

Zn²⁺ and Cd²⁺ removal from wastewater using clinoptilolite as adsorbent

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Abstract

The demographic growth and rapid industrialization of the last decades have contributed to increasing the presence of heavy metals in wastewater. Treatment processes involving adsorbent materials are appropriate to increase efficiency in removing heavy metals. Activated carbon adsorption is considered to be a particularly competitive and effective process for the removal of heavy metals at trace quantities; however, the use of activated carbon is not suitable in developing countries due to the high costs associated with production and regeneration of spent carbon. Then, in order to minimize processing cost, recent investigations have been focused on the use of low cost adsorbents as zeolites. In particular, clinoptilolite is known to have high selectivity for certain heavy metal.

In this paper, the capability of clinoptilolite as a low cost adsorbent for the removal of zinc and cadmium ions from wastewater was analysed in a batch system. Tests in batch for analyzing adsorbing capacity of clinoptilolite were carried out varying zinc and cadmium concentrations between 10 and 200 mg/L with different amounts of sorbent in the solution (10-60 g/L). For both zinc and cadmium ions, complete adsorption was reached when the concentration was equal to 10 ppm and adsorption capacity decreased increasing metals amount. In particular, clinoptilolite permitted high Cd²⁺ abatement. Binary system was then analyzed and, contrary to previous tests, the adsorbent in the simultaneous presence of the two metals demonstrated a greater affinity towards zinc, showing a higher percentage of absorption.

Keywords

wastewater, natural zeolite, heavy metals, adsorption.

Introduction

A rapid expansion in industries took place over the last century. Several industrial processes generate metal containing waste. Heavy metal contamination can be found in the aqueous waste of many industries, such as metal plating, mining operations, tanneries, chloralkali, radiator manufacturing, smelting, alloy industries and storage battery industries, etc. [1]. The effluents generated by these industries are therefore rich in heavy metals which should be treated before being discharged into common waste water.

The conventional method for the removal of heavy metal from industrial wastewater generally involves a chemical precipitation process [2-6]. Studies on the treatment of effluents containing heavy metals have shown that adsorption is a highly effective technique for the removal of heavy metals from waste streams and activated carbon has been extensively used as an adsorbent [7]. However, the use of activated carbon is not suitable in developing countries due to the high costs associated with production and regeneration of spent carbon [8]. Then, in these last years, the possibility to remove heavy metals by means of adsorption using different and low cost adsorbents has been evaluated.

In this context natural zeolites gain a significant interest among scientists, mainly due to their valuable sorption characteristics provided by combination of ion-exchange and molecular-sieve properties which can be relatively easily modified. Zeolite use as ion exchangers for environmental protection and other applications is stimulated by the good results obtained, the nontoxic nature of these materials, their availability in the many parts of the world, and the low cost [9]. Clinoptilolite is probably the most used natural zeolite for the adsorption of either organic molecules or metal ions in the wastewater treatment [9-12]. Clinoptilolite is the most abundant natural zeolite and has the chemical formula $(\text{NaKCa})_4(\text{Al}_6\text{Si}_{30}\text{O}_{72}) \cdot 24\text{H}_2\text{O}$ along with other cations (e.g. Fe, Mg). The aluminum ion is small enough to occupy the position in the center of the tetrahedron formed by the four oxygen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (sodium, potassium, or calcium) and the fact that these ions are relatively innocuous makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters [13].

The main risk for human health from heavy metals is due to exposure to zinc, cadmium, chromium, mercury and arsenic. These metals and their effects on human health have been widely studied even by international organizations [4-6].

In this work, the attention has been focused on zinc and cadmium present as pollutants in wastewater.

Zinc is a Persistent Bioaccumulative Toxic (PBT) chemical. PBT chemicals are chemicals that do not breakdown easily or decrease in potency after they are released into the environment. They tend to accumulate in the environment, be absorbed or ingested by plants and animals, accumulate in animal and plant tissues and pass through the food chain and cause long-term human health or ecological problems [14]. Zinc is an essential element for human life, but too much zinc is harmful and can also damage human health. In natural surface water, the concentration of zinc is usually below 10 $\mu\text{g}/\text{L}$, and below 10 – 40 $\mu\text{g}/\text{L}$ in groundwaters. In tap water, the zinc concentration can be much higher as a result of the leaching of zinc from pipes and fittings. Considering the industrial wastewater, i.e. in the United States, the main sources of zinc are found at many industrial facilities as galvanized metal surfaces, motor oil and hydraulic fluids and tyre dust [15]. Moreover, due to the toxicity of metals, the Ministry of Environment and Forests, of the Indian Government has set the Minimal National Standards of Zn at 5.0 mg/L for the safe discharge of effluents containing these metal ions into surface water [16].

Cadmium is a product of the refining of lead, zinc and copper metals; it is normally used in electronic and chemical industry, in the production of pigments and coated surfaces. Cadmium in the air is mainly the result of industrial activities (refining of non-ferrous metals, combustion of carbon and petroleum products, burning of household waste, metallurgy). The Cd presence in water is due to the soil erosion and human activities [6].

Basing on X Annex of Directive 2000/60/EC [1], cadmium and its compounds are considered very hazardous substances. According to the WHO Guidelines for Drinking Water Quality [5], guideline value in drinking water for cadmium is 0,003 mg/L. In Italy the maximum cadmium limit values for emissions into the surface water and the drain in sewage are 0.2 mg/L [1,6].

This study aims to evaluate the capability of clinoptilolite, as a low cost adsorbent, for the removal of zinc and cadmium ions from wastewater.

Materials and methods

The clinoptilolite, used as adsorbent, was provided from the Zeolado Company (Greece). It presented the typical flake-like shape and the average dimensions of these flakes were 35 nm of thickness and 3 mm of length.

The clinoptilolite X-ray diffraction patterns were collected on an X'Pert Philips PW3040 diffractometer using Cu K α radiation (2θ range = 5°-50°; step = 0.05° 2 θ ; time per step = 0.2 s). The diffraction peaks were indexed according to the Powder Data File database (PDF-2 1999, International Centre of Diffraction Data, PA, USA).

The specific surface area (SBET) and total pore volume (V_p) were measured by the N₂ physisorption at -196 °C (Micromeritics Tristar II 3020) on samples previously outgassed at 200 °C for 4 h.

The adsorbent was moreover characterized by means of Field Emission Scanning Electron Microscopy (FESEM Zeiss MERLIN, Gemini-II column) to evaluate morphology of fresh and used material.

Then X-Ray Fluorescence analysis was carried out to determine elemental composition of clinoptilolite before and after metals adsorption. A RIGAKU ZSX100E apparatus, equipped with a Rh X-ray tube and TAP, PET, LiF1, Ge, RX61 and RX45 analysis crystals, was used. Samples were prepared by pressing powder into thin discs with a diameter of 20 mm and a thickness of 2 mm. The samples were analyzed in at least 20 different points.

Synthetic wastewater solutions were prepared by dissolving analytical grade Cd(NO₃)₂·4H₂O and ZnSO₄·7H₂O in distilled water to obtain different metal concentrations in the solution (between 10 and 200 mg/L), respectively for Zn and Cd. The adsorbent (concentration was varied between 10 and 60 g/L), dispersed in the metal solution (pH₀ = 4.5), was agitated on a heater-stirrer and at different time intervals it was allowed to settle for about 1 min and the supernatant solution was analyzed for its Zn²⁺ and Cd²⁺ concentration, using an Inductively Coupled Plasma Mass Spectrometer (iCAP Q ICP-MS). Removal of the two metals was studied separately and in the binary system. Adsorption capacity was reported in percentage, calculated as:

$$\frac{C_0 - C}{C_0} \times 100$$

where:

C₀ = metal initial concentration in the solution

C = metal concentration for each collection at different time

Experimental

Physico-chemical proprieties of clinoptilolite were analysed before adsorption processes. In Figure 1, XRD pattern was reported. The high crystallinity of the clinoptilolite sample was observed: at $2\theta = 22.3^\circ$ there was the most intense peak of the clinoptilolite and other intense peaks, characteristic of the clinoptilolite material (reference code of the clinoptilolite: 00-039-1383), were identified at $2\theta = 9.8^\circ$, 11° and 29.9° .

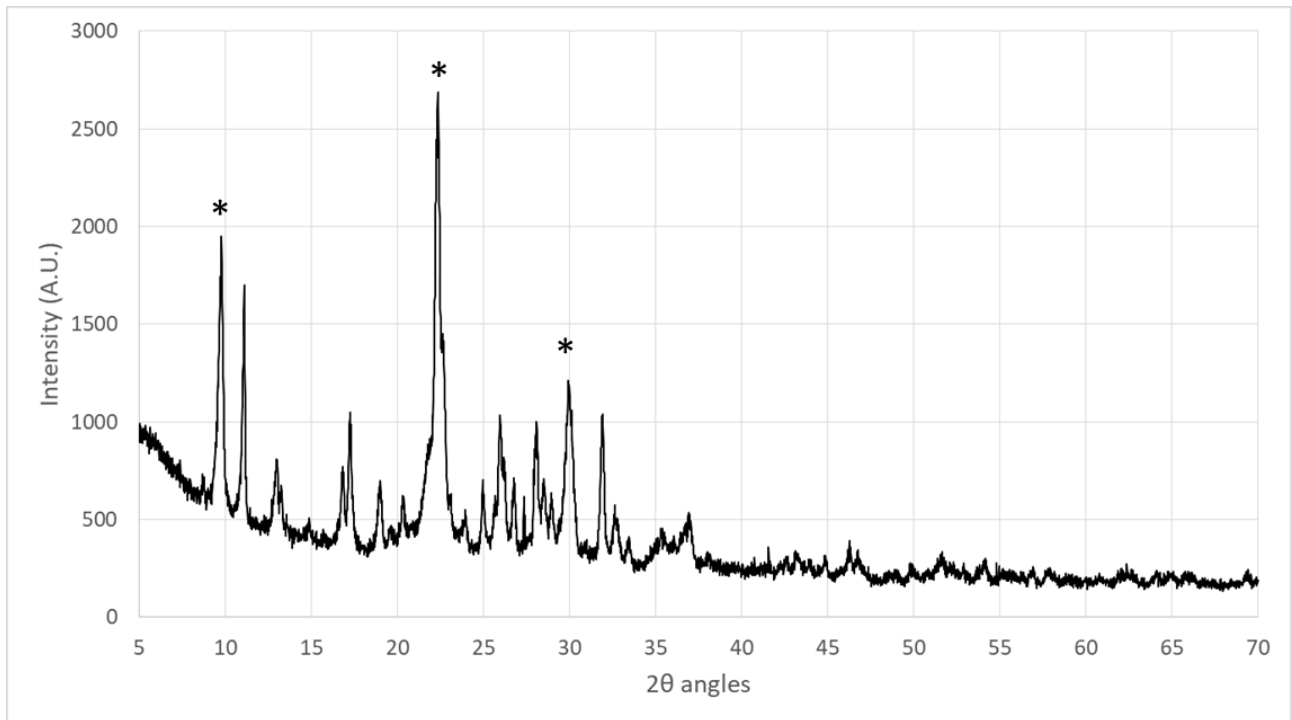


Fig. 1 XRD diffractogram of Clinoptilolite ($2\theta = 5-70^\circ$)

The BET surface area was measured equal to $41.8 \text{ m}^2\text{g}^{-1}$ and the total pore volume was calculated equal to $0.076 \text{ cm}^3\text{g}^{-1}$, by BJH method during the desorption phase. Moreover, in Fig. 2 are shown the N_2 adsorption/desorption isotherms for the zeolite previously outgassed at $200 \text{ }^\circ\text{C}$ for 4 h. The sample exhibited type-IV isotherms and the capillarity condensation was followed by the hysteresis, in agreement with the literature [17].

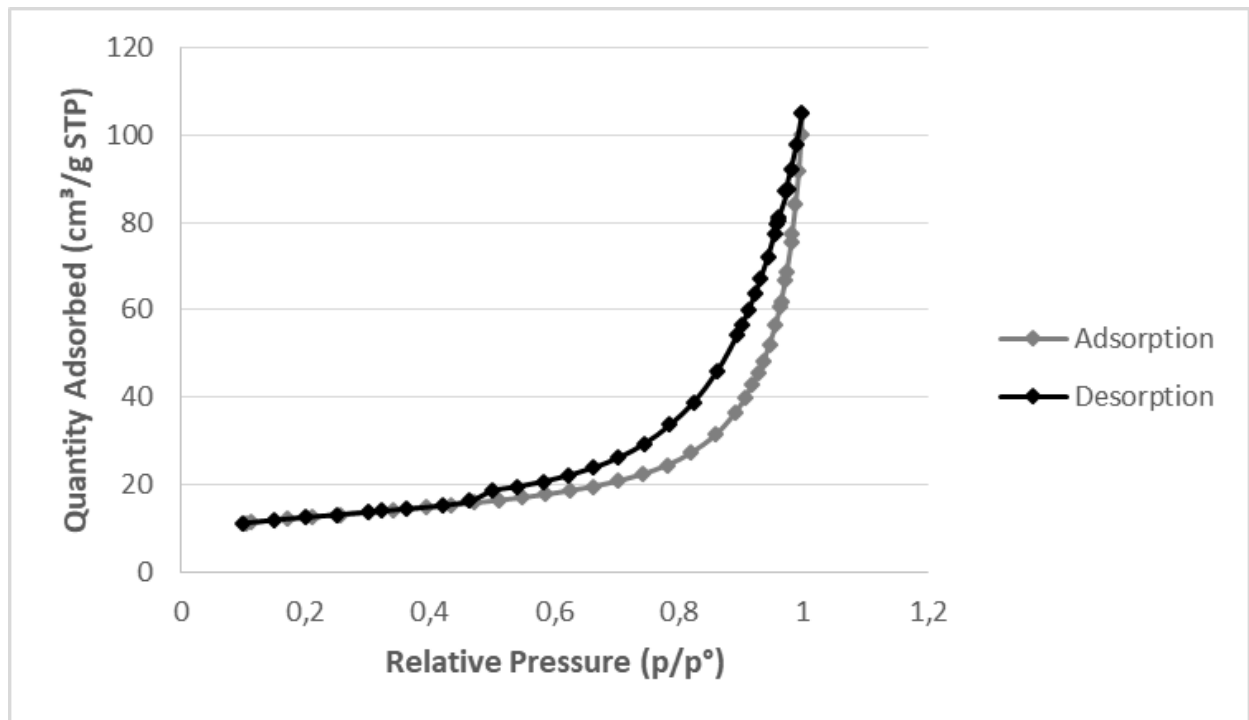


Fig 2 N_2 adsorption/desorption isotherms at $-196 \text{ }^\circ\text{C}$.

In order to study the morphology of the clinoptilolite fresh and after adsorption process, Field Emission Scanning Electron Microscopy (FESEM) was used. In Figure 3 the FESEM images of the samples at comparable magnification (200 nm) are illustrated. The clinoptilolite exhibited the typical “flake” structure: the particles appeared flat, and they were assembled on the top of each other [18]. Moreover, these particles were characterized by grains with no well-defined crystal faces. After the adsorption of the metals, the clinoptilolite showed flatter and smoother surfaces, more tidy in the case of zinc adsorption. Furthermore, grains on surfaces were still present, much smaller in the case of cadmium adsorption. When adsorption process was performed in binary system grains and flat surfaces were combined.

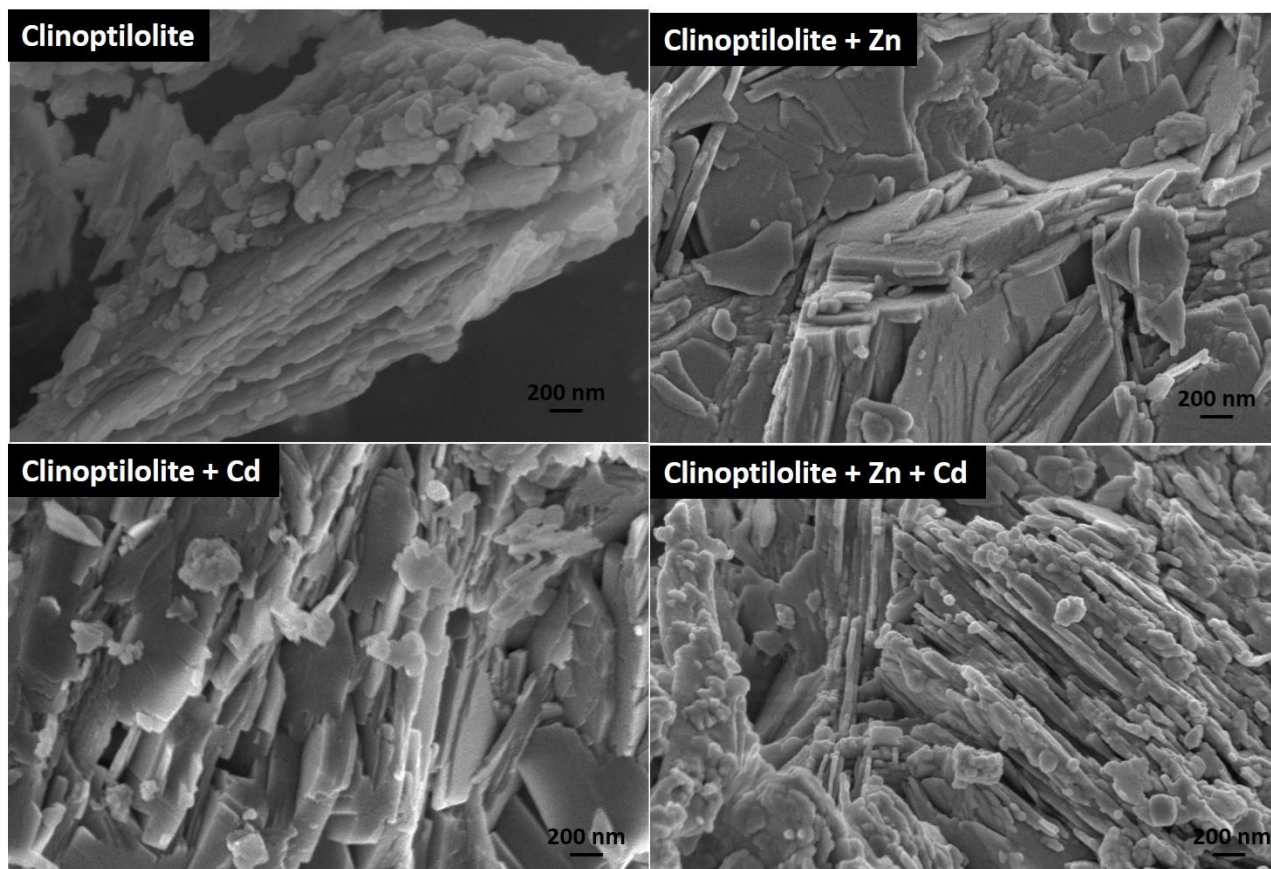


Fig 3 FESEM images of fresh clinoptilolite and after adsorption process with zinc, cadmium and both the metals.

Subsequently, in order to evaluate the elemental composition of the clinoptilolite, XRF spectrophotometry was used. Fresh and used samples were pulverized with a mortar and pelletized for the analysis. The results are presented in Table 1.

Table 1 XRF results on fresh and used clinoptilolite.

	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	ZnO	CdO
	% mass	% mass	% mass	% mass	% mass	% mass
clinoptilolite	12,6	76,6	4,77	3,92	-	-
clinoptilolite+Zn	12	77,2	4,82	3,78	0,876	-
clinoptilolite+Cd	13,5	74,6	4,85	3,42	-	0,619
clinoptilolite+Zn+Cd	12,6	76,7	5,02	4,09	0,337	0,201

As expected, the main elements of clinoptilolite were silica and alumina, potassium and calcium were present in minimum quantities. Cadmium and zinc, however, were not present in the fresh zeolite, but only after adsorption processes.

Since in the literature pH was considered a very influencing parameter on adsorbing capacity, first tests were carried out comparing adsorption in solutions with original pH (≈ 3.6) and by adjusting initial pH between 4.5 and 5 [19]. At lower pH values H^+ ions competed with metal ions for sites on the surface of the adsorbent, thereby hindering Zn and Cd ions from reaching such sites through the action of repulsive forces. At higher pH values, the metal ions could precipitate as hydroxide [20] and did not get adsorbed.

Results are reported in Figure 4, maintaining the clinoptilolite concentration equal to 10 g/L in solutions containing 10 mg/L of metal. For both the metals, adsorption capacity increased when pH was adjusted to 4.5.

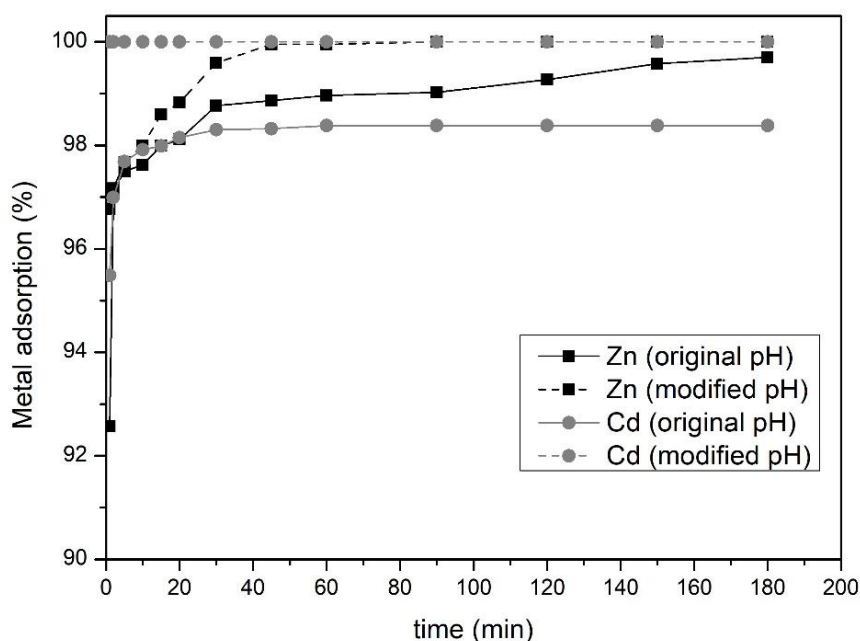


Fig 4 Percentage of adsorbed metal ions vs. time at different solution pH.

Then, for all the tests initial pH was adjusted to 4.5.

Preliminary analyses for both zinc and cadmium ions adsorption were carried out in two different batch, with an adsorbent amount in the solutions equal to 10 g/L, by varying metal concentrations between 10 to 200 mg/L. Results of maximum metal abatement are plotted in Figure 5.

For both zinc and cadmium ions, complete adsorption was reached when the metal concentration in the solutions was equal to 10 ppm. Increasing metal amount progressively to 50, 100 and 200 ppm, adsorption capacity decreased, most for Zn^{2+} , down to 35% with 200 ppm of metal in the starting solution. Cadmium ions removal was reduce much less, always remaining above 50% even at high metal concentrations.

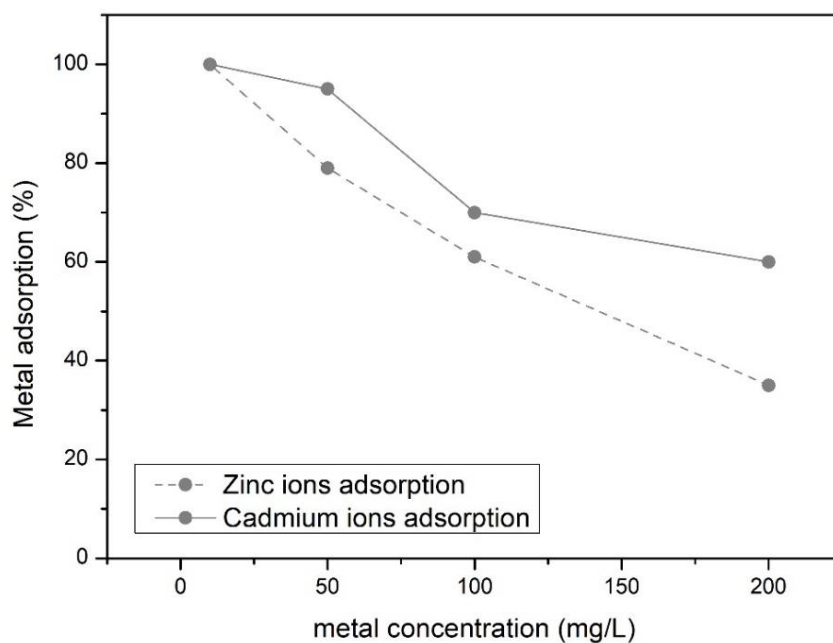


Fig 5 Maximum adsorption of zinc and cadmium ions on 10 g/L of clinoptilolite varying metal concentrations

Moreover, by considering the acceptable performance of clinoptilolite at high metal ions concentration (in particular for Zn^{2+}), maximum value, equal to 200 mg/L in the solution, was maintained and adsorbent amount was increased till 60 g/L in order to verify if clinoptilolite performance improved. Results are reported in Fig. 6. As expected, maximum adsorption percentages increased for the both zinc and cadmium and in particular, according to previous results, zeolite shown higher abatement capacity towards cadmium.

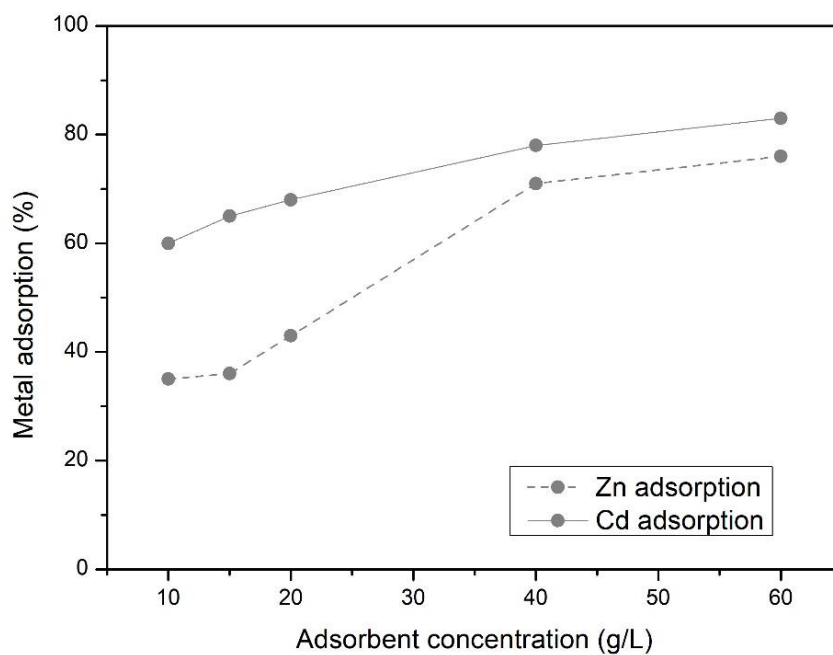


Fig 6 Maximum percentage of adsorbed zinc and cadmium ions ($C_0 = 200$ mg/L) varying adsorbent concentrations

By increasing clinoptilolite concentration to 40 g/L, ions abatement exceeded 50%, for both the metals, not varying much more enhanced concentration to 60 g/L.

Adsorption of zinc and cadmium ions onto clinoptilolite had a ion-exchange nature and the obtained results confirmed better natural zeolite performance for cadmium ions adsorption [21-23].

Conversely, the molecular sieve effect of zeolite did not influence adsorption as the metals ionic radius was much lower (about 100 times) than the pores of clinoptilolite (99 Å).

Then, for binary system, a natural zeolite amount equal 40 g/L was used in the tests, starting from a metal solution containing an equal amount of the two metals (100 mg/L). Contrary to previous tests, the adsorbent in the simultaneous presence of the two metals demonstrated a greater affinity towards zinc, showing a higher percentage of absorption. Results, reported in Figure 7, showed that, if the two metals were present in solution individually, they were adsorbed over time with a very similar trend, while in the binary system there was a greater affinity of zinc with clinoptilolite. This latter could be explained by considering the smaller ionic radius of the zinc, which would allow the Zn^{2+} to saturate the zeolite sites first.

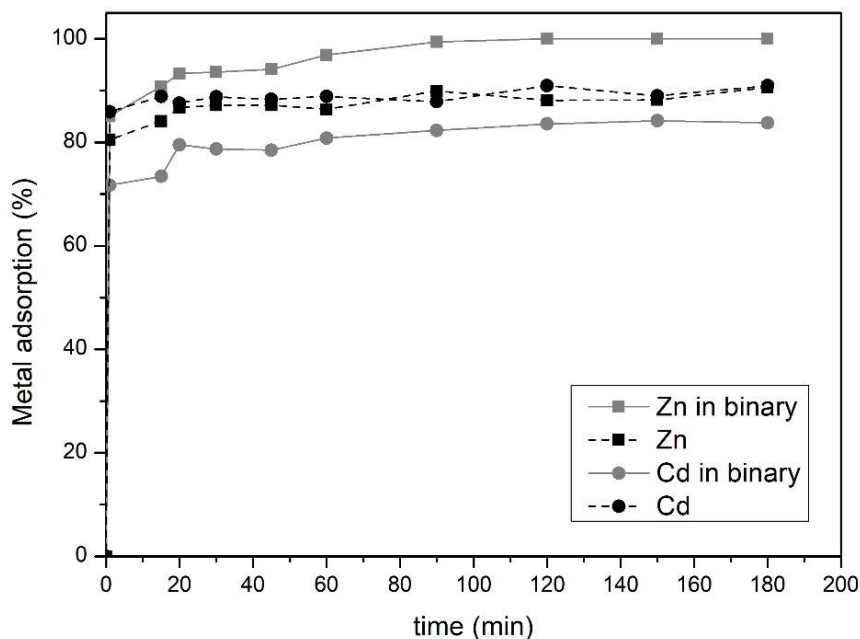


Fig 7 Percentage of adsorbed zinc and cadmium ions in single and binary systems vs. time

Finally, in order to reduce zeolite amount and consequently costs, adsorbent concentration was halved (20 g/L), obtaining similar curves trend and a slight reduction in performance but still maintaining absorption values higher than 70% for both the metal ions.

Conclusions

The capability of clinoptilolite as a low cost adsorbent for the removal of zinc and cadmium ions from wastewater was analysed in single and binary system, starting from different metal concentrations and using different adsorbent amounts. Starting from a clinoptilolite concentration equal to 10 g/L, for both zinc and cadmium ions, complete adsorption was reached when the metal concentration in the solutions was very low. Then, increasing metals amount progressively,

adsorption capacity decreased, most for Zn^{2+} . Tests with initial metal concentrations equal to 200 ppm was performed increasing adsorbent amount till 40 and 60 g/L, and results showed maximum abatements higher than 50%, in particular better performance was reached for cadmium ions.

Finally, adsorption tests in binary system were performed, showing a greater affinity of clinoptilolite towards Zn^{2+} , otherwise respect single metal system. This result was probably due to the smaller ionic radius that allowed the zinc a privileged absorption on the available sites of the natural zeolite.

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