

DECONTAMINATION OF WATERS POLLUTED WITH HEAVY METALS USING WASTES OF MEDICINAL HERBS

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Abstract. *This paper presents a purification method for waters infested with heavy metals by using dry and milled waste of medicinal herbs resulted from the extraction processes. There were used FT IR spectrophotometric methods of analysis (spectrophotometer Varian 640-IR) and atomic absorption methods (spectrophotometer AA-6200 Shimadzu).*

Keywords: plant powders, basic lead acetate, polluted water

1. Introduction

Following the extraction process of certain active principles from the medicinal herbs, annually results tones of plant wastes, which are thrown at the ecological garbage hole. These wastes get rid of active compounds and microelements, leaving behind cavities of the size of chemical compound structures or microelements issued. These cavities may capture other chemical elements, as well as organic chemical structures present in the waste waters.

In a study concerning contamination with hard metals of mountainous waters [8] there were observed concentrations of certain heavy metals (lead, cadmium and zinc) exceeding the normal limit, which endangers the river fauna. The literature in the area indicates a number of waste water treatment methods, among which we mention:

a) Bio-remediation of waste waters with a series of compounds resulted from the pharmaceutical industry. The method is based on the ability of degrading organic matter and to assimilate certain heavy metals by some aerobic and anaerobic microorganisms;

b) Phyto-remediation of waste waters represent a purification method using wastes from plants (roots, stems, leaves and so on). This is a method practiced even by nature, which overflow and deposit various plant debris in their bed;

c) The treatment of waste water with two substances: ZCTAG195 (0.25mL/L) as coagulant and MOGNAFLOC 919 (0,615 mL/L) as flocculants [4]. This is a purification and cleaning method for waste waters resulted from washing coal and minerals from specific exploitation;

d) Filtration of polluted waters with heavy metals through composite membranes based on nanomaterials of the MCM [4] and SAPO [3] class. The quality of the resulted waters depends on the performances of the used membranes. The application of this method in various industries (food, chemical,

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textile, electrochemical, leather industry) proved more economical and efficient than the use of classical purification technologies. In the highly industrialized countries, such as France, USA, Finland, the membrane procedures were applied at the level of pilot stations;

e) The physico-chemical process of waste water treatment. This process applies when the pollutants are dissolved or in the form of suspensions in water. The pollutants in fine suspension that did not settle in the first decanter are eliminated with the help of chemical coagulants [2]. The application of the decanting process with coagulants removes the suspensions in 95% percentage;

f) A waste water treatment method uses "filter plants", such as water hyacinth (*Eichornia crassipes*), water salad (*Pistia stratiotes*), certain algae, which can retain both classical pollutants and the radioactive ones. In proper thermal conditions, these plants grow in abundance and if they do not have in their contents dangerous substances, can be administered in animal feed [3].

2. Materials and methods

- *Materials*

- Dry oregano waste (*Origanum vulgare*) resulted from the extraction process and transformed into powder;
- 0.05 and 1.0% solutions of basic lead acetate;
- Distilled water.

Method for obtaining oregano powder is presented in Fig. 1.

Wet waste of oregano → drying of the waste → grinding of the waste → sieving of the waste → oregano powder

Fig. 1. Scheme for obtaining oregano (*Origanum vulgare*) powder

- *Methods*

There were prepared two different solutions of basic lead acetate, of: 0.05% and 1.00%. These solutions were put in contact with the plant powder. The contact time for the powders with the tested solutions varied between 20 minutes and 120 minutes. We obtained a set of samples presented in Table 1.

After the contact time between powder and solution has elapsed, each sample was filtered, the solution was measured and the remained powder was dried for 2 hours in an oven at 80°C. Both the powder and the solutions resulting from the filtration were analyzed by spectral photometry. We used spectrophotometer with atomic absorption AA-6200 Shimadzu/2006 and the spectrophotometer Varian FT IR 640/2008.

Table 1. Characteristics of the analyzed sample

Nr. crt.	Name of sample	Quantity of powder (g)	Quantity of solution (mL)	Time of contact (min.)
1	SAMPLE 1- Oregano powder Initial sample	1g	-	-
2	SAMPLE 2 With basic lead acetate 0.05% - 20'	1 g	20 mL	20'
3	SAMPLE 3 With basic lead acetate 0.05% - 40'	1 g	20 mL	40'
4	SAMPLE 4 With basic lead acetate 0.05% - 60'	1 g	20 mL	60'
5	SAMPLE 5 With basic lead acetate 0.05% - 80'	1 g	20 mL	80'
6	SAMPLE 6 With basic lead acetate 0.05% - 100'	1 g	20 mL	100'
7	SAMPLE 7 With basic lead acetate 0.05% - 120'	1 g	20 mL	120'
8	SAMPLE 8 With basic lead acetate 1 % - 20'	1 g	20 mL	20'
9	SAMPLE 9 With basic lead acetate 1 % - 40'	1 g	20 mL	40'
10	SAMPLE 10 With basic lead acetate 1 % - 60'	1 g	20 mL	60'
11	SAMPLE 11 With basic lead acetate 1 % - 80'	1 g	20 mL	80'
12	SAMPLE 12 With basic lead acetate 1 % - 100'	1 g	20 mL	100'
13	SAMPLE 13 With basic lead acetate 1 % - 120'	1 g	20 mL	120'

- *Spectrophotometric method of atomic absorption*

- *Powder analysis*

The powder to be analyzed was burnt in an electrical oven(at 400°C), and the resulted ash was dissolved in concentrated chloride acid and dried on sand bath. This operation was repeated twice. The obtained sample was dissolved in distilled water, then introduced in a vial of 50mL and came to the mark with distilled water. Before being analyzed, the solution was filtered using a glass funnel provided with a G₅ porous plate.

- *Building the standard curve*

There were prepared solutions of lead, having the following concentrations: 0.4; 1.0; 2.0 and 10.0 ppm. The solutions were analyzed by spectral photometry, thus setting the relation between the absorbance and solution concentration. The obtained values are presented in Table 2 and Fig. 2.

Table 2. Concentration and absorbance of lead acetate solutions

Concentration (ppm)	0.40	1.00	2.00	10.00
Absorbance	0.0113	0.0283	0.0584	0.2945

(1) The equation of the regression line: $Abs = 0.0294 \text{ conc.} + 0r = 1.00$

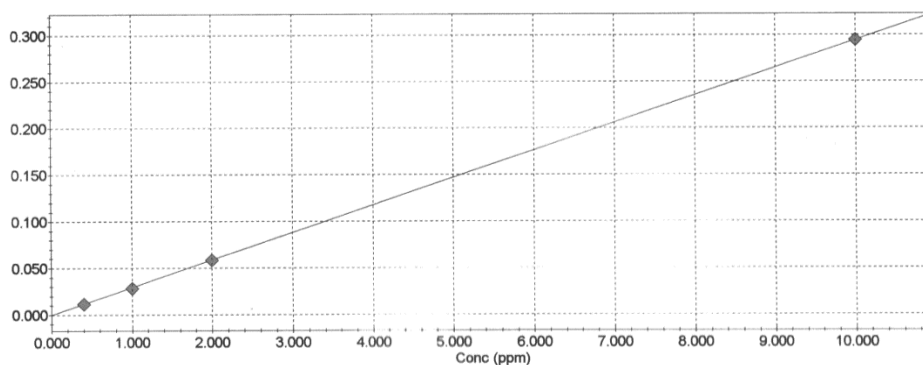


Fig. 2. Standard curve

3. Results

The results obtained from these analyses are presented in Tables 3 and 4.

Table 3. Powder lead analysis after the contact with the 0.05% solution of lead acetate

Sample	Conc. of the calibration curve (ppm.)	Abs.	Weight factor	Volume factor	Dilution factor	Correction factor	Final sample conc.	Conc. measure unit	Curve deviations	Standard deviations
STD 1	0.40	0.0113								0.000
STD 2	1.00	0.0283								0.000
STD 3	2.00	0.0584								0.000
STD 4	10.00	0.2945								0.000
Sample 1		0.0318	0.9956	10.00	1.00	1.00	10.8538	ppm	2.8952	0.000

Sample 2		0.4254	0.6871	10.00	10.00	1.00	2103.886	ppm	0.4987	0.002
Sample 3		0.2010	0.6938	10.00	25.00	1.00	2461.192	ppm	0.3165	0.000
Sample 4	-	-	-	-	-	-	-	-	-	-
Sample 5		0.1691	0.6813	10.00	25.00	1.00	2108.579	ppm	0.9200	0.001
Sample 6		0.2853	0.5714	10.00	10.00	1.00	1696.692	ppm	0.2479	0.000
Sample 7		-	-	-	-	-	-	-	-	-

Table 4. Powder lead analysis after the contact with the 1.00% solution of lead acetate

<i>Sample</i>	<i>Conc. of the calibration curve (ppm.)</i>	<i>Abs.</i>	<i>Weight factor</i>	<i>Volume factor</i>	<i>Dilution factor</i>	<i>Correction factor</i>	<i>Final sample conc.</i>	<i>Conc. measure unit</i>	<i>Curve deviations</i>	<i>Standard deviations</i>
STD 1	0.40	0.0113								0.000
STD 2	1.00	0.0283								0.000
STD 3	2.00	0.0584								0.000
STD 4	10.00	0.2945								0.000
Sample 8		0.2783	0.6423	10.00	25.00	1.00	3680.951	ppm	0.9147	0.002
Sample 9		0.2734	0.6019	10.00	25.00	1.00	3858.863	ppm	1.0345	0.002
Sample 10	-	-	-	-	-	-	-	-	-	-
Sample 11		0.2210	0.6514	10.00	25.00	1.00	2882.215	ppm	0.5759	0.001
Sample 12		0.4341	0.9844	10.00	25.00	1.00	3746.292	ppm	0.7819	0.003
Sample 13		-	-	-	-	-	-	-	-	-

- *Liquid phase analysis*

Analysis of the liquid phase resulting from the extraction of lead from waste water with oregano powder was performed with the atomic absorption spectrophotometer, and the obtained results are given in Table 5.

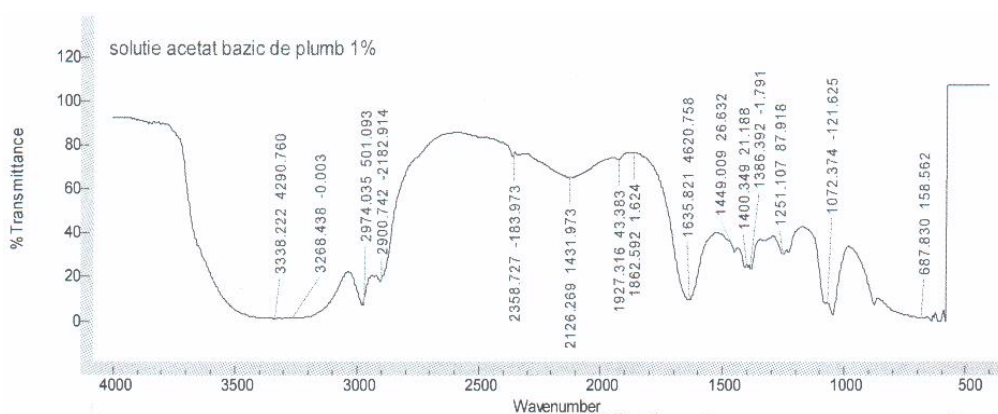
The data in the Table 5 show that waste waters resulted from the lead extraction have a very low content of lead, varying between 0.7 and 4.0 ppm/L. These values are within the European quality standards which at the 1st category are: for Zn = 0.03 mg/L, and for Pb = 0.05 mg/L.

Table 5. The values obtained from the analysis of waste water after the lead extraction

Sample	Conc. of the calibration curve (ppm.)	Abs.	Weight factor	Volume factor	Dilution factor	Correction factor	Final sample conc.	Conc. measure unit	Curve deviations	Standard deviations
STD 1	0.40	0.0113							1.8368	0.000
STD 2	1.00	0.0283							1.2740	0.000
STD 3	2.00	0.0584							1.4572	0.000
STD 4	10.00	0.2945							0.2183	0.000
Sample 2		0.1114	1.0000	1.00	1.00	1.00	3.7855	ppm	0.0635	0.000
Sample 3		0.0972	1.0000	1.00	1.00	1.00	3.3030	ppm	1.2361	0.000
Sample 4		0.0962	1.0000	1.00	1.00	1.00	3.2690	ppm	0.5148	0.000
Sample 5		0.1098	1.0000	1.00	1.00	1.00	3.7312	ppm	0.6440	0.000
Sample 6		0.1194	1.0000	1.00	1.00	1.00	4.0574	ppm	0.2369	0.000
Sample 7		0.0305	1.0000	1.00	1.00	1.00	1.0364	ppm	0.4637	0.000
Sample 8		0.0442	1.0000	1.00	1.00	1.00	1.5020	ppm	1.5998	0.000
Sample 9		0.0362	1.0000	1.00	1.00	1.00	1.2301	ppm	2.1516	0.000
Sample 10		0.0288	1.0000	1.00	1.00	1.00	0.9787	ppm	0.7378	0.000
Sample 11		0.0298	1.0000	1.00	1.00	1.00	1.0127	ppm	0.7130	0.000
Sample 12		0.0232	1.0000	1.00	1.00	1.00	0.7884	ppm	1.2191	0.000
Sample 13		0.0178	1.0000	1.00	1.00	1.00	0.6049	ppm	1.5890	0.000

FT IR spectrophotometer analysis

Among all the analyzed samples, three representative samples were chosen, showing that using this method we can evaluate the purification efficiency of waste water infested with heavy metals (Pb).

**Fig. 3.** FT IR spectrum of the basic lead acetate solution 1.0%

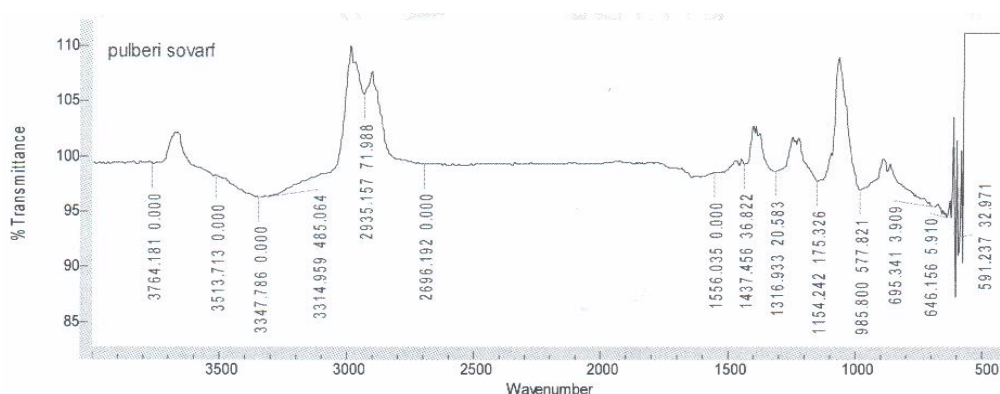


Fig. 4. FT IR spectrum of the powder from vegetable waste

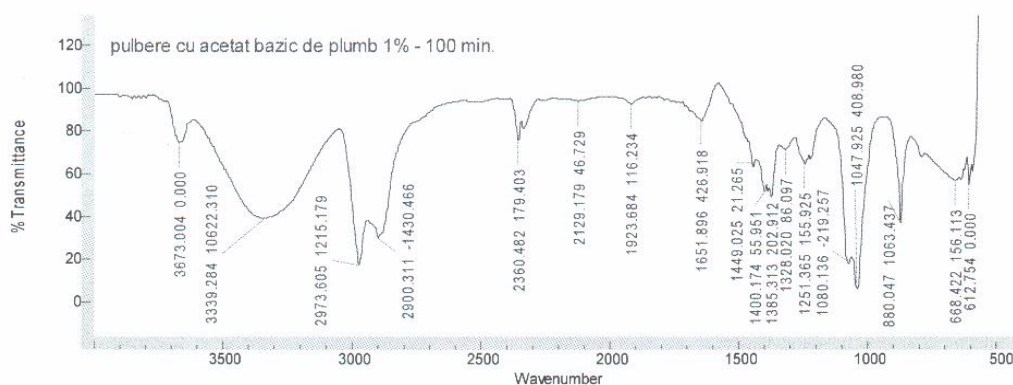


Fig. 5. FT IR spectrum of the vegetable powder after the operation of absorbing lead from waste water

In Fig. 3 the band $\lambda=1927.316 \text{ cm}^{-1}$ is given to C=O extended from the carbonyl group; $\lambda=1449.009 \text{ cm}^{-1}$ is given to the group CH_3 deformed, which is part of the carboxylic acids; $\lambda=1400.349 \text{ cm}^{-1}$ is OH deformed from carboxylic acids; $\lambda=1251.207 \text{ cm}^{-1}$ is assigned to the group C-O extended from the molecule of the basic lead acetate.

In Fig. 4, $\lambda=3764 \text{ cm}^{-1}$, $\lambda=3513 \text{ cm}^{-1}$ are assigned to OH (banding vibration) alcoholic or water; $\lambda=3347.786 \text{ cm}^{-1}$, $\lambda=3314.959 \text{ cm}^{-1}$ are assigned to OH (banding vibration) specific to certain amino acids, carboxylic acids, found in plants. Given band of $\lambda=1556,035 \text{ cm}^{-1}$ is assigned to the group N-H stretching vibration specific to the amide structures found in plants in various forms. Given strip of $\lambda=1154.242 \text{ cm}^{-1}$ is specific to the group C-O (banding vibration) specific to certain saturated alcohols or carboxyl esters. The band $\lambda=985.341 \text{ cm}^{-1}$ is given to the group C-H stretching vibration, specific to certain monosubstituted unsaturated compounds.

Fig. 5 represents a spectrum of an oregano powder after being in contact to the 1.00% solution of basic lead acetate for 100 minutes. This spectrum contains both specific bands from the basic lead acetate solution, and the specific strips from the oregano powder spectrum, such as: $\lambda=3339\text{ cm}^{-1}$, $\lambda=2975.63\text{ cm}^{-1}$, $\lambda=2900.311\text{ cm}^{-1}$, $\lambda=1449.025\text{ cm}^{-1}$, $\lambda=1386.12\text{ cm}^{-1}$, $\lambda=1328.21\text{ cm}^{-1}$, $\lambda=1071.75\text{ cm}^{-1}$.

Conclusions

1. In this paper, there are presented the results of some experiments related to the retention of heavy metals (Pb) from waste waters, using medicinal plant debris resulting after the extraction of specific active principles. For the assessment of the efficiency of using waste powders from medicinal plants in purification processes we used spectrophotometric methods of atomic absorption and FT IR spectrophotometry.

2. Our experiments showed that 1 gram of oregano (*Origanum vulgare*) powder debris retains over 4000 ppm Pb from waste waters. The results we obtained confirmed that medicinal plant debris can be successfully used in the purification processes of waste waters infested with heavy metals.

3. Using these depolluting agents in the purification processes have the advantage of a superior biodegradation, compared to the method that uses plant roots, stem and leaves.

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