Synthesis of Monolith Hydroxysodalite from Low Grade Kaolin and its Application as an Adsorbent for Lead

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ABSTRACT

Low grade kaolin is converted to monolith hydroxysodalite dihydrate by hydrothermal treatment with 10M NaOH solution i.e., higher Na concentration, Na/Si =1.3. The X-ray diffraction and infrared methods are used to determine the chemical formula of cured material which is $Na_8Al_6Si_6O_{24}(OH)_2.2H_2O$. The CEC values do not correlate with that of SSA values, where for uncured kaolin the CEC have increased from 6.52 to 89.13 meq/100g for the cured kaolin or synthetic hydroxysodalite; on the other hand, the SSA values have decreased from 87 to 10 m^2/g. An adsorption experiment shows that the expansion of the framework of hydroxysodalite is due to the replacement of Na^+ by Pb^{2+}; moreover, about 91% of Pb is effectively removed. To get optimum removal, the solution must be buffered to about pH=4.5.

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.$Na_8Al_6Si_6(OH)_2.2H_2O$:

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INTRODUCTION

Large quantities of low grade kaolin are available in Hussainiyat Formation/ western desert of Iraq (Fig. 1); and most of this kaolin is used for refractory industries. Kaolin is a ready source of Al and Si and is necessary for the synthesis of zeolites which are natural alumino-silicates with SiO_2 and Al_2O_3 ratio near unity (Woolard et al., 2000; Hassan et al., 2002).

Zeolites including hydroxysodalite have a wide range of materials of both natural and synthetic origins. Generally, the crystalline alumino-silicates have a three dimensional framework in which silicon and aluminum atoms are tetrahedrally coordinated with oxygen atoms (TO_4 tetrahedra, T=Al, Si), where each apical oxygen atom is shared with an adjacent tetrahedron (Hassan et al., 2002). Thus, the ratio O/T always equals 2 (Woolard et al., 2000).

The three dimensional framework gives the zeolites some peculiar properties, e.g. adsorption and catalytic ion exchange reactions, and molecular sieving which find variety of industrial applications. Zeolites can exist either as minerals found in natural sediments, volcanic and metamorphic rocks or as synthetic materials made by hydrothermal synthesis (Bonaccorsi and Provebio, 2004). The synthesized materials have a superior retention ability for alkali, alkaline earth and heavy metal ions; they have also the ability to sequester ions in lattice positions or within their networks of channels and voids; as such they are nearly perfect waste forms, where, the zeolite can host alkali, alkaline earth and a variety of higher valance cations (Grutzeck, 1999, 2004). However, hydroxysodalite is more stable for common use than other zeolite under wider range of pH conditions. Vucinic et al. (2003) reported that pure hydroxysodalite can be formed at $Na_2O/SiO_2=1$ and at low H_2O/Na_2O ratio. It forms with sodalite octahydrate a binary system of $Na_{6+x}(AlSiO_4)_6(OH)_x.nH_2O$ composition with 0=x=2 and 0<n<8.

The aim of this work is to investigate conversions of low grade kaolin which is of considerable quantity to the more economically hydroxysodalite in Hussainiyat Formation in the Iraqi western desert. It also aims to determine the efficiency of the product to remove a high toxic metal, i.e. Pb in aqueous waste products.

EXPERIMENTAL ASPECT

Hydroxysodalite Preparation:

Hydroxysodalite products is prepared by using 10g of Hussainiyat low grade kaolin powder (65μ) which is added to 50ml of 10M NaOH solution, and then heated to $150^{\circ}C$ for 24h in a teflon autoclave. The product is collected by filtration, washed with hot distilled water and dried at $80^{\circ}C$ for 24h.
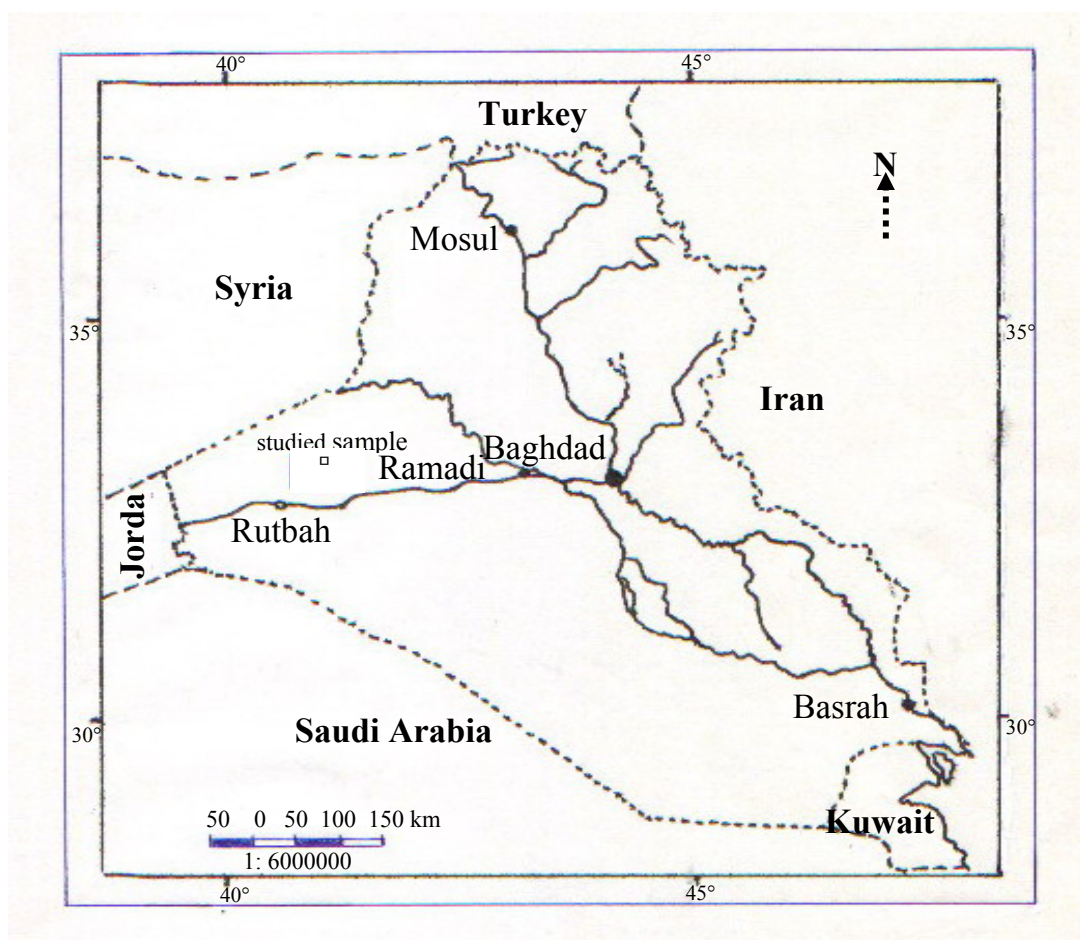
Fig. 1: Location of the studied sample, Hussainiyat Formation/ Iraqi western desert.

X-Ray Diffraction (XRD):

The collected samples are again washed with hot distilled water to remove any possible remaining NaOH prior to X-ray diffraction analysis. After drying, a diffraction pattern is obtained by using a Philips PW 1410 X-ray diffractometer; the apparatus is set at 40kV and 20mA using CuKα radiation (λ=1.541A$^{°}$). The JCPDS files are used to identify the resultant crystalline phase which is a monolithic hydroxysodalite (Fig. 2).

Cation Exchange Capacity (CEC):

CECs are determined following the procedure of Chapman (cited in Black et al.,1965). 4gms of low grade kaolin are shaken for 5min with 33ml of 1M sodium acetate followed by centrifuging. The shaking and centrifuging, are repeated three times. The precipitate is then shaken for 5min with 33ml of 50% ethanol three times for removing excess Na^{+}. Replacement of Na^{+} is then carried out with NH_4^{+} by shaking the precipitate three times with 33ml of 1M ammonium acetate. The sodium extracts are then collected, and analyzed for Na content by flame photometry using 410 Flame Photometer, provided by Sherwood Company.

Specific Surface Area (SSA):

SSA measurements are determined by using the procedure of Bower and Goertzen (1959 cited in Black et al., 1965). 5gms of the sample are treated with ethylene glycol (EG); the SSA is calculated using the following equation:

SSA= W$_g$. W$_s$/ 0.00031   where;

SSA: specific surface area (m^2/g)
W$_g$: wt. of ethylene glycol (gm) used.
 W$_s$: wt. of the sample (gm)
0.00031: amount of EG adsorbed per m^2

Infrared Spectroscopy Study:

   The infrared transmission spectrum of the solid sample is obtained by the KBr method. The spectrum was recorded on a Beckmann model 4250 spectrometer in region of 300 to 1800 cm^{-1}.

Lead Adsorption Experiments:

   The adsorption (or substitution) of lead by synthetic hydroxysodalite was carried out at different pH values and Pb concentrations using 0.5gm of cured material, which was shaken with 100 ml of 100, 300 and 500ppm of Pb^{2+} solutions. After 24h, the solid precipitate was separated from the solution by filtration. The concentration of lead in the filtrates was then determined by using Perkin-Elmer 503 Atomic Absorption Spectroph-otometer. However, adsorption (or substitution) was determined by the difference between the initial and the final concentration of lead in the filtrates.
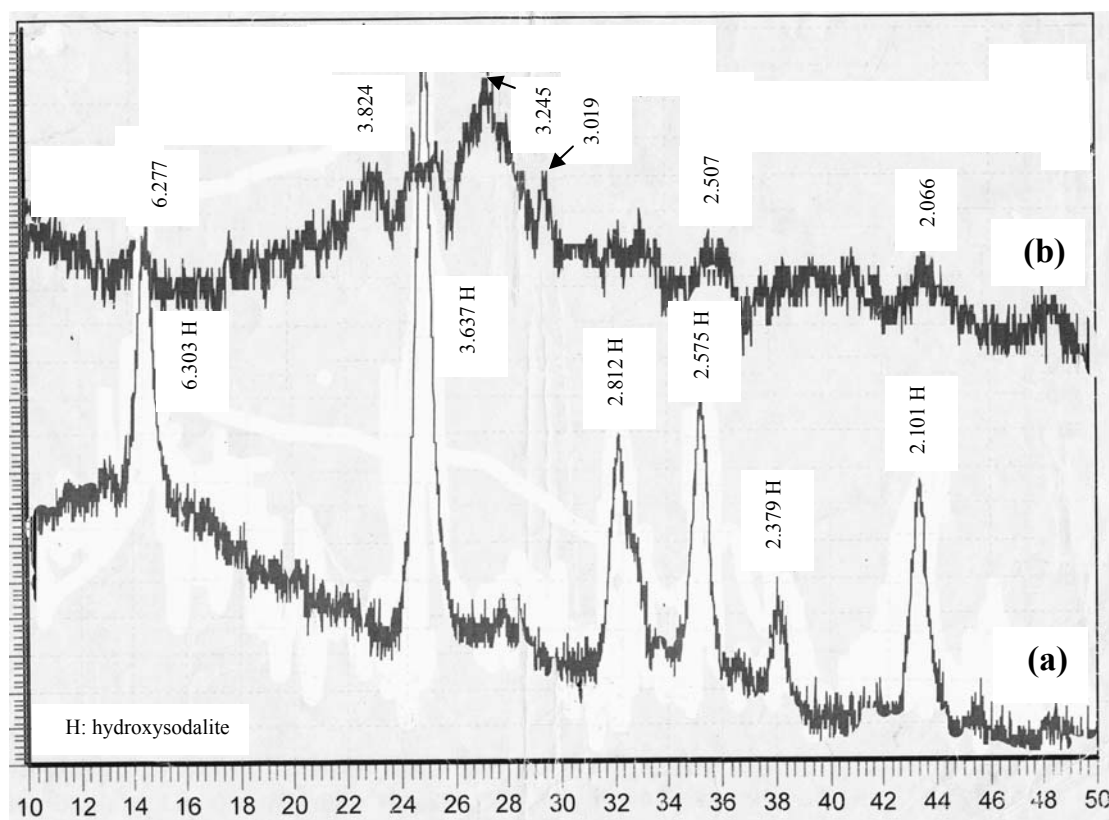

Fig. 2: XRD patterns of synthetic hydroxysodalite, (a) untreated hydroxysodalite (b) treated with 1000ppm of Pb^{2+} solution.

RESULTS AND DISCUSSION

The chemical analysis of the kaolin used as the starting material (untreated) and the cured material (treated) are shown in table 1. The mole ratios Na/Si and Si/Al for the cured material (prepared hydroxysodalite) are 1.318 and 1.031, respectively. The X-ray diffraction pattern for the hydrothermally treated kaolin is shown in Figure 2a. Only monolith phase of sodalite is identified at the most three intense peaks of (112), (110), and (114) reflections of d-spacing 3.629, 6.285 and 2.095A$^\circ$, respectively (Yamzin, 1978) as illustrated in table 2. According to the obtained chemical analysis (Table 1), X-ray diffraction and infrared data, the phase can be classified as hydroxysodalite dihydrate type of cubic system belonging to P43n space group with the chemical formula of $Na_8Al_6Si_6O_{24}(OH)_2.2H_2O$ and the a lattice parameter is 8.903A$^\circ$. The latter is plotted on Figure 3 to confirm the final chemical formula for the synthetic phase. The predicted angle Si-O-Al is equal to 139.5° (140-150° for zeolite).
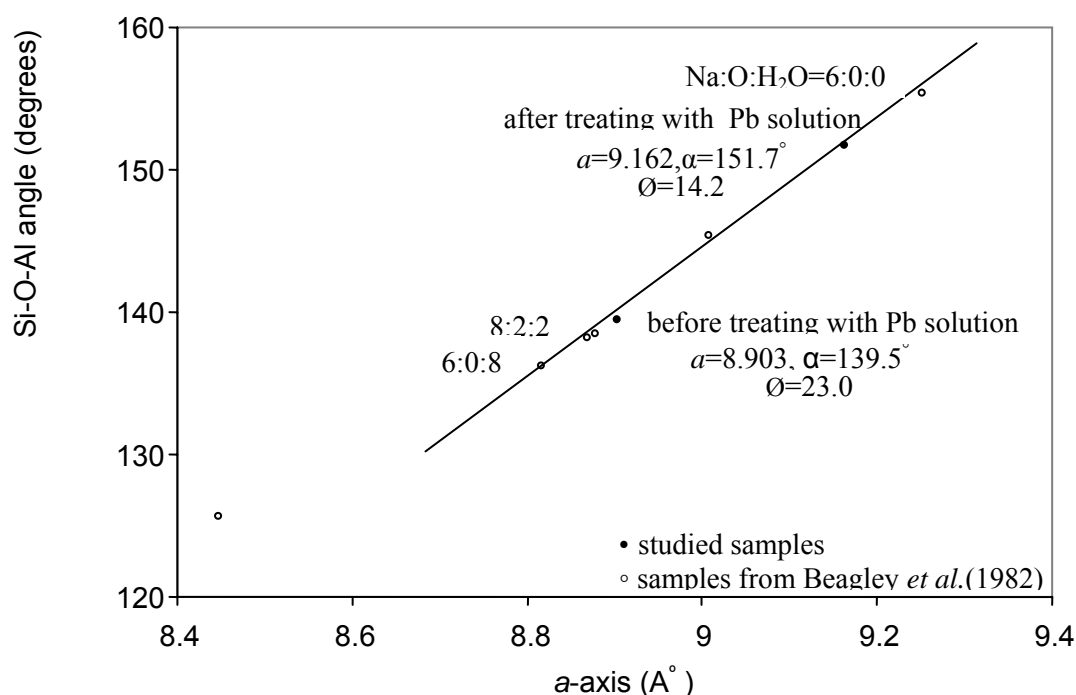

Fig. 3: Relationship between lattice parameter a and Si-O-Al angle for different kinds of sodalite (based on Beagley et al., 1982; Aswad, in preparation) and studied hydroxysodalite. Ø= the tilt angle in Figure 7.

Table 1: Chemical analysis of low grade kaolin sample (untreated) and synthetic hydroxysodalite (treated).

	Wt(%)									
	SiO$_2$	Fe$_2$O$_3$	Al$_2$O$_3$	TiO$_2$	CaO	MgO	Na$_2$O	K$_2$O	L.O.I	Total
untreated	.	.	.	.	.	.	.	.	.	95.85
treated	.	.	.	nil	nil	.	.	.	.	97.03

A systematic investigation has been carried out in the 300- 1800 cm^{-1} region, since it contains the fundamental vibrations of TO_4 tetrahedra. Interpretations of these spectra are based on the assignment of the infrared bands to certain structural groups in the various zeolite frameworks. Hence, this method is complementary to x-ray analysis. The infrared spectrum of the obtained zeolitic material is a result of the new crystal phase vibrations (Fig. 4). The band between 950- 1250 cm^{-1} confirms the tetrahedral coordination of aluminum in the zeolite framework. This band is the main asymmetric stretching vibration of the tetrahedra, the frequency of which decreases with increasing amount of Al in the tetrahedral sites of the alumino-silicate framework of the zeolite (Araujo et al., 1999; Vucinic et al..2003).
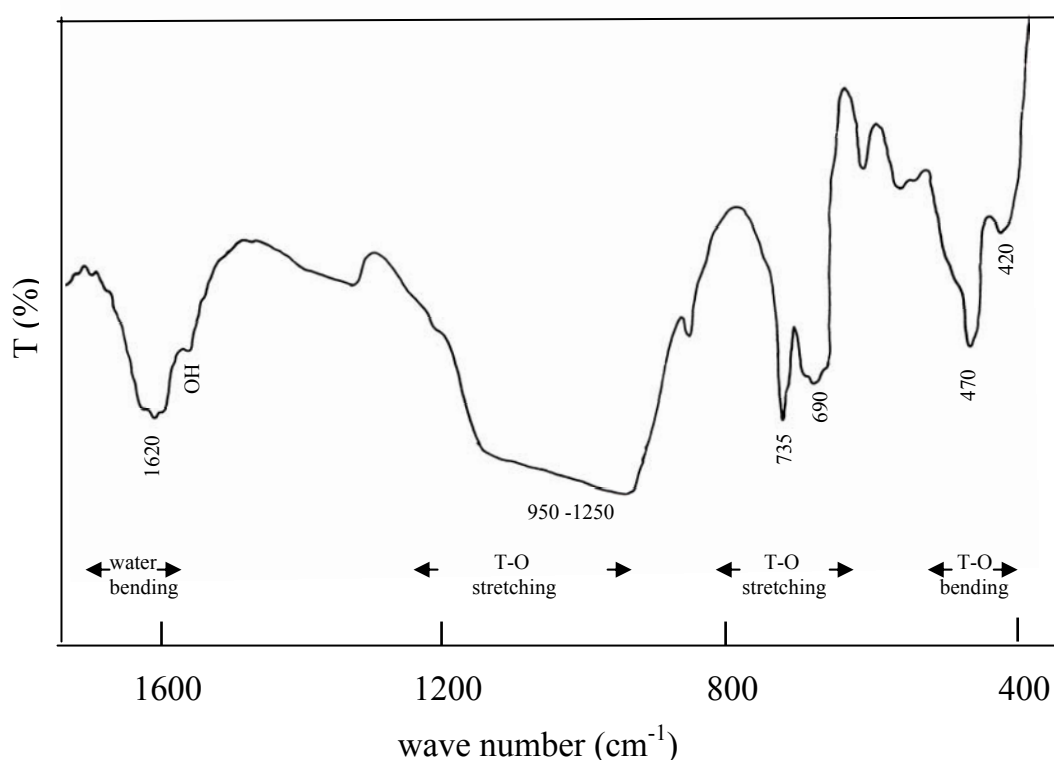

Fig. 4: Adsorption infrared spectrum of the prepared hydroxysodalite.

Table 2: Miller indices (hkl) and d-spacing reported by Yamzin (1978) and the present study for prepared hydroxysodalite.

hkl	(Yamzin,1978)		(present study)	
	d- published	intensity	d- observed	intensity
	.		.	
	.	.	.	.
	.	.	.	.
	.	.	.	.

	.	.	.	.
	.	.	.	.

Moreover, the shoulder in the 1150- 1200 cm^{-1} region in the pure zeolite spectra is the result of asymmetric stretching vibrations of external linkages of primary structural units. The band 470 cm^{-1} is assigned to T-O bending mode. Stretching modes involving mainly the tetrahedral atoms are assigned in the region of 650- 820 cm^{-1} (Araujo et al., 1999); these are sensitive to the Si-Al composition of the framework and may shift to a lower frequency with increasing number of tetrahedral Al atoms. The presence of the band at 1620 cm^{-1} (stretching vibration) is attributed to the both water and hydroxyl ion (OH) of hydroxysodalite.

Table 3 shows the cation exchange capacity and specific surface area of the low grade kaolin and the synthetic hydroxysodalite. The CEC values do not correlate with that of SSA values. The CEC for synthetic hydroxysodalite (prepared) is much higher than the unconverted kaolin but lower than those obtained by Chang and Shih (1998) (151 to 186 meq/100g) and the maximum of 300 meq/100g observed by Woolard et al. (2000). However, cation exchange capacity for hydroxysodalite which is restricted to room temperature may lead to low values (Singer and Bertgaut, 1995).

Table 3: Cation exchange capacity and specific surface area for low grade
kaolin (untreated) and synthetic hydroxysodalite (treated).

	SSA (m^2/g)	CEC (meq/100g)
untreated		.
treated		.

The rather high specific surface area of low grade kaolin compared with that of synthetic hydroxysodalite may be due to the kind of organic material (ethylene glycol) used in the measurement, which may prevent the molecules from penetrating the voids and channels, leading to lower values of SSA.

Table 4 and Figure 5 illustrate the relationship between Pb^{2+} and pH of the solutions before and after treatment with the hydroxysodalite. Figure 5 indicates that cured (treated) kaolin has the greatest affinity for lead at pH= 4.5. The ion exchange study were carried out without pH control in order to avoid the addition of a competing exchangeable cation. Table 4 shows the initial pH decreases with increasing of Pb concentration. The pH increases about twice after 24h. The higher percent of Pb exchange (91.2%) was at 100 ppm of Pb concentration in solution where pH is the higher (3.5).

The shape of the isotherms in Figure 6 suggests that the adsorption (substitution) behavior could be modeled by using the Langmuir isotherm.

$$q = \frac{KCN_{max}}{\text{------------}}$$ (Woolard et al., 2000)

$$1 + KC$$

where:

q: the amount per gram of solid Pb adsorbed

Pb in solution at equilibrium   C: the concentration of

K: the Langmuir adsorption constant

N_{max}: the total number of sites available for adsorption on the solid surface. Moreover, figure 6 illustrates the adsorption behavior of various modified samples which are pH dependent. It is obvious that in all cases the percentage of adsorbed lead increases as pH increases. This is likely to be via an ion-exchange mechanism, where the Pb^{2+} cations replace H^+ ions in the zeolite structure (Woolard et al., 2000):

$$\equiv Z\text{-}H + Pb^{2+} \quad \equiv Z\text{-}Pb^{2+} + H^+$$
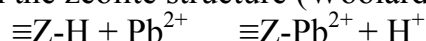
where $\equiv Z$- represent an exchange site in the zeolite framework. Furthermore the pH of the experiment does not exceed (6) because figure 6 contains a curve for the theoretical precipitation of amorphous $Pb(OH)_2$. This curve was based on the MINEQL+ program (Schecher and McAvoy, 1991 in Woolard et al., 2000) and in this study is included to determine whether the ion exchange of Pb has been taken place rather than adsorption. Figure 6 shows that the Pb is effectively removed by hydroxysodalite at pH<5

Table 4: Concentrations of added, resident and exchanged lead in the solutions and pH values before and after treatment.

	Pb conc. in solution (ppm)/log (C_{oA})	initial pH of (C_{oA})	pH after 24h of C_A	(ppm)/log (C_A)	(ppm)/log $(C_{oA}\text{-}C_A)$	Pb exchanged %
a	100/2.000	.	.	8.8/0.944	91.2/1.960	.
b	300/2.477	.	.	105/2.021	195/2.290	.
c	500/2.699	.	.	288/2.460	42.4/1.627	.

C_{oA}= Initial concentration of A (Pb cation).
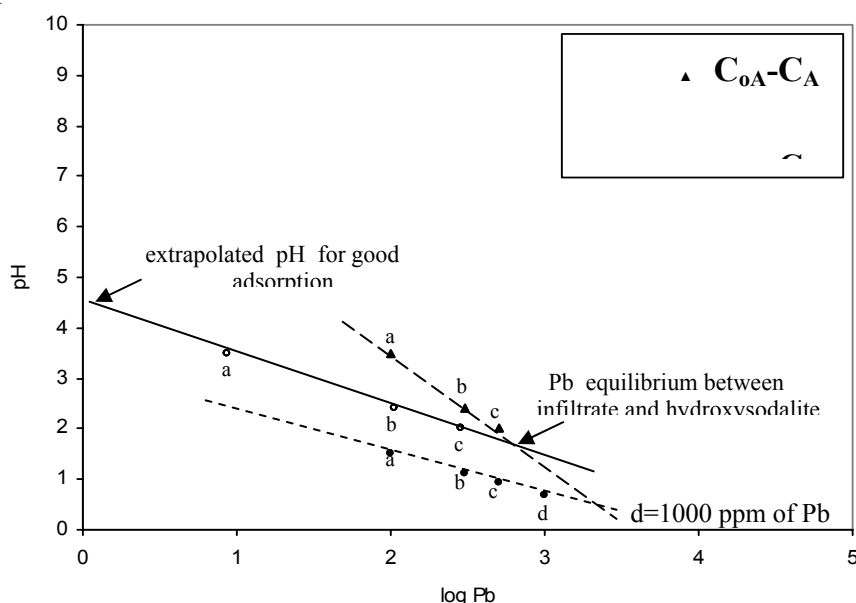
C_A= Equilibrium concentration of A.

Fig. 5: Relationship between pH and Pb concentration, and the condition of good adsorption (substitution). Data from Table 4.
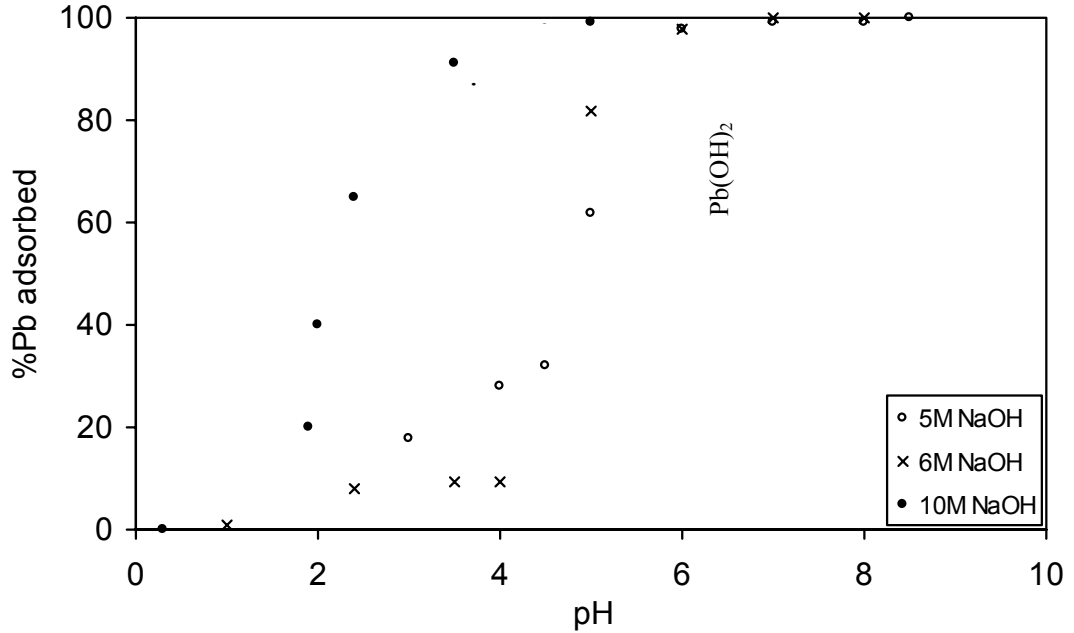

Fig. 6: Adsorption edges for the adsorption of Pb onto different treated samples as a function of pH (5M, 6M NaOH and $Pb(OH)_2$ from Woolard et al., 2000, and 10M NaOH for this study presented in table 4).

The study of XRD patterns of Pb treated hydroxysodalite (Figure 2b) with 1000 ppm of Pb^{2+} (as $PbCl_2$) shows shifting in the pattern and broadening of the peaks and a little increase in the background because of the emission. This may be due to the replacement of Pb^{2+} for H^+. It could also be attributed to the fact that the lead has higher scattering coefficient compared with sodium (about 7.5 times).

Consequently, this accounts for the difference in d-spacing and relative integrated intensity; but the crystal system is still cubic. The lattice parameter a expanded from 8.903A° to 9.162A°; this means that the framework of the phase has a partially collapsed structure. However, it becomes nearly fully expanded structure (Figure 7) after treating it with Pb^{2+} solution. Figure 3 also shows clearly that the tilt angle ø decreases (from 23.0° to 14.2°) and the Si-O-Al angle (α) increases (from 139.5° to 151.7°) due to the cavity ion increase in size (Na^+= 0.93 A°, Pb^{2+}= 1.20 A°).

The measured equilibrium data are plotted as ion exchange isotherm (Figure 8) reporting the equivalent fraction of the in-going cation A in the solid phase (X_{AZ}) as a function of the equivalent fraction of the same cation in solution (X_{AS}). The isotherm data were calculated by:

$$X_{AS}= C_A/C_{oA} \text{ and } X_{AZ}= (C_{oA}- C_A)/ CEC_{mz} \qquad \text{(de Barros et al.,2002)}$$

Where; C_A stands for the equilibrium concentration of cation A in the solution phase; C_{oA} stands for the initial concentration of A (Table 4) and CEC_{mz} is the cation exchange capacity of the hydroxysodalite (Table 3).
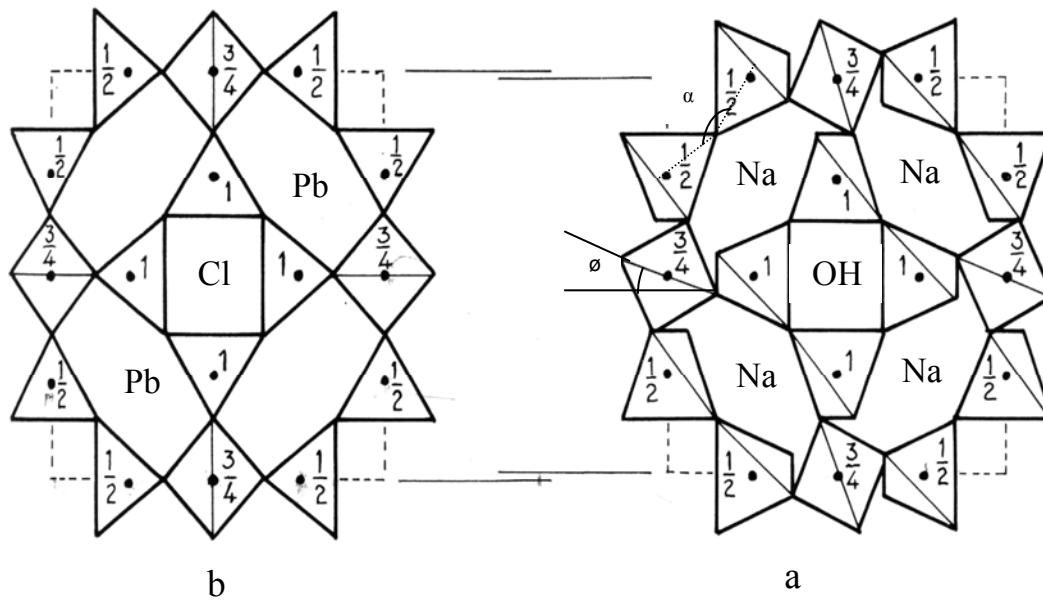

Fig. 7: Schematic diagrams for the partially-collapsed (a) and fully- expanded structure (b) of sodalite (modified after Taylor, 1972).
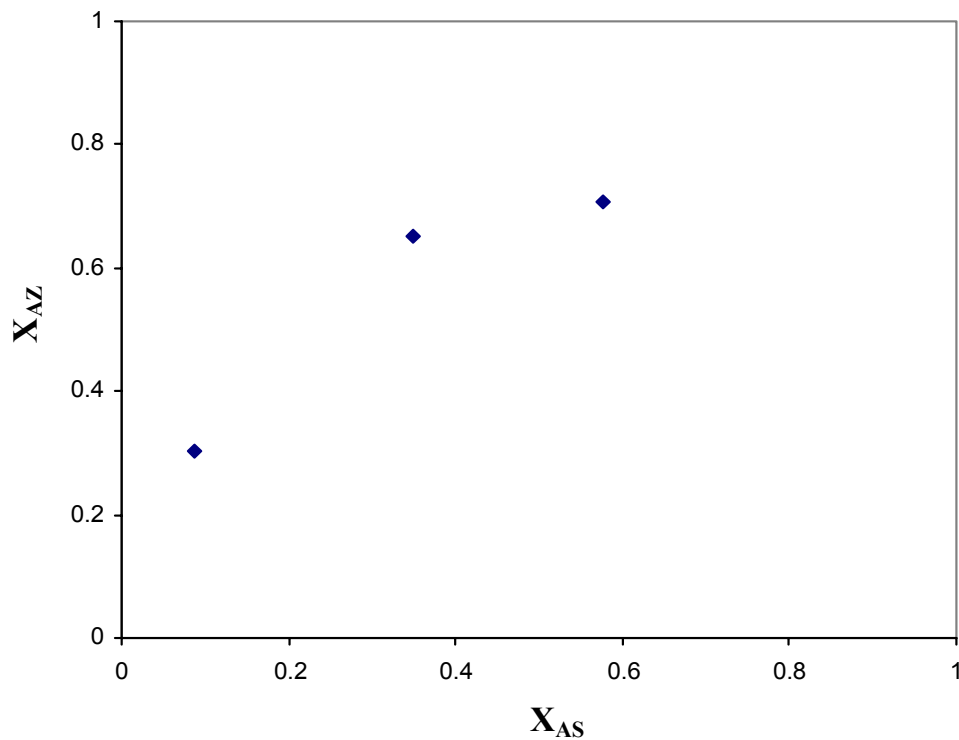
Fig. 8: Lead exchange isotherm on prepared hydroxysodalite.

This isotherm shows convexly upward curvature, because the hydroxysodalite is more selective towards the in-going cation A (Pb). The ion exchange isotherm shown in Figure 8 (the isotherm is failed to completion) is terminated slightly in value at about 70% which is related to the full occupancy of the β-cage. Therefore, it may be concluded that although the hydroxysodalite is very selective to Pb ions, the progress of exchange is limited by the diffusion of the large hydrated cation Pb through the cage apertures.

CONCLUSIONS
The hydrothermal treatment of low grade kaolin by high alkaline solutions with Na/Si mole ratio =1.3 results in a monolithic hydroxysodalite dihydrate which has been examined by X-ray diffraction and infrared spectra with the formula of $Na_8Al_6Si_6O_{24}(OH)_2.2H_2O$. The resultant modified kaolin or synthetic hydroxysodalite has a greater cation exchange capacity and lower specific surface area than the untreated kaolin.

The synthetic hydroxysodalite shows a greater adsorption (as substitution in the cages) of lead bearing solutions, in which about 91% of Pb is effectively removed at pH=3.5. Finally, the study shows that the Pb removal is pH dependant, and the efficiency of Pb removal from the solution increases as pH increases. Hence, to get optimum Pb removal the solution must be pH buffered, this might add a competing exchangeable cation provided by the buffering solution. Hydroxysodalite, however, could be used as alkaline internal buffer.

REFERENCES

Araujo,de,L.R.G., Cavalcante,Jr,C.L., Farias,K.M., Guedes,I., Sasaki,J.M., Freire, P.T.C., Melo,F.E.A. and Mendes-Filho,J.(1999) Synthesis of cubic Y zeolite using a pulsed microwave heating system, *Minerals Research*,Vol.2, No.2, pp.105-109.

Beagley,B., Henderson,C.M.B. and Taylor,D.(1982) The crystal structures of aluminosilicate-sodolite: X-ray diffraction studies and computer modeling, *Mineralogical Magazine*,Vol.46, pp.459-464.

Black,C.A., Evans,D.D., White,J.L., Ensminger,L.E. and Clark,F.E.(1965) Methods of soil analysis, chemical and microbiological properties, Part 2, *Amer. Soc. of Agronomy*, USA, 1571p.

Bonaccorsi,L. and Proverbio,E.(2004) Hydrothermal synthesis of zeolite LTA by microwave irradiation, *Mat. Res. Innovat.*, Vol.8, No.1, pp.53-57.

Chang,H.L. and Shih,W.H.(1998) A general method for the conversion of fly ash into zeolites as ion exchangers for cesium, *Ind. Eng. Chem.Res.*, Vol.37, pp.71-78. de Barros,M.A., Zola,A.S., Arroyo,P.A., Sousa-Aguiar,E.F. and Tavares,C.R. (2002) Equilibrium and ion exchange studies of Cr^{3+} on zeolites NaA and NaX, *Maringa*, Vol. 24, No. 6, pp. 1619-1625.

Grutzeck,M.(2004) Physical, chemical and structural evolution of zeolite- containing waste forms produced from metakiolinite and calcined HLW, *Env. Manag. Sci. Program*, Project no.65366.

Hassan,M.S., Ismail,I.S. and Ibrahim,I.A.(2002) Synthesis of zeolite Al Na from low grade Kalabsha kaolin, *Erzmetall*, Vol 55, No.9.

Singer,A. and Berkgaut,V.(1995) Cation exchange properties of hydrother- mally treated coal fly ash, *Envi. Sci. Tech.*, Vol.29, pp.1748-1753 .

Vucinic,D., Miljanovic,I., Rosic,A. and Lazic P.(2003) Effect of Na_2O/SiO_2 mole ratio on the crystal type of zeolite synthesized from coal fly ash, *J. Serb. Chem. Soc.*, Vol.68, No.6, pp.471-478.

Woolard,C.D., Petrus,K. and Horst,M.(2000) The use of modified fly ash as an adsorbent for lead, *Water S.A.*, Vol.26, No.4, pp.53-536 .

Yamzin,E.A.(1978) Kristallogr., *Soviet Physc. Cryst.*, Vol.23, pp.27-29.