MODIFIED LOW COST ADSORBENT (CEDAR) FOR THE REMOVAL OF Pb (II), Ni (II) AND Zn (II) FROM AQUEOUS SOLUTIONS

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ABSTRACT
Increased industrialization and population have a negative impact on the environment through the discharge of waste containing heavy metals. The aim of this work is to assess the sorption capacity of a modified low cost adsorbent (cedar) on the removal of lead, nickel and zinc ions from aqueous solutions at 60 mg/L for each metal. Alkaline treatment was applied to cedar to improve the adsorption process by the activation of the sorption sites. Kinetic assays were performed in batch mode at different adsorbent concentrations, from 0.5 g/L to 7.5 g/L. The pH of zero point of charge obtained for modified cedar was 5.13. Scanning Electron Microscopy-Energy Dispersive Spectroscopy was used to compare the morphology and chemical composition of the unmodified and modified cedar. The results revealed that alkaline treatment with potassium hydroxide is effective on the removal of these metals from aqueous solutions. The adsorption of lead (II), nickel (II) and zinc (II) onto modified cedar is dependent on the adsorbent concentration, being the maximum uptake reached for each ion at 2.5 g/L, 25.8 mg/g for Pb and 7.7 mg/g for Ni and Zn.

Keywords: Heavy metals, adsorption, cedar, alkaline treatment

INTRODUCTION
Heavy metal contamination in groundwater and sediments is one of the most relevant threats to environmental quality and human health. Their presence in the aquatic environment has attracted global attention due to their toxicity, persistence in nature, non-biodegradability and ability to bio-accumulate in food chains. The traditional treatment methods for heavy metal removal have been used but chemical methods are often restricted due to the technical or economic problems. Various biomaterials have been used to entrap those ions from water and wastewater such as industrial and/or agriculture wastes, becoming a good alternative to industrial wastewater treatment due to of their inexpensive and nonhazardous character [1,2]. In a few recent reports, some authors have documented the use of sawdust for the removal of metals from aqueous solutions. Additionally, wood sawdust has been reported as effective for heavy-metal uptake, especially after chemical treatments, appearing to be a promising adsorbent [3]. It is the case of cedar, a wood whose surface contains functional groups found efficient to bind cations [2]. Following this line of research, it is therefore necessary to look for cost-effective treatments for the optimization of the sorbent character of the biomaterial for the removal of hazards substances, as heavy metals. The aim of this study is to evaluate the sorption capacity of cedar, subject to an alkaline chemical activation, on the removal of Pb (II), Ni (II) and Zn (II) in aqueous solutions.

EXPERIMENTAL
Cedar (*Cedrus atlantica Manatti*) sawdust from Morocco with an average particle size of ≤1 mm, was used for the sorption experiments, with an alkaline chemical pre-activation. Aqueous solutions of Pb (II), Ni (II) and Zn (II) were prepared by dissolution of lead nitrate (II), nickel nitrate hexahydrate (II) and zinc chloride (II), respectively, purchased from Sigma-Aldrich, in distilled water.
For the alkaline chemical pretreatment of adsorbent, potassium hydroxide pellets were purchased from Sigma-Aldrich and used for solution preparation. The process was performed in a 0.5 L Erlenmeyer flask in batch mode, at a temperature of (25ºC±1ºC). 3 g of washed, dried and sieved

adsorbent was treated with 0.3 L of 0.2 M solution of reagent (pH=13.27). The mixture was stirred at 180 rpm for 24 h. The treated adsorbent was centrifuged at 9000 rpm, at 25°C for 7 min, and then washed twice with sterile MilliQ water to remove excess of chemical. In the next step, centrifuged cedar was mixed with distilled water and the pH value was adjusted to 5 so as not to interfere with the adsorption processes, using 0.1 M NaOH/HCl. Next, the cedar was again centrifuged and dried in the oven at 28°C, until all the humidity evaporated (3 days) and stored in a vacuum desiccator until use.

The samples were characterized using a scanning electron microscope (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS), phenom ProX with EDS detector (Phenom-World BV, Netherlands)). All data were processed using the ProSuite software integrated with Phenom Element Identification software, allowing the quantification of the elements present in the samples, expressed in either weight or atomic concentration. Modified cedar samples were added to aluminium pin stubs with electrically conductive carbon adhesive tape (PELCO Tabs™), with the excess being removed by compressed air. Samples were observed without coating. The aluminium pin stub was then placed inside a Phenom Charge Reduction Sample Holder, and different areas for each sample were analysed for elemental composition. EDS analyses were conducted at 15 kV with intensity map.

The pH of zero point of charge (pHzpc) of modified cedar was measured by preparing a solution of 0.01 M NaCl (99.5%, Panreac), previously bubbled with nitrogen to stabilize the pH by preventing the dissolution of CO_2.The pH was adjusted at different values between 1 and 9 by adding 1.0 M H_2SO_4 (95%, Fisher Chemical) or 1.0 M NaOH (≥ 97% Fisher Chemical). For each pH value, the adsorbent (0.10 g) was added to 25 mL of NaCl solution in conical flasks and left under moderate agitation (140 rpm) at (25ºC±1ºC) for 48 h. The samples were then filtered using 0.2 µm nylon filters (Whatman Ltd, USA) and the final pH of filtrate was measured and plotted against initial pH. The pH at which the curve crosses the line $pH_{initial} = pH_{final}$ was taken as pHpzc.

The adsorption capacity of modified cedar was investigated at different adsorbent doses (0.1, 0.5, 1.0 and 2.5 g). Kinetic experiments were carried out in batch system, in 250 mL stoppered polypropylene Erlenmeyer flasks containing 200 mL of Pb (II), Ni (II) and Zn (II) solution with initial concentration of 60 mg/L for each metal. Solution pH was monitored over time. The Erlenmeyer flasks were kept at (25ºC±1ºC) and 160 rpm, for 29 h, until equilibrium was reached. Samples were periodically taken, filtered with 0.2 µm nylon filters (Whatman Ltd, USA) and analyzed for Pb, Ni, and Zn concentration by Inductively coupled plasma optical emission spectroscopy ICP-OES (Optima 8000, Perkin-Elmer). The adsorbed amount of Pb, Ni, and Zn at time t, qt (mg/g) was calculated by Eq. 1:

$$q_t = (C_0 - C_t)V/m \quad (1)$$

where C_0 (mg/L) is the initial concentration of Pb, Ni, or Zn, C_t(mg/L) is the concentration of lead, nickel or zinc in solution at time *t*, *V*(L) is the volume of the Pb, Ni, or Zn solution and *m*(g) is the mass of modified cedar.

RESULTS

Determination of pH of zero point of charge

The pHzpc corresponds to the pH value at which the net surface charge of the adsorbent becomes electrically neutral and it plays an important role during the sorption of ionic species on solid surfaces from aqueous systems. At pH < pHzpc, the adsorbent surface becomes positively charged, while at pH > pHzpc, the adsorbent surface is negatively charged. The pHzpc value obtained for modified cedar was 5.13.

Characterization of morphology and chemical composition

SEM-EDS analysis was performed to compare the surface structure morphology (at 5kV), through visual analysis of the pores and elemental composition (at 15kV) of unmodified and modified cedar. In Fig. 1A and B the SEM images of the surface of unmodified and modified cedar are presented, respectively, with the same amplification. EDS analyses indicated an percentage average of the weight concentration, 51.98% of carbon, 38.96% of oxygen and 9.06% of nitrogen for unmodified cedar and 48.33% of carbon, 46.96% of oxygen, 4.19% of nitrogen and 0.51% of potassium for modified cedar.

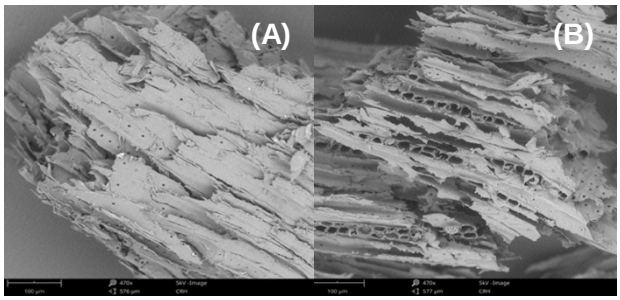

Fig. 1 SEM images of samples surface, demonstrating different details in morphology, (A) unmodified cedar, with *Field-of-View (FOV)*: 576 µm, (B) modified cedar, with *FOV*: 577 µm.

Sorption experiments

Sorption experiments were performed to determine the uptake of Pb (II), Ni (II) and Zn (II) onto modified cedar at different adsorbent concentrations, ranging from 0.5 g/L to 7.5 g/L. The adsorption assays for Pb (II), Ni (II) and Zn (II) take between 2-5 hours to reach the equilibrium. During the experiments, solution pH was measured, not changing substantially (4.4±0.2). The maximum uptake was achieved at 0.5 g/L, with 25.8 mg/g for Pb (II), 7.7 mg/g for Ni and Zn. As shown in Fig. 2, the removal efficiency of Pb (II), Ni (II) and Zn (II) increased as the dosage of modified cedar increased from 0.1 to 1.5 g. This may be explained by the increase of absolute number of available active sites of the adsorbent, thus facilitating the binding of Pb (II), Ni (II) and Zn (II) ions. Modified cedar is efficient on the removal of these metals, mainly Pb (II), presenting 90.2% as the maximum removal percentage, achieved with 1.5 g of the adsorbent.

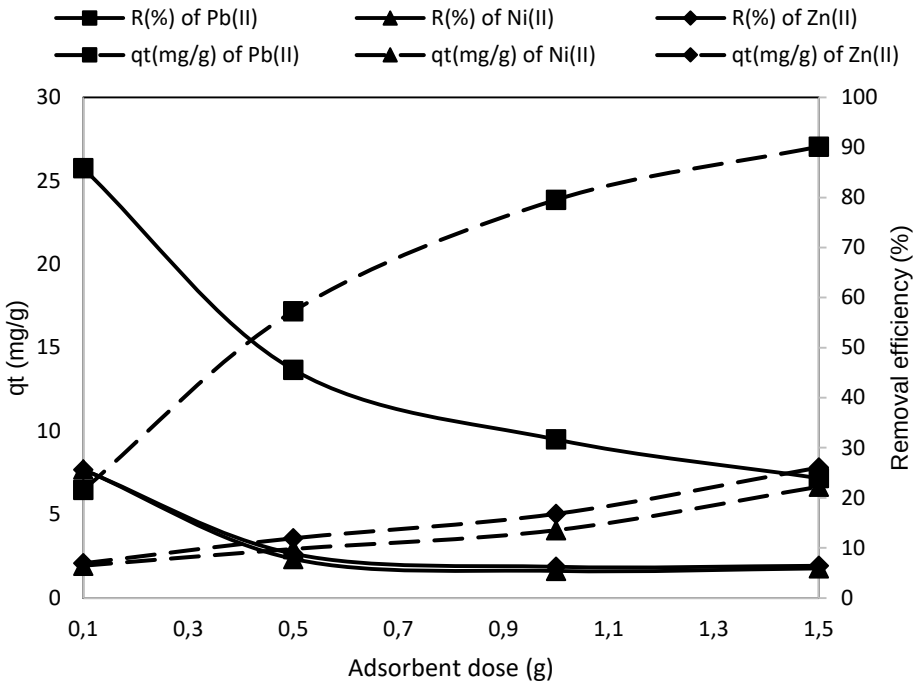

Fig. 2 The effect of adsorbent dose on Pb (II), Ni (II) and Zn (II) removal efficiency and uptake.

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