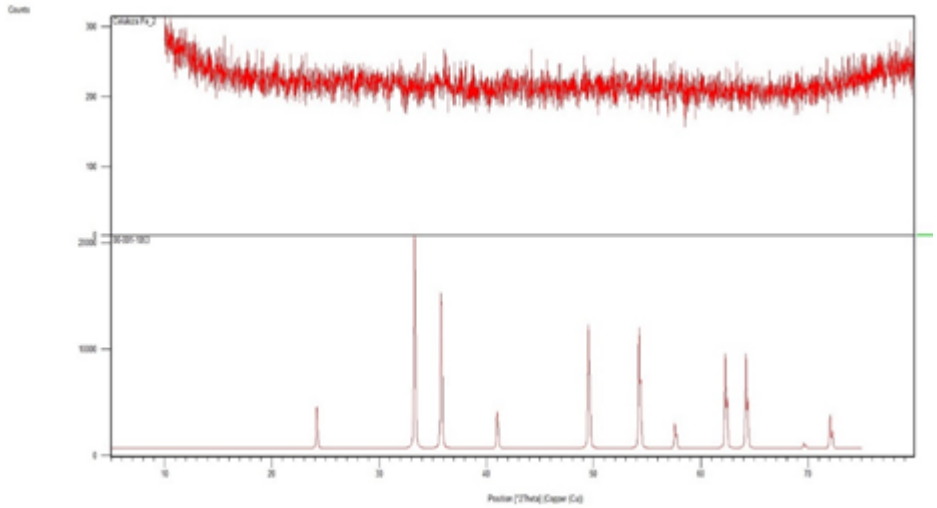

Fig. 4. X-ray diffraction spectrum of CeAmFe material

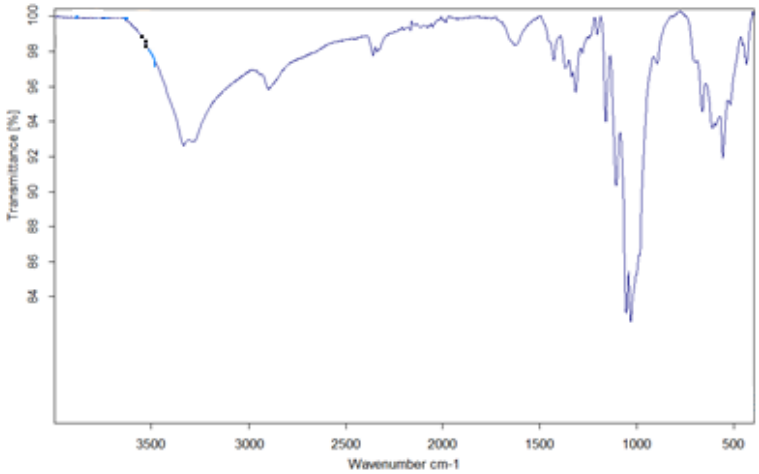

Fig. 5. FT-IR spectra for the CeAmFe material

From the spectra depicted in figure 5 can conclude that the iron oxides are presented into the synthesized material. Presence of iron oxides can be proved by the presence into the FT-IR spectra of a specific band located between 800 and 450 cm^{-1}. Band located between 1700 and 1200 cm^{-1} contains lines specific for C-C and C-OH bonds. Also, can observe the disappearance of the band located into the range of 3500 - 3000 cm^{-1} from the FT-IR spectra of composite material, band characteristic for the OH and water groups [16, 17].

Applications of CeAmFe material

In order to determine the adsorption performance of CeAmFe material, was studied the influence of some physical-chemical parameters. So it was studied the influence of the contact time and after that the influence of the initial concentration of As(V) ions onto the adsorption capacity of the material. Also, kinetic and equilibrium studies were performed in order to establish the mechanism of the adsorption process of As(V) onto the CeAmFe material.

Influence of contact time and kinetic studies

The influence of contact time onto the adsorption capacity of CeAmFe material for the As(V) ions removal from aqueous solutions is depicted in figure 6.

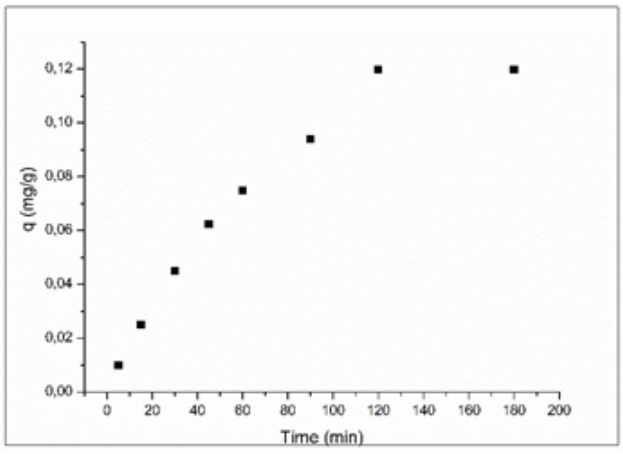

Fig. 6. The influence of contact time on the adsorption capacity of CeAmFe material m=0.1g, v=25mL, C_0=1mgAs(V)/L, *p*H=7, T=298K

A sudden increase of the adsorption capacity can be noted over a period of 120 minutes, after which the adsorption capacity remains constant. The high adsorption capacity of the material in the first 120 min is due to the availability of a large number of adsorbent sites onto the surface of the adsorbent material at the beginning of the adsorption process. For steady-state studies, a contact time of 120 min was used. The kinetics of the adsorption process describes the degree of elimination of As(V) ions and is one of the most important characteristics defining the efficiency of the adsorption process [18-21].

In order to determine the mechanism that controls the adsorption process, pseudo-first-order and pseudo-second-order kinetics models were used to fit obtained experimental data. Curves obtained by fitting obtained experimental data with pseudo-firs-order and pseudo-second-order models are depicted in figure 7. a-b.

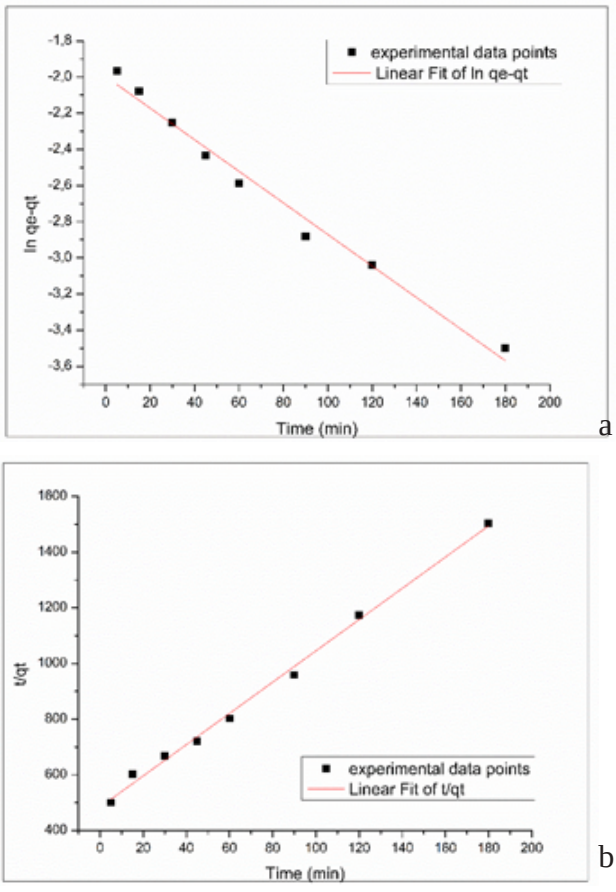

Fig. 7. The linear representation of the kinetic model

By using these linear representations were evaluated the parameters associated with used kinetic models. Pseudo-firs-order speed constant (k_1) and adsorption

$q_{e,exp}$, mg/g	The pseudo-order one kinetic model			The pseudo-order two kinetic model		
	$q_{e,calc}$, mg/g	k_1 min^{-1}	R^2	$q_{e,calc}$, mg/g	k_2 $min^{-1}(mg/g)^{-1}$	R^2
0.15	0.07	0.0087	0.9848	0.17	$6.6 \cdot 10^{-3}$	0.9957

Table 1
KINETIC PARAMETERS FOR ADSORPTION OF As (V) IONS ON CeAmFe MATERIAL

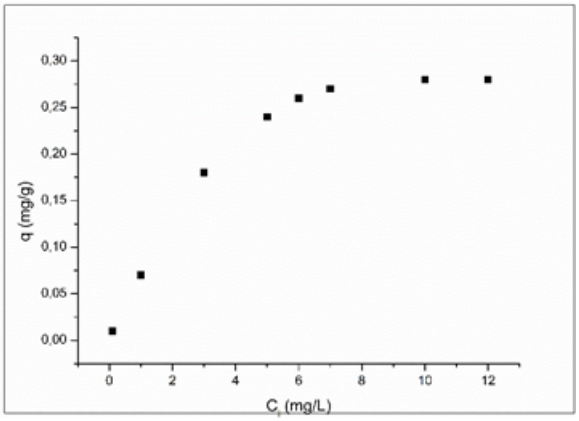

Fig. 8. Influence of the initial concentration of As(V) on the adsorption capacity of the CeAmFe material; m = 0.1g, v = 25mL, t = 120min, *p*H = 7, T = 298K

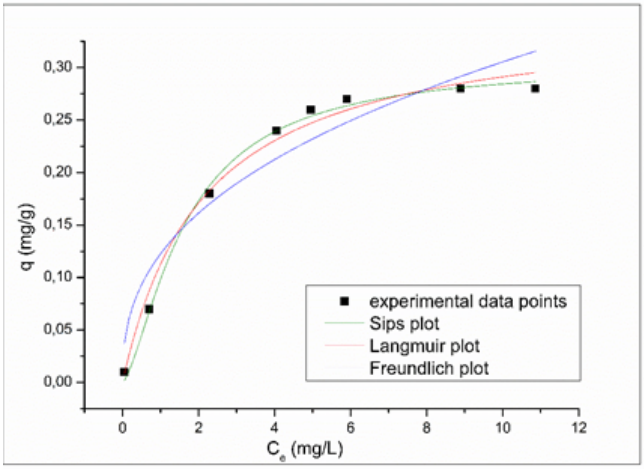

Fig. 9. As (V) adsorption isotherms onto CeAmFe material

Table 2
PARAMETERS OF FREUNDLICH, LANGMUIR AND SIPS ISOTHERMS FOR ION ADSORPTION As(V) ON THE CeAmFe MATERIAL

$q_{m,exp}$, mg/g	Freundlich Isotherm			Langmuir Isotherm			Sips Isotherm			
0.28	K_F, mg/g	$1/n_F$	R^2	K_L, L/mg	q_L, mg/g	R^2	K_s	q_s, mg/g	$1/n_s$	R^2
	0.1226	0.396	0.9143	0.469	**0.35**	0.9859	0.48	**0.31**	0.46	0.9954

capacity (q_e) were calculated from slope and from the intercept of the linear representation of q_e-q_t versus time (fig. 7. a) and the kinetic pseudo-second-order speed constant (k_2) and the material adsorption capacity (q_e) associated to the pseudo-second order model were calculated from the slope and from the intercept of linear representation t/q_t versus time (fig. 7. b).

In table 1 are presented the experimental and calculated values of the equilibrium adsorption capacities q_e, speed constants (k_1 and k_2) and the regression coefficients R^2.

From data presented in table 1 can note that the correlation coefficient obtained when the experimental data were fitted using pseudo–first-order kinetic model is lower (R^2 = 0.9848) than the correlation coefficient obtained when the experimental data were fitted using the pseudo-second-order kinetic model which is close to 1 (R^2 = 0.9957). At same time calculated equilibrium adsorption capacity ($q_{e,calc}$ = 0.07mg/g) for the pseudo-first-order kinetic model is not close to the experimentally obtained adsorption capacity ($q_{e,exp}$ = 0.15 mg/g). When the pseudo-second-order kinetic model was used to fit the experimental data, can observe that the theoretical value of adsorption capacity ($q_{e,calc}$ = 0.17 mg/g) is close to the experimentally obtained one ($q_{e,exp}$ = 0.15 mg/g).

These demonstrates that the kinetics of the As(V) ion removal process by adsorption on the CeAmFe material is better described by the pseudo–second-order kinetic model.

This suggests that the process may be chemical adsorption or chemisorption involving valence forces by sharing or by exchange electrons between adsorbent and adsorbate.

Influence of initial concentration of As(V) ions and equilibrium studies

The influence of the initial concentration of the As(V) solution on the adsorption process is presented in figure 8.

From data presented in figure 8 can observe that the adsorption capacity increases with the increase of As(V) initial concentration until a constant value is reached, known as the equilibrium concentration. The maximum adsorption capacity is an important parameter for designing an efficient adsorption system. Thus, the maximum adsorption capacity of synthesized material is 0.28 mg As(V)/g for an initial concentration of As(V)/L equal with 7 mg/L.

Adsorption isotherms present a great importance in the analysis and optimization of the adsorption processes. Adsorption isotherms determine the relationship between the concentration and the amount of metallic ion adsorbed per adsorbent mass unit at constant temperature. Langmuir, Freundlich and Sips isotherms have been used in order to establish the maximum adsorption capacity of the material for As(V) removal from aqueous solutions.

Sips isotherm represent a combination between Freundlich and Langmuir isotherms [22-24].

Figure 9 presents Freundlich, Langmuir and Sips adsorption isotherms obtained for As(V) adsorption onto CeAmFe adsorbent, and in table 2 are presented the parameters associated with these isotherms, parameters which describe As(V) adsorption process on CeAmFe material.

It is noted that the highest regression coefficient (R^2) belongs to the Sips model (0.9954) unlike the Langmuir model (0.9859) and the Freundlich model (0.9143), proving that the As(V) adsorption process onto CeAmFe material is better described by Sips model.

From Sips model was also evaluated the maximum adsorption capacity of used material, which have a value of 0.31 mg/g, value situated realy close to the experimental one (0.28 mg As (V)/g). These values represent a confirmation that the adsorption process of As (V) on the studied material is better described by Sips model.

Conclusions

Results obtained in this study have shown that the new material obtained from environmental friendly precursors (starch, ferric chloride and cellulose) present a good efficiency for As (V) removal from aqueous solutions. By using soluble starch and cellulose to stabilize the iron oxide particles, was obtained a composite adsorbent material with good adsorption capacity with iron oxide particle dimensions located from 200 to 500 nm. The use of cellulose and starch as a precursor of the carbon support leads to obtain an inexpensive composite material from renewable raw materials.

Produced material was characterized by scanning electrone microscopy (SEM), X-ray dispersion (EDX), X-ray diffraction (XRD), thermogravimetric analysis (TG-DTG) and Fourier Transform Infrared Spectroscopy (FTIR).

The maximum adsorption capacity of the material was 0.28 mg As(V)/g for a maximum concentration of As(V) of 7 mg/L, and the required contact time was 120 minutes.The mechanism of the adsorption process was also evaluated by performing kinetic and equilibrium studies. Obtained data showed that the As(V) ions adsorption process on the CeAmFe material is best described by pseudo-second-order kinetic model and the adsorption isotherm that best covers the process is Sips. When the experimental data were fitted using Sips isotherm were obtained a regression coefficient R^2 of 0.9954 and a maximum adsorption capacity of 0.31 mg/g, value very close to the maximum experimental adsorption capacity ($q_{m,exp}$=0.28 mg/g). These suggest that the process is spontaneous and adsorption is accomplished by physical-chemical interactions between the metal ion and the active centers of the material.

Acknowledgements: This work was supported by research grants PCD-TC-2017

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Manuscirpt received: 9.12.2018