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## REMOVAL OF Cr(VI) AND Cd(II) FROM AQUEOUS SOLUTIONS USING NATURAL SORBENTS: VOLCANIC TUFF AND WALNUT SHELLS

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### Abstract

Some natural adsorbents were evaluated for the advanced removal of pollutants from aqueous systems. The sorption capacity of walnut shells and volcanic zeolite tuff (from Mirsid-Cluj Romania) to remove the chrome and cadmium at different experimental conditions was studied. The concentration of metal ions in aqueous systems was evaluated with an inductively coupled plasma mass spectrometer (ICP-MS) and an atomic absorption spectrometer. The effect of time, initial concentration of the metals and solution pH on the adsorption at room temperature was studied. pH of the solutions was found to influence the adsorption. Higher Cr(VI) adsorption was observed at lower pH and at low concentration of metal ions. The maximum efficiency of volcanic tuff in acidic media was 97.12% for chrome and 57.04% for cadmium, respectively, for 0.1 mg/L initial concentration. Moreover, in the same experimental conditions, the maximum efficiency of walnut shells was 61.24% and 44.51% for chrome and cadmium. The two low-cost natural sorbents were efficient for the remove of pollutants from aqueous systems.

**Keywords:** *adsorption, heavy metals, volcanic tuff, walnut shells*

### Introduction

Conventional sorbents used in water treatment are activated carbons, polymers, oxides, zeolites, etc. (Worch 2012). Engineered sorbents can be very expensive and in recent decades, the interest in using alternative low-cost sorbents can be observed. Some of the reported low-cost sorbents with high absorbency for metals include chitin/chitosan (Lazaridis et al. 2007), natural zeolite (Wanga & Pengb 2010), lignin (Srivastava et al. 1997), seaweed/algae/alginate (Anastopoulos & Kyzas 2015), and others with less efficiency like dead biomass (Niu et al. 1993), clay (Azejjel 2009), fly ash (Banerjee 1997), yeast (Stanila 2016) etc. These natural sorbents are more suitable for wastewater treatment and less for use in drinking water treatment due to quality requirements for adsorbents in this case. Although many studies have been conducted on low cost adsorbents, it is necessary to continue this work in order to better understand adsorption processes involved and to demonstrate the technology. The mean research goal is to identify and develop inexpensive and effective adsorbents from plentiful sources of raw material. The aim of this paper is to study the potential of some natural (organic / inorganic) adsorbents as low-cost adsorbents for the removal of heavy metals from aqueous systems. The adsorption capacity of walnut shells and volcanic tuff is studied under different experimental conditions. Metals of interest were Cr and Cd. They were chosen based on their potential pollution

impact on the environment. The effect of contact time between sorbent and metal ions, pH of the sorption medium and initial concentration of ions on the adsorption parameters at room temperature were investigated.

In the past years, volcanic tuff of different origins has been explored as adsorbent for removal of various heavy metals and organic substances (Inglezakis 2003; Wanga & Peng 2010; Taffarel & Rubio 2010). Also walnut shells were studied and presented in different articles (Pehlivan & Altun 2008; Kazemipour 2008; Petuhov 2015) as alternative adsorbent for pollutants removal.

### **Experimental**

Walnut shells (WS) from an area close to Botosani in northern Romania were used as raw material. The volcanic tuff (VT) comes from Mirsid near Cluj. Synthetic aqueous solutions containing Cr(VI) or Cd(II) were prepared by diluting the 1g/L stock monoelement solution (CPAChem) metal salt by ultrapure water. Nitrogen acid of analytical grade was used to set the right pH of the aqueous systems. The concentration of metals was measured using an atomic absorption spectrophotometer (Perkin Elmer PinAAcle 900T) and an inductively coupled plasma mass spectrometer (Bruker Aurora M90).

The walnut shells, were first washed extensively with deionized water, then crushed rough with a hammer. Pieces of nut shells 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 and dehydrated at 105 °C for 24 hours. The volcanic tuff was also ground using the same protocol as in the case of walnut shells in order to obtain a fine powder of micrometers and dehydrated at 105°C for 2 hours.

Batch adsorption tests were carried out at room temperature by adding 2 g of adsorbent to 100 ml flasks containing synthetic aqueous solutions of desired metal salt, at room temperature. The mixture was stirred with a magnetic stirrer at 150 rpm. With the aid of a syringe and a filter, samples were collected at given intervals of time and analyzed.

The concentrations of heavy metals in aqueous solutions before and after adsorption were measured and the adsorption efficiency was calculated as follows:

$$Q = (C_i - C_e) * V / m \quad (1)$$

where Q (mg/g) is the adsorption capacity of the adsorbent, C<sub>i</sub> and C<sub>e</sub> (mg/L) are the initial and final concentrations of metal ion in solutions, respectively. V (L) is the volume of the adsorption medium and m (g) is the mass of the adsorbent. The adsorption efficiency can also be expressed in percent:

$$\eta = (C_i - C_e) * 100 / C_i \quad (2)$$

where η (%) is the adsorption efficiency of the adsorbent.

### **Results and Discussion**

Volcanic tuff is composed of zeolites who can be considered as derivatives of silicates where Si is partially substituted by Al. The framework structure containing pores occupied by water, alkali and alkaline earth cations (Wanga & Peng 2010). The

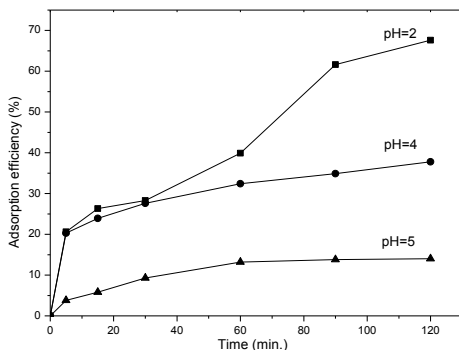
zeolite framework carries negative charges, which are compensated by metal cations. The Mirsid volcanic tuff contains mainly clinoptilolite (about 70%), and as extra minerals eulandite. The chemical and mineralogical composition of the tuff is presented in reference (Rusu & Rusu 2009).

The walnut shells are composed of cellulose, hemicellulose and lignin. Cellulose is a common material in plant cell walls and lignin is relatively hydrophobic and aromatic in nature. WS sorbent carry the some polar functional groups such as alcoholic, carbonylic, carboxylic and phenolic groups which are believed to be the active sites for metal ions attachment.

The behaviours of volcanic tuff and walnut shells in aqueous acidic media were analysed in aqueous medium in order to predict the ionic charge released by the adsorbent. To carry out this analysis some solutions were prepared, one with 2 g of volcanic tuff and the other with 2 g of walnut shells in 100 ml deionised water in which nitric acid was added in order to bring pH value in 5 to 2 range. After 120 min of stirring the final solutions were analysed. The results shows that the adsorbent are stable at pH 4-5. When pH decreases to 2, some metallic ions from volcanic tuff (Al, Fe, Mn, Cu) migrate in the aqueous system and the aluminosilicate crystalline network silicates is affected.

#### *Adsorption activity of volcanic tuff*

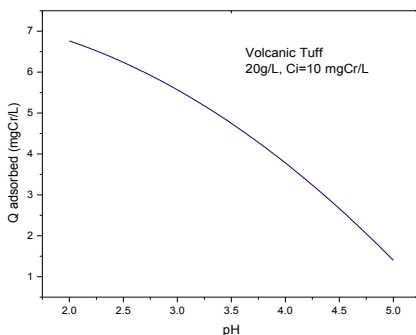
The adsorption capacity of volcanic tuff was tested on synthetic solutions containing chromium and cadmium under different experimental conditions. In Fig. 1 is presented the evolution of the amount of chromium adsorbed in time, starting from a initial concentration of 10 mg/L and 2 g of adsorbent. The influence of pH on the adsorption were studied. The results showed that the percentage of Cr(VI) ion adsorption by VT increased with increasing adsorption time. In terms of kinetics, adsorption of Cr(VI) by volcanic tuff occurs in two stages: one fast during the first 5 minutes, then the rate of adsorption is slowing down until the equilibrium is reached.



**Figure 1.** Effect of contact time on the adsorption of Cr(VI) by VT. Initial concentration of Cr (VI): 10 mg/L

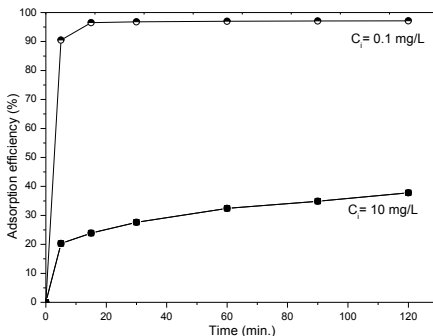
The aqueous systems appear to stabilize after 60 min for the solutions at pH 4 and 5. At pH 2 the adsorption process seems to continue after 120 minutes.

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**Figure 2.** Effect of pH on the adsorption of Cr(VI) using the VT. Initial concentration of Cr (VI): 10 mg/L

The effect of Cr(VI) concentration on the sorption by the VT sorbent was investigated by using two ions concentrations : 0.1 mg/L and 10 mg/L, at a pH of 4 for 120 minutes equilibrium time (Figure 3).

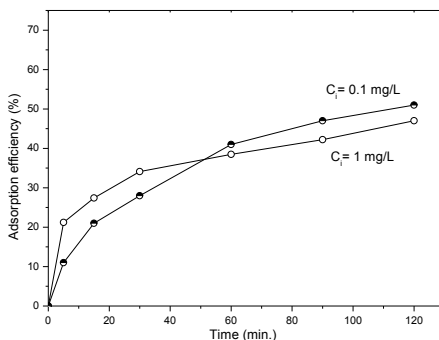


**Figure 3.** Effect of initial concentration on the adsorption of Cr(VI) using the VT. pH=4

As it can be seen from the shape of the kinetic curves, the first stage of the adsorption corresponding to 10 mg Cr/L initial concentration is much faster and the maximum adsorption capacity is reached after 10 minutes. In addition, it is observed that the lower the initial concentration, the greater the efficacy. This may be due to the fact

that the most easily accessible adsorption sites on zeolite volcanic tuff are quickly occupied by the smaller amount of Cr ions. Also, the fractional sorption became independent of initial concentration for the low concentration of Cr(VI) in adsorption media. In other words, the ratio between the number of Cr(VI) ions and the number of adsorption sites is much larger in case of higher concentrations. The amount of Cr(VI) ions adsorbed per unit mass of the VT increased with the initial Cr(VI) concentration as expected. The adsorption capacity was 3.40 mg/g for 10 mg Cr/L initial concentration.

The evolution in time of **cadmium** amount adsorbed by volcanic tuff is presented in Fig. 4, starting from a initial concentrations of 0.10 mg/L and 1 mg/L Cd(II) using and 2 g of volcanic tuff at pH=2.

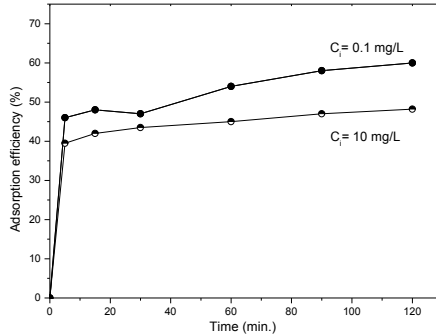


**Figure 4.** Effect of initial concentration on the adsorption of Cd(II) using the VT at pH=2

The cadmium adsorption efficiency is lower than in chromium case. As it can be seen, the rate of cadmium adsorption is slower. In what concerning the initial concentration factor, the values for cadmium adsorption efficacy is relatively close, around 50%. The difference consists in the initial rate of adsorption, in the case of 1 mg/L the first stage is faster. A maximum adsorption capacity of 0.23 mg/g was measured.

#### *Adsorption activity of walnut shells*

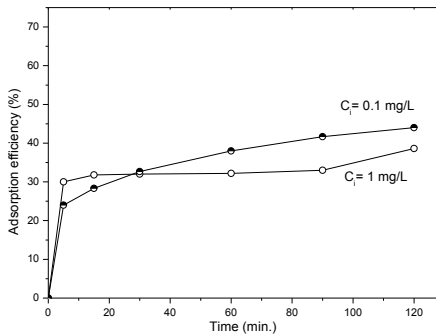
The adsorption capacity of walnut shells was tested on synthetic solutions of chromium and cadmium with different concentrations at pH = 2. The effect of Cr(VI) concentration on the adsorption by the WS was investigated using starting concentrations of 0.1 mg/L and 10 mg/L. The results of adsorption efficiency are plotted in Fig. 5. Two stages of adsorption can be distinguished, one fast the first 15 minutes, and a slower stage until 120 minutes. As it can be seen from the slope of the curves, the equilibrium is still not reached at the end of the batch experiment. The adsorption of Cr(VI) on walnut shells occurred on the lignin molecules containing hydroxyl and phenol functional surface groups.



**Figure 5.** Effect of initial concentration on the adsorption of Cr(VI) using the WS at pH = 2

The adsorption of chromium on walnut shells is also fast. Comparing the curves for 10 mg Cr(VI)/L, using VT (Figure 1) and WS (Figure 5) at pH=2, the adsorption is more efficient in the volcanic tuff case, the difference in behavior is due to the different type of adsorption mechanism. In Fig. 5 the adsorption efficiency value corresponding to 30 minutes is probably due to a sampling error. A maximum adsorption capacity of 2.34 mg/g was measured.

The evolution of **cadmium** adsorption on walnut shells at pH=2, starting with two solutions with 0.1 mg/L and 1 mg/L, is plotted in Fig. 6. The efficiency values in both cases are comparable. Adsorption is initially faster for the 1 mg/L solution, but in the long term, adsorption at lower concentrations is slightly more efficient.



**Figure 6.** Effect of initial concentration on the adsorption of Cd(II) using the WS at pH=2

As can be seen from Fig. 5 and Fig. 6, chromium adsorption on walnut shell is more efficient than cadmium in 0.1-1 mg/L range of concentration, at pH=2, using 2 g of adsorbent, 100 mL of adsorption medium, temperature: 23°C and agitation speed: 150 rpm. The maximum adsorption capacity was 0.19 mg/g.

## Conclusions

The toxic Cr(VI) and Cd(II) ion sorption on the inexpensive and natural sorbents as walnut shells and volcanic tuff have been investigated as alternative to conventional adsorbent for wastewater treatment. Volcanic tuff consisting mainly of clinoptilolite are in general a good natural adsorbents. The adsorption behavior of these sorbents depends on the nature of the metals studied. The adsorption of Cr(VI) onto VT is strongly pH dependent, the uptake of the chromium decreases with the increase in pH from 2 to 5. Volcanic tuff demonstrated to have very good performance at low concentration of Cr(VI) in acidic media. The cadmium adsorption on this adsorbent is lower than in chromium ions case. This is certainly due to the nature of the specific charge of cadmium and chrome ions.

Having a lower efficiency than volcanic tuff, the walnut shells showed to be an effective natural adsorbent for the removal of cadmium and especially chromium ions from aqueous systems. Walnut shells in 10 mg/L chromium solution (pH=2) reached 48.2% the efficiency, compared with 67% in case of volcanic tuff, but the adsorption is faster in case of walnut shells use. The cadmium adsorption onto WS is slightly smaller (10%) than in adsorption onto volcanic tuff at pH = 2 using 0.1 mg/L or 1 mg/L starting concentrations. Adsorption of chromium and cadmium ions was generally more effective at low concentrations.

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