ECO-FRIENDLY ELDERBERRY BASED SORBENT FOR REMOVING Pb²⁺ IONS FROM AQUEOUS SOLUTIONS

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Abstract

Elderberry (Sambucus nigra) pith was modified with polyethyleneimine (PEI) in order to improve the adsorption properties. Characterization of both dried Sambucus nigra pith (DSNP) and amino modification of elderberry pith with branched PEI (PEI/DSNP) was performed by: Fourier-transform infrared spectroscopy (FTIR), optical microscopy, and porosity determination. The amine and ester number, as well as acid value, were determined on DSNP and PEI/DSNP samples using standard volumetric methods. The samples were used as adsorbents for Pb²⁺ ions from an aqueous solution in a batch system. The obtained results were fitted using suitable equilibrium isotherm and kinetic models. The maximum adsorption capacity for Pb²⁺ ions on DSNP and aminated sample, obtained using Langmuir adsorption isotherm at 298 K, are 18.9 and 47.8 mg g⁻¹, respectively. Based on the kinetic studies, the adsorption process follows the pseudo second-order model. Thermodynamic parameters showed that the adsorption process is endothermic and spontaneous. In general, the overall adsorption process was improved by modifying starting material with branched PEI modifier by introducing large numbers of amino functionalities having high affinity to cations.

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Introduction

One of the biggest problems that humanity has been facing in recent years is the pollution of water resources from various sources. Heavy metal ions and organic pollutants pose a great danger to the environment [1, 2]. Those ions are highly toxic and belong to the group of stable pollutants. Toxic compounds enter groundwater and surface water mostly as a result of human activity [3]. During production processes in the pulp industry, metallurgy, mining, automotive, aerospace industry, there is an increased use of chemicals, with increasing production of wastewater containing large amounts of heavy metals, such as Ni, Pb, Fe, Cr, Cu, Hg, etc. [4, 5]. Heavy metals, as non-biodegradable pollutants, are persistent in ecosystems adversely affect humans living organisms, causing a large number of diseases. The goal is to find materials, as well as improve their properties, in order to reduce the concentration of heavy metals in water. In recent years, biomaterials, including elderberry, due to low cost, availability, environmental friendliness, are increasingly being used as sorbents in the removal of heavy metal ions from polluted waters. Elderberry (also called a perennial woody plant) originates from Europe (Sambucus nigra) and North America (Sambucus canadensis) [6]. Organic acids, sugars (primary metabolites), phenols (secondary metabolites), vitamins A, C, cytokines make up the chemical composition of elderberry fruit. However, elderberry pith is not well enough studied, and the first scientific research was performed during the Second World War, where the pith and wood of elderberry were studied [7]. Also, in Great Britain, during the Second World War, elderberry wood was used to produce coal. The resulting coal was high in calories, hard, granular in structure [7].

A very big advantage compared to other biomaterials is that elderberry pith is a cheap material, highly porous, widespread, and has good throughput. Unlike woody, older stems, the proportion of elderberry pith is much higher in young stems, which are grown in protected localities with a large amount of sunlight. The pith of elderberry may be easily dispart from the wood, as it is known that elderberry grows in the form of bundles containing from 12 to 20 sticks, whereas the length of pith in each stick is about 1 m. Pith is most often used for the manufacture of very small spindles, watches, and similar industries, in polishing. Previous research has noted that the best piths are isolated from straight, long, vertical stems, which originate from the lower parts of the tree [7]. For example, if young stems are cut, the pith is very easy to isolate due to the presence of secondary xylem in small quantities. However, the pith obtained in this way is not of great importance because it decomposes very quickly. While in older trees, where the amount of secondary xylene is higher, the separation of pith is much more difficult, but thus its decomposition is slower.

In order to achieve satisfactory water quality, it is necessary to constantly monitor the concentrations of metals and other impurities that are present. Therefore, many conventional techniques have been developed for heavy metal removal, such as filtration, membrane technologies, precipitation, electrochemical treatment, and others [8]. Materials that contain a large amount of cellulose slowly degrade during use and the right polymer solutions are formed. In this case, the materials structure becomes less consistent, and as a result of that, it is harder to remove the biosolvent from the system. Some of the products are oxidative α-isosaccharinic acid and β-isosaccharinic acid [9, 10]. Unlike expensive conventional techniques, the adsorption process is a relatively efficient, simple, and inexpensive method. A large number of sorbents show an affinity for metal ions [11, 12]. Many factors, such as the type of metal and the composition of the sorbent, affect the

removal of metal ions. Natural materials are increasingly used due to the possibility to improve the adsorption properties by structural modifications, as well as due to the low cost of cutting [13, 14]. Biosorbents have appropriate functional groups, which originate from available organic compounds and biopolymers, which readily uptake metal ions by complexation [15, 16]. Such a group of biosorbents includes the elderberry pith, which, thanks to functional groups, such as phenolic, hydroxyl, carboxyl, and amino, erase which have the ability to bind metal ions [14].

The aim of this study is to develop a cost-effective DSNP modified adsorbent with PEI used to remove Pb^{2+} ions from water. Its adsorption properties towards lead ions should be improved by inserting amino functionalities of PEI, which may be bonded on ester groups of DSNP structure.

Experimental

Acid, esterification numbers, total amines were determined by standard test methods. Standard volume methods used are ASTM D1980-87(1998) (acid value number), ASTM D94 - 07(2017) (ester value number), D2074-07 (total amine value).

Materials preparation

The preparation of the adsorbent is as follows: in the first step, 0.579 g of dried elderberry pith was measured. In order to aminate the material, the ester groups present were converted to the amide by reaction with branched PEI (0.20 g, 0.00464 mol). During the amination process (6h at 80 ℃), the material received a large number of functional amino groups derived from the PEI modifier. The volume of ethanol used is sufficient for all particles to be completely wetted by the liquid phase of the reaction mixture, in this case, $m/V = 16.5$ g dm^{-3}. The elderberry sample, modified with PEI was inserted into a glass flask, after which it was subjected to ultrasound treatment and vacuuming with a water jet vacuum pump for 5 minutes.

After this, the system was gradually heated until a temperature of 80°C was reached. The amination process was completed after eight hours of total ethanol reflux. Finally, the sample was washed with ethanol, filtered, and dried at atmospheric pressure at 50°C for four hours. The dried sample was stored in a plastic closed container.

Characterization section

Characterization of both dried Sambucus Nigra pith (DSNP) and its aminated modification (PEI/DSNP) was performed by: Fourier-transform infrared spectroscopy (FTIR) optical spectroscopy, while pH point of zero charge (pH_{PZC}) Sontheimer porosity measurement was determined using standardized methods described. Optical micrographs were obtained using BTC STM-8T Trinocular Stereo Microscope ZOOM. Both samples were utilized as Pb^{2+} absorbent. Adsorption properties were determined performing equilibrium adsorption, kinetic and thermodynamic studies in the batch system following Taguchi model used for experimental design [17].

Optical micrographs of DSNP and PEI/DSNP are given in Figure 1.
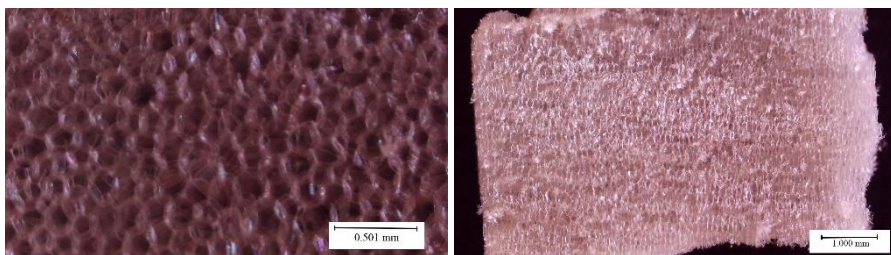
Fig. 1. Cross-section and longitudinal section of a DSNP sample on an optical microscope.

Figure 1. shows the shape and size of the DSNP sample obtained by optical microscopy, using a BTC STM-8T Trinocular Stereo Microscope ZOOM microscope, on which a transverse and longitudinal section of a DSNP sample can be seen. The cell walls are thin, about 8 microns thick. The diameter of the smallest and largest cell is about 50 and 200 microns, respectively.

The FTIR spectra of the sample were recorded using Fourier transforms infrared (FTIR) spectra, using a Nicolet^{TM}iS^{TM}Spectrometer (ThermoFisherSCIENTIFIC) spectrometer with Smart iTR™ Attenuated Total Reflectance (ATR) Sampling accessories, within a range of 400-4000 cm^{-1}, at a resolution of 4 cm^{-1}and in 20 scan mode. FT-IR spectra of PEI/DSNP before and after adsorption of Pb^{2+} ions are presented in Figure 1. PEI/DSNP spectra were analyzed and compared before and after Pb^{2+} adsorption depending on the shape, frequency, and intensity of the characteristic peaks. The change in intensity is recorded at 1035 and 1160 cm^{-1}which is the characteristic peak for C-O stretching vibration of carbohydrate structure and C-N groups. The wide band at about 3335 cm^{-1} in the FT-IR spectra of the elderberry pith refers to O-H and NH_2 stretching vibrations. Also, changes occur at about 1737cm^{-1} (1735 cm^{-1}), 1591cm^{-1}(1593 cm^{-1}), 1459cm^{-1}(1455 cm^{-1}), and 1109 cm^{-1}for DSNP (1103 cm^{-1}for PEI/DSNP) as a results of chemisorption between Pb^{2+} ions and functional groups present in adsorbent. Namely, bonded lead ions decrease the energy needed for bonds to vibrate or bend therefore almost all changes for PEI/DSNP occurred at smaller wave number. The small change of wavelength value, from 1591 cm^{-1} to 1593 cm^{-1}, is due to N-H bond vibration affected by interaction with Pb^{2+}. Assuming that lead is covalently bonded *via* free electron pair on amino groups, it is expected that those hydrogen bonds with nitrogen are shorter and therefore stronger leading to higher energy demand for bond excitation.
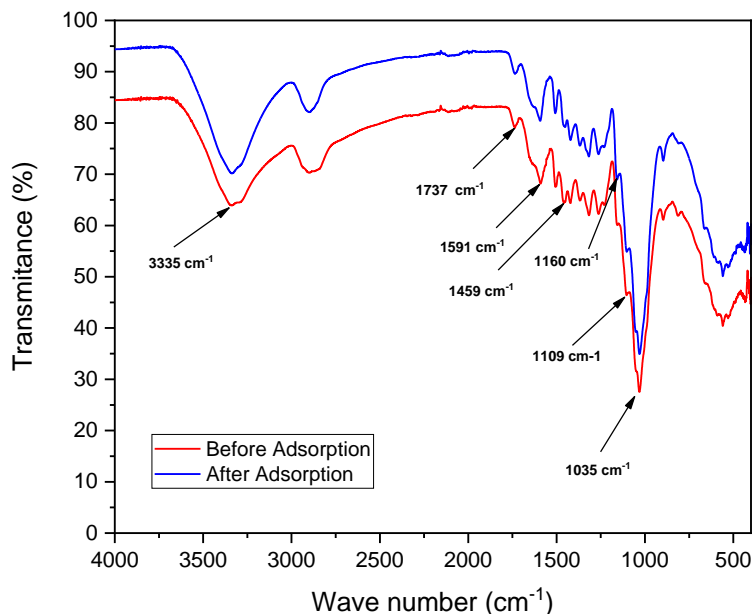
Fig. 2. FT-IR spectra of PEI/DSNP before and after Pb²⁺adsorption.

Results and discussion

Adsorbent characterization

Measured values of acid, ester, total amine number, bulk density and porosity determined for DSNP are given in Table 1.

Table 1. Acid, ester number, total amine number, bulk density and porosity of DSNP and PEI/DSNP adsorbent.

Adsorbent	Acid Value Number	Ester Value Number	Total Amine Value	Bulk density	Porosity
DSNP	2.9mgKOH/g	370.2 mg KOH/g	8.3mgKOH/g	8.2×10^{-2} g/cm^3	61.8 %
PEI/DSNP	<1 mg KOH/g	-	72.8 mg KOH/g	8.4×10^{-2} g/cm^3	58.9 %

According to the results from Table 1, it is obvious that an appropriate extent of ester groups transformation to amide was obtained, but from the point of the successfulness, i.e. maximum of possible amine value with respect to ester group in DSNP only 20% of the ester groups are transformed into amide (taking into count PEI and both samples total amine value together with the assumption that every ester group of PEI is transformed into amide group). The amination procedure should be further improved for the development of PEI/DSNP adsorbent with a higher extent of amino groups, which is well known to have a high affinity to cation.

The pH value at which the net charge of the surface of the dispersed particle is zero, i.e. neutral, is called point of zero charge pH (pH_{PZC}) [18]. The net charge of the adsorbent surface is positive for pH values that are less than pHpzc and negative if pH is above pH_{PZC} value. The value of pH_{pzc} is determined from a wide set of initial pH values, and as can be seen in Figure 3, the PEI/DSNP retains its surface neutral on a wide range of pH values (5<pH<9). In determining the pH_{pzc}, a KNO_3 solution with concentrations of 0.1, 0.01, and 0.001 M, respectively, were used. The obtained results are given in Figure 3, with a determined pH_{PZC} value of 6.74.
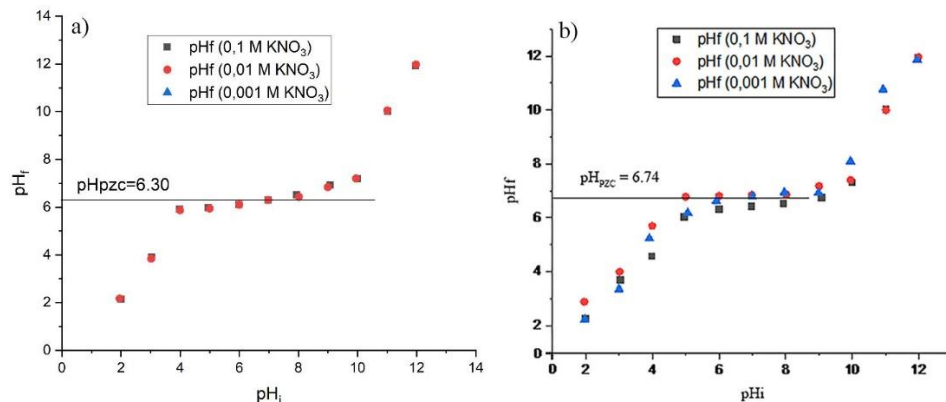

Fig. 3. The final pH(pH_f) versus initial pH(pH_i) change for: (a) DSNP, and (b) PEI/DSNP.

The pHpzc depends on the ion activity of the aqueous solution, but this dependence is negligible in 5<pH<9 region, as can be seen in Figure 3. Such almost flat plateau is due to the extent of the ionization of surface functionalities at appropriate pH, i.e., proton donating/accepting capability of primarily amino and carboxyl groups present at PEI/DSNP surface (Table 1). Similar pH_{PZC} values were found for a wide set of similar materials: waste cellulose 6.6, lignin 6.2, and other plant-based materials [19,20]. The value of pH for zero net charge is a useful parameter for adsorption management since it may point to the optimal application of selected material. Used material should be oppositely charged from the pollutant on the selected pH value, which would promote its adsorption on the surface. The Pb^{2+} adsorption is enhanced by the negatively charged surface of the adsorbent. According to this and the known fact that the pH of natural water is in the range 6-8, a pH of 6 was selected for adsorption experiments.

Adsorption kinetics

The effect of time on Pb^{2+} adsorption was monitored in the range of 5 to 180 minutes. The final equilibrium was established after 220 minutes, but since the difference in the removal of Pb^{2+} ion for 180 and 220 minutes was less than 3%, this fact allowed us to select 180 minutes for further kinetic experiments. Different kinetic rate law equations: pseudo-first, pseudo-second-order (PSO) and second-order models [21] were used for fitting kinetic data.

Results obtained from selected kinetic models data fitting, evaluated according to the regression coefficient (R^2) and standard error for all model parameters, indicate that

the studied kinetic is best described using a PSO model. PSO model is given by equation (1):

$$q_t = \frac{t}{1/k_2 q_e^2 + 1/q_e} \qquad\qquad 1$$

The kinetic parameters for Pb^{2+} adsorption on PEI/DSNP are given in Table 2.

Table 2. The kinetic parameters for Pb^{2+} ions adsorption on PEI/DSNPadsorbent ($Ci_{[Pb}$$^{2+}$$_]$ = 9.00 mg L^{-1}, pH = 6; m/V = 135 mg L^{-1}, T = 25 °C).

Adsorbent	Model parameters	Pseudo-first	Pseudo-second	Second-order
PEI/DSNP	q_e(mg g^{-1})	16.663	41.826	41.826
	k (k_1, k_2) (g mg^{-1} min^{-1})	0.01926	0.00221	0.00016
	R^2	0.815	0.997	0.527

Similar result for PSO rate constant was obtained for DSNP (0.00286g mg^{-1} min^{-1}). The PSO rate constant is slightly lower due to the presence of voluminous side chains originating from PEI structure. Since the best fitting was performed with PSO model, it may be concluded that at least three chemical species are involved during the adsorption of lead ions; since lead is a cation of 2+ net charge it is bonded with at least two covalent bonds on the surface of PEI/DSNP.

The rate constants from the intra-particle diffusion model, i.e. Weber-Morris model, for Pb^{2+} ions adsorption on PEI/DSNP adsorbents is given in Table 3.

Table 3. Parameters of Weber-Morrismodel ($Ci_{[Pb}$$^{2+}$$_]$ = 9 mg L^{-1}, pH =6; m/V = 135 mg L^{-1}, θ = 25 ^{o}C).

Model parameters	PEI/DSNP
k_{p1} (mg g^{-1} min$^{-0.5}$)	4.77352
C_1(mg g^{-1})	2.805
R^2	0.997
k_{p2}(mg g^{-1} min$^{-0.5}$)	0.25201
C_2(mg g^{-1})	35.6753
R^2	0.953

The Weber-Morris model reveals two linear steps that describe the adsorption process: fast kinetics in the first step and slower in the second. The first linear part describes the external mass transfer to the adsorbent surface, while the second part describes the process of material transfer into the porous structure of the adsorbent, and strictly depends on the size and shape of the pores as well as the density of PEI/DSNP adsorbent pore network. Intra-particle and film diffusion slow down the transport of adsorbate. In the final phase of the process, adsorption takes place slowly until saturation is achieved on the entire available surface of the adsorbent.
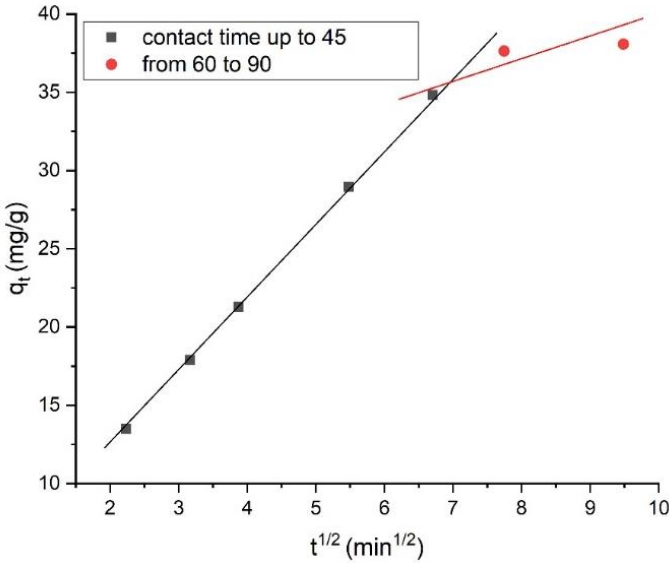
Fig. 4. Correlation of experimental data of adsorption kinetics of the Weber-Morris model.

The evaluation of the adsorption capacity of the elderberry-based adsorbent was performed using a batch experiment for the adsorption of Pb^{2+} ions. Adsorbents whose masses are, m = 1.0, 2.5, 5.0, 7.5 and 10.0 mg, was placed in vials containing 15 ml of standard Pb^{2+} ion solution (conc. 9 mg/L) and pH = 6.0. Adsorption experiments were performed at 298 K. In Table 4, certain isotherm parameters are presented. Adsorption experimental data is fitted using various isotherm models [22], and according to the highest F value and other statistical parameters (ANOVA parameters), Freundlich and Langmuir isotherms are selected, and the results for these two isotherm models are presented (Table 4).

Table 4. Parameters of adsorption isotherms of Pb^{2+} ions adsorption on PEI/DSNP.

	Isotherm models and parameters		Temperature		
			25 °C	35 °C	45 °C
PEI/DSNP	Langmuir isotherm	q_m (mg g^{-1})	47.800	52.198	56.311
		K_L (L mg^{-1})	0.57501	0.59709	0.63262
		R^2	0.973	0.960	0.945
	Freundlich isotherm	K_F (mg g^{-1}) (dm^3 mg^{-1})$^{1/n}$	16.404	18.203	20.168
		$1/n$	0.475	0.465	0.451
		R^2	0.998	0.999	0.993

The Langmuir and Freundlich isotherm models are given by Eq. (2) and (3), respectively:

$$q = (bq_{max}C)/(1+bC) \quad_{or}\quad C/q = 1/(bq_{max}) + C/q_{max} \qquad 2$$

$$q = k_f C^n \quad or \quad \log q = \log k_f + n \log C \qquad\qquad\qquad 3$$

The results from Table 4 indicate that the PEI/DSNP have a 1/n value in the range 0.451-0.475, which means that PEI leads to an improvement in the adsorption properties of the DSNP surface but also increases the heterogeneity of sorbent surface, which is expected because bonded PEI side chains increase the disorder of the system.

Thermodynamic study

Gibbs free energy (ΔG^{Θ}), enthalpy (ΔH^{Θ}) and entropy (ΔS^{Θ}) were calculated by Van't Hoff equation (4) and (5):

$$\Delta G^{\Theta} = -RT \ln(b) \qquad\qquad\qquad 4$$

$$\ln(b) = \frac{\Delta S^{\Theta}}{R} - \frac{\Delta H^{\Theta}}{RT} \qquad\qquad\qquad 5$$

where T is the absolute temperature in *K, R* is the universal gas constant (8.314 mol⁻¹ K⁻¹) and the adsorption constant b is calculated using the Langmuir isotherm (Table 4). ΔH^{Θ} and ΔS^{Θ} were calculated from the slopes and sections in the diagram $\ln(b)$ - T⁻¹, assuming that the adsorption kinetics are stationary. The calculated thermodynamic parameters are shown in Table 5.

Table 5. Calculated Gibbs free adsorption energy, enthalpy and entropy for Pb²⁺ adsorption on PEI/DSNPat 25, 35 and 45 °C.

Adsorbent	ΔG^{Θ} (kJ mol⁻¹)			ΔH^{Θ}	ΔS^{Θ}	R^2
	25°C	35°C	45°C	(kJ mol⁻¹)	(J mol⁻¹ K⁻¹)	
PEI/DSNP	-38.93	-40.33	-41.79	3.76	143.13	0981

Negative values of Gibbs free energy (ΔG^{Θ}) and positive values of entropy (ΔS^{Θ}) at all temperatures indicate that reactions in the adsorption process take place spontaneously. A decrease in the Gibbs free energy (ΔG^{Θ}) with an increase in temperature also indicates that the spontaneity of the reaction increases. A positive value of ΔH^{Θ} reveals a higher affinity of Pb²⁺ to PEI/DSNP with temperature increase indicating appropriate participation of chemisorption to overall adsorption process.

Conclusions

In this work, DSNP was modified with PEI and obtained material was tested as adsorbent for Pb²⁺removal from water. Physico-chemical properties of dry biosorbent were investigated using different methods. It is determined that the sample possesses low content of both amino and carboxyl groups but the high presence of ester groups which are susceptible to a wealth of chemical modification. However, those ester groups are not that available for reaction with amino groups of PEI due to steric hindrance and voluminosity of PEI modifier. Due to the lower extent of DSNP modification with PEI showed appropriate increase of adsorption capacity, from 18.9 for DSNP to 47.8 mg g⁻

[1]for PEI/DSNP, obtained by Langmuir isotherm data fitting. Additionally, thermodynamic and kinetic studies confirmed the high potential of PEI/DSNP as an adsorbent. Due to this, future studies will be focused on the development of more efficient activation of ester functional groups and promoting adsorbent reusability and its use in a continuous system.

Acknowledgement

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