STUDIES REGARDING COPPER IONS REMOVAL FROM WASTEWATERS USING OAK WOOD ASH AND THE EFFECT OF EXHAUSTED ASH AS SOIL AMENDMENT

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ABSTRACT. In this work it was studied the removal of copper ions from wastewater by adsorption on oak wood ash and the effect of the ash resulting from adsorption process as a soil amendment. The process variables such as pH, contact time and adsorbent dose were optimized for maximum Cu^{2+} removal. It was establishing the mathematical correlation between this factors and the metal ions removal efficiency using specific 3D software. Adsorption process is described by Freundlich isotherm and pseudo-first order kinetic model. The effect of the wood ash, previously used as adsorbent, as soil amendment was studied using barley crop, *Hordeum vulgare* L. The values of the specific parameters: germination percent, plant average length, biomass and relative growth rate proving the beneficial effect of the use of wood ash (resulted from the adsorption process) on plant growth.

Keywords: *Cu^{2+} adsorption; Oak woods ash; Mathematical correlation; Equilibrium; Kinetics; Soil amendment.*

INTRODUCTION

Heavy metal pollution has become one of the most serious environmental problems, in many countries, especially in aquatic environments [1-3]. Unlike most organic pollutants, heavy metals are persistent environmental pollutants and cannot be degraded naturally [4-6].

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GIANNIN MOSOARCA, COSMIN VANCEA, SIMONA POPA, SORINA BORAN,
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Heavy metals are discharged into the environment from different industrial activities and the resulting effluents can contain Cd, Cr, Cu, Co, Pb and Zn. These effluents have been excessively released into the environment and caused serious problems because heavy metals are recognized as major contaminants to plants, animals and human beings [1-6].

Copper is an essential trace element for living organisms. Copper is ubiquitous in the environment and an important trace element in biogeochemical cycles in soils and sediments. However, it becomes extremely toxic when presented at a high concentration. The presence of copper ion in drinking water causes abdominal pain, nausea, and more. Excessive copper intake may be responsible for severe mucosal irritation and corrosion, widespread capillary damage, hemolysis, liver and kidney damage, central nervous system irritation followed by depression, weakness and lethargy [6-11].

Copper and its compounds are widely used in many industries: metallurgy, electrical, electroplating, paper and pigments manufacturing, fertilizer, pesticides, herbicides, tannery. Wastewaters discharged from these industries have contributed to a progressive increase of copper concentrations in environments [6,7,11-13]. Therefore, the copper ions removal from contaminated waters became an important issue for the environmental protection [11].

Several methods, namely chemical precipitation, ion exchange, membrane filtration, electrochemical treatment, biological treatment and hydrogel were currently used to remove Cu^{2+} from aqueous solutions [1-5,7,9,10]. However, these methods have disadvantages and limitations due to high reagents or energy requirements, incomplete metal removal, complex operations, production of high amounts of sludge and unacceptable operating cost [1,2,4,6,14].

In addition to the methods mentioned above, adsorption process is one of the most widely used methods for the removal of metal ions from an aqueous solution. Adsorption is generally preferred due to its high efficiency, simplicity, moderate operational conditions, fast response, the availability of different adsorbents, and its cost effectiveness [1,2,4-6,10,14].

Technical and economic concerns have led to a focus on low-cost adsorbents. These materials include clay minerals, agricultural by-products, some aquatic plants and microorganisms. Industrial solid disposals and agricultural by-products such fly ash, wood ash, lignite, zeolite, clarified sludge, red mud, clay, rice husk ash, fuller's earth, sawdust, cellulose, chitosan, starch, sugarcane bagasse, neem-bark, coconut shell, orange peel, tea leaves have been used to remove heavy metals from wastewaters [1,2,4,14-18].

Wood ash is produce in high quantity every year by combustion of wood in industrial power plant or in home fireplaces [19,20]. It was found that wood ash was a promising adsorbent for the removal of pollutants from waters. [21,22].

An advantage of the adsorption is that it is suitable for mathematical modeling, leading to a better understanding of the factors that influence the process [18].

To the best of our knowledge, only few articles have studied the adsorption of Cu^{2+} on wood ash [23,24], but mathematical correlations between the main factors influencing the adsorption process was not followed.

On the other hand, the adsorption process generates a new waste, exhausted wood ash. The reuse of this material, resulted from copper adsorption, as soil amendment has not yet been reported in the literature.

The first objective of this research was to determine the effect of the solution pH, contact time, and adsorbent doses on the removal of Cu^{2+} from water and to establish a mathematical correlation between these factors and copper ions removal efficiency. In addition, the kinetic and equilibrium parameters of the adsorption process were computed and discussed. The second objective was to reuse wood ash resulted from the copper adsorption process as soil amendment. Therefore, it was studied the effect of wood ash application on a barley crop, *Hordeum vulgare* L.

RESULTS AND DISCUSSION

SEM analysis can be used to characterize the surface morphology of an adsorbent, serving to determine the particles shape and size distribution. Wood ash has a very porous surface, having a relatively uniform dimensional distribution, providing large surface area for Cu^{2+}-surface interaction as it is illustrated in Figure 1a. After adsorption, the surface is saturated, the pores being covered by copper ions (Figure 1b).
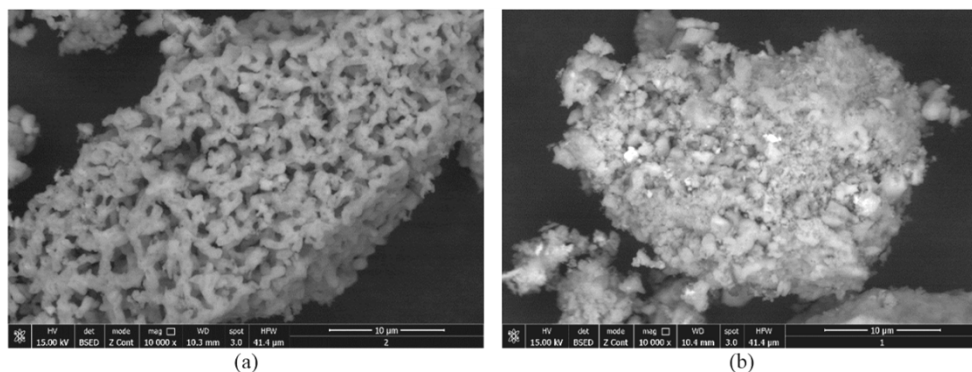

Figure 1. SEM images of wood ash: (a) before and (b) after copper ions adsorption

GIANNIN MOSOARCA, COSMIN VANCEA, SIMONA POPA, SORINA BORAN,
PETRU NEGREA, MARIA ELENA RADULESCU-GRAD

pH is one of the most important parameter that influence the metal sorption processes, due to its influence on surface properties of the adsorbent and on ionic species chemistry in solution (hydrolysis, complexation by organic and/or inorganic ligands, precipitation, redox reactions) [16,25]. The amount of the adsorbed metal also depends on contact time. In adsorption kinetics this parameter determines the time required to transport adsorbates to the adsorption sites [25,26]. Adsorbent dosage is an important parameter because it determines the adsoption capacity of an adsorbent for a given concentration of the adsorbate [16].

In order to represent a mathematical model between these factors and the copper ions removal efficiency, the experimental data were processed by means of the Table Curve 3D software. In view of choosing the best mathematical model, the following criteria were taken into account: the shape of the response surface, the simplicity of the characteristics mathematical equation and the determination coefficient (R^2) as close as possible to unity [27].

The effects of pH, contact time, wood ash dosage on adsorption process and mathematical correlation between these and the Cu^{2+} removal efficiency are presented in the Figures 2-4.
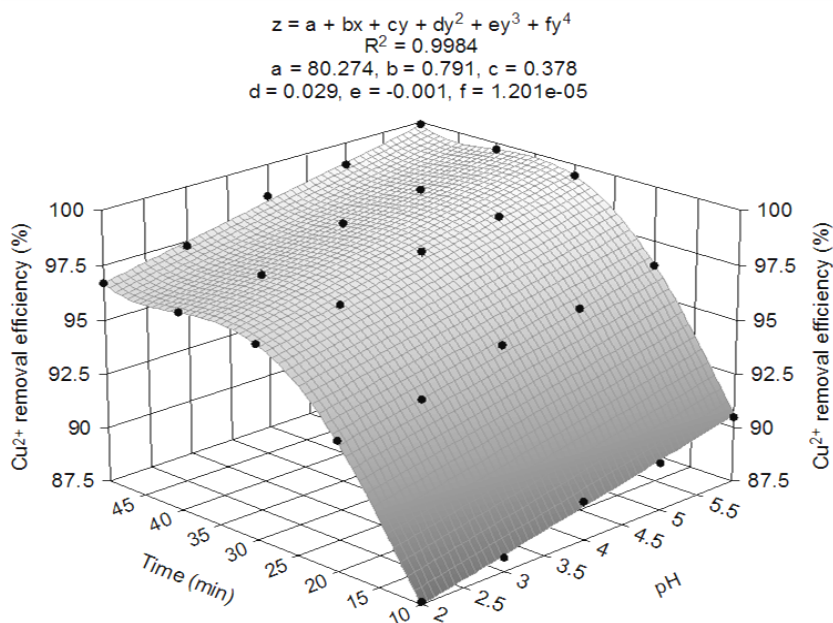

$$z = a + bx + cy + dy^2 + ey^3 + fy^4$$
$$R^2 = 0.9984$$
$$a = 80.274, b = 0.791, c = 0.378$$
$$d = 0.029, e = -0.001, f = 1.201e\text{-}05$$

Figure 2. The mathematical correlation between pH, contact time and the copper ions removal efficiency from wastewater using wood ash

$$z = a + bx + cy + dy^2 + ey^3$$
$$R^2 = 0.9991$$
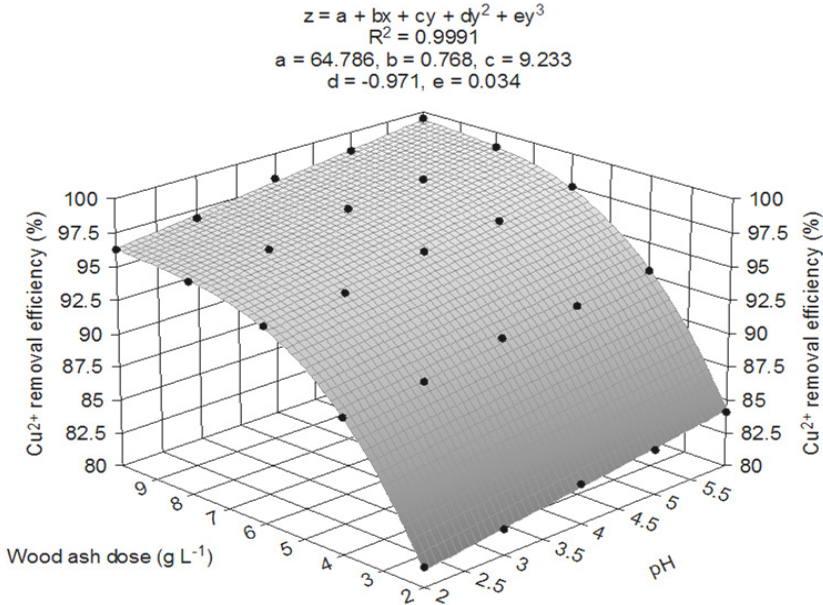$$a = 64.786, b = 0.768, c = 9.233$$
$$d = -0.971, e = 0.034$$

Figure 3. The mathematical correlation between pH, adsorbent dose and the copper ions removal efficiency from wastewater using wood ash

$$z = a + bx + cx^2 + dx^3 + ey + fy^2 + gy^3$$
$$R^2 = 0.9983$$
$$a = 50.578, b = 9.171, c = -0.963, d = 0.034$$
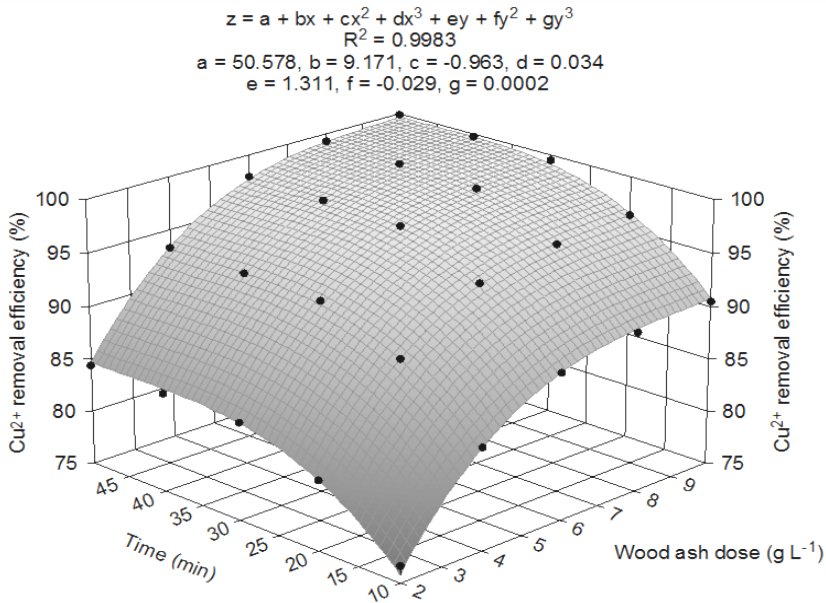$$e = 1.311, f = -0.029, g = 0.0002$$

Figure 4. The mathematical correlation between contact time, adsorbent dose and the copper ions removal efficiency from wastewater using wood ash

197

Due to the high basicity of the used ash, the removal of copper ions varies slightly by increasing the initial pH of the wastewater, reaching the highest value at pH = 6 (Figure 2 and Figure 3). Electrostatic adsorption and precipitation can be involved in the expected mechanism of metal ions removal from aqueous solutions by wood ash [28,29]. At higher pH values, a negatively charged surface sites of the ash favour the adsorption of copper metal ions based on the electrostatic attraction [16,23].

At these pH values, the ash could act as a precipitant agent because of it's alkalization properties. The most important characteristic of the wood ash is the Ca^{2+} content, that generates alkalinity. This means that at higher pH values precipitation could be involved in the mechanism of toxic metal ions removal. Since Ca^{2+} in the ash is present as CaO, it can be assumed that the following reaction occur: $CaO + H_2O + Cu^{2+} = Cu(OH)_2 + Ca^{2+}$ [29].

According to the experimental data, the copper ions removal efficiency increases by increasing the contact time. The effect is more obvious up to 30 minutes, after this time the copper removal yield is practically constant (Figure 2 and Figure 4).

The initial Cu^{2+} adsorption rates are high due to the availability of a large number of vacant surface sites for adsorption or to a higher diffusion rate towards the pores at the beginning of the adsorption process. As the contact time increases further, the available active sites for adsorption are gradually occupied and the driving force is weakened. As a result, the adsorption presents a slower rate, taking a longer time to achieve adsorption equilibrium [5,29].

Along with increasing of the adsorbent dose from 2 to 10 (g L^{-1}) the adsorption efficiency of Cu^{2+} on the wood ash increases gradually until 99.8% (Figure 3 and Figure 4). This phenomenon could be explained by the fact that along with increasing the amount of adsorbent the active surface increase. At initial stages, there is a large number of reactive sites leading to an efficient copper ions removal [7,16].

Adsorption isotherm is very useful in giving information on adsorption behavior, surface properties and adsorbent-adsorbate interactions [30,31].

Figure 5 ilustrate the Langmuir, Freundlich and Temkin adsorption isotherms for copper ions adsorption on wood ash. The adsorption isotherms constants and the corresponding error parameters are detailed in Table 1. It was observed that the adsorption is best described by the Freundlich isotherm (highest determination coefficient R^2 and lowest chi-square χ^2, sum of square error SSE, and average relative error ARE). The adsorption intensity calculated value, n = 2.13, is greater than unity, that indicates a favorable adsorption [6].
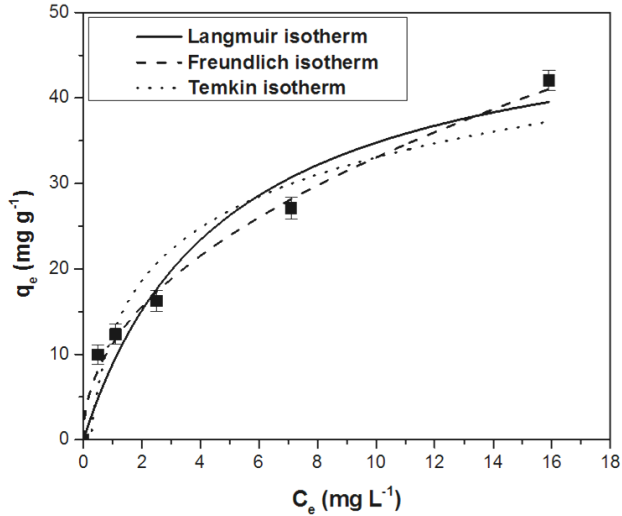
Figure 5. Langmuir, Freundlich and Temkin isotherms
for copper ions adsorption on wood ash

Table 1. The adsorption isotherms constants
and the corresponding error parameters

Isotherm model	Parameters	Value
Langmuir	K_L (L mg^{-1})	0.208 ± 0.031
	q_{max} (mg g^{-1})	51.43 ± 4.25
	R^2	0.9542
	χ^2	6.96
	SSE	58.95
	ARE (%)	26.88
Freundlich	K_f (mg g^{-1})	11.26 ± 2.74
	1/n	0.46 ± 0.05
	R^2	0.9926
	χ^2	0.60
	SSE	8.19
	ARE (%)	8.23
Temkin	K_T (L mg^{-1})	3.96 ± 0.47
	b (kJ g^{-1})	272.25 ± 16.54
	R^2	0.957
	χ^2	4.33
	SSE	69.11
	ARE (%)	22.74

Kinetic of the adsorption process represents an important aspect because it provides information about the uptake rate and controls the residual time of the entire process. The adsorption rate is influenced by different processes including: transfer of solute to the sorbent surface, diffusion from the surface to the internal sites (surface or pore diffusion) and retention of the adsorbate which can involve sorption, complexation or intraparticle precipitation phenomena [6,30,31].

Figure 6 shows the pseudo-first order, pseudo-second order and Elovich kinetic models for copper ions adsorption on wood ash. The kinetic models constants and the corresponding error parameters are presented in Table 2. The pseudo-first ordel model best describe the adsorption process. The highest R^2 value and the lowest values for χ^2, SSE, and ARE were obtained for this kinetic model. Also, the q_e calculated values, 1.71 (mg g^{-1}) is in good agreement with the q_e experimentally determined values, 1.70 (mg g^{-1}). This model assumes that physisorption limits the adsorption rate of the adsorbate on the adsorbent surface [32].
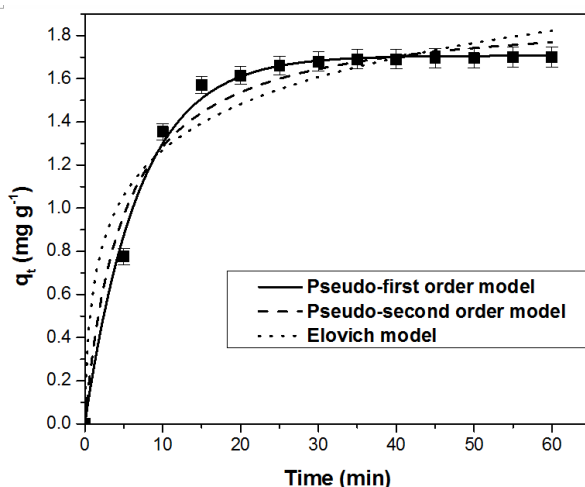

Figure 6. Pseudo-first order, pseudo-second order and
Elovich kinetic models for copper ions adsorption on wood ash

The scientific literature mentions that pseudo-first order model also described the adsorption process of some heavy metal ions on different biomasses such as: Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+} on wood ash [23], Cu^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+} on agroforestry waste mixtures (fern, rice husk, oak leaves) [33], Cu^{2+} on garden grass [34] and chemically modified Neem (*Azadirachta indica*) sawdust [35], Ni^{2+} on *Peganum harmala*-L seeds [36] and orange peel, pineapple peel, passion fruit wastes [37], Cd^{2+} on natural and modified *Posidonia oceanica* leaves [38].

Table 2. The kinetic models constants and
the corresponding error parameters

Kinetic model	Parameters	Value
Pseudo-first order	k_1 (min^{-1})	0.143 ± 0.024
	$q_{e,calc}$ (mg g^{-1})	1.71 ± 0.08
	R^2	0.9946
	χ^2	0.01
	SSE	0.01
	ARE (%)	1.77
Pseudo-second order	k_2 (min^{-1})	0.106 ± 0.015
	$q_{e,calc}$ (g mg^{-1} min^{-1})	1.91 ± 0.14
	R^2	0.9739
	χ^2	0.06
	SSE	0.08
	ARE (%)	4.85
Elovich	a (g mg^{-1})	3.23 ± 0.54
	b (mg g^{-1} min^{-1})	1.85 ± 0.11
	R^2	0.9395
	χ^2	0.14
	SSE	0.18
	ARE (%)	6.69

The general characteristics of the wood ash used in this work (determined in other previously study [25]) were follows: pH = 11.7, $[Ca^{2+}]$ = 61980 (mg kg^{-1} d.m.), $[Mg^{2+}]$ = 13310 (mg kg^{-1} d.m.), $[Na^+]$ = 1890 (mg kg^{-1} d.m.), $[K^+]$ = 94293 (mg kg^{-1} d.m.), [P] = 19452 (mg kg^{-1} d.m.), $[Fe_{total}]$ = 2100 (mg kg^{-1} d.m.), $[Mn^{2+}]$ = 7490 (mg kg^{-1} d.m.), $[Cu^{2+}]$ = 95 (mg kg^{-1} d.m.).

The wood ash, resulted from adsorption, had the following characteristics: $[Ca^{2+}]$ = 34328 (mg kg^{-1} d.m.), $[Mg^{2+}]$ = 7684 (mg kg^{-1} d.m.), $[Na^+]$ = 1193 (mg kg^{-1} d.m.), $[K^+]$ = 53689 (mg kg^{-1} d.m.), [P] = 12281 (mg kg^{-1} d.m.), $[Fe_{total}]$ = 788 (mg kg^{-1} d.m.), $[Mn^{2+}]$ = 3220 (mg kg^{-1} d.m.), $[Cu^{2+}]$ = 7225 (mg kg^{-1} d.m.). The pH of this material was alkaline (9.12).

The experimental results show a decrease of the main chemical elements concentrations from the ashes after the adsorption process due to the lixiviation effect. The exhausted wood ash presents a large increase of the copper concentration from 95 to 7225 (mg kg^{-1} d.m) due to the retention of the copper ions.

Also, it can be noted that this exhausted wood ash contains high concentrations of chemicals, useful in plant growth. Calcium and potassium are useful for cell division and formation. Many plants enzymes are activated by potassium, magnesium and manganese. Potassium and phosphorus are involved in protein synthesis and activity. An important role in photosynthesis is held by magnesium, phosphorus and copper. Calcium and manganese increase plant resistance to various diseases. Also, phosphorus and copper have a major function in respiration and reproductive stages [39].

In order to establish the effect of the exhausted wood ash, resulted from cooper adsorption, as a soil amendment, *Hordeum vulgare* L. was used, this plant being a well-known bio-indicator [40,41].

Figure 7 summarizes the percentage of germination for each sample. It can be observed the beneficial effect of the copper ash addition. In the control sample, 82 % (mean) of seeds were germinated. In the samples with ash addition, the germination percentage is higher, reaching up to 95 % when the ash was added as a layer above ground, in the ratio ash : soil = 1: 50.
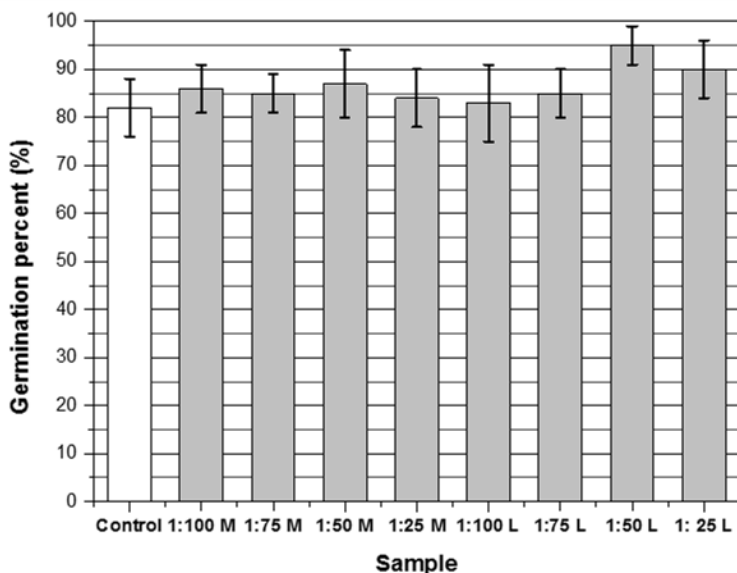

Figure 7. The germination percentage for control and sample with ash addition in both variant studied: soil mixed with ash (M) and ash as a layer above the soil (L) for different ash : soil ratio

Figure 8 presents the average lengths of the plants at 21 days after sowing. The experimental results show the positive effect of the ash addition on length of plants.
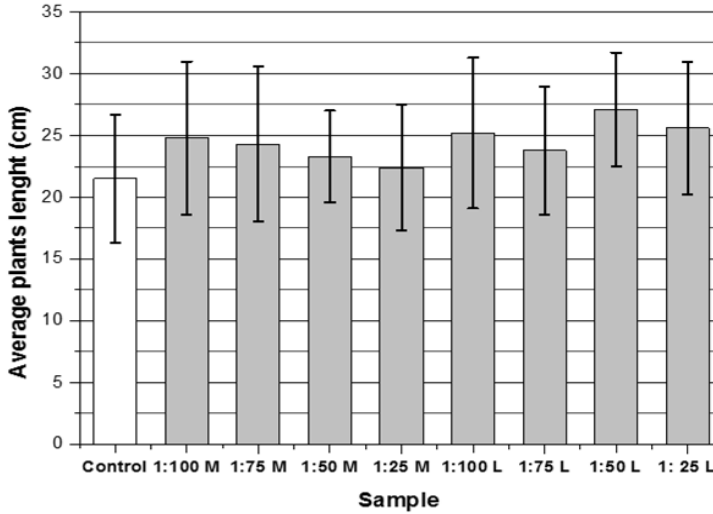
Figure 8. The average lengths of the plants at 21 days after sowing
in both variant studied: soil mixed with ash (M) and ash as a layer
above the soil (L) for different ash: soil ratio

Another followed parameter was the amount of the obtained biomass.
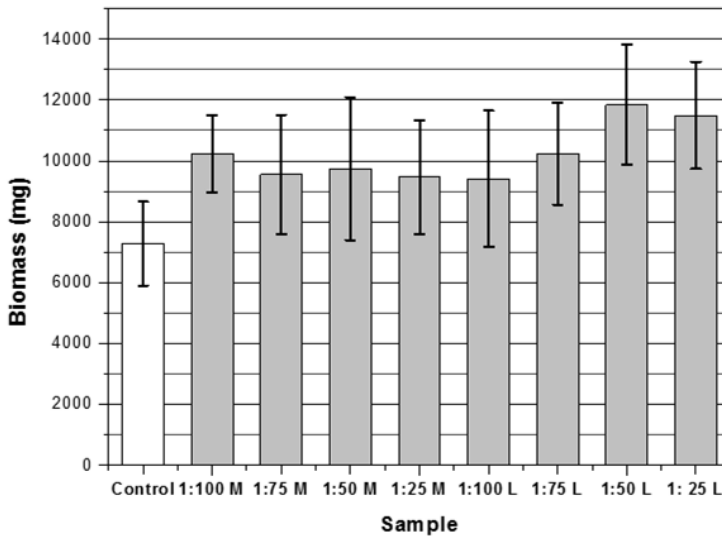The biomass mean value, after 21 days of sowing is presented in Figure 9.

Figure 9. The biomass mean value after 21 days of sowing in both variant
studied: soil mixed with ash (M) and ash as a layer above the soil (L)
for different ash: soil ratio

Addition of ash leads to an increase of the biomass in all samples. The amount of biomass was higher by 30 - 62 % compared to the control sample. For the samples where the ash was added as a layer above ground, in the ratio ash: soil equals with 1: 50 and 1: 25, were recorded the biomass highest values.

The most used parameter for assessing the growth of plants is relative growth rate [42]. Figure 10 presents the relative growth rate of plants at 21 days after sowing. In all samples containing exhausted wood ash this parameter was higher than the control sample. The wood ash application method, soil mixed with ash (M) and ash as a layer above the soil (L) have no sensible effect upon the relative growth rate of the plants.
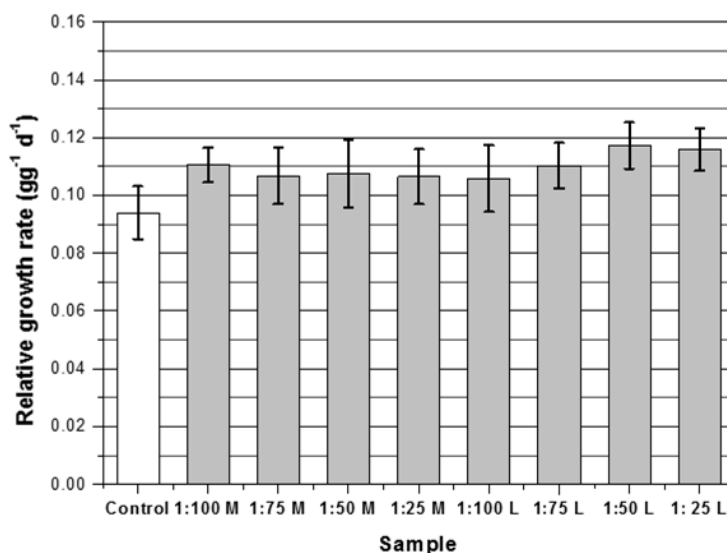

Figure 10. Relative growth rate after 21 days in both variant studied: soil mixed with ash (M) and ash as a layer above the soil (L) for different ash: soil ratio

CONCLUSIONS

Wood ash has a high efficiency in the removal of copper ions from wastewater (more than 99 %). Maximum efficiency was obtained under the following experimental conditions: pH = 6, mixing time 30 minutes and adsorbent dose 10 (g L^{-1}). Developed mathematical models that describe the dependence between copper removal efficiency and the main factors that influence the adsorption process have correlation coefficients close to unity.

Adsorption process is best described by Freundlich isotherm and pseudo-first order kinetic model.

The use of exhausted wood ash, resulted from the adsorption process of copper ions from waste water, as soil amendment has a beneficial effect for the barley crop. The germination percent, the plant average length, the amount of biomass and relative growth rate of plants were higher in the samples containing wood ash compared to the control sample. This fact can be explained by the high content of essential elements in the nutrition and development of plants from the ash (calcium, magnesium, potassium, phosphorus and manganese). The copper adsorbed on the ash is, also, a trace element in plant growth. Wood ash application method (soil mixed with ash and ash as a layer above the soil) does not significantly influence the plant development.

EXPERIMENTAL SECTION

Analytical grade reagents (purchase from Merck) were used in experiments. A Cu^{2+} stock solution, 100 (mg L^{-1}) was prepared from distilled water and an appropriate quantity of $CuSO_4 \cdot 5H_2O$.

The wood ash for the present assay was derived from the combustion of oak wood (*Quercus robur* L.) in a home fireplace. BET analysis showed that the majority of pores are mesopores [25]. Quanta FEG 250 SEM microscope was employed to analyze the adsorbent surface morphology, before and after adsorption, at 10000x magnitude.

For determination of the general characteristics of the wood ash this material was digested with aqua regia and the concentrations of metals were determined using an atomic absorption spectrophotometer Varian SpectrAA 110 with graphite furnace. The vanadomolybdophosphoric acid method and UV-VIS spectrophotometer (Varian Cary 50) were used for the phosphorous determination. The measure of the wood ash pH, in distilled water (pH_{H2O}), was realized according to USEPA Method 9045D, Soil and waste pH.

The adsorption experiments were carried out in 150 mL Erlenmeyer flasks at room temperature using an M.T.A. 609/A shaker. Mixing intensity was maintained constant throughout the experiments. The batch experiments were conducted at 2 - 6 pH range, contact time between 10 - 60 minutes and adsorbent dose between 2 - 10 (g L^{-1}). The pH was measure with an Ino-lab pH-meter and was adjusted using 0.1 N solutions of NaOH/HCl. After mixing, the samples were filtrated and the copper concentration was determined by atomic absorption spectroscopy.

Three independent replicates were performed for each adsorption experiment. In order to describe the adsorption behavior of Cu^{2+} ions on wood ash, three of the most commonly used adsorption isotherm models were applied to analyze the adsorption data obtained from the experiments, Langmuir, Freundlich and Temkin isotherms.

The non-linear forms of these isotherms models are expressed by the following equations:

Langmuir isotherm $$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \qquad (1)$$

Freundlich isotherm $$q_e = K_F \cdot C_e^{1/n_F} \qquad (2)$$

Temkin isotherm $$q_e = \frac{R \cdot T}{b} \cdot ln(K_T \cdot C_e) \qquad (3)$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent; C_e is the equilibrium concentration of the adsorbate; K_L, K_F, and K_T are the Langmuir, Freundlich and Temkin isotherms constants; $1/n_F$ is an empirical constant indicating the intensity of adsorption; R is the universal gas constant; T is the absolute temperature; b is Temkin constant which related to the adsorption heat [43].

Pseudo-first order, pseudo-second order and Elovich kinetic models were applied in order to investigate adsorption process of Cu^{2+} onto the wood ash. The non-linear forms of these kinetic models are expressed by equations:

Pseudo-first-order kinetic model $$q_t = q_e(1 - exp^{-k_1 \cdot t}) \qquad (4)$$

Pseudo-second-order kinetic model $$q_t = \frac{k_2 \cdot t \cdot q_e^2}{1 + k_2 \cdot t \cdot q_e} \qquad (5)$$

Elovich kinetic model $$q_t = \frac{1}{a} ln(1 + a \cdot b \cdot t) \qquad (6)$$

where q_e is the equilibrium adsorption capacity, q_t is the adsorption capacity at time t, k_1 and k_2 are the rate constants of pseudo-first-order and pseudo-second-order kinetic models; a is the desorption constant of Elovich model; b is the initial velocity [44].

The proper isotherm and kinetic models was determined using values of determination coefficient (R^2), sum of square error (SSE), chi-square (χ^2) and average relative error (ARE) [43].

The exhausted wood ash, resulted from adsorption, was dried at room temperature and use as soil amendment.

The soil used in experiments was collected from the surface layer of a public garden in Timisoara town and had the following main characteristics: pH_{H2O} = 6.7, sand = 34.2 %, clay = 39.4 %, silt = 26.4 % [25].

Seeds of *Hordeum vulgare* L. (purchase from a local farmer) were surface sterilized with 80% (v/v) ethanol and then were rinsed with distilled water for two to three times. Sterilized seed were kept at room temperature to make them completely dried.

Various wood ash: soil weight ratios have used in the experiment, from 1:100 to 1:25, in two variants, soil mixed with ash (M) and ash as a layer above the soil (L). For a correct analysis of the results, a soil control sample without ash addition was prepared for comparison. For each treatment, three independent replicates were performed.

In order to evaluate the addition effect of the wood ash, the germination percent, plant height, biomass and relative growth rate were determined, after 21 days from *Hordeum vulgare* L. seeds sowing.

Equation (7) was used for the relative growth rate determination:

$$RGR = \frac{\ln W_2 - \ln W_1}{t_2 - t_1} \tag{7}$$

where W_1 is fresh biomass of plants at time one (g), W_2 is fresh biomass of plants at time two (g), t_1 is time one (days) and t_2 is time two (days) [42].

The data consists of the mean values of three replicates. The one-way ANOVA was used in the statistical analysis in order to assess significant differences among the various wood ash: soil ratios. Considering P < 0.01 as a significant value, a comparison of mean using the least significant different test was calculated for P-values.

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