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POTENTIAL VALORISATION OF PROTOBIND 1000 AS ADSORBENT FOR Pb^{2+} AND Zn^{2+}

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ABSTRACT. The adsorption of metal ions from increasing concentrations in aqueous solutions by modified straw lignin Protobind 1000 was studied. The effect of metallic ion concentrations (from 20.72 to 207.2 $mg \cdot L^{-1}$ for Pb^{2+} and from 6.538 to 65.38 $mg \cdot L^{-1}$ for Zn^{2+}) and contact time (30, 60 and 90 minutes) were studied at pH = 6 and 20^0C. Langmuir and Freundlich isotherm equations were applied to assess equilibrium data and the kinetics of the adsorption processes were analysed using Lagergren pseudo first order and Ho&McKay pseudo second order models. The results show that the adsorption processes reached equilibrium after 90 minutes, but similar values were registered after 60 minutes. The Freundlich isotherm described the process better, denoting chemisorption with the formation of ion-lignin complex structures. The Ho&McKay model fit the adsorption data better with regression coefficients equal to 1 compared to the Lagergren model, where the regression factors varied between 0.72 and 0.95. For the maximum concentration of lead solution and the longest adsorption time of 90 minutes, the Ho&McKay model predicted an equilibrium capacity q_e of 13.1406 $mg \cdot g^{-1}$ compared to the 13.1398 $mg \cdot g^{-1}$ obtained. For zinc adsorption, the same maximum concentration and time were considered, and the pseudo-second order model predicted a q_e of 12.6743 $mg \cdot g^{-1}$ compared to the obtained value of 12.6714 $mg \cdot g^{-1}$.
The uptake of lead was greater on 0.15 g of adsorbent (a maximum of 27.23 $mg \cdot g^{-1}$) than the zinc uptake (a maximum of 8.28 $mg \cdot g^{-1}$), for all analysed concentrations.

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Keywords: adsorption, Protobind 1000 (PB 1000), lead, zinc.

INTRODUCTION

Heavy metals are known to cause severe damages to animal organisms (Rao *et al.,* 2011). Different methods are used for their removal (ion exchange, precipitation, separation, or reverse osmosis) (Amer *et al.,* 2010; Saleh 2021), but they are expensive or inefficient at low concentrations. Therefore, adsorption is usually preferred because it is efficient, easy to use and different adsorbents are available (activated carbon, zeolites, clay minerals or resins) (Rao *et al.,* 2011; Saleh, 2021). Efforts have been taken to use phytoremediation (Bello *et al.,* 2018) or to obtain low-cost adsorbents, nanomaterials, polymers, and green materials to remove metals from waste waters of household or industrial origin (Esmaili *et al.,* 2003; Janyasuthiwong *et al.,* 2015; Kurniawan *et al.,* 2006; Saleh, 2016, 2021; Sani *et al.*, 2017; Al Hamouz *et al.*, 2017).

The highest amount of lead acceptable in water is 0.05-0.1 $mg \cdot L^{-1}$ and for zinc, 5 $mg \cdot L^{-1}$. These ions are not biodegradable and can accumulate in plants and animals, causing multiple effects (Depci *et al.,* 2012). Studies have been made on the ability of plant or animal-based biochar to retain heavy metal ions. This is due to the hydroxyapatite content of biochar(Xue *et al.,* 2020; Sellaoui *et al.,* 2019; Xu *et al.,* 2013; Meng *et al.,* 2018; Trakal *et al.,* 2011).

The objective of this study is to determine if lead and zinc at different concentrations in aqueous solutions can be retained on thermally treated Protobind 1000.

MATERIALS AND METHODS

Material and reagents

Protobind 1000 (PB 1000) lignin derivative is a commercial product supplied by Granit Recherche Développement S.A. from Lausanne, Switzerland. It is residual lignin separated by the process of alkaline descaling of some annual plants (cereal straws such as wheat or barley). It is heat-treated at 70 ºC in order to increase its stability to the action of environmental factors. The properties and an SEM image of the surface of this modified lignin are presented in *Table 1* and *Figure 1* (Gîlcă *et al.*, 2013)

Lignin is an amorphous natural resin with a three-dimensional aromatic polymer structure bearing various functional groups (alkyl and aromatic hydroxylic groups, carbonyl, methoxy etc.) These functional groups are capable of forming bonds with metallic ions and therefore have ion-exchange ability. This makes lignin a potentially useful adsorbent material for retaining heavy metals from different solutions.

Table 1 - Protobind 1000 properties

Properties	
Relative humidity, %	4.2
Ash, %	1.4 - 1.8
Solubility in acids %	1,2
Insolubility in acids %	91.5
Solubility in aqueous alkali %	94
Solubility in furfuryl alcohol, %	40.1
T softening, °C	200
pH (10% aqueous suspension)	3.5
Particle size	>99% <210 μm
Density (g/cm^3)	0.3
Aryl OH, mmoles / g	1.8 - 1.9
COOH, mmoles / g	2.1 - 2.3

Figure 1 – SEM image of the PB 1000 surface

Table 2 contains the distribution of PB 1000 functional groups.

Table 2 - Functional groups content of Protobind 1000

T^0C	-	90	90	50	50
pH	-	12.0	10.5	10.5	12.0
OH total groups	1.11	1.23	1.15	1.14	1.16
Ar-OH groups	0.89	0.98	0.98	0.98	0.99
OCH_3 groups	1.05	1.15	1.13	1.12	1.14
Alk/Ar ratio	1.17	1.27	1.20	1.22	1.21
C=O groups	0.89	0.95	0.91	0.95	0.94
Siringyl/ Guaiacyl ratio	0.83	0.96	0.96	0.96	0.96

Thermogravimetry is well-known and it is often used to analyse lignin's thermodynamic properties. *Table 3* shows the decomposition temperature of PB 1000.

Table 3 - Characteristics of Protobind 1000 thermal degradation process

Stage	I	II	III
T_i (°C)	52	229	330
T_{max} (°C)	77	267	383
T_f (°C)	106	330	532
W (%)	3.31	17.05	42.47

T_i - initial temperature - degradation starts; T_{max} – temperature at the maximum rate of degradation, T_f – final temperature and W – mass loss %.

Among spectral analysis techniques, nuclear magnetic resonance (NMR) provides the most complex structural information for organic compounds. For the ^1H NMR spectroscopic characterization, shown in *Figure 2,* PB 1000 was first acetylated to ease dissolution in hexa deuterium dimethyl sulfoxide (DMSO-D6) (Ungureanu *et al.*, 2016).

For the initial solutions used in the experiment, concentrations in the range of 20.72 - 207.2 $mg \cdot L^{-1}$ for Pb^{2+} ions and in the range 6.538 - 65.38 $mg \cdot L^{-1}$ for Zn^{2+} ions were chosen. From each solution a volume of 20 mL was measured and mixed with 0.15 g of adsorbent (modified lignin PB 1000). The contact intervals of time selected after the preliminary tests were 30, 60 and 90 minutes, at a temperature of 20^0C, considering that the influence of temperature variation (± $5\ ^0C$ from the considered one) on the adsorption on lignin varieties is insignificant, according to Guo *et al.* (2008).

The adsorption was performed in a dynamic procedure, at 120 rotations per minute, followed by separation of the phases by filtration on Whatman quantitative filter paper.

The determination of Pb^{2+} concentration was performed spectrophotometrically, using PAR (4- (2-pyridylazo) - resorcinol), in alkaline medium (pH = 10, ammonia buffer) as a colouring reagent that forms a red-orange complex with a maximum absorption at 530 nm.

Reagents

Pb

10^{-2} M PAR reagent (dissolve 0.273 g of monosodium PAR into 100 ml);

Buffer solution (pH 10). A mixture of 85 ml NH_4OH and 26 g NH_4Cl was used to insure a pH of 10 in 1 L of solution.

10 ml Pb solution, 15 ml buffer and 1 ml PAR are mixed and shaken for 30 seconds and then brought to 50 ml with distilled water in a volumetric flask.

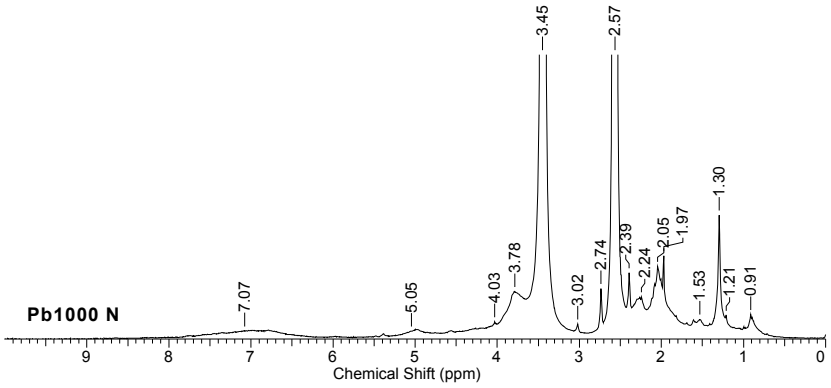

Figure 2 - PB 1000 ^{1}H NMR spectrum

Samples could be analysed immediately or up to 24 hours later (Dagnall *et al.*, 1965).

The spectrophotometric determination of Zn^{2+} was performed using xylenol orange, which forms a red complex with Zn^{2+} ions, with a maximum absorption at 570 nm.

Zn

Stock xylenol orange solution ($1.58 \cdot 10^{-3}$ M in deionized water);

Buffer solution (pH = 6.00) was prepared using KH_2PO_4 (0.1 M) + $Na_2B_4O_7 \cdot 10H_2O$ (0.05 M).

In a 10 mL volumetric flask we measured 5 mL Zn solution and added 2 mL of $1.58 \cdot 10^{-3}$ M xylenol orange solution; the flask was filled to the mark with buffer solution and mixed (Tehrani *et al.*, 2012).

Instruments

The pH values for the initial samples were determined with an analog pH-meter / ORP-meter HI83141 from Hanna Instruments and were established at pH 6 to ensure a higher efficiency of adsorption (in terms of enabling the dissociation for the surface functional groups) and not to exceed the values at which precipitations of the considered metal ions can take place (pH values > 6.5), according to Chen *et al.*, (2008) and Erdem *et al.*, (2013).

A VIS spectrophotometer V1000 SN: YA07151909217 and glass vats with a 1 cm optical path were used for the spectrophotometric measurement of the solutions resulting from the adsorption.

RESULTS AND DISCUSSION

Thermodynamic studies

1. Freundlich isotherm

The Freundlich isotherm model usually applies to sorption processes on heterogeneous surfaces and also to multilayer sorption. It is expressed by the following equation (*Eq. 1*):

$$q_e = k_F C_e^{1/n} \quad (1),$$

where n and k_F are the Freundlich constants.

We applied the linear form of the Freundlich isotherm (*Eq. 2*):

$$\log q_e = \log k_F + 1/n \log C_e \quad (2),$$

where q_e is the adsorption capacity ($mg \cdot g^{-1}$), Ce is the concentration at equilibrium ($mg \cdot L^{-1}$) and k_F and $1/n$ are Freundlich constants (Ayawei *et. al.*, 2017).

Experimental data complying with a Freundlich isotherm indicates the heterogeneity of the PB 1000 surface. The value of the $1/n$ factor shows the adequacy and efficiency of the adsorbent/adsorbate system. The linear plot of $\ln q_e$ versus $\ln C_e$ (presented in *Figure 3* for Pb^{2+} and in *Figure 4* for Zn^{2+}

after 60 minutes adsorption time) shows that the adsorption fits the Freundlich model.

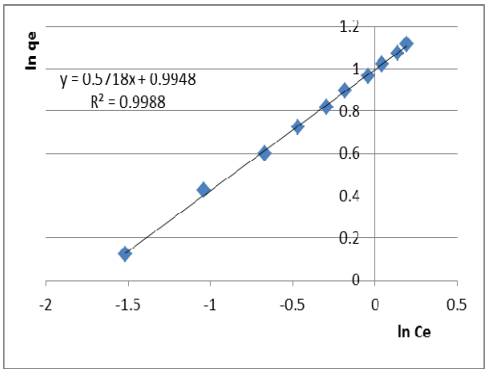

Figure 3 – Linear Freundlich isotherm for Pb^{2+} adsorption after 60 minutes

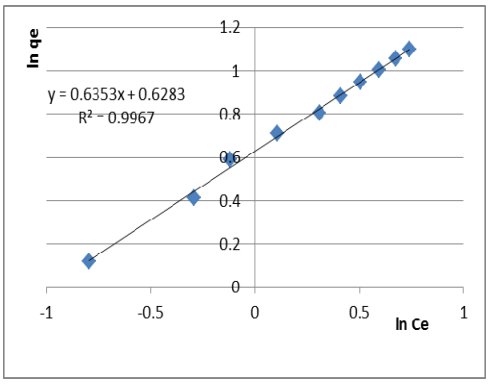

Figure 4 – Linear Freundlich isotherm for Zn^{2+} adsorption after 60 minutes

k_F and *1/n* were determined and presented in *Table 4*.

2. Langmuir isotherm

Langmuir adsorption serves to quantify the adsorption capacity of various adsorbents. The following equation was applied (*Eq. 3*):

$$q_e = k_L\, q_{max}\, C_e/(1 + q_{max}\, C_e) \quad (3),$$

The Langmuir constants k_L and q_{max} relate to the adsorption capacity and energy. The linear form of the Langmuir equation we used to calculate the specific parameters is as follows (*Eq. 4*):

$$1/q_e = 1/(k_L \cdot q_{max} \cdot C_e) + 1/q_{max} \quad (4),$$

where q_e is concentration of adsorbate at equilibrium ($mg \cdot g^{-1}$), q_{max} is the maximum sorption capacity ($mg \cdot g^{-1}$) and C_e is the equilibrium concentration in $mg \cdot L^{-1}$.

The characteristics of the Langmuir isotherm are expressed by the separation factor R_L (*Eq. 5*):

$$R_L = 1/(1+k_L\, C_0) \quad (5),$$

where k_L is the Langmuir constant ($mg \cdot g^{-1}$) and C_0 represents the initial concentration of ions ($mg \cdot L^{-1}$). R_L values indicate the process to be unfavourable when $R_L > 1$, linear when $R_L = 1$, favourable when $0 < R_L < 1$, and irreversible when $R_L = 0$. (Cara *et al.*, 2016)

The variation of $1/q_e$ versus $1/C_e$ was applied for the selected time intervals (presented in *Figure 5* for Pb^{2+} and in *Figure 6* for Zn^{2+} after the 60 min adsorption time). k_L, q_{max} and R_L were determined from the Langmuir isotherm plots and they are presented in *Table 4*.

The experimental data fit with the Freundlich isotherm model better. This proves that chemisorption is involved in retaining the lead and zinc ions, resulting complex structures with the functional groups on the sorbent's active sites.

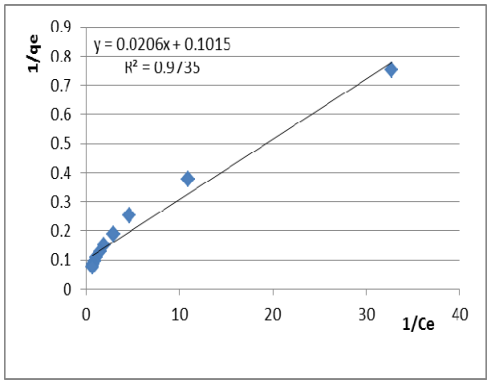

Figure 5 – Linear Langmuir isotherm for Pb^{2+} adsorption after 60 minutes

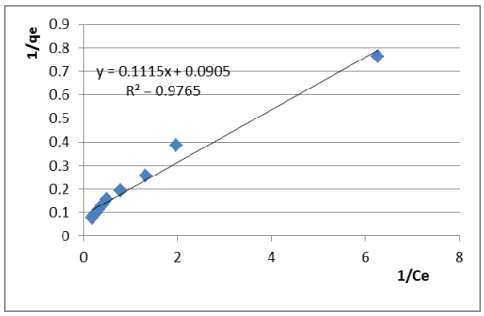

Figure 6 – Linear Langmuir isotherm for Zn^{2+} adsorption after 60 minutes

Kinetic modelling

We applied two kinetic models to assess the experimental data:

(a) Lagergren (pseudo first order) model, characterized by the following linear equation (*Eq. 6*):

$$ln(q_e - q_t) = ln\ q_e - k_1 \cdot t \quad (6),$$

where k_1 represents the rate constant of this model (min^{-1}).

(b) Ho and McKay (pseudo second order) model, expressed in the following linear form (*Eq. 7*):

$$t/qe = 1/k_2 \cdot qe^2 + 1/qe \quad (7),$$

where k_2 is the pseudo-second order (mg g^{-1} min^{-1}) rate constant.

For both models, q_e is the quantity of retained ion (mg g^{-1}) at equilibrium and q_t is the quantity of retained ion (mg g^{-1}) at a certain time t (Hanif *et al.*, 2017).

The linear plot of *t(min)* versus $ln(q_e - q_t)$ in the Lagergren model was used to calculate q_e, k_1 and R^2 for each initial concentration of the two considered ions. For the Ho and McKay model, the linear plot of *t(min)* versus t/q_t was used to determine the characteristic parameters q_e, k_1 and R^2. All of the data obtained are presented in *Table 5*.

Table 4 - Isothermal parameters determined by adsorption of Pb^{2+} and Zn^{2+} ions on PB 1000 modified lignin

Time (min)	Freundlich isotherm			Langmuir isotherm			
	1/n	k_F	R^2	q_{max}	k_L	R_L	R^2
				Pb^{2+} adsorption			
30	0.648	2.574	0.9906	9.634	0.103	0.045	0.9429
60	0.572	2.704	0.9988	9.852	0.101	0.045	0.9735
90	0.643	1.922	0.996	11.074	0.089	0.051	0.9741
				Zn^{2+} adsorption			
30	0.659	1.722	0.9956	10.225	0.096	0.137	0.9609
60	0.635	1.874	0.9967	11.050	0.089	0.146	0.9765
90	0.643	1.922	0.996	11.050	0.089	0.146	0.9765

Analysing the kinetic parameters, the pseudo-second order model describes better than the pseudo-first order model the adsorption process of both lead and zinc ions, with very small differences between the estimated (q_e) and realized (q_t) adsorption capacities, as seen in *Table 5*.

Regarding the efficiency of the lead and zinc ions' adsorption on modified PB 1000 lignin, we present in *Table 6* the quantities of ions retained on the adsorbent depending on the contact time and initial concentration.

Lead retention on lignin-based materials takes place during two steps of the sorption mechanism. In the first step, a quite fast adsorption occurs at the surface, and a slower step, involving intra particle diffusion follows. The Pb^{2+} binding to the adsorbent's active sites takes place by ion exchanges in the first

step and then, the diffusion of Pb^{2+} into the pores occurs in the second step (Bulgariu *et al.,* 2016).

A study comprising 102 publications during 1984 - 2005 showed that cheap adsorbents obtained from agricultural waste proved to be very efficient in removing heavy metal ions (Cr^{6+} - 170 mg/g on hazelnut shell ash, Ni^{2+} - 158 mg/g on orange peel ash, Cu^{2+} - 154.9 mg/g on soybean hull activated with NaOH and citric acid, Cd^{2+} - 52.08 mg g^{-1} on jackfruit ash) compared to activated carbon (Cd^{2+} - 146 mg g^{-1}, Cr^{6+} - 145 mg g^{-1}, Cr^{3+} - 30 mg g^{-1}, Zn^{2+} - 20 mg g^{-1}). Therefore, these materials may prove to be useful alternatives to activated carbon in contaminated water treatment procedures (Kurniawan *et al.,* 2006).

Due to its structure and capability of retaining heavy metal ions, lignin (*Figure 7*, Ruthran *et al.*, 2021) may be added to the list of alternative adsorbent materials, as previous studies have shown (Nacu *et al.*, 2015; Bulgariu *et al*, 2016). Lignin - based adsorbents can have great advantages for the environment because they are biocompatible, stable and abundant in nature (Ge *et al.*, 2018).

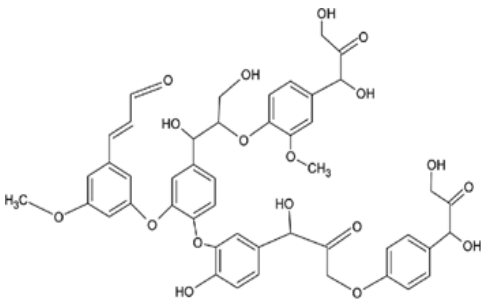

Figure 7 - Lignin structure

However, the capacity of lignin materials to retain pollutants is lower than the commercial adsorbents and the resin materials' one. Composite lignin-based materials with added functional groups were created in order to increase the sorption capacity of lignin (Ruthran *et al.*, 2021).

Usually, chemical modification is applied to improve the reactivity and enrich the functionality of lignin for valorisation.

Recent progress in studying lignin and its derivatives stated that chemical improvements might very well stabilise and enrich the lignin surface to make it a viable wastewater treatment agent, next to other adsorbents, flocculants and sterilants (Wang *et al.*, 2021).

To obtain an efficient adsorbent for the retention of Pb^{2+}, Cd^{2+} and Ni^{2+}, Ponomarev *et al.*, (2019) developed a nanocomposite using hydrolytic lignin and magnesium hydroxide. Also, they considered regeneration after metal removal. The nanocomposite proved that ion exchanges occurred between all three retained metals and the magnesium – lignin material.

Lin (2022) developed an enhanced lignin adsorbent by demethylation and introducing phenol and amine groups from γ-polyglutamic acid and ε-poly-L-lysine, respectively. These modified lignin materials had higher reactivity and a larger number of surface active sites. They were tested and good results were obtained for removing heavy metals from aqueous solutions. The kinetic and isothermal aspects of the adsorption showed that a pseudo-second-order model and the Langmuir model described both processes better.

Table 5 - Parameters determined from kinetic models for adsorption of Pb^{2+} and Zn^{2+} ions on modified lignin PB 1000

Initial conc. (mg/L)	Lagergren pseudo-first order			Ho & McKay pseudo-second order			
	q_e	k_1	R^2	q_e	q_t	k_2	R^2
Pb^{2+} adsorption							
20.72	0.7378	-0.0015	0.9347	1.3307	1.3306	20.7630	1
41.44	2.3284	-0.0019	0.9214	2.6567	2.6558	5.6898	1
62.16	5.4173	-0.0022	0.8600	3.9746	3.9733	4.0065	1
82.88	3.1689	-0.0019	0.8913	5.2910	5.2902	3.9690	1
103.6	2.4552	-0.0017	0.8840	6.6050	6.6038	3.8203	1
124.32	6.1306	-0.0022	0.8268	7.9177	7.9164	3.3233	1
145.04	2.8974	-0.0017	0.8661	9.2251	9.2199	2.5001	1
165.76	4.2224	-0.0018	0.8229	10.5374	10.5315	2.1443	1
186.48	3.9531	-0.0018	0.8249	11.8343	11.8289	2.1001	1
207.2	0.7343	-0.0008	0.9550	13.1406	13.1398	1.9304	1
Zn^{2+} adsorption							
6.538	1.3134	-0.0017	0.9312	1.3142	1.3138	9.9308	1
13.076	3.3248	-0.0018	0.8844	2.6055	2.6028	2.4428	1
19.614	6.6048	-0.002	0.8331	3.9108	3.9063	1.1696	1
26.152	7.5595	-0.002	0.7969	5.1840	5.1792	1.0279	1
32.69	3.07499	-0.0014	0.8607	6.4185	6.4148	0.8370	1
39.228	6.7619	-0.0018	0.7887	7.6923	7.6854	0.5868	1
45.766	10.2267	-0.0019	0.7674	8.9525	8.9411	0.4159	0.9999
52.304	7.6492	-0.0017	0.7637	10.2041	10.1939	0.3904	1
58.842	7.8170	-0.0017	0.746	11.4548	11.4456	0.3496	1
65.38	7.8995	-0.0017	0.7469	12.6743	12.6714	0.3773	1

The highest uptakes for Pb^{2+} (following esterification of lignin materials with carbon sulphide) were 275.9 mg g^{-1} and 231.8 mg g^{-1} at 25^0C. The added functional groups, like amino, hydroxyl, dithiocarbamate or methoxyl formed bonds with Pb^{2+}.

Another method of lignin modification lead to phosphorylated alkali lignin microparticles. Their adsorption capacity for Pb^{2+} reached 349.2 mg·g^{-1}, as reported by Gong *et al*. (2021).

Song *et al.*, (2018) tested the Pb^{2+} removal capacity (the uptake per unit mass) of activated carbon adsorbents obtained from waste materials and observed a decrease in their efficiency when the amounts of the adsorbent increased. This is due to lower adsorbate / adsorbent ratio. Therefore, 0.1 g of adsorbent was used for all experiments. With regard to the adsorption conditions, the temperature varied between 25 – 45 °C and the pH was 7, but the results proved that temperature had no visible effect on Pb^{2+} uptake. Also, the influence of adsorption time (ranging from 10 to 60 min) on Pb^{2+} uptake was tested,. The adsorption efficiency of activated carbon materials obtained from sawdust, acrylic fabric, tire powder and rice husk tended to stabilize at longer adsorption time, achieving equilibrium after 60 min. The maximum Pb^{2+} uptake for the four studied adsorbents was 58.25 mg·g^{-1}, 31.25 mg·g^{-1}, 50.48 mg·g^{-1} and 59.73 mg·g^{-1}, respectively.

Table 6 - Quantities of Pb^{2+} and Zn^{2+} adsorbed on modified lignin PB 1000

Initial conc.($mg \cdot L^{-1}$)	30 min	60 min	90 min
Pb^{2+} adsorption			
20.72	2.7502	2.7542	2.7570
41.44	5.4741	5.5000	5.5028
62.16	8.1921	8.2283	8.2327
82.88	10.9203	10.9563	10.9613
103.6	13.6427	13.673	13.683
124.32	16.3563	16.3925	16.4029
145.04	19.0424	19.0874	19.1036
165.76	21.7541	21.796	21.8213
186.48	24.4402	24.4824	24.5096
207.2	27.1535	27.1938	27.2257
Zn^{2+} adsorption			
6.538	0.8541	0.8578	0.8589
13.076	1.6810	1.6991	1.7017
19.614	2.5107	2.5490	2.5539
26.152	3.3392	3.3756	3.3862
32.69	4.1361	4.1816	4.1940
39.228	4.9431	5.0052	5.0247
45.766	5.7288	5.8235	5.8457
52.304	6.5448	6.6309	6.6648
58.842	7.3542	7.4346	7.4831
65.38	8.1672	8.2345	8.2846

Amer *et al.*, (2011) found that the sorption capacity on sodium polyphosphate kaolinite clay was 40.00 mg g^{-1} for Pb^{2+} and f, 27.78 mg g^{-1} or Zn^{2+}.

Chen *et al.*, (2008) found that the maximum biosorption capacity for Pb^{2+} by waste brewery biomass was 0.413 mmol $Pb^{2+} \cdot g^{-1}$.

Another study on Pb^{2+} and Zn^{2+} removal showed that the adsorption capacity of lead was 15.56 $mg \cdot g^{-1}$ and the one for zinc was 11.72 $mg \cdot g^{-1}$ on activated carbon derived from Van apple pulp. A film diffusion process was responsible for the adsorption, which proved to be endothermic, feasible and thermodynamically favoured. Depci *et al.* (2012) and Erdem *et al.* (2013) found that the maximum monolayer adsorption capacity of activated carbon obtain from soybean oil cake activated with K_2CO_3 was 476.2 $mg \cdot g^{-1}$. From the kinetics point of view, the Ho and McKay model best suited the experimental data and the thermodynamic study showed the adsorption process to be spontaneous and endothermic.

Adsorption mechanism

There are five mechanisms proposed for metal retention from water on different adsorbents. They are the following: - electrostatic interactions between metallic ions and active sites on the surface; - cation exchange between metallic ions and other cations on the surface, including protons; - complexes formed with the functional groups of the sorbent's structure; - precipitation of the

metallic ions and - reduction and sorption of the reduced species on the active sites. The adsorption mechanisms and the amount of metal adsorbed vary with the surface properties, adsorption conditions (as pH) and the selected metals.

The highest adsorbed amounts were observed at pH 6.0 (provided by acetate buffer), when over 96% of Pb^{2+} was removed from solution. The competition between Pb^{2+} and H_3O^+ for the active sites of the surface is mainly responsible for the process. The strong pH-dependence of the adsorption process suggests that the specific adsorption mechanism may be explained by electrostatic interactions between metallic cations and negatively charged functional groups.

The metal ion biosorption on lignin takes place through sequential equilibrium steps: first, very fast biosorption at the surface and second a slower intra-particle diffusion. Ion exchanges in the first step are responsible for retaining cations on the surface, while their diffusion into the adsorbent's pores occurs effectively in the second step. The fact that the retention of Pb^{2+} on the surface of lignin-based adsorbents takes place mainly by electrostatic interactions (ion-exchange or complexation) is confirmed by the short contact time needed to reach equilibrium.

The pH greatly affects the adsorbents' capacity for Pb^{2+} removal. The efficiency increases with the increase of pH, because at lower values, the amount of H_3O^+ that can compete for the oxygen - containing functional groups is larger, therefore reducing the possibility of Pb^{2+} ions to occupy active sites on the surface. When pH increases, the active sites become available again for the metallic ions, leading to higher amounts retained per mass unit (Bulgariu *et al.*, 2013).

Ungureanu *et al.* (2021) showed that the adsorption of Pb^{2+} and Zn^{2+} ions from aqueous solutions on unmodified Sarkanda grass lignin probably occurs in two successive stages: - by ion-exchange surface interactions followed by ion retention on the functional groups of lignin which takes place through intraparticle diffusion.

CONCLUSION

As an alternative to activated carbon and other expensive adsorbents, PB 1000 modified lignin can retain heavy metal ions from aqueous solutions, even when the concentrations of the ions are low.

The adsorption processes for both lead and zinc were best described by the Freundlich isotherm, allowing us to conclude that chemisorption occurred with the formation of ion-lignin complex structures. The kinetics of the adsorption process were best fitted by the pseudo-second order Ho&McKay model, with regression coefficients equal to 1. Considering the maximum concentration of lead solution applied and the longest adsorption time of 90 minutes, the pseudo second order model predicted an adsorption capacity q_e of 13.1406 $mg \cdot g^{-1}$ compared to the 13.1398 $mg \cdot g^{-1}$ obtained. For the zinc adsorption, the Ho and McKay model predicted a q_e of 12.6743 $mg \cdot g^{-1}$ compared to the obtained value of 12.6714 $mg \cdot g^{-1}$.

The uptake of lead on the Protobind 1000 lignin reached a maximum of

27.23 $mg \cdot g^{-1}$ which is greater than the zinc uptake (a maximum of 8.28 $mg \cdot g^{-1}$).

Considering the fact that the adsorption takes place with good results after one hour, using small quantities (5 to 7.5 $g \cdot L^{-1}$) and minimum conditioning, modified lignin PB 1000 can be taken into consideration as a promising material for further studies on activation and surface enhancement in order to increase its sorption potential.

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