



ASPECTS REGARDING THE CONSTITUTIVE EQUATIONS FOR FEM ANALYSIS OF ADVANCED METAL FORMING PROCESSES

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ABSTRACT

The main aim of this paper is to review some different models, from simple to very complicated, for computing the changes in flow stress depending on the deformation conditions. Some of the models can be applied to cold forming and some to hot and warm forming. A finite element analysis (FEA) of the dieless drawing process was undertaken. The FEA simulation was carried out using Forge3, a FEA software, specifically produced for metal forming simulation. An axisymmetrical 3D geometric model of the tooling and billet was constructed for the analysis. The data obtained from the FE model included temperature, equivalent von Mises stress, equivalent strain and material deformation velocity.

KEYWORDS: metal forming, constitutive equations, Forge3, dieless drawing

1. Introduction

Cold and hot forging are regarded as two of the most important processes for the manufacturing of products with good mechanical properties and fine metallurgical structures.

An important objective of the deformation processing of metals and alloys is the production of defect-free parts, with the desired microstructure and properties. This goal can be achieved by better design and calculation methods and better control of the parameters of the deformation processes. This should be based on a deeper knowledge of the phenomena that accompany the deformation of materials and of the relationships between the properties of the deformed materials and the conditions of deformation.

The progress in computer hardware and simulation tools has, in recent years, enabled complicated simulations of industrial forming processes. However, the accuracy of such simulations will remain dependant on the reliability of the material data, most important of all the true flow stress. Experimental tests at different strains, strain rates and temperatures reached during metal forming application are performed to reveal this constitutive relationship, which relates the deformation behavior to stress.

The most important aspect of mechanical design in metal forming processes is the determination of forces and forming energy, which requires the knowledge of the flow stress of alloys. Experiments to find the flow stress of alloys at different loading

conditions, i.e. various strain rates and temperatures, are necessary but very expensive and time consuming. Therefore, developing mathematical models to predict the stress-strain curves under different forming conditions is of great importance. Many researchers tried to model the stress-strain curves for different alloys. The main difference between these models is the level of physical theories which is used to obtain them.

One of the most important elements of a computer simulation of plastic deformation processes is the model of deformed materials, usually describing the flow stress as a function of the deformation conditions. The accuracy of such a material model depends on both the mathematical structure of the model and the proper experimental determination of the material parameters used in the model. The mathematical structure should take into account the physical phenomena occurring in the material and depending on its kind, the conditions of forming, the history of deformation. Considering the different structural phenomena, cold, warm, and hot forming processes should be distinguished. Recently, the progress in computer hardware and simulation tools led to a wide application of FEM simulations to study the forging process [1, 4, 6, 7, 12,13].

Constitutive equations are used to describe the changes in strength observed to occur in materials being deformed. These formulations are empirical and relate changes in strength produced by variation in strain, temperature or strain rate. Such equations are used to predict forces, distortions, stresses, etc. that



THE USE OF MAGNETIC NANOMATERIALS FOR THE RETAINING OF Cu(II) IONS OUT OF RESIDUAL WATER

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ABSTRACT

In the developed countries the removal of hard materials from residual waters using advanced technologies such as ionic change, precipitation, ultrafiltration or electrochemical deposits seems inconvenient from the economic point of view for the industry because its high costs. Therefore, it is necessary to introduce new technologies that imply low costs.

By linking chitosan and magnetite particles (Fe_3O_4), a new magnetic adsorbent with 100-200 nm particles and of great efficiency to move off the metallic ions is obtained. That is why this study aims to obtain a new magnetic material with great efficiency to retain copper out of synthetic solutions, and then to compare it, from the retaining point of view, with simple synthesized magnetite (Fe_3O_4).

KEYWORDS: nanomaterial, composite, chitosan, water

1. Introduction

Water is an important factor in the ecological balance and its pollution is a contemporary issue with more or less serious consequences on the population. The effects of the pollution of water resources are complex and various depending on the nature and concentration of impurification substances.

The presence of heavy metals in the environment is a problem of great significance because of the great volume of residual water with metallic ions, of their ionic nature and of the negative effects that they have on natural waters. For the human health, one of the most dangerous materials in industrial residual waters (metals industry, cellulose and paper industry, fertilizers industry, electronic industry, photographic industry, copperfield) is copper.

Copper is a necessary microelement for the human body; the daily dose is 2-3 mg of copper for adults and 0.05 mg/kilogram for children. When it is swallowed in great amounts, it becomes toxic thus leading to such manifestations as icterus, anaemia or to an exaggerated consumption of water, etc.

One of the less expensive methods to remove copper from residual waters is adsorption. An adsorbent for copper could be chitosan, a natural polysaccharide with various properties such as

hydrophilicity, biocompatibility, biodegradability, antihæterian properties and a remarkable affinity towards various biomacromolecules. The chitosan and its derivatives have various potential applications in such domains as: biotechnology, biomedicine, food ingredients and cosmetics. Furthermore, the chitosan is capable to retain a great number of metallic ions because it contains nano groups used as chelating points.

This biosorbent has also disadvantages such as: the tendency to heap up, a low capacity of getting soaked, the capacity of making gels into watery solutions thus making unavailable the linking reactive centers.

These are the reasons that have prevented this potential adsorbent from being used at an industrial scale except in laboratory experiments. In order to overcome these restrictions and other difficulties during the sorption process, a compound, called magnetite-chitosan, has been obtained as a new potential sorbent to retain the Cu(II) from watery solutions efficiently.

Therefore the purpose of this study was to obtain a new magnetic material with great efficiency in retaining copper out of synthetic solutions and comparing it with simple synthesized magnetite, from the retaining capacity point of view.

Consequently:

- two materials have been obtained: magnetite and chitosan, joined by the coprecipitation method, which have been characterized by using well-known methods;

- a study has been carried out to identify the characteristics of the obtained composite material (magnetite/chitosan);

- the composite has been used to retain copper ions out of synthetic solutions in static situations;

- the influence of some parameters has been established: the initial concentration of the Cu(II) synthetic solution, the contact time on the absorption of Cu(II) using the composite material with magnetic properties – magnetite – chitosan.

Besides fixing the humidity, the materials have also been analyzed by FTIR (Fig. 2), spectrography diffraction analysis, transmission electron microscopy (TEM).

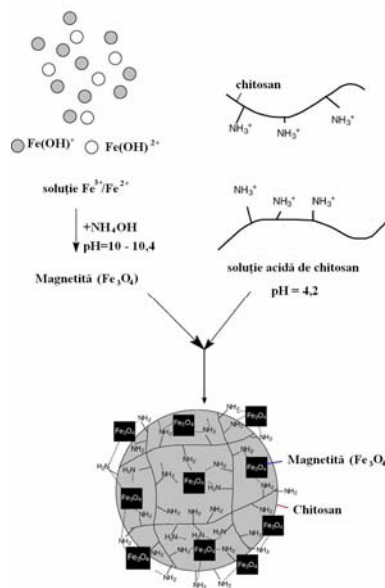


Fig. 1. Sketchy plotting of the process of making magnetite/chitosan composite.

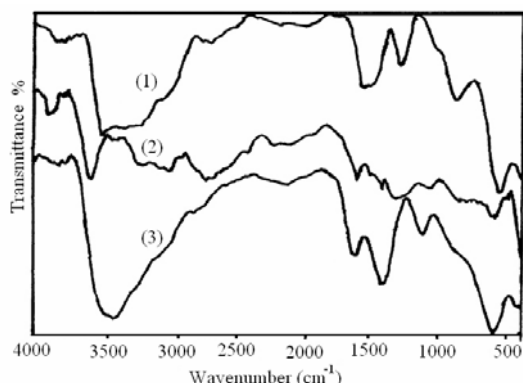


Fig. 2. FTIR spectroscopy magnetite (1) chitosan (2) and magnetite–chitosan (3).

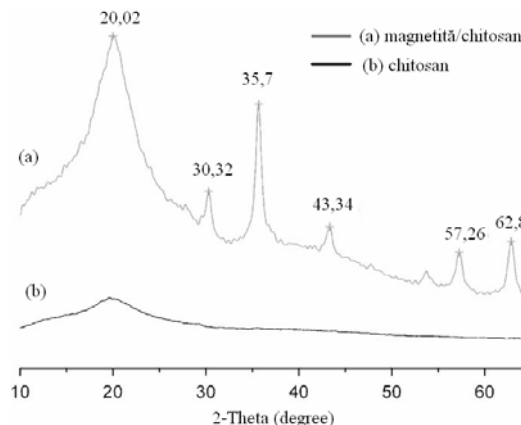


Fig. 3. Diffraction analysis.

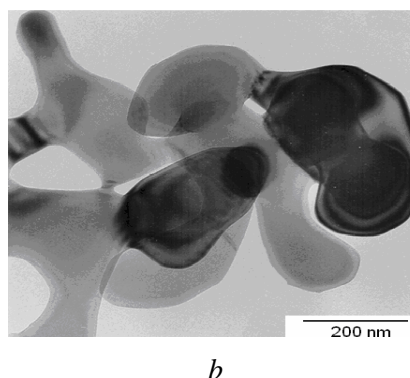
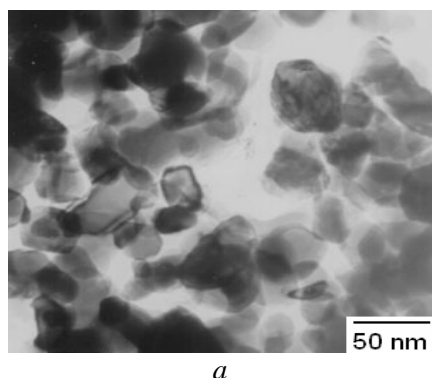


Fig. 4. TEM images for magnetite (a) and magnetite - chitosan (b).

IR spectroscopies have been recorded in the 400 - 4000 cm^{-1} domain, using a FT-IR 620 spectrometer (Jasco, Japan).

Figure 2 presents FTIR spectroscopy of the magnetite, chitosan and the composite made up in the reaction between the magnetite and the chitosan.

In spectroscopy (1), characteristic to the magnetite, the presence of bands in the area 3250-3600 cm^{-1} and 1550-1700 cm^{-1} is associated to the water molecules net. This indicates the presence of crystallization of water in the magnetite test. The 610 cm^{-1} band is characteristic to the stretching vibration of the M-O joint which confirms the presence of Fe-O joints in the magnetite.

The presence of a characteristic band at the 3594 cm^{-1} wavelength in the chitosan spectroscopy shows the existence of the HO hidroxil groups in the chitosan molecule, while the bands appearing at the 1650 cm^{-1} and 1449 cm^{-1} wavelengths correspond to the frequency of stretching vibrations characteristic to the amid group in the chitosan molecule.

Spectroscopy (3) in Figure 2 shows all the characteristic bands of magnetite and chitosan, and more than that the bands characteristic to water molecules are much more intense, which proves the existence of the magnetite – chitosan composite.

The diffraction analysis of unmodified chitosan in Figure 3b shows only one band of diffraction of 20°. This band is due to reflections (2 0 2) according to the literature data.

The sharp diffraction bands appearing at angles $2\theta = 30.32; 35.7; 43.34; 57.26$ and 62.8 in the diffraction analysis of magnetite chitosan composite correspond to the magnetite. Consequently the iron oxide in the obtained composite is the magnetite. The difference of the band intensity from angle $2\theta = 20.02$ indicates that the degree of crystallinity of the chitosan rises because of the orientation of the chitosan chains. The oriented magnetite particles lead to the formation of an ordered structure regarding the chitosan composite. These are according to the scientific literature.

The transmission electron microscopy (TEM) was used to fix the morphology of the reaction product obtained through a method specific to the study of crystallin dust. The obtained dust was spread into alcohol and then deposited on a TEM grid with carbon support. The TEM study was realised by the help of an electronic microscope, Jeol 200CX. One can notice in Figure 4 that the magnetic particle have an average diameter of 30-70 nm.

Figure 4b shows that the magnetite particles are in the chitosan particles because of two simultaneous processes. The first process refers to the formation of magnetite and the second process to the precipitation of chitosan in an alkaline solution.

In Figure 4a it is to be noticed that both stages (magnetite and chitosan) are visible. The agglomeration of magnetite – chitosan composite is probably due to the lack of a stabilizing agent in the reaction system and also to the tendency of the chitosan to agglomerate.

2. The use of the magnetite – chitosan composite for the retaining of Cu(II) ions from residual waters

In order to realise the absorption of copper on magnetite/chitosan composite experiments, synthetic solutions prepared in the laboratory have been used. The stored solution of concentrated Cu(II) 0.1M was diluted and solutions of Cu(II) with concentrations of 800 mg/L, 400 mg/L, 200 mg/L, 100 mg/L were obtained.

The spectrophotometric determination of copper (a method based on the reaction of copper with ammonia) showed a blue complex that has gone to spectrometry to the $\lambda = 620$ nm wavelength.

The absorbed copper quantity on the magnetite/chitosan composite was calculated according to the contact time between the two stages; the data obtained can be seen in Figures 5 and 6.

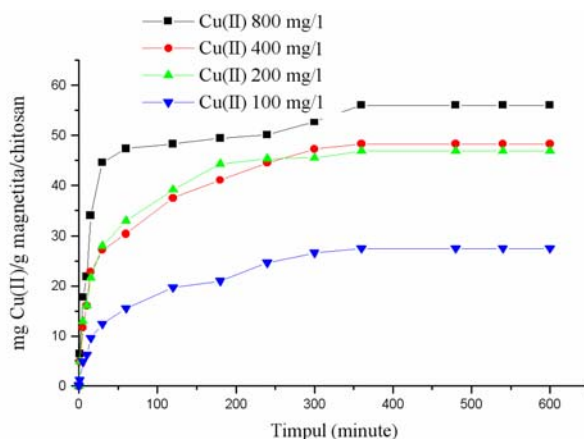


Fig.5. Cu(II) quantity retained on the magnetite/chitosan composite according to contact time.

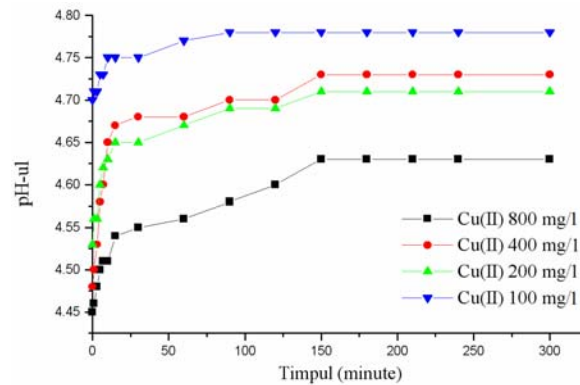


Fig.6. Variation of the pH of Cu(II) of 800 mg/L, 400 mg/L, 200 mg/L, 100 mg/L at contact with 0.1 g magnetite/chitosan composite according to time.

Studying Figure 5, the first conclusion is that the Cu(II) quantity retained on each gram of magnetite/chitosan composite grows with the contact time between the two stages. The process of moving copper off watery solutions by using magnetite/chitosan composite is a slow process, the equilibrium reaching 5 hours. This is a very important result, because the time necessary to reach the equilibrium is a very important parameter in creating an economic water treatment system. Figure 6 shows that there is a very small variation of the pH solution according to the contact time between the two stages. This variation is about 0.08-0.25 units, which leads to the conclusion that the process of retaining copper out of synthetic solutions by the magnetite/ chitosan composite is not a process that implies a chemical reaction but physical sorption.

The Kinetics of the copper ion sorption process by the magnetite/ chitosan composite

In order to identify the checking mechanisms of

adsorption processes as a transfer of mass and chemical reaction, the equations of order I, order II and intraparticle diffusion have been used to test the experimental data.

The first order kinetic model is given as:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} \cdot t \quad (1)$$

where Q_e and Q_t are the amounts of Cu(II) adsorbed on adsorbent (mg/g) at equilibrium and at time t ; k_1 is the rate constant of first-order adsorption (min^{-1});

The second-order equation may be expressed as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (2)$$

where: k_2 – is the rate constant of second-order adsorption ($\text{g/mg}\cdot\text{min}$); Q_e and Q_t are the amounts of Cu(II) adsorbed by the magnetite/chitosan composite (mg/g) at equilibrium and at time t .

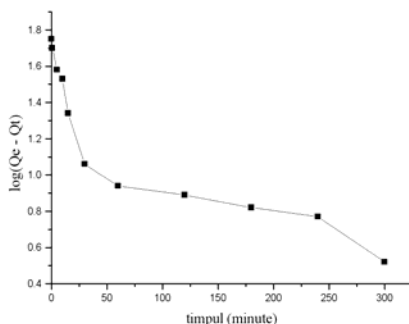


Fig.7. Kinetics of first-order adsorption of the Cu(II) on the magnetite/chitosan composite (0,1 g) at an initial concentration of 800 mg/L

The diagram of the proportion t/Q_t according to time t shows the following parameters: the speed constant k_2 and the correlation coefficient R^2 for the

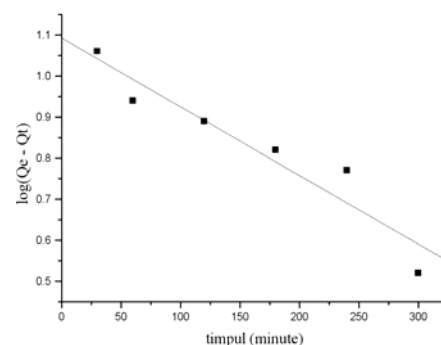


Fig. 8. Kinetics of pseudo first-order adsorption of the Cu(II) on the magnetite/chitosan composite (0,1 g) at an initial concentration of 800 mg/L at an interval of 30-300 minutes

adsorption of copper by the magnetite/chitosan composite.

The rate of the intraparticle diffusion is described by the equation:

$$Q_t = k_i t^{0.5}$$

where k_i is the intraparticle diffusion rate ($\text{mg g}^{-1} \text{min}^{-0.5}$).

The k is the slope of straight-line obtained in the diagram of the intraparticle diffusion rate, Q_t according to the time of dividing into halves, $t^{0.5}$. The obtained data are shown in Figures 7-16.

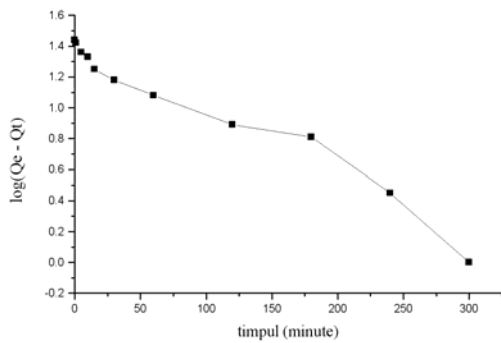


Fig. 9. Kinetics of first-order adsorption of the Cu(II) on the magnetite/chitosan composite (0.1 g) at an initial concentration of 100 mg/L.

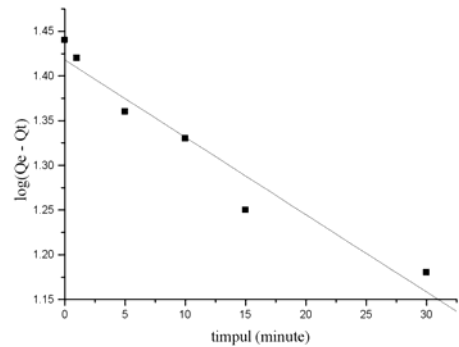


Fig. 10. Kinetics of pseudo first-order adsorption of the Cu(II) on the magnetite/chitosan composite (0.1 g) at an initial concentration of 100 mg/L at an interval of 0-30 minutes.

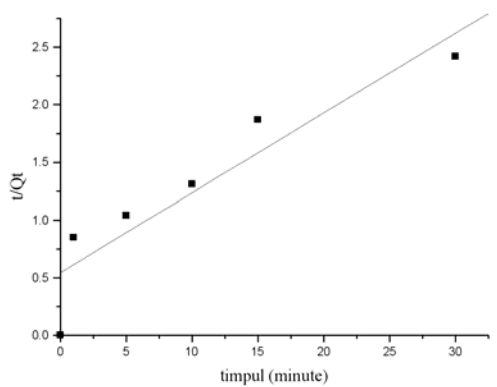


Fig. 11. Kinetics of pseudo second-order adsorption of the Cu(II) on the magnetite/chitosan composite (0.1 g) at an initial concentration of 100 mg/L at an interval of 0-30 minutes.

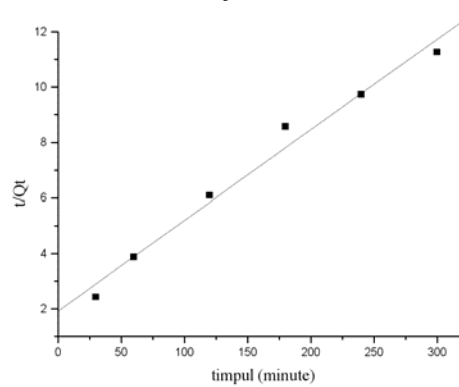


Fig. 12. Kinetics of pseudo first-order adsorption of the Cu(II) on the magnetite/chitosan composite (0.1 g) at an initial concentration of 100 mg/L at an interval of 30-300 minutes.

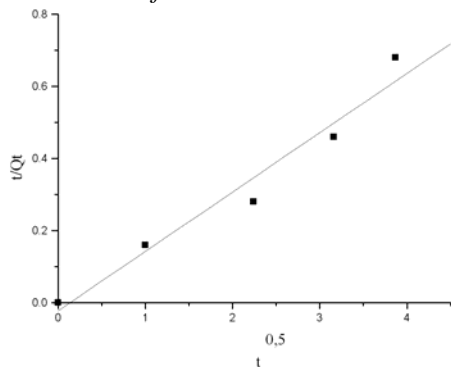


Fig. 13. Kinetics of sorption of intraparticle diffusion of Cu(II) on the magnetite/chitosan composite (0.1 g) at an initial concentration of 800 mg/L in an interval of 0-30 minutes.

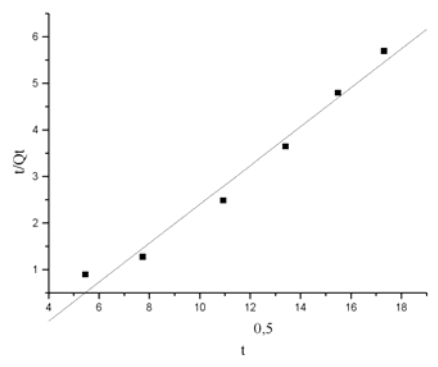


Fig. 14. Kinetics of sorption of intraparticle diffusion of Cu(II) on the magnetite/chitosan composite (0.1 g) at an initial concentration of 800 mg/L in an interval of 30-300 minutes.

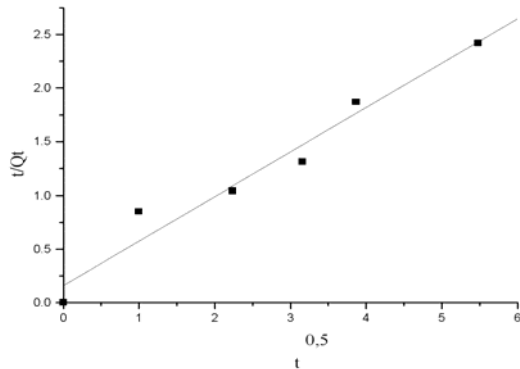


Fig. 15. Kinetics of sorption of intraparticle diffusion of Cu(II) on the magnetite/chitosan composite (0.1 g) at an initial concentration of 100 mg/L in an interval of 0 -30 minutes.

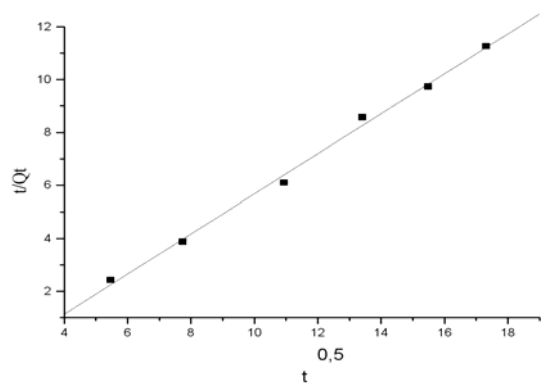


Fig. 16. Kinetics of sorption of intraparticle diffusion of Cu(II) on the magnetite/chitosan composite (0.1 g) at an initial concentration of 100 mg/L in an interval of 30-300 minutes.

The constant rate and the correlation coefficient of the models Lagergren (the pseudo first-order), the

pseudo second-order and the intraparticle diffusion in the mentioned intervals are shown in Tables 1 and 2.

Table 1. The constant rate and the correlation coefficients for Cu(II) adsorption on chitosan and an initial concentration of Cu(II) of 800 mg/L, the amount of magnetite/chitosan composite is 0.1 g

The kinetic model	0 – 30 min.		30 - 300 min.	
	k_i	R^2	k_i	R^2
Lagergren (pseudo first-order)	$5.2185 \cdot 10^{-2}$ (min ⁻¹)	0.9851	$3.846 \cdot 10^{-3}$ (min ⁻¹)	0.9979
Pseudo second-order	$2.8617 \cdot 10^{-2}$ (g/mg min)	0.9735	$1.1903 \cdot 10^{-3}$ (g/mg min)	0.9104
Intraparticle diffusion	0.1646 (mg g ⁻¹ min ^{-0.5})	0.9608	0.4176 (mg g ⁻¹ min ^{-0.5})	0.9795

Table 2. The constant rate and the correlation coefficients for Cu(II) adsorption on chitosan and an initial concentration of Cu(II) of 100 mg/L, the amount of magnetite/chitosan composite is 0.1 g

The kinetic model	0 – 30 min.		30 - 300 min.	
	k_i	R^2	k_i	R^2
Lagergren (pseudo first-order)	$1.9943 \cdot 10^{-2}$ (min ⁻¹)	0.9451	$9.3732 \cdot 10^{-3}$ (min ⁻¹)	0.9361
Pseudo second-order	$8.7892 \cdot 10^{-3}$ (g/mg min)	0.8573	$5.5713 \cdot 10^{-4}$ (g/mg min)	0.9816
Intraparticle diffusion	0.4147 (mg g ⁻¹ min ^{-0.5})	0.9601	0.7568 (mg g ⁻¹ min ^{-0.5})	0.9960

According to the correlation coefficients, it can be seen that on the entire time interval (0 – 300 minutes) the adsorption of Cu(II) on the magnetite/chitosan composite is best described by the first equation Lagergren ($R^2 = 0,9851; 0,9979$) for the Cu(II) solution of 800 mg/L concentration, which leads to the conclusion that the important stage of rate is the physic adsorption.

Table 2 shows that for the Cu(II) solution of 100 mg/L the Cu(II) sorption on magnetite/chitosan may be best described by the equation characteristic to the

intraparticle diffusion on the entire time interval because the values of the correlation coefficient R^2 are 0.9601 și 0.9960.

3. Conclusions

The results of this study prove the possibility of using a magnetic material such as the magnetite/chitosan composite to remove Cu(II) from aqueous solutions.



Taking into account the experiments and their results, here are the conclusions:

- based on a simple method, a magnetic material magnetite/chitosan composite has been obtained;
- the material was morphologically and structurally characterized;
- the experimental data show that a magnetite/chitosan composite with magnetic properties and 100-200 nm particles has been obtained;
- the material was used in the process of retaining Cu(II) ions out of synthetic solutions;
- the kinetic studies show that the equilibrium in adsorption of Cu(II) was reached after five hours of contact between the composite and the aqueous solution; consequently, the process of retaining Cu(II) is slow;
- the amount of Cu(II) retained by the composite grows with the Cu(II) concentration in the initial solution;
- according to the correlation coefficients, the sorption of copper on the composite in the 0-300 minutes interval is well described for a high concentration (Cu 800 mg/L) by the first equation ($R^2 = 0.9851$; 0.9979), which leads to the conclusion that on this time interval, for the respective concentration, the important stage of rate is the physic sorption (adsorption);
- for the solution of a small concentration (100 mg/l) it may be seen that on this time interval, the sorption of Cu(II) on the composite is best described by the third equation ($R^2 = 0.9601$ și 0.9960), which means that the important stage of rate is the intraparticle diffusion;
- the results are also established by the studies on variations of pH according to the contact time between the two stages;
- the experiments show that there was not a significant variation of the pH value of the solution at the contact between the two stages according to the time contact and that is why the sorption process

between the Cu(II) ions and the composite is a physic process not a chemical one, this implying a chemical reaction between the Cu(II) ions and the sorbent.

Consequently, the composite magnetic material may be used in the process of retaining Cu(II) ions out of residual waters, its separation being an easy process when a magnetic field is used.

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