ADSORPTION OF LEAD AND ARSENIC FROM AQUEOUS SOLUTIONS USING VOLCANIC TUFF AND WALNUT SHELLS

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Abstract: Volcanic tuff and walnut shells were tested as natural adsorbents materials for the removal of Pb(II) and As(V) from waste water. Inductively coupled plasma mass spectrometer (ICP-MS) and an atomic absorption spectrometer were used to monitor the concentration of metal ions in aqueous systems. The sorption capacity of these adsorbents were evaluated at different experimental conditions. The effect of time, initial concentration of the metals and the adsorbent dose on the adsorption was studied. The lead removal efficiency using volcanic tuff at pH value of 4 was more than 99 % in all concentration range investigated, while in the case walnut shells at pH value of 2, the maximum efficiency was 53.2%. Regarding the arsenic uptake at low concentration, the best performance was registered for walnut shells (50.15%). The two low-cost natural sorbents were efficient to remove both pollutants from aqueous systems and may be considered as a viable alternative to conventional adsorbents.

Keywords: natural adsorbents, heavy metals, volcanic tuff, walnut shells

1. INTRODUCTION

Lead and arsenic are part of the heavy metals category and are present in water bodies generally due to human activities [1]. These pollutants are persistent in water and are not biodegradable, causing problems in removing them from the environment. The conventional wastewater treatment system uses several chemical techniques such as precipitation, membrane filtration, ion exchange, activated carbon adsorption and co-precipitation for water treatment [2]. The use of inexpensive natural adsorbents has been studied to replace the current very expensive engineered sorbents. Industrial and agricultural (natural) wastes are readily available in large quantities and are potentially effective as inexpensive natural adsorbents. Use of low cost natural sorbent have been reported such as activated carbon produced from nuts shells [3], chitin/chitosan [4], natural zeolite [5], lignin [6], algae [7], etc.

In this paper we tested the potential of some natural (organic/inorganic) adsorbents as a low-cost adsorbent for the removal of heavy metals from aqueous systems. The adsorption capacity of nut hulls and volcanic tuff is studied in this report under different experimental conditions. The experimental parameters were: contact time (adsorbent-adsorbate), the initial concentration of heavy metals, and the dose of adsorbents.

2. EXPERIMENTAL

2.1. Material and chemicals

Walnut shells (WS) were collected from Botosani area in northern Romania and the volcanic tuff (VT) comes from Mirsid near Cluj. Volcanic tuff is composed of zeolites having a framework structure containing pores occupied by water, alkali and alkaline earth cations [5]. The Mirsid volcanic tuff contains mainly clinoptilolite (about 70%), and as extra minerals eulandite [8]. The walnut (Juglans regia L.) shells are composed of cellulose, hemicellulose and lignin [9]. The functional groups (alcoholic, carboxylic, carbonyl, and phenolic) from lignin can act as active sites for metal ions bonding.

In order to increase the specific surface of the adsorbent, the walnut shells and the volcanic tuff, were firstly crushed manually with a hammer, after that were grinded in two steps using Rotor Beater Mill SR 300 – Retsch and Vibratory Disc Mill RS 200 – Retsch. The resulting fine powder was sieved through a 100 micron sieve.

Synthetic aqueous solutions containing As(V) or Pb(II) were prepared by dilution, starting with a 1 g/L stock monoelement standard solution (CPAChem). Nitrogen acid was used to adjust the pH of the aqueous systems. For the metal concentration measurements an atomic absorption spectrometer (Perkin Elmer PinAAcle 900T) and an inductively coupled plasma mass spectrometer (Bruker Aurora M90) were used.

2.2 Adsorption experiments

2 g of adsorbent were loaded in flask containing 100 ml of synthetic aqueous solutions of metal salt stirred at 150 rpm, at room temperature. Samples were collected at given intervals of time with the aid of a syringe and a filter and analysed. The removal efficiency percent is expressed as:

$$\eta = (C_i - C_e) * 100 / C_i \quad (1)$$

where η (%) is the removal efficiency percent of the adsorbent, C_i and C_e (mg/L) are the initial and concentration at equilibrium of metal ion in solutions.

The adsorption efficiency was defined as:

$$Q = (C_i - C_e) * V / m \quad (2)$$

where Q (mg/g) is the adsorption capacity of the adsorbent, V (L) is the volume of the adsorption medium and m (g) is the mass of the adsorbent.

3. RESULTS AND DISCUSSION

3.1 Lead removal

Lead adsorption on volcanic tuff experiments were conducted at pH=4 and 23 ºC analysing the effect of adsorbent dose or the initial lead concentration in the solution. As can be seen from the results presented in Table 1, the adsorption of lead on volcanic tuff is very fast, achieving an uptake of 90 % since the first few minutes in all cases of concentration and regardless of the adsorbent dose ranging from 2.5 g/L to 20 g/L.

Table 1 The influence of initial lead concentration and adsorbent dose on adsorption kinetics

Time (min.)	conc.(mg/L)				
0	0.1	10	10	10	10
5	0.004	0.079	0.088	0.09	0.133
15	0.004	0.044	0.044	0.062	0.071
30	0.003	0.023	0.03	0.036	0.042
60	0.003	0.014	0.018	0.210	0.024
90	0.002	0.008	0.01	0.013	0.016
120	0.001	0.007	0.009	0.01	0.01
Adsorbent dose (g/L)	20	20	10	5	2.5
Ƞ (%)	99.00	99.93	99.91	99.90	99.90

These results reveal that volcanic tuff have huge number of active sites availabe for Pb^{2+} ions and even a small dose of volcanic tuff can be very efficient, the optimal dose of adsorbent should be calculated based on the concentration of competing ions in wastewater.

The experiments on the uptake of lead on walnut shells were conducted at pH=2, an initial concentration of 10 mg/L and the adsorbant dose was 20 g/L.

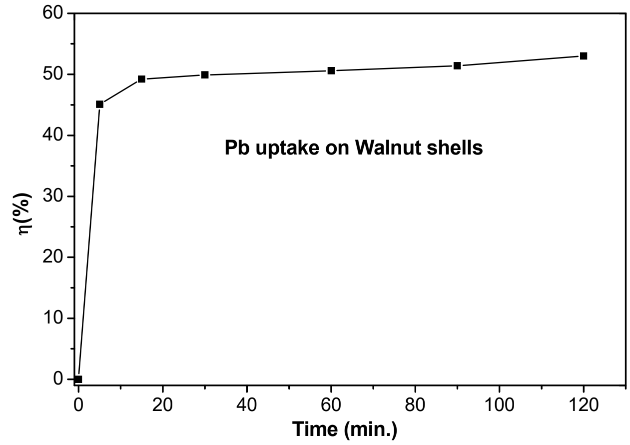

Fig. 1 Lead removal efficiency evolution over time using walnut shells

Fig. 1, illustrates the kinetiks of lead adsorption on walnut shells. As can be seen, the process is aslo fast, the curve stabilizes very fast and reaches a value of 53.20 % removal efficiency.
Comparing the adsorption efficiencies for 10 mg Pb/L, using volcanic tuff and walnut shells, the adsorption is more efficient in the volcanic tuff case, the difference in behavior is due to the different type of mechanism involved in removal process.

3.2 Arsenic removal

For the arsenic adsorption study on volcanic tuff, 100 ml acidic solution of 0.1 mg/L arsenic at pH=4 were prepared and after the addition of 2 g of ground volcanic tuff the concentration in solution of arsenic remains unchanged. In this case the volcanic tuff seems to be ineffective for arsenic removal in these experimental conditions.

The effect of As(V) concentration on the sorption on the walnut shells sorbent was investigated using two ions concentrations: 0.1 mg/L and 1 mg/L, at a pH of 2 for 120 minutes equilibrium time (Figure 2). These concentration values were chosen taking into account the arsenic concentrations range found usually in wastewater.

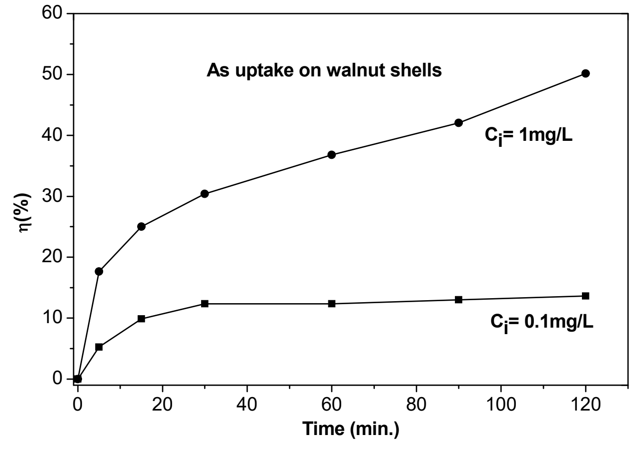

Fig. 2 Arsenic removal efficiency evolution over time using walnut shells

In the case of arsenic, the adsorption have a slower rate and this type of adsorbent is more efficient for wastewater having high initial concentrations of arsenic. The maximum removal efficiency percent is 50.15 % for C_i =1 mg/L and of 13.66 % for Ci =1 mg/L.

The adsorption efficiency Q was calculated to be of 8.16 mgPb/g volcanic tuff, 2,21 mgPb/g walnut shells and 1.17 mgAs/g walnut shells

4. CONCLUSIONS

The sorption of toxic Pb(II) and As(V) on inexpensive and natural sorbents as walnut shells and volcanic tuff have been investigated as alternative to expensive conventional adsorbents for wastewater treatment. The adsorption behavior of these sorbents depends on the nature adsorbent-adsorbate pair. Volcanic tuff consisting mainly of clinoptilolite has demonstrated good performance in removal of lead ions in acidic media. High values of removal efficiency were recorded using both adsorbents, but the most effective proved to be the volcanic tuff. The adsorption of arsenic from liquid phase was more efficient in case of walnut shells in concentrated synthetic solutions.

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