

A Preliminary study of removal of some heavy metals from aqueous medium by a mesoporous hydroxysodalite zeolite prepared from basalt rich in calc-plagioclase by alkali activation

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This research is dedicated to Professor Dr. Mahmoud Alawi on his retirement from the University of Jordan. Professor Alawi will be remembered by generations of Jordanian students, environmentalists and educators for his contributions and services in education and environmental awareness.

Abstract

This work presents an exploration of the use of hydroxysodalite zeolite prepared from basalt rich in calc-plagioclase by alkali activation for removal of some heavy metals from aqueous medium. The preliminary results of batch and column experiments indicated a quantitative and fast removal of the three investigated ions, Cu^{2+} , Pb^{2+} and Zn^{2+} from aqueous solutions. The data from the batch experiments and the column experiments jointly support the notion that hydroxysodalite zeolite prepared from basalt rich in calc-plagioclase is an efficient adsorbent for the investigated heavy metals. Almost quantitative removal of the ions was achieved within a period of 15 min of exposure of the solution to the adsorbent in batch experiments and through passing a small column filled with the adsorbent. The highest removal efficiency by the zeolite prepared from basalt rich in calc-plagioclase of the three tested heavy metal Cu^{2+} , Pb^{2+} and Zn^{2+} were 99.98% ,99.76% and 99.93 % respectively.

Keywords: hydroxysodalite zeolite, basalt utilization, heavy ions removal, pollution remediation

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1. Introduction

The adverse effects of accumulation of heavy metals in the environment as a result of increasing industrial and domestic applications presents a global environmental and public health threat [1,2,3]. Heavy metals which originate from industrial activities and the overuse of agricultural fertilizers are considered as the most hazardous ground water pollutants. The quest for inexpensive, abundant, environmental friendly sorbents is a hot area in environmental and chemical research. [4,5,6]

In this study, a hydroxysodalite (H-SOD) zeolite was prepared in our laboratory from locally abundant Jordanian basalt powder rich in calc-plagioclase by alkali-activation method. This method is an inexpensive and green methodology for preparation of inorganic polymers [7]. As Esaifan et al, mentioned in their paper [7] the prepared Hydroxysodalite (H-SOD) microcrystalline particles were synthesized from basalt powder rich in calc-plagioclase (anorthite) by alkali activation at 80 °C/24 h. Sodium hydroxide (NaOH) solution was used as alkaline activator. The reactivity of the natural solid precursor basalt was studied using differential scanning calorimetry (DSC), and a maximum reaction enthalpy of (DH) of 170 J/g was obtained. The chemical, mineralogical, and textural properties were obtained by using X-ray powder diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR) fig 1(a,b) , scanning electron microscopy (SEM) thermogravimetric analysis (TGA), and N_2 -adsorption-desorption measurements fig 2 (a ,b ,c) [7] .

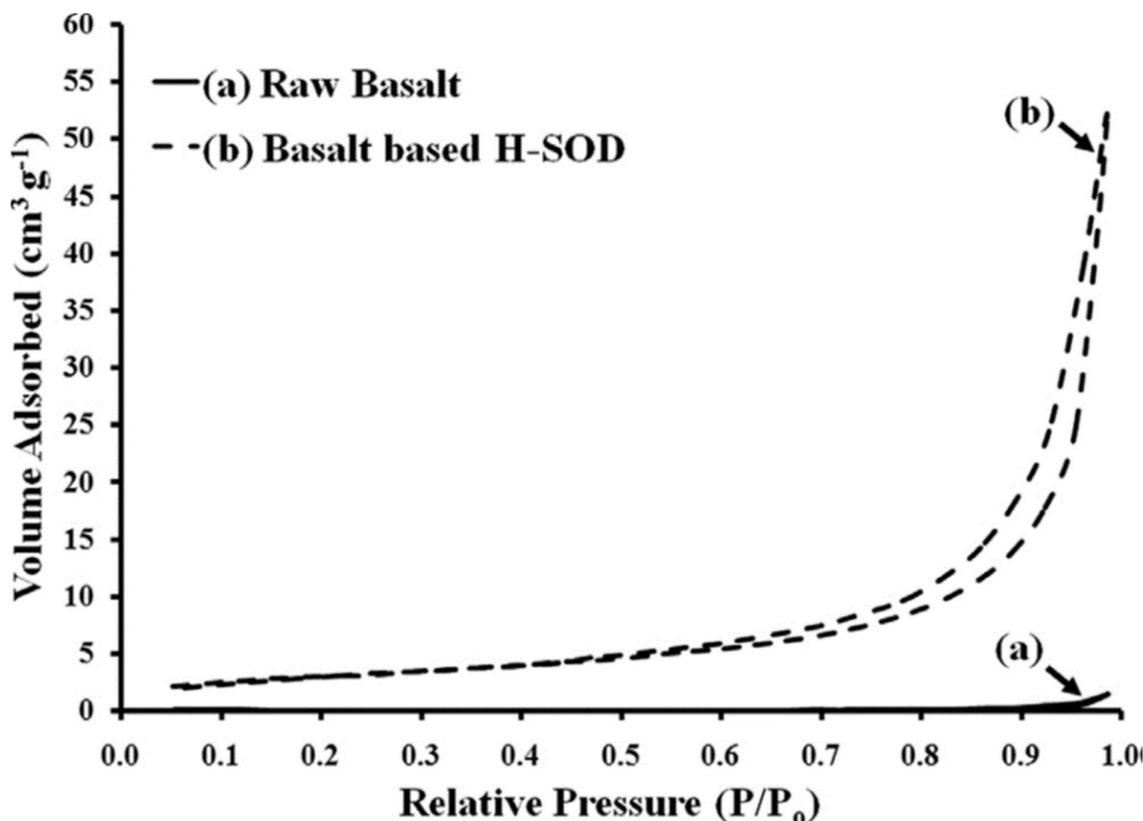


Fig 2\c- Adsorption/desorption isotherm curves of N₂ for; (a) raw basalt material and (b) basalt based H-SOD synthesized using NaOH/basalt ratio of 0.3.[7]

The synthesized material has a specific BET surface area of 20.5 m² g⁻¹ approximately 200 times higher than raw basalt material (0.1 m² g⁻¹). The compressive strength of basalt based H-SOD/sand composite samples cured at 80 °C for 24 h upon using different amounts of the activator (NaOH) was evaluated under dry and saturated conditions. The dry samples with NaOH/basalt mass ratio of 0.12 have reached a compressive strength of 57 MPa. Wet samples, on the other hand, showed a compressive strength of 25 MPa after seven days of soaking in water and four episodes of wetting and drying material in addition the Porosity of the prepared hydroxyl sodalite was investigated by adsorption/desorption isotherms of nitrogen [7]. Its porosity (0.21 g/cm³) which give it a high mechanical characteristics that present an excellent candidate for adsorption of some pollutants.

On the premise that the mesoporous hydroxysodalite zeolite prepared from basalt is a good candidate for removal of pollutants from aqueous media compared to many other sorbent and technique used for removal of heavy metal [8,9,10,11,12], the present work was undertaken. The main goal of this study was to investigate the adsorption capabilities of the hydroxysodalite zeolite prepared from basalt raw materials by alkali-activation [4]. This work was tempting because hydroxysodalite zeolite can be prepared from locally abundant raw material by an inexpensive environment friendly methodology; the alkali-activation which allows polymerization of the silicate-rich materials at low temperature [13]. The chosen test pollutants for the present work were three heavy metals, lead (Pb), zinc (Zn) and copper (Cu) because of their expansive use and their adverse effects on the environment and presence in many waste water from different sources [15,16,17]. Also, Khalil I et al mentioned that natural faujasite-phillipsite and phillipsite-chabazite tuffs is efficient in removing Mo and Ni from contaminated drinking water with 80%, 76%, and 78%, respectively and the maximum removal efficiency of Ni by the zeolitic tuffs is up to 90% compared to the original groundwater sample. [18]

2. Methods and materials

Preparation and characterization of the sorbent specimens has been performed as described in the procedure performed in Esaifan et al work [7]. The hydroxysodalite zeolite was prepared in powder form and sieved to collect the fraction of particles of a diameter between 100 and 50 mesh (150 – 300 μm). Standard solutions of Pb²⁺, Cu²⁺ and Zn²⁺ were prepared from Pb(NO₃)₂ (99.0% minimum purity) Cu(NO₃)₂.3H₂O (99.0% minimum purity) and ZnSO₄.7H₂O (99.0% minimum purity) respectively. All of these reagents were supplied by Riedel-de Haen

(Germany) and used as received without further purification. All solutions were prepared by dissolving the above-mentioned reagents in Milli-Q water (Millipore, Merck) and all experiments were conducted at ambient conditions. For all experiments, the concentrations of Cu^{2+} , Pb^{2+} and Zn^{2+} in the test solutions were determined by atomic emission spectrometry with an inductively coupled plasma source (ICP-AES) (GBC E1475, USA). The 212.603 nm, 220.353 nm and 206.2 nm emission lines were used for quantitative determination of copper, lead and zinc respectively. Calibration curves for the three metals were established with an excellent linearity ($R^2 > 0.990$).

In order to study the effect of exposure time batch experiments were conducted with 50 mL of 50 ppm metal ion concentration in contact with 1.0 g specimens of hydroxysodalite zeolite placed in 100 mL conical flasks, mixed thoroughly and stirred for a preset period of time 2, 6, 8, 10, 12, 15, 30, 60, 90 minutes. At the end of the specified period, the solutions were filtered through 0.45 μm PTFE filter. The concentrations of the three heavy metals were determined by inductively coupled plasma optical atomic spectrometry (ICP-AES) (GBC E1475, USA). However, the effect of changing the concentration and solution volume on metal uptake was also explored. For the purpose of studying the effect of concentration, on the adsorption process measured volumes (25, 50 mL) of different concentrations (25, 50, 75, 100 ppm) of Cu^{2+} , Zn^{2+} and Pb^{2+} standard solutions were added to the hydroxysodalite zeolite specimens, stirred for 15 min, filtered through 0.45 μm PTFE filter, and final concentration of individual ions was again determined by (ICP-AES) (GBC E1475, USA).

To study the effect of adsorbent dosage on the heavy metal removal efficiency, batch experiments were conducted with 50 ml of 50 ppm metal ion concentration placed in 100 ml erlenmeyer flasks. The hydroxysodalite zeolite was dosed at 0.1, 0.5, 1.0, 2.0 g. the solutions were stirred for 15 min at room temperature (25 ± 0.1 °C)

The column experiments were performed on a small cylindrical column 8 cm(length) x 1 cm diameter filled with the hydroxysodalite zeolite particles sieved between 150 and 300 μm (100 and 50mesh). 50.00 mL of 100 ppm solutions of each of the three test ions; Cu^{2+} , Pb^{2+} , and Zn^{2+} were allowed to pass through the hydroxysodalite zeolite column separately. The column was washed with 50.00 mL of fresh Millipore water. The two fractions were combined to make a volume of 100.0mL. The concentrations of the three metals were determined in the final solutions and the percent removal of the metals from the sample was calculated.

3. Results and Discussion

3.1 Effect of time of adsorption

Table (1) shows the results of exposure of a set of standard solutions of the three test ions to 1.0 g of the hydroxysodalite zeolite adsorbent at different adsorption times

Table (1) The adsorbent removal efficiency (%) of the three metals ions (Cu^{2+} , Pb^{2+} , Zn^{2+}) by 1.0 g hydroxysodalite zeolite based on alkali-activated basalt powder. The metal ions concentration = 50 ppm, volume of solution = 50 mL at different exposure times.

Time of exposure (min)	% Cu^{2+} Removal	% Pb^{2+} Removal	% Zn^{2+} Removal
2	88.58	92.41	78.74
8	92.54	94.88	80.48
12	98.63	98.84	95.45
15	99.85	99.76	99.30
30	99.66	99.75	99.92
60	99.51	99.61	99.93
90	99.85	99.59	99.89

The adsorbent removal efficiency (%) was calculated using equation (1).

$$\text{Removal efficiency (\%)} = (C_i - C_f) / C_i \times 100 \quad (1)$$

where C_i (ppm) is the initial concentration of heavy metal ions and C_f (ppm) is the final concentration of metal ions in solution after stirring with hydroxysodalite zeolite.

These results indicate that the hydroxysodalite zeolite has high adsorption capability for the three ions and the uptake of the metals is almost quantitative and complete removal of the three metals is established from the first 15 min of contact between the hydroxysodalite zeolite and the test ion solution. As Figure 3 (a,b, and c) shown that 15 min optimum time of removal achieved even for different concentrations of the three metal ion .This removal efficiency percentage still high and give a promising result for high scale experiment for Pb^{2+} , Cu^{2+} and Zn^{2+} environmental problem, also 15 min time period consider to be a good time to perform removal experiment of high acceptable removal efficiency without time consuming long range experiment.

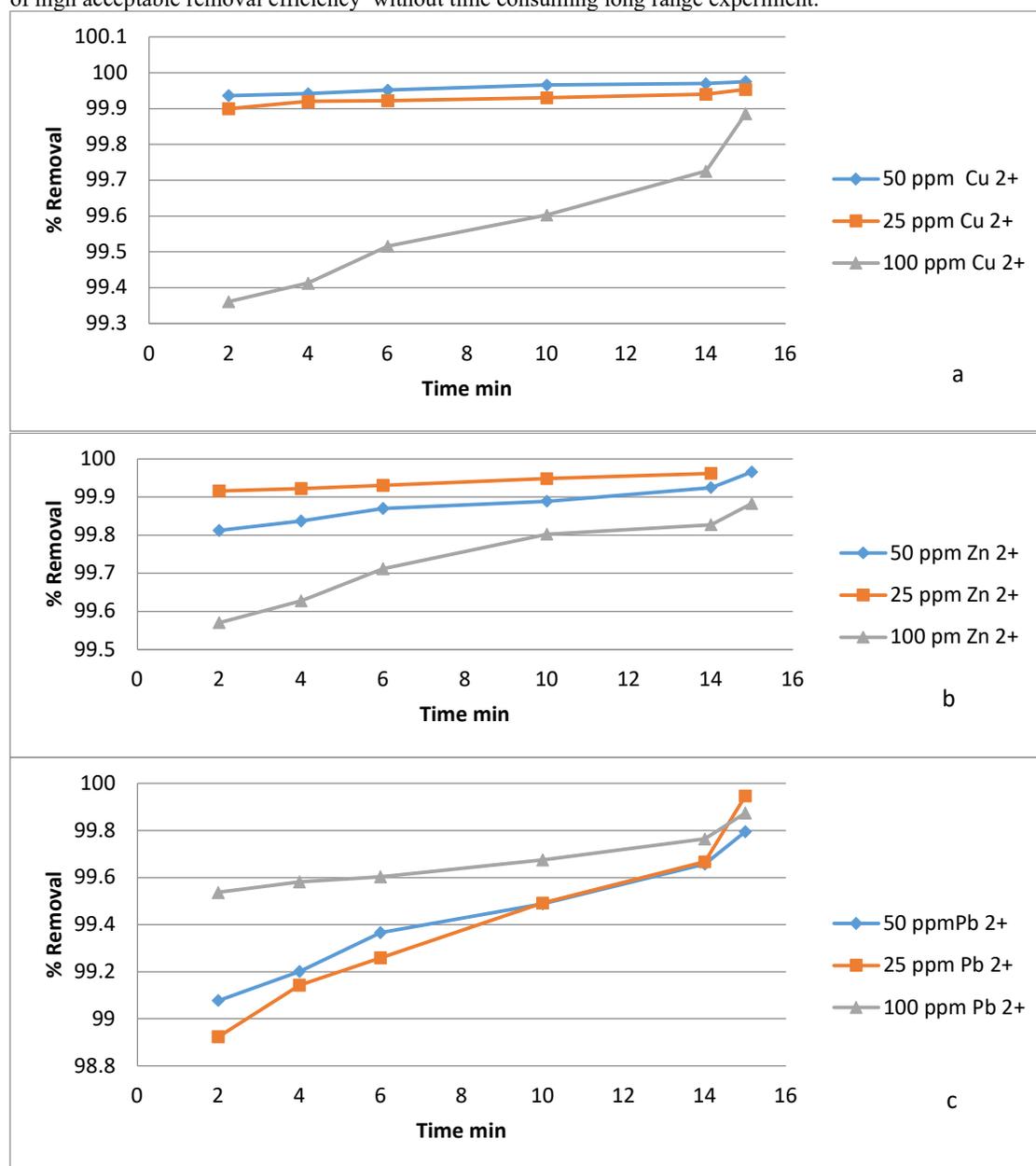


Fig 3(a,b,c) Percent removal of the three metals by hydroxysodalite zeolite as function of time(different time of exposure , Mass of hydroxysodalite = 1.0 g, volume = 50 mL. initial concentration = 25 ,50 ,100 ppm)

3.2 Effect of volume and concentration of the heavy metal ion

Table 2 shows the percent removal of the ions from the solution as a function of concentration for two different times of exposure. Almost quantitative removal of the ions was achieved at all added concentrations at 15 min compared to 2 min which show lowest removal efficiency. The difference between 2 min and 15 min on one hand and the difference according to increasing the concentration on other hand showed that as we increase the concentration for 15 min time period the removal efficiency falls within the limits of uncertainty and we reach almost the highest removal efficiency as shown in Figure 4 (a,b, and c) variation of concentration 25,50 and 100 ppm give a very approximate removal efficiency values with some variation depend on concentration ; Cu^{2+} , Zn^{2+} and Pb^{2+} metal ions removal efficiency increase with increasing the concentration. These results present a manifestation of the strong interaction between the three ions and the hydroxysodalite adsorbent and offer the capability to use the hydroxysodalite zeolite for waste water treatment to remove Cu^{2+} , Zn^{2+} and Pb^{2+} metal ion .

Table (2) The adsorbent removal efficiency (%) of the three metals ions (Cu^{2+} , Pb^{2+} , Zn^{2+}) by 1.0 g hydroxysodalite zeolite based on alkali-activated basalt powder. At different concentrations 25, 50, 75, 100 ppm, volume of solution = 50 ml, exposure time = 2, and 15 min.

Concentration (ppm)	% Pb^{2+} Removal		% Cu^{2+} Removal		% Zn^{2+} Removal	
	Time (2 min)	Time (15 min)	Time (2 min)	Time (15 min)	Time (2 min)	Time (15 min)
25	85.72	99.67	84.66	99.75	75.63	99.95
50	92.41	99.76	88.58	99.85	78.74	99.30
75	94.86	99.90	94.08	99.62	89.64	99.92
100	96.83	99.89	95.53	99.64	92.81	99.91

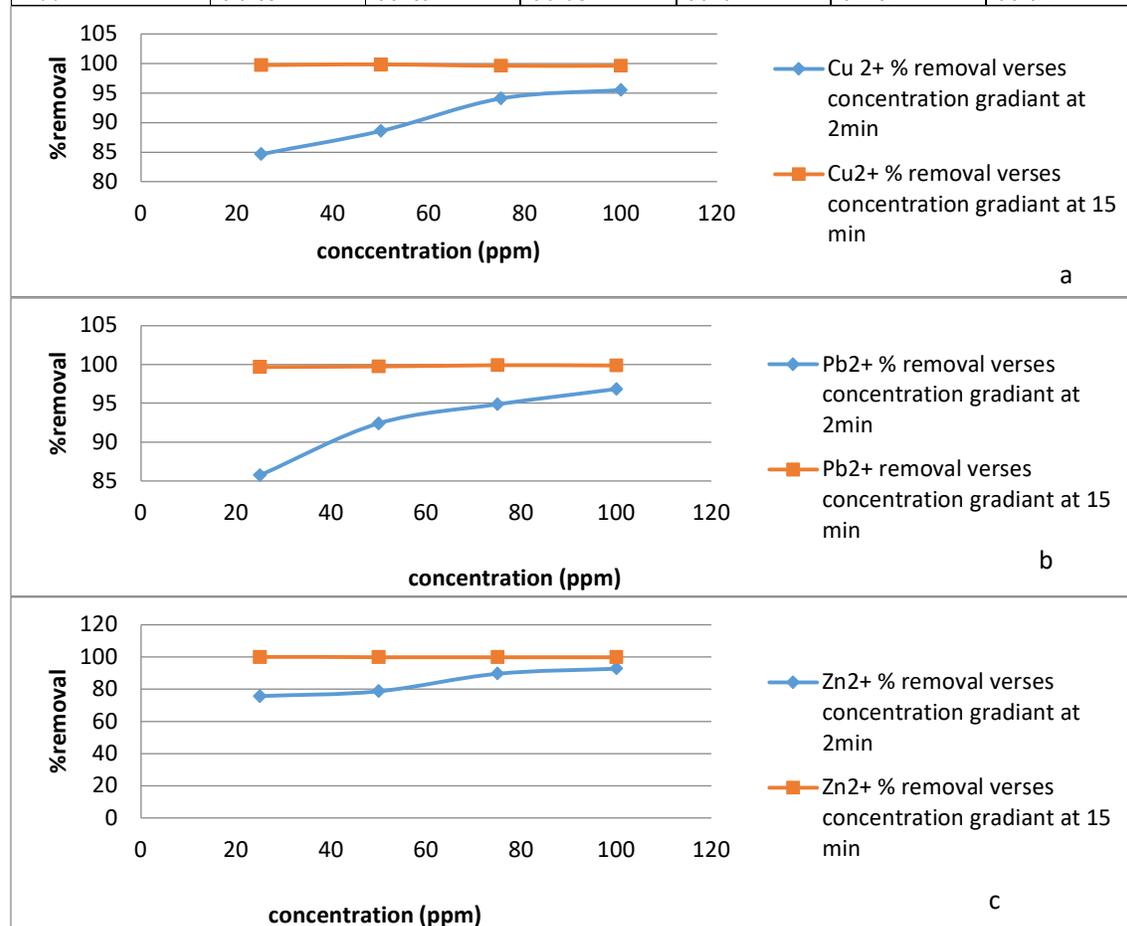


Fig 4 (a,b,c) Percent removal of the Cu^{2+} , Pb^{2+} and Zn^{2+} by hydroxysodalite zeolite as function of concentration at (2 and 15 min) (different concentration of the metal ion solutions. Mass of hydroxysodalite = 1.0 g, Volume of solution = 50mL)

The results of percent removal upon changing the volume of the metal ion Solution are shown in Table 3. The differences as a function of the volume is negligible and falls within the uncertainty limits. These results also indicate almost quantitative removal of the three ions regardless of the volume of the standard solution of the metal ions and also attest to the strength of interaction between the investigated ions and adsorbent. The % of removal of Cu^{2+} , Pb^{2+} , and Zn^{2+} increase as the concentration increases this may be as a result of increase in the driving force of the concentration gradient.[19]

Table 3 Percent removal of the three metals by hydroxysodalite zeolite (different volumes of the metal ion solutions(25,50,75,100mL). Mass of hydroxysodalite = 1.0 g, time of exposure = 15 min. initial metal concentration = 50 ppm)

Volume /mL	Ion Percent Removal		
	Cu^{2+}	Pb^{2+}	Zn^{2+}
25	99.93	99.75	99.95
50	99.85	99.76	99.93
75	99.63	99.79	99.95
100	99.43	99.73	99.95

3.3 Effect of mass of adsorbent

Variation of the mass of the H-SOD adsorbent were studied using different masses of the H-SOD with constant concentration of Cu^{2+} , Pb^{2+} , and Zn^{2+} (50ppm) at constant time 15 min. As shown in fig 5 as the mass of the adsorbent increased the % removal efficiency increased to reach its maximum at almost 1g of the H-SOD. the maximum removal efficiency for 1g of the adsorbent were 99.85%, 99.76% and 99.93% for Cu^{2+} , Pb^{2+} , and Zn^{2+} respectively. These result open the eyes about availability of using the lowest amount of the H-SOD adsorbent to remove as much as possible of Cu^{2+} , Pb^{2+} , and Zn^{2+} heavy metal ion from any aqueous solution

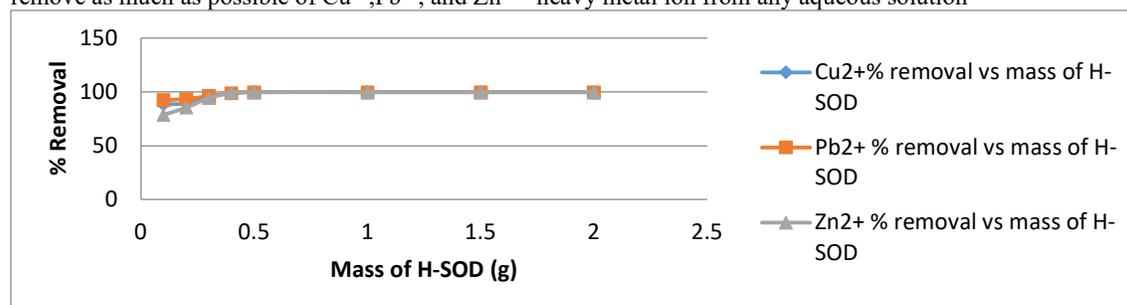


Fig 5 Percent removal of the Cu^{2+} , Pb^{2+} and Zn^{2+} by hydroxysodalite zeolite as function of mass variation (concentration of the metal ion solutions = 50 ppm., Volume of solution = 50mL, time of exposure =15 min)

3.4 Column experiment

Table 4 shows the results of the column experiment. The concentrations of the ions were determined and the percent removal of the ions from the solutions (or the uptake of the ions by the adsorbent) was calculated. Analysis of the data in Table 4 indicates that quantitative removal of the three ions had been achieved upon passing the sample through the hydroxysodalite zeolite adsorbent. These results reinforce the conclusions obtained from the batch experiments.

Table 4 Concentration of Zn^{2+} , Pb^{2+} and Cu^{2+} in the solution after passing through the hydroxysodalite zeolite(8.0- cm x 1.00-cm i.d column)

Ion	Initial concentration, ppm	Initial Volume added, mL	Volume of washing Water, mL	Volume of final eluates	Concentration in the final solution, ppm	% Removal
Cu^{2+}	100	50.00	50.00	100.00	ND	100%
Pb^{2+}	100	50.00	50.00	100.00	ND	100%
Zn^{2+}	100	50.00	50.00	100.00	ND	100%

4. Conclusions

Hydroxysodalite zeolite was prepared by alkali-activation from basalt raw materials demonstrated high efficiency in removal of Cu^{2+} , Pb^{2+} and Cu^{2+} from aqueous solutions. The data from the batch experiments and the column experiments jointly support the notion that hydroxysodalite zeolite prepared from basalt rich incalc-plagioclase is an efficient adsorbent for the investigated heavy metals. Almost quantitative removal of the ions was achieved within a period of 15 min of exposure of the solution to the adsorbent in batch experiments and through passing a small column filled with the adsorbent. The strong interaction between the ions and the adsorbent is attributed to the strong ion-dipole interaction or ion-ion interaction between the three ions and the Hydroxysodalite zeolite which contains polar water molecules and ionic hydroxyl groups^[14]. A major strength in the present work is the fact that the hydroxysodalite zeolite is prepared from naturally occurring rocks by alkali-activation, an inexpensive and green methodology for preparation of inorganic polymers. The present work also opens the window for applications of the prepared hydroxysodalite zeolite for micro-extraction, and macro-extraction in analysis of heavy metals and some other organic pollutants.

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