UTILIZATION OF AGRICULTURAL WASTE (*Phasoleus Vulgaris L*, *Prunus Cerasifera – Myrobalan*) FOR WASTEWATER TREATMENT HIGH IN Cd, Cr, Pb AND Zn BY SORPTION

VYUŽITÍ ODPADU ZE ZEMĚDĚLSTVÍ *(Phasoleus vulgaris L*, *Prunus cerasifera – myrobalan*) JAKO SORBENTU PRO ČIŠTĚNÍ ODPADNÍCH VOD S VYŠŠÍM OBSAHEM Cd, Cr, Pb A Zn

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Abstract

The use of sorption technology for the removal of contaminants of waste streams is favorable when biological treatments are not applicable. Utilization of agricultural waste for sorption is one of the alternative technologies for cleaning of industrial wastewaters. This part of the utilization of industrial wastes for wastewater treatment project aims to investigate the use of bean-pods *Phasoleus vulgaris L* and plum nuts *Prunus cerasifera – myrobalan* as a sorbent, verify the chemical and thermal activation of the sorbent and investigate the sorption of Cd, Cr, Pb and Zn from syntheticaly prepared waste water.

Abstrakt

Technologie adsorpce kontaminantů z vodného prostředí se využívá převážně tam, kde nelze využít jejich biologického čištění. Využití zemědělského odpadu je jednou z možných alternativ čištění průmyslových odpadních vod. Zde budou prezentovány dílčí výsledky projektu, který se zabývá využitím fazolového lusku *Phasoleus vulgaris L* a pecky švestky *Prunus cerasifera - myrobalan* jako sorbentu pro sorpci Cd, Cr, Pb a Zn z modelových roztoků, při různorodé modifikaci jejich chemické úpravy.

Key words: adsorbent, heavy metals, agriculture waste, sorption kinetics, isotherms

1 INTRODUCTION

Toxic metal contamination of soil and water is a significant environmental and human hazard, and therefore its removal from the environment in a safe and efficient manner is of utmost importance. There are many available processes for toxic metal decontamination - chemical precipitation, evaporation, cementation, flotation, reverse osmosis and ion separation to name a few - but most of these methods suffer from some drawback such as high capital and operational costs or diposal of residual metal sludges. Hence, there is need for research and development of low cost and readily available sorbents which can remove toxic metals economically.

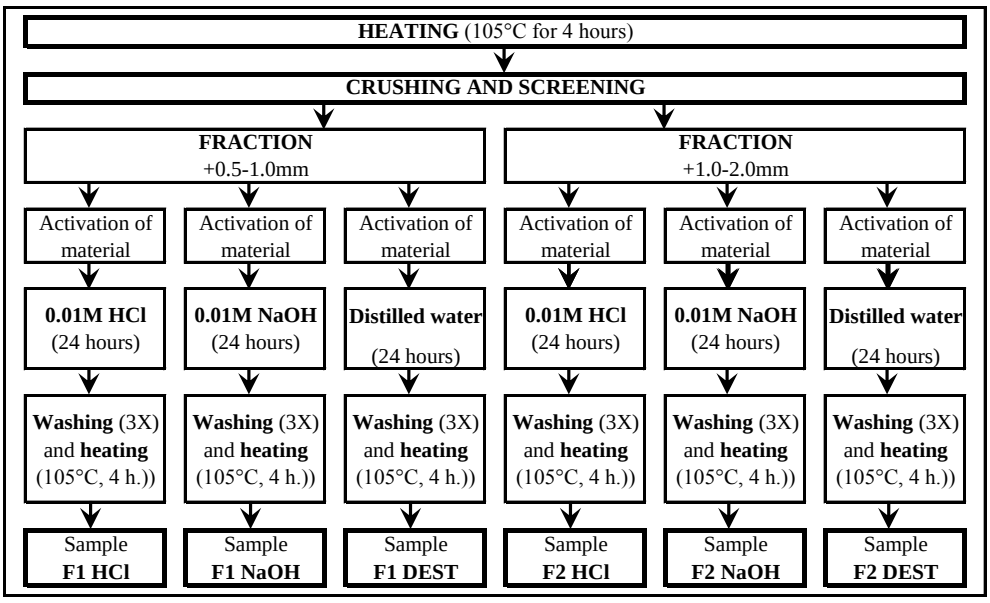
A cheaper alternative for removal of toxic metals from industrial wastewaters is to use agricultural waste materials with suitable sorption characteristics. In this study, the use of bean-pods (*Phasoleus vulgaris L)* and plum nuts (*Prunus cerasifera – myrobalan)* for the sorption of Cd, Cr, Pb and Zn, and Pb respectivley from synthetic industrial waste waters was investigated.

2 EXPERIMENTAL PART

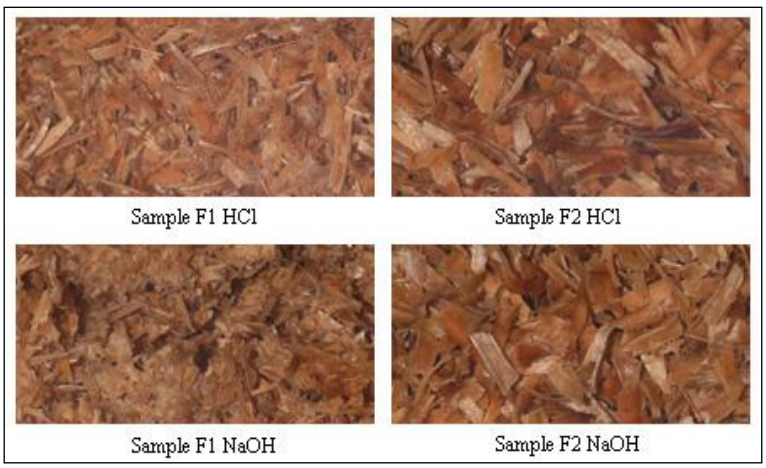
2.1 BIOMASS PREPARATION

Samples of the bean-pods and plum nuts were collected in Ostrava, Czech Republic (see scheme 1). Biomass preparation is shown in Scheme 2 and 4 and structure of prepared samples is shown in scheme 3 and 5.

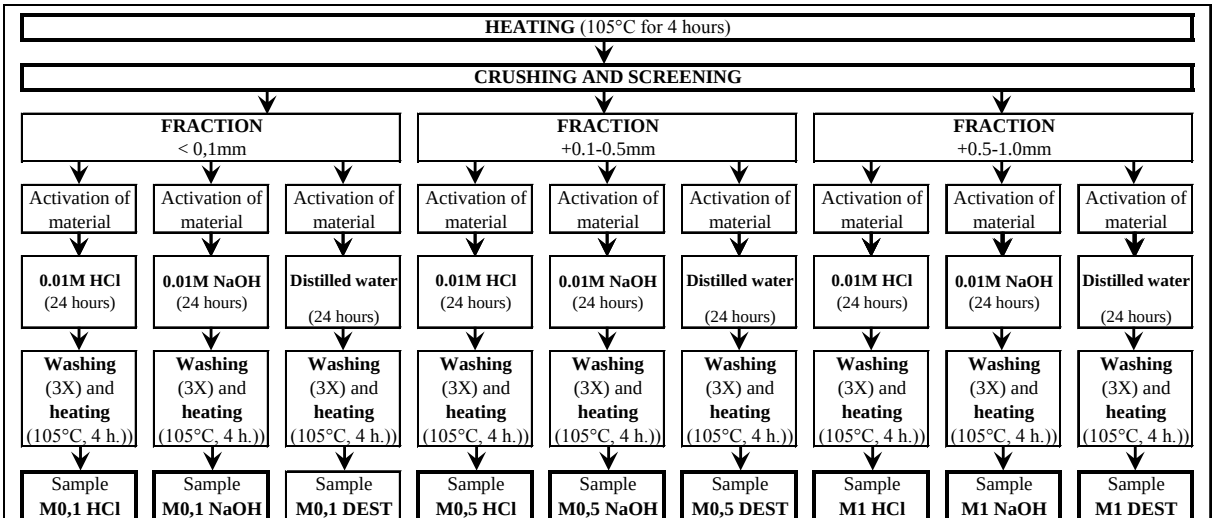
Scheme 1. Bean-pods *Phasoleus vulgaris L* and plum nuts *Prunus cerasifera - myrobalan* collected in Ostrava (Czech Republic) for sorption tests



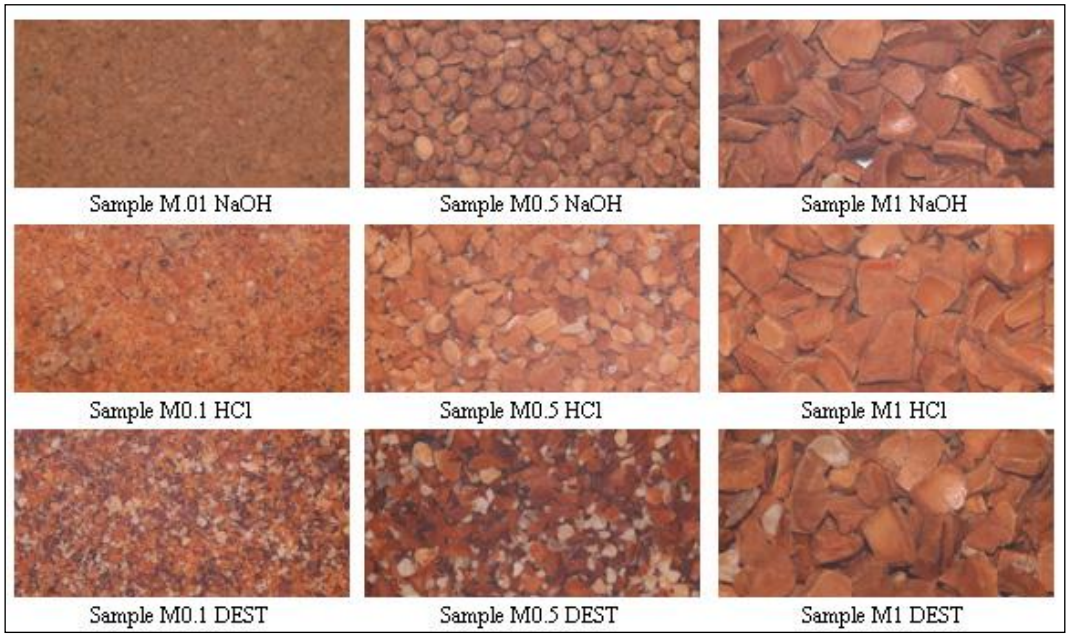
Scheme 2. Characteristic of prepared sorptive matter from bean-pods



Scheme 3. Structure of the samples prepared from plum nuts *Prunus cerasifera - myrobalan*



Scheme 4. Characteristic of prepared sorptive metter from plum nuts



Scheme 5. Structure of the samples prepared from bean pods *Phasoleus vulgaris L*

Plum nuts were washed, heated and then crushed and screened so that the test were carried out on fraction: (1) <0.1mm, (2) +0.1-0.5mm and (3) +0.5-1mm. Bean-pods were washed, heated and then crushed and screened so that tests were carried out on the size fractions: (1) +0.5-1.0mm and (2) +1.0-2.0mm.

Finer material was not used owing to filtration problems and also swelling that affected the reaction kinetics. The treatment techniques that were investigated were thermal and chemical (acidic and caustic) techniques. For thermal treatment, the material was heated to 105ºC whilst being soaked. For chemical treatment, materials were soaked in the chosen solution (0.01M NaOH, 0.01M HCl, distilled water). Swelling issues were encountered, but were alleviated by thermal treating the sorbent in distilled water for 24 hours, after which it was filtered, charged and used for the sorption test. A flow-sheet detailing the preparation of sorptive matter is shown in Scheme 2 and 4.

2.2 ENTRY ANALYSES

There was determined iodine adsorbing number for individual fraction, like the indicator of the physical adsorption. (See Table 1) Samples M0.1 NaOH, M0.5 NaOH, M1 NaOH and F1 NaOH (soaked in 0.01M NaOH solution) and sample M1 HCl achieved the best results – the highest iodometric numbers (over 100) - using these samples is possible expect the best sorption chracteristics – the best sorption results.

Tab. 1 Iodometric numbers for all prepared sorption metters

Sample labeling	V1	V2	V3	cI2	M	mE	I
-	ml	ml	ml	mol/l	g/mol	g	mg/g
M0,1 DEST	25.0	18.03	24.12	0.0238	253.809	0.3930	**97.098**
M0,1 HCl	25.0	18.05	24.12	0.0238	253.809	0.4016	**94.706**
M0,1 NaOH	25.0	17.56	24.12	0.0238	253.809	0.3988	**103.070**
M0,5 DEST	25.0	19.49	24.17	0.0239	253.809	0.4005	**73.220**
M0,5 HCl	25.0	19.53	24.12	0.0238	253.809	0.4027	**71.420**
M0,5 NaOH	25.0	17.03	24.17	0.0239	253.809	0.3954	**113.148**
M1 DEST	25.0	17.97	24.105	0.0238	253.809	0.4002	**96.055**
M1 HCl	25.0	17.46	24.17	0.0239	253.809	0.3992	**105.322**
M1 NaOH	25.0	17.53	24.105	0.0238	253.809	0.4053	**101.649**
F1 DEST	25.0	18.45	24.105	0.0238	253.809	0.4081	**86.8267**
F1 HCl	25.0	19.5	24.24	0.0239	253.809	0.3746	**79.286**
F1 NaOH	25.0	18.5	24.24	0.0239	253.809	0.3511	**102.439**
F2 DEST	25.0	18.79	24.24	0.0239	253.809	0.3533	**96.658**
F2 HCl	25.0	20.35	24.24	0.0239	253.809	0.3527	**69.108**
F2 NaOH	25.0	20.,11	24.24	0.0239	253.809	0.3548	**72.938**

V_1 - is the volume of the iodine solution, which was in the activation process with the mass of the sample, V_2 – is the volume of $Na_2S_2O_3$ solution (c = 0.0395 mol/l) used for titration of the iodine solution after its activation with sample of the adsorbent, V_3 – is the volume of the $Na_2S_2O_3$ solution (c = 0.0395 mol/l) used for titration of the iodine solution without activation (standard test), cI2 – concentration of the iodine solution, *mE* – the mass of the adsorbent used for the testing, *M* – molecular mass of iodine

2.3 SORPTION KINETICS

Batch sorption tests were conducted at temperature of 25°C. For the investigation of adsorption kinetics, synthetic industrial wastewaters were prepared and contained Cd, Cr, Pb and Zn in initial concentrations ±200 mg/L. All tests were conducted with constant agitation, with samples being collected as required and later analyzed by AAS. Figures 1-4 show data of Cd, Cr, Pb and Zn sorption as a function of the time with the sampless of bean-pods in all chemical treatment and figure 5 kinetic parameters for the chemical treatment using NaOH (the best decrease). From Figures 1-4 is evident that sorptive equilibrium is acheived within 24 hours in all cases. In all experiments a decrease in the solution pH during the metal sorption was observed.

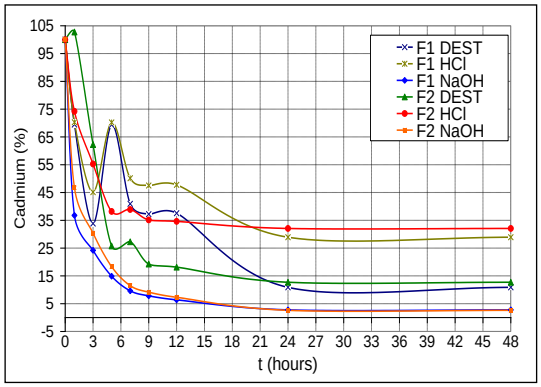


Fig. 1 Decrease of Cd concentration in time

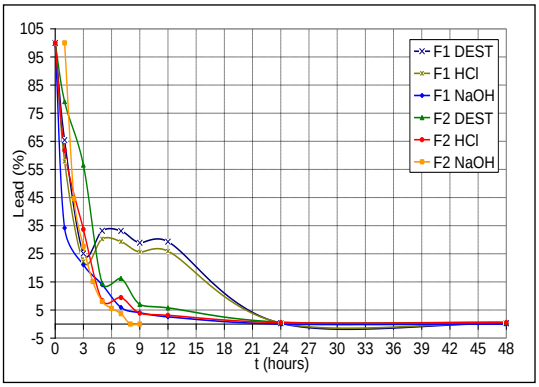


Fig. 2 Decrease of Pb concentration in time.

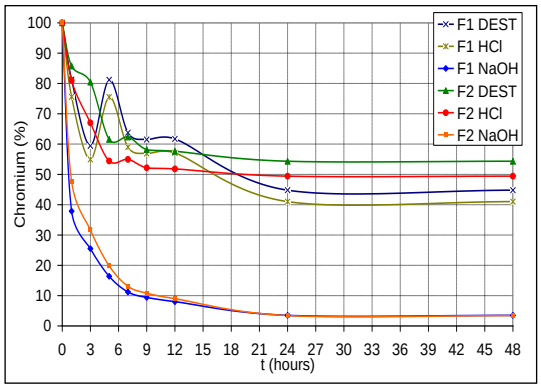


Fig. 3 Decrease of Cr concentration in time.

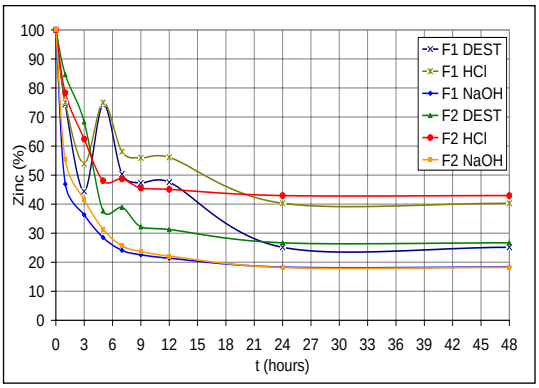
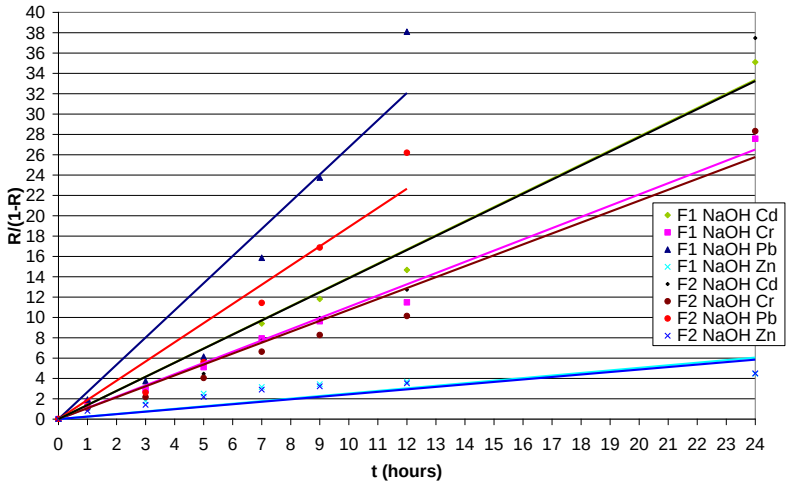


Fig. 4 Decrease of Zn concentration in time



Sample labeling	Correlation coeficient
F1 NaOH Pb	0.95
F2 NaOH Pb	0.96
F1 NaOH Cd	1.00
F2 NaOH Cd	0.98
F1 NaOH Cr	1.00
F2 NaOH Cr	0.99
F1 NaOH Zn	0.77
F2 NaOH Zn	0.61

Fig. 5 Kinetic parameters of Cd, Cr, Pb and Zn biosorption for chemical treatment by NaOH

Values of pH during the analyses were between 2.58–3.706 for Cd, 2.955-3.358 for Cr, 4.090-6.596 for Pb and 3.318-3.749 for Zn. It means that in all reactions chemical precipitation was not expected. Figures 6 and 7 summarize the decreases of all metals for all chemical treatment of sorbents.

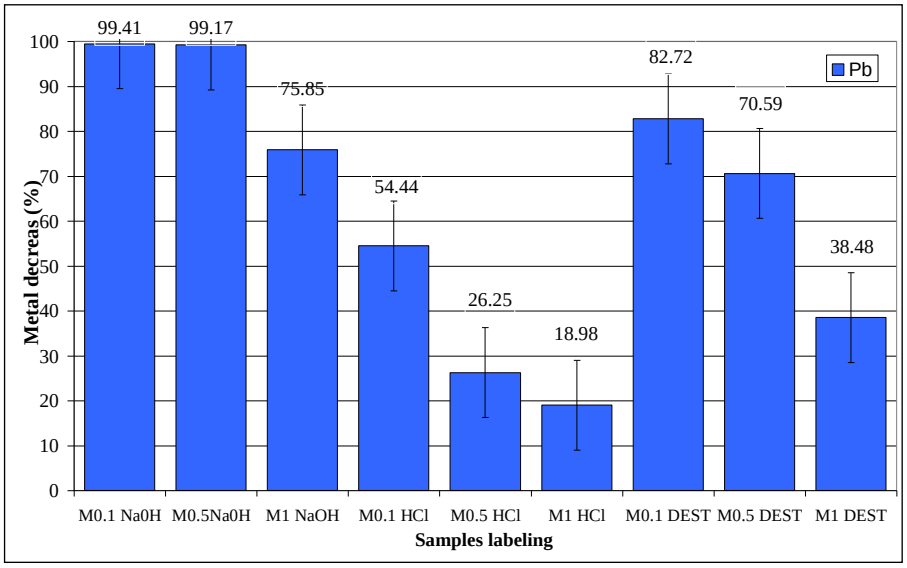


Fig. 6 Summarized tests of lead sorption factors for all chemical treatment

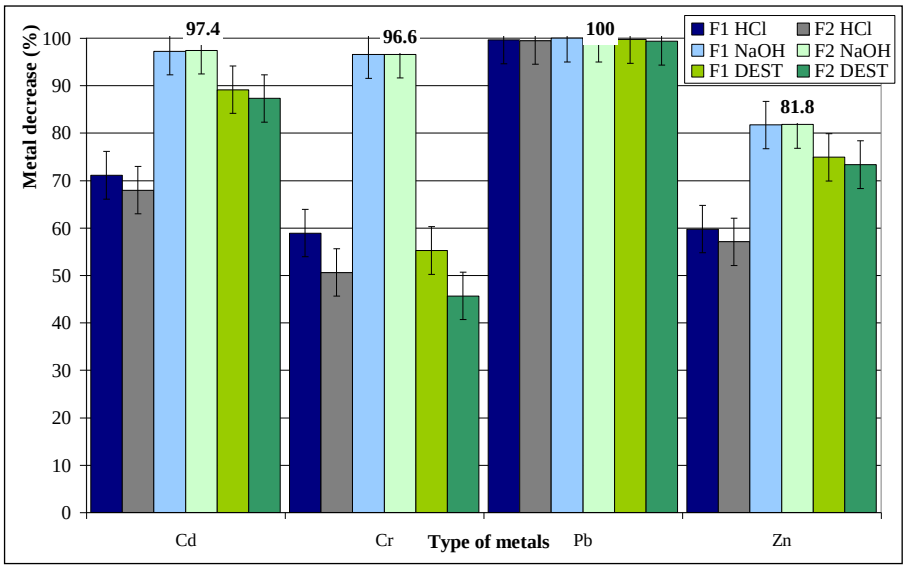


Fig. 7 Summarized tests of metals sorption factors for all chemical treatment.

2.4 ADSORPTION ISOTHERMS

Sorption isotherms were measured by varying the initial metal concentration from 50 to 200 mg/L. All tests were conducted with constant agitation, with samples being collected as required and later analyzed by AAS.

For isotherm design Langmuir models – L1 and L2 – were used. Figure 8 shows lead sorption isotherms on plum nuts for all chemical treatment. The sorption isotherms were designed using both types of Langmuir models.

Lagmuir model - I. type (L1): $$y = \frac{a \cdot b \cdot x^{1-c}}{1 + b \cdot x^{1-c}} \quad \text{and} \tag{1}$$

Langmuir model - II. type (L2): $$y = \frac{1}{a + b \cdot x^{c-1}}, \tag{2}$$

where *a*,*b* and *c* are parameters of the Lagmuir isotherms.

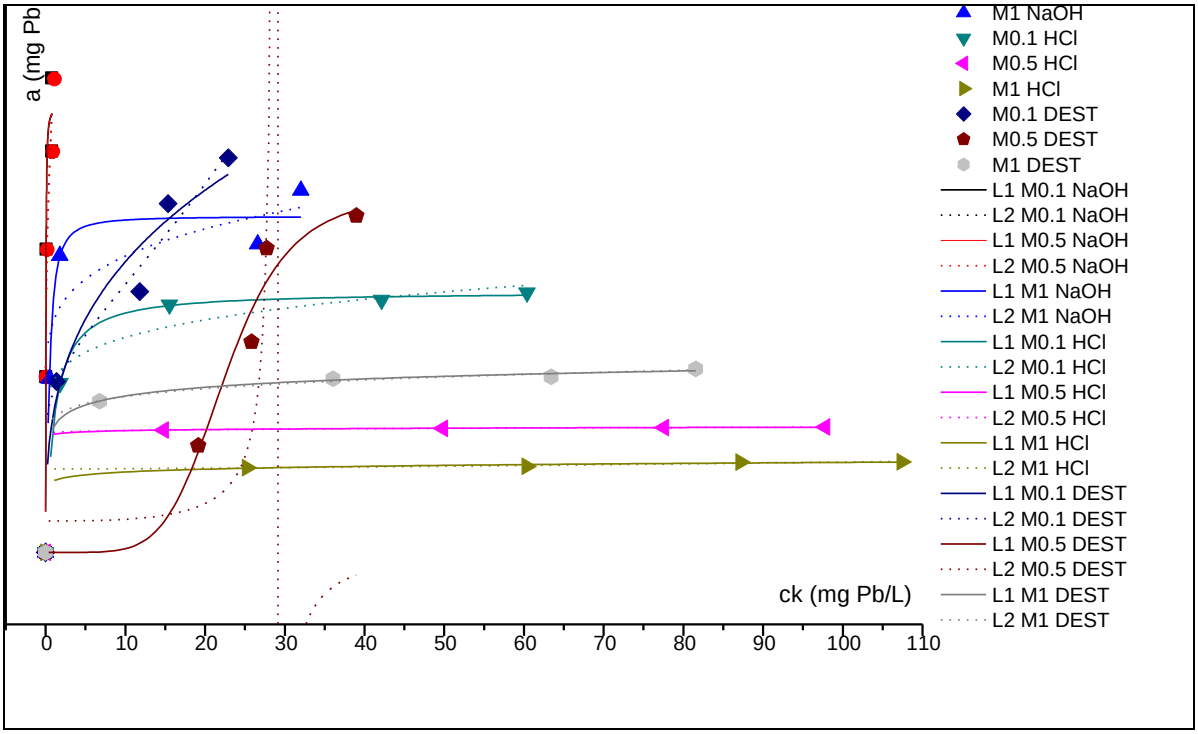


Fig. 8 Lead sorption isotherms on plum nuts biomass for all chemical treatment

Figure 8 shows that it is possible to model both of types of Langmuir isotherms, the way this type of isotherm follows the original model is much more important, see table 2. For design isotherms for all the samples prepared by caustic leaching in 0.01M NaOH – samples M0.1 NaOH, M0.5 NaOH and M1 NaOH - and sample 0.1M HCl and M0.5 DEST is possible to use model L1 and for the rest of the samples it was necessary to use the model L2.

In figures 8-12 we can see the sorption isotherms of Cd, Pb, Cr and Zn by bean-pods biomass for all chemical treatment. The isotherm characterisitcs (parameters) are shown in Tables 3–6. The correlation coeficients in tables 3-6 demonstrate that sorption follows the Lamgmuir model – type L1 well.

Tab. 2 Characteristics of the both types of Langmuir isotherms for lead

Sample labeling	Parameter	L1			R	L2			R
	a	6.18076	±	0.64552		226.8729	±	1728680	
M0.1 NaOH	**b**	88.05697	±	274.6788	**0.917**	-226.722	±	1728680	0.761
	c	-0.39891	±	0.94357		1.00022	±	1.66181	
	a	6.18076	±	0.64552		226.8729	±	1728680	
M0.5 NaOH	**b**	88.05697	±	274.6788	**0.917**	-226.722	±	1728680	0.761
	c	-0,39891	±	0.94357		1.00022	±	1.66181	
	a	4.66867	±	0.39435		114.8514	±	954940.7	
M1 NaOH	**b**	3.19872	±	2.65681	**0.880**	-114.541	±	954940.7	0.357
	c	-0.44497	±	0.9966		1.00026	±	2.13978	
	a	3.61843	±	0.09058		70.78344	±	116994.8	
M0.1 HCl	**b**	0.97972	±	0.14881	**0.995**	-70.3653	±	116994.7	0.786
	c	-0.06278	±	0.30369		1.00051	±	0.85425	
	a	2.52955	±	9.60523		0.61207	±	0.01177	
M0.5 HCl	**b**	1.84719	±	19.84396	0.993	-0.01251	±	0.00933	**0.999**
	c	0.96186	±	0.30681		1.23914	±	0.09484	
	a	6.22896	±	959.3467		0.86432	±	0.04483	
M1 HCl	**b**	0.18987	±	34.61474	0.736	-0.00023	±	0.00184	**0.869**
	c	0.93936	±	2.25057		2.23032	±	1.58157	
	a	1058.432	±	857950		0.72889	±	1.24217	
M0.1 DEST	**b**	0.00184	±	1.49355	0.841	-0.28209	±	1.14619	**0.923**
	c	0.68151	±	0.87498		1.21271	±	0.58156	
	a	4.97733	±	1.01198					
M0.5 DEST	**b**	2.55E-08	±	2.43E-07	**0.892**		*Unreal*		
	c	-4.60407	±	3.13262					
	a	3.57914	±	5.48484		6.79631	±	730.3674	
M1 DEST	**b**	0.95564	±	2.46764	**0.959**	-6.26175	±	730.2865	0.954
	c	0.79166	±	0.58624		1.00502	±	0.57649	

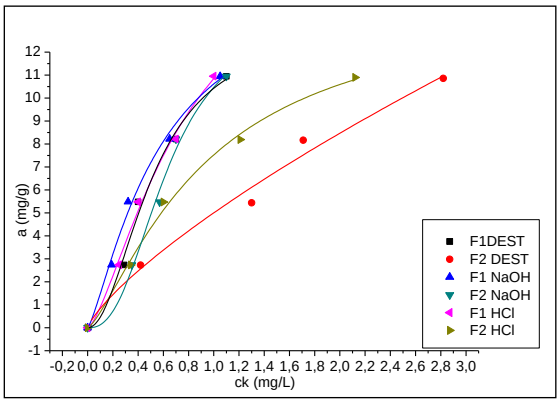


Fig. 9 Lead sorption isotherms on bean-pods biomass for all chemical treatment

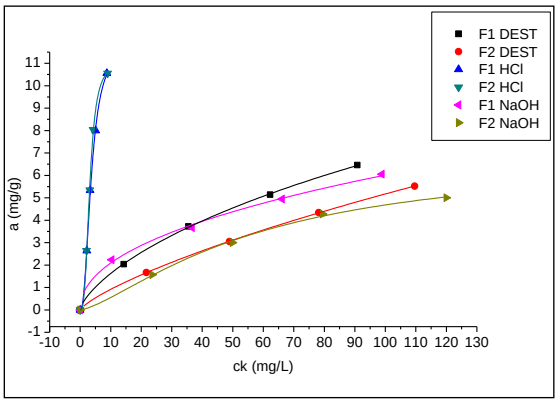


Fig. 10 Chromium sorption isotherms on bean-pods biomass for all chemical treatment

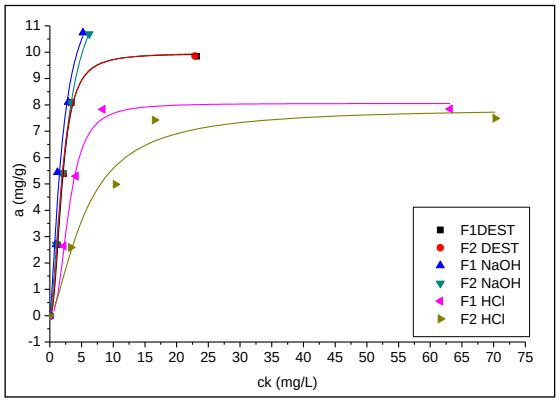


Fig. 11 Cadmium sorption isotherms on bean-pods biomass for all chemical treatment

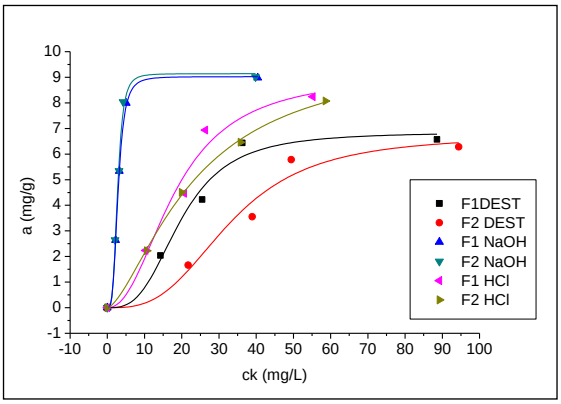


Fig. 12 Zinc sorption isotherms on bean-pods biomass for all chemical treatmen

Tab. 3 Characteristics of the Langmuir isotherms for cadmium

Sample labeling	a	b	c	R
F1 DEST	9.949 ± 0,477	0.224 ± 0.063	-1.28 ± 0.385	1.00
F2 DEST	9.997 ± 0.495	0.27 ± 0.071	-1.137 ± 0.371	1.00
F1 HCl	8.056 ± 0.4445	0.063 ± 0.042	-1.51 ± 0.608	0.99
F2 HCl	7.88 ± 1.361	0.071 ± 0.1	-0.54 ± 0.854	0.96
F1 NaOH	13.33 ± 8.404	0.379 ± 0.309	-0.44 ± 3.065	0.97
F2 NaOH	13.62 ± 0.898	0.233 ± 0.017	-0.51 ± 0.136	1.00

Tab. 4 Characteristics of the Langmuir isotherms for chromium

Sample labeling	a	b	c	R
F1 DEST	32.68 ± 24.86	0.01 ± 0.006	0.299 ± 0.083	1.00
F2 DEST	63.32 ± 38.17	0.002 ± 0.001	0.217 ± 0.029	1.00
F1 HCl	11.85 ± 0.861	0.047 ± 0.015	-1.356 ± 0.35	1.00
F2 HCl	11.02 ± 0.396	0.031 ± 0.01	-2.044 ± 0.328	1.00
F1 NaOH	656.7 ± 49303	0.001 ± 0.082	0.538 ± 0.218	1.00
F2 NaOH	6.86 ± 1.1	0.004 ± 0.003	-0.39 ± 0.257	1.00

Tab. 5 Characteristics of the Langmuir isotherms for lead

Sample labeling	a	b	c	R
F1 DEST	13.2 ± 3.805	3.76 ± 4.837	-1.011 ± 0.886	0.99
F2 DEST	242.3 ± 6742	0.021 ± 0.599	0.219 ± 0.675	0.99
F1 HCl	18.29 ± 10.67	1.465 ± 1.994	-0.45 ± 0.588	1.00
F2 HCl	14.4 ± 3.678	1.095 ± 0.693	-0.34 ± 0.405	1.00
F1 NaOH	15.8 ± 7.137	2.048 ± 2.69	-0.296 ± 0.55	0.99
F2 NaOH	13.75 ± 3.332	3.128 ± 3.078	-1.51 ± 0.898	0.99

Tab. 6 Characteristics of the Langmuir isotherms for zinc

Sample labeling	a	b	c	R
F1 DEST	6.85 ± 0.823	1E-04 ± 5E-04	-2.004 ± 1.227	0.98
F2 DEST	6.72 ± 1.309	3E-05 ± 1E-04	-2.015 ± 1.619	0.97
F1 HCl	9.11 ± 1.986	0.002 ± 0.005	-1.186 ± 1.117	0.98
F2 HCl	9.98 ± 0.922	0.008 ± 0.004	-0.536 ± 0,207	1.00
F1 NaOH	9,023 ± 0.137	0.026 ± 0.006	-2.432 ± 0.208	1.00
F2 NaOH	9.139 ± 0.564	0.022 ± 0.019	-2.786 ± 0.842	0.99

3 CONCLUSIONS

The experiments have shown that bean-pods are suitable for the sorption of Cr, Cd, Zn and Pb and plum nuts are suitable for soprtion of Pb. It is possible to affect its sorption property by working chemical reagents. The most metals decrease came, that means the highest sorption were achieved, at starting concentration about ±200 mg/L. For lead the best sorption values were achieved for fraction +0.5-1.0 mm and chemical treatment by 0.01M NaOH (10.948 mg Pb/g) and 0.01M HCl (10.950 mg Pb/g). For chromium, zinc and cadmium was the best chemical treatment by 0.01M NaOH, where the both fractions had similar sorption results. Sample F1 NaOH had these results: 10.653 mg Cr/g, 8.981 mg Zn/g and 10.793 mg Cd/g. Sample F2 NaOH had the results lower 10.55 mg Cr/g, 9.010 mg Zn/g and 10.690 mg Cd/g.

The experiments have shown that sorption isotherms of the samples prepared by caustic leaching in 0,01M NaOH do not rich their maximum at the end of the model L1 or L2. That is why it is possible to say, that for samples fraction <0.1mm, +0.1-0.5mm and +0.5-1.0 mm soaked in 0.01M NaOH is possible to use much more higher starting concentration of the model solution – starting concentrationg could be higher then ±200 mg/l of Pb (Cr, Cd or Zn). Sorption isotherms of the samples prepared by caustic leaching in 0.01M NaOH do not reach their maximum in the end of the model L1 or L2.

There is an evidence that bean-pods and plum nuts like adsorbents have sorption properties much more lower than the industrially prepared sorbents. But we can use them everywhere, where is necessary to use clean technology (without chemical inputs) and where it is necessary to find cheap variant for cleaning (reclamation areas).

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RESUMÉ

Provedené experimenty prokázaly, že fazolový lusk je vhodným adsorbentem pro adsorpci Cr, Cd, Zn a olova, stejně tak jako je vhodná pecka švestky mirobalan pro adsorpci olova. Sorpční vlastnosti jednotlivých materiálů lze ovlivnit volbou aktivačních postupů a roztoků, využitých pro jejich úpravu.

Výsledky dosažené adsorpcí na upraveném fazolovém lusku *Phasoleus vulgaris L*

K největšímu úbytku, resp. největší adsorpci vykazují všechny materiály při vstupní koncentraci ±200 mg/l. Nejlepší výsledek pro adsorpci olova z modelového roztoku dosáhla frakce +0.5-1.0mm chemicky upravené pomocí 0.01M NaOH (10.948 mg Pb/g) a stejná frakce chemicky upravená pomocí 0.01M HCl (10.950 mg Pb/g). Pro chrom, zinek a kadmium byla nejlepší úpravou zvolena chemická aktivace pomocí 0.01M NaOH, ale v tomto případě dosáhly obdobných výsledků obě takto upravené frakce, resp. +0.5-1.0mm i +1.0-2.0 mm. Pro vzorek F1 NaOH – 10.653 mg Cr/g, 8.981 mg Zn/g and 10.793 mg Cd/g a vzorek F2 NaOH jsou výsledky následující – 10.55 mg Cr/g, 9.010 mg Zn/g and 10.690 mg Cd/g.

Výsledky dosažené adsorpcí na upravené pecce švestky myrobalan *Prunus cerasifera – myrobalan*

K největšímu úbytku olova v tomto případě došlo s využitím frakce <0.1mm a frakce 0.1-1.0mm a chemické úpravě 0.01M NaOH. Obě tyto frakce dosáhly obdobných výsledků, a lze tedy říci, a z grafu 8 vyplývá, že modelované izotermy mají obdobný průběh. Nejlepší výsledky pro adsorpci olova při úpravě *Prunus cerasifera – myrobalan* jsou následující – pro M0.1 NaOH (6.69mg Pb/g) a pro M0.5 NaOH (6.60 mg Pb/g)

Z grafu 8–12 vyplývá, že v obou případech (aktivace jak pecky švestky myrobalan, tak fazolového lusku) s využitím 0.01M NaOH je možné vstupní koncentrace všech modelových roztoků navýšit – izotermy zde nevykazují své max. hodnoty.

Lze tedy říci, že sorpční vlastnosti vybraných zemědělských odpadů jsou dle předpokladu nižší, než u průmyslově využívaných adsorbentů. Ovšem lze je využít všude tam, kde je třeba využít čistých technologií (bez dalších chemických úprav) a všude tam, kde je třeba najít nějakou z levnějších alternativ pro čištění odpadních vod (např.rekultivace).