

Efficiency of a zeolitized pumice waste as a low-cost heavy metals adsorbent

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Abstract

The unextracted residue obtained after a countercurrent two-step extractive process of silica from pumice lapillus, at 100 °C and room pressure, has been found mainly crystallized to the pseudo-cubic form typical of zeolite P. This residue could be active as a low-cost agent for the removal of heavy metals from wastewater.

In this paper the removal capacity of six metallic cations (i.e. Cu²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Pb²⁺ and Cr³⁺) was studied in a stirred batch reactor. Results obtained showed that the removal of metal ions (100–500 mg g⁻¹) from wastewater is achieved in a short time and the concentration lowered under the legal limits.

The adsorption mechanism mainly involves an ionic exchange between sodium ions from the solid phase and heavy metals in solution. However, if wastewater was accompanied by free acidity, it first should be neutralized to pH 4–5 to prevent zeolite destruction.

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1. Introduction

The presence of heavy metals in wastewater means that at the end of many industrial processes it is frequently necessary to use adsorbents to bring their concentration down to below the prescribed legal limit. The most commonly adsorbent used in the treatment of wastewater is still active carbon; though expensive and requiring the help of complexing agents, it undeniably remains an efficient (0.5–2.5 meq g⁻¹) [1] means of removing inorganic material from water. The high cost would not be a burden if it was regenerated and reused many times. However, regeneration is not suitable for use with contaminated adsorbents as returning heavy metals to water, should not, in our view, be preferred to the immediate inertization and disposal.

The above consideration led scientists to focus attention on identifying efficient low-cost throw-away adsorbents. Thanks to occasionally high local availability, chitosan has been classified as a low-cost adsorbent [1] but, in fact, it is not; though

having excellent adsorption capacities for various metals, including some of the most difficult, its market price ($\cong 12\text{--}13 \text{ € Kg}^{-1}$) [2] is not significantly lower than that of active carbon ($\cong 16\text{--}18 \text{ € Kg}^{-1}$) [3]. On the other hand, natural zeolites are an interesting option at between 100 and 200 times cheaper [4] although their adsorption capacity is 10–20 times lower [1] and, sometimes, the adsorption kinetics, as well [5].

This paper describes a study of the adsorbent capacity of a synthetic zeolite obtained as a sub-product of a treatment of lapillus (a waste in mining pumice) aimed to the extraction of the amorphous silica content with an aqueous solution of caustic soda and production of sodium silicates [6,7]. A cost evaluation suggests that the zeolitized residue could be marketed almost the same price as common natural zeolites (Internal report).¹

We are therefore looking at a possible low-cost adsorbent if its efficacy at adsorbing heavy metals from water is demonstrated.

¹ The main product of the pumice waste process is sodium silicate, the sale of which may by itself cover the costs of the processing. The zeolitized residue is a co-product obtained without any additional processing. Thus, its selling price can be limited as also the saving of disposal costs (in Italy $\cong 0.15 \text{ € Kg}^{-1}$) supports the overall return.

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Tests were carried out using both synthetic wastewater and industrial aqueous effluents contaminated with chrome, lead, copper, zinc, cadmium and/or nickel with the aim of establishing the adsorbent capacity of the synthetic zeolite towards each metal species and identifying the conditions necessary to reduce concentrations to below the environmentally safe limits. Finally, we examined the problem of how to dispose of the metal-loaded residue according to current Italian regulations or stricter future legislation.

2. Experimental part

A sample of unextracted residue deriving from a countercurrent double extraction of silica from pumice lapillus [6,7] was characterized by elementary EDS microprobe, SEM morphological and X-ray diffractometric analysis.

Capacity trials were carried out by contacting 1 L of synthetic aqueous solutions containing from 100 to 600 mg L⁻¹ of one of the following ions: Cr³⁺, Pb²⁺, Cu²⁺, Zn²⁺, Ni²⁺ and Cd²⁺ with 1 g of the adsorbent, dried at 110 °C. The above procedure is designed to determine the maximum adsorption capacity of the adsorbent towards each heavy metal where an excess of unadsorbed metal ion is not a problem.

In order to determine if the adsorbent was able to reduce the heavy metals concentrations to below legal limits [8], 1 g of adsorbent per litre of water was contacted with a lower amount (10–100 mg L⁻¹) of heavy metals, even as industrial wastewater concentrations usually are within this interval.

The trials were performed under stirring at room temperature and pressure for time periods of up to 1 h and, sometimes, 24 h. Samples were taken at 15-min intervals, the solids separated from solutions by filtration and the residual heavy metal concentrations redetermined.

The synthetic aqueous solutions were prepared by dissolving heavy metal nitrates in distilled water. The concentrations of heavy metals in these solutions and in wastewater before and after the adsorption treatment were determined by atomic absorption and the data used to establish the metal fraction adsorbed. pH values and Na⁺, Ca²⁺, Mg²⁺ and K⁺ concentrations were measured as well both before and after the adsorption in order to identify the mechanism involved.

The contaminated solid residues were then submitted to release tests according to the UNI 10802 regulation in order to determine which type of waste disposal site they should be sent to and whether they should undergo inertization tests.

3. Results and discussion

The images in Figs. 1 and 2 show that after two steps of the silica countercurrent extraction from pumice lapillus [6,7], the unextracted residue has become a powder crystallized in the pseudo-cubic form typical of zeolite P (it should be remembered that the original material is in an overall amorphous state) [6,7], with the composition reported in Table 1.

The exchange capacity of the sodium ion (outgoing) with calcium (incoming cation) in various samples has been measured to range between 2.8 and 3.3 meq g⁻¹ of the dry residue, which

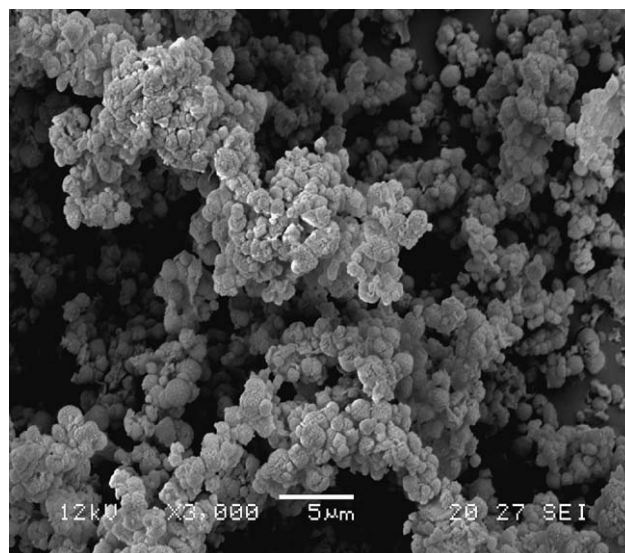


Fig. 1. SEM image of the unextracted pumice residue after step II.

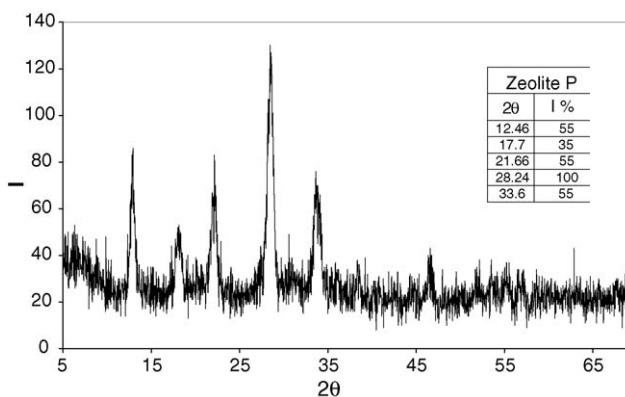


Fig. 2. XRD pattern of the unextracted pumice residue after step II and X-ray powder data of pure zeolite P for comparison.

confirms a good, though incomplete, crystallization to zeolite. When the powder was pelletized to grains having 2 ± 0.5 mm, the observed capacity was 10–15% less.

The values obtained after 1 h contact of the synthetic aqueous solutions containing each of the heavy metals being tested and 1 g of the unextracted residue as a fine powder are shown in Table 2. Heavy metals concentrations were deliberately kept above adsorbent capacity in order to determine maximum capacity.

Table 1

Percentages of the main constituents of pumice before and after extraction treatment

Oxide	Pumice (wt.%)	Zeolitized residue (wt.%)
SiO ₂	70.90	50.68
Al ₂ O ₃	12.76	25.65
FeO	0.64	4.36
CaO	1.36	2.11
MgO	0.60	0.90
Na ₂ O	3.23	15.35
K ₂ O	3.83	1.85

Table 2

Results of tests of adsorption of metal ions from aqueous solutions using a 1 g sample of zeolitized pumice lapillus (contact time = 1 h)^a

Metal ion	In initial solution		In final solution		Adsorbed		Na ⁺ (mmol g ⁻¹)	Na ⁺ + K ⁺ + Mg ²⁺ + Ca ²⁺ (meq g ⁻¹)
	(mg L ⁻¹)	(pH)	(mg L ⁻¹)	(pH)	(mg g ⁻¹)	(mmol g ⁻¹)		
Cr ³⁺	141	3.4	134	4.0	7	0.13	2.52	2.91
Pb ²⁺	543	4.5	31	4.8	512	2.47	3.43	4.92
Cu ²⁺	134	5.4	30	5.1	104	1.64	3.10	3.28
Zn ²⁺	140	5.3	42	5.7	98	1.50	3.08	3.08
Ni ²⁺	131	5.6	104	5.6	27	0.45	0.57	0.89
Cd ²⁺	312	5.7	109	5.5	203	1.80	3.10	3.55

^a For contact times of up to 24 h the amounts of metal adsorbed increase by 5–20%, except for chrome (no increase) and nickel (50% increase).

With the exception of nickel (II) and chrome (III), the data show that the residue is able, in an hour, to adsorb between 1.5 and 2.5 mmol (equivalent to 100–500 mg) of metal per gram of dry adsorbent, making it, in terms of speed and efficiency, a better alternative to competing low-cost materials such as clays and natural zeolites [1,9,10]. The different affinities of the metal ions towards the residue (Pb > Cd > Zn ≅ Cu ≫ Ni > Cr) seems consistent with the factors that influence ionic exchange in zeolites and with the known tendency of metals with high hydration free energy to remain desorbed in the solution phase [10,11].

Indeed, the zeolitic nature of the material, its high adsorption capacity and speed of action, the minimal changes in pH and the release into solution of a slightly less than equivalent quantity of Na⁺ ions are indicative of an ion exchange mechanism [12,13]; whereas, in cases where sodium ions are significantly less than equivalent to the amount of heavy metal adsorbed (Table 2) and the gap is compensated for by the presence of K⁺, Mg²⁺ and Ca²⁺ ions, this is probably a sign that the non-zeolitized part of the residue also contributed to the adsorption by a different mechanism; with nickel, for example, adsorption appears to take much longer. On the other hand, the adsorption of chrome seems to have been hindered by the low pH caused by metal hydrolysis [14], which compromised the stability of the zeolite (a not reported XRD pattern shows flat at the end of contact time) [12,13,15]; this hypothesis was confirmed by the observation that if the wastewater was accompanied by free acidity (pH < 4), the adsorbent proved inefficient.

Once adsorbent capacity was established, we set out to determine how complete was the extent of adsorption. For this purpose, we simulated industrial wastewater samples containing between 10 and 100 mg L⁻¹ of heavy metals and again contacted them with 1 g of adsorbent to bring heavy metal concentrations down to below prescribed minimum tolerable limits.

As can be seen from Fig. 3 in all cases metal concentrations were brought to below detectable and legal limits [8]. The same result could be obtained with the previous concentrations but using two or more adsorption stages. The abatement process was also very fast and was complete within the first 15 min and possibly even within the first few minutes. Surprisingly, even the chrome was removed completely, probably because the wastewater used, containing only 15 mg L⁻¹ of chrome, had a pH 4.5, which is not sufficient to destroy zeolite P in the short space of time before adsorption. If wastewater's pH is less than 4, it is necessary to neutralize it at least to pH 4 or, ideally 5 before

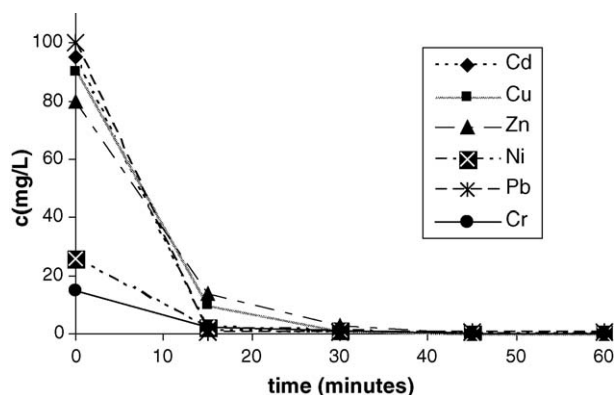


Fig. 3. Performance vs. time of unextracted lapillus in removal of heavy metals from simulated industrial wastewater.

adding the adsorbent. If it is accompanied by sodium or potassium ions, they do not appreciably interfere with adsorption.

The release tests prescribed by Italian legislation (UNI 10802) were performed on the heavy metal-loaded materials (dangerous waste) according to Gazzetta Ufficiale 2003 [16]. The results indicate that heavy metals remain stably adsorbed on the substrate used. Where current Italian legislation was thought too permissive to ensure lasting and efficient protection of the environment, the heavy metal-loaded material could be rendered inert with lime [9,17,18].

4. Conclusions

The study described in this paper revealed that an unextracted residue zeolitized to zeolite P (obtained after extracting the amorphous silica from pumice lapillus using sodium alkali) possess a pronounced ability to attract and retain the heavy metal ions present in wastewater, making it one of the most efficient and low-cost single-use adsorbents available.

Within an hour 1 g of residue is able to adsorb between 100 and 500 mg of heavy metal according to the following sequence of affinity: Pb > Cd > Zn ≅ Cu ≫ Ni > Cr and with complete adsorption of pollutants if heavy metal concentrations are lower than adsorption capacity.

Its efficiency is better than (or equal to) that of the expensive adsorbents, such as activated carbon and chitosan, and the cost lower than (or equal to) that of low-cost adsorbents, such as natural zeolites and clays.

The adsorption mechanism mainly involves the exchange of sodium ions from the solid phase with the metal ions drawn from solution, but for some ions a slower mechanism, determined by the non-zeolitized solid, is also involved.

If wastewater is accompanied by free acidity, it must first be neutralized to pH 4–5 to avoid destruction of the zeolite. Alkali and/or alkali-earth metal cations have much lower affinity.

The release tests performed enabled us to establish that the heavy metal-loaded adsorbent can be placed in disposal sites for non-hazardous waste since none of the heavy metals studied were released in amounts exceeding the legal limits currently in force in Italy [16]. In any case, lime inertization is possible when a higher level of safety is required.

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