Uptake of heavy metal ions in aqueous solution by chitosan modified biochar

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Introduction

Heavy metals are hazardous for health and life of people and animals due to mutagenous action and capability of bioaccumulation.

Sources of heavy metals are:

- **mining,**
- **battery production,**
- **motor industry,**
- **textile industry.**

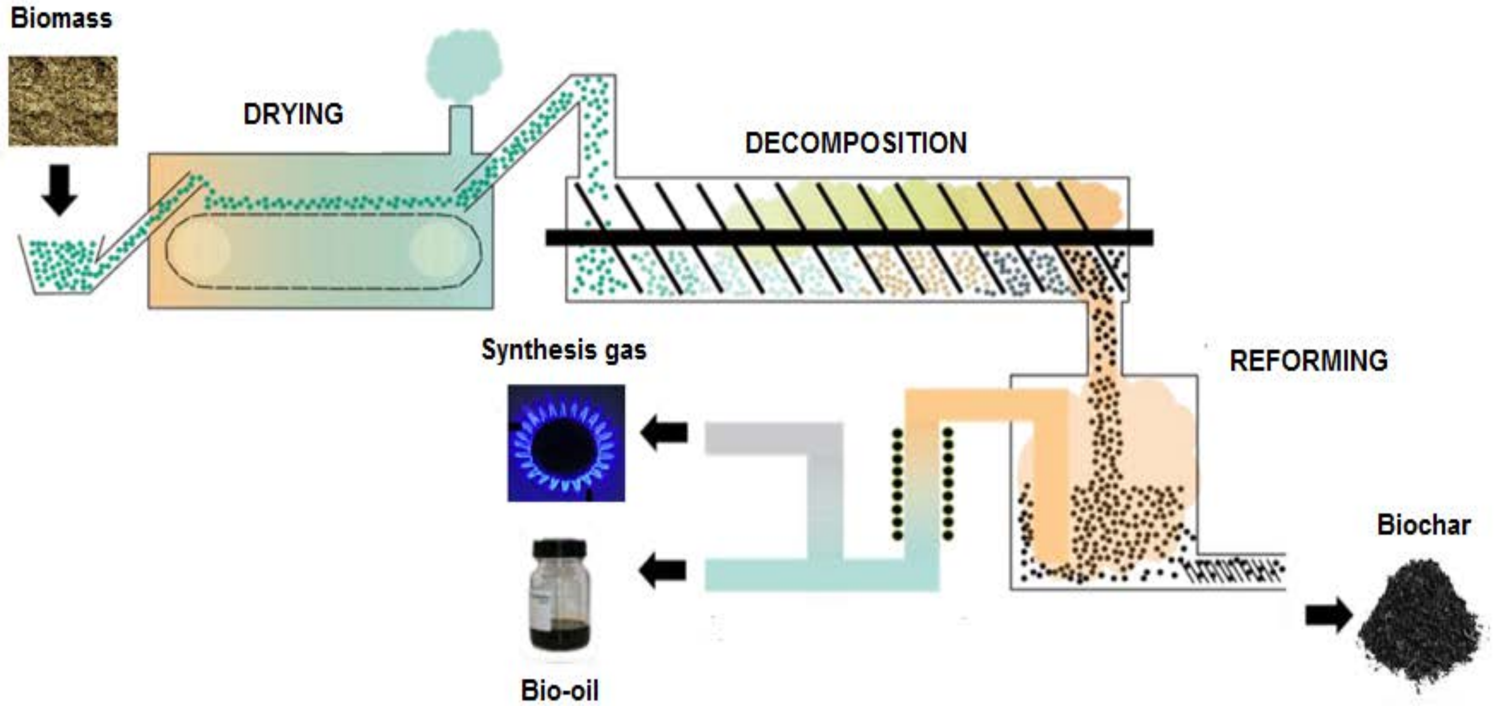
Methods used to remove heavy metals from waters and wastewaters are: chemical precipitation, coagulation, filtration, ion exchange, adsorption and membrane processes.

Adsorption proved to be an effective and economical method used for heavy melal ions removal.

The sorbent used for the study was biochar. Biochar is a solid product most frequently obtained due to biomass pyrolysis in nitrogen atmosphere. During pyrolysis besides biochar, bio-oil and synthesis gas are obtained.

The other thermochemical processes leading to biochar preparation are:

- **gasification,**
- **hydrothermal carbonization,**
- **calcination.**

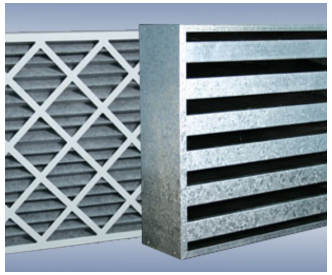


Biochar is characterized by:

- large specific surface area,
- porous structure,
- presence of functional groups,
- low production costs.

APPLICATION:

- filtration material



- renewable fuel in power industry

ADVANTAGES:

- sorbent used in the process of heavy metal ions and organic compounds removal from waters and wastewaters

- combustion in heat and power generating plants
- alternative to mineral fuels

- raw material improving soil properties

- reduction in the loss of nutritious components
- increase of carbon content in soil
- fertility improvement
- increase of soil water capacity and pH
- increase of soil microorganisms activity

- in animal breeding

- fodder additive
- water treatment in fish keeping

- cosmetic industry

- soap production
- cream production

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Aim of the studies

Investigates of the possibility of application of chitosan modified biochar in sorption of heavy metals: Cu(II), Cd(II), Zn(II), Co(II) and Pb(II) ions from waters and wastewaters.

Materials and methods

Biochar (BC) - Coaltec Energy (Illinois, USA).

COALTEC ENERGY

It has been designing and implementing systems of wastes gasification in the USA and Europe on the commercial scale since 2000.
Annually from 6 to 75 thousand tons of wastes is subjected to gasification in the Coaltec Energy.
A ton of biochar costs up to $ 350 in the USA whereas a ton of active carbon is from 1500 to 2000 US dollars.

In the Coaltec Energy biochar is obtained from agriculture industry wastes.

The quality of the obtained biochar in the gasification process is affected by:

- **raw material used for biochar production,**
- **monitoring of gasification parameters:**
  - **time of biomass stay in the reactor,**
  - **storage temperature.**

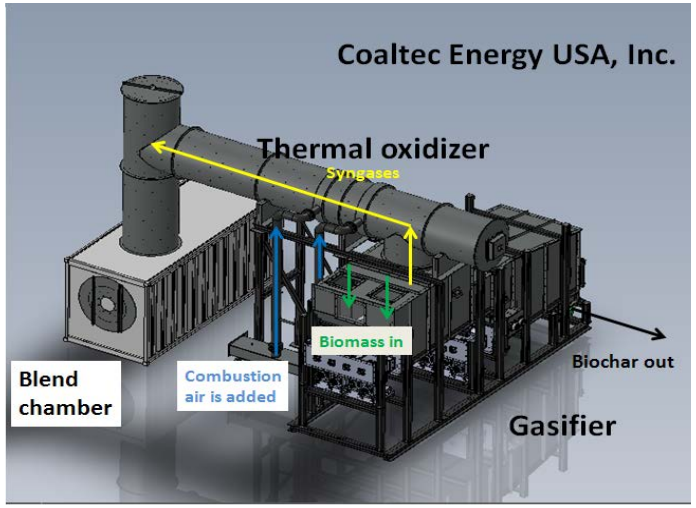


Fig.1. Gasification process in Coaltec Energy.

Fig.2. View of the biomass loading process in Coaltec Energy.

Fig.3. View of the gas generator in Coaltec Energy.

Chitosan (CS) is a polysaccharide produced by the deacetylation of chitin which is a component of crustacean shells. It belongs to the most widespread biopolymers in nature.

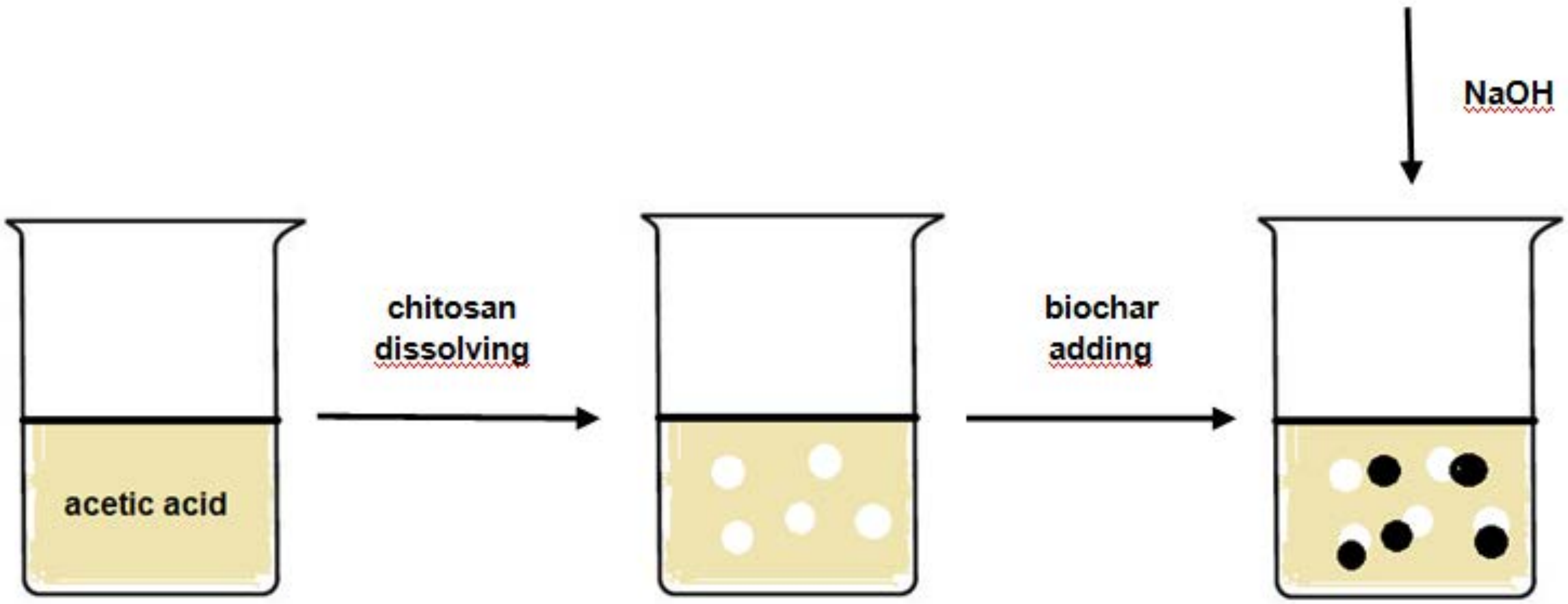
Chitosan is characterized by:

- **biodegradability,**
- **non-toxicity,**
- **availability,**
- **low price,**
- **the presence of reactive functional groups such as: amino and hydroxyl ones.**

Due to the appropriate sorption capacity it is used to remove heavy metals and organic pollutants from waters and wastewaters.

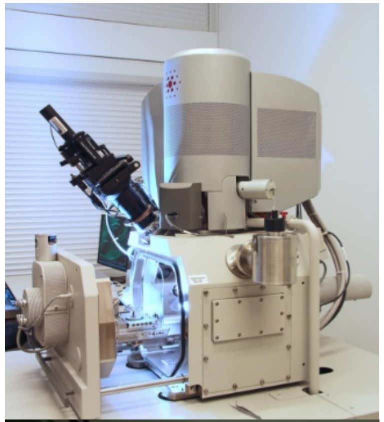
Biochar modification by chitosan combines the advantages of the both, keeping low production cost.

Preparation of chitosan modified biochar



In order to determine the properties of the biochar, it was analyzed using the methods:

- scanning electron microscopy (Quanta 3D FEG, FEI, USA),



- infrared spectroscopy (Cary 630 FTIR, Agilent Technologies, USA),

- determination of the zero point charge by the potentiometric method.

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Sorption process

Sorption process was studied using the static method. There were investigated the effects of:

- **mass ratio of biochar to chitosan (1:1, 2:1, 4:1, 8:1),**
- **pH (2-6),**
- **initial concentration of solution (50-200 mg/dm^3),**
- **phase contact time (1-360 min.),**

on effectiveness of simultaneous Cu(II), Cd(II), Zn(II), Co(II) and Pb(II) ions sorption in the solution using an emission spectrometer with inductively coupled plasma excitation ICP-OES (type 720, Varian).

In order to determine sorption kinetics and mechanism there were applied

the kinetic models:

- **pseudo first order (PFO),**
- **pseudo second order (PSO),**
- **intraparticle diffusion model (IPD).**

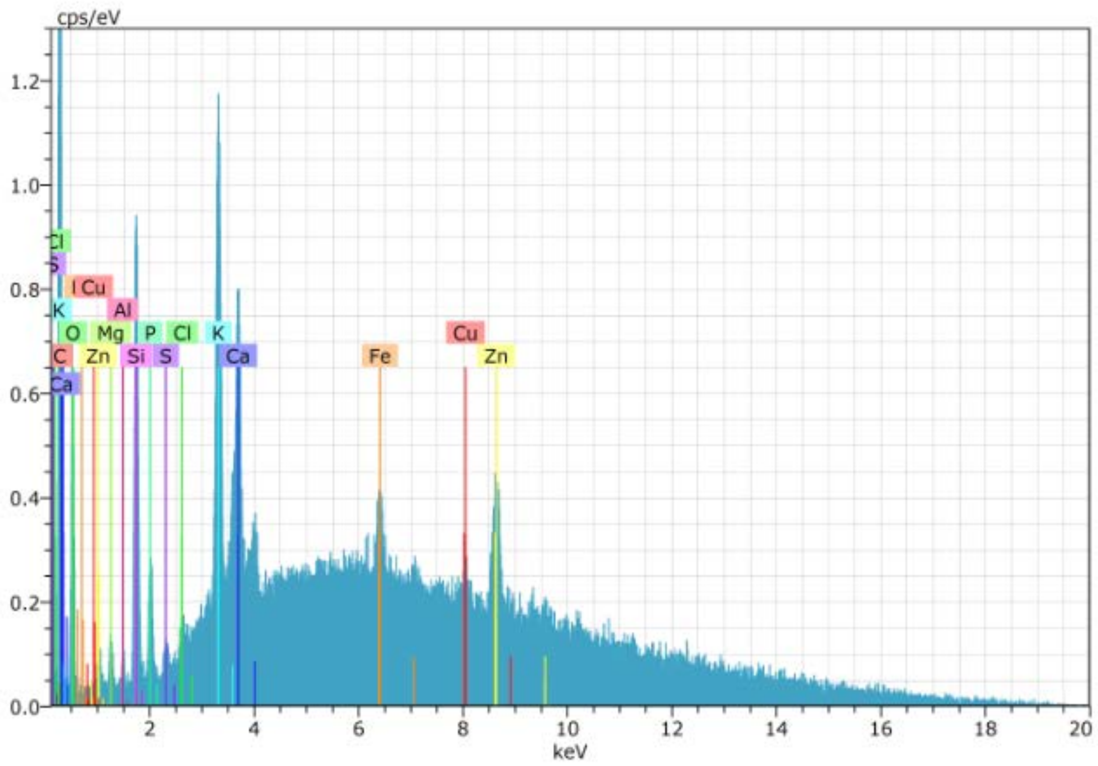
the isotherm models:

- **Langmuir,**
- **Freundlich.**

Desorption process

- application of the desorbing agents: HNO_3, HCl, H_2SO_4,
- studies of the dependence of desorption percentage on time using HNO_3.

Results



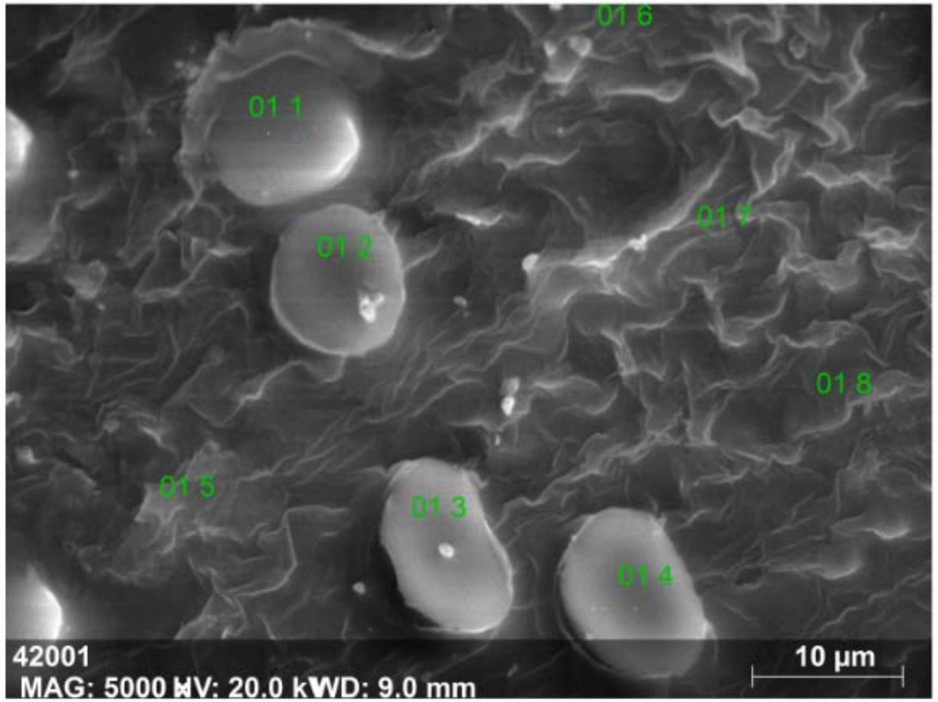


Fig.4. SEM-EDS analysis for BC.

- the analysis points out that biochar includes the following elements: C, Ca, O, K, Zn, Mg, Al, Si, P, S, Cl, Ca, Fe, Cu, Zn. These elements are typical of plant material.

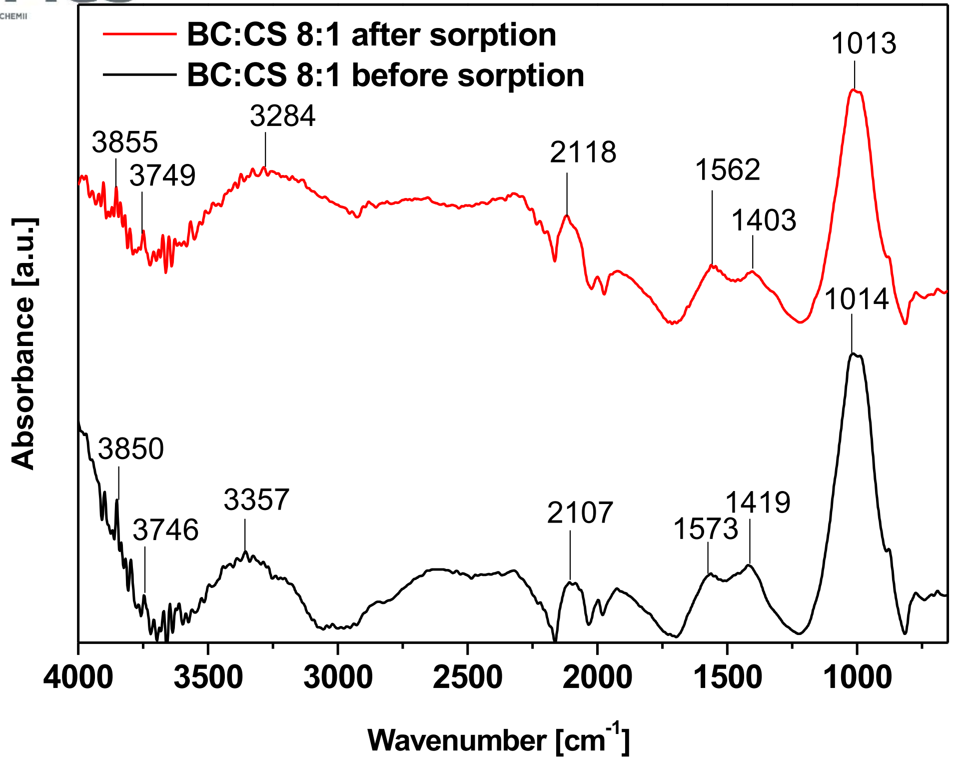


Fig.5. FTIR spectra of chitosan modified biochar (BC:CS 8:1) before and after sorption of ions from the mixture.

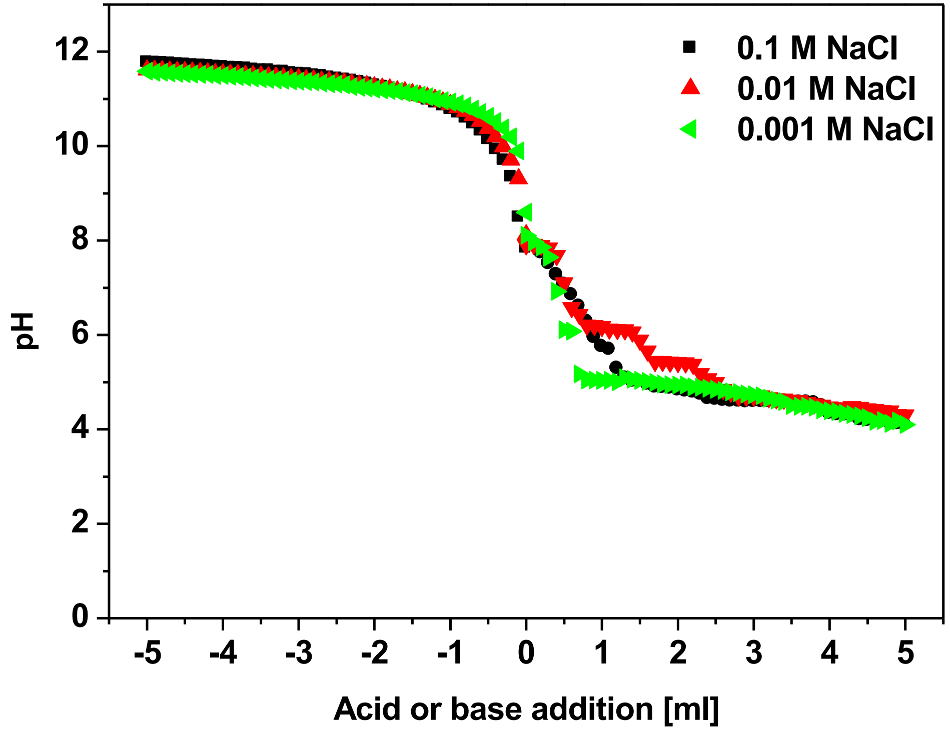


Fig.6. Point of zero charge of chitosan modified biochar (BC:CS 8:1).

- peaks at wavenumbers of 3850 to 3200 cm^{-1} are assigned to the stretching vibrations of -OH groups,
- from 3400 to 3200 cm^{-1} there appear the peaks associated with the –NH groups,
- peaks in the range 2500-2000 cm^{-1} evidence the presence of C≡C and C≡N bonds or cumulative double bonds of C=C=C i N=C=O,
- peaks in the range 1650-1550 cm^{-1} come from the stretching vibrations of asymmetric carboxyl groups,
- peaks at 1400 $cm^{-1}$are assigned to the presence of stretching vibrations of symmetric carboxyl groups,
- strong peaks at approximately 1014 cm^{-1}- bending off the plane of C-H bonds in the aromatic ring,
- the value of point of zero charge of chitosan modified biochar (BC:CS 8:1) is 8.58.

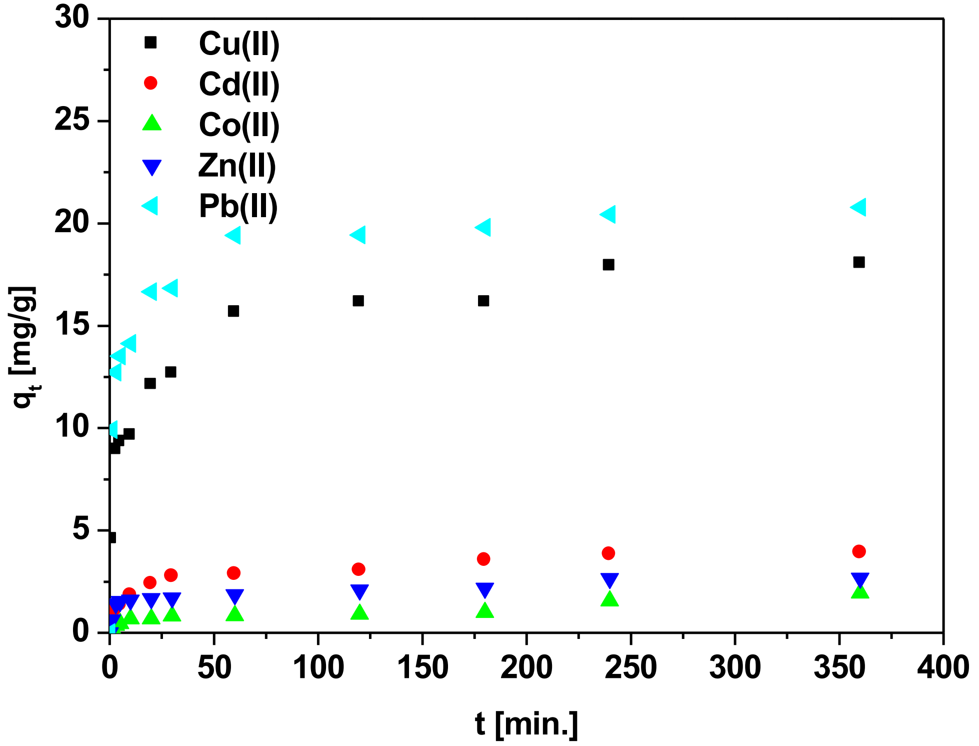


Fig.7. Effect of phase contact time on simultaneous sorption of heavy metal ions at the mass ratio of BC:CS 8:1 (t 1-360 min, C_0 100 mg/dm^3, pH 5, 180 rpm, 295 K).

Table 1. Summary of equilibrium capacities for simultaneous sorption of heavy metal ions for different mass ratios of BC to CS.

Heavy metal ions	BC:CS			
	1:1	2:1	4:1	8:1
	q_e [mg/g]			
Cu(II)	17.46	16.22	17.66	18.05
Cd(II)	2.91	2.59	2.88	3.92
Co(II)	1.77	1.52	1.83	1.95
Zn(II)	2.16	1.89	2.61	2.67
Pb(II)	20.37	17.78	19.85	20.78

- the range of heavy metal ions affinity is as follows: Pb(II) > Cu(II) > Cd(II) > Zn(II) > Co(II),
- the highest amounts of adsorbed ions were observed for the mass ratio of BC:CS 8:1.

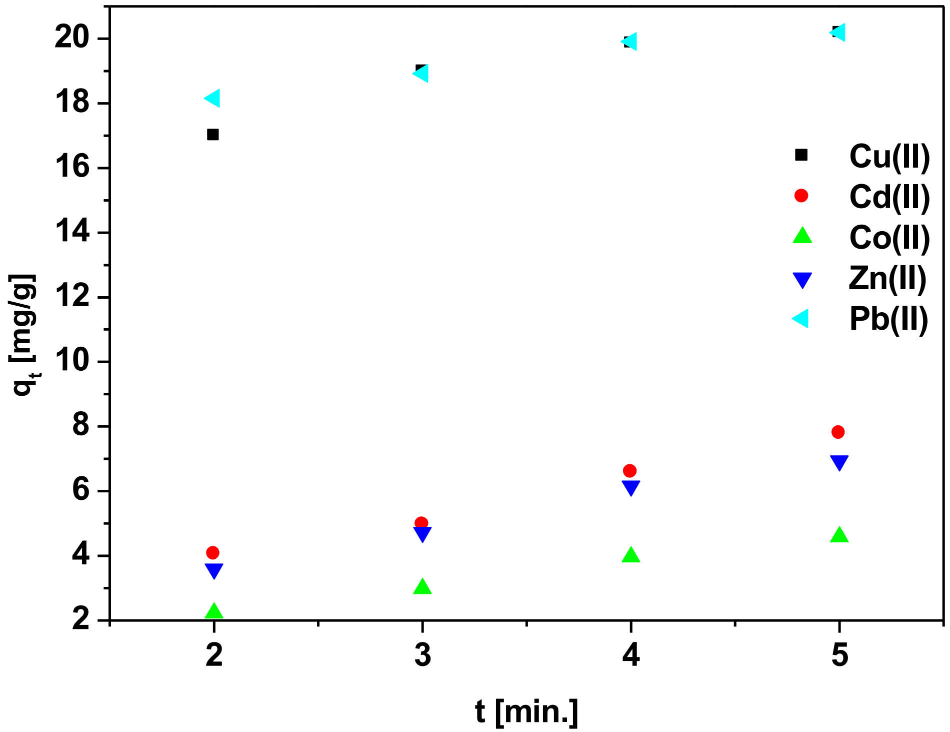


Fig.8. Dependence of equilibrium capacity on the initial pH for simultaneous heavy metals sorption at the mass ratio of BC:CS 8:1 (t 360 min, C_0 100 mg/dm^3, 180 rpm, 295 K).

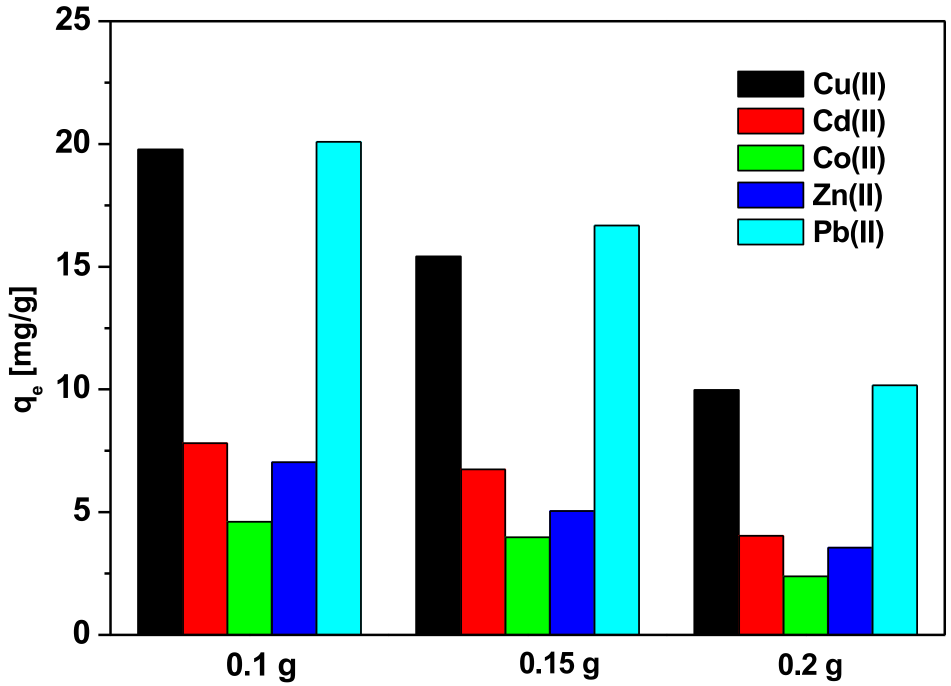


Fig.9. Dependence of the equilibrium capacity on mass sorbent for heavy metal simultaneous sorption on BC:CS 8:1 BC (t 360 min., C_0 100 mg/dm^3, pH 5, 180 rpm, 295 K).

- the sorption efficiency increases with the increasing pH and the highest value is reached at pH 5 because this pH value was chosen for further research,
- at pH 2, the amount absorbed is very low due to competition with oxides on the sorbent surface,
- the optimum sorbent weight for sorption of heavy metals is 0.1 g.

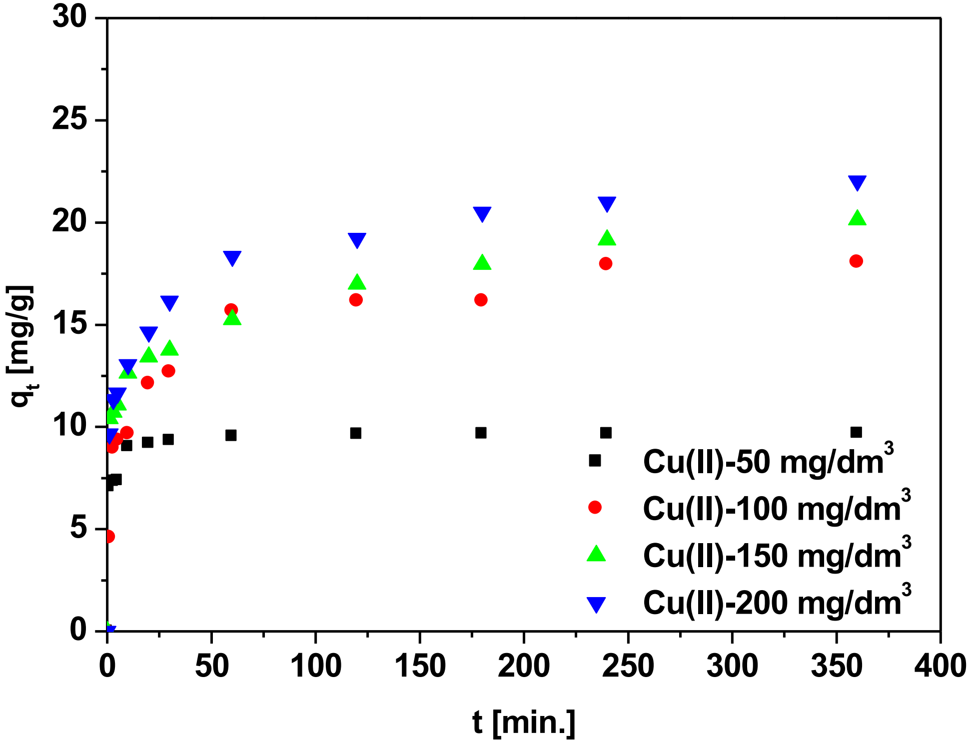


Fig.10. Effect of phase contact time and initial solution concentration on Cu(II) ions from the mixture sorption at the BC:CS ratio 8:1 (t 1-360 min, C_0 50-200 mg/dm^3, pH 5, 180 rpm, 295 K).

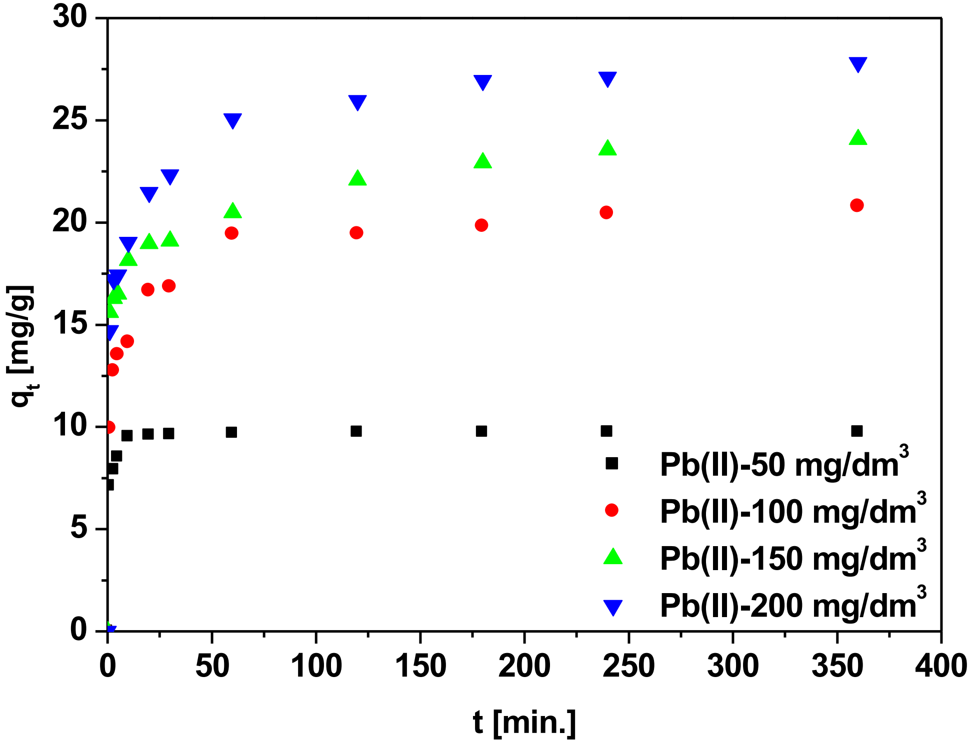


Fig.11. Effect of phase contact time and initial solution concentration on Pb(II) with mixture ions sorption on BC:CS 8:1 (t 1-360 min, C_0 50-200 mg/dm^3, pH 5, 180 rpm, 295 K).

- the amount of adsorbed Cu(II) and Pb(II) ions increases with the increasing phase contact time and initial concentration of solution,
- the lower the initial concentration, the faster the balance is reached. At an initial concentration of 50 mg/dm^3, the equilibrium is reached after about 30 minutes, and for a concentration of 200 mg/dm^3, after 180 min,
- comparing the values of q_t, it can be stated that Pb(II) sorption on the obtained sorbent is more efficient than Cu(II) sorption.

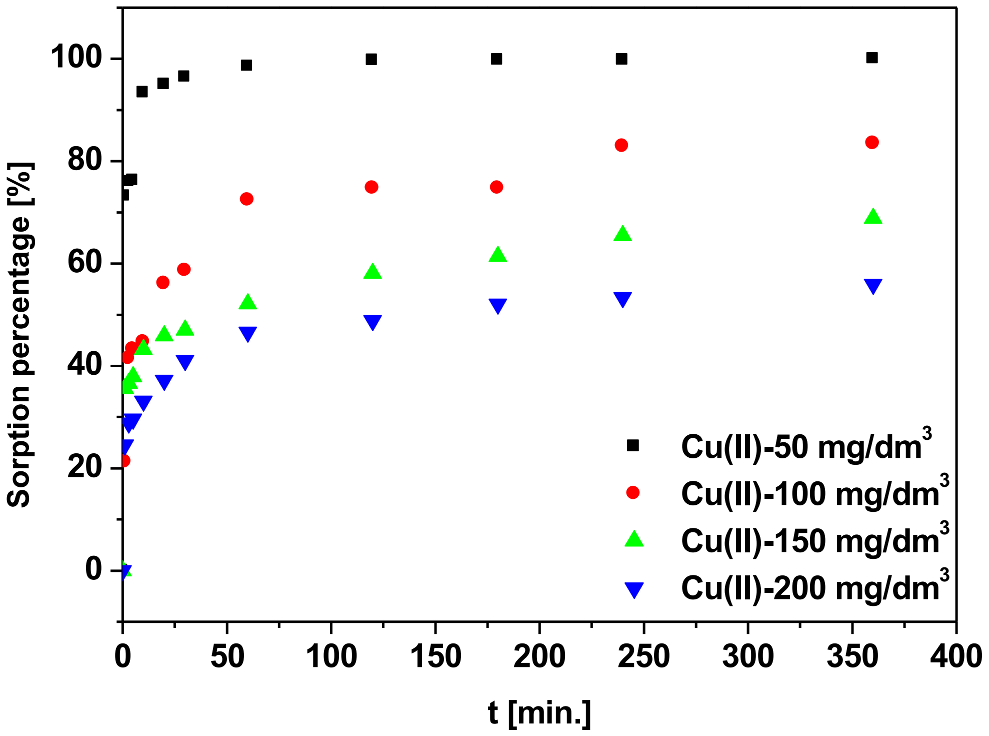


Fig.12. Relationship of sorption percentage from the initial concentration for Cu(II) sorption from mixture at the BC:CS ratio 8:1 (t 360 min., C_0 50-200 mg/dm^3, pH 5, 180 rpm, 295 K).

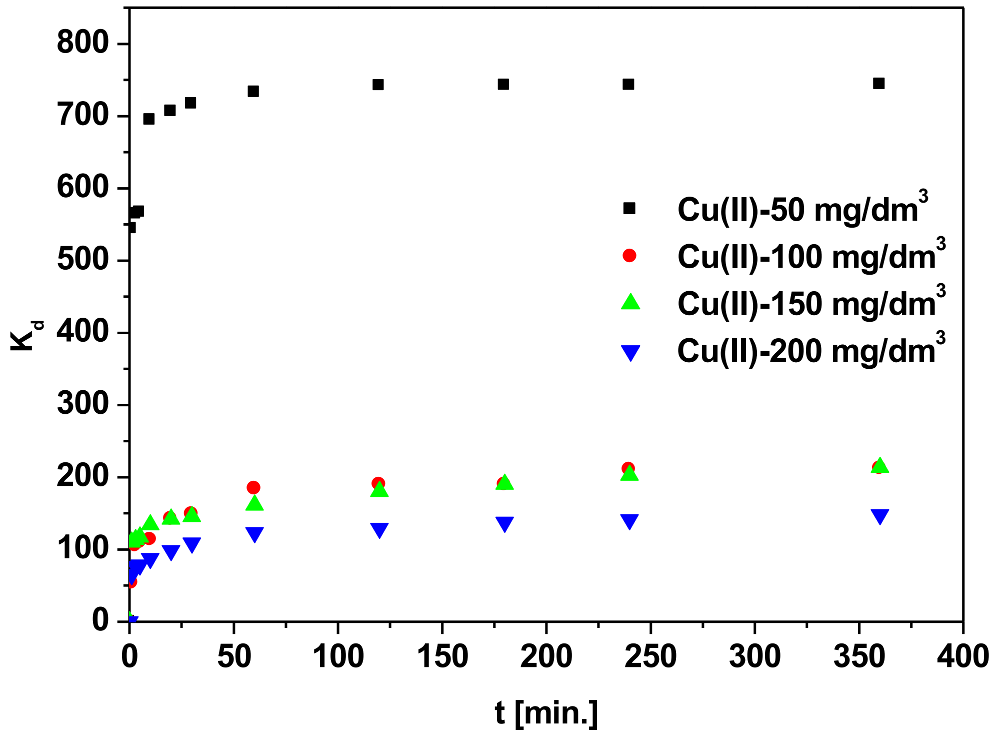


Fig.13. Dependence of the partition coefficient K_d on time for Cu(II) sorption from mixture at the BC:CS ratio 8:1 (t 360 min., C_0 50-200 mg/dm^3, pH 5, 180 rpm, 295 K).

- the percentage of sorption and partition coefficient values increase with the increasing phase contact time and gradually reach a constant value,
- the percentage of sorption and partition coefficient values decrease as the concentration of the initial solution increases.

Tabela 2. Kinetic data for Cu(II) sorption from mixture at the BC:CS ratio 8:1.

c_0 [mg/dm^3]	q_{exp}	Parametry									
		PFO $\log(q_1 - q_t) = \log(q_1) - \frac{k_1 t}{2.303}$			PSO $\frac{t}{q_t} = \frac{1}{k_2 q_2^2} - \frac{t}{q_2}$				IPD $q_t = k_i t^{1/2} + C$		
		q_1	k_1	R^2	q_2	k_2	h	R^2	k_i	C	R^2
50	9.67	1.12	0.021	0.835	9.69	0107	10.071	1.000	0.703	4.227	0.859
100	18.05	9.72	0.015	0.869	18.19	0.006	2.074	0.997	0.817	4.350	0.805
150	20.14	8.89	0.009	0.983	20.02	0.005	2.069	0.995	0.950	7.260	0.954
200	22.03	9.66	0.008	0.955	22.01	0.005	2.688	0.998	1.381	8.590	0.982

- the k_1 and k_2 reaction rate parameters slightly decrease as the initial concentration increases, indicating that the reaction speed decreases with the increasing concentration,
- the reaction speed parameter k_i and the parameter C determining the effect of the boundary layer on the sorption process increase with the increasing initial concentration of the solution which proves that the sorption process is a step limiting the reaction rate,
- comparing the detemination coefficient R^2, it can be concluded that the Cu(II) sorption process follows the pseudo second order model (> 0.99).

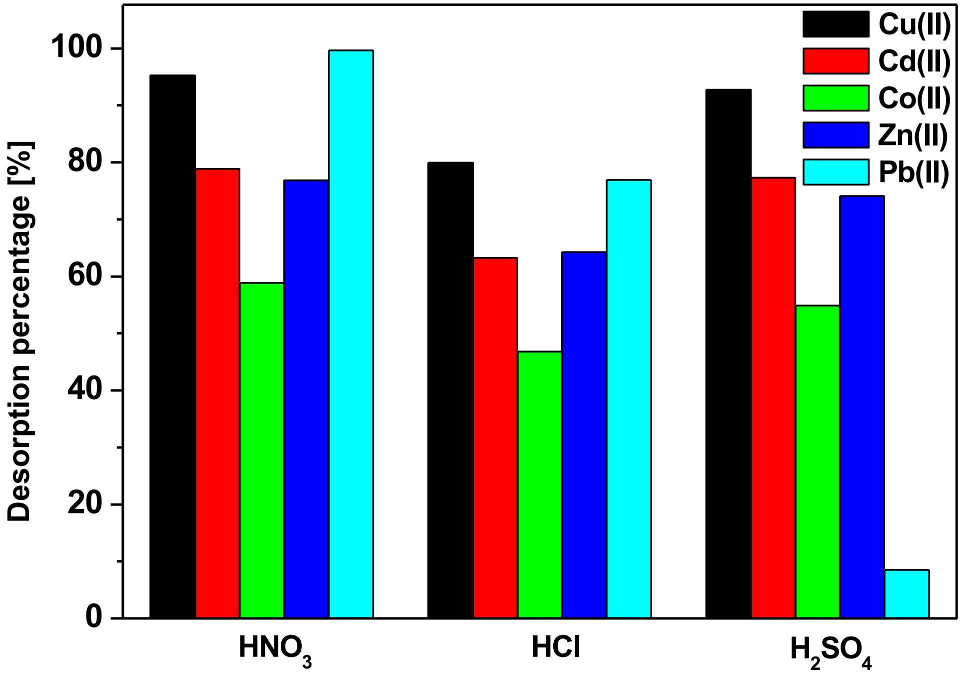


Fig.14. Dependence of heavy metal ions desorption capacity on the acid at the BC:CS ratio 8:1 on the desorption agents: HNO_3, HCl and H_2SO_4 at 1 mol/dm^3 concentration.

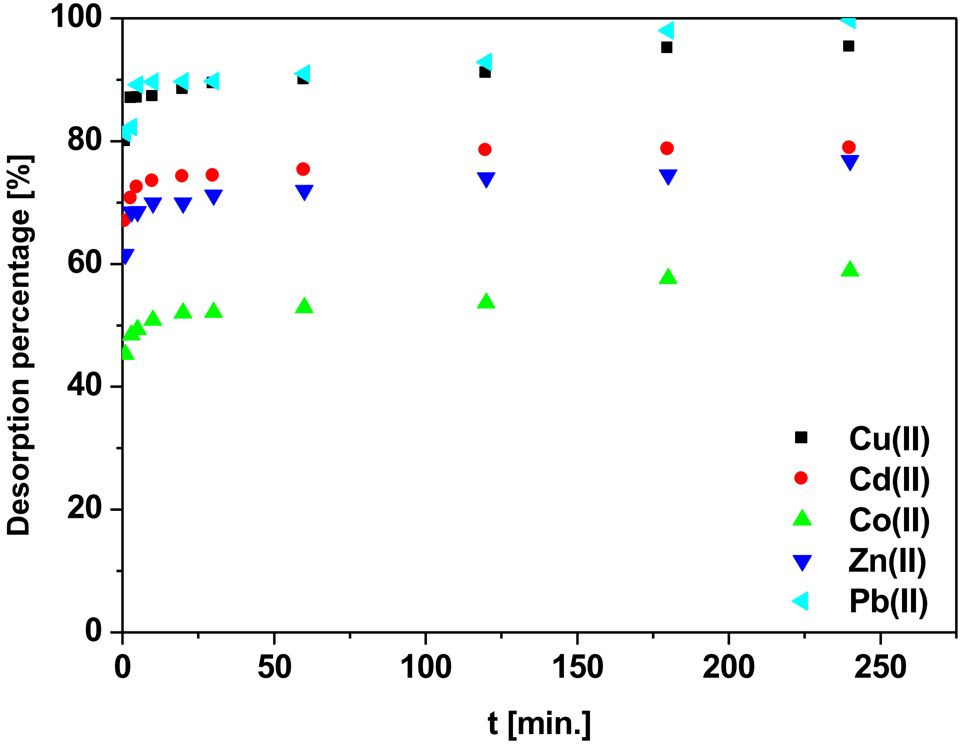


Fig.15. Effect of phase contact time on the desorption efficiency of Cu(II), Cd(II), Co(II), Zn(II) and Pb (II) ions deposited on BC:CS 8:1.

- the best desorption efficiency was obtained using nitric acid, so it was chosen for further desorption kinetics,
- Pb(II) ions adsorbed on the above sorbent are the easiest to wash while Co(II) ions are the most difficullt,
- the use of acidic desorbing agents results in appearance of the additional functional groups.

Sorption mechanism

Coinsidering the sorption mechanism it can be concluded that carboxyl, hydroxyl and phenolic groups are the main groups contributing to the coordination of metal ions on the surface of biochar in accordance with the equations:

$$R\text{-}COOH + M^{n+} \rightarrow R\text{-}COOM^{n+} + H^+$$
$$R\text{-}OH + M^{n+} \rightarrow R\text{-}OM^{n+} + H^+$$

Studies of sorption of heavy metal ions on chitosan have demonstrated that the amine functional groups of chitosan could immobilize various metal ions, from aqueous solution through chelation of amine functional groups as follows from the equation:

$$RNH_2 + M^{n+} \rightarrow [RNH_2\text{-}M]^{n+}$$

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Conclusions

- The simultaneous sorption of Cu(II), Zn(II), Cd(II), Co(II) and Pb(II) ions on chitosan modified biochar was the highest at pH 5 and the sorbent mass 0.1 g. The amount of adsorbed q_t increases with the increasing phase contact time and initial concentration of the solution. *%S* and K_d values increase with the increasing phase contact time and decrease as the initial solution concentrations increase.
- Comparing the sorbents with different biochar to chitosan ratios, the highest amounts of adsorbed ions were observed for the mass ratio of BC:CS 8:1.
- The determined kinetic parameters of the process indicate that it follows a typical pseudo secondary reaction mechanism. The state of equilibrium is determined after approximately 30 min. for the initial concentration 50 mg/dm^3 and approximately 180 min. for 200 mg/dm^3.
- The affinity of the above mentioned metal ions is as follows:

  Pb(II) > Cu(II) > Cd(II) > Zn(II) > Co(II)
- The most preferred washing agent is nitric acid Pb(II) ions are the easiest to be washed whereas Co(II) ions are the most difficult.

Thank you for your attention