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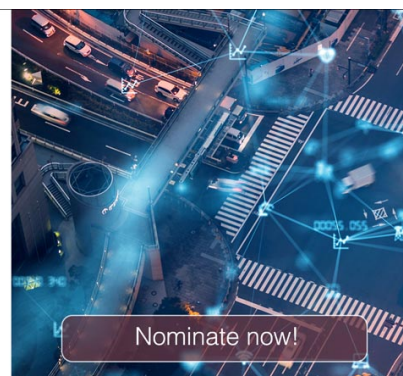


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Natural Zeolite Sample and Investigation Its Use in Oil Bleaching Sector

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Abstract. In the sector of oil bleaching, the stored raw oil is subjected to physical and chemical methods such as degumming, neutralization, bleaching, deodorization and winterization. In the process of oil bleaching, the selection of correct bleaching earth in accordance with oil characteristics matters so much. Bleaching earth is an inorganic product used in removing impurities being available within the structures of vegetable, animal oil (sunflower, soya, corn, palm, tallow, rapeseed, fish oils...etc.) and fatty acids, mineral oils (glycerine, paraffin, mineral motor oils. etc.) with the adsorption process. The factors such as low cost of oil bleaching earth, low ratio of oil retaining, high bleaching capacity in spite of using them in small amounts, filter's delayed blocking by the earth and non-increase of the free acidity of the oil should be taken into consideration. Bleaching earths are processed with some acids in order to widen their surface areas. During this process, a certain amount of acid is left within oil bleaching earths even if it is very little. These acids also increase oil's acidity by oxidizing oil in the course of bleaching process. In this study, zeolite sample taken from Manisa -Demirci region was used. Following the processes of crushing and sieving, zeolite sample was subjected to chemical analyses according to their grain thickness, microscopic examination, the analyses of XRD and cation exchange capacity and their ore characteristics were determined. Afterwards, it was searched whether zeolite sample has oil bleaching ability or not or whether it can be used as oil bleaching earth or not.

1. Introduction

The refining process in oil production is a purification process. It is one of the most important stages in bleaching or oil refinement. The most crucial element in bleaching process is selecting the bleaching soil that is most viable for the properties of the oil that needs to be bleached. Performing the bleaching with the right soil type with the least cost has been the primal goal for the companies. When calculating the cost, indicated above, the oil retention rate of the soil being low, high bleaching capacity even when using a low amount of soil, the soil clogging up the filter as late as possible, not increasing the free acidity of the oil etc. should be taken into account. The bleaching soil is processed with several types of acids in order to widen the surface area. During this process, a small amount of acid remains within the bleaching soil even if just a bit of it. This remaining acid oxidizes the oil during the bleaching process, leading to an increase in the acidity of the oil. The physical activation method contains the following processes; custom shaping, drying, grinding to the suitable surface area and pore size respectively. As the result of the indicated processes, various ideal bleaching soil types are produced in order to remove the color compositions and impurities in the cooking oil [1]. For example, the tonsil (oil bleaching soil) is sodium based and contains 90% montmorillonite. It has high swelling



capacity. (15-20 fold in volume) It is used as a clarification agent for the clarification of various liquid chemicals and for the recycling of the vegan waste oil.

2. Material and method

The Chabazite (zeolite) material; with the chemical formula of $(Ca,Na)_2(Al_2Si_4O_{12}) \cdot 6H_2O$ is found in hexagonal form in rhombohedral shape with cube looking crystals. Its hardness is 4.5 and its specific gravity is 2.1. It is transparent in glass radiance, semi transparent, colourless, white and reddish. This compound is dissolved with HCl and is isolated with silicate. It is found in the grooves and cracks of the basalts. When left in a closed tube, it gives off water. The clearance volume in its system is %47. The structure of the Chabazite is in the form of bonding hexa rings to each other with inclined quad rings. They are formed by the sedimentary bedding and by the alteration of the glass containing tuff [2]. In this study, the material properties (as raw material) of the Chabazite sample, obtained from the Manisa - Demirci region of Turkey is analyzed and its utilization as the oil bleaching soil is discussed. Figure 1 shows the flow chart, displaying the experimental works.

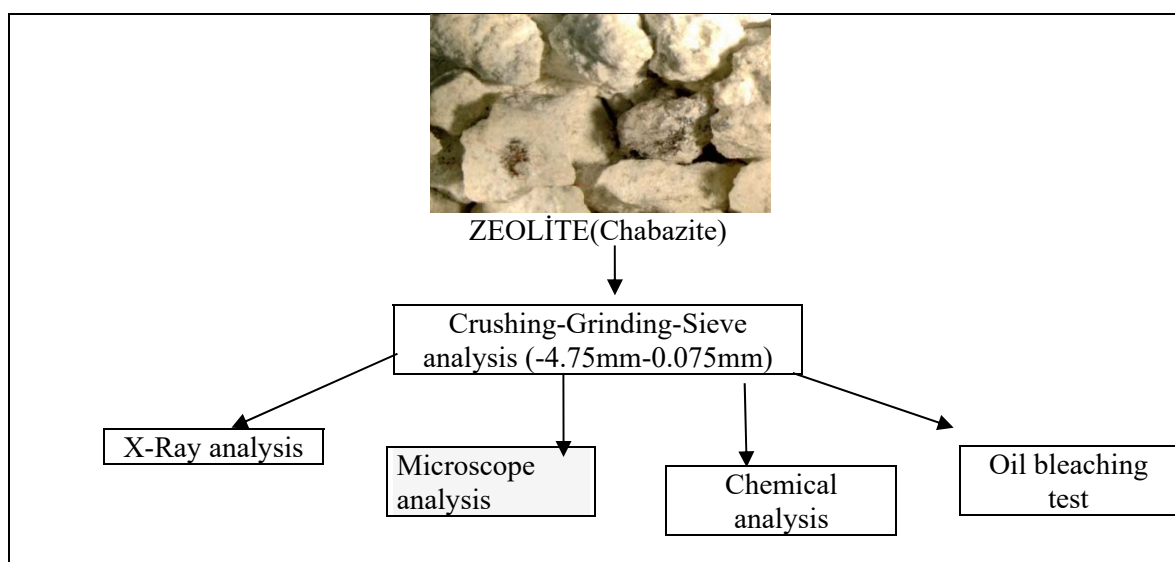


Figure 1. Flow chart of experimental work

2.1 Obtaining the Sample and Chemical Analysis

The site that the Chabazite (zeolite) samples were obtained is located in Guneşli area of Aliagaç Village of Demirci County in Manisa Province. The samples were obtained between those coordinates; Y: 54000-54085 , X: 3.927-4.060 The samples, after the crushing - screening process were analyzed in the size range of +4.75mm - 0.075 mm in 11 grain fraction and the chemical weight of compounds were tested (%). The chemical analysis results of the Chabazite (zeolite) samples by grain size is given in Table 1 [3].

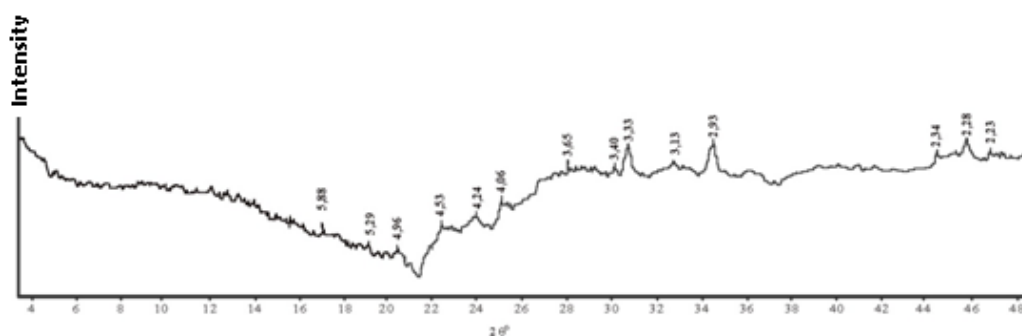
When the chemical analysis of the aforementioned samples is reviewed, it was found that the SiO_2 ratio (%) s found out to be between 72.97 – 77.42 while the ratios of the other elements were found to be in similar values. However, due the fact that the carbonate values within the structure of the zeolite sample turned out to be low, it was concluded that this sample may provide a lower ignition loss value of %7.29 compared to the ignition loss values of the other samples. In addition, the high SiO_2 ratio in the zeolite sample creates a possible fragmentability. It can also be concluded that this zeolite sample, thanks to its relatively high K_2O value of %3.66; may be a rather desired type of zeolite for the agricultural sector [3].

Table 1. The chemical analysis results of the Chabazite (zeolite) sample.

| Particle Size | SiO ₂ (%) | Al ₂ O ₃ (%) | Fe ₂ O ₃ (%) | CaO(%) | MgO(%) | Na ₂ O(%) | K ₂ O(%) | Lost Head(%) |
|---------------|----------------------|------------------------------------|------------------------------------|--------|--------|----------------------|---------------------|--------------|
| Feed material | 77.42 | 9.30 | 0.96 | 0.48 | 0.11 | 0.66 | 3.66 | 7.29 |
| +4.75 | 77.09 | 9.21 | 1.06 | 0.45 | 0.13 | 0.69 | 4.00 | 7.24 |
| -4.75+3.35 | 77.19 | 9.26 | 0.89 | 0.51 | 0.13 | 0.70 | 3.70 | 7.48 |
| -3.35+2 | 77.66 | 8.85 | 0.78 | 0.46 | 0.12 | 0.62 | 3.89 | 7.46 |
| -2.0+1.0 | 77.75 | 8.94 | 0.92 | 0.40 | 0.12 | 0.65 | 3.87 | 7.15 |
| -1+0.85 | 77.52 | 9.35 | 1.08 | 0.42 | 0.12 | 0.68 | 3.86 | 6.80 |
| -0.85+0.5 | 78.19 | 8.53 | 0.89 | 0.39 | 0.11 | 0.69 | 3.88 | 7.10 |
| -0.5+0.4 | 78.07 | 8.85 | 1.06 | 0.41 | 0.09 | 0.68 | 3.82 | 6.78 |
| -0.4+0.3 | 79.01 | 8.44 | 1.03 | 0.50 | 0.10 | 0.71 | 3.58 | 6.39 |
| -0.3+0.2 | 78.12 | 9.30 | 0.87 | 0.46 | 0.08 | 0.78 | 3.86 | 6.41 |
| -0.2+0.1 | 77.96 | 9.26 | 1.15 | 0.38 | 0.10 | 0.80 | 4.16 | 5.97 |
| -0.1+0.075 | 78.5 | 8.66 | 0.89 | 0.48 | 0.09 | 0.77 | 3.96 | 6.41 |
| -0.075 | 78.21 | 9.03 | 0.85 | 0.49 | 0.10 | 0.67 | 3.98 | 6.53 |

2.2 X Ray Graphic and Binocular Microscope Analyses of the Sample

The zeolite sample from Manisa - Demirci region was subjected to X Ray Diffractometer tests. This test shows which 2θ does the diffraction distribution, obtained by the X Ray Diffractometer shots correspond to the peaks over the continuous spectrum. The dhkl distances between the hkl planes that correspond each 2θ that meet the Bragg refraction condition ($n\lambda=2d\sin\theta$) and the refraction intensity are determined from the catalogues. In order to confirm the phases, from which the peaks are derived, the Refraction Index, compiled by the American Society for Testing Material (ASTM) is used. These standard cards are used to determine the phases of the samples, which have a crystalline structure. The X Ray Analyses of the samples were performed at Dokuz Eylül University, The Department of Mining Engineering. Figure 2 shows the X Ray Graph of the Zeolite sample. Based on the results of the X Ray Analysis, it was determined that the sample is Chabazite mineral [3].

**Figure 2.** The X ray diffraction diagram of the chabazite (zeolite) sample

According to the binocular microscope analysis of the zeolite sample, it was concluded that the samples was contaminated in terms of surface cover, the contamination was found in the form of scattering and punctual contamination by iron oxide minerals. Considering the rate of the removal of the contaminating minerals in selected dry and wet environment after the sample is selectively fractured or pulverized, it is recommended to determine this by further studies. Figure 3 is given the image of the binocular microscope analysis of the zeolite sample [3].

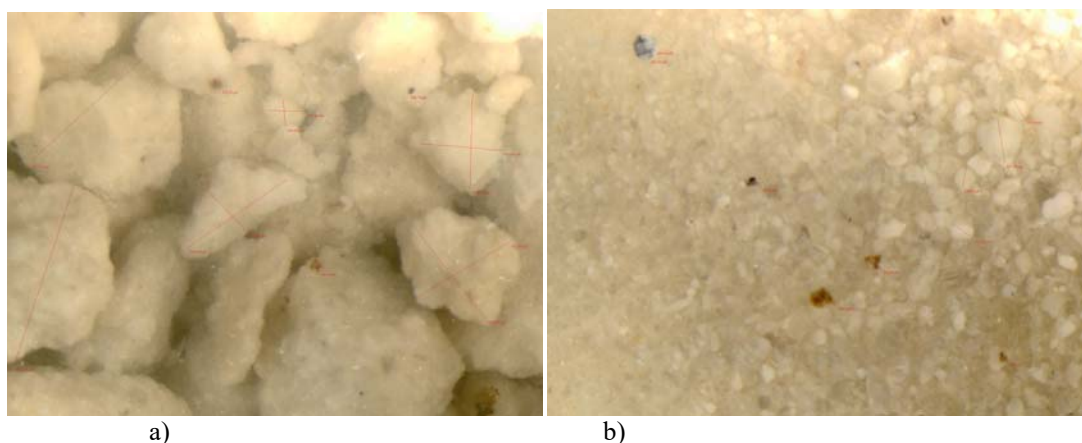


Figure 3. a), b) The image of the binocular microscope analysis of the zeolite sample

The punctual contamination of the zeolite sample is revealed to be due to 100 – 150 μm particles. It was observed the zeolite sample is considerably clean. However, a higher quality production can be achieved with a punctual reduction below 150 μm to render the contaminating minerals free and as the result of an enrichment to be performed in wet or dry environment; very high quality zeolite concentrations can be produced. (Figure 3-a) As the clean zeolites that are in a free state after pulverizing, were displayed, the free contaminating minerals were also observed. As it was indicated before, it was established that those contaminants become free below 150 – 200 μm . The production of a high quality zeolite concentration will be possible by grinding the zeolite down to this size and by enriching it in wet and dry environments. As the result of the microscopic exams and the digital imaging, it was proved that the clean zeolite particles are rendered in a free state in high incidents within a wide particle range from 600 μ to 300 μ and below. Therefore, it was concluded that a high quality zeolite concentration can be obtained by grinding the zeolite down to the indicated size range and by enriching it in dry and wet environment (Figure 3-b). As understood from the Figure 4; volcanic rock shards are detected thin the Zeolite sample [3].

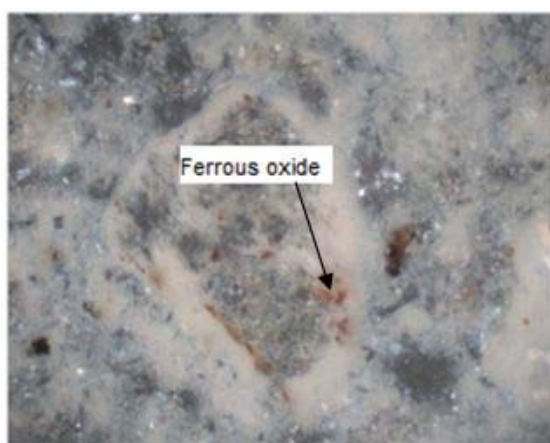


Figure 4. The thin section image of the zeolite sample

2.3 Determination of the Cation Exchange Capacity and the determination of the exchangeable cations in the sample

The organic and inorganic soil colloids (organic matter, clay and low amounts of amorphous silica acids as well as Al and Fe oxides and their hydroxides) have the ability to absorb the cations. The absorbed cations can be exchanged. The cation absorption is highly important in terms of soil reaction,

the amount of the nutrients in the soil and the soil formation events (such as podsolization and alkalinization). The unit of the exchange capacity is “m.e./100 gr soil and its amount varies depending on the amount and type of the clay and organic matter. In order to determine the cation exchange capacity, the ore is thoroughly treated with Na-acetate, which contains a certain cation (Na^+) and which has a Ph value of 8.2, and its absorption complex is saturated with this cation. In addition, the same cation is mixed with another cation (NH_4^+) to determine how much it is retained. (“m.e./100 gr soil) [3].

For example, there are various cations in the exchange complex. They are exchangeable cations. (Such as Ca^{+2} , Mg^{+2} , K^+ , Na^+ , H^+) The retention rate of a cation is influenced by various factors. Those factors are the valency of the cations, its atomic weight, polarization characteristics the concentration of a cation within a solution, the concentration of the other cations in the solution and the specific features of the colloid. For example, the increase in Na^+ saturation leads to alkalinity while the increase in the saturation of H^+ and Al^{+3} leads to acidity. The total of the Ca, Mg, Na and K in the cation exchange capacity (%) is called “the base saturation” The nomination of the exchangeable cations is exchanging the exchangeable cation with this specific cation after saturating the ore with NH_4^+ at the pH value:7 and determining the amount of the exchanged cations within a solution. Table 2 shows the CEC and EC (meq/100 g. zeolit)

Table 2. The CEC and EC values of the zeolite. (meq/100 g. zeolit)

| Name of Sample | CEC | EC_{Na} | EC_{K} | EC_{Ca} | EC_{Mg} | Base Saturation (%) | pH |
|--------------------|-------|-------------------------|------------------------|-------------------------|-------------------------|---------------------|-----|
| Zeolite(chabazite) | 80.58 | 0.41 | 1.80 | 3.24 | 0.58 | 7.49 | 7.6 |

When the cation exchange capacities of the zeolite samples were analyzed, we can conclude that all four samples have high cation exchange capacities (CEC) and as the result, have high Ph values. Having a high Ph value in the soil means the easy exchange of the H^+ and Al^{+3} ions that are retained by the soil colloids. It is also safe to say that the cation exchange capacity of the Zeolite sample as well as its Ph value is high. The base saturation in the soil is an indicator of the fertility of the soil [3].

2.4 Oil Bleaching Experiment

The oil bleaching processes: Olive oil is undergone various processes in oil production facilities. The stored raw oil gets an edible flavour by physical and chemical methods after undergoing the following processes;

- Degumming: (Flushing) The phosphatides in raw olive oil is removed by this process.
- Neutralization: The free fatty acids in the raw olive oil, treated with sodium hydroxide, are removed from the oil in the form of soap.
- Bleaching: In this process, the oil is undergone a procedure with an active clay – active coal, which is called neutral oil bleaching soil under vacuum (80 – 100°C). The resulting mix of soil – oil is cooled down and filtered, then is separated from the soil.
- Deodorization: The oil is treated with steam under low vacuum (2-5Hg) and high temperature (84 – 230 °C) and is cleansed of substances that give off scent. The result is neutral oil in terms of odour and flavour.
- Winterization (Clarification): This is the filtering of the oil that are cooled down to very low temperatures (1-2 + 2°C) in order to cleanse from the wax and sterides to have a better overall appearance.

After those processes are completed, the refined oil that is packed in tin canisters is stored or sale. In Figure 5; an example of the flow chart of an olive oil production process can be seen [4].

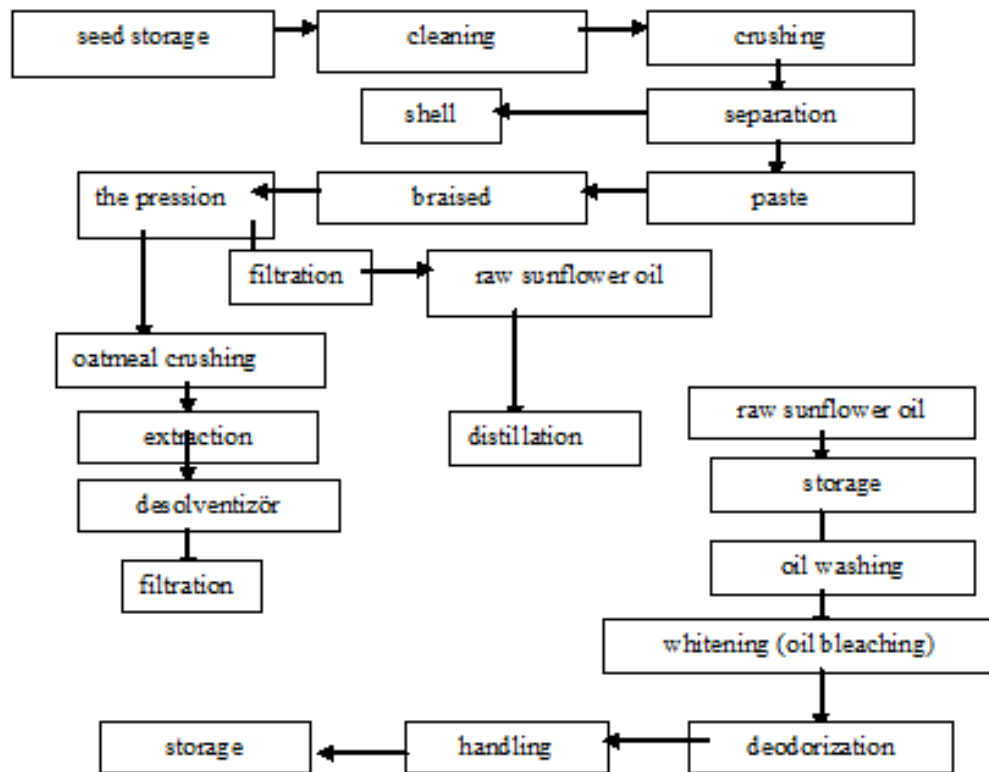


Figure 5. Flow chart for olive oil production

In the oil bleaching experiment, whether the zeolite (Chabazite) material can be used as bleaching soil or not was analyzed. Several experiments were conducted in relation to the bleaching process, which has a pivotal role in the sun flower oil. The task of preparing the solutions was undertaken at the Chemistry Labs in Dokuz Eylul University the Department of Mining Engineering as the results of the experiments were measured by a Lovibond Tintometer at Altinyag Facilities in Cigli. In the experiment, 100 ml of raw oil is heated up to $90 \pm 2^\circ\text{C}$ and is added raw zeolite.

The zeolite, used as 1.0 g, 1.5g and 2.5g, are mixed in a magnetic stirrer for 30 minutes. The resulting mix of oil - zeolite is screened through a screening paper and visible parts of the filtered oil is measured by a spectrophotometer. The neutral sunflower oil that was used for the bleaching experiments was obtained from Tariş cotton seed oil facilities.

The zeolite samples were in different grams. (1.0 g, 1.5g and 2.5g respectively). Furthermore, in order to be able to make a comparison, the same experiment was repeated in raw oil and in zeolite sample, activated by a 5M acid. The oil bleaching results of the zeolites according to the amount of the absorbent is shown in Table 3.

The data, accumulated as the result of the oil bleaching experiments was measured in Lovibond Tintometer. The Lovibond Tintometer colour determination is a process that is performed in order to check the state of the natural colour that the pigments within the composition of the oils give off to oil, to determine how effective was the bleaching and whether the colouring agents (such as Beta Carotene) that are subsequently added to the oil are sufficient or not and in order to check whether the oil gets the desired look and appearance or not. The colour determination is performed by instruments such as the tintometer, which automatically measures the colour. The container of the tintometer is filled completely with the sample. This container is then inserted to the instrument. The adjustments

are made depending on whether the sample is raw oil of a produce and the instrument is powered on. The color value in the scale is read. The colour is read as yellow or red. The finished oil is read after placed on a 5.25 inch container as the raw oil is placed inside a 1 inch container. The raw sunflower oil should be read as Red 1.5-3.0 - Yellow 3.0-8.0 and the refined sunflower oil should be read as Red 1.0 - 1.3 - Yellow 8.0 - 11.0 [3].

Table 3. The oil bleaching results of the zeolites according to the amount of the adsorbent

| Name of Sample | Amount of adsorbent(gr) | Colour | | |
|---------------------|-------------------------|-------------|----------|------|
| | | Yellow | Red | Blue |
| Raw oil | - | 10 | 2 | - |
| Standard oil | - | 8-10 | 1 | - |
| With using tonsils | 1 | 10 | 1 | - |
| 5M Acid-activated | 1 | 10 | 1 | - |
| Zeolite (Chabazite) | 1 | 8 | 1 | - |
| Zeolite (Chabazite) | 1.5 | 8 | 1 | - |
| Zeolite (Chabazite) | 2 | 8 | 1 | - |
| Zeolite (Chabazite) | 2.5 | 9 | 1 | - |

When the color measurements, obtained as the result of the oil bleaching experiment for the zeolite (Chabazite) are analyzed according to Table 3; it is seen that the standard oil values are 8-10 for yellow color while the red color value turned out to be 1. The color values for the neutral sunflower oil, obtained from the factory is Yellow: 10 and Red:2. The purpose of this experiment is to obtain a value for the raw oil that is close to the values of the standard oil. In addition, it was understood that by using a sample called Tonsile and using a zeolite sample, activated with 5M acid, a value that is conformable with the desired value of the standard oil. It is observed that the raw material features close to the properties of a standard oil [3].

3. Results

The zeolite sample that constitutes the subject of the study was obtained from Manisa Demirci region of Turkey. Experiments, aiming to determine its raw material were conducted and fields of use that are in compliance with its structural properties were sought. It was seen that the samples, used in the experiments represented the raw material %85. As the result of the studies, it was shown that the zeolite has high mineral purity and high cation exchange capacity. In order to improve the farmlands of Turkey and to increase the agricultural yield, the utilization of zeolite should be spread and increased. The importance of the zeolite, which releases the fertilizers and water to the plants and which acts like a storeroom, is most obvious. In addition, the zolite is a natural source that adjusts the water consumption in a balanced way thus saving water. Therefore, it prevents the air, water and soil pollution and provides great benefits to the humans, allowing them to live within healthier environments. As the structural properties of zeolite are dissected further, new findings regarding its use are revealed. This study is also aims at this purpose.

According to the data, obtained from the oil absorption experiments, conducted in order to create new areas for use in a different sector; when the raw zeolit is used without being activated with an acid, the sample provides values that are closed to the desired outcome and without the need for activation with an acid, it will be possible to use it in oil bleaching process.

4. Conclusions

As the conclusion; the industries, in which the zeolite (Chabazite) material can be used, are listed below;

- It is known that the nitrogenous manure is lost in the forms of wash out and NH_3 gas. However, the high selectivity of the Chabazite against the ammoniac and its high ammonium exchange capacity decreases the wash out effect of the nitrogenous manure.
- Chabazite, by absorbing the NH_4 , which may have toxic effects in excess amounts, into its pores, decreases the ammonium poisoning. It is known that especially the Chabazite tuff can be used for this purpose.
- By utilizing the water exchange (intake - outlet) property of the Chabazite; its use for heating up small structures and conditioning their air, in other words, its use as a heat exchange agent for the transfer of solar energy increases.
- Due to its high cation exchange capacity, it can be used in oil bleaching process.
- As it can be used for soil reclamation due to its Ph balancing / increasing effects, it can also be used for plant breeding due to the fact that it will increase the tendency of absorbing and desorption of humidity if the zeolite tuffs are activated. In addition, it can be used to separate methane from other gases and to absorb the urine and feces based scent in places, where livestock farming is undertaken. Finally, due to its insulation properties, it can be used as a building element in multistorey buildings and animal shelters.
- In Drying Process: Processed, dry Chabazite products have ability to absorb 15% of the water (% by weight / minimum) at 25°C under 15% relative humidity. Due to this feature, it is an important element in terms of protecting the equipment and products in humid environment. Chabazite, when compared to the other preservatives such as silica gel and various types of clay, used in humid environments, is a superior mineral in terms of the capability to remove the moisture within the environment completely in a swift manner. It can also be used in various motor systems against the corrosion that may be resulted from the environmental moisture and the moisture that can be generated during the process.
- Heating / Cooling Systems (Air Conditioners): Water is used as the fluid in saturation based heating / cooling systems. Such systems, where the petrol, gas, wood or solar energy is used as the heat source, are especially important in terms of energy efficiency. Using Chabazite mineral in such systems proves to yield better results compared to other synthetic zeolite derivatives due to its high absorption capacity, its effect on decreasing the costs and its resistance against corrosion.
- Radioactive Waste: One of the most important areas of application for Chabazite is to remove radioactive matters such as Cs 137, Sr 90 in the radioactive waste. The Chabazite products, which are especially selective for Sr 90; is far more effective in the removal of radioactive waste compared to the other natural or synthetic Chabazite derivatives.
- Ion exchange applications: Chabazite products are used to refine the ammonium nitrate within the aqueous solutions. The Chabazite has a capability to remove 2,3 meq/gm or %9 by weight in the solution. It is especially superior in hydrometallurgical applications for recovery of various metals in solutions. It was observed that the Chabazite is effective in the recovery of silver (21.9% by weight), copper (15% by weight) and other metals (2.8 by weight).
- The Chabazite mineral is a material that is used to purify all kinds of liquid matter such as petrol, natural gas, liquid industrial waste, waste water and utility water in an effective manner.

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