# Synthesis of sodalite from sepiolite by alkali fusion method and its application to remove $Fe^{3+}$, $Cr^{3+}$, and $Cd^{2+}$ from aqueous solutions

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## Abstract

The potential for pure zeolite formation was investigated by using sepiolite as starting material via alkaline fusion method followed by hydrothermal process. NaOH and KOH as activators were chosen for mixing with staring material at 650°C to prepare fused primary alkaline mixture. The fusion step was followed by a hydrothermal process which was performed at determined temperatures of 100, 140, 180, 220°C. Pure sodalite was obtained through synthesis experiments by application of NaOH, and KOH activators, at 140 and 180°C and reaction times of 48 and 72 hours. The XRD, SEM and FT-IR analyses were used to characterize the pure phase. Subsequently, a series of batch experiments were determined to evaluate the pure sodalite capability to remove $Fe^{3+}$, $Cr^{3+}$, and $Cd^{2+}$ from aqueous solutions. The results obtained through these adsorption experiments demonstrated that the optimum adsorption of $Fe^{3+}$ and $Cr^{3+}$ gained at the presence of 0.001M also 0.01M solutions and that of $Cd^{2+}$ under the influence of 0.1M solutions. In this regard the maximum adsorption amount through applying 0.001M solutions, has been occurred from 1 to 2 hours for pure sodalite 1 and from 30 minutes to 1 hour for pure sodalite 2. Whereas, by the usage of 0.01M and 0.1M solutions, the most adsorption obtained from 30 minutes to 1 hour, for applying pure sodalite 1 as well as using pure sodalite 2.

## Introduction

Sodalite, $Na_8Al_6Si_6O_{24}Cl_2$, is sodium an aluminosilicate with isometric crystal system having three-dimensional structure consisting of β-cages as polyhedral structural units [Li et al., 2015; Rabiller et al., 2004). This mineral is a zeolite with six-membered ring aperture framework

structure with a pore size of 2.8Å (Jiang et al., 2012). The six membered rings define a series of tunnels whose intersections lead to formation of large cavities which are occupied by chloride ions coordinated with sodium ions (Rabiller et al., 2004). This mineral has drawn scientists' attention to focus on its potential applications such as optical material (Arieli et al., 2004), adsorption and ion exchange (Mirfendereski & Mohammadi, 2011), catalyst support (Ogura et al., 2008) arisen from small pore sizes and high ion exchange capacity (Sari et al., 2018). Accordingly, numerous studies have been widely performed on the synthesis of this microporous zeolite. Scientists (Sari et al., 2018), investigated direct synthesis of sodalite from kaolinite. In this study, the synthesis was done by stirring for 6 hours, without aging, and crystallization time was 24 hours under hydrothermal method (100 °C). In this regard, some scientists (Li et al., 2015), studied synthesis of the pure sodalite with ball morphology from alkali fused kaolinite. Pure sodalite crystals were synthesized in their study under hydrothermal reactions, and after aging at room temperature. The controllable synthesis of submicron sodalite crystal from palygorskite clay also was studied using a two step-approach (Jiang et al., 2012). In this regard, zeolite materials synthesized by earlier researchers are collected in Table 1.

Using clay minerals as natural sources of alumina-silica for synthesis of zeolites is profitable due to their low price and availability. Sepiolite clay with ideal theoretical structural formula of $Mg_8Si_{12}O_{30}(OH)_4(OH_2)_4.8H_2O$ is a trioctahedral phyllosilicate in which the octahedral sites have been occupied by Mg (Brauner & Presinger, 1956; Inagaki et al., 1990). Naturally, sepiolite is considered as an end member of the palygorskite-sepiolite group of minerals with layer ribbon structures which can be classified as intermediates between the chain/ribbon structures of pyroxene and amphiboles and the layer structures of smectites (Velde, 1985; Jones & Galán., 1988). The stability of the palygorskite-sepiolite mineral group was investigated under laboratory conditions, as well. Such studies show that these fibrous minerals directly transform to other clay minerals namely smectite under the laboratory conditions, like treatment of 100mg of palygorskite with 1mmol of NaOH solution at 150°C for 24 hours which yielded smectite (Golden et al., 1985).

Industrial activities, hazardous chemical substances such as heavy metals or organic compound give rise to pollution in the environment and lead to some ecosystems drastic deterioration. Among the other types of pollution, the contamination of heavy metals causes serious health problems since they are accumulated in living tissues and affect food chain (Volesky, 1990). In this regard, iron is among metals which give rise the widest damage to the environment, since excessive amount of $Fe^{3+}$ in public water supplies causes turbidity, an unpleasant taste and odour and its supporting role for the growth of iron bacteria subsequently leads to the clogging pipes and increasing the flow characteristics (Ostroski et al., 2007). Chromium is one of the toxic heavy metals whose trivalent form, $Cr^{3+}$, is chiefly found in natural environments and its compounds are largely bound to floating particles in water and has a monumental influence upon drinking water quality. In the case of toxicity, Chromium (III) is retained to a greater extent in lungs than is chromium (IV) (Edel & Sabbioni, 1985) and Chromium compounds identified to increase the risk of bronchiogenic cancer, which is well documented in chromate workers (Tandon, 1982). Cadmium is one of the most toxic metals even in low concentration. It is frequently formed waste streams discharging from metallurgical alloying, ceramics and sewage sludge and its toxicity leads to disorders such as lung cancer, anemia, skin,

pulmonary edema, brain damage, bone as well as heart diseases (Voegelin and Kretzschmar, 2003; Tsang and Lo, 2006; Mohan et al., 2005; Deng and Ting, 2005).

Chemical precipitation and filtration, solvent extraction, reverse osmosis and, chemical oxidation or reduction are traditionally used to clean up wastewaters (Volesky, 2001). Nowadays, ion exchange is widely investigated in several studies as profitable process for treatment of metal bearing effluents. Among materials applied for this objective, zeolites play momentous role, which have three-dimensional open microporous structures consisting of aluminum, silicon and oxygen with regular arrangement of $SiO_4^-$ and $AlO_4^-$ tetrahedral units forming tunnels, channels and cavities whose intersections form regular pores (Zaarour et al.,2014; Shirani Lapari et al., 2015). This regular arrangement causes them to have negative charge balanced with cations such as $Na^+$, $K^+$, $Ca^{2+}$ or $Mg^{2+}$ and have numerous applications like acting as molecular sieves in separation of gases; using as catalyst for chemical reactions (Pal et al., 2013), and having high thermal stability and high adsorption capacity due to their large surface area (Stein, 1992).

Synthesis of zeolites is a promising field of interest since synthetic zeolites have shown significant environmental and industrial applications due to their well-adjusted properties than the natural zeolites enabling them to remove various contaminants with wide range of molecular sizes from wastewaters (Wang, 2012; Li et al., 2015). Various types of zeolites with different systems of channels can be obtained through synthesis reactions defined according to different laboratory synthesis techniques which are determined considering various influential parameters. In the present research, the authors proposed Alkaline fusion approach as a tentative technique for the formation of pure zeolites and determined effective parameter of time and activator type through application of NaOH and KOH activators with defined concentrations. The main reason for applying sepiolite as primary material in this study was to investigate its ability to produce zeolites specifically pure phases of zeolite that could be considered as one of its industrial and environmental applications. The efficiency of synthesized sodalites for $Fe^{3+}$, $Cr^{3+}$, and $Cd^{2+}$ ions removal from wastewater was evaluated, in the current work, through establishing the batch type adsorption experiments taking the advantages of artificially made monometallic solutions.


**Materials and method**

*Materials*

Sepiolite used as starting material in this research, was sampled from Eeliato Sepiolite Mine a Pliocene–Quaternary sepiolite deposit located at Fariman County, NE Iran. The activators applied in this study were sodium hydroxide, NaOH, as pellets (97.5%, BDH Laboratory Supplies GPR and 98%, Merck Index-No. 011-002-00-6) and potassium hydroxide, KOH, in the form of pellets (97%, BDH Laboratory Supplies, AnalaR and extra pure, Merck EC-Index-N.019-002-00-8) and Aluminum Chloride, $AlCl_3.6H_2O$, (BDH Laboratory Supplies, GPR, and extra pure, Merck EG-Nr. /EC-No.201-705-8) which was used to control the $SiO_2/Al_2O_3$ ratio in the synthesis process. The adsorption experiments were conducted by the application of $FeCl_3$, Ferric Chloride anhydrous (Iron (III) Chloride), (Ferrous Chloride 96%, BDH Limited Poole England); $CrCl_3.6H_2O$, Chromium (III) chloride hexahydrate, (98.0%≥, Aldrich); and Cadmium Chloride $CdCl_2.xH_2O$, (98.0%, Aldrich) which used for artificial heavy metals polluted aqueous solutions.

*Starting material preparation for synthesis step*

Powdered sepiolite was ground and sieved to size <200 mesh and particles of <~75μm were selected for synthesis experiments. With this regard, NaOH and KOH pellets were powdered and then added to powdered starting material (starting material/alkaline activator in 1:1.2 weight proportion) then put in a temperature controlled furnace to prepare a fused primary material. Meanwhile, (1, 2, 3 N) aluminum chloride solutions used to control $SiO_2/Al_2O_3$ ratio were prepared through dissolving $AlCl_3.6H_2O$ in distilled water by using standard purification methods.

## Methods

Starting and synthetic materials were characterized using standard methods of phase and morphology determination.

*Characterization methods*

*X-ray fluorescence spectrometry:* The bulk chemical composition of the initial material, sepiolite, was evaluated by using XRF, PANalytical Energy-dispersive (PANanalytical Epsilon 3XL) with operating ambient temperature of 5-35° C; Tube settings: Software controlled, max. voltage 50kV, max. 3mA; Electrical specifications: main supply voltage: 90-264 V; Frequency: 47-63 Hz; power consumption: 250 VA; HT generator power: Max. 15 W. In this technique, 10mg of powdered primary material put in a sample cup to carry out the elemental analysis.

*X-ray powder diffraction:* The crystalline structure of both starting material and synthetic products and their precise mineralogy was determined by XRD (PANalytical Empyrean, multipurpose X-ray diffractometer. Data collection was carried out with continuous scanning type; Measurement Temperature [°C]: 25.00; Ratio: 0.50000; Generator Settings: 40 mA, 40 kV; Minimum step size: 2Theta:0.0001; Minimum step size Omega:0.0001; Start Position [°2Th.]:5.0064; End Position [°2Th.]: 79.9904. In this method studied materials were ground to powder form (<5μm) and mounted in aluminum plate sample holders.

*Scanning Electron Microscopy:* The morphology of the raw material and synthetic products was characterized using the instrument Scanning Electron Microscope (SEM) (ZEISS EVO50) under the analytical conditions as following magnification**:** 5 to 1,000,000x; field of view: 6mm at Analytical Working Distance (AWD); 35° take-off angle; EHT: 20.00 kV; Signal A: VPSE, WD: 8.5mm; Image Processing: Resolution: up to $3072 \times 2304$ pixel. In this technique, specimens were prepared by spraying dried raw material or products powder onto aluminum stubs applying double-sided adhesive carbon discs.

*Fourier Transform Infrared spectroscopy*: The framework quality of the starting material and synthetic products was identified by the application of Fourier Transform Infrared spectrometer using a Bruker Alpha FT-IR, which was used in transmission. Standard KBr beam splitter $500 – 6,000$ cm$^{-1}$, Signal - to- noise ratio: typically, >50,000:1 (1 min measurement time, spectral resolution 4 cm$^{-1}$). Samples were analyzed in the region of 4000-400 cm$^{-1}$ as powdered form (particle size < 5μm) and were placed onto the diamond ATR crystal surface. Then a force applied to the sample with the usage of one finger clamp mechanism for spectrum collection.

*ICP-OE spectrometry:* The heavy metal cationic concentration in the final leachates was detected using an Inductively Coupled Plasma-Optical Emission Spectrometer, Agilent 5100 ICP-

OES, with 167 to 785nm wavelength range; Robust, solid-state 27MHz RF generator; 400mm focal length thermostatted to +35°C, Mass Flow controlled polychromator purge; plasma gas, auxiliary gas; Vertically oriented torch gives high matrix capability. The standard solutions for metal analysis were prepared to determine the amount of $Fe^{3+}$, $Cr^{3+}$, and $Cd^{2+}$ ion concentrations. The leachate sample volume was 10ml in 15ml centrifuge vial provided for ICP-OES analysis.

*Synthesis method*

*Alkaline fusion method:* Alkaline fusion method was applied prior to the hydrothermal treatment because of its critical role in enhancing hydrothermal conditions for dissolving aluminosilicates as well as the synthesis of zeolites (Ríos et al., 2009). Moreover, in this procedure, some of the inert crystalline phases in the raw materials can fully react and products of the fusion can be highly pure up to 100%. In these sets of experiments which were performed in the chemistry laboratory of the school of applied sciences, University of Wolverhampton, powdered alkaline reagents (sodium hydroxide, potassium hydroxide), were added to powdered raw material to act as activator agents during the fusion process and provide a fused mixture. For more explanation, at first, 6 g of powdered sepiolite as the primary material was dry mixed with powdered NaOH or KOH (raw material/alkaline activator in 1:1.2 weight proportion) and the resulting mixture was put in a ceramic crucible and fused at 650°C for 90 minutes in a temperature controlled furnace. Then, the fused product was ground by a ceramic mortar and pestle and then prepared powder was dissolved in distilled water for 30 minutes under stirring conditions then stirred for another 30 minutes when aluminum chloride solution added to the mixture to form the homogeneous precursor. Then the result mixture was poured in an autoclave and put in oven for determined period of time, 24, 48, 72 and 96 hours, at temperatures of 100, 140, 180 and 220°C. subsequently after the certain period of time, the autoclave remove from the oven then the inside mixture was filtered with a filter paper then rinsed several times with distilled water. Then the mixture dried at 80 °C, overnight and was powdered and prepared for further characterizations. Flowchart regarding process of primary material conversion into synthesis products has been presented in Fig. 1.

*Batch type adsorptive experiments*

A series of batch adsorption experiments were carried out for adsorptive properties evaluation of synthesized sodalities. In this regard, the adsorption characteristics of sodalities was investigated through using 0.001, 0.01 and 0.001M heavy metals, Fe, Cr, and Cd solutions within determined various contact time, 1, 2, 4, 8, 12, and 24 hours. In this adsorptive experiments contact time and initial concentration were the influential parameters to scrutinize their impact on the synthesized sodalite adsorption efficiency. The percentage of these heavy metals removal was measured via the equation (1)

$$Removal\% = (C0 - Ce) \times 100/C0 \qquad\qquad (1)$$

Where, Ce (mg/L) and C0 (mg/L) are equilibrium concentration and initial concentration of adsorbate in the solution, respectively.

**Results**

The mineral phases in sepiolite clay are exactly dependent on its original bulk chemical composition. So, the bulk chemical composition of the primary material was characterized by using XRF (Table 2).

*Alkaline fusion products synthesized by the application of NaOH activator*

Products formed through the alkaline fusion method with application of NaOH activator are listed in Table 3.

*Alkaline fusion products formed by the usage of KOH activator*

Some synthetic phases which have been produced through alkaline fusion method with KOH activator are listed in Table 4.

The pure zeolite phases and primary material were characterized using XRD, X-ray diffractometer analysis, and obtained XRD patterns of natural raw material, sepiolite, and pure sodalities representing their mineral compositions are shown in Fig. 2.

The SEM images (Fig. 3) illustrate the morphology of various phases of this experiment including sepiolite, which is applied in the present research as raw material, and pure synthesized zeolite phases both sodalite formed with application of NaOH and that synthesized under the effect of KOH activators.

Infrared spectra for sepiolite as starting material, and those of pure sodalite phases obtained in current research are presented in Fig. 4.

Batch experiments results including adsorption percentages as well as selectivity orders for Fe, Cr, and cd removal (Table 5 & 6) and graphs regarding removal percentage of $Fe^{3+}$, $Cr^{3+}$, and $Ni^{2+}$ from monometallic solutions (Figs. 5, 6 & 7), presented in the following.

**Discussion**

Zeolites are usually synthesized in the presence of an amorphous gel phase. The solubility of this gel phase depends on the alkalinity. Moreover, the alkalinity is the one of the most important parameters for controlling the crystallization of zeolites and determines their compositions. It is also responsible for the type of crystallizing products (Robson, 1998). Therefore, zeolite synthesis typically occurs in an alkaline medium and accordingly, most synthesis studies focus on the alkaline environment.

*Investigation on alkaline fusion products*

Experimental studies in this research defined using alkaline fusion approach by the application of NaOH in powder form. According to Table 2, sodalite (pure phase) synthesized using 7.72g powdered NaOH, at 140°C.

XRD patterns regarding pure products (Fig. 2) demonstrated no impurity peaks in samples synthesized at both 140 and 180°C, under the effect of NaOH and KOH activators for time durations of 48 and 72 hours, respectively. Accordingly, sodalite can be synthesized in the

presence of low to medium amount of NaOH powder, 7.32-7.72g in the fused reaction gel, at 100-220°C. This can reveal the influence of alkaline environment in zeolite formation and alkalinity of the reaction medium was proven to be an important parameter affecting the synthesis of sodalite (Sari et al., 2018). Meanwhile, from the theoretical point of view, higher alkalinity condition, there would be a high concentration of OH⁻ in the experimental environment. If there is a high concentration of OH⁻ in experimental condition, more Si and Al will be dissolved. Subsequently, if more Si and Al are dissolved, there would be a less possibility for zeolite crystallization. In this case, because high level of alkalinity causes low stability of Si-Al bonds in an aluminosilicate framework and high solubility of Si and Al, there would be a small yield of the synthesized product and sodalite was not crystallized in high alkaline condition and in the presence of high OH. In an experiment with regard to the synthesis of sodalite (Lou et al. 2016), synthesized sodalite through alkali fusion method followed by a desilisication-hydrothermal process using fly ash as starting material. According to their results, sodalite with high crystallinity was prepared at the basicity of 2mol/L, crystallization duration of 12 hours, and crystallization temperature of 90°C.

In this regard, KOH was also used in this study as an activator in the fusion method to provide fused reaction gel and evaluate the possibility of zeolite formation in the presence of KOH activator. In this case, sodalite (pure phase) formed by the application of 9.2g KOH, at 180°C. Regarding the results, temperature in alkaline fusion step may be also an effective parameter with regard to pure phase formation. Fusion step causes raw materials to fully react with alkaline activator then this enhancement of primary material's reactivity results in obtaining products that can be highly pure up to 100%. In the presence of KOH activator, in this research, sodalite was formed as a pure phase, at 180°C, for time duration of 72 hours. To understand sodalite formation in the aforementioned conditions and considering the ideal composition of sodalite which can be shown as $Na_8[AlSiO_4]_6(ClO_4)_2$ (Borhade et al., 2012), sodium is the main exchangeable cation in sodalite structure balancing the charge of the aluminosilicate lattice (Franus et al., 2014). In this case, if another cation like $K^+$ would be present in its formation environment, its formula will be defined as for example $Na_{3.2}K_{4.8}[AlSiO_4]_6(ClO_4)_2$. In this regard, scientists (Borhade et al., 2012) performed a study on the synthesis of perchlorate enclathrated sodalite with aluminogermanate host framework through hydrothermal synthesis. They used a mixed gel of $NaAlO_2$, as a source for aluminum, and germanium oxide, as a source of germanium, along with sodium hydroxide and they kept them in an oven at 373K for 5 days in a Teflon autoclave. Subsequently, they applied aqueous cation exchange method [Eiden-Assmann, 2002] to produce a sodium, potassium and silver perchlorate sodalite.

The SEM images, in the present study, showed fiber bunches of sepiolite as primary material (Fig. 3a) with an intermediate length of fibers (according to the fiber length classification (Del Río et al., 2011), and morphology of synthesized products produced by using different activators NaOH (Fig. 3b) and KOH (Fig. 3c). In this regard, via an experimental study (Franus et al., 2014), the sodalite crystals appear in spherical form like zeolites formed through hydrothermal process from fly ash used as primary material. In their research, pure sodalite phase was formed in spherical shape similar to desert roses. Moreover, through another research (Li et al., 2015), sodalite with rhombic dodecahedron particles having smooth surfaces was reported to form from alkaline fused kaolinite. furthermore, scientists (Shirani Lapari., et al 2015) who investigated the influence of different types of organic structures like organosilane on formation of mesoporous sodalite

reported formation of sodalite with regular spherical morphology out of aluminum-silicate mixture prepared by mixing fumed silica and $NaAlO_2$ with NaOH alkaline solutions through hydrothermal synthesis.

In the present research, Fourier Transform Infrared Spectroscopy spectrum of pure sodalite synthesized at presence of NaOH activator, (Fig. 4a), revealed absorption bands at 430 and 462 $cm^{-1}$ wavenumbers which were ascribed to O-T-O bending vibration. The bands observed at 668, 712 and almost 735 $cm^{-1}$ were attributed to T-O-T (T=Si, Al) symmetric stretching vibration, while the absorption band at 963 $cm^{-1}$ was assigned to asymmetric stretching vibration. In this regard, the characteristic band of sodalite at wavenumber of 997 $cm^{-1}$ was assigned to the T-O-T asymmetric stretching (T=Si, Al) (Inada et al., 2005), adsorption bands at wavenumbers of 715 and 657 $cm^{-1}$ were attributed to the T-O-T symmetric stretch, and those at 459 and 430 $cm^{-1}$ were related to bending vibration of O-T-O and the bending vibration of single four-membered ring of sodalite, respectively (Inada et al., 2005).

Infrared spectrum of pure sodalite synthesized at presence of KOH activator in the present study (Fig. 4b) revealed absorption bands at 432 and almost 463 $cm^{-1}$ which were related to O-T-O bending vibrations. Furthermore, adsorption bands at 669, 716 and 737 $cm^{-1}$ wavenumbers were assigned to T-O-T symmetric stretching vibrations when the absorption band observed at 965 $cm^{-1}$ was related to asymmetric stretching vibrations. Typically, the positions of symmetric and asymmetric T-O-T modes are dependent on the framework expansion, (Henderson & Taylor, 1979). In the aluminogermanate sodalite, for instance, one asymmetric stretching at 850 $cm^{-1}$, two modes for symmetric stretching at 600 $cm^{-1}$, and bending mode is visible at 380 $cm^{-1}$ (Eiden-Assmann, 2002; Buhl et al., 2006). In this case, the framework band of an aluminogermanate sodalite revealed at the wavenumber of 874, 617 and 592 $cm^{-1}$. In this regard, weak bonds at about 3500 $cm^{-1}$ was correspond to the amount of $OH^{-}$ found as impurities arising from the hydrothermal process of crystallization (Borhade et al., 2012). Besides, depending on a research (Borhade et al., 2012), the enclathrated guests can be detected according to their intensive absorption band for perchlorate at 1112 $cm^{-1}$. Besides, the absorption band at 620 $cm^{-1}$ is also characteristic of the enclathration of perchlorate in sodalite cages, (Borhade et al., 2012). The framework bands at almost 874, 617, and 592 $cm^{-1}$ were revealed in the infrared spectrum of the potassium exchanged sodalite formed at the presence of KOH activator. For the potassium exchanged sodalite, the asymmetric vibration for $ClO_4^{-}$ was found at 1114$cm^{-1}$. This shift in the IR frequency as a function of cation exchange can be explained on the basis of cell constants (Borhade et al., 2012; Jin et al., 2008).

In the infrared spectrum of sepiolite raw material (Fig. 4c), absorption band at 3562 $cm^{-1}$ is attributed to OH groups in the octahedral sheet of sepiolite framework and according to (Frost et al., 2001, Chahi et al., 2002) it is related to the OH stretching vibration in the surface of sepiolite. The band at 1657 $cm^{-1}$ was ascribed to the presence of OH stretching, representing the zeolitic water in the channels and bound water which is coordinated to magnesium in the octahedral sheet. Absorption band at 1435 $cm^{-1}$ was related to asymmetric stretching vibrations and developed due to the hydroxyl bending vibration reflecting the presence of bound water. The Si-O coordination bands at 1210, 1050 and 1015 $cm^{-1}$ represent the stretching of Si–O in the Si–O–Si groups of the tetrahedral sheet. The absorption in the region appearing at 728, 883 and 975 $cm^{-1}$ were related to T–O (T=Al, Si) symmetric stretching vibrations and correspond to the band characteristics of

silicate minerals as well as the absorption band which occurs at 427 cm$^{-1}$ that is associated with T–O bending vibration. In this regard, according to a research (Hojati & Khademi, 2013), three wavenumber regions in 4000 to 2800 cm$^{-1}$; 1800 to 1400 cm$^{-1}$, and 1400 to 400 cm$^{-1}$ were observed in infrared spectrum of sepiolite. The absorption bands of 4000 to 2800 cm$^{-1}$ correspond to vibrations of different types of hydroxyl groups (Frost et al., 2001; Cheng et al., 2011; Mora et al., 2010) and those ranging from 1800 to 1400 cm$^{-1}$ are asymmetric and represent OH bond deformation. Previous studies have demonstrated two partially resolved peaks at 1630 and 1656 cm$^{-1}$ attributed to the adsorbed and zeolitic water (Farmer et al., 1974). Absorptions revealed at 1400 to 400 cm$^{-1}$ correspond to typical stretching vibrations of Si-O bonds and deformation vibrations of O-H bonds (Mora et al., 2010; Murray, 2007; Perraki & Orfanoudaki, 2008).

*Batch type adsorption experiments data*

Considering the ICP results obtained through analyzing the final leachates (Tables 5 & 6 and Figs. 5, 6 & 7), pure sodalite 1, which synthesized through using NaOH activator, at 140°C, remove $Fe^{3+}$ and $Cr^{3+}$ ions with highest amount from 1 and 2 hours then constantly up to 24 hours from 0.001M solution. While, this pure sodalite clean up $Cd^{2+}$ up to highest amount up to 8 hours then continuously to 24 hours. By the application of pure sodalite 2 formed applying KOH activator at 180°C, $Fe^{3+}$, $Cr^{3+}$, and $Cd^{2+}$ was constantly removed with highest amount from less than 1 hour up to 24 hours. Regarding the amount of uptake cations from 1 to 24 hours by pure sodalite 1, $Fe^{3+}$ changed within 95.7%-99.9%, $Cr^{3+}$ from 97.6% up to 99.9%, and $Cd^{2+}$ within the range of 80.3%-95.8%. Pure sodalite 2 removed $Fe^{3+}$ with percentages changed from 99.85 to 99.87%, $Cr^{3+}$ from 99.8% up to 99.9%, and $Cd^{2+}$ with the range of 98.8%-99.6%. In the case of selectivity order considering these cations removal during determined contact time, both pure sodalites 1 and 2 adsorbed $Fe^{3+}$ and $Cr^{3+}$ with highest amount and $Cd^{2+}$ with amount less than the aforementioned cations.

In the presence of 0.01M solutions, pure sodalite 1, removed $Fe^{3+}$ and $Cr^{3+}$ constantly with highest amount and $Cd^{2+}$ increasingly up to 2 hours then with continuous to inalterable rate to 24 hours. While, pure sodalite 2 adsorbed $Fe^{3+}$ and $Cr^{3+}$ with additive rate from 1 to 2 hours then constantly to 12 hours subsequently increasing up to 24 hours and $Cd^{2+}$ continuously from 1 to 8 hours then with growing rate to 12 hours, finally permanently up to 24 hours. Considering the percent of removal, pure sodalite 1 adsorbed $Fe^{3+}$ within the range of 86.7%-87.4%, $Cr^{3+}$ from 91.8% to 92.1%, and $Cd^{2+}$ from 82.4% to 83.3% within 1 hour up to 24 hours. Pure sodalite 2 cleaned $Fe^{3+}$ with the percentages of 93.5% to 98.2%, $Cr^{3+}$ from 93.9% to 99.6% and $Cd^{2+}$ within the range of 83.6%-88.2%, from 1 to 24 hours. With regard to selectivity orders of cations, pure sodalites 1 & 2 uptake $Cr^{3+}$ and $Fe^{3+}$ with highest amount and $Cd^{2+}$ with the amount less than that of $Fe^{3+}$ and $Cr^{3+}$ from artificial monometallic solutions.

Pure sodalite 1 under the influence of 0.1M solutions adsorbed $Fe^{3+}$ with highest amount and additive to permanent rate from 1 to 24 hours and $Cr^{3+}$ and $Cd^{2+}$ with the highest amount continuously from early 1 hour up to 24 hours. When pure sodalite 2 removed $Fe^{3+}$ and $Cr^{3+}$ with highest amount incessantly from early 1 hour to 24 hours and $Cd^{2+}$ with growing rate to obtain the highest amount of adsorption up to 2 hours then firmly to 24 hours. The results related to the removal percent demonstrated that pure sodalite 1 adsorbed $Fe^{3+}$ within the range of 82.9%-83.1%, $Cr^{3+}$ from 90.7% to 90.8% and $Cd^{2+}$ with percentages changed from 96% to 96.1%. while, pure

sodalite 2 removed $Fe^{3+}$ from synthetic metallic solutions with the percent of 86.9%-87%, $Cr^{3+}$ within the range of 90.5%-90.9%, and $Cd^{2+}$ from 91.7% to 94.1%. In this case the adsorptive cations selectivity orders, pure sodalite 1 removed $Cd^{2+}$ & $Cr^{3+}$ with highest amount and $Fe^{3+}$ with less amount from 1 to 24 hours. When, pure sodalite 2 adsorbed $Cd^{2+}$ with the highest amount, and $Cr^{3+}$ and $Fe^{3+}$ with less amount, respectively.

The adsorption results obtained from the current study demonstrated that for both pure sodalite 1 and pure sodalite 2, the optimum adsorption of $Fe^{3+}$ and $Cr^{3+}$ was at the presence of 0.001M while that of $Cd^{2+}$ was under the effect of 0.1M artificial metallic solutions. In this regard and by the application of 0.001M solutions, the maximum amount of adsorption has been occurred between 1 to 2 hours for pure sodalite 1 and was mostly between 30 minutes to 1 hour for pure sodalite 2. By the application of 0.01M and 0.1M solutions, the most adsorption happened from 30 minutes up to the first 1 hour, for both pure sodalite 1 & 2. Based on the obtained results of a research carried out on clinoptilolite efficiency for Cd, Fe, and Ni removal from industrial wastewater (Abd El-Azim, and Mourad, 2018), clinoptilolite has a great potential to remove $Cd^{2+}$, $Fe^{3+}$, and $Ni^{2+}$ ions from industrial effluents. Moreover, the effect of retention time on adsorption ratio demonstrated adsorption percent of 80% for Cd, Fe, and Ni, during the first 120 minutes. In the aforementioned study by applying clinoptilolite as the adsorbent, the removal efficiency order became as Fe > Cd > Ni, each metal has unique electronegativities, ionic size and bond strength affecting the adsorption capacity of this zeolite (Gomes et al., 2001). In this regard, the influence of the initial chromium concentration on removal efficiency can be investigated through a study conducted on the removal of Cr (VI) cation from aqueous solutions and tannery wastewater using Polymer-Clay composites (Sallam, 2017). According to the obtained results, the removal efficiency of Cr (VI) ion decreased with an increase in its initial ionic concentration indicating the occupation of the available binding sites for chromium ions, subsequently, prevention of their further adsorption onto the adsorbent. Numerous studies have been also performed on productiveness of zeolite application for heavy metals removal from wastewater considering various parameters of pH, temperature, granular phase volume, concentration, and induction speed (Trgo & Perić, 2003; Perić et al., 2004; Salunkhe & Raut, 2012; Shaheen et al., 2012; Visa & Popa, 2015; Hesnawi et al., 2017).

Results obtained through current adsorption study demonstrated that the exchange of $Fe^{3+}$, $Cr^{3+}$, and $Cd^{2+}$ cations might be as the steps of diffusion of cations through the solution to the zeolite particles; diffusion through the zeolite particles to active sites through exchange process; chemical exchange between $Fe^{3+}$, $Cr^{3+}$, and $Cd^{2+}$ and exchangeable cations ( $Na^+$, $K^+$) at the exchange site in the interior of zeolite (β cage of sodalite); and partial dissolution of $Fe^{3+}$, $Cr^{3+}$, and $Cd^{2+}$, accordingly the ion uptake could be mainly attributed to the ion-exchange reaction referring to a study (Ćurković et al., 2014) conducted on the ability of natural clinoptilolite and its Na-enriched form to remove $Fe^{3+}$ from acid aqueous solutions in the batch system, at the concentration of 100 mg $Fe^{3+}$/L, and 30-300 min equilibrium time, whose results verified a higher selectivity of Clinoptilolite for iron than the modified Na-Clinoptilolite.

Contact time and its effect on the adsorption efficiency could be clarified through the fact that contact time needed to reach the maximum removal of metals uptake by zeolite which is dependent on the type of heavy metal (Taamneh & Sharadqah, 2017). This parameter's impact can be showed as a rapid adsorption rate in the first 30 minutes followed by a gradual increase with

time until equilibrium adsorption that can be observed within 90 minutes (Abd El-Azim, and Mourad, 2018). In this case, the fast adsorption rate at the initial stage might be due to the initial concentration gradient between adsorbate (cations) in solution and the number of available vacant sites on the adsorption surface. Besides, obtaining equilibrium of the adsorption might have been due to decline in the available active sites on the adsorption with time (Mehdizadeh et al., 2014).

The initial ion concentration plays a significant role in the adsorption process and can be as a driving force to conquer the mass transfer residence between the liquid phase and solid phase; accordingly, an increase in metal ions causes increase the metal uptake (Ziyath et al., 2011). In this regard, at low metal ions concentration, available adsorption sites can be easily occupied since ratio between the number of metal moles and the accessible surface area is low. Hence, adsorption is independent of the initial concentration. All the same, at high metal ion concentrations, the efficiency of adsorption is dependent on the initial concentration since the number of available site is less than the number of metal moles; in this case, when the initial concentration increases, the removal rate decreases (Horsfall, 2006). At higher concentrations, the number of ions competing for available sites to bind on the surface of the adsorbent increases and subsequently reduces the number of binding sites; meanwhile, the average distance between the adsorbed ions will be reduced affecting the surface charge distribution. Likewise, adsorbate (cations) ability to migrate to the surface of the adsorbent (zeolite) changes resulting in reduction of stabilization (Quintelas et al., 2009).

**Conclusions**

Evaluation of the pure zeolites synthesis through alkaline fusion method leads to the conclusion that the application of alkaline fusion step before hydrothermal process is a profitable method which can be effectively used for pure zeolites formation. The results in this research confirmed the critical effects of temperature and alkaline medium in the zeolites formation. Hence, these factors can be considered as influential parameters for zeolite synthesis process.

The determined conditions in synthesis experiments lead to the formation of sodalite as the pure phase through using both NaOH and KOH activators at different temperatures caused the authors to find out sepiolite potential to produce pure zeolite phases regardless of the type of applied activators and subsequently its industrial and environmental applications.

The efficiency for heavy metals removal of pure sodalites was evaluated through batch adsorptive experiments. Contact time and initial ionic concentration were influential factors affected the general reaction rate of adsorption. The pure sodalities demonstrated their impressiveness in $Fe^{3+}$, $Cr^{3+}$, and $Cd^{2+}$ removal from aqueous solutions.

It was found that by the application of 0.01M and 0.1M solutions, the optimum adsorption occurred from 30 minutes to 1 hour, for both pure sodalite 1 & 2. Whereas, by the usage of 0.001M solutions, the maximum adsorption was between 1 hour and 2 hours for pure sodalite 1 and was chiefly between 30 minutes and 1 hour for pure sodalite 2. Accordingly, the application of these synthetic pure sodalities for environmental purposes besides their potential as catalysts is strongly recommended since they can be promising minerals due to their capability to get recovered after cation exchange process.

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## Author Disclosure Statement

No competing financial interests exist.

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**Table captions**

**Table 1** previous investigations on zeolites synthesis

**Table 2** Chemical composition of sepiolite sample determined by XRF

**Table 3** Products synthesized with varying amounts of NaOH and $AlCl_3 \cdot 6H_2O$; Sdl: sodalite; Cal: Calcite; Zeo A: zeolite A; MgCal: magnesium calcite; Brc: brucite; Hl: halite; Mag: magnetite

**Table 4** Products synthesized applying varying amounts of KOH and of $AlCl_3 \cdot 6H_2O$; Sdl: sodalite; Cal: calcite; Zeo A: zeolite A; Bay: bayerite; Qz: quartz; Ame: amesite; MgCal: magnesium calcite

**Table 5** removal percent of Fe, Cr, and Cd from metallic solutions using pure sodalite

**Table 6** Fe, Cr, and Cd removal selectivity orders

**Figure captions**

**Figure 1** Flowchart process of primary material conversion into synthesis products, (Kamyab, 2019)

**Figure 2** XRD patterns of pure sodalities and starting material; (a) sodalite formed by using KOH activator; (b) sodalite formed by using NaOH activator; (c) starting material; Sdl: sodalite; Sep: sepiolite, Dol: dolomite; Qz: quartz;

**Figure 3** SEM images: (a) staring material, (b) pure sodalite formed by applying NaOH activator, (c) pure sodalite synthesized using KOH activator

**Figure 4** Infrared spectra: (a, b) synthesized pure sodalities, (c) sepiolite

**Figure 5** adsorption percent on pure sodalites 1 & 2 vs time, 0.001M solutions

**Figure 6** adsorption percent on pure sodalites 1 & 2 vs time, 0.01M solutions

**Figure 7** adsorption percent on pure sodalites 1 & 2 vs time, 0.1M solutions