

Removal of Lead from Aqueous Solutions by Adsorption Using Sphagnum Moss Peat

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Abstract: In this study, the adsorption experiments were carried out on laboratory scale, to evaluate the adsorption capacity of sphagnum moss peat (Poiana Stampei, Romania) for lead, as a function of several experimental parameters. The aqueous solution influence of various pH, also the initial metal ion concentration, peat dose and contact time was studied in batch experiments. The obtained results indicate that for an initial solution pH = 6.0 (acetate buffer), sphagnum moss peat was effective in removing 98 % of lead, and still increase with the increasing of peat dose. With the increasing of initial lead concentration, the residual Pb(II) content from aqueous solution increase the same, but the removal percent is higher than 95 % only in case of solutions with an initial concentration lower than 350 mg/L. In addition was also observed that the retained lead ions could be easily leaching from sphagnum moss peat using 0.5 N HCl solution. The interferences caused by several ions (Na(I), K(I), Ca(II), Mg(II), Cu(II), Zn(II), Co(II), Ni(II)) which are present in most environmental samples were determined. The validation of this procedure was done by recovery test of lead in tap water and lake water (free of SO_4^{2-}). The results of recovery test showed that the constituents of water samples do not interfere significantly with the lead removal by sphagnum moss peat.

Keywords: lead removal, sphagnum moss peat, adsorption, aqueous solutions

1. Introduction

Environmental protection must require the use of natural products instead of chemicals to minimize pollution. Thus, this investigation studies the use of natural materials for the removal of lead ions from aqueous solutions.

Lead is a toxic element, which is conservative and has cumulative characteristics [1, 2]. The majority of lead discharged into environment comes from atmospheric and particulate sources [3]. However, there are a range of industries which generate waste waters containing significant concentration of lead. For example, the battery manufacturing industry, smelting, printed wiring board manufacture and papers mills, are only few sources of lead pollution [4, 5].

The presence of lead and other heavy metals in the environment has become a major treat to plant, animal and human life, due their bioaccumulation tendency and toxicity, and therefore must be removed from waste waters before discharged. Excessive amount of lead in the human body can cause hypertension and brain damage, and for this reason, the permissible limits for lead discharged are low (0.2 mg/L in inland surface water and 5.0 $\mu\text{g/L}$ in drinking water) [6].

Various methods are currently used for the treatment of aqueous effluents containing heavy metals; the most important are chemical precipitation, electrochemical treatment, ion exchange, adsorption and biosorption [7-9]. But, many of these are relative expensive and non-environmental friendly, require additional reagents or

generate secondary waste. Even the utilization of activate carbon, the most used sorbent, is economically feasible only for small-scale industries, prevalent in developing economies due to huge capital instrument [10]. As such, it is necessary to search for alternative adsorbents, which are low-cost, that have good adsorbent properties and low value to the inhabitants.

The sorbent used in this study is sphagnum moss peat (from Poiana Stampei, Romania). This is a complex material, obtained by partial degradation of vegetables and where the major constituents are cellulose, lignin, humic and fulvic acids [11]. Due to those components, the sphagnum moss peat has in its structure different polar groups (such as: carboxylic, phenolic, alcoholic, etheric, etc.) which can chemical bind metal ions from aqueous solutions.

In this paper, we have investigated the effectiveness of sphagnum moss peat as sorbent in removal of lead from aqueous solutions. The influence of different experimental parameters (initial solution pH, initial metal ion concentration, peat dose, contact time) was considered. The proposed procedure showed high efficiency, good selectivity for lead and was evaluated for lead removal from water samples.

2. Experimental

2.1. Materials

Experiments were carried out using sphagnum moss peat, drawing from Poiana Stampei, Romania. The material

was dried for 4 hours at 90 ± 2 °C and the grounded and sieved to particles with size of 1-2 mm.

All chemical reagents used in this study were of analytical degree and were used without further purifications. The stock solution of lead, containing 2000 μg Pb(II)/mL was prepared by lead nitrate (Reactivul Bucharest) dissolving in double distilled water, following by solution standardization [12]. The working solutions were obtained by diluting the stock solution with double distilled water. The initial solution pH values of work aqueous solutions were obtained using 2N HNO₃ solution or acetate buffer (CH₃COOH/NaOH).

2. 2. Methods

The adsorption experiments were performed by batch technique, mixing samples of cca. 0.125 g of sphagnum moss peat with volumes of 25 mL solution of known concentration of lead (34 – 507 mg Pb(II)/L), in a 10 mL conical flasks. The initial pH of work solutions was obtained adding 2.5 mL of 2N HNO₃ solution (for pH=2.0) and 5.0 mL of acetate buffer (for pH = 4.0 and 6.0), and was measured with a Radelkis OK-281 pH/ion-meter, equipped with a combined glass electrode. After a determined time (usually 24 hours) with intermittent stirring, the phases were separated by filtration and the Pb(II) concentration in filtrate was analyzed spectrophotometrical with 4-(2-pyridylazo)-resorcinol (Digital Spectrophotometer S 104 D, $\lambda = 530$ nm, 1 cm glass cell, against a blank solution [13]), using a prepared calibration graph.

In the experiments concerning the effect of peat dose, a range of sorbent samples from 0.125 to 1.000 g were used. For the contact time experiments, we use the same procedure as described above, with the differences that the samples were filtrated after a specific period of time.

The residual lead concentration (C_{Pb}^r , mg/g) and the percent of lead removal (R, %) were calculated according with their definition.

The selectivity coefficients was calculated as the ration between the lead concentration and interfering ions concentration which gives a 5 % change of removal percent, in a reference solution. The recovery test was done using tap water obtained from Technical University "Gh. Asachi" of Iasi laboratories and lake water, from Ciric Lake (Iasi, Romania), after a preliminary treatment.

3. Results and discussion

The optimum conditions for lead removal using sphagnum moss peat were obtaining by varying several experimental parameters, and determining the residual lead concentration in each case.

3. 1. Effect of initial solution pH

It is known that the solution pH is an important experimental parameter in the removal of metal ions from

aqueous solutions, because affect both the speciation form of metal ion and the ionization degree of functional groups from sorbent surface [14, 15].

In this study, the initial solution pH was varied in the 2.0 and 6.0 pH range. According with the lead speciation diagram [16], in this pH domain Pb(II) is predominantly as divalent free ions (Pb²⁺), and this species can be involved in chemical processes during of sorption by sphagnum moss peat.

The experimental results concerning the influence of initial solution pH on the Pb(II) sorption by sphagnum moss peat are presented in Fig. 1.

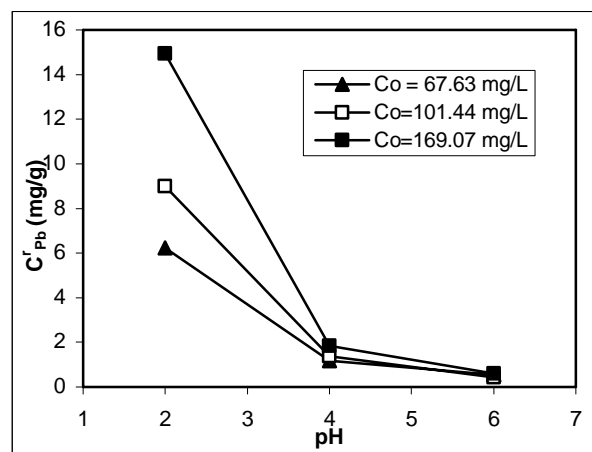


Figure 1. Effect of initial solution pH on removal of Pb(II) by sphagnum moss peat (sorbent dose = 10 g/L; time = 24 h; C_0 -initial lead concentration)

It can be observed from Fig. 1, that the residual Pb(II) concentration in aqueous solution decrease with the increasing of initial solution pH; and this tendency is much pronounced as higher initial Pb(II) concentration is. This variation could be simply explained by considering ionic state of functional groups involved in sorption process. Thus, at pH = 2.0 (acid media), most functional groups are undissociated and the obtained value of Pb(II) removal percent is lower (11.52 %). The increasing of initial solution pH determined the increasing of functional groups dissociation degree, and thus the Pb(II) ions can be more easy bonded. In consequence, the residual lead concentration decreases. Because the maximum efficiency of lead removal (97.75 %) is obtained at initial solution pH = 6.0 (acetate buffer), this value was considered for the further sorption experiments.

3. 2. Effect of sphagnum moss peat dose

The variation of the removal percent and residual concentration of lead as a function of the sorbent dose are show in Fig. 2. It can be seen that if the Pb(II) residual concentration from aqueous solution decrease with the increasing of sorbent dose, the Pb(II) removal percent values varied more slowly (between 96.66 % and 99.06 %). Under these conditions, from economically reasons, a 5 g peat/L was considered sufficient for the quantitative removal of lead from aqueous solutions and was used in all following experiments.

3.3. Effect of contact time

The influence of contact time between sphagnum moss peat and the aqueous solution which contains lead ions, on Pb(II) removal efficiency is presented in Fig. 3. The experimental results indicate that, in mentioned experimental conditions, the sorption process is a very fast one; most of lead ions being retained in the first 25 – 30 min. After this short period, the equilibrium stage is practically obtained; the difference between lead quantities retained after 24 h and 25 min is not higher than 1.45 %.

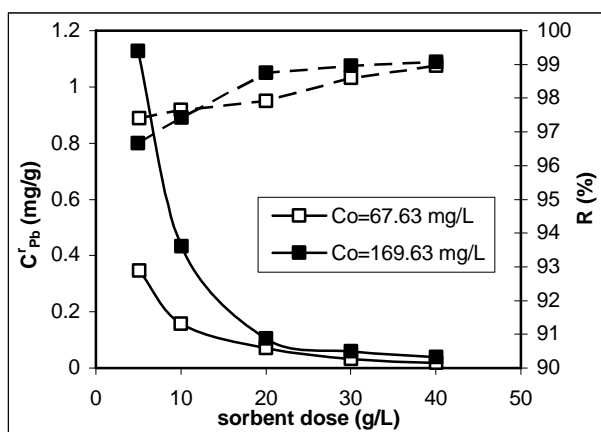


Figure 2. Effect of sphagnum moss peat dose on the Pb(II) removal from aqueous solution (pH = 6.0; time = 24 h; C_o -initial lead concentration)

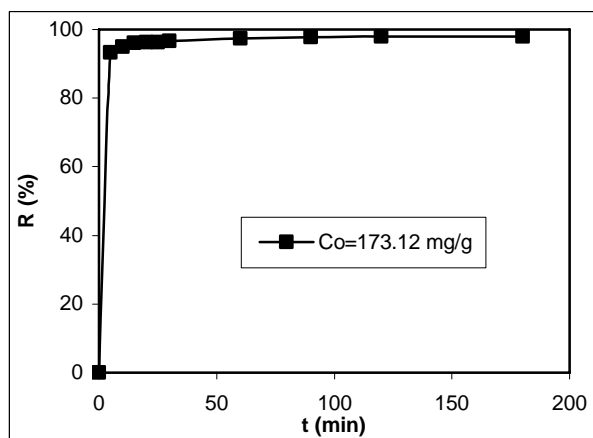


Figure 3. The influence of contact time on Pb(II) removal percent (R %) by sphagnum moss peat (sorbent dose = 5 g/L; pH = 6.0; C_o -initial lead concentration)

3.4. Effect of initial lead concentration

The lead removal efficiency by sphagnum moss peat was studied as a function of its initial concentration, under optimum experimental conditions. The effect of initial Pb(II) concentration on the sorptive removal of lead is presented in Fig. 4.

The increasing of initial Pb(II) concentration from 33.81 mg/L to 507.21 mg/L determined the decrease of removal percent value from 97.69 % to 87.22 %, at a sorbent dose of 5 g/L. A good retention of lead takes place at initial metal ion concentration lower than 70 mg/L,

where the residual lead content is lower than the permissible limit for lead discharge. With the increasing of initial lead concentration, the residual Pb(II) content from aqueous solution increase, the same. This suggest that for waste waters with a lead content higher than 70 mg/L, is necessary two or more adsorption steps on sphagnum moss peat, for that the lead content to be lower than the permissible limit.

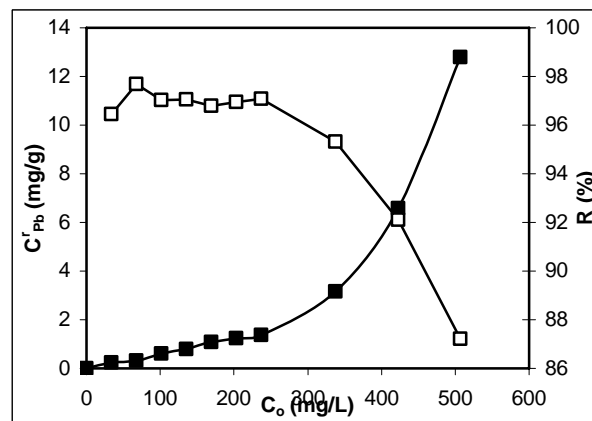


Figure 4. Effect of initial Pb(II) concentration on its removal onto sphagnum moss peat (pH = 6.0; sorbent dose = 5 g/L, time = 24 h)

In order to investigate if the retained lead ions could be leaching from the sphagnum moss peat, the de-sorption studies were realized.

For this five samples of sphagnum moss peat, obtained after lead adsorption, (0.125 – 0.625 g sphagnum moss peat) were treated with 10 mL of 0.5 N HCl solution. Each sample was intermittent stirred for two hours, then filtrated and in filtrate the concentration of lead ions was determined. In all cases was observed than more of 99.7 % from lead (Table 1) can be leaching from sphagnum moss peat.

TABLE 1. The de-sorption experiments

Sphagnum moss peat (g)	Pb(II) adsorbed (mg/g)	Pb(II) leaching (mg/g)
0.1254	13.2028	13.1865
0.2565	25.9411	25.9276
0.4012	39.4354	39.4157
0.5324	43.7834	43.7699
0.6245	67.1478	66.9876

This indicate that the sorption of lead ions is a reversible process, and in consequence the sorbent (sphagnum moss peat) can be regenerated and eventually used for another sorption experiments.

3.5. The validation procedure

An important step in characterization of the lead removal procedure using sphagnum moss peat is the selectivity of adsorption process towards Pb(II) in comparison with other interfering ions. For the quantification of this characteristic, the selectivity coefficients were used. The selectivity coefficients ($a_{pb, j}$)

are defined as the ratio of lead concentration (C_{pb}) and interfering ions concentration (C_j) which gives the same change of removal percent, in a reference solution with a constant Pb(II) concentration [17].

In this study, the interfering ions were added to an identical reference solution with a constant lead content (173.12 mg/L) until a change of 5 % in lead removal percent was obtained. The calculated values of the selectivity coefficients are summarized in Table 2.

TABLE 2. The logarithmic values of the selectivity coefficients

Interferent, j	$\log a_{pb,j}$	Interferent, j	$\log a_{pb,j}$
Na(I)	-3.121	Cu(II)	-1.854
K(I)	-2.898	Zn(II)	-0.143
Ca(II)	-2.424	Co(II)	-1.705
Mg(II)	-1.973	Ni(II)	-0.238

Only Zn(II) and Ni(II) ions interfere seriously in the sorption process of lead on sphagnum moss peat. The other studied ions (Na(I), K(I), Ca(II), Mg(II), Cu(II), Co(II)) that were fairly abundant in environmental samples, practically do not interfere. This means that in presence of these ions the sorption process of lead by sphagnum moss peat is not affected.

For to use the selectivity advantages, the recovery test was done using two categories of water samples: the first, tap water from Technical University "Gh. Asachi" laboratories and the second, lake water from Ciric Lake (Iasi, Romania). Both water samples were filtrated using a G4 glass crucible, in order to remove the solid impurities and then was treated with 0.5 M BaCl₂ solution for to eliminated the SO₄²⁻ ions. After this preliminary treatment 15 mL from each water sample was used for to obtained the aqueous solutions (25 mL) with a known lead content and an initial solution pH = 6.0. These solutions were mixed with cca. 0.125 g of sphagnum moss peat and after filtration, the lead concentration was measured in filtrate. The results of recovery test are presented in Fig. 5.

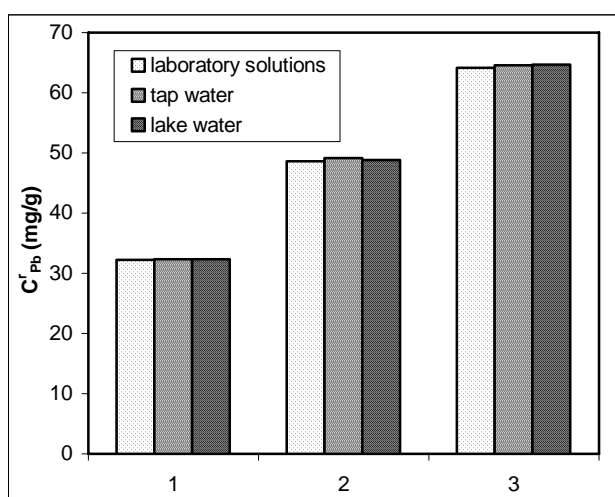


Figure 5. The recovery test (1: Co = 173.11 mg/L; 2: Co = 259.68 mg/L; 3: Co = 346.24 mg/L)

It can be observed that for all the three cases, the obtained residual lead concentrations have appropriate values. This means that, the constituents of water samples do not interfere significantly with the lead removal using sphagnum moss peat. Thus, this natural sorbent can be successfully used for the removal of lead ions from aqueous solutions.

4. Conclusions

The results of this study show that the sphagnum moss peat (from Poiana Stampei, Romania) can be used as a cheaper and efficient sorbent for to removal of lead ions from aqueous solutions.

The sorption process was studied at laboratory scale in batch conditions, as a function of several experimental parameters: initial solution pH, sorbent dose, contact time and initial lead ions concentration. The experimental results have show that the optimum pH for the lead removal is 6.0 (acetate buffer); a dose of 5 g peat/L retained almost quantitatively Pb(II) ions from aqueous solutions and the contact time for the for the maximum of adsorption is around 25 – 30 min. The residual concentration of lead increase with the increasing of initial metal ion concentration, but the removal percent is higher than 95 % only in case of solution with a lead content lower than 350 mg/L. In addition, was observed that the retained lead ions can be easy leaching from sphagnum moss peat using a 0.5 N HCl solution.

The interferences caused by several ions (Na(I), K(I), Ca(II), Mg(II), Cu(II), Zn(II), Co(II), Ni(II)) which are present in most environmental samples were evaluated using the selectivity coefficients. The validation of this procedure was done using recovery test of lead in tap water and lake water (free of SO₄²⁻). The results of recovery test showed that the constituents of water samples do not interfere with the lead removal using sphagnum moss peat.

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REFERENCES

- Goyer R.A., Lead toxicity: current concerns. *Environ. Health Perspect.* **1993**, Vol. 100, pp. 177 – 187.
- Coupal B. and Spiff A.I., The treatment of waste waters with peat moss. *Wat. Res.* **1999**, Vol. 33(2), pp. 1071 – 1076.
- Londrigan P.J., Silbergeld E.K. and Froisnes J.R., Lead in modern world. *Am. J. Public Health.* **1990**, Vol. 80(8), pp. 907 – 908.

4. Srivastava S.K., Gupta V.K. and Mohan D., Removal of lead and chromium by activate slab – A blast-furnance waste. *J. Environ. Eng.* **1999**, Vol. 123(5), pp. 461 – 468.
5. Quek S.Y., Wase D.A.J. and Forster C.F., The use of Sago Waste for the sorption of lead and copper. *Water SA.* **1998**, Vol. 24(3), pp.251 – 256.
6. NTPA 001 / **2005**; NTPA 002 / **2005**.
7. Horsfall M. and Spiff A.I., Effect of metal ion concentration on the biosorption of Pb(II) and Cd(II) by *Caladium bicolor*. *African J. Biotech.* **2005**, Vol. 4(2), pp. 191 – 196.
8. Orumwense F.F.O., Removal of lead from water by adsorption on kaolinic clay. *J. Chem. Tech. Biotech.* **1996**, Vol. 65, pp. 363 – 369.
9. Bailey S.E., Olin T.J., Bricka M.R. and Adrian D.D., A review of potentially low cost sorbents for heavy metals. *Wat. Res.* **1999**, Vol. 33(11), pp. 2469 – 2479.
10. Babel S. and Krniavan T.A., Low cost adsorbants for the heavy metals uptake from contaminated water: a review. *J. Hazard. Mater.* **2003**, Vol. B 97, pp. 219 – 243.
11. Brown P.A., Gill S.A. and Allen S.J., Metal removal from waste waters using peat. *Wat. Res.* **2000**, Vol. 34, pp. 3907 – 3916.
12. Dean J.A., *Analytical Chemistry Handbook*. 3rd ed. McGraw-Hill Inc. New York. **1995**. pp 3.105 – 3.109.
13. Flaska A.H. and Barnard A.J., *Chelates in Analytical Chemistry*. Marcel Dekker Inc. New York. **1976**. pp 16 – 28.
14. Bulgariu L., Robu B. and Macoveanu M., The Pb(II) sorption from aqueous solutions by sphagnum moss peat. *Rev. de Chimie.* (in press).
15. Ho Y.S., John Wase D.A. and Forster C.F., Kinetic studies of competitive adsorption by sphagnum moss peat. *Environ. Tech.* **1996**, Vol. 17, pp. 71 – 77.
16. Lead speciation diagram calculated using EpH-web, accessed at 15 February 2008: <http://www.crct.pdymtl.ca/ephweb.php>.
17. Bulgariu L., Bulgariu D. and Sarghie I., Spectrophotometric determination of cadmium (II) using p,p'-Dinitro-Sym-Diphenylcarbaid in aqueous solutions. *Anal. Lett.* **2005**, Vol. 38(14), pp. 2365 – 2375.