Section: Environmental protection

Effect of pH for lead removal from polluted water applying peat

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Abstract

Sorption is often applied as heavy metals removal from polluted water method. However, still remain the need for low cost, efficient sorbents, which are able to remove heavy metal ions from contaminated water. In the present work cheap biological material – peat have been investigated with respect to its capacity to adsorb metals from contaminated waters. The peat showed the high sorption capacity for lead form single-metal solutions.

The key parameters characterizing sorbent and affecting its sorption properties –average values of total carbon, pH were determined – TC(peat) =51.83%, $pH_{KCl} = 4.80$, $pH_{H2O} = 5.90$. Determined quantity of lead in dry peat is equal to 3.31 ppm. Average value of moisture of peat was 44.67%. Modelling solution was used in research, inserting a known quantity of Pb salt and identifying peat sorption capacity under static conditions, after 72 hours. Effect of pH (pH = 2, pH = 4 and pH = 6) for lead removal from aqueous solution was studied. Best adsorption of Pb from aqueous solution applying peat was fixed when pH = 4 and pH = 6. The results of the research showed that maximum sorption capacity of peat is reached at pH = 4 and is equal to 9.976 mg/g.

Keywords: heavy metals; peat; sorption; lead; pH.

Nomenclature	
φ	moisture (%)
TC	total carbon (%)
a	adsorption capacity (mg/g)
HM	heavy metals
MAC	maximum allowable concentration

1. Introduction

The objective of the environment protection of the Republic of Lithuania – to guarantee proper environmental quality for the inhabitants of the country and to allow the regular territorial development – is anticipated in the country's strategic documents. This objective cannot be obtained, if one of the most important environmental elements is not guaranteed – good condition of surface-water pools (rivers, lakes, ponds, the Curonian Bay, sea shore waters) [1].

An increased input of metals and synthetic chemicals in the terrestrial environment due to rapid industrialization coupled with inadequate environmental management in Europe has led to large-scale pollution of the environment. In the terrestrial environment, these chemicals clearly pose a significant risk to the quality of soils, plants, natural waters and human health [2]. Metals are considered to be among the most dangerous environmental pollutants, because they do not disintegrate with physical processes and therefore remain for long time period [3]. Large amounts of HM are transported via natural processes from technogenic pollution sources to air, water, soil and natural ecosystems. Commonly, the concentration of HM exceeds maximal available concentration in water (wastewater) and soil [4]. Many industrial effluents are contaminated with heavy metals (e.g. lead, etc.). Lead pollution sources: natural − erosion (11 000 t/year are washed into the oceans), anthropogenic from agriculture (33 000 t/year in the world) – mining (4 mln. t/y are mined), lead fusion, industry (140 000 t/y get into the water), production and transportation of alkyl-lead (e.g., tetraethyl-lead) (300 000 t/y) [5].

Natural or synthetic sorbents, for their high sorption capacity, selectivity, properties of caption exchangeability, low price and affordability, are used to remove HM from wastewater [6].Sorption of metals onto biological materials (biosorption), including peat, is well-recognized as an alternative to "traditional" wastewater treatments processes. Peat is a heterogeneous

organically formed substance that results from the incomplete decomposition of plants in a wet or humid environment. The organic content in peat is more than 75%, it has a large specific surface area (>200 m^2/g) and is highly porous (95%), therefore, peat has long been known for its ability to remove metals from water. As a result, metal concentrations in peat have been used as a geochemical prospecting tool and peat ended up being tested for its ability to treat wastewater [7]. Peat can be described as fibrous mass of fossilized plant matter in various decomposition stages, it generally occurs in wet areas where there is a deficiency of oxygen thereby promoting the accumulation of plant matter over its decomposition. Peat is a complex material consisting predorninantly of lignin and cellulose. These constituents, especially lignin, bear polar functional groups such as alcohols, ketones, aldehydes, acids and phenolic residue which can be involved in chemical bonding and complexation roles during meta1 ion fixation from solutions. The use of peat in wastewater treatment has been extensively studied and it has ken proven that peat is an effective adsorbent for the removal of heavy metals from wastewater. Peat has a natural capacity for exchange adsorption with heavy metals such as lead, zinc, chromium, nickel, copper and cadmium. Exchange adsorption takes place as a result of either solvent motivated force, which relates to surface tension or adsorbent motivated force which combines chemical electrostatics and physical interaction between adsorbate and adsorbing surface. Adsorption is generally driven by the two forces. Peat strongly adsorbs various metal cations using their caboxylic, phenolic and hydroxylic functional group [8, 9].

Compared to "traditional" techniques (such as precipitation, ion exchange and reverse osmosis), biosorption offers the advantages of low cost, good efficiency and it does not produce sludge of high metal content. Biosorption may be simply defined as the removal of substances from solution by biological material [10].The number of scientific publications related to biosorption increased from 75 in 2002 to 248 in 2011 [11].

The aim of the work is to investigate influence of pH for removing of lead from aqueous solutions applying peat.

2. Water pools attributed to the risk group

Such surface water pools which cannot reach a good state till 2015 because of negative human influence are called risk water pools [12].

Surface risk water pools were distinguished because of these significant loads of human activity [13]:
− diffusive pollution (evoked by the agricultural activity);
− concentrated pollution (water pollution by urban and industrial object sewage);
− riverbed lining (here are attributed the water pools flowing in non-urbanized territories);
− water-power plants.

Those surface water pools were also attributed to the risk group in which greater concentrations of some materials were found than provided in the Directive of dangerous materials [14] and the Directive of freshwater fish [15].

At the moment, in Lithuania, 790 surface water risk pools were tentatively distinguished. Even 694 of these pools were distinguished for the risk group really approximately therefore their list will be revised in the future. The number of water pools, attributed to the risk group, in separate river-basin regions is presented in Table 1 [12].

The greatest number of risk pools (even 75%) is determined by the concentrated pollution – water pollution by urban and industrial object sewage. Risk water pools, distinguished for the diffusive pollution (evoked by the agricultural activity), make 22% of all pools attributed to the risk group, but their pools take even about one fourth of the Lithuania's area.

Table 1. The number of risk water pools in separate river–basin regions [12]

River basin region	Water pools, attributed to the risk group	Water pools, attributed to the potential risk group
Dauguva	2	8
Nemunas	63	499
Venta	5	96
Lielupė	26	91
In total:	96	694

Thus it is very important to increase the efficiency of sewage cleaning in our country and to reduce the agricultural pollution [14].

3. Methodology of investigation

− Materials, reagents and instruments
  1. Samples of peat;
  2. Deionized water according to European Standard ISO 3696:1987 (electric conductivity – 0.05–0.08 µS/cm);
  3. Aqueous solutions of lead 25 mg/L, 50 mg/L 75 mg/L, 100 mg/L. Solutions were prepared from nitrate of lead (pure for analysis);

4. HNO_3 (65%, pure analysis);

5. H_2O_2 (30%, pure analysis);

6. KOH 0.1 N;

7. HNO_3 0.1 N;

8. Standard Pb solution (~1000 mg/L) in 2% HNO_3;

9. 50 ml; 100 ml and 1000 ml measuring flasks, A class;

10. Percolators;

11. Atomic absorption spectrophotometer "Buck Scientific", 210 VGP;

12. Water purification system ''Demiwa 3 Roi'';

13. Analytical balance "KERN-770";

14. pH-meter S47K"Mettler Toledo";

15. Sieve shaker, "Retsch, AS 200";

16. Mechanical shaker "Gerhardt, Rotoshake RS 12".

‒ Preparation of peat samples and moisture determination

Peat samples were sieved through 1 mm diameter sieve (Retsch, As 200). Peat samples were heated at a temperature of 100–105 °C up to a stable weight. According to mass difference of sample before and after heating quantity of moisture in peat (%) was determined. Heated sorbent was cooled up to room temperature. It was weighed out 1±0.001 g of peat with the analytical balance KERN-770 for the sorption of Pb from an aqueous solution researches.

‒ Determination of the pH of peat

For one peat pH determination method 30 g (±0.01) of peat sample was weighted. For peat: water method – 15 g peat samples were mixed with 75 ml of deionized water (1:5 peat: water). Water and peat suspension was shaken for 60 min, using the mechanical shaker Gerhardt, Rotoshake RS 12. Mixed suspensions were left for 1 h to settle. For peat: KCl method 15 g (±0.01) of peat was diluted with 75 ml of 1 M KCl solution. This suspension also was stirred with mechanical shaker for 60 min and after that left to sit for 1 h. Peat pH was measured with pH meter – S47K, Mettler Toledo".

‒ Determination of the total carbon (TC) of peat

About 30 mg (±0.1) of dry peat was weighted. The total carbon content was analysed with total organic carbon analyser (TOC-V by Shimadzu) in 900 °C temperature.

‒ Determination of Pb quantity in peat

Total Pb quantity determination in peat analysis was performed with Buck Scientific 210 VGP Atomic Absorption Spectrophotometer after peat digesting in mixture of HNO_3:H_2O_2 (10 ml: 2 ml) extraction solution using ETHOS microwave digestor (Milestone) (Fig. 1). Then, the mixture of the sample and acid is filtered through 0.45 µm glass filters [16,17], diluted with deionized water till 50 ml and lead concentration determined using Atomic absorption spectrophotometer presented in Figure 2 applying GAAS method.
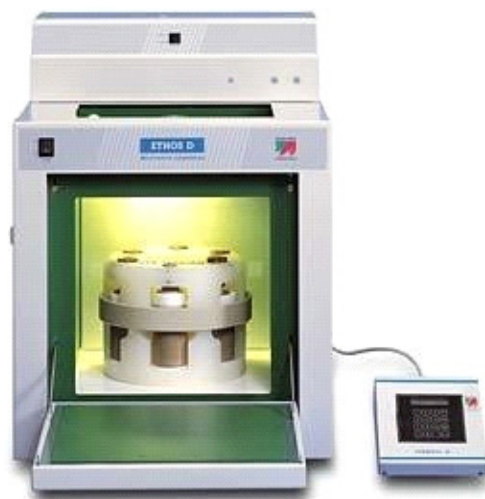

Fig. 1. Microwave digestion system "Milestone Ethos Touch Control"

‒ Lead sorption researches

Adequate salts of Pb (nitrate) were chosen as a source of HM. Lead nitrate salt was dissolved in 800 ml of deionized water and diluted till the sign in a 1000 ml capacity flask. Different initial concentrations of lead were used for experiments: C_{Pb} – 25 mg/L; 50 mg/L; 75 mg/L and 100 mg/L. PH of solution was regulated with 0.1 N HNO_3 or 0.1 N KOH solutions. 1 g of peat was mixed with 100 ml of aqueous lead solution containing different concentrations of Pb(II) ions, using capped bottles (100 ml). Contact time between sorbent and sorbate – 72 hours. The suspensions were filtered and the concentration of Pb (II) in the filtrates as well as in the initial solutions was determined.

Fig. 2. The atomic absorption spectrophotometer "Buck Scientific" 210 VGP

Analysing samples with FAAS or GFAAS method 283.2 nm wavelengths is set for Pb determination.

– Statistical analysis

Each concentration of lead in polluted water, in peat, also pH, total carbon and humidity measurements were measured five times. Some descriptive statistics of samples were carried, namely average, minimum (min), maximum (max), median and standard deviation at a $p<0.05$. Pearson's coefficient was calculated between peat sorption capacity and lead concentration in solution. The differences were considered significant at $p <0.05$. All calculations were performed using the statistical package Statistica 7.0 and Excel 2007 program.

4. Results and discussion

Ion exchange is a common water treatment technology and a wide variety of commercial resins are available for specific applications. Commercial resins are expensive and need to be regenerated either on site or sent back to the supplier. On-site regeneration is often problematic, particularly for small companies, and generates solutions that require disposal and possibly additional treatment. The search for low-cost ion exchange materials has led to tests of a wide variety of products including peanut hulls, sawdust, algae, pecan shells and corn cobs [7, 18]. Peat is a natural material formed from the partial decomposition of mosses, sedges, grasses, shrubs, or trees in waterlogged conditions. Peat has also been considered and tested as a low-cost ion exchange material in a variety of studies [7]. Data has shown that it can effectively remove metals from solution.

Peat can be used for wastewater treatment of polluted waters because of its natural characteristics that ensure high removal efficiencies, little pre-treatment required, it is inexpensive and available in large quantities, and there is also a need to explore new areas where peat could be used.

Peat with a low degree of decomposition for the production of sorbents should be used, because it exhibits higher porosity, specific surface area, and more developed structure. Results of peat properties study presented in Table 2.

Table 2. Properties of peat

| Parameter | pH | | Moisture | Total Carbon, (TC), | Pb, ppm |
	pH_{KCl}	pH_{H2O}	(φ), %	%	
Min	4.71	5.83	40.54	51.03	3.02
Max	4.88	6.04	50.71	52.88	3.74
Med	4.805	5.88	43.72	51.71	3.24
Average	4.80	5.90	44.67	51.83	3.31
Standard deviation	0.060	0.082	3.76	0.68	0.277
Confidence interval	±0.059	±0.072	±1.11	±0.19	±0.313

Peat mixed with fixed volumes solutions of lead ions of different concentrations. Residual concentration of lead in solution and lead quantity in peat after sorption has been reached. The results of experimental investigation on Pb sorption from aqueous solutions depending on the lead concentration at different solution pH presented in Figs 3–5.
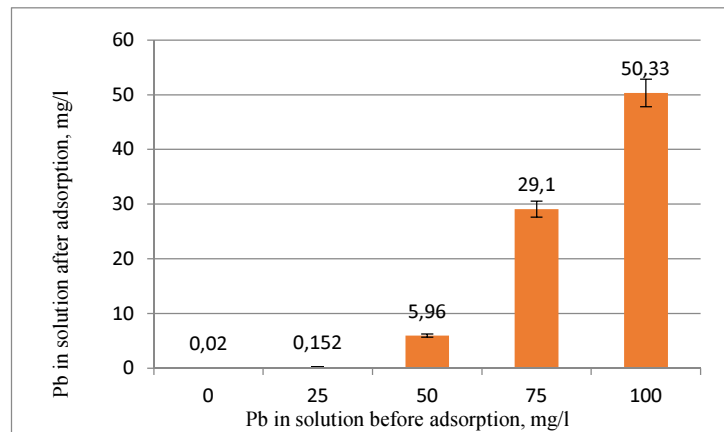
Fig. 3. Effect of initial Pb (II) concentration on lead sorption on peat (t = 20 °C, pH = 2, m(peat) = 1 g)

According to Kalmykova *et al.* [19] the fibre sludge ash and the Sphagnum peat showed the highest sorption capacities for metals among the materials studied in batch experiments with single-metal solutions. The Figure 3 clearly illustrate that lead adsorption on peat in acid environment (pH = 2) is limited, with initial Pb concentration increasing residual Pb concentration in solution also. It can be seen when Pb concentration in solution is 0 mg/g small concentration of Pb is fixed (0.020 mg/L). It can be due to these factors; purity of reagents, or metal leaching from peat at acid environment. When Pb concentration in solution is equal to 100 mg/L the degree of water treatment is less than 50% (49.67%). The column study indicated that adsorbed lead ions could be eluted from peat using 0.05 N nitric acid solution (it is approximately equal to pH = 1.3) [8]. It is also possible that pH of solution after added peat into solution increased.

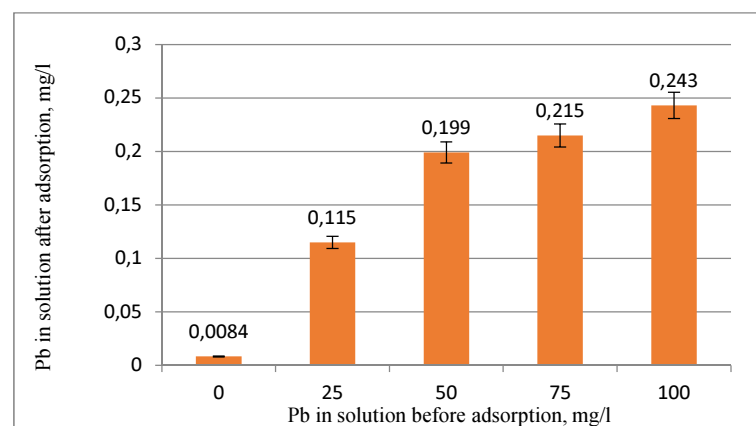Fig 4. Effect of initial Pb (II) concentration on lead sorption on peat (t = 20 °C, pH = 4, m(peat) = 1 g)

The Figure 4 clearly illustrate that peat can be used as effective sorbent for lead adsorption from pH = 4 solution. With initial Pb concentration increasing residual Pb concentration in solution also. It can be seen when Pb concentration in solution is 0 mg/g small concentration of Pb is fixed (0.008 mg/L). It can be due to these factors; purity of reagents, or metal leaching from peat at acid environment. This value is smaller than registered at pH = 2 due to bigger pH of solution. When Pb concentration in solution is equal to 100 mg/l the degree of water treatment is more than 99% (99.76%).
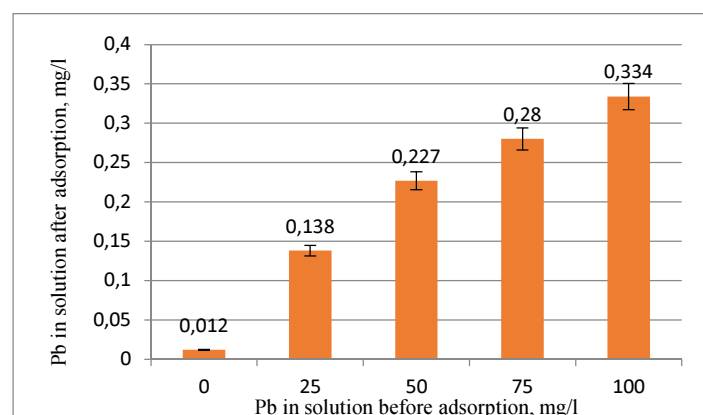

Fig. 5. Effect of initial Pb (II) concentration on lead sorption on peat (t = 20 °C, pH = 6, m(peat) = 1 g)

The Figure 5 clearly illustrate that peat can be used as effective sorbent for lead adsorption from pH = 6 solution. With initial Pb concentration increasing residual Pb concentration in solution also. It can be seen when Pb concentration in solution is 0 mg/g small concentration of Pb is fixed (0.012 mg/L). It can be due to these factors: purity of reagents, or metal leaching from peat. This value is smaller than registered at pH = 2 due to bigger pH of solution. When Pb concentration in solution is equal to 100 mg/l the degree of water treatment is more than 99% (99.66%). Adsorption capacity values for peat at different pH presented in Table 3.

Table 3. Adsorption capacity for peat at different pH values

C_{Pb}, mg/l	a, mg/g		
	pH = 2	pH = 4	pH = 6
25.0	2.485	2.489	2.486
50.0	4.404	4.980	4.977
75.0	4.590	7.479	7.472
100.0	4.967	9.976	9.967

It can be seen form Table 3 that sorption capacity of peat increasing with increasing Pb concentration in solution. The maximum sorption capacity of peat is equal to 9.976 mg/g when pH = 4. The biggest influence of solution pH was determined when pH = 2.

Pearson's coefficient for peat sorption capacity dependence on lead concentration in solution is 0.888 when pH = 2. Also big Pearson's coefficient values determined for pH = 4 and pH = 6–1.000 and 1.000 accordingly. The factors that influence the sorption process can be grouped as: physical and chemical properties of metal ions (i.e., molecular weight, ionic radius, oxidation state); properties of biosorbent (i.e., the structure of the biomass surface); and the experimental conditions (i.e., pH, temperature, concentration of biosorbent, the concentration of sorbate). Peat can be modified in order to reduce several deficiencies, which are: low chemical stability, low mechanical strength, tendency of its particles to expand or shrink. The influence of initial metal ions concentration and equilibrium contact time was studied in a series of batch experiments, in comparison with natural peat. An increasing of adsorption capacity of alkaline treated peat was obtained for all studied heavy metals (23.07% – Pb(II), 23.53% – Co(II), and 26.19% – Ni(II)). Peat exhibited relatively higher metal removal efficiencies at pH 4.5 compared to pH 2.9 [20]. Effect of potential interferents to lead sorption is important. L. Bulgariu with colleagues [21] studied effect of citrate and acetate on Pb (II) sorption onto peat, and the results showed that presence of citrate improved the efficiency of the Pb (II) sorption onto peat, while the presence of citrate in the aqueous solutions decreased the efficiency of the Pb (II) sorption onto peat. The values of maximum sorption capacities (a_{max}) were 135.13 mg/g for Pb (II) complexed with acetate, a>79.36 mg/g for uncomplexed Pb.

5. Conclusion

1. It was estimated main properties of peat: moisture – 44.67%, pH_{H20} = 5.90, pH_{KCl} = 4.80, total carbon – 51.83%.
2. After carrying out the research on removal of lead from aqueous solutions the capacity of peat to sorb heavy metals was estimated. The results of the research showed that maximum sorption capacity of peat is reached at pH = 4 and is equal to 9.976 mg/g.
3. By the results of investigation it was observed that, while the purification of contaminated with lead water by peat, the maximal removal of lead ions from the solution is reached at pH = 4 and pH = 6, when water treatment level researches up to 99.7%.

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