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Comparative assessment of adsorbents performances of plant biomasses grown on different sites: Case study of invasive *Acer negundo* L.

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Abstract: With the increasing global spread of invasive species, collecting their biomass could be a promising source for adsorbent development and water remediation. Therefore, the ability of adsorbent based on biomass of invasive plant *Acer negundo* L. originating from different habitat types was investigated for the lead removal from aqueous solution, in order to observe if different growing sites have effect on adsorbent performances. Three sites were selected for sampling: forest edges on Mt. Avala, riparian forests at Great War Island and banks of coal separation pond in Piskanja, Serbia. Characterisation was performed *via* pH_{pzc}, zeta potential, cation exchange capacity, SEM-EDS and FTIR analysis. Optimization of sorption parameters was done and the best performance was at pH 5.0, adsorbent dosage 2.0 g/dm^3 at 298 K for 60 min. Fitting of isothermal experiment data showed best correlation with Sips model (q_{max} is 94.92–131.52 mg/g, according to growing site). Among three reaction kinetic models, pseudo-second-order kinetics model showed best results. Since sample taken from the most anthropogenic influenced area have almost 30 % lower adsorption capacity than others, it can be concluded that growing site characteristics reflect on biomass performances, which is important factor for any further biomass usage.

Keywords: adsorption; invasive plants; *Acer negundo* L.; lead; kinetics.

INTRODUCTION

Acer negundo L., which originates from North America, was introduced to Europe as a cultivated woody species in the 17th century and was planted in the cities due to its rapid growth and resistance to weather extremes. It is still one of the most common species in parks, street tree lines and spontaneously occurs along roads and in other disturbed habitats. However, it has become invasive in both

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natural and urban habitats.[1] *A. negundo* has broad ecological amplitude: it tolerates air pollution, soils with wide range of pH values, extreme cold and drought.[2] In Serbia, *A. negundo* is considered as one of the most aggressive invasive tree species in forest ecosystems and its presence has also been detected in many areas with preserved natural values.[3]

Abundant biomass of invasive plant species is nowadays recognized for its potential benefits in providing various environmental services. Adsorption, as one of the sustainable and efficient remediation technique could be potential field for its application. Moreover, adsorption is considered as a cost-effective and reliable method for purification of contaminated water, especially in the case of common water metal pollutants.[4] Plant-derived materials such as wood, leaves, fruits, or seeds have been studied for this purpose, where adsorbents based on leaf biomass showed the best adsorption performance.[5] Biomass of *Acer* species have been tested as adsorbents for metal removal from aqueous solutions,[6] but no such studies have been conducted on invasive *A. negundo*. Also, so far there has been lack of investigations concerning sorption performance of biomasses of the same species collected from different habitats. Therefore, the research questions aimed to answer were: a) is invasive *A. negundo* leaf biomass suitable adsorbent for metal aqueous pollution? b) Does the *A. negundo* leaves originated from sites with contrasting ecological, edaphic and anthropogenic differ in their composition? And c) does the leaf composition variability impact metal adsorption capacity?

EXPERIMENTAL

Three different growing sites were selected for sampling *A. negundo* leaves. First sampling site, Mt. Avala, represents protected area in the vicinity of Belgrade, with environment that supports a large diversity of species. It is recognized as Emerald Network site and as a Serbian ecological network site.[7] Seven allochthonous invasive tree species were recorded on Mt. Avala, including *A. negundo*.[8] Area of the natural landscape Great War Island, the second sampling site, represents unique example of protected area located in the urban environment of Belgrade. The island is habitat for many species and it is being annually flooded by the Danube River. It is recognized as one of the central areas of Serbia's ecological network and the ecological Network within the Danube ecological corridor.[7,9] However, research of Kašanin *et al.*[10] showed increased pollution of Great War Island sediments with Cu and Cd, as well as with oil pollutants. In the area of Great War Island 17 invasive tree species, among which is *A. negundo*, are registered.[11] Third sampling point is placed on the banks of former coal separation pond in Piskanja, which is a part of industrial setting at Ibar coal mining basin in South–Central Serbia. This area is nowadays sporadically colonized by various plant species, including invasive ones.[12] Sampling points are presented in Fig. S-1 of the Supplementary material to this paper.

Composite soil samples were taken at each sampling site from the upper layer (0–20 cm) of the rhizosphere zone. Soils were air-dried and sieved through 2 mm sieve. Pseudo-total content of elements was determined by using aqua region digestion following ISO 11466:1995 standard[13] and measured by atomic absorption spectroscopy (AAS). The content of soil organic carbon (SOC) was determined by oxidation with a solution of $KMnO_4$ according to the Kotzman method.[14]

Up to 100 fully developed leaves from mature *A. negundo* trees were collected during June from middle canopy section and each side of the crown of 3–5 individuals of approximately similar age, in order to make representative composite samples for each sampling site. Leaves were collected by pruning following methodology described elsewhere.[15] They were rinsed with distilled water and air-dried. Leaves were then grinded in blade grinder (20.000–30.000 rpm) and powdered prior to analysis (particle size < 0.2 mm). Samples from Mt. Avala, Great War Island and coal separation pond Piskanja were labelled as ANA, ANV and ANS, respecttively, as presented in Fig. S-1. In order to determine the content of elements, the samples were dissolved using standardized microwave-assisted acid dissolution procedure for this type of material in high-performance microwave digestion system Ethos UP, Milestone and the concentrations of elements were determined by AAS, while K, Ca and Na were determined by atomic emission spectrometry using PerkinElmer PinAAcle 900T, USA, directly from the prepared solution. Bioconcentration factor (*BCF*) was used to determine the efficiency of metal accumulation in leaves, and it was calculated as a ratio between metal concentration in leaves and pseudo-total concentration of the same element in the soil.[16] Cation exchange capacity (*CEC*) was determined by method that involves saturation of the cation exchange sites by ammonium acetate.[17] Determination of pH value of suspensions (pH_{sus}) was performed according to standard ASTM D6851-02. Determination of the point of zero charge (pH_{pzc}) was done in accordance to methodology described elsewhere.[18] In order to determine zeta potential of samples Zetasizer Nano Z (Malvern, UK) was used in the pH range from 2.0 to 10. In order to observe surface morphology and elemental composition of leaf powder, scanning electron microscopy combined with the energy dispersive spectroscopy (Jeol JSM 6460, Jeol Ltd., Japan) was used. The dried samples were coated with thin layer of gold under vacuum conditions. Attenuated total fourier transform infrared spectroscopy was used for determination of samples surface functional groups by using Thermo Nicolet 6700 FTIR (Thermo Fisher Scientific, USA). The spectra were recorded in range from 4000 to 400 cm^{-1}. The region between 1900 and 2200 cm^{-1} is interrupted due to strong diamond IR absorption.

Batch sorption experiments were performed through the sets of the experiments where one parameter was varied, while the others remained constant. Experiments were performed by mixing sample with metal solution and stirring it on orbital thermostatic shaker (HeidolphUnimax 1010, USA) at 200 rpm. Lead stock solution (1.0 mmol/dm^3) was prepared from $\text{Pb(NO}_3\text{)}_2\cdot 3\text{H}_2\text{O}$ (analytical grade). After investigated period of time suspension was filtrated and the filtrate was analysed using AAS. The effects of following parameters on sorption capacity were analysed: a) effect of initial pH in the range from 2.0 to 5.0; b) effect of contact time in range from 2 to 180 min; c) effect of sorbent concentration in range from 1 to 20 g/dm^3; d) effect of initial lead concentration in range from 5 to 600 mg/ dm^3; e) effect of temperature in range from 288 to 328 K. The sorption capacity was calculated using the following equation:

$$q_{\text{e}} = \frac{(C_0 - C_{\text{e}})V}{m} \tag{1}$$

where q_{e} is the amount of lead absorbed (mg/g); C_0 and C_{e} are the initial and equilibrium lead concentrations (mg/dm^3); V – the sorbate solution volume (dm^3); m – the sorbent mass (g). The involvement of ion-exchange mechanism during the sorption process was investigated by following the release of cations (Ca^{2+}, Mg^{2+}, Na^+, K^+ and H^+) from sorbents after process of lead sorption. The ratio was calculated by using the following equation:

$$R_{\mathrm{b/r}} = \frac{\left[\mathrm{Pb}^{2+}\right]}{\left[\mathrm{Ca}^{2+}\right]+\left[\mathrm{Mg}^{2+}\right]+\left[\mathrm{Na}^{+}\right]/2+\left[\mathrm{K}^{+}\right]/2+\left[H^{+}\right]/2} \tag{2}$$

where $R_{\mathrm{b/r}}$ is the ratio of the bonded lead ions and released cations, while in brackets are amount of bonded lead ions and amounts of specific cations released from sorbents.

Kinetic and isotherm investigations were performed in order to analyse the sorption process, fitting the experimental sorption data by various isotherm and kinetic models, which might elucidate the nature of sorption process. Kinetic and isothermal experimental data were obtained from the experiments performed under optimised operational parameters ($C_{\mathrm{Pb}^{2+}}$ = 200 mg/dm^3, m/V = 2.0 g/dm^3, pH = 5.0, T = 298 K and t = 180 min). Isothermal sorption experiments were conducted under the same operational parameters, varying initial lead concentration from 5.0 up to 600 mg/dm^3. Models/equations which have been used in this paper are presented in Table S-I of the Supplementary material. All sorption experiments were performed in triplicate and results were reported as arithmetic mean values. The statistical analysis was performed and nonlinear correlation coefficient (R^2) and the reduced chi square test (χ^2) were applied to measure the appropriateness of applied kinetic and isotherm models.

Soil and plant analysis were carried out in triplicates, and the results are presented as arithmetic means ± standard deviations. Statistical differences between sites and concentration of elements in plant leaves were determined by using one-way analysis of variance (ANOVA) in Statistica 8.0 (StatSoft 2007).

RESULTS AND DISCUSSION

Characterization of samples

Invasive plant species exhibit broad ecological amplitude that allows them to colonize ecologically diverse habitats. Due to developmental plasticity, the same plant species grown on ecologically different habitats might show significant variation in structural and physiological traits.[19] Plant leaves are considered to be among most sensitive organs to the influence of environmental factors, showing differences in chemical components and presence of functional groups.[20] In relation to that, characterization of collected samples of soil and leaf biomass was conducted. The measurements of the soil pH, content of soil organic carbon (SOC), concentration of potentially toxic elements (PTE) and macroelements in topsoil layers (0–20 cm), together with concentrations of PTE in leaves are presented in Table S-II (Supplementary material). Soil pH ranges from neutral (ANA$_{\mathrm{S}}$) and slightly acid (ANV$_{\mathrm{S}}$), to acidic (ANS$_{\mathrm{S}}$), while content of SOC shows higher values on ANA$_{\mathrm{S}}$. On this site, value of Pb content is high, which is in line with results of Stanković *et al.*[21] for the same site. Highest concentration of Fe and Ni due to the present technogenic pollution is recorded for soils of separation pond (ANS$_{\mathrm{S}}$), which is in accordance with investigation of Ranđelović *et al.*[12] Content of macroelements varies significantly between the sites, whereas all of them, except Na, show the lowest concentration at ANS$_{\mathrm{S}}$. The content of measured elements in plant leaves remains in the range of normal[22] except in the case of Ni that shows excess values for all sites. As expected, the highest concentration of Ni and Cd are recorded on *A. negundo* leaves from coal separation pond (ANS_L). Content of Ca and Mg significantly differs in leaves originating from different sites, showing the lowest concentration in ANS_L, while concentration of K exhibited highest values on the same site. Similarly, Liu *et al.*[23] compared leaf mineral content in healthy and declining *Acer saccharum* stand and find out significantly lower concentration of leaf Ca and Mg in declining stand in comparison to healthy and higher concentration of leaf K in declining in comparison to healthy stand. Role of K is recognized in the synthesis of protein and carbohydrate metabolism for alleviation of increased abiotic stresses[24] and Drzewiecka *et al.*[25] have found that K was mainly transported and accumulated in the aerial organs of *Acer platanoides* cultivated on polluted mine sludge, accompanied by ROS scavenging and accumulation of secondary metabolites in plant leaves.

Metal uptake from the soil by plant, expressed as *BCF* factor is presented in Table S-III of the Supplementary material. A value of *BCF* below 1 refers to the low accumulation of element in plant organs which is the case for all investigated elements, except Mn, on sites ANA and ANV.

In order to determine capability of leaf samples (future adsorbents) to exchange cations under chemically neutral conditions, *CEC* was detected. It is evident from Table I that ANS, originating from most antrhropogenically influenced area, has the lowest total *CEC* despite the fact that it has 40 and 15 % higher amount of K ions in comparison to ANA and ANV, respectively.

TABLE I. The values of *CEC* (meq/100 g), pH_{pzc}, pH_{sus} for ANA, ANV and ANS

Site	K	Na	Ca	Mg	Total ∑	pH_{pzc}	pH_{sus}
ANA	36.57	7.35	52.40	73.84	170.16	4.14	3.95
ANV	45.91	7.44	49.90	62.11	165.36	4.12	4.07
ANS	52.62	7.33	37.43	47.72	145.09	4.08	3.72

According to Kashyap *et al.*[27] excess K may induce deficiency of other nutrients like Mg and Ca, which is in accordance with results from Table S-II (amount of Ca and Mg is noticeably lower in ANS). Lower value of Ca and Mg content in leaves was noted by Liu *et al.*,[23] in declining *Acer saccharum* stands developing on acidic soil, too. It is recognized that Ca and Mg deficiencies are commonly distributed on acid soils, as such environment promotes leaching of these cations[28] which is in accordance with obtained result of ANS soil pH value (4.76). The results of point of zero charge (pH_{pzc}) were explained elsewhere.[29] The results of zeta potential values (Fig. S-2 of the Supplementary material) indicate that in all samples the negatively charged surface functional groups are predominant.

In order to observe and analyse surface morphology and chemical composition of investigated samples, SEM micrographs and corresponding EDS spectra of samples are presented in Fig. 1. Heterogeneous structures of samples (cracks, irregular pores and rough surface with parts of tracheid) have been described elsewhere.[30] Such morphology promotes metal ions diffusion into internal layers where numerous active sites become more available for ions, and thus increase adsorption performances of sorbent.

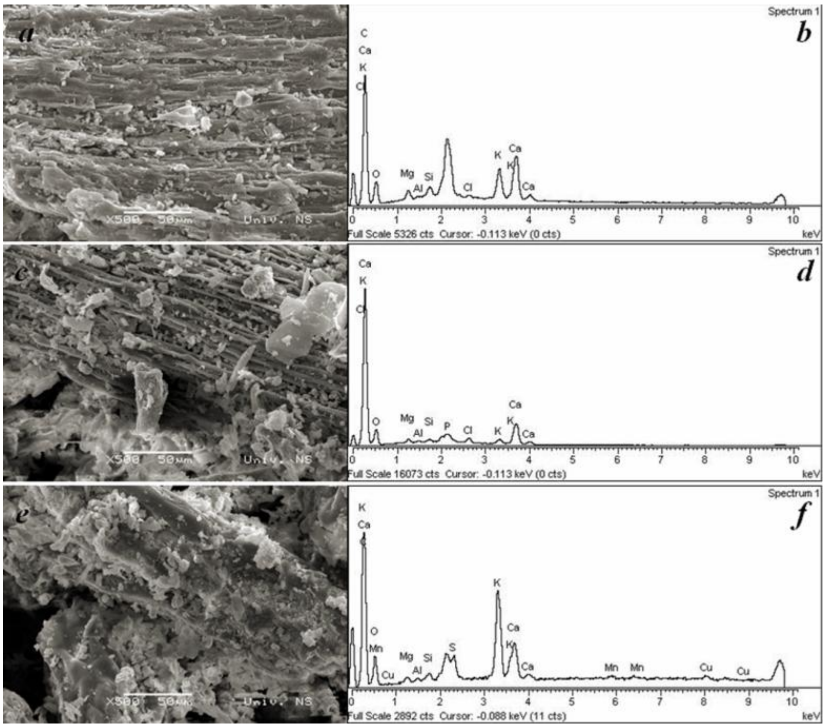

Fig. 1. SEM micrographs and EDS spectrums of: ANA (a/b), ANV (c/d) and ANS (e/f).

ATR-FTIR characterization (Fig. S-2) was carried out, in order to understand changes that occurred in surface functional groups from populations from different habitats. Despite ATR-FTIR spectra of ANV and ANA samples appear to be very similar, certain differences in spectra of ANS sample can be noticed: *i*) higher relative intensity of 1731 cm^{-1} bend (that refers to the C=O stretching vibration of esters from lipid and protein components of cell walls, according to Deng *et al.*[31]), *ii*) the appearance of the shoulder on 1645 cm^{-1} (also C=O stretching of amide I proteins, according to Azuma *et al.*[32]), *iii*) absence of 1548 cm^{-1} peak related to N–H or C–N stretching of amide II[33]), *iv*) presence of 1516 cm^{-1} peak related C=C stretching of proteins (amide II), *v*) lower intensity of the band 1317 cm^{-1} related to the C–H of the methyl functional groups and *vi*) appearance of the new band at 1205 cm^{-1}, due to C–O bending vibration of carbohydrate functional groups.[31]

This result points out to the involvement of different mechanisms of leaves in coping with metal stress common to various plant species, such as impact on protein synthesis and their modification, as well as change in carbohydrate metabolism and signalling to oxidative stress regulation.[34]

Sorption studies

Investigation of the effect of pH onto sorption capacity (Fig. 2a) showed the same trend for all three samples: low sorption capacity of sorbents at pH 2.0, which slowly rises with increase of pH value of the solution. It is well known that solution pH affects the dissociation of functional groups present on the sorbent surface: as the pH value increases, de-protonation of functional groups occurs and the negative charge density increases, increasing the removal of cations from the solution. Since the sorption process is the most efficient at pH 5.0 and in order to avoid formation of hydroxides which may occur at higher pH values, all further experiments were carried out at that pH value. The effect of contact time was examined in order to define required time for equilibrium to be reached. As can be seen from Fig. 2b, the initial sorption of Pb^{2+} occurs very rapidly due to available and abundant active sites present on sorbents surface, sorption of lead ions increases over time and reaches equilibrium after 60 min. The effect of sorbent concentration on sorption capacity and removal percentage was also investigated and results are presented in Fig. 2c. At sorbent concentration of 1.0 g/dm^3, lead removal percentage was 58, 53 and 49 % for ANA, ANV and ANS, respectively. However, when sorbent concentration was raised to 2.0 g/dm^3 the percentage of lead removal increased up to 87, 84 and 73 %, respectively. With further increase of sorbent concentration (up to 20 g/dm^3), the percentage of lead removal went up to 93, 93 and 84 %, while the sorption uptake decreased drastically (from 90, 87 and 70 mg/g to 8.3, 7.5 and 8.9 mg/g, respectively). In relation to that, sorbent concentration of 2.0 g/dm^3 was used in all further experiments. Rise of sorbent concentration induces particle aggregation and stirring difficulties, consequently reducing effective surface area and number of available active sites and slowing down the mass transfer.[15] The results of effect of initial lead concentration on sorption capacity are presented in Fig. 2d. Noticeably, the sorption capacity increased, at initial concentration 2.0 mg/dm^3, from 2.3, 2.4 and 1.8 mg/g to 90.5, 86.25 and 73.75 mg/g at initial concentration 200 mg/dm^3, for ANA, ANV and ANS, respectively. It is well known that increase of initial metal concentration is a driving force for overcoming mass transfer resistance of cations in solid/liquid phase.[15] Effect of temperature on lead sorption capacity of tested sorbents was investigated and the obtained results are presented at Fig. S-4 of the Supplementary material. As the temperature increases, the biosorption capacity decreases from 89.5, 87.7 and 75.7 mg/g at 288 K to 84.1, 81.7 and 69.25 mg/g at 328 K for ANA, ANV and ANS, respectively. Sorption process of lead ions onto investigated sorbents is an exothermic process:

an increase in temperature lead to decrease in ions removal and temperature rise weakens attractive forces between active sites on the sorbent surface and lead ions in solution.

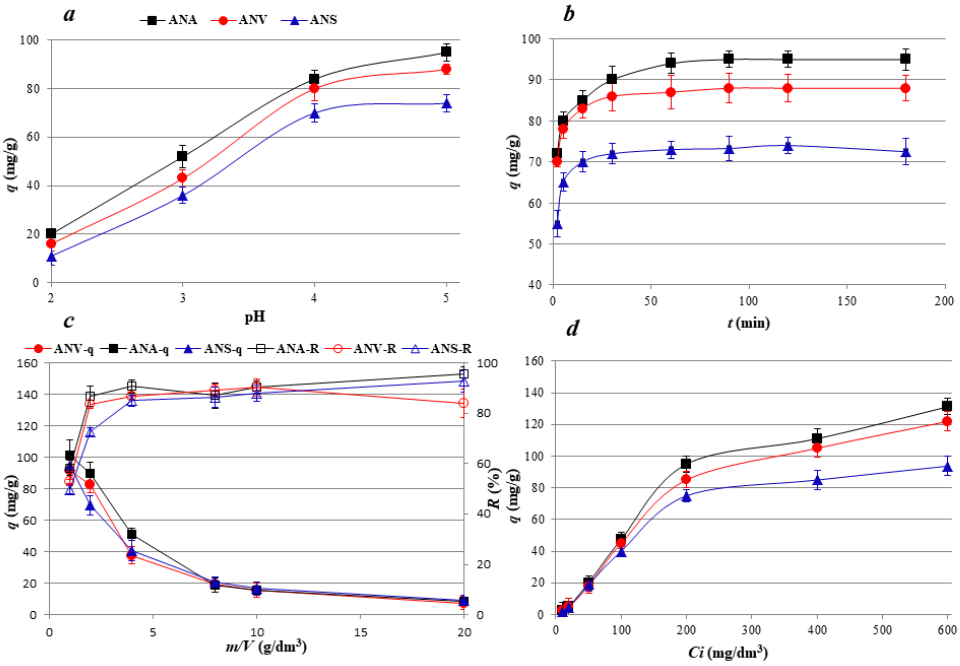

Fig. 2. Effect of operative parameters onto sorbent capacity: effect of pH (a), contact time (b), sorbent concentration (c) and initial Pb^{2+} concentration (d).

Investigation of ion exchange mechanism

Since analyses of the *CEC* showed that all samples have cations in exchangeable positions, the participation of the ion-exchange mechanism in sorption process is expected. Consequently, releases of the exchangeable cations from all materials, together with solution pH value before and after the sorption process, were investigated and the data are presented in the Table S-IV of the Supplementary material. Fig. 3 revealed that the sum of cations, released from ANA and ANV samples, was almost equal to the amount of Pb^{2+} bound on the same sorbents, except at lowest metal concentration, suggesting that ion-exchange mechanism is dominant during the lead sorption process in both samples. However, the sum of the released cations from sorbent ANS is higher than concentration of bonded lead ions. ANS bonds reduce lead ions which are in correlation with lower amount of exchangeable cations on its surface (Table I). These results are in accordance with Table S-IV. Also, the measured final pH value of the solution after sorption process was 3.77 (lower than initial pH value – pH 5.0) indicating that ANS releases a significant amount of competitive hydrogen (hydronium) ions, which reduces binding of lead. This phenomenon might reflect differences in composition of functional groups and active binding sites of sorbents originating from different growing sites, as supported by FTIR analysis.

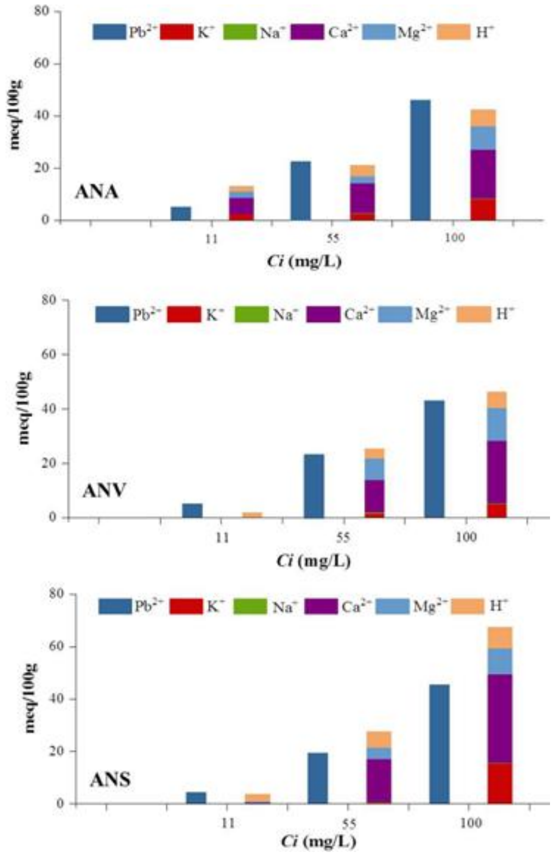

Fig. 3. The amount of sorbed lead ions and released cations from ANA, ANV and ANS at different initial metal concentrations.

Kinetic, sorption isotherm and thermodynamic studies

Table II summarizes data for experimental sorption capacity at maximum time investigated (q_e), together with the kinetic and isotherm model parameters and corresponding determination coefficients (R^2) and χ^2 values. The results of fitting experimental data showed that the best fit was obtained by using the pseudo second order kinetic model, with the highest values of correlation coefficient (R^2) and the lowest chi-factor (χ^2) among the all models applied. This indicates that the sorption mechanism is limited by bonding forces through sharing electrons between the sorbate and the sorbents. As can be seen from Table II, Lagergren pseudo-first order equation, as well as Elovich model, cannot be used to predict the sorption kinetic of lead by any sorbent investigated; the application of these models resulted in the lower values of R^2 and the higher χ^2 values, but also calculated q_m values differ from experimental q_e values. The graphs of kinetics models are presented in Figs. S-5 to S-7 of the Supplementary material.

TABLE II. Kinetic and isotherm parameters calculated for lead sorption by different sorbents

Kinetic model	ANA	ANV	ANS	Isotherm model	ANA	ANV	ANS
Exp. q_e / mg g^{-1}	86.62	83.81	73.25				
Pseudo-first-order				Langmuir			
q_m / mg g^{-1}	84.76	83.10	71.86	q_m / mg g^{-1}	138.99	129.42	105.28
k_1 / min^{-1}	0.9584	1.410	0.6893	K_L / dm^3 mg^{-1}	0.0295	0.0360	0.0224
R^2	0.8320	0.7205	0.8035	R^2	0.995	0.991	0.988
χ^2	3.5754	1.1044	8.4628	χ^2	12.42	19.20	17.14
Pseudo-second-order				Freundlich			
q_m / mg g^{-1}	86.04	83.66	73.67	K_F / mg g^{-1} (dm^3/g)^n	14.53	15.96	5.472
k_2 / g mg^{-1} min^{-1}	0.0323	0.0830	0.0198	$1/n$	2.597	2.770	2.570
R^2	0.9744	0.9449	0.9706	R^2	0.920	0.904	0.895
χ^2	0.5446	0.3380	1.2682	χ^2	210.18	221.78	149.18
Elovich				Sips			
q_m / mg g^{-1}	89.93	84.60	76.31	q_m / mg g^{-1}	131.52	120.18	94.92
a / mg g^{-1} min^{-1}	4.00E12	1.66E29	8.99E6	K_s / dm^3 g^{-1}	0.0205	0.0181	0.0090
b / g mg^{-1}	0.3780	0.8548	0.2601	s	1.159	1.297	1.345
R^2	0.8108	0.8623	0.8531	R^2	0.997	0.998	0.985
χ^2	4.0270	0.5442	6.3276	χ^2	8.610	4.914	6.912

The applicability of pseudo-second order kinetics model suggested that the lead removal by *A. negundo* sorbents is based on chemical reaction, involving the exchange of electrons between the sorbents and the metal ions present in sorbate solution. The highest value of the pseudo-second reaction rate constant, k_2, is obtained for ANV sorbent (0.0830 g/(mg min)), indicating the fastest removal for this sorbent. This can also be seen from the Fig. S-4, where the fitting of the experimental data by pseudo-second order model is presented. Although the highest rate is observed for ANV, the ANA sorbent has higher overall maximum sorption capacity under applied operational parameters, 86.04 mg/g, while the lowest one is found to be the capacity of ANS (73.67 mg/g). Previous reports on sorption kinetics by the similar biomasses suggest that pseudo-second order kinetics govern most of the sorption processes. For example, Qaiser *et al.*[35] have investigated the potential of *Ficus religiosa* leaves in lead sorption, and find out that the sorption process is well described by the pseudo-second order model, with maximum removal capacity of 19.76 mg/g at 20 °C. Sangi *et al.*[36] have investigated the potentials of *Ulmus* sp. and *Fraxinus* sp. tree leaves for lead removal and obtained the kinetic results which indicated that second-order kinetics best describe the experimental data, relying on the assumption that the rate limiting step involves valence forces through sharing or exchange of electrons between the sorbent surface sorbent and sorbate ions.

Additional, two-parameter model were used to correlate isotherm data: the Langmuir[37] equation which is valid for monolayer sorption onto a surface with a finite number of identical sites and the empirical Freundlich[38] isotherm based on sorption on a heterogeneous surface. Beside them one three-parameter model, named Sips[39] isotherm was used. This model represents combination of Langmuir and Freundlich expressions: at low metal concentration it approaches Freundlich isotherm, while at high concentrations it predicts a monolayer adsorption capacity characteristic for the Langmuir isotherm. Graph of all isotherm models are presented in Figs. S-7 and S-8. Looking at the data (Table II), on the basis of the R^2 closest to 1 and the lowest values of χ^2, the following order of fitting equations is found to be: Sips>Langmuir>Freundlich. The equilibrium parameters, R_L, calculated as $R_L = 1/(1+K_LC_0)$, are falling in the range from 0.047 up to 0.889 in the investigated concentration range. These values indicate that the removal of lead ions onto *A. negundo* sorbents is favourable for all sorbents applied. The best fitting model (Sips) of the sorption equilibrium is presented at Fig. S-7. ANA has maximum sorption capacity of 131.52 mg/g at 298 K while the lowest removal was achieved by ANS application, 94.92 mg/g. Sips model implies that, in the same time, monolayer sorption and heterogeneous energetic distribution of active sites on the surface of the sorbent is possible.[40] Moreover, Sips model has been proven to be applicable in cases of pH dependent sorption, such is the case of lead removal by *A. negundo* sorbents.[41] Table III contains comparative data of investigated materials sorption capacity with other similar lead sorbents found in the literature. As can be seen, among three sorbents investigated in this study, the highest sorption capacity is detected in ANA which is grown in uncontaminated habitat. This indicates that the majority of the presented functional groups are available for adsorption of Pb^{2+}. The lowest sorption capacity is detected in ANS, which indicates lower availability of functional groups for Pb^{2+} adsorption due to their current involvement in metal immobilization and/or different chemical composition of leaves and different proportion of functional groups to which Pb^{2+} show high binding affinity.

TABLE III. Comparison of lead sorption on various leaves sorbents

Sorbent (leaf powder)	q_m / mg g^{-1}	pH	C_i / mg dm^{-3}	Model
Bael tree[42]	4.065	5.0	25–100	Langmuir
Cocos nucifera[43]	8.475	5.0	10–150	Langmuir
Ficus religosia[44]	37.45	4.0	10–1000	Langmuir
Cinnamomum camphora[45]	73.15	5.0	50–400	Langmuir
Broussonetia papyrifera[46]	84.74	5.5	10–500	Langmuir
Aegle marmelos[47]	104.0	5.1	8.7–180.2	Langmuir
Citrus grandis[48]	207.2	4.1	0–1000	Sips
Acer negundo (this study)				
ANA	131.5	5.0	5–600	Sips
ANV	120.2	5.0	5–600	Sips
ANS	94.92	5.0	5–600	Sips

Although this study showed that the sorption capacity of *A. negundo* leaf powder in comparison to other sorbents with similar structure found in literature is very high, it primarily emphasizes the importance of growing site on plant material properties and its sorbent capacity. As found in this investigation, the variability in sorption capacity may be significantly different among different samples and it even reached 30 %.

CONCLUSIONS

The presented investigation has shown that sorbents based on *A. negundo* L. leaves are the promising sorbents for the removal of lead ions from contaminated waters, but has also highlighted the importance of growing site as a factor affecting the sorption performance of the future sorbent. Prior to the sorption experiments, characterization of soils and leaves revealed differences between samples from selected growing sites, particularly with respect to the content of PTE and *CEC*, as well as differences in the presence of certain functional groups in *A. negundo* leaves, responsible for sorption. The adsorption process was pH dependent and the optimum pH for lead removal was 5.0, after 60 min of contact time, at optimized sorbent dose of 2.0 g/dm^3. The results of fitting experimental data showed that the best fit was obtained by using the pseudo second order kinetic model, indicating that the sorption mechanism is limited by binding forces through electrons sharing between the lead ions and the sorbents. It was show that lead ions were removed with a maximum lead loading capacity of the samples of 131.52, 120.18 and 94.92 mg/g for ANA, ANV and ANS, respectively, which is either comparable to or better than the lead loading capacities of other reported similar sorbents. This research indicated that the differences in growing sites should be taken into account when studying the sorption process, as they affect the adsorption performance of the chosen biomass. Future studies could reveal the extent of this influence on different sorbents and uncover the most influential site factors and physiological mechanisms responsible for such outcome.

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/13367, or from the corresponding author on request.

ИЗВОД

ПОРЕЂЕЊЕ АДСОРПЦИОНИХ СВОЈСТВА БИЉНЕ БИОМАСЕ ПОРЕКЛОМ СА РАЗЛИЧИТИХ СТАНИШТА – СТУДИЈА СЛУЧАЈА ИНВАЗИВНЕ ВРСТЕ *ACER NEGUNDO*

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На природним стаништима инвазивне биљне врсте имају снажан утицај на биодиверзитет, примарну продуктивност екосистема, мрежу исхране, кружење хранљивих материја. Услед њиховог глобалног ширења, њихова употреба се намеће као атрактивно решење. Развој адсорбента за пречишћавање вода, је једно од могућих решења. У складу са тим, у овом раду, испитана су својства адсорбената на бази биомасе инвазивне биљке *A. negundo,* са три различита станишта, у сврху уклањања олова из воденог раствора, како би се показало да ли карактеристике станишта утичу на својства адсорбента. За узорковање су одабране три локације: ободне шуме на Авали, приобалне шуме на Великом ратном острву и обод базена за сепарацију угља у Пискањи. Карактеризација материјала је извршена коришћењем $\mathrm{pH}_{\mathrm{pzc}}$, зета потенцијала, капацитета за измену катјона, SEM-EDS и FTIR анализа. Оптимизацијом параметара сорпције утврђено је да је најбољи учинак при pH 5,0, дози адсорбента 2,0 g/dm^3 на 298 K током 60 min. Применом изотермних модела на податке добијене у сорпционим експериментима, утврђена је најбоља корелација са Сипсовим изотермним моделом ($q_{\max}$ је 94,92–131,52 mg/g, у односу на станишта). Такође, међу три коришћена кинетичка модела, најбоље резултате показао је модел кинетике псеудо-другог реда. Резултати ове студије су показали да узорак који је узет са подручја које је под највећим антропогеним утицајем, има скоро 30 % нижи капацитет адсорпције у односу на друга два узорка. Можемо се закључити да се утицај станишта огледа на физичко–хемијска својства биомасе, а са тим у вези и на сорпционе одлике биомасе, што је важан фактор за даљу употребу у сврху развоја сорбената.

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