



## Heavy metal removals from industrial wastewater using modified zeolite: study the effect of pre-treatment

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### Abstract

Pre-treatment processes were performed in order to investigate the behavior of modified clinoptilolite (natural zeolite) as adsorbents and understand the removal mechanisms involved in the adsorption process. The pre-treatment of clinoptilolite is carried out to increase the metal removal efficiency from solution. For this purpose, both hydrothermal and chemical pre-treatment of clinoptilolite were carried out in order to investigate whether pre-treatment could increase the adsorption capacity of clinoptilolite. The zeolite samples were characterized by using different analytical techniques such as Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), X – Ray Diffraction (XRD), X – Ray Fluorescence (XRF), Thermogravimetric Analysis (TGA), Fourier Transform Infrared (FT-IR) Spectroscopy and Inductively Coupled Plasma-Optical Emission Spectrometers (ICP-OES). The thermal pre-treatment process of clinoptilolite was carried out by heating clinoptilolite samples in a furnace for 30 minutes under a slow heating rate of 200, 400 and 600°C. The chemical pre-treatment of the clinoptilolite were carried out by mixing clinoptilolite sample with 200 ml of 0.5M NaCl. Then 4g of modified clinoptilolite samples were in contact with 100 ml of multi- component solutions for 360 minutes. The data obtained from the kinetic adsorption tests the shows that the efficiency of Cu<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup> metal ions removal was enhanced with the application of pre-treatments.

## 1. Introduction

Zeolites are an inorganic microporous crystalline solid substance contains silicon, aluminium and oxygen in its framework [1, 2]. Usually, large cavities and channels inside the zeolite framework are contain water molecules forming hydration spheres around exchangeable cationic. Clinoptilolite can be modified using thermal or chemical treatment separately or can be treated as a combined process [3, 4, 5, 6 and 7]. Thermal treatment depends on the zeolite structure and

rate of temperature used in the processes. Thermal treatment result in improve pore volume by removing water molecules and hydroxyl group present in cavities and channels of the clinoptilolite framework which contributes 10 – 25 % to the total mass of clinoptilolites [4]. To determine the adsorption capacity of clinoptilolite in wastewater treatment, it is important to study the dehydration and

dehydroxylation processes with structural stability of natural zeolitic materials.

Clinoptilolite can be chemically modified by using various type of inorganic salts (e.g. NaCl, CaCl<sub>2</sub>, BaCl<sub>2</sub>, NH<sub>4</sub>Cl, FeCl<sub>3</sub>) to activate the zeolite and increase its efficiency in water treatment [8, 9, 10, 11, 12 and 13]. Among those inorganic salts, NaCl solution is the most commonly used as a pre-treatment agent for the conversion of clinoptilolite to harmonic or near harmonic form [14, 15, 16 and 17]. Using NaCl solution result in cation migration from clinoptilolite framework and it is well-known as an effective technique to increase ion exchangers overall cation exchange capacity for water treatment applications [18]. Previous studies showed that the most widely used concentration ranges are 0.5-2.0 M NaCl [14, 19, 20, 21 and 22].

Zeolites can be used in various industrial applications due to its high cation-exchange ability and molecular sieve and catalysis properties. The adsorption and ion exchange process are the most widely used techniques that have attracted increasing interest in different companies [17, 23]. Different type of synthetic zeolites were developed such as (4A, mordenite, X, Y zeolites, etc.) which they have higher adsorption capacities and higher performances, compared to clinoptilolites, but they are usually very expensive [17, 23]. In the meantime, modified zeolites have been developed that can be rated as having a median adsorption capacity, while they do not cost as much as synthetic zeolite and have a better adsorption capacity than clinoptilolite [24].

Experiments were carried out in order to investigate the impact of pre-treatment on the efficiency of zeolite for the removal of Cu<sup>2+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> ions from synthetic industrial wastewater.

## 2. Experimental procedure

In this study clinoptilolite was used. The natural clinoptilolite was mined in Anaconda and supplied by the Anaconda mining company, Denver Colorado, USA it is 97% pure. The clinoptilolite samples were used as received without any modification from their natural state, unless stated. Kinetic studies were performed in order to investigate the behaviour of adsorbents

and understand the removal mechanisms involved in the adsorption process. The present work involves the study of the removal of Cu<sup>2+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> from synthetic metal solutions using natural zeolite. Laboratory experiments were cured out at university of Wolverhampton and kinetic test used to investigate the efficiency of adsorbents in the uptake of heavy metals from industrial wastewater.

### 2.1 Thermal pre-treatment process

The thermal pre-treatment process of clinoptilolite was performed by heating clinoptilolite samples in a furnace for 30 minutes under a slow heating rate of 200, 400 and 600°C to avoid destroy the zeolite structure. Then 4g of the thermally modified clinoptilolite samples were in contact with 100 ml of multi- component solutions. Agitation was carried out in a beaker using a stirrer at a speed of 150 rpm for 360 minutes at room temperature. The pH of the solution was adjusted to  $4 \pm 0.1$ .

### 2.2 Chemical pre-treatment process

The chemical pre-treatment of the clinoptilolite were carried out by placing clinoptilolite sample with 200 ml of 0.5M NaCl. The zeolite sample was agitated in a beaker using a stirrer at a speed of 150 rpm for 24 hours at room temperature. Thereafter the sample was rinsed three times in ample deionised water for a total period of 15 minutes and put in an oven to be dried at 100°C. Then 4g of chemically modified clinoptilolite samples were in contact with 100 ml of multi-component solutions for 360 minutes. The agitation speed applied was 150 rpm at room temperature. The pH of the solution was adjusted to  $4 \pm 0.1$ . For successful modification 0.5 M NaCl solutions were used to modify the clinoptilolite. Washing the zeolite samples after the pre-treatment process using deionised water is essential in order to remove excess NaCl entrapped within the zeolite structure [25].

## 3. Results and discussion

### 3.1. Scanning Electron Microscopy (SEM)

The surface morphologies of the different clinoptilolite samples before and after modification were analysed. Fig. 1(a, b) show the micrographs of the “as received” clinoptilolite samples. The images were taken under the

following SEM analytical conditions: EHT =10.00 kV and Signal A = SE1, WD 6.5mm at a magnification of 1000x, 5000x. The micrographs clearly show that the clinoptilolite structure contains a number of different diameter size macro-pores ( $1\ \mu\text{m} \leq d \leq 3\ \mu\text{m}$ ).

The effect of chemical pre-treatment was also analysed (Fig. 2) under the following SEM analytical conditions: EHT =10.00 kV, Signal A = SE1, WD 6.5mm at a magnification of 1000x and 5000x. The micrographs below show a clean surface and well defined crystal structures of clinoptilolite.

Fig.3 (a) shows that there is not significant change in the microstructure of thermally treated clinoptilolite at 200 °C. The images were taken under the following SEM analytical conditions: EHT =10.00 kV, Signal A = SE1, WD 6.5mm at a magnification of 5000x. The SEM figures show some well-defined zeolite crystals but the surface of the crystals seem to have considerably decomposed due to direct heating at 400 °C; this can be noticed in Fig.3 (b). The macro-pores on the clinoptilolite structure also seem to have slightly collapsed and the distinct crystal structures of clinoptilolite have disappeared. This was lead to appearance more solid less porous surface on the clinoptilolite structure.

Fig.4 shows the clinoptilolite sample that was exposed to extreme thermal conditions. The images were taken under the following SEM analytical conditions: EHT =10.00 kV, Signal A = SE1, WD 6.0 mm at a magnification of 3000x. The sample heated to 600 °C shows how thermal radiation has had a negative impact on the structure of clinoptilolite. As the heating rate increased, the structure became more distorted and the macro-pores on the clinoptilolite structure have collapsed.

### 3.2. Energy dispersive spectroscopy (EDS)

EDS is an analytical technique that was used to identify the elemental composition and chemical characterization of clinoptilolite. An electron beam was randomly directed onto different parts of the clinoptilolite samples in order to get a more accurate analysis Fig.5. The main elements and their corresponding oxides were determined by EDS.

The results of the EDS analysis also shows that the predominant exchangeable cations in the

clinoptilolite structure were found to be Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and Ca<sup>2+</sup> (Table 1).

Element	Na <sub>2</sub> O %	MgO %	Al <sub>2</sub> O <sub>3</sub> %	SiO <sub>2</sub> %
EDS	3.98	0.69	14.23	29.22
XRF	4.12	0.89	16.53	37.97

Element	K <sub>2</sub> O %	CaO %	TiO <sub>2</sub> %	Fe <sub>2</sub> O <sub>3</sub> %
EDS	2.39	0.84	0.06	0.54
XRF	2.12	0.96	0.06	0.74

### 3.3. X-Ray Fluorescence (XRF)

XRF analytical analysis of the clinoptilolite samples also was carried out to determine the elemental composition of the samples. The results of the XRF analysis are presented in Table 1. The result shows that SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and K<sub>2</sub>O are main components of clinoptilolite but higher rate compared to EDS analysis result. The results of the XRF analysis are similar to EDS analysis result which showed that the predominant exchangeable cations in the clinoptilolite structure were Na<sup>+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and Ca<sup>2+</sup>.

### 3.4. X – Ray Diffraction (XRD) results

X-ray diffraction (XRD) analytical technique was used for phase identification of the clinoptilolite. The procedure was carried out and data were collected in the range 0-50 degrees, with a scanning step of  $2^\circ$ . The crystalline patterns were compared with the standard line patterns from the powder diffraction file database supplied by the International Centre for Diffraction Data (ICDD). Thus the XRD result showed that the sample contained clinoptilolite in the majority (Fig. 6).

### 3.5. Thermogravimetric Analysis (TGA) result

Thermal analysis methods were used to gain information about the mass loss change and structural stability of clinoptilolite of. The results

obtained from the TG/DTG analysis clearly show that the zeolite structure was stable up to 750 °C and dehydration process appeared up to 400°C continually this is an agreement with is the result presented by Breck (1974). Fig.7. shows the dehydration and dehydroxylation process of clinoptilolite and their mass loss rate (13 wt. %). Results obtained from TGA/DTG show that, clinoptilolite samples were continually losing weight after heating up to 900 °C (Fig. 8). The main reasons of this are due to dehydration and dehydroxylation processes. According to Perraki and Orfanoudaki (2004) weight losses at 20–100 °C and 100–200 °C are due to hygroscopic water and loosely bonded water, respectively [2,27 and 28]. Then dehydroxylation took place in the range 400–600 °C [29]. Kurkuna et al. (2006) reported two forms of water molecules and hydroxyl groups existing in the structure of silicate minerals such as clinoptilolite [30]. The total loss calculated from the thermogravimetric analysis was 13 wt. %. Similar values were obtained by other authors [30, 31, 32 and 27].

### 3.6. Fourier Transform Infrared (FT-IR) Spectroscopy results

FT-IR Spectroscopy technique was used to obtain an infrared spectrum of absorption of clinoptilolite. Only the 1200–400 cm<sup>-1</sup> region was investigated; this is where the all spectra showed remarkable changes. A broad band between 3500 and 3700 cm<sup>-1</sup> is indicative of the presence of OH groups on the clinoptilolite surface. In the OH stretching region, infrared spectra of zeolites provide a wealth of information on hydroxyl groups attached to zeolite structures (Li, 2005). FT-IR results demonstrate (Fig. 9) that zeolites are significantly hydrated. The bands, which were located at 3444 cm<sup>-1</sup> refer to OH group and 1637 cm<sup>-1</sup> refer to H<sub>2</sub>O molecules associated with Na and Ca in the channels and cages in the of the zeolite structure [33]. The 1015 cm<sup>-1</sup> band corresponds to asymmetric stretching vibration modes of internal Si-O-Si or Si-O-Al bonds. The 796 and 448 cm<sup>-1</sup> bands indicative of the stretching vibration modes of Si-O-Si or Si-O-Al bonds groups and the bending vibrations of Si-O bonds, respectively [34]. These results are similar as those obtained by other authors [35, 27].

### 3.7. Inductively Coupled Plasma-Optical Emission Spectrometers (ICP-OES) results

The heavy metal ion concentrations in the waste water solution were determined using ICP-OES. Results shows the behavior of adsorbents and the pre-treatment factor that affect the rate of adsorption and maximum effective capacity of clinoptilolite towards Fe<sup>3+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> ions removal. Every hour 15 ml of the sample was taken for metal ion concentration analysis using the ICP-OES. Microsoft office excel were used for data interpretation. After a mathematic calculation the results were presented either by plotting a chart or presenting data in a table.

The data obtained from the kinetic adsorption tests were used to determine the removal capacity,  $q_e$  (mg/g) of the different adsorbents using the following equation:

$$q_e = (C_o - C_e) \times V / m$$

The percentage removal of metal ions from solution was also determined using the equation below:

$$\text{Percentage Adsorbed (\% removal)} q_e = \{(C_o - C_e) \times 100\} / C_o$$

where,

$q_e$  amount of adsorbate adsorbed per unit weight of adsorbent (mg/g)

$C_o$  and  $C_e$  are the initial and final metal ion concentrations in solution (mg/l) respectively,  $V$  is the solution volume (l) and  $m$  is the weight of the zeolite used (g).

The results of the effect of the pre-treatment on the removal of the cations from the solution are shown in Fig.10. Although the thermal treatment process can affect the adsorption capacity, mostly up to 200°C, as the temperature rate increases more, there is a decrease in the level of the effect of the thermal treatment process on adsorption and the adsorption process gets slower.

It was observed that the thermal treatment samples at 200°C adsorbed more metal ions of Cu<sup>2+</sup>, Fe<sup>3+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> ions from solution, around %50 better than the thermal treatment samples at 400°C adsorbed less metal ions as shown in Fig.10. Also, the rate of adsorption by calcined zeolite up to 200°C was %10 better compared to the untreated zeolite, but the efficiency decreased when zeolite was treated at very high temperatures.

The increase in the efficiency of heavy metal removal from solution as a result of thermal treatment may be due to the removal of water and hydroxyl groups from the clinoptilolite structure. This removal of water and hydroxyl group results in a change in the surface area of the samples and also leaves the channels more vacant and available. Hence the adsorption capacity is improved since the heavy metal ions had better access to exchangeable sites within the clinoptilolite [36, 37]. However, the decline in the efficiency for zeolite treated at very high temperatures was related to the possible collapse of the zeolite structure and the loss of porosity, which reduced the activated surface area [37].

The adsorption capacity as a result of the chemical treatment processes was higher compared to the untreated zeolite or thermal pre-treatment zeolites as shown in Fig 7 and 8. This may be due to decationization process which is exchange of ( $H^+$  or  $Na^+$ ) from solution with exchangeable cations ( $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) from the zeolite framework which they can be easily removed.

### 3 Conclusion

- The removal efficiency of  $Cu^{2+}$ ,  $Fe^{3+}$ ,  $Pb^{2+}$  and  $Zn^{2+}$  ions from synthetic industrial wastewater, was enhanced with the application of pre-treatments.
- Application of any temperature above  $200\text{ }^{\circ}C$  is not suitable in thermal treatment process. Further thermal treatment may lead to lose some porosity and decomposition of some crystalline structure due to.
- Modified zeolites have high adsorption capacities for removal of heavy metals from solutions and can reach adsorption equilibrium level in short periods of time while pre-treatment process applied.
- The adsorption capacity as a result of the chemical treatment processes was higher compared to the untreated zeolite or thermal pre-treatment zeolites.

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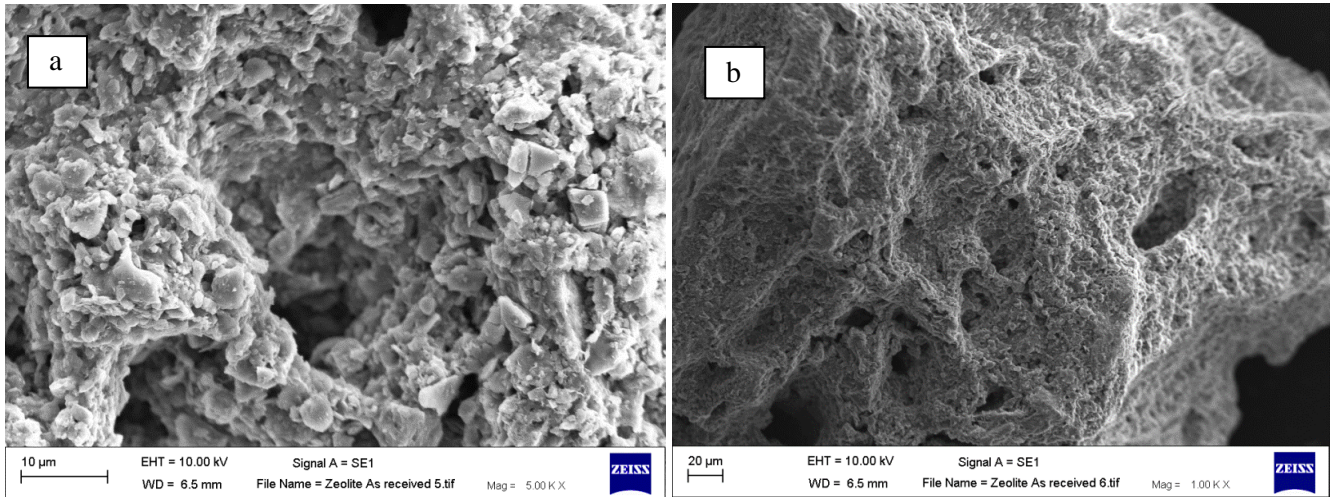
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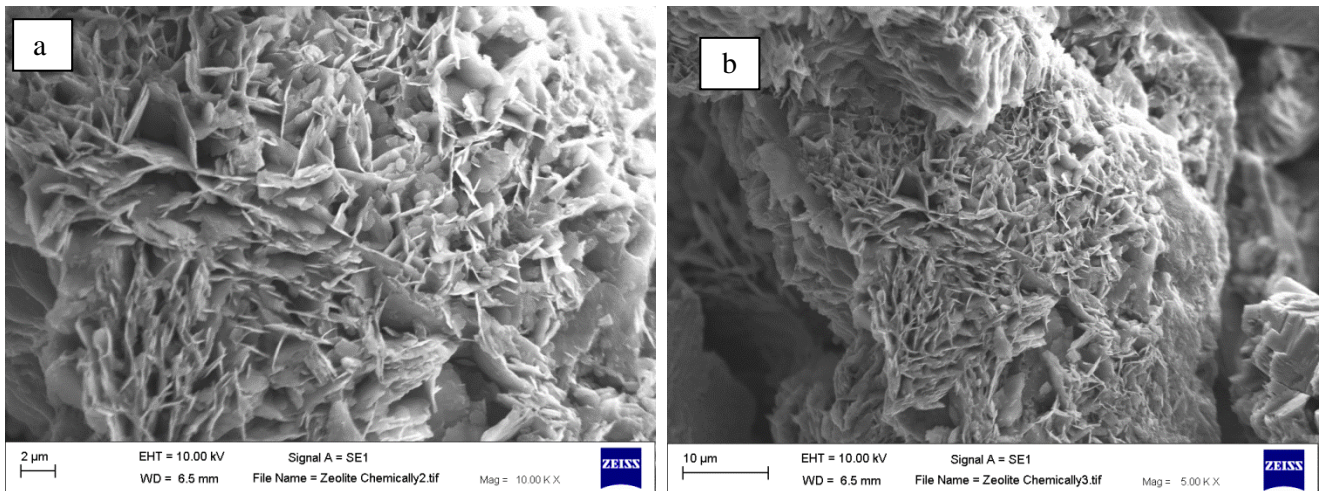
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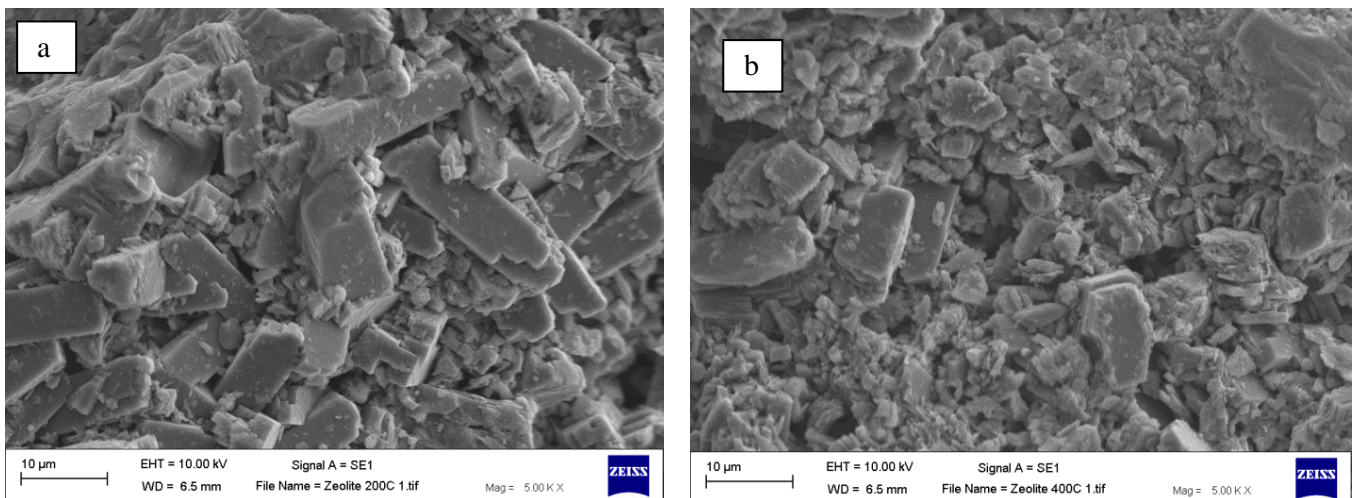
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**Fig. 1.** Showing the SEM micrograph of as-received clinoptilolite at a magnification of: (a) 5000x and (b) 1000x.

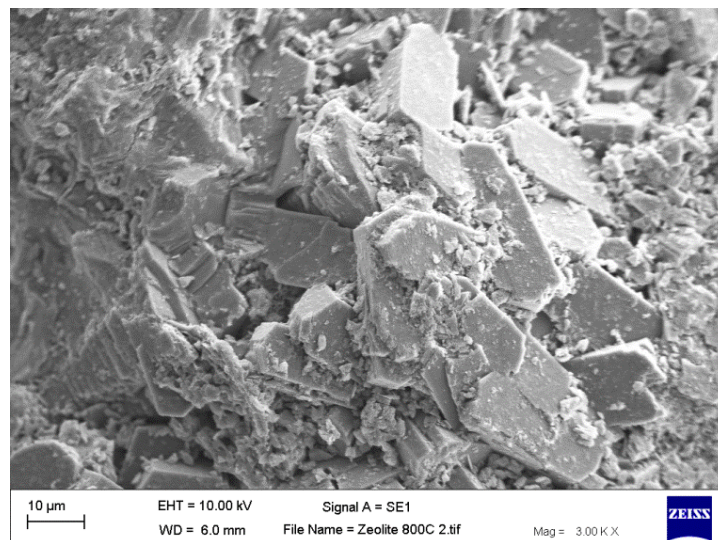


**Fig. 2.** SEM micrographs of chemical pre-treatment of clinoptilolite at different magnifications: (a) 10000x and (b) 5000x.

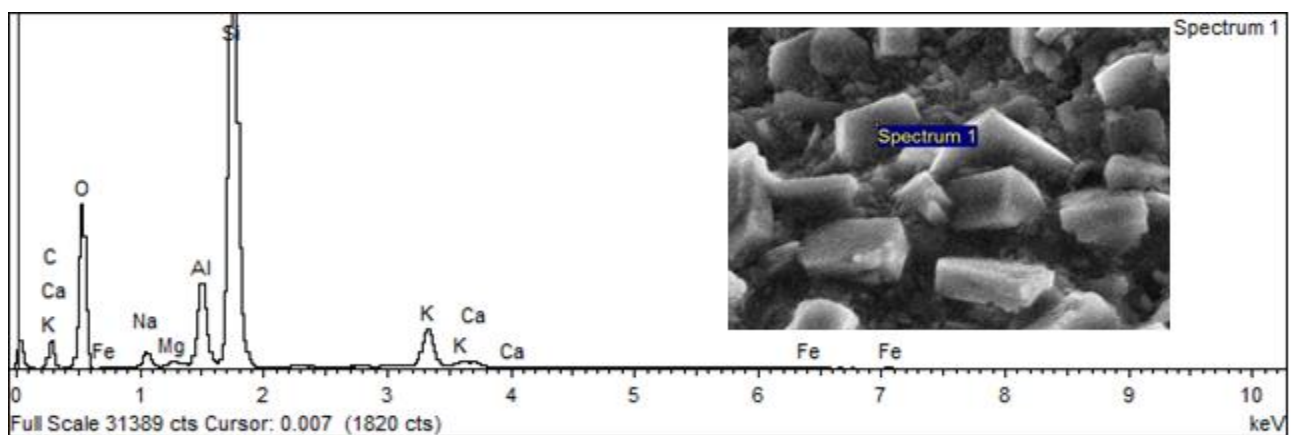


**Fig. 3.** SEM microstructure of thermally pre-treated clinoptilolite in a muffle furnace at (a) 200 °C (b) 400 °C, at a magnification of 5000x.



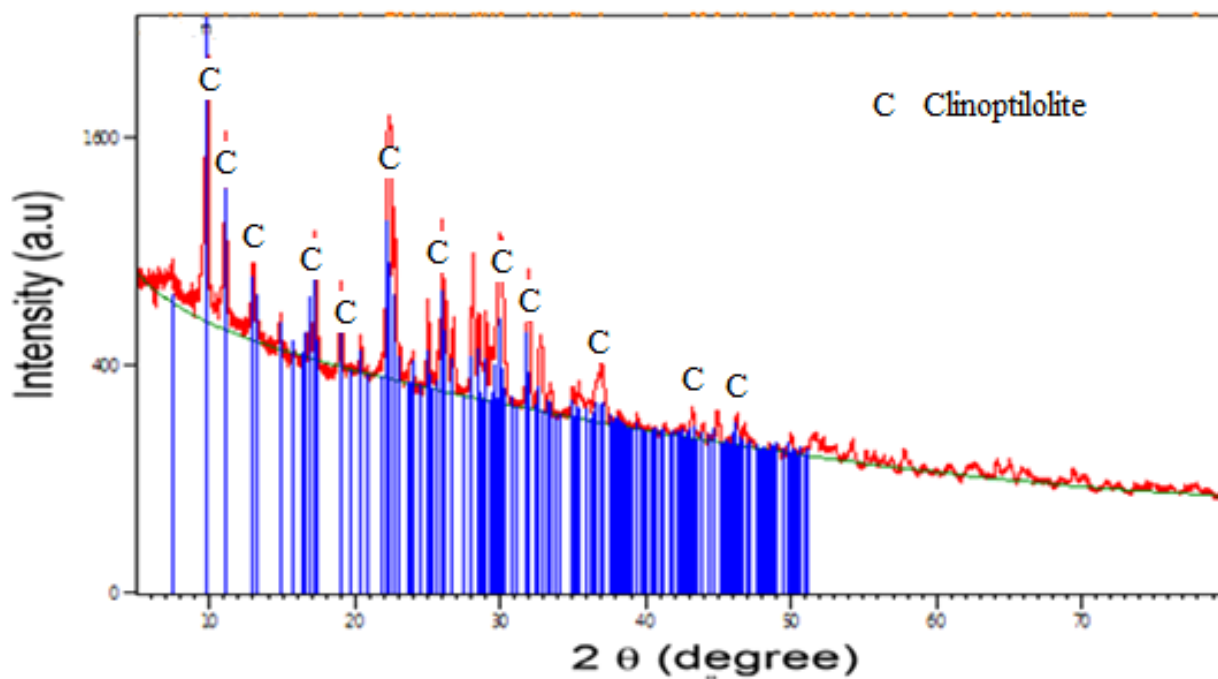


**Fig. 4.** SEM microstructure of clinoptilolite showing the collapse of the structure of clinoptilolite due to thermal treatment at 600 °C, at a magnification of 3000x.

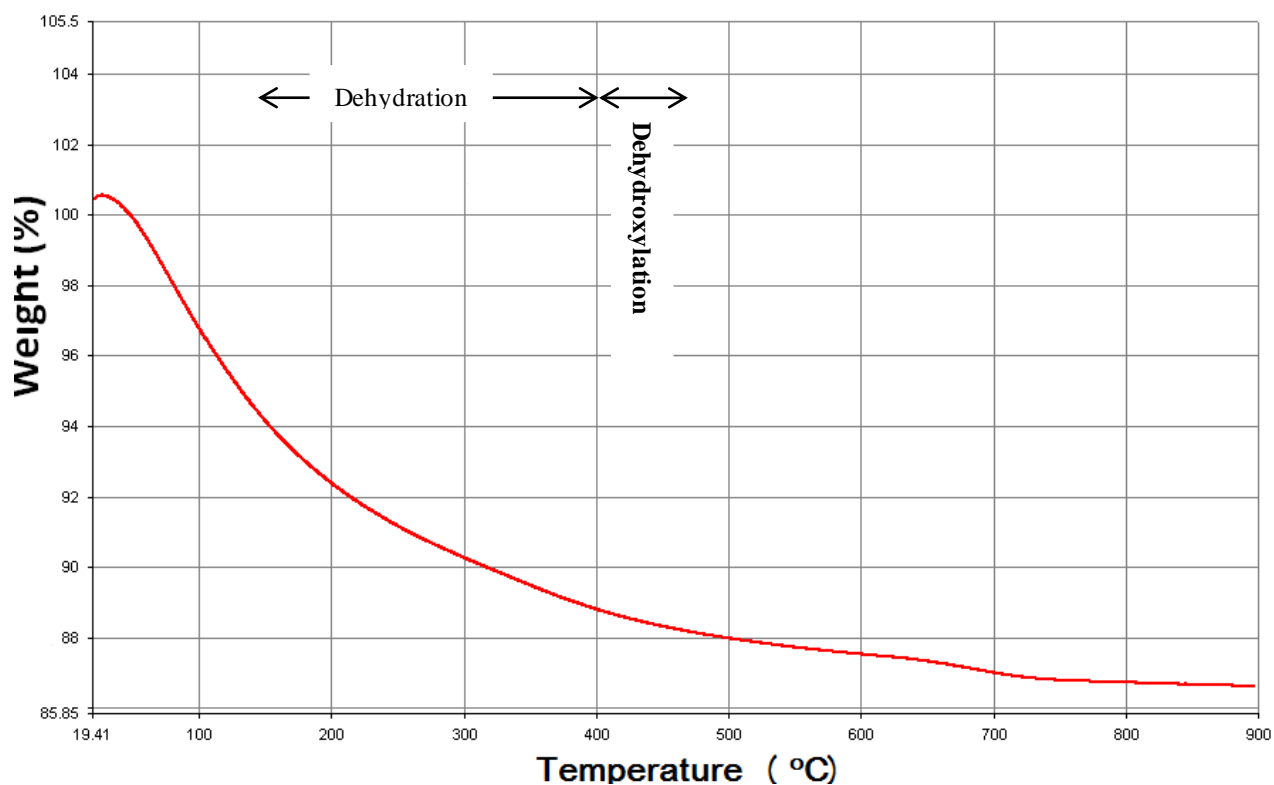


**Fig.** Error! No text of specified style in document.. EDS analysis showing the elemental composition and the scanned image for clinoptilolite.

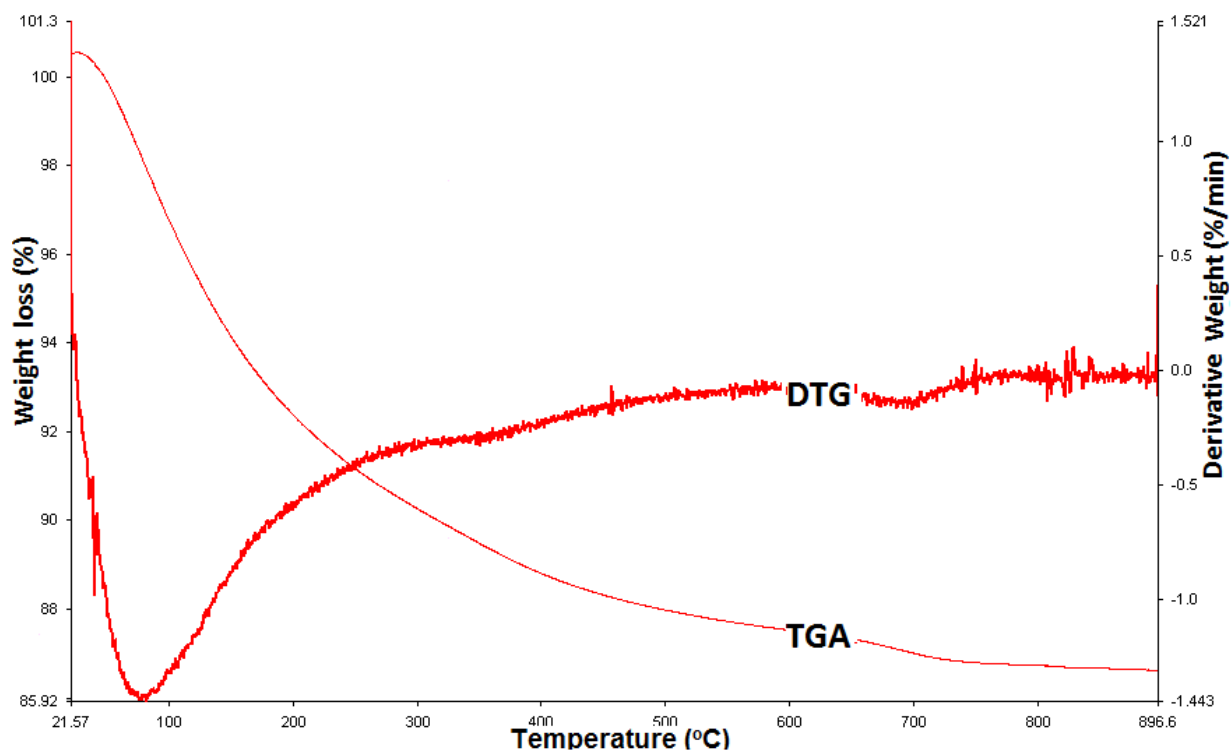




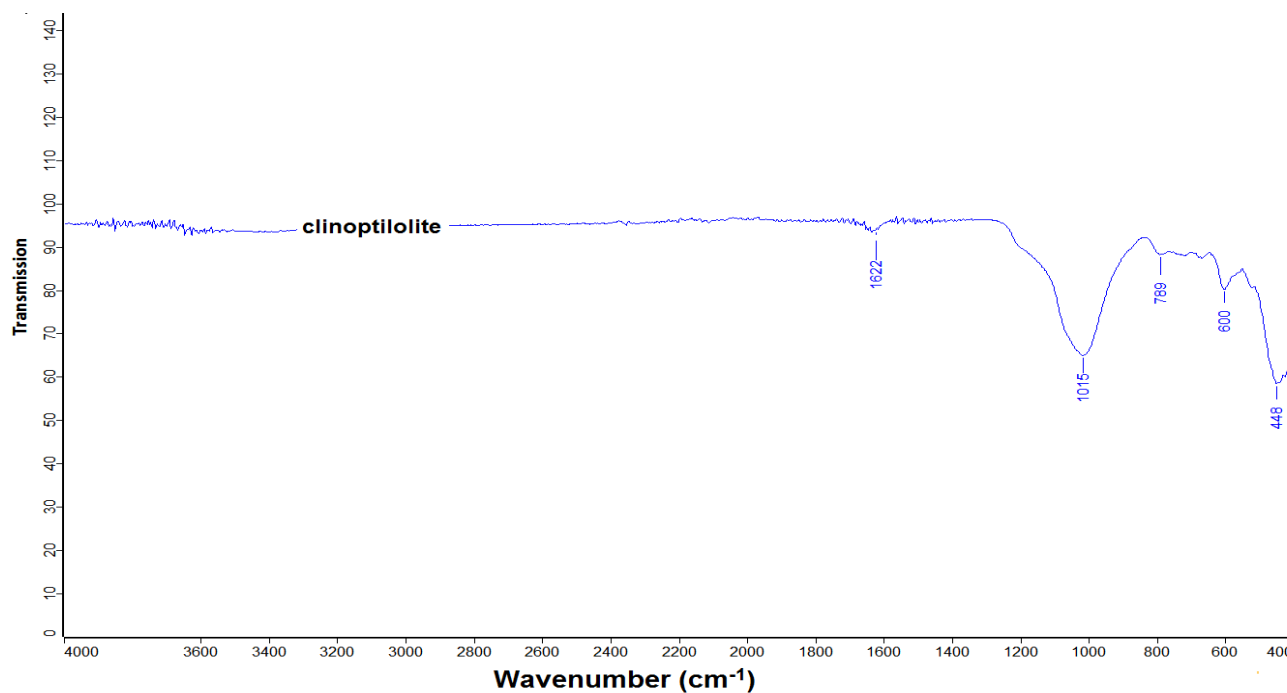
**Fig.6.** XRD analysis showing the mineralogical analysis of Clinoptilolite.



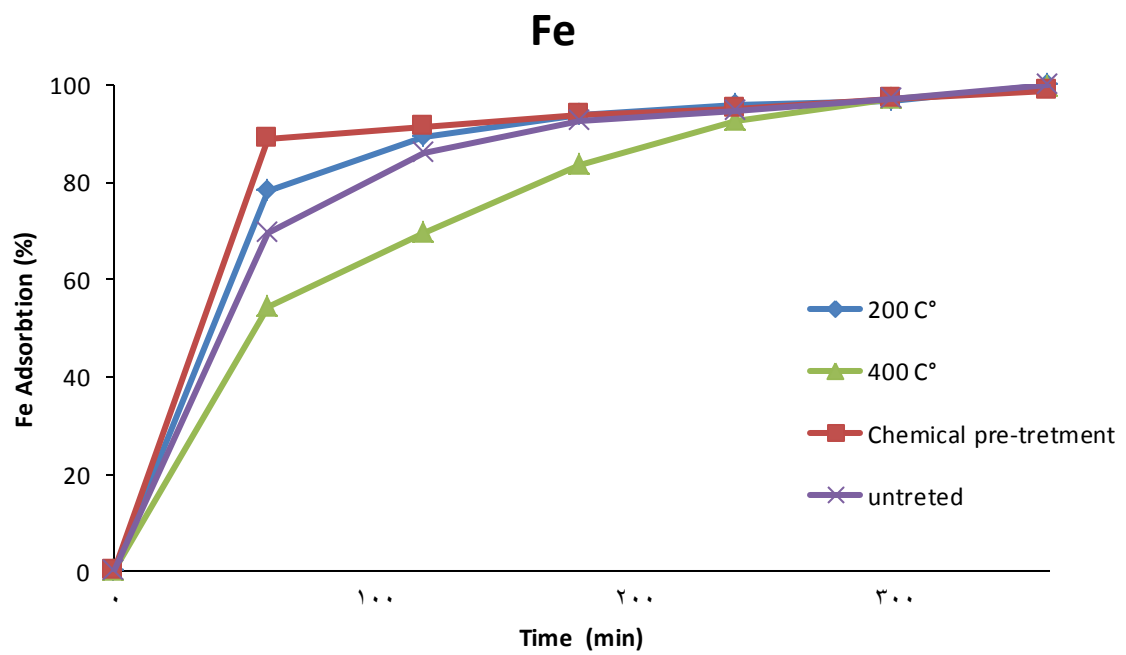
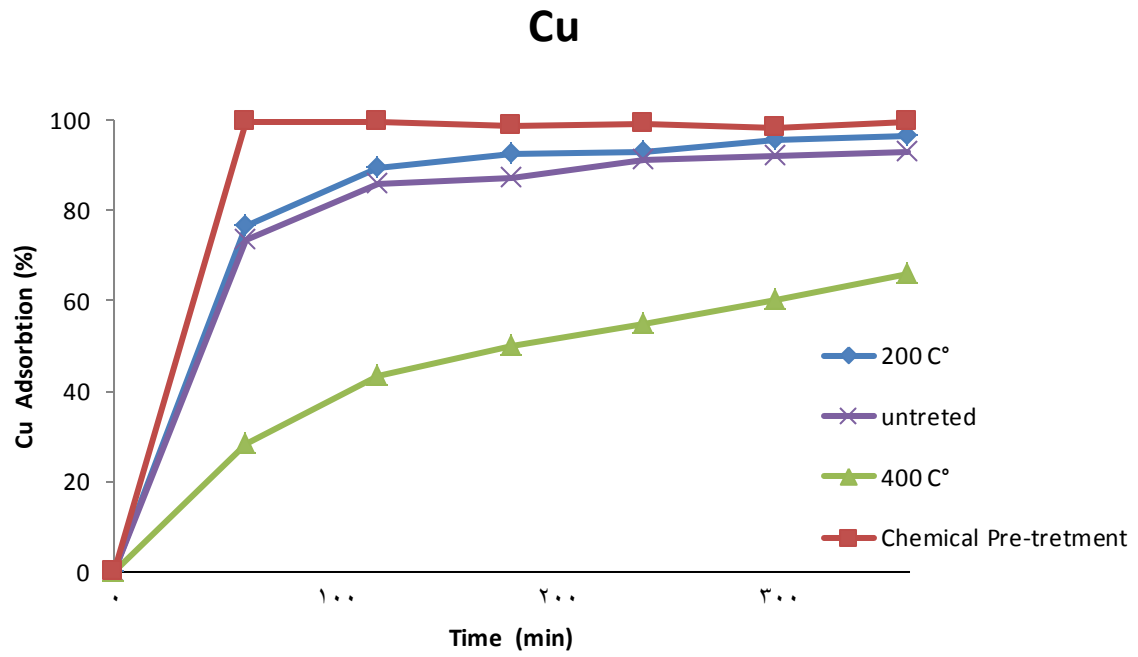
**Fig. 7.** Shows the loss of mass of clinoptilolite by thermogravimetric analysis (TGA) which show curves between 20-900°C.



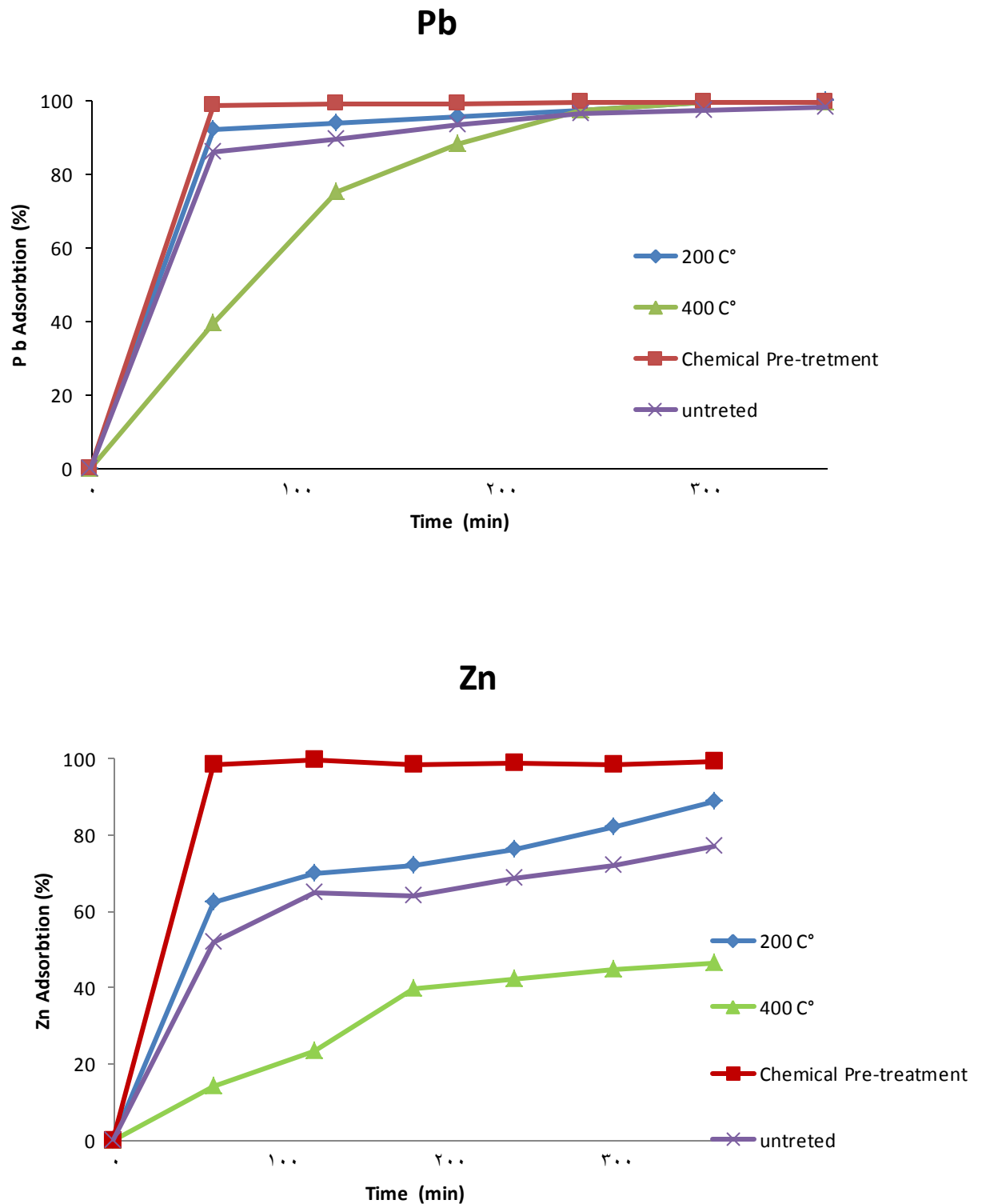
**Fig. 8.** Thermogravimetric analysis (TGA/DTG) of clinoptilolite between 20-900°C.



**Fig.9.** Shows the FT-IR spectra analysis of the as received clinoptilolite.







**Fig.10.** Shows the comparison of un-treated and treated clinoptilolite.