

TOWARDS A SAFER ENVIRONMENT: ZEOLITIZATION OF BENTONITE AND ITS POTENTIALITIES FOR REMOVING HEAVY METALS FROM WASTEWATER

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ABSTRACT

Zeolites have several applications in many fields related to pollution control, radioactive waste management, petroleum refining, purification of gases, agriculture and others. The production of zeolites using clay minerals as a resource constitutes one important issue of waste management. To convert bentonite clay to zeolitic materials, sodium hydroxide at different concentrations with two different treatments (magnetic stirring and autoclave treatments) were used. Obtained results indicated that alteration was carried out and zeolitic materials appeared. X-ray diffraction analysis, Infra-red spectroscopy, chemical composition, cation exchange capacity and accessibility of internal sites were used to characterize the produced zeolitic materials. Natures of obtained zeolitic materials depend on the method of contact between clay and alkaline agent. Autoclave treatment showed the conversion of montmorillonite and kaolinite in the bentonite clay sediment to sodalite and analcime zeolitic materials, while magnetic stirring converted the same mineral to sodalite only at 3M of NaOH. The C.E.C values of produced zeolitic materials increased with the rise in NaOH concentration until 2M only and decreased when increasing NaOH concentration in both clay sediments by both treatments (stirring and autoclave). Obtained results indicated that although ammonium is widely used to measure C.E.C, it seems inappropriate to apply to materials having smaller pores than the diameter of ammonium ion such as sodalite. Produced zeolitic materials have internal sites accessible to exchange with different ions and suitable to utilize in removing heavy metals or other ion toxicants from wastewater. Potentialities of produced zeolitic materials to remove heavy metals from industrial wastewater were studied as a function of contact time. The maximum percentage of metals removed was increased more than two to more than three times than initial bentonite with different arrangement of metals removed. The current study indicated that zeolitic materials not only had highly percentage of metals removed but also had highly selectivity for certain ions.

Keywords: Zeolitization – bentonite sediments – sodalite – analcime – wastewater treatment – heavy metals – X-ray diffraction analysis – infra-red spectroscopy.

INTRODUCTION

Clay minerals represent excellent natural barriers due to their small grain size, their specific surface area and their diagenetic processes (which cause high natural density), Abdallah *et al.* (2007). Besides, their ability to close fissures and cracks (which may form paths for leachates). In addition, their chemical reactivity permits them to immobilize important contaminants i.e. vanadium, uranium and boron Abdallah *et al.* (2005), (2009 a and b). Zeolite considers any member of a family of hydrated aluminosilicate minerals that have a framework structure enclosing interconnected cavities occupied by large metal cations (positively charged ions) generally sodium,

potassium, magnesium, calcium and barium and water molecules. The ease of movement of ions and water within the framework allows reversible dehydration and cation exchange properties that are exploited in water softeners and molecular sieves for pollution control, among other uses.

The structures of zeolites consist of three-dimensional frameworks of SiO_4 and AlO_4 tetrahedral. The aluminum ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (sodium, potassium, or calcium). These cations are exchangeable with certain cations in solutions such as lead, cadmium, zinc, and manganese Erdem *et al.* (2004). Natural zeolites are mined in many parts of the world but most of zeolites used at industrial level are synthesized in alkaline media with different sources of silicon and aluminum components. Many techniques have been investigated and several processes have been proposed by several authors to produce zeolite from clays and clay minerals, Zhao *et al.* (2004), Ruiz *et al.* (1997), Baccouche *et al.* (1998), Tounsi *et al.* (2009) and Zwingmann *et al.* (2009). The most common method is used for the conversion of clay minerals into zeolites involves a hydrothermal process, whereby the clay mineral is mixed with an alkali solution such as sodium hydroxide at different conditions of concentration, temperature, pressure and contact time. The resulting materials vary widely and usually are confirmed by a mix of zeolites. The structural heterogeneity together with the poor properties as ion exchange of stable zeolites, limits their applications. According to Molina and Poole (2004) both natural and synthetic minerals are known for their ability to act as catalysts, to adsorb liquids, gases and to exchange ions.

Heavy metals like Fe^{3+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+} have been discharged into the environment as industrial wastes, causing serious soil and water pollution, Petrus and warchol (2003). Heavy metals cannot be destroyed chemically. Therefore approaches to treat metal-contaminated water and soils aim to methods to reduce the availability of polluting heavy metals, e.g. by precipitation of insoluble compounds, sorption to solids or extraction Abdallah (2004), (2006) and Hakan and keya (2006).

The fact that zeolite exchangeable ions are relatively innocuous (sodium, calcium, and potassium ions) makes them particularly suitable for removing undesirable heavy metal ions from industrial effluent waters. Zeolites are a suitable choice as they have a large cation exchange capacity and an affinity for heavy metals.

Therefore, the objectives of the current study are to:

- 1 - Alteration of some bentonite clay sediments in Egypt to zeolitic material
- 2- Investigate the accessibility of internal sites in the produced zeolitic material
- 3- Evaluate the potentialities of produced zeolitic material for removing some heavy metals from wastewater

MATERIALS AND METHODS

1 Materials

1.1 Bentonite sediments

Two bentonite clay sediments were used in the current study as follows:

a – Abu- Tartur bentonite (western desert Egypt)

Abu- Tartur plateau lies between latitudes 29° 00' , 30° 30' N. and longitudes 25° 00' , 26° 00' E. The sample was taken from Nuclear Materials Authority, Katamya, Cairo, Egypt.

b – Estern Sebaia bentonite (upper Egypt)

Bentonite sediment from eastern part of Eastern- Esna region, Upper Egypt was taken from Geological Survey and Mining Authority, Cairo, Egypt. The area lies between: Latitude 25° 26' 18" N and longitude 32° 34' 11" E.

Both bentonite sediments were used without any purification. Preliminary treatment consisted of grinding and sieving to 100 µm. The clay powder was oven dried at 105°C and kept in desiccant.

1.2 Wastewater source:

Non treated wastewater samples were collected from industrial city of Khamis-mushayt, Asir district, southwestern of Saudi Arabia. Wastewater samples were prepared and analyzed according to Greenberg *et al.* (1992) for both chemical analysis and heavy metal determination. Wastewater samples were evaluated according to Pescod (1992), the main heavy metal contaminants were Cd, Mn, Co, Cr, and Pb. The current study focused on the first three heavy metals Cd, Mn and Co which represented the highly levels of contaminants ions.

2 Methods:

2.1 Zeolitization procedures (Alteration experiment):

Each bentonite sample was treated in two different ways according to Ruiz *et al.* (1997) as follows:

In the first treatment method, 15 g of each source of bentonite samples were treated by 100 ml sodium hydroxide solution (at the boiling point) with different concentrations: 1,2,3,4,5 and 6 M. The reaction was maintained with magnetic stirring for 24 h.

In the second treatment method, the suspensions with the same solid / liquid ratio and concentration of sodium hydroxide as the first treatment method were heated at 160°C in the autoclave without stirring for 60 h.

Thus generating a set of 4 samples were altered from two initial bentonite sediments. To express the initial bentonite clay sediments and their altered clay, the following symbol used in the current study: SB :(sebaia bentonite clay), SS:(sebaia clay altered by stirring treatment), SA: (sebaia clay altered by autoclave treatment), AB: (Abu-tartur bentonite clay), AS:(Abu-tartur clay altered by stirring treatment), AA: (Abu-tartur clay altered by autoclave treatment).

In both treatment methods the final mixture was centrifuged to 10000 rpm. The solid phase was washed several times with distilled water until pH 9.5 –

10, filtered and dried at 80 °C. The solid was then ground and sieved to 40 µm.

2.2 Characterization of altered solid phases:

a) X-ray diffraction analysis

XRD analysis was carried out prior to and after each treatment for sodium hydroxide concentration from 3 to 6M. Thin slurry of the separated clay deposited on a glass slide, air dried at room temperature and subjected to X-ray diffraction analysis. XRD analysis was done using SHIMADZU XRD 6000 x-ray apparatus, with Ni filter and Cu-K α radiation.

Constant criteria for all samples X-rayed used as follows: - KV=40, MA=20, Gain=60, Range=1000, time constant were 2

b) Infra red spectroscopy analysis

Infra red absorption spectra in the region of 400 cm⁻¹ to 4000 cm⁻¹ were recorded using K Br sample pellets. The samples were prepared as pellet method according to Russell and Fraser (1994)

c) Chemical analysis

Except of silicon, the samples were digested with hydrogen fluoride in conjunction with perchloric acid and dissolved later by hydrochloric acid. While for the analysis of silicon, the samples were melted with sodium hydroxide. The elemental concentrations were then measured in digestions by Inductively Coupled Plasma Spectrometry. The dissolved silica was determined by the colorimetric method using the silicomolybdate complex. The dissociated iron oxide and aluminum oxide were determined by the dithionite – citrate – bicarbonate (DCB) extraction method according to Jackson and Lim (1986). Soluble sodium ion was analyzed by emission spectroscopy.

d) Cation exchange analysis

Cation exchange capacity was carried out on the initial clay sediments and their solid phases obtained by each concentration of sodium hydroxide in both treatments.

The cation exchange capacity was determined using the ammonium acetate method according to Van Reeuwijk (1992). About 0.4 g of the samples was washed five times with 1.0 mol/L ammonium acetate. To remove residual ammonium that was not held by the sample, the solid was further washed with doubly distilled water and ethanol until be free from chloride ion (checked with 1N AgNO₃). Finally, the residue was washed five times with 1.0 mol/L NaCl and the released ammonium was determined by the Nessler method according to APHA (1995). The C.E.Cs were thus calculated and expressed as meq per one hundred gram of solids.

e) Accessibility of internal sites in produced zeolitic material

To test if the internal sites in produced zeolitic material are accessible by different ions, 0.05 g of samples (SS, SA, AS and AA) were mixed with 15 ml of 0.5 KNO₃ or 0.25 Ca(NO₃)₂ solution in a 40 ml. centrifuge tube according to the method of Zhao *et al.* (2004). The tubes were kept in an oven at 80°C for 24 h. During the day time of the 24 h storage, the tubes were shaken for 20 min every 2 h. At the end of the 24 h treatment, the tubes were centrifuged, and ~15 mL of supernatant solution from each tube were

collected for Na⁺ quantification with the atomic absorption spectrometer. An additional 15 mL of the corresponding KNO₃ or Ca (NO₃)₂ solutions were added to the tubes. The tubes were stored, shaken and centrifuged as in the first washing. The washing process was repeated six times in total.

2.3 Potentialities of produced solids for removing heavy metals from wastewater

0.4 gram from two bentonite sediments used(SB and AB) and solid produced after the treatment with 6M of NaOH (SS, SA, AS and AA) were equilibrated with an aliquot of 40 ml from wastewater separately for various times intervals 30, 60, 90,120,180 and 240 min. according to Abdallah (2004). All measurements run in triplicate. According Chen *et al.*(1997) the slurries were discarded and acidified to pH=2 with concentrated nitric acid for metal determination by inductive coupled plasma. The amount of ion removed was taken as the difference between the initial concentration in wastewater and that remaining in solution after the equilibration.

RESULTS AND DISCUSSION

Characterization of new mineral phase:

Five parameters were used to characterize the produced zeolitic materials as new solid phases after zeolitization processes were carried out as follows:

a) X-ray diffraction analysis:

Both bentonite sediments were dominated by montmorillonite mineral followed by kaolinite then feldspars and quartz. Fig.1 represents the X-ray diffraction patterns of the solids obtained after reaction of sebaia bentonite clay fraction with 3 to 6 M NaOH solution in autoclave at 160°C for 60 h. The most distinct changes reflected on the X-ray diffraction patterns were the reduction in intensity of montmorillonite and kaolinite peaks and the appearance of sodalite and analcime peak. The intensity of the montmorillonite and kaolinite peaks reduced progressively with increasing NaOH concentration with sodalite and analcime peaks enhanced accordingly. The montmorillonite and kaolinite peaks were negligible after the treatment of 6M NaOH carried out. Sodalite mineral have several common X-ray diffraction peaks located in 2θ values at (14.5 and 24.5) as strongest intensity, (35 and 43.5) as medium intensity and (32 and 38) as weak intensity as suggested by Tounsi *et al.* (2009), Zhao *et al.* (2004), Baccouche *et al.* (1998) and Ruiz *et al.*(1997), the last two authors confirmed that these diffraction patterns referred to sodalite octahydrate zeolite.

Analcime mineral can be identified by its characteristics diffraction patterns located in 2θ values at 15.75, 26 and 32 as high diagnostic intensity patterns as recommended by Baccouche *et al.* (1998) and Ruiz *et al.*(1997). Zhao *et al.* (2004) considered the stability diffraction patterns of sodalite at 2θ = 32 indication of its thermodynamically stability although the peak appeared as too small intensity.

Obtained results indicated that the relative height of the diffraction patterns of sodalite at 2θ values (14.5, 24.5 and 43.5) and analcime mineral at 2θ values

(15.75, 26 and 30.5) seem to be similar to sediments treated with NaOH at 3, 4 and 5M. After the treatment of 6M NaOH carried out the enhanced previous diffraction patterns indicated that both sodalite and analcime minerals were stable under the experimental conditions.

Figure 1 revealed that once clay sediments treated with 3M NaOH and autoclaved for 60h the shape of diffraction patterns were different and new zeolitic materials were formed.

Many previous studies were carried out to determine the suitable concentration of NaOH to convert montmorillonite and kaolinite to zeolite like material, beside, other conditions to make conversion. The current study recommends the treatment with 3M NaOH was enough to convert montmorillonite and / or kaolinite to sodalite octahydrate zeolite.

Abu-tartur bentonite clay treated by autoclave treatment with different concentration of NaOH showed the same new zeolitic materials formed in sebaia bentonite clay as shown in figure (2). The treatment of 6M NaOH increased the intensity of analcime mineral as the case in Sebaia bentonite clay. The diffraction patterns of analcime mineral at $2\theta = 30.5$ appeared only after the treatment of NaOH was 5M or higher. The diffraction patterns intensity of all sodalite and analcime zeolitic materials may be lower than sebaia clay. The lower percent of montmorillonite, kaolinite and higher percent of quartz and feldspars mineral in Abu-trarur sediment may be the reason beside, the lower silica / alumina ratio in Abu-tartur clay table (1).

When the bentonite clays subjected to the second treatment by stirring treatment method, conversion of montmorillonite and kaolinite were appeared as indicated by the reducing their peak intensity and appearing new mineral as shown in figures (3) and (4) for Sebaia and Abu-tartur bentonite clay, respectively. Obtained results by this treatment indicated that both bentonite sediments were converted to sodalite zeolitic material only and analcime mineral did not appear in all different concentrations of NaOH.

The intensity of diffraction patterns may be the same in the two clay sediments used. The differences between them may be the shape of diffraction patterns on montmorillonite in the Abu-tartur sediment especially at low grade angle of 2θ which appearing as heap shape and appearing the diffraction patterns of feldspars mineral as the present in the initial sediments.

b) Infra – red spectroscopy analysis

To confirm the previous finding Infra-red spectroscopy analysis was carried out on both bentonite clay sediments used. Treatment with 5 and 6M of NaOH in both autoclave and magnetic stirring were subjected to infra-red spectroscopy.

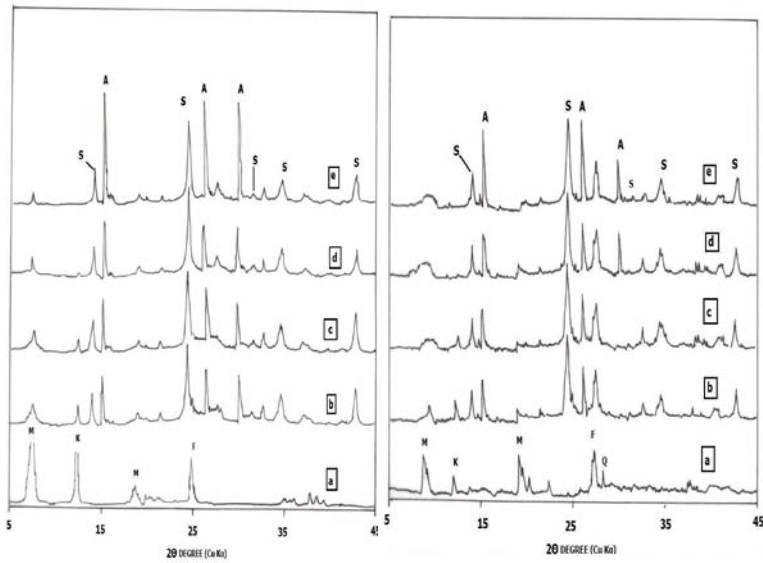


Figure (1): XRD patterns of Sebaia bentonite clay (a) and its solid phases obtained after autoclave treatment with different concentration of NaOH: (b) 3M.

Figure (2) XRD patterns of Abu-tartur bentonite clay (a) and its solid phases obtained after autoclave treatment with different concentration of NaOH: (b) 3M (c) 4M

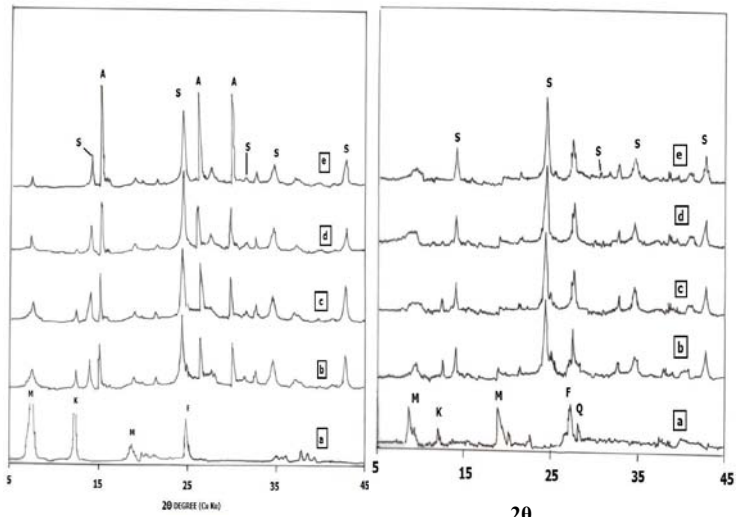


Figure (3) XRD patterns of Sebaia bentonite clay (a) and its solid phases obtained after stirring treatment with different concentration of NaOH: (b) 3M, (c) 4M, (d)5M, (e)6M S (sodalite mineral), A (analcime mineral)

Figure (4) XRD patterns of Abu-tartur clay (a) and its solid phases obtained after stirring treatment with different concentration of NaOH: (b) 3M, (c) 4M, (d)5M, (e)6M S (sodalite mineral) A (analcime mineral)

The I.R spectra of the initial bentonite clay and its transformation are shown in Figures 5 and 6 for Sebaia and Abu-tartur bentonite clay sediments, respectively. The figures revealed several distinct changes on the Fourier Transform Infra-Red (FTIR) spectra when bentonite clay reacted with different concentration of NaOH. The characteristics OH-stretching vibrations of montmorillonite and kaolinite at 3652 and 3627 cm^{-1} disappeared in Sebaia clay Figure 5 or weakened as the case of Abu-tartur clay Figure 6. Other diagnostic band at 915 cm^{-1} of inner OH bending also weakened.

The reduction of the montmorillonite and / or kaolinite bands in the solid phase formed in Sebaia clay was more extensive than that in Abu-trarur clay. This is similar to the obtained results by X-ray diffraction analysis.

Weak montmorillonite bands at $\sim 3620 \text{ cm}^{-1}$ were still visible in the Abu -tartur clay. Coincident with the reduction of disappearance of montmorillonite and kaolinite bands, sodalite and analcime zeolitic material bands appeared.

Obtained data also revealed that sodalite mineral can be distinguished by five diagnostic bands at 1096, (730 – 760), (660 – 670), 535 and 460 cm^{-1} . Each diagnostic band may explain as follows: band at 1096 refers to asymmetric Al – O stretch of sodalite which may be located in the range of 980 – 1120 cm^{-1} , the symmetric Al – O stretch of the sodalite mineral located in the range of 660 – 670 cm^{-1} . The band at 535 cm^{-1} arose from the parallel four of six membered double rings of sodalite which also may be appeared in the region (530 – 668). The diagnostic band at 460 cm^{-1} arose from bending vibrations of Si – O and Al – O of the tetrahedral of feldspathoids. The previous interpretation was confirmed by several authors among them, Ruiz *et al.* (1997), Baccouche *et al.* (1998), Yining Huang (1998), Zhao *et al.* (2004) , Nibou *et al.* (2009) and Tounsi *et al.* (2009). In the literature, the previous diagnostic bands have some wave number slightly different from obtained results. Also the band positions are different in case of pure mineral, presumably due to crystallinity differences between natural samples , synthetic minerals and altered minerals.

Several authors suggested some of diagnostic bands of sodalite mineral for example, Zhao *et al.* (2004) mentioned that sodalite can be distinguished by its diagnostic bands at 733 and 707 cm^{-1} , 560 – 630 cm^{-1} and $< 500 \text{ cm}^{-1}$. On the other hand, Nibou *et al.* (2009) added two bands area of sodaite mineral , the first between (200 to 450 cm^{-1}) are known to assignable to (Si – O – Al) ,(Si – O – Si) , (Si – O) and (Si – Al) . The second band area between (3750 to 3450 cm^{-1}) is attributed to (Si – OH), (Si – OH – Al) and (– OH) groups. The author referred the band of 660 cm^{-1} to assignable to (Si – O – M) where M is exchangeable Na^+ ion metal species. Moreover, Tounsi *et al.* (2009) suggested four diagnostic bands of sodalite mineral at 1003, 668, 553 and 462 cm^{-1} . The authors interpreted the bands at 1003, 668, and 462 cm^{-1} bands are asymmetric stretching vibration and the bending modes of (T – O) bonds in (TO_4) tetrahedral (where T = Si or Al).

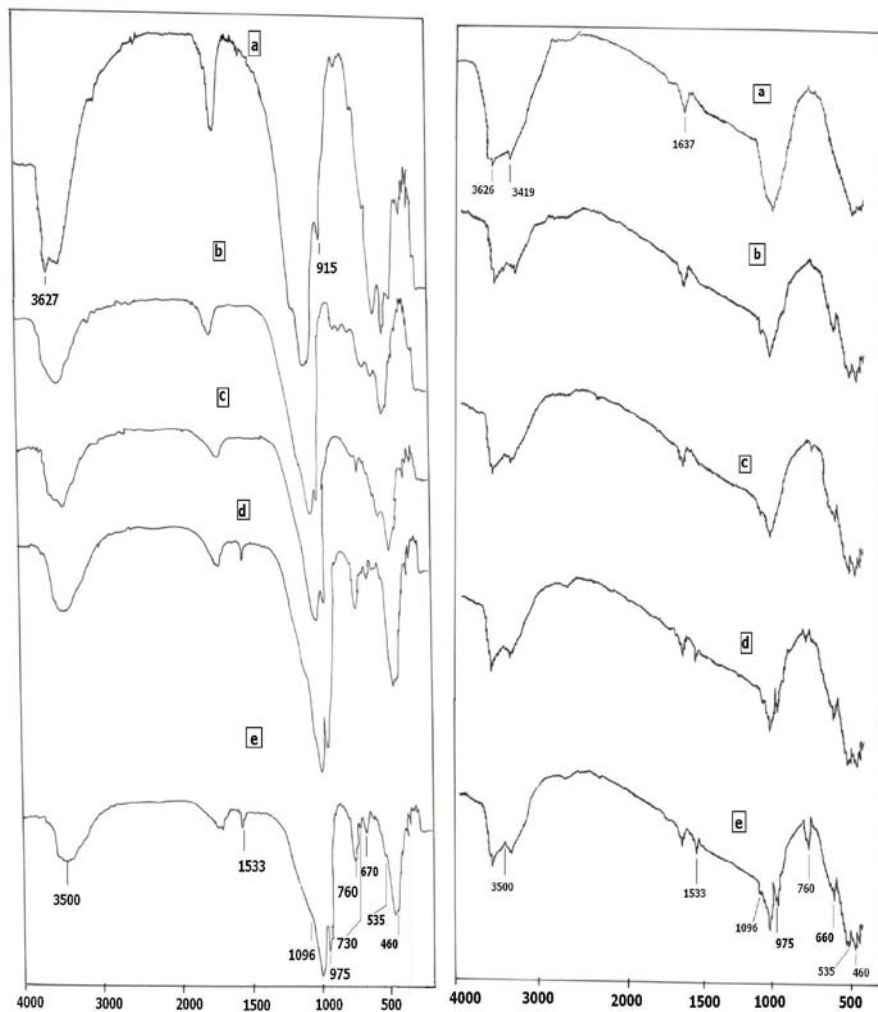


Figure (5) I.R spectra of sebaia bentonite clay (a) and its solid phases obtained after treated with NaOH (b)5M stirring (c)6M stirring (d)5M autoclave (e) 6M autoclave

Figure (6) I.R spectra of abu-tartur bentonite clay (a) and its solid phases obtained after treated with NaOH (b)5M stirring (c)6M stirring (d)5M autoclave (e) 6M autoclave

With the great harmony obtained infra-red spectra represented the same zeolitic material detected by X-ray diffraction analysis. Analcime mineral appeared only in autoclave treatment as shown in figures (5 and 6

patterns d and e) for both clay sediments used. Analcime mineral can be distinguished by diagnostic bands at 760, 975 and 1533 cm^{-1} . These obtained results confirmed by early study of Harada and Nagashima (1972), which put the new data of the analcime – wairakite mineral series and Ruiz *et al.* (1997). The first authors drawn typical spectra of analcime mineral and suggested different bands at (616 – 660 cm^{-1}), (730 – 760 cm^{-1}), (798 cm^{-1}), (1020 cm^{-1}) and (1630 cm^{-1}). The study of Ruiz *et al.* (1997) indicated that the characteristic bands of analcime mineral were located between (775 and 670 cm^{-1}) and (975 cm^{-1}). In the Abu-tartur bentonite clay Figure 6, the bands were not so strong and some bands appeared as shoulders in contrast with the Sebaia clay sediment. This feature was happened in X-ray diffraction analysis, the decreasing of silica / alumina ratio in Abu-tartur clay sediment may be the reason.

In all cases, the broad bands around 3500 cm^{-1} indicated that water remained in the feldspathoids which confirmed the alteration of montmorillonite to zeolite. Zhao *et al.* (2004) supported the obtained data and added that this band still observed after heating overnight at 150°C, but heating the samples at 350°C reduced the moisture content and reflected by the near disappearance of the broad band around 3500 cm^{-1} . Libowitzky and Rossman (1997) used I.R absorption data from polarized measurements on single crystal minerals with stoichiometric water contents (in the form of H₂O or OH groups) in the structure and suggested the same locations of obtained band as indication of zeolite minerals.

In Sebaia bentonite clay Figure 5 the band at 3627 cm^{-1} became broader after the alteration of montmorillonite taken place and the band at 3500 cm^{-1} may joined with 3627 cm^{-1} and appeared as broad band.

From the previous discussion, one can conclude that the alkalinity and the method of the contact between clay and alkaline agent were important variables and can change the nature of obtained zeolite. Autoclave treatment showed the conversion of montmorillonite and kaolinite to sodalite and analcime zeolite mineral, while magnetic stirring converted the same mineral to sodalite only. The reason may be referred to the contact time between clay and solution (60 h). enable ions to recrystallization in new zeolite form. Ruiz *et al.* (1997) revealed that montmorillonite structure converted from laminar structure to spherical units in the zeolitic products. The resulting modifications were greater when the samples were treated in autoclave rather than with reflux system.

Also Tounsi *et al.* (2009) prepared Na-A (LTA) zeolite from aluminosilicate gel obtained by a mixture of metasilicate and aluminate solutions. They concluded that, the alkalinity is an important sed, whereas the crystallization of some zeolite mineral i.e. sodalite were promoted at higher NaOH concentration. On the other hand, it was pointed out that the synthesis of zeolite (sodalite) depends on the rate of gel dissolution which is directly related to the high concentration of OH⁻ ions in the reaction mixture.

c) Chemical composition of produced zeolitic materials

The changes in elemental composition in the treated clay are shown in Table 1; the values were expressed as molar ration. An attack on the

montmorillonite structure is evidenced by a decrease in the silica/alumina ratio. The Abu-tartur clay samples have a smaller ratio. There are some increases in the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratio in all treated clays. This may be explained by the incorporation into the new structure of the iron present as an impurity in the starting sediments. The $\text{MgO}/\text{Al}_2\text{O}_3$ ratio does not change significantly because both metals are present in octahedral sheet of the montmorillonite, they persend in a similar way. The slight increase observed in the Sebaia clay after autoclave treatment was apparently caused by the incorporation of Mg as an exchangeable cation. Another interpretation presented by Deyi Wu et al. (2008) which in their study on hydrothermal conversion process of coal fly ash into zeolite. The ratios of $\text{MgO}/\text{Al}_2\text{O}_3$ remained quite stable, probably due to the insolubility in NaOH media. Our results showed that the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio increased after zeolitic materials had formed in both clay sediments used. The reason may be due to the Ca captured by negatively charged zeolite formed evident so significant increase in the Ca content following the zeolite conversion. Another reason confirmed the previous hypothesis that there are relationship between CaO content and C.E.C of zeolite. This correlation strongly supports the view that high calcium content is the consequence of a high C.E.C of zeolite and vice versa. Deyi Wu et al. (2008) and Ruiz et al.(1997) supported our result and the first authors added that the previous correlation happened although the Ca content is expressed by the form of CaO, Ca in zeolite exists principally as cations on zeolite surface, not oxides. The $\text{CaO}/\text{Al}_2\text{O}_3$ ratio was higher in autoclave treatment than stirring one, in both clay sediments used. Increasing temperature at 160°C in autoclave treatment may be the reason as confirmed by Deyi Wu et al. (2008). The decrease in $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio by both treatments was expected owing to the solubility property of the potassium oxid in alkaline solution. The $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio increased in both clay sediments by both treatments, and it is getting close to (1) which the theoretical ratio for a zeolite mineral in accordance with Baccouche et al. (1998).The hydrothermal treatment of bentonite clay in NaOH solution resulted in the rise of the Na content. Following the alteration process, the products were initially saturated by Na^+ due to the use of high NaOH concentration in alteration process.

d) Cation exchange capacity of altered zeolitic materials

The variations of C.E.C for the reaction products corresponding to various NaOH concentrations were presented on Figure 7. The initial C.E.C of clay sediments used represented in the figure as zero NaOH concentration. In all cases, the C.E.C of obtained solids was increased in both clay sediments by all treatments. The increase was greater for the clay treated by stirring than those treated by autoclave treatment. This is due to highly temperature used with autoclave treatment (160°C). As it has been shown by Berggaut and Singer (1996) the cation exchange capacity of sodalite octahydrate zeolite is temperature-dependent. Deyi wu et al. (2008) reported that within the temperature range adopted, the C.E.C value of synthesized zeolite increased as a function of temperature until the temperature of 110°C . However, this increase in C.E.C then began to slow down when temperature increased up to 110°C .

Table 1: Chemical composition of the final solids products after a reaction concentration of 6M NaOH

pH (1:2.5)	Ec ds/m (1:5)	Total dissolved solids (TDS) mg L ⁻¹	Total Solids (TS) (mgL ⁻¹)	Chemical oxygen demand (COD)(mgL ⁻¹)	Biological oxygen demand (BOD)(mgL ⁻¹)
4.56	31.76	618	637	543	217
element	concentration (mgL ⁻¹)	element	concentration (mgL ⁻¹)	element	concentration (mgL ⁻¹)
Co	15.45	Mn	17.37	Cd	13.08
Cr	8.4	Zn	11.79	Ni	10.14
pb	9.75	Cu	12.04	Fe	176

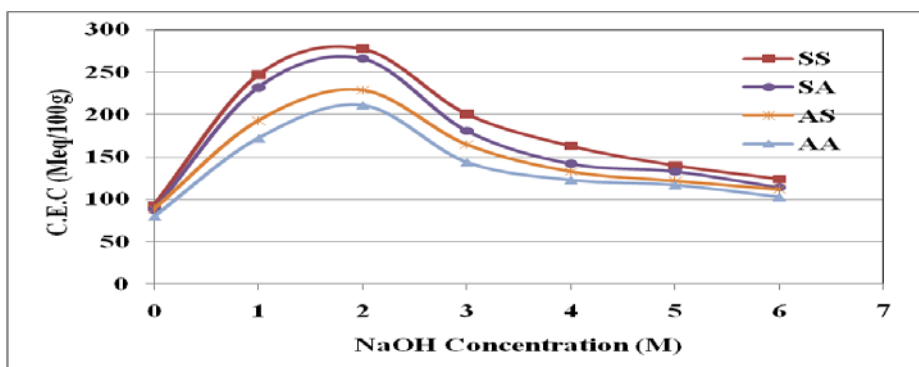


Figure (7): Cation exchange capacity of produced zeolitic materials as a function of NaOH concentrations

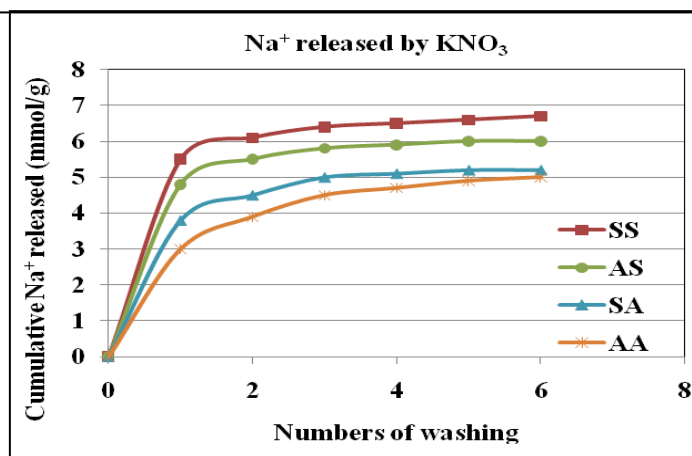


Figure (8): Na⁺ released from produced zeolitic materials by KNO₃

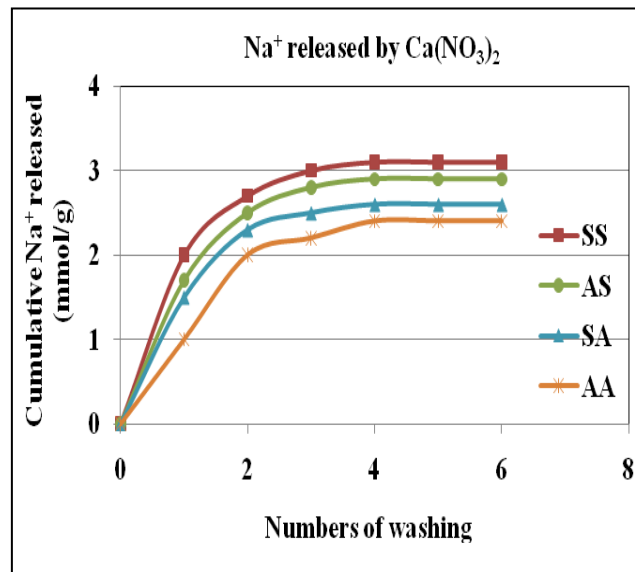


Figure (9): Na⁺ released from produced zeolitic materials by Ca(NO₃)₂

The C.E.C value increased initially with the rise in NaOH concentration until 2M only. Increasing NaOH concentration above 2M the C.E.C values decreased in both clay sediments by both treatment (stirring and autoclave). Obtained results are in harmony with the results obtained by both Baccouche et al. (1998), Molina and poole (2004) and Deyi Wu et al. (2008). This attributed to the C.E.C method determination by ammonium acetate, sodalite octahydrate have small pore size (0.23nm), that does not allow the penetration of ammonium (0.28nm). Therefore, although ammonium is widely used to measure C.E.C, it seems inappropriate to apply to materials having smaller pores than the diameter of ammonium ion such as sodalite. The decrease in C.E.C value at 3M NaOH concentration was reported by Molina and poole (2004). It should be noted that through there was no notable appearance of characteristic X-ray diffraction patterns due to zeolite at low NaOH concentration (1 and 2M), zeolite may be formed as evidenced by the C.E.C values. Molina and poole (2004) reported that the formed zeolite crystals could be so small as be undetectable or may be present in line broadening of X-ray reflections when the reaction temperature is not sufficient high.

e) Accessibility of internal sites in altered zeolitic materials:

Zeolitic materials produced under the current study may are not considered as a typical zeolite minerals because of the difficulty of molecular diffusion in their framework as suggested by Coombs *et al.* (1997). This

experiment carried out to examine the accessibility of internal sites in altered zeolitic materials by inorganic ions. After both clay sediments used (treated with 6M NaOH by both stirring and autoclave treatments) were washed with KNO_3 and $\text{Ca}(\text{NO}_3)_2$ solution containing 0.5M NO_3^- , a large amount of Na^+ was released in the first 24 h washing Figures 8 and 9, respectively, indicating that Na^+ in the cages of sodalite and analcime was exchangeable. In all cases, the amount of Na^+ released by stirring treatment was higher than released by autoclave treatment and followed the order $\text{SS} > \text{AS} > \text{SA} > \text{AA}$. More than twice the amount of Na^+ was released by the first KNO_3 washing than by $\text{Ca}(\text{NO}_3)_2$ indicating that K^+ is the more efficient than Ca^{2+} in the ion exchange reaction. Substantial amounts of Na^+ were still released from the third through the sixth washings with two extractants. After the third washing the changes in Na^+ released was negligible. The different amounts of Na^+ released from the sequential washings indicate that Na^+ ions can readily migrate out of or into the cages and channels of sodalite and analcime minerals. Both K^+ and Ca^{2+} ions can access the internal part of the minerals, yet they had different abilities to access those sites. Potassium ions can easily diffuse into the minerals whereas calcium ions take longer to reach the same sites. Calcium cations appeared to have the most difficulty in fully replacing the Na^+ even though the ionic radii of Ca^{2+} and Na^+ are about the same (0.099 and 0.097 nm, respectively). Sebaia bentonite clay released more Na^+ than Abu-tartur bentonite clay by both stirring and autoclave treatments indicating that the internal sites of zeolitic materials produced from Sebaia clay may have more accessible internal sites for ion exchange than those produced by Abu-tartur clay. Obtained results indicated that zeolitic material have internal sites accessible to exchange with different ions and suitable to utilize in removing heavy metals or other ion toxicants from wastewater.

Potentialities of solids produced for removing heavy metals from wastewater

The main aim of this experiment was examine the potentialities of produced zeolitic materials for removing heavy metals from industrial wastewater. Some characteristics of industrial wastewater from Khamis-mushyat, Asir district, southwestern of Saudi Arabia were presented in Table 2 indicated that there are many heavy metals pollutants as they over the permissible limits according to Pescod (1992). Exception iron, the highly contaminants heavy metals in the wastewater were Co, Cd and Mn, the current study focused on these heavy metals. Wastewater treated with initial bentonite clay sediments (SB and AB) and the solids produced from these sediments (SS, SA, AS and AA) after alteration process by 6M NaOH was carried out. The percentage of metal removed as a function of contact time was studied in the room temperature and plotted in Figure 10. In the initial bentonite clay (SB and AB), the percentage of metal removed was increased with increasing time contact until 120 min. then almost was constant. The percentage of removed metals was highly in (SB) than (AB) and followed the descending order: $\text{Mn} > \text{Cd} > \text{Co}$. The maximum percentage of removing Mn by (SB, AB) was (24, 21), Cd (21, 17) and Co (19, 15), respectively.

Produced zeolitic material represented highly removed percentage of all heavy metals studied with increasing time contact and did not reach the level off even at 240 min. After zeolitic materials were produced the maximum percentage was increased as follows, Co was the highly removed percentage (73, 71) and (68, 65), Mn was intermediate percentage (63, 59) and (55, 52), Cd was the least one (57, 52) and (48, 44) for (SS, SA) and (AS, AA), respectively.

These results indicated that energetically more favorable sites become involved with increasing contact time between wastewater and zeolitic materials.

Ion exchange capacity of studied heavy metals cations drawn in Figure 10 indicated the following selectivity sequence by zeolitic material produced: $Co^{+2} > Mn^{+2} > Cd^{+2}$. This arrangement was different from those obtained before alteration processes. This also indicated that zeolitic materials not only had highly percentage of metals removed but also had highly selectivity for certain ions. The heavy metals cations were present as hexaaqua complex ions with six surrounding water molecules in the solution and they passed the channel of zeolite in this form according to Jama and Yücel (1990). Since the adsorption phenomena depend on the charge density of cations, the diameter of hydrate cations is very important. The charges of the metal cation were the same (+2), therefore, Cd^{+2} ions (the biggest diameter $0.97A^{\circ}$ have minimum adsorption or by other word have minimum removal by zeolitic materials. Co^{+2} ions (the least diameter $0.72 A^{\circ}$ have maximum removal percent from wastewater, Mn^{+2} ions $0.81 A^{\circ}$ which have in between diameter between Co^{+2} and Cd^{+2} have also in between removing percentage. Erdem et al.(2004) supported the obtained results and indicated that the removal of heavy metal cations by natural zeolite followed the descending order $Co^{+2} > Cu^{+2} > Zn^{+2} > Mn^{+2}$. They considered that the metal cations are formed as high spin aqua complexes and the hydration ion diameter is the same diameter of aqua-complex ions. Moreover, Ulla wingen felder *et al.* (2005) confirmed the obtained interpretation. They interpreted their results through the differences in hydration energies. With the great harmony percentage of heavy metals removed by initial clay sediments (SB and AB) and their produced zeolitic material followed the same sequence of cation exchange capacity.

Table 2 : Some chemical characteristics of industrial wastewater used

Molar ratio	Abu-tartur			Sebaia		
	Initial (AB)	Stirring (AS)	Autoclave (AA)	Initial (SB)	Stirring (SS)	Autoclave (SA)
SiO_2/Al_2O_3	4.82	4.1	3.85	5.7	4.8	5.1
Fe_2O_3/ Al_2O_3	0.33	0.39	0.36	0.12	0.15	0.13
MgO/ Al_2O_3	0.27	0.25	0.24	0.46	0.44	0.49
CaO/ Al_2O_3	0.11	0.44	0.51	0.09	0.12	0.14
K_2O/ Al_2O_3	0.057	0.049	0.051	0.16	0.13	0.15
Na_2O/ Al_2O_3	0.56	0.93	0.91	0.64	0.95	0.97

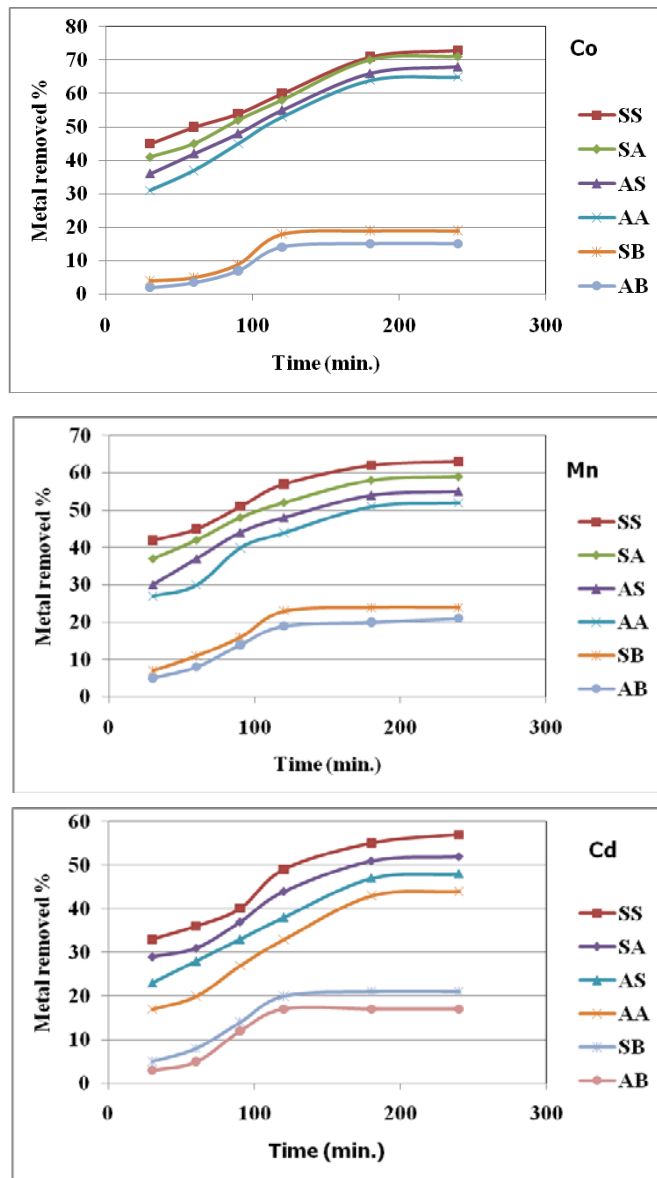


Figure (10): percentage of ions removed from wastewater by initial bentonite sediments and their produced solid phases by

The heavy metals uptake is attributed to different mechanisms of ion-exchange processes as well as to the adsorption process. During the ion-exchange process, metal ions had to move through the pores of the zeolite mass. But also through channels of the lattice, and they had to replace exchangeable cations (mainly sodium and calcium). Diffusion was faster through the pores and was retarded when the ions moved through the smaller diameter channels. In this case the metal ion uptake could mainly be attributed to ion-exchange reactions in the microporous minerals of the zeolite samples. Several authors confirmed the previous mechanism for zeolite among them Erdem *et al.* (2004), Ulla Wingenfelder *et al.* (2005) and Paola Castaldi *et al.* (2008).

In general, Sebaia clay (SB) and its produced zeolitic material (SS and SA) removed all studied heavy metals with higher percentage than Abu-tartur clay (AB) and its produced zeolitic material (AS and AA). Of course, the cation exchange capacity played important role in this case but also the higher Si/Al ratio of sebaia clay (5.7) than Abu-tartur (4.82) may be considered the second reason. This may be interpreted by the selectivity of zeolitic material which increased with increased the Si/Al ratio. In this respect, Erdem *et al.* (2004) supported the obtained results but for another zeolite mineral (clinoptilolite), they added that the high Si/Al ratio of clinoptilolite results in a typical low anionic field that gives rise to good selectivity.

Conclusion

Zeolitization of bentonite clay was carried out through different concentrations of NaOH starting from 3M with two different treatments, magnetic stirring for 24h and autoclave treatment at 160°C for 60h. This was confirmed by X-ray diffraction analysis, Infra-red spectroscopy, chemical composition and cation exchange capacity. Natures of obtained zeolitic materials depend on the method of contact between clay and alkaline agent. Autoclave treatment showed the conversion of montmorillonite and kaolinite in the bentonite clay to sodalite and analcime zeolitic materials, while magnetic stirring converted the same mineral to sodalite only. Zeolitic materials produced under the current study may be not considered as a typical zeolite minerals because of the difficulty of molecular diffusion in their framework. Examination of the accessibility of internal sites in altered zeolitic materials by inorganic ions indicated that both K⁺ and Ca²⁺ ions can access the internal part of the minerals, yet they had different abilities to access those sites. Potassium ions can easily diffuse into the minerals whereas calcium ions take longer to reach the same sites.

Potentialities of produced zeolitic materials to remove heavy metals from industrial wastewater were studied as a function of contact time. In the initial bentonite clay (before alteration) the percentage of metal removed was increased with increasing time contact till 120 min. then almost was constant. Removed metals followed the descending order: Mn > Cd > Co. Produced zeolitic materials represented highly removed percentage of all heavy metals studied more than two to more than three times with increasing time contact and did not reach the level off even at 240 min. Ion exchange capacity of studied heavy metals cations indicated the following selectivity sequence by

zeolitic material: $\text{Co}^{+2} > \text{Mn}^{+2} > \text{Cd}^{+2}$. This also indicated that zeolitic materials not only had highly percentage of metals removed but also had highly selectivity for certain ions. The cation exchange capacity played important role in this case beside the higher Si/Al ratio. This finding may interpreted through the selectivity of zeolitic material increased with increased the Si/Al ratio. The high Si/Al ratio of zeolitic materials results in a typical low anionic field that gives rise to good selectivity. The heavy metals uptake is attributed to different mechanisms of ion-exchange processes as well as to the adsorption process. During the ion-exchange process, metal ions had to move through the pores of the zeolite mass. But also through channels of the lattice, and they had to replace exchangeable cations (mainly sodium and calcium). Diffusion was faster through the pores and was retarded when the ions moved through the smaller diameter channels. In this case the metal ion uptake could mainly be attributed to ion-exchange reactions in the microporous minerals of the zeolite samples.

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**نحو بيئة أكثر أماناً: (8) تحويل البنتونيت إلي زيوليت وإختبار مدي قدرته علي إزالة العنصر الثقيلة من مياه الصرف
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تتكون معادن الزيوليت طبيعياً من سليكات الألومنيوم معتمدة في تركيبها علي كل من وحدة السليكا $(SiO_4)^{-4}$ ووحدة الألومينا $(AlO_4)^{-4}$. وترتبط هذه الوحدات مع بعضها عن طريق الأركان منتجة بذلك تراكيب مفتوحة تحتوي علي العديد من الفتحات (الفجوات) الداخلية والتي تسمح للأيونات والجزينات ذات الأحجام المختلفة من أن تسكن أو تحتجز داخل هذه الفجوات الداخلية. ولمعادن الزيوليت تطبيقات عديدة في كثير من المجالات البيئية المختلفة (معالجة التلوث البيئي - وإدارة ومعالجة المخلفات النووية – مجالات البترول وتنقية الغازات – والتطبيقات الزراعية وغيرها) مما يكسب الزيوليتات صفات متفردة عن باقي المعادن الأخرى إلا أن معظم معادن الزيوليت المستخدمة علي النطاق الصناعي ناتجة من التحول وليست طبيعية النشأة. ونظراً لأن معادن الزيوليت ليست منتشرة في مصر كمصادر طبيعية عكس رواسب البنتونيت الواسعة الإنتشار لذلك فإن إنتاج الزيوليت عن طريق التحويل من رواسب البنتونيت يعتبر من الأمور الهامة والتي لها تطبيقات مباشرة في مختلف المجالات.

لتحويل رواسب البنتونيت إلى مواد شبيهة بالزيوليت تم استخدام التحول الحراري باستخدام تركيزات مختلفة من الصودا الكاوية (من 1 إلى 6 مولر) عن طريق معاملتين مختلفتين (باستخدام الرج magnetic stirring لمدة 24 ساعة – باستخدام الأوتوكلاف علي درجة حرارة °C 160 لمدة 60 ساعة). وتم استخدام العديد من الوسائل لتوصيف وتشخيص المواد الزيولتية الناتجة مثل x-ray diffraction chemical – cation exchange capacity – infra-red spectroscopy – analysis composition). ونظرا لإختلاف المواد الزيولتية الناتجة عن تلك الطبيعية تم إختيار طبيعة المواقع الداخلية internal sites للمواد الزيولتية الناتجة لمعرفة مدي إمكانية وصول الأيونات المختلفة إليها وقابليتها لحدوث التبادل عليها حتي يتسني للمواد الزيولتية الناتجة إستخدامها في التطبيقات البيئية المختلفة. أظهرت النتائج حدوث تحولات واضحة وكبيرة لمعادن المونثوموريلونيت والكاولينيت المكونة لرواسب البنتونيت إلى معادن شبيهة بالزيوليت وإختلفت نوعية المواد الزيولتية الناتجة علي حسب المعاملات المستخدمة. أظهرت النتائج بوضوح وجود معادن الصوداليت في معاملة magnetic stirring بينما ظهر معدن الصوداليت والأنالسيم في معاملة الأوتوكلاف حيث أظهرت نتائج x-ray diffraction وكذلك infra-red spectroscopy تقريبا معظم الخطوط المميزة للمعدنين بل وأكدت علي ثباتهما. أوضحت نتائج السعة التبادلية الكاتيونية للمواد الشبيهة بالزيوليت الناتجة أنها تزداد بزيادة تركيز الصودا الكاوية حتي 2 مولر فقط ثم تقل بزيادة التركيز عن ذلك. ولقد أكدت نتائج الدراسة علي أن بالرغم من الإستخدام الواسع للأمونيوم في تقدير السعة التبادلية الكاتيونية للطين إلا أنه غير ملائم للإستخدام إذا كانت المواد الطينية ذات مسام أقل من قطر أيون الأمونيوم نفسه كما في معادن الصوداليت. أكدت نتائج الدراسة أيضا علي أن المواد الشبيهة بالزيوليت الناتجة تقريبا مشابهة إلي حد كبير للتركيب الداخلي للمعادن الزيولتية الطبيعية وأن المواقع الداخلية لها قابلة لحدوث تبادل للأيونات المختلفة وهو مادعي إلي إجراء تجارب لإختبار مدي قدرة هذه المواد علي إزالة بعض العناصر الثقيلة من مياه الصرف وعلاقة ذلك بزمن التلامس. وأكدت النتائج المتحصل عليها أن هذه المواد لها قدرة أعلى من البنتونيت العادي (قبل التحول) بأكثر من الضعفين إلي أكثر من ثلاثة أضعاف في إزالة العناصر الثقيلة من مياه الصرف. كما أظهرت النتائج وجود إختيارية selectivity عالية لبعض العناصر الثقيلة فعلي سبيل المثال : كانت أعلى نسبة للعناصر المزالة قبل التحول كالتالي: Mn (21-24%) و Cd (17-21%) و Ni (15-19) وكانت نسب هذه العناصر بعد التحول ونتاج المواد الشبيهة بالزيوليت كالتالي: Mn (52-63%) و Cd (44-57%) و Co (65-73%) وأكدت الدراسة علي أن المواد الشبيهة بالزيوليت الناتجة ليست فقط ذات قدرة عالية علي إزالة المعادن الثقيلة من مياه الصرف ولكن أيضا لها قدرة إختيارية عالية لبعض الأيونات وتم تفسير ذلك وربطه بالتركيب الكيماوي للمواد الزيولتية الناتجة وبنسبة SiO_2/Al_2O_3 .

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