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Sudanese Thomsonite as Ion Exchanger to Removal Pb^{2+}, Fe^{3+} and Ni^{2+} from Artificial Wastewater

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Abstract

Zeolite samples were collected from Wadkawly in Gadarif region. These samples were characterized with respect chemical properties by AAS, SEM and X-ray Diffraction Analysis (XRD) showed these samples to be composed of Thomsonite zeolite, exclusively. The sample was treated with strong brine solution to ensure that Na-zeolite was generated and used as the stationary ion exchanger phase. Solutions containing 100 ppm of heavy metal ions (Pb^{2+}, $Fe^{3+}$and Ni^{2+}) were artificially prepared and then processed with Na-zeolite. Excellent extraction was achieved, with final residual concentration of 0.02 ppb, 3.0 ppb and 1.38 ppm for (Pb^{2+}, Fe^{3+} and Ni^{2+}) respectively and retention time 180 seconds for decreasing concentrations. This gives extraction efficiency of ~ 100%, 99.9%, and 98.6%, for Pb^{2+}, Fe^{3+} and Ni^{2+}, respectively. The relative efficiency is, therefore: Pb^{2+} > Fe^{3+} > Ni^{2+}.

Keywords: Thomsonite; Natural zeolite; Ion exchange; Heavy metals; X-ray diffraction analysis

Introduction

Thomsonite is a zeolite belonging to the "fibrous zeolites group," often found in amygdaloidal vugs of massive volcanic rocks (e.g., basalt) and tuffs as an alteration product of volcanic glass [1-3]. Thomsonite specimens occur often as spherules or rosettes, composed of platy or blocky crystallites, often associated with gonnardit [4]. The ideal chemical formula of Thomsonite is $Ca_2Na[Al_5Si_5O_{20}]\cdot 6H_2O$ [1]. Small amounts of Fe, Mg, Sr, Ba, and K also may be found [4].

Ion exchange is a chemisorption process, whereas adsorption may be physical sorption or chemisorption. The ion exchange reaction may be defined as the reversible interchange of ions between a solid phase (the ion exchanger) and a solution phase. The ion exchanger is usually insoluble in the medium in which the exchange is carried out [5]. All ion exchange processes are extremely rapid and they follow the general well known kinetic laws as shown in the equation below, however, the mathematical treatment of the reaction rates become quite cumbersome and difficult in heterogeneous systems [6]. The following two reactions illustrate the basic interactions that take place between the solid phase and the ions in solution.

Cationic Exchanger:

M-A+ (solid) + B+ (solution) <=> M–B+ (solid) +A+ (solution) (1)

Anionic Exchanger:

M+A-(solid) + B-(solution) <=> M+B- (solid) + A- (solution) (2)

Due to their structural characteristics, natural zeolites can be used in several applications, from which [7] reviewed those of environmental interest. For example [8] used clinoptilolite to remove Al, Fe, Cu, and Zn from copper mine wastewater to below drinking water standards. Natural zeolites are especially attractive for removing heavy metal ions from effluent wastewaters mainly of industrial origin [9]. Natural zeolites have been investigated for removal of Mn^{2+}, Fe^{2+}, Hg^{2+}, Cr^{3+}, Ag^{+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Co^{2+}, and Ni^{2+} from various wastewaters [10-12].

It is well known that ion exchange selectivity depends on the ion concentration of the metals in the water to be treated. Cation exchange selectivity sequences of Clinoptilolite rich samples for heavy metals:

Cs > Pb > Fe > Cu > Zn, Cd, Co > Ni > Mn >Cr [13]. Pb > Cd > Cu > Co > Cr^{3+} >Zn > Ni > Hg [10]. They also report that. Our objective in this study is to investigate the removal of heavy metals Ni^{2+}, Pb^{2+}, and Fe^{3+}. The retention time was 180 seconds for artificial solutions by the Thomsonite natural zeolite.

Materials and Methods

Materials

Samples of zeolites deposits were obtained from two different areas, and will be referred to as "Khadarif sample". From Wad Kawly. Samples of waste were artificially prepared by diluted standard solutions containing 1000 ppm 100 ppm of the heavy metal ion (Fe^{3+} or Pb^{2+} or Ni^{2+}).

Instruments

1) X-Ray Diffracotmeter: System: Phillips, Model: X'-pert PRO Stress XRD analyzer Cu-target radiation.

2) Scanning Electron Microscopy (SEM): Model: TESCAN. Oxford Instrument Company, use energy dispersive spectrometery (EDS) system.

3) Atomic Absorption spectrophotometer (AAS): Perkin Elmer Model: 2380, flame double-beam system was used to determine chemical composition reported as oxides. 4- SHIMADZU, AA-6800, Fernus and flame double-beam system air/ acetylene, was used to determine concentrations of (Pb^{2+}, Fe^{3+}, Ni^{2+}) after extraction.

Processing natural Thomsonite

Natural thomsonite treated by (0.1 M) HCl for 5 hours, after that it washed with tap water roughly (1-2%) of Zeolite was lost (since carbonates, clays leached). Then treated by NaCl (1.0 M) for 24 hours.

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All the conditioning is done before grinding. Sample is reduced by crushing, and ground to grain size of (315-500 µm).

Removal of the heavy metal ions

A sample of 4 gm Na- Thomsonite (315-500 µm) grain-size is placed in a beaker. Then is added 30 ml of one of the heavy metal ions (Fe^{3+}, Pb^{2+} or Ni^{2+}) standard solution (100 ppm). To facilitate extraction of the heavy metal ions, vigorous shaking is applied for (5, 10, 30, 60, 120, or 180 seconds) by magnetic stirrer. The solution then filtered, and the filtrate was transferred to the AAS to determine the residual concentration of the metal ion.

Results and Discussion

For the present study, efforts were made to locate zeolite deposits in the Sudan. Three positions were identified in Wadkwly area near Gallabat town Table 1, was shown latitude and longitude of zeolite deposites Results of Thomsonite were shown in Figures 1-3. Phase analysis was achieved by using Phillips, Model: X' pert PRO XRD analyzer Cu-target radiation (λ=1.54 Å). Only samples from "Road 1" and "Road 2" were analyzed. These were labeled as "K3-a" and "K3-b". Both of them were found to be Thomsonite zeolite (hydrated sodium-calcium aluminum silicate), Scanning Electron Microscopy (SEM) has been employed to probe the internal structure of the zeolite samples. The cellular microstructure of grains is clearly and it is clear that particles are rectangular in shape with sharp edges. It were shown in Figures 2 and 3. In Table 2 show the chemical composition of the natural zeolite as oxides. SiO_2 percentage was found high in sample. This indicates that silicate is important component in natural zeolites.

A solution containing 100 ppm of (Pb^{2+}) was injected into Thomsonite powder, and agitated for a given period of time, when a sample was removed and analyzed. A plot of this data is shown in Figure 4. It is seen that the concentration of (Pb^{2+}) decreased to (0.02 × 10^{-3}%) of its initial value. This gives an extraction of ~ 100% after 3 minutes retention time. In Figure 5 is seen that the concentration of (Fe^{3+}) decreased to (0.003%) of its initial value. This gives an extraction of 99.997% after 3 minutes. In Figure 6 is seen that the concentration of (Ni^{2+}) decreased to (1.4%) of its initial value. This gives an extraction of 98.6% after 3 minutes. The Table 3 shows that almost all of the heavy metal ions were extract-ed by the zeolite in 3 minutes, indicating remarkable efficiency.

Location	Latitude	Longitude
Road 1	13° 36´ N	36° 19´ E
Road 2	13° 13´ N	36° 14´ E
Valley	13° 14´ N	36° 17´ E

Table 1: Coordinates of Zeolite Deposits.

Component	Percentage (%)
Al_2O_3	4.37
CaO	3.02
K_2O	2.28
Na_2O	13.26
MgO	2.38
SiO_2	65.73
LOI	8.96

Where LOI: loss of ignition.

Table 2: The Chemical Composition of Zeolite.

Ion	Initial Concentration	Final Concentration	% Extraction
Fe^{3+}	100 ppm	3 ppb	99.997%
Pb^{2+}	100 ppm	0.02 ppb	~ 100%
Ni^{2+}	100 ppm	1.38 ppm	98.6%

Table 3: Extraction Efficiency for Fe, Pb and Ni.

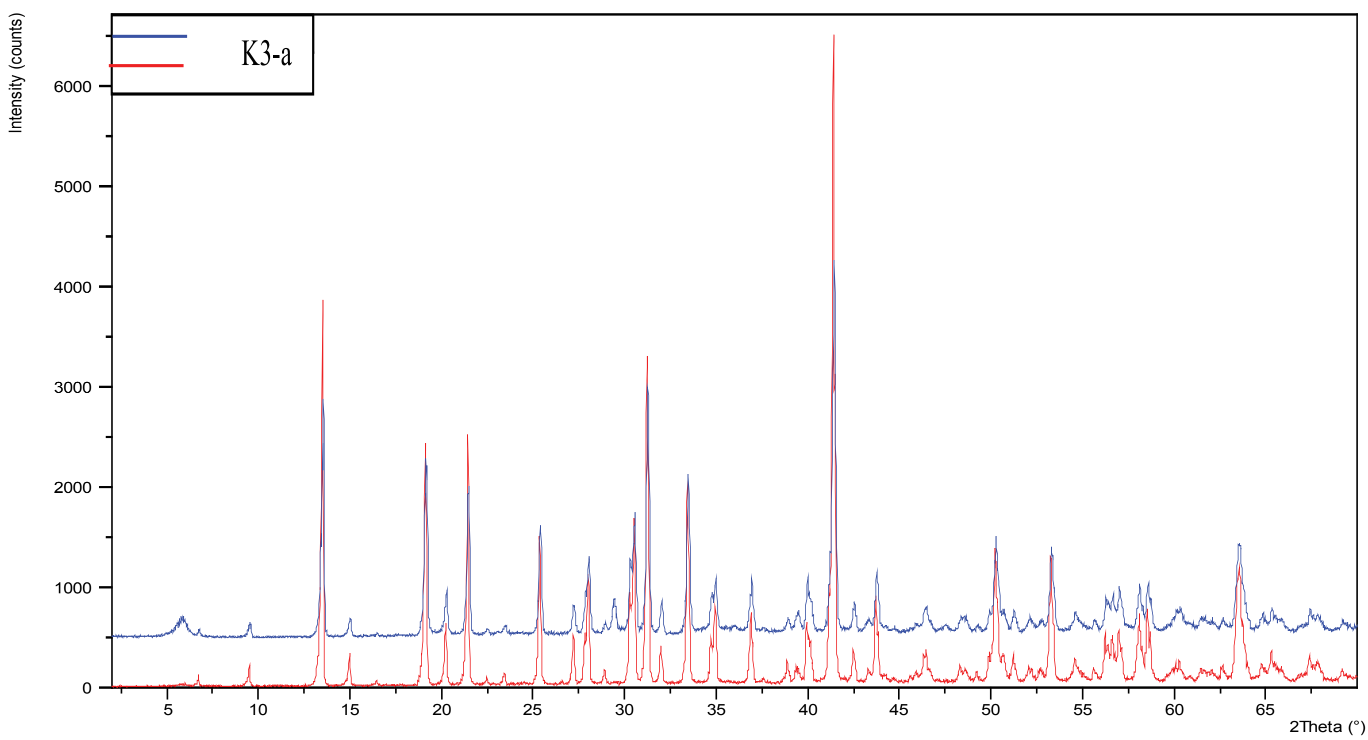

Figure 1: XRD Patterns for Thomsonite deposites.

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The Sudanese Standards and Metrology Organization (SSMO) in 1999 reported that the safe levels of these ions in drinking water are: Lead 7 ppb, Iron 300 ppb, Nickel 14 ppb.

When these are compared with the final concentration values obtained in the present study, it is found that Zeolite will be an excellent

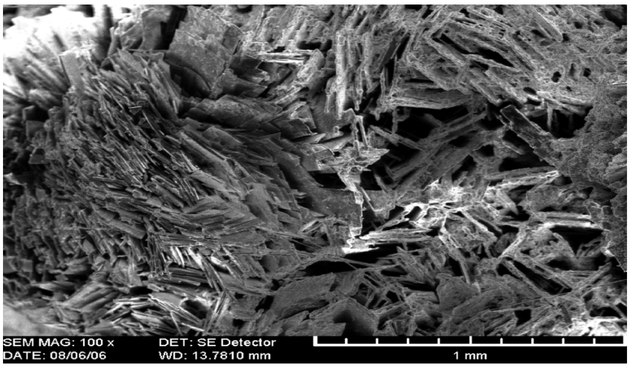

Figure 2: SEM image of Thomsonite.

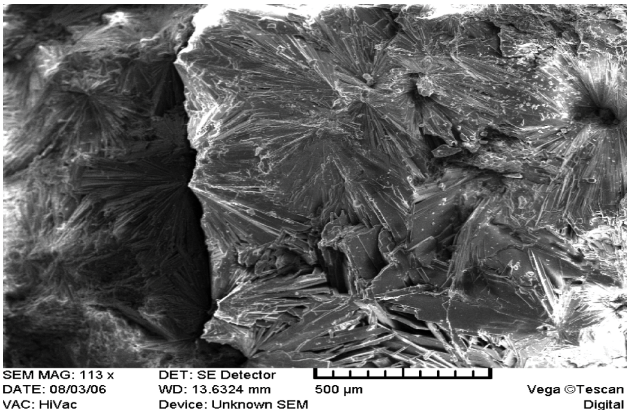

Figure 3: SEM image of Thomsonite.

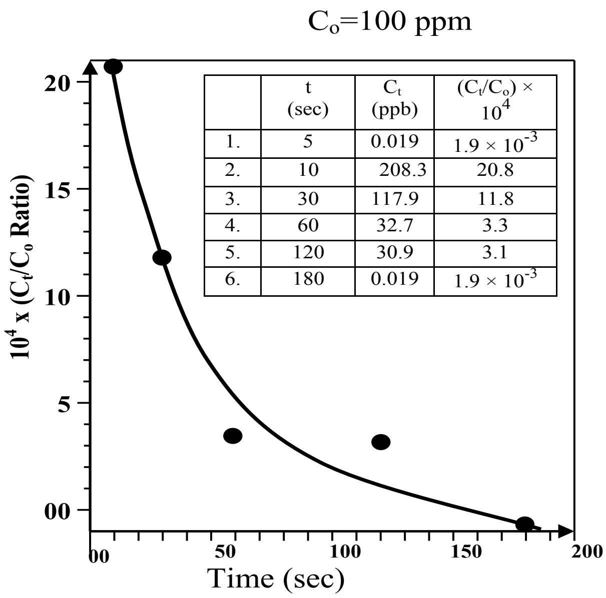

Figure 4: Effect of Retention Time On The Extraction of Pb^{2+} by Thomsonite.

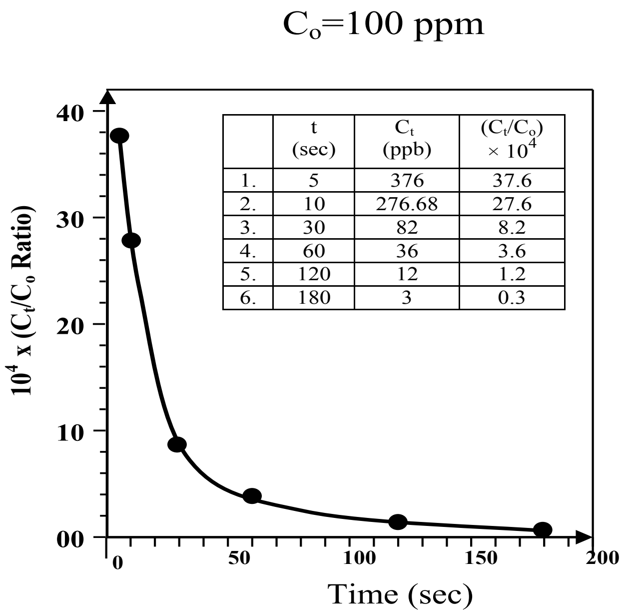

Figure 5: Effect of Retention Time on the Extraction of Fe^{3+} by Thomsonite.

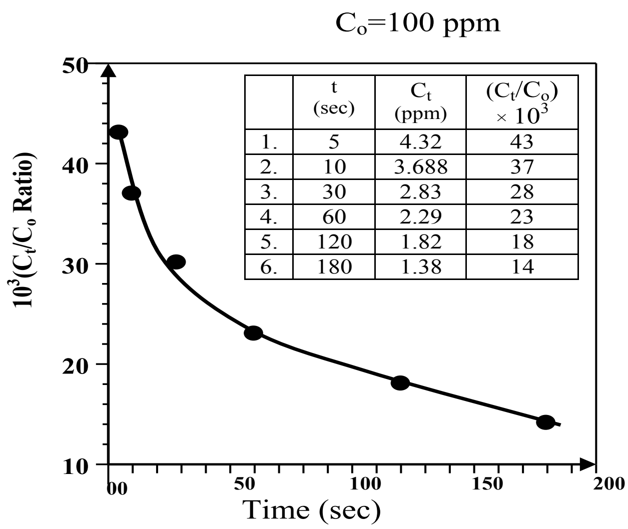

Figure 6: Effect of Retention Time on the Extraction of Ni^{2+} by Thomsonite.

medium for removing heavy metal ions from drinking water. This may not be said for (Ni^{2+}), for reasons that are not clear at present. The ion exchange selectivity for the three ions found in this study is:

Pb^{2+} > Fe^{3+} >Ni^{2+}

This is in excellent agreement with a study by that the ion exchange selectivity of various ions was reported that [13]:

Cs> **Pb** > **Fe** >Cu > Zn, Cd, Co> **Ni**> Mn > Cr

Conclusion

The Thomsonite samples collected from Wadkawly in Gadarif area, are found to provide an excellent medium for the extraction of heavy metal ions (Pb and Fe), reducing their concentration to levels that satisfy the Sudanese Standards. Nickel need more retention time for extraction. Na- Thomsonite would be suitable for purification of ground water. More studies are recommended to determine the extraction of other heavy metal ions. Thomsonite has been the Zeolite used in the present study, other Zeolite need to be studied.

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