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THE PRELIMINARY ADSORPTION INVESTIGATION OF *URTICA DIOICA* L. BIOMASS MATERIAL AS A POTENTIAL BIOSORBENT FOR HEAVY METAL IONS

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ABSTRACT. The removal of Cu(II) ions from aqueous solutions by adsorption onto nettle after incomplete incineration (IIN) has been studied in batch mode. The experimental isotherm results have been fitted using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich equations. A comparison of kinetic models applied to the adsorption of Cu(II) ions on the adsorbent was evaluated for the pseudo-first order, the pseudo-second order and Elovich kinetic models. The pseudo-second order kinetic model was found to correlate the experimental data well. To evaluate competitive adsorption the batch experiments were carried out among the Cu(II), Pb(II) and Cd(II). The affinity order for the ternary system was Pb(II) > Cu(II) > Cd(II). FTIR and SEM analysis indicated that IIN could be used as an efficient biosorbent whose chemical structure and morphology is not altered during adsorption process.

Keywords: *biosorption, heavy metals, kinetic study, thermodynamic study, Urtica dioica L.*

INTRODUCTION

Heavy metal pollution has become one of the biggest problems in the context of environmental pollution due to their solubility, mobility and ability to accumulate in the soil. Wastes with high content of metals directly or indirectly discharged into the environment which causes its pollution. [1]

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Chemical vapor deposition and electrochemical treatment are not effective for highly diluted solutions and produce a large amount of sludge. On other side, ion exchanges, as well as technology based on purification by membrane, belong to expensive technology.

All rigorous standards of allowable concentrations of contaminants and environmental protection have caused the quest for better and cheaper methods of purification of polluted water. For this purpose, develop various kinds of substances capable to adsorb pollutants. As a particularly significant adsorbent must be mentioned activated charcoal. Activated carbon can be produced starting from different precursors such as peat, wood, stone fruits, etc. [2-6]

The maximum allowed concentration of copper for drinking water which is regulated by the United States Environmental Protection Agency in 2010 is 1.3 mg dm^{-3}. [1]

Lead belongs to the group of the highly toxic elements, with a cumulative-toxic effect. Prolonged exposure to low-level toxicity (< 240 µg dm^{-3}) can lead to various psychological disorders and learning disabilities among children.

Cadmium is one of the most dangerous poisons of the working and living environment. Once it enters the body, cadmium is transported into the blood by red blood cells and a highly molecular blood protein – albumin. The maximum allowed concentration for drinking water which is regulated by the United States Environmental Protection Agency in 2010 is 5×10-3 mg dm^{-3}. [1]

Heavy metal adsorption onto some biomass, such as nettle, grapevine, marigold, linden, geranium, chestnut and maple naturally dried [7], Salvinia [8], Ludwigia stolonifera [9], Urtica dioica and Sedum spectabile [10], nettle [11,12], Neem leaves [13].

Nettle is traditionally used as a medicinal plant. In modern phytotherapy are known different preparations based on nettles. Medicinal raw materials are leaves and above-ground part.[14] In the literature, is also known that this plant is used for phytoremediation. In several studies authors used a nettle ash as a low cost adsorbent for the removal heavy M(II) metals from aqueous solution. [11,12,15-17]

The aim of this study was to show that the product of incomplete combustion obtained from a disused plant material nettle can be used as a potentially inexpensive and readily available biosorbent for the removal of heavy metals from aqueous solutions. A model system for studying the biosorption was a solution of M(II) metal ions (Cu, Pb and Cd) concentration in the range of maximum concentration that could occur in polluted waters from the surrounding city of Nis due to industrial processes. The effect of various experimental parameters such as contact time, initial Cu(II) concentration, biosorbent dosage and metal ions competition has been investigated. The equilibrium data were fitted to Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models, while the kinetics data were correlated according to various kinetics models (pseudo-first order, pseudo-second-order and Elovich model).

RESULTS AND DISCUSSION

FTIR characterization of nettle biosorbent

FTIR spectra of raw nettle, after incomplete combustion, such as complete combustion and after adsorption treatment are given in Figure 1.

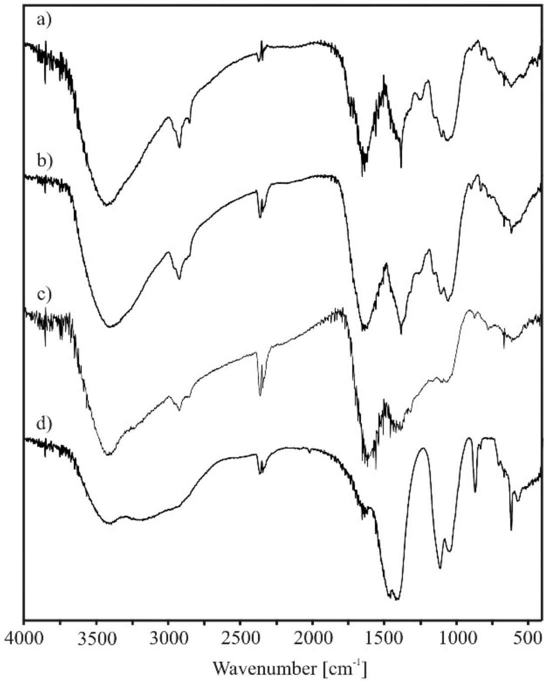

Figure 1. FTIR spectra of: a) raw nettle, b) after incomplete incineration nettle, c) after Cu(II) adsorption treatment and d) after complete incineration

The spectrum of raw nettle shows characteristic adsorption bands for a plant material (Fig. 1a). A broad band between 3200 and 3600 cm^{-1} attributed to the hydroxyl groups in phenol and aliphatic structures, bands centered around 2920 cm^{-1}, predominantly arising from CH stretching in –CH$_3$ or

$–CH_2–$ groups, a band at 1640 cm^{-1} indicates the fingerprint region of CO, C–O and O–H groups. The band at 1383 cm^{-1} corresponding to C-O stretching. The region between 1250 and 1000 cm^{-1} is the fingerprint region, OH, and C-H bending vibration and C-O stretching vibration absorption bands. The intense band at 1061 cm^{-1} can be assigned to the C-O of alcohols and carboxylic acids. Bands in the region from 700 to 400 cm^{-1} are attributed to halogen compounds. [18-23] In the FTIR spectrum of incomplete burning/ incineration nettle shown in Fig. 1b there is no significance changes compared to spectrum of raw plant material, which indicates that it is made incomplete incineration of plant, and all organic functional groups are put on hold. After completed incineration in oven (500-600 °C) all organic matter (functional group) were removed from nettle, which are confirm with presentation of inorganic biomineral bands in FTIR spectra: 3400-3100 cm^{-1} Si-OH vibrations; 1636 cm^{-1} calcium oxalate; 1456 and 1419 cm^{-1} asymmetric calcite stretching; 1112 and 1052 cm^{-1} biogenic silica; 870 cm^{-1} out of plane deformation calcite; 618 cm^{-1}, halogenides (Fig. 1d). [24]

The FTIR spectra for the copper loaded biosorbent (Fig. 1c) showed wavenumbers and intensity of some peaks that were shifted or substantially lower than those before biosorption. A band assigned to O–H stretching vibrations showed a decrease in intensity and shift from 3420 to 3428 cm^{-1} probably indicating copper ions interacted with hydroxyl groups. A shifting of band from 1640 cm^{-1} to 1623 cm^{-1} indicates involvement of CO, C–O and O–H groups in copper(II) binding. The band corresponding of C-O stretching was shifted to 1450 cm^{-1}, and the bands from region of 1250 and 1000 cm^{-1} showed a decrease in intensity (practically disappear in the spectrum), which also suggests the involvement of C–O and -OH group in binding copper(II) ions. [21,23]

SEM-EDX characterization of nettle biosorbent

The morphological characteristics of biosorbent surfaces were examined by scanning electron microscopy (Fig. 2). It can be observed that material is of fibrous and stripes structure which is characteristic for cellulosic material. After incomplete incineration nettle structure became uneven rugged and porous. These structure characteristics allow better diffusion of solution and probably increase possibility for investigated metal ions to penetrate into the biosorbent and their adsorption onto numerous active sites of biosorbent. There are no differences in the biosorbent structure before and after copper adsorption, and the presence of adsorbed metal ion with SEM cannot be verified due to scale of this micrographs and the dimension of copper ion.

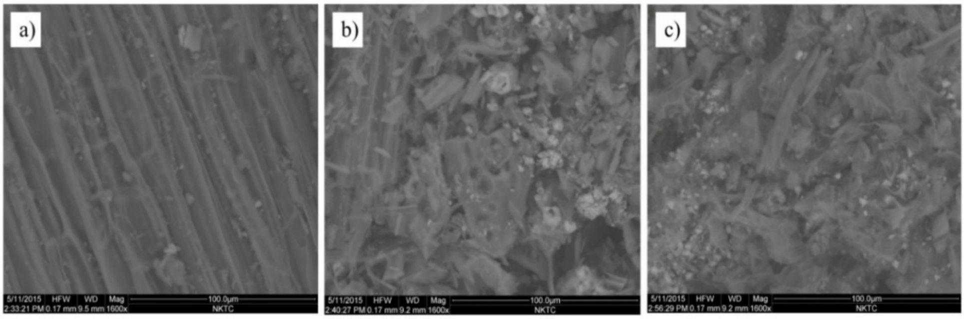

Figure 2. SEM micrographs of: a) raw nettle, b) after incomplete incineration nettle and c) after Cu(II) adsorption treatment

EDX analysis of a raw nettle, after incomplete incineration nettle (hereafter IIN) and after biosorption of Cu(II) ions was shown in Figure B. This analysis provides information about elemental content of investigation biomaterial. The presence of C (wt% ca. 60), O (wt% ca. 23) and K (wt% ca. 14) as major elements and other minor elements (P, S, Cl, Mg, and Ca) indicate the chemical composition characteristic for plant material (Fig. 3a). Increase peak intensity (pi) from 1030 to 1740 and weight percent from 60% to 68% for C; and decrease the same parameters for O (pi: from 330 to 240; and wt: from 23 wt% to 14%) compared to untreated nettle indicate incomplete burning treatment of biomaterial (Fig 3b). The presence of peak of copper (Fig 3c) indicate the adsorption of the metal ion to the surface of the nettle biosorbent.

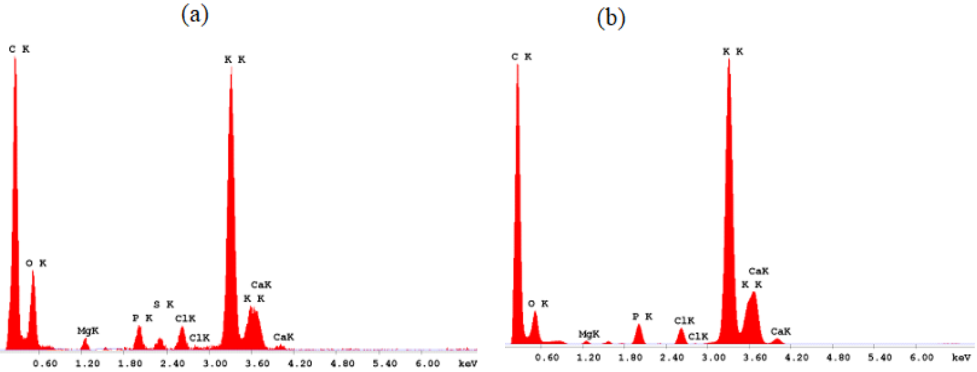

Figure 3. EDX spectra of: a) raw nettle, b) after incomplete incineration of nettle

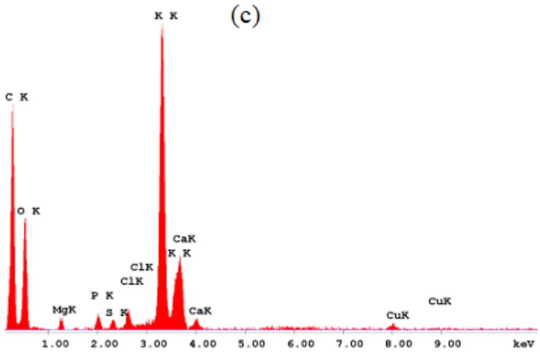

Figure 3. EDX spectra of c) after Cu(II) adsorption treatment

Effect of biosorbent type on adsorption process

The effect of contact time on the residual concentration of Cu(II) ions in aqueous solution with raw nettle and nettle after incomplete incineration is shown at Fig. 4.

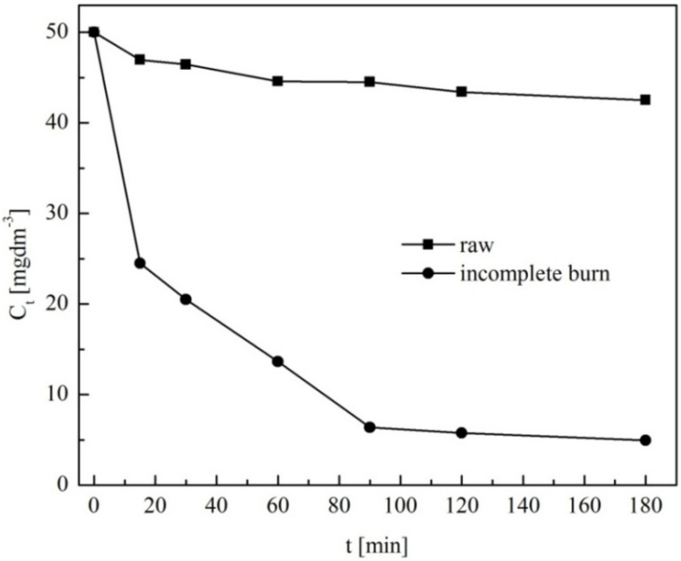

Figure 4. Effect of contact time on removal Cu(II) by raw nettle and nettle after incomplete incineration (initial Cu(II) concentration 50 mg dm^{-3}, temp. 20±0.5 °C, pH 5.0±0.1, biosorbent dose 4.0 g dm^{-3})

Experiments were performed with model wastewaters containing Cu(II) ions at an initial concentration of 50.0 mg dm^{-3}, a biosorbent dose of 4.0 g dm^{-3}, at 20±0.5°C and pH 5.0. These results indicate that raw nettle is not efficient biosorbent, but after incomplete incineration it became a very efficient biosorbent for removal Cu(II) ions from wastewater. The concentration of copper declined sharply with contact time in the first 10 min, then decreased slightly to 90 min, and after that reached equilibrium. The initial fast phase occurs due to a high availability of the number of active binding sites (functional groups) on the biosorbent surface, and it is typically controlled by the diffusion process from the solution to the surface. A further increase in contact time did not show a significant decrease of Cu(II) concentration, which occurs due to diffusion of the copper ions into the inner part of the biomass. [21]

Effect of initial Cu(II) concentration

The influence of initial Cu(II) concentration on pollutant removal from aqueous solution by INN (4.0 g dm^{-3}) was studied in the concentrations range from 10.0 to 200.0 mg dm^{-3} at 20±0.5 °C and pH 5.0±0.1. The effect of initial Cu(II) concentration on removal efficiency is shown in Fig. 5.

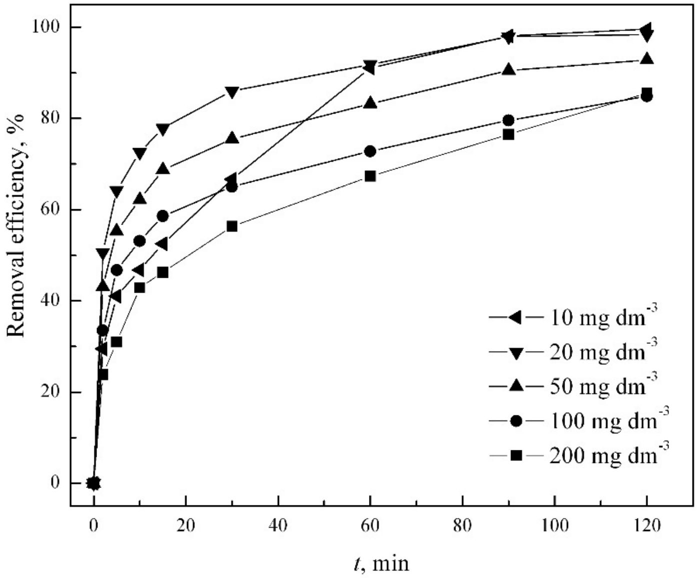

Figure 5. Effects of initial Cu(II) concentration on removal Cu(II) by IIN (initial Cu(II) concentration 10.0-200.0 mg dm^{-3}, temp. 20±0.5 °C, pH 5.0±0.1, biosorbent dose 4.0 g dm^{-3})

The initial copper concentration is a driving force to overcome mass transfer resistance for metal ion transport between the solution and the surface of the adsorbent. The amount of Cu(II) uptake increased by increasing the initial Cu(II) concentration (Table 1), but adsorption percentages decrease with increase in the Cu(II) concentration. At low concentrations of copper(II) ions, greater availability of the exchangeable sites on the surface area interact with all adsorbate ions present in the solution more rapid reaching the almost 100% adsorption. On the other side saturation of the available active sites on the surface functional groups prevent further copper ion uptake with increase of Cu(II) concentration. [11]

Effect of biosorbent dosage

Batch experiments were performed at different biosorbent dosage ranging from 1.0 to 8.0 g dm^{-3} in contact with model waste waters containing Cu(II) ions at an initial concentration of 50.0 mg dm^{-3} at 20±0.5 °C and pH 5.0±0.1. The influence of biosorbent dosage on removal efficiency is shown in Fig. 6.

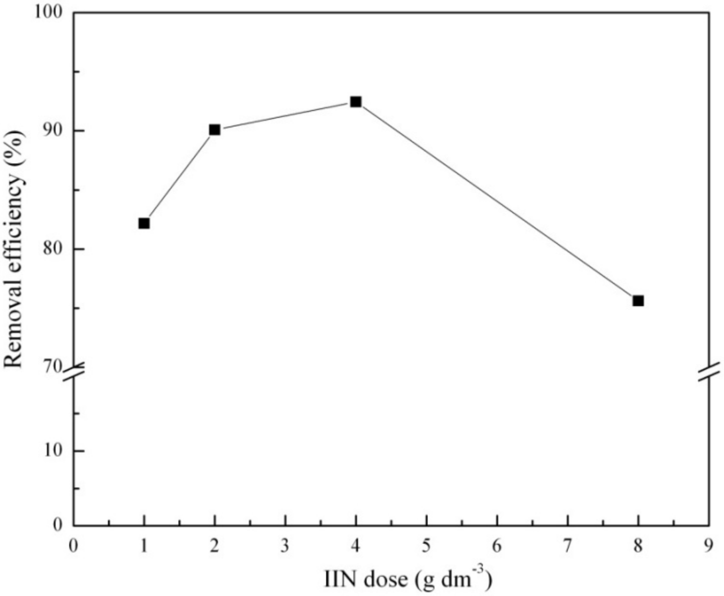

Figure 6. Effect of biosorbent dosage in a removal of Cu(II) ions (initial Cu(II) concentration 50.0 mg dm^{-3}, temp. 20±0.5 °C, pH 5.0±0.1)

The biosorbent dosage determines the capacity of a biosorbent for a given initial concentration. The biosorption efficiency for Cu(II) ions as a function of biosorbent dosage was investigated. The efficiency of biosorption sharply increases with the biosorbent loading up to 4.0 g dm^{-3}. This result can be explained by the fact that the biosorption sites remain unsaturated during the biosorption because the number of sites available for biosorption increases by increasing the biosorbent dosage. [21] However, the copper uptake decreased when the biosorbent concentration exceeded 4.0 g dm^{-3}. For the optimum biosorbent dosage 4.0 g dm^{-3} was taken. This dosage showed the highest removal efficiency as shown in Figure 6.

Sorption kinetics

Kinetics studies provide information on the rate of the sorption metal uptake which is very important for biosorption process design. [25]

Pseudo-first-order model

The pseudo-first order rate equation is represented in logarithmic form as: [26]

$$\ln(q_e-q_t)=\ln q_e-kt \tag{1}$$

where q_e is the mass of metal ions adsorbed at equilibrium (mg g^{-1}), q_t is the mass of metal adsorbed at time t (mg g^{-1}), and k is the pseudo-first order reaction rate equilibrium constant (min^{-1}).

A straight line of $\ln(q_e-q_t)$ vs t indicates that the pseudo-first order kinetics model should be applied. However, in a true pseudo-first order process, $\ln q_e$ should be equal to the intercept and k equal to the slope of plot of $\ln(q_e-q_t)$ against t, respectively.

Pseudo-second-order model

The pseudo-second-order equation based on equilibrium adsorption can be expressed in linearized form as [27]

$$\frac{t}{q_t}=\frac{1}{k_2q_e^2}+\frac{1}{q_e}t \tag{2}$$

where k_2 is the pseudo-second order reaction rate equilibrium constant (g mg^{-1} min^{-1}). For the applicability of the pseudo-second-order kinetics model a plot of t/q_t against t should give a linear relationship.

Table 1. Pseudo-first, pseudo-second-order and Elovich model parameters for biosorption of Cu(II) ions using IIN

	Concentration Cu(II), mg dm^{-3}				
	10.0	**20.0**	**50.0**	**100.0**	**200.0**
q_e^{exp}	2.49	4.92	11.60	21.22	42.81
Pseudo-first model					
k_1	0.0359	0.0485	0.0338	0.0256	0.0312
q_e	2.11	2.80	6.64	12.52	15.53
R^2	0.9941	0.9644	0.9665	0.9560	0.5907
Pseudo-second model					
k_2	0.0296	0.0527	0.0161	0.0070	0.0075
q_e	2.76	5.04	11.91	21.65	43.40
R^2	0.9950	0.9995	0.9987	0.9974	0.9990
Elovich model					
β	2.1277	1.7146	0.6629	0.3353	0.1547
α	0.7681	27.1794	27.5691	26.088	25.749
R^2	0.9783	0.9957	0.9987	0.9970	0.9449

The values of $q_{e,exp}$ and the $q_{e,cal}$ from the pseudo-second-order kinetic model were very close to one another. The calculated coefficients of determination for pseudo-second-order kinetics (R^2) were closer to 1 than coefficient for the pseudo-first-order kinetics. Overall conclusion is that the pseudo second-order mechanism is predominant and that the adsorption process of the copper(II) ions is most likely to be controlled by the chemisorption process. [11,12]

Elovich model

The Elovich model describes many of reaction mechanisms including bulk and surface diffusion and the activation and deactivation of catalytic surfaces: [28]

$$q_t = \frac{1}{\beta}(\ln\alpha\beta) + \frac{1}{\beta}\ln t \tag{3}$$

where α is the initial adsorption rate (mg g^{-1} min^{-1}), and β is the desorption constant (g mg^{-1}). If the Elovich equation is applicable with a slope of (1/β) and an intercept of (1/β)ln(αβ), plot of q_t versus ln$t$ should give a linear relationship.

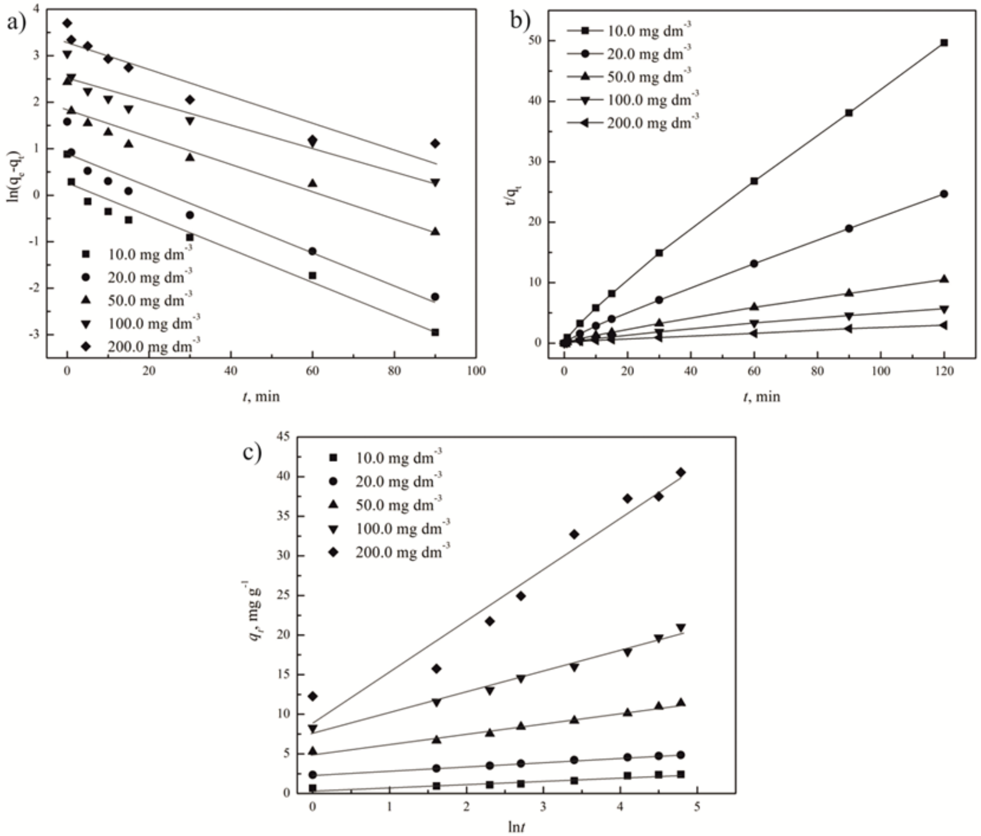

Figure 7. Kinetic models a) pseudo-first, b) pseudo-second, c) Elovich

Fig. 7c depicts a plot of the Elovich equation for the investigated data. In this case, a linear relationship between Cu(II) biosorbed, q_t and *lnt* was not obtain for overall concentration range. However, good correlation with the Elovich model was observed for initial copper(II) concentrations of 20.0 mg dm^{-3}, 50.0 mg dm^{-3} and 100.0 mg dm^{-3} with determination coefficients of 0.9957, 0.9987 and 0.9970, respectively. Table 1 lists the kinetic constants obtained from the Elovich equation. It can be observed that with increasing the initial copper(II) concentration from 10.0 to 200.0 mg dm^{-3} the value of β decreased from 2.1277 to 0.1547. Nevertheless, the determination coefficients obtained from Elovich equation are lower than those calculated from the pseudo-second-order equation.

Adsorption isotherms

Adsorption isotherm is a graphical representation that maps the distribution of adsorbable solute between the liquid and solid phases at various equilibrium concentrations. [29] The adsorption isotherm data have been got by varying the initial metal concentration while the other parameters are kept constant. Besides to the Langmuir and Freundlich isotherm models, which are commonly used in describing adsorption, the experimental data were fitted to the Temkin and Dubinin-Radushkevich isoterm models.

Langmuir isotherm model

This isotherm model describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thus, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases. [30] The Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions. [31] Based upon these assumptions, Langmuir represented the following equation:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{4}$$

The Langmuir parameters can be determined from a linearized form, by plotting C_e/q_e vs. C_e:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} C_e \tag{5}$$

where C_e is the equilibrium concentration of adsorbate (mg dm^{-3}), q_{max} is the Langmuir equilibrium constant related to maximum monolayer coverage capacity (mg g^{-1}), and K_L is the Langmuir constant which is related to the enthalpy of adsorption (dm^{-3} mg^{-1}).

The values of q_{max} and K_L were calculated from the slope and intercept of the Langmuir plot of C_e/q_e vs. C_e. [31] This is the most often used isotherm applied for explaining the adsorption equilibrium. However, the Langmuir isotherm offers no insights into the mechanism aspects of biosorption. [32]

Freundlich isotherm model

This is commonly used to describe the adsorption characteristics for the heterogeneous surface. It is represented by the equation: [33]

$$q_e = K_F C_e^{\frac{1}{n}} \tag{6}$$

where K_F is Freundlich isotherm constant (mg g^{-1}), and n is adsorption intensity.

This model assumes that the uptake of metal ions occurs by multilayer adsorption where the stronger binding sites are occupied first and the binding strength decreases with increasing degree of site occupation. [34,35] This reason it is more indicative for the physical mechanism of adsorption.

Freundlich empirical adsorption isotherm equation can be expressed in the logarithmic, linear form as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{7}$$

The constant K_F is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process. [36] If n = 1 then the partition between the two phases are independent of the concentration. If value of 1/n is below one it indicates a normal adsorption. On the other side, 1/n being above one indicates cooperative adsorption. [37] 1/n is a heterogeneity parameter, the smaller 1/n, the greater heterogeneity should be expected. This expression reduces to a linear adsorption isotherm when 1/n = 1. If n lies between 1 and 10, this indicates a favorable sorption process. [38]

Temkin isotherm model

This isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. [30,31,34] This equation implies that the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. [39] The model is given by the following equation: [30,31]

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \tag{8}$$

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \tag{9}$$

where A_T is Temkin isotherm equilibrium binding constant ($dm^3\ g^{-1}$) which corresponds to the maximum binding energy, b_T is Temkin isotherm constant related to heat of sorption ($J\ mol^{-1}$), R is universal gas constant ($8.314\ J\ mol^{-1}K^{-1}$), and T is absolute temperature (K).

Dubinin–Radushkevich isotherm model

The Dubinin-Radushkevish isotherm was chosen to estimate the characteristics porosity of the biomass and the apparent energy of adsorption. [40] Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. [41,42] The model has often successfully fitted high solute activities and the intermediate range of concentrations data well. The model is represented by the equation below:

$$q_e=(q_s)\exp(-K_{ad}\varepsilon^2) \tag{10}$$

$$\varepsilon=\left[RT\ln\left(1+\frac{1}{C_e}\right)\right] \tag{11}$$

where q_s is theoretical isotherm saturation capacity ($mg\ g^{-1}$), K_{ad} is Dubinin - Radushkevich isotherm constant ($mol^2\ kJ^{-2}$), and ε is Dubinin–Radushkevich isotherm constant.

Dubinin–Radushkevich isotherm equation can be expressed in the logarithmic, linear form as:

$$\ln q_e=\ln q_s-K_{ad}\varepsilon^2 \tag{12}$$

Table 2 shows the isotherm parameters for Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The fitting of the data to the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms shows that the biosorption of Cu(II) ions by IIN follows Freundlich model better than the others based on the coefficients of determination (R^2). This phenomenon suggests that multilayer sorption takes place on the surface of biomass. KF and n were calculated from the slope of the Freundlich plot and were found to be 5.2588 L mg-1 and 1.8468, respectively. The value of KF and n shows high adsorption capacity i.e. easy separation of heavy metal ions from wastewater. The fact that the magnitude of n (which is related to the distribution of bonded ions on the sorbent surface) is greater than 1 represents that adsorption of Cu(II) is favorable. [11,12,23]

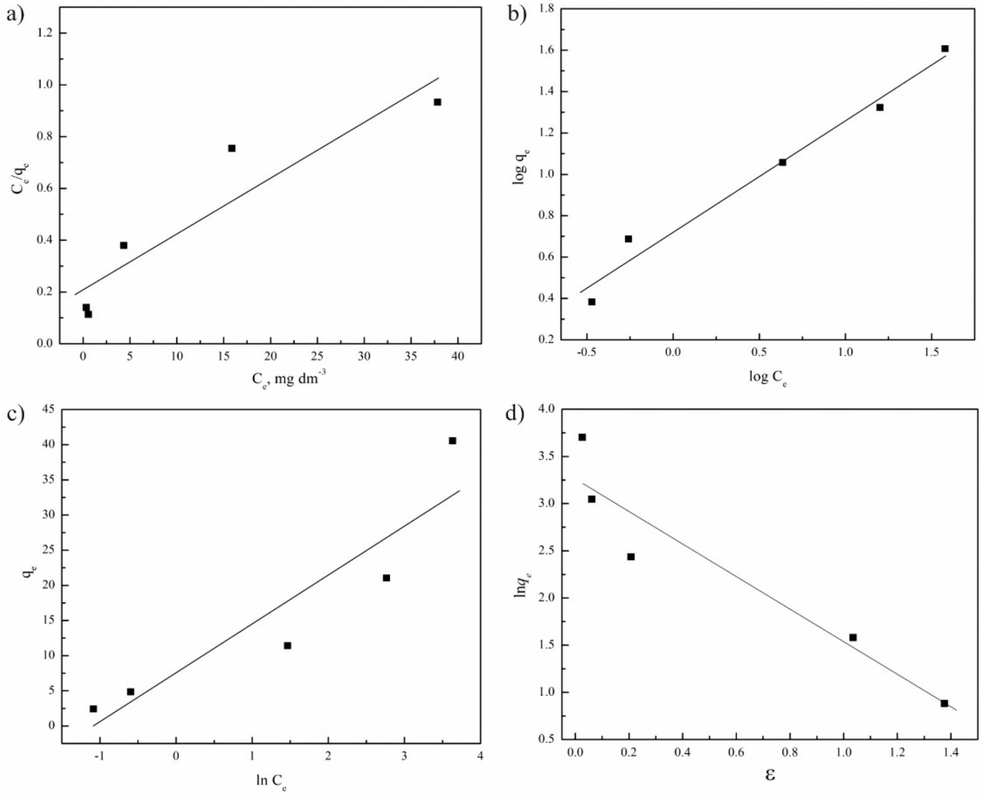

Figure 8. The isotherm model plots for adsorption Cu(II) ions onto IIN: a) Langmuir, b) Freundlich, c) Temkin, and d) Dubinin-Radushkevich

Table 2. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich parameters for the adsorption isotherms of Cu(II) by IIN

Isotherms	**Constants**		
Langmuir	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2
$C_e/q_e=1/K_Lq_{max} + C_e/q_{max}$	46.47	0.1023	0.8193
Freundlich	n	K_F (L mg^{-1})	
$\log q_e = \log K_F + (1/n)\log C_e$	1.8468	5.2588	0.9698
Temkin	b_T (kJ mol^{-1})	A_T (L mg^{-1})	
$q_e = (RT/b_T)\ln A_T + (RT/b_T)\ln C_e$	352.64	2.9208	0.8041
Dubinin-Radushkevich	q_s	K_{ad} (mol^2 kJ^{-2})	
$\ln q_e=\ln q_s-K_{ad}\varepsilon^2$	26.08	2.86×10^{-7}	0.8741

Adsorption behaviour in ternary solutions

Wastewaters usually contain more than one metal ion and the examination of multiple metal interactions simultaneously is very important for precise interpretation of adsorption data. [43] The competitive adsorption among the Cu(II), Pb(II) and Cd(II) (1:1:1) in the ternary systems were conducted in batch systems with initial total concentration of 50.0 mg dm^{-3} and the biosorption was performed in the same conditions as it is described for a single ion solution. The single metal ion removal efficiency of IIN was 92.0%, 86.8%, and 99.9% for Cu(II), Cd(II) and Pb(II), respectively. The efficiency of metal removal of IIN were found to be 77.4%, 66.6% and 93.0% for Cu(II)–Cd(II)–Pb(II) system (Fig. 9). Therefore, adsorption order in ternary system was found to be Pb(II) > Cu(II) > Cd(II), which is in agreement with previous studies. [44-47] These results indicated the highest decline of 20% in removal efficiency for Cd(II) followed by 15% for Cu(II) and 6% for Pb(II) in comparison to single metal system. It has been already concluded that the metal with the highest uptake capacity in the single metal system showed greater effect of inhibition on the biosorption of other metal ions in the multi-metal system, and when the lead ions exist in aqueous solution, the uptake of copper and cadmium decreased significantly. [48]

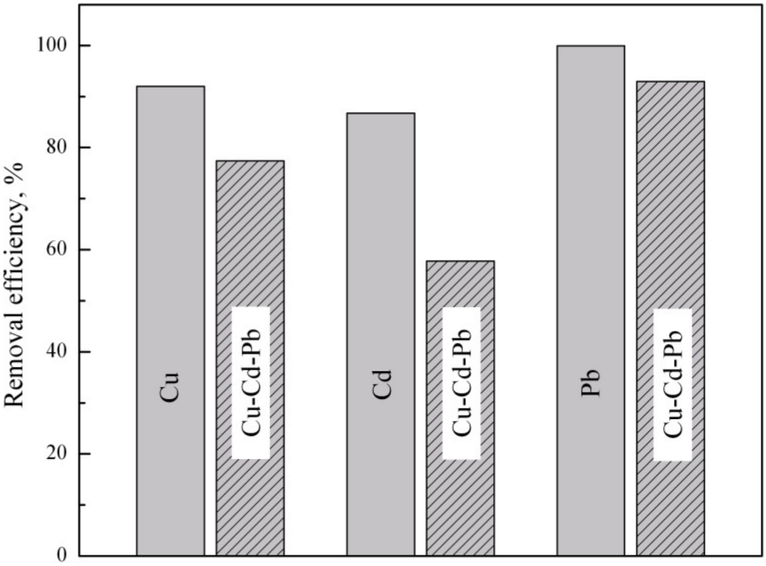

Figure 9. Removal efficiency of IIN for Cu(II), Cd(II) and Pb(II) ions for the sorption from the single-metal system and ternary-metals system

CONCLUSIONS

The present study indicated that the nettle after incomplete incineration (IIN) is an effective adsorbent for the removal of Cu(II) from aqueous solutions. SEM results indicate that surface of raw material has fibrous structure. IIN structure became unequally rugged and porous which presents a suitable morphological profile to bind Cu(II) ions. The effect of contact time on the residual concentration of Cu(II) ions in aqueous solution with raw nettle and IIN indicated that raw nettle is not efficient biosorbent, but after incomplete incineration it became very efficient. Batch experiments with different initial Cu(II) concentrations showed that copper uptake was increased by increasing the initial Cu(II) concentration, but, in the same time, removal efficiency decreases. The optimum biosorbent dosage was determined to be 4.0 g dm^{-3}. The sorption kinetics followed the pseudo-second order model. The batch adsorption data was successfully correlated with Freundlich isotherm model ($R^2 = 0.9698$). The competitive adsorption of Cu(II), Pb(II) and Cd(II) (1:1:1) in the ternary systems indicated that in all cases, there was an inhibitory effect of one metal on binding others and that the adsorption order was Pb(II) > Cu(II) > Cd(II).

Nettle is very cheap material and the created sludge could be easily eliminated so nettle can be used as a potentially good biosorbent for the removal of heavy metals from wastewaters.

EXPERIMENTAL SECTION

Reagents and Chemicals

All chemicals ($CuSO_4 \times 5H_2O$, $Pb(NO_3)_2$, $Cd(NO_3)_2$, Merck) were of analytical grade and used without further purification. Deionized water (<5 µS cm^{-1}) was used to prepare all aqueous solutions. Standard stock solutions of metal ions of 1000 mg dm^{-3} were used to prepare appropriate concentrations for the sorption studies. The pH of the solutions was adjusted pH-metrically to the required value with nitric acid or sodium hydroxide (0.1/0.01 M), without buffering. The pH of solutions was determined by a SensION3 (HACH, USA) pH meter.

Preparation of biosorbent

Biosorbent was obtained by incomplete incineration of dried nettle in covered porcelain pot. Nettle of the same levels of vegetation were collected from localities in vicinity of city of Niš (Serbia) and air dried prior to testing.

FTIR Characterization of biosorbent

The functional groups available on the surface of nettle before and after preparation, as well as adsorption of Cu(II) ions were detected by KBr technique using FTIR spectroscopy (Bomem Hartman & Braun MB-100 spectrometer). The spectra were recorded at room temperature in a range from 4000 to 400 cm^{-1}. The KBr pellets were prepared from 1.5 mg of finely powdered biosorbent dispersed in 150 mg of anhydrous KBr. The obtained FTIR spectra were analyzed using ACD/Labs 10 software.

SEM-EDX Characterization of biosorbent

A Scanning Electron Microscope (FEI Quanta 200 microscope) was used to examine the surface morphology of the biosorbent. An energy dispersive X-ray spectrometer with the scanning electronic microscope (SEM-EDX) was used to determine the chemical composition of the biomass before and after metal uptake.

The batch adsorption experiments

The adsorption experiments were conducted in 250 cm^3 Erlenmeyer flasks, containing 125 cm^3 different concentrations (from 10.0 to 400.0 mg dm-3) of the model solution containing Cu(II) ions during 120 min. Aliquots of solutions were withdrawn at preset time intervals, the biomaterial was removed by filtration through a 0.45 µm membrane filter and the filtrates were analyzed for metal ions. All experiments were conducted at ambient temperature (20.0±0.5°C), at initial pH 5.0±0.1 and carried out in triplicates. The experiments were performed using magnetic stirrer on 200 rpm.

Competitive biosorption of Cu(II), Pb(II) and Cd(II) was investigated in ternary system, in 250 cm3 Erlenmeyer flasks containing metals in mass ratio 1:1:1 with total concentration of 50 mg dm^{-3} to avoid increasing of the ionic strength compared to single metal experiment. The experiment was performed during 120 min period.

The concentrations of residual M(II) ions in the solution before and after adsorption were determined by using an atomic absorption spectrophotometer (AASAnalyst 300, Perkin–Elmer, USA) at standard wavelengths for investigated metals.

The adsorption capacity of the biosorbent, q_e (mg g^{-1}), at equilibrium was calculated as:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{13}$$

where qe is the amount of M(II) ion adsorbed per unit weight of the adsorbent, V is the volume of solution, C_0 is the initial concentration of metal ion (mg dm^{-3}), C_e is the equilibrium metal ion concentration (mg dm^{-3}), and m is the mass of the adsorbent (g).

The metal removal efficiency, RE (%), of the adsorbent was estimated according to the following equation:

$$RE = \frac{C_0 - C_e}{C_0} \times 100\% \tag{14}$$

where C_0 and C_e are the initial and equilibrium concentrations (mg dm^{-3}) of M(II) ions in solution, respectively.

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