



Activation of Kosovo Bentonite with Sulphuric Acid for Recycling of Used Motor Oils

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Received August 11, 2015; Accepted November 24, 2015

Abstract: The main objective of this publication is to handle the recycling of used motor oil, introducing optimal methods of processing acid activated bentonite compared with natural bentonite. Comparative results of chemical analysis of the oil samples analyzed after treatment with these absorbent enabled significant estimates issued on changes specific parameters before and after treatment of the oil. This process consists in removing unwanted components of the oil through the bentonite adsorptive properties of the Republic of Kosovo. And at the same time related to generated oil production, based on a practice ecologically safe, therefore renewed oils or recycled may turn into products, to be reused as base oils or as fuel in the engines of cars or industrial machinery. Results showed that bentonite activation increases specific surface and the cumulative volume, at the same time with increasing the concentration of sulphuric acid. This shows that with increasing concentration up to 30% do not have limits or the optimal amount of acid concentration that takes to obtain as large as possible specific surface area. For extended time of activation to these parameters grow in activated acid samples of 10% and 20% while the acid activated samples of concentration 30% their values are decreased. Also it turns out that oil is not damaged or altered, but rather their effect is best shown regenerative abilities. This method has shown that the basic components of motor oil are maintained and their consistency is not damaged.

Keywords: *recycling used motor oil; sulphuric acid; natural bentonite, activation*

Introduction

Different types of clay as natural products are free and environmentally friendly, so these raw material mining are characterized and used as bleaching clays for discoloration of used motor oil. Clays which base mineral contains smectite or montmorillonite are generally called bentonite. Bentonites are among the most important industrial unprocessed materials, which are used in more than 25 different applications (Asllani *et al.*, 2011). During the activation process of bentonite, chemical and mineralogical structure undergoes significant transformations by increasing adsorptive properties, and catalytic ion exchangeability. In this research study are used activated bentonite of Kamenica region (V. Karaqeva) and the region of Vitia (V. Goshicë), Kosovo.

During the process of recycling used motor oils, de-colorization process, through the use of activated bentonite, is shown as a very important step that is used to remove unwanted components from oil, through adsorption. Indicating that specific exchangeable cations can generate active centers in mineral bentonite, characterizing them as good adsorbent which can then be used for adsorption and bleaching of a large number of chemical pollutants such as used lubricating oils also as used vegetable oils and other types (animal and fish oils, waxes, *etc.*).

Activated bentonite show higher activity compared to natural active bentonite. So acid treatment of clay is applied to increase its adsorption properties and this treatment is usually with mineral acids. Desired changes achieved precisely through their activation, which differ depending on activated conditions specifically by selecting the concentration, treatment time and temperature (Malja *et al.*, 2002). This study was conducted to examine the structural properties of Kosovo bentonite by comparing samples from two different regions after acidic activation and to assess their suitability on de-colorization process in used lubricating oils.

Materials and Methods

Bentonite of Kamenica region-Karaqeva and region of Vitia-Goshica, are used as the primary material. These types of bentonite have shown bleaching activity and are appeared with high capacity

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adsorption surface because of their large specific surface. by consulting literature and practical work has shown that this type of activated adsorbent with mineral acids, when during this process a number of metal ions in octahedron layers and pollutants like calcite are removed by acid treatment but at high temperature (Temuujin *et al.*, 2006). All chemicals used were of analytical grade of purity from Merck manufacturing company. In all experiments it is used distilled water. Discoloration important criteria for used motor oil are activated bentonite quantity, time, mixing, temperature and pressure. The amount of activated bentonite should be the minimum amount which makes removal of impurities (Wiedermann, 1981).

Acid activation

Initially the grounded bentonite is passed through the filter paper of 0.5 mm and then it is washed in order to remove free sand which it contains. Then there is a suspension prepared 10% shale and clay acid activation is done with sulphuric acid concentration of 10%, 20%, and 30% versus dry mass.

Terms of activation: Activation time: 2 hours; Activation temperature: 99-105 °C; Humidity of bentonite wash: 44.35%.

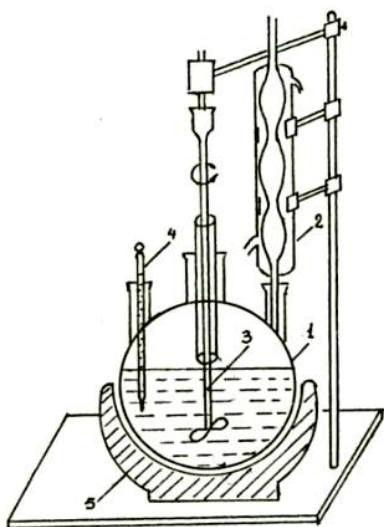


Figure 1. Scheme of activation device (1.Three neck round bottom glass flask, 2.Refrigerator, 3.Glass mixer with rod, 4.Thermometer, 5.The electric heater)

Into three neck round bottom glass flask of 2 dm³ volume were added 378.3 g of washed clay, 834.46 cm³ of water, and finally 2.13 cm³ 96% H₂SO₄. Three neck round bottom glass flask with suspension is placed under electric heater after being set in its neck glass rod mixer, refrigerator and thermometer, while the heating temperature were maintain between 99-103 °C. The suspension mixing is carried out continuously with rotation speed of 150 rot/ min for two hours from the start of his boiling. After activation is completed, the clay washing was accomplished with distilled water through decantation until negative reaction of sulphate ions and later dried at a temperature when thermostat shows 105 °C to constant weight.

In this paper are explored some parameters of Goshicë's bentonite and that the Karaqeva. The possibility of changing them through the activation acid with sulphuric acid concentration versus dry mass of 10%, 20% and 30% for two and three hours. The recycling process is started with the removal of contaminants from used motor oil. Sulphuric acid is mixed with used motor oil using a ratio of 100 ml of sulphuric acid in 1 L used motor oil. This was followed by a mixture in a sealed container at room conditions (temperature and pressure) for two hours. The mixture is left for 24 hours at room conditions and then is subjected to centrifugation for one hour to separate base oil from pollutants. Decanted base oil is then mixed with activated Goshicë's bentonite and Karaqeva in acidic environment in the same reports for all, then 0.5 liters of oil in 200-400 g bentonite. Bentonite is added to remove the dark colour and odour resulting from the oxidation of some components of the

oil. This is achieved by heating at a temperature slightly higher than 250 ° C, followed by centrifugation for 30 min. This process produced yellow base oil and a quantity of sludge clearly very close to the initial weight of bentonite used plus 5% weight. Waste lubricating oils in this research refer to motor oil after use. Also refer to the degradation of the lubricant fresh ingredients that become contaminated by metals, ash, carbon residues, water, varnish, corrosion, and other contaminated materials except asphalt-compounds (Kajdas *et al.*, 2000).

Experimental results

In Tables 1 and 2 are the experimental results of chemical analysis natural bentonite and activated with acid concentrations respectively of 10, 20 and 30% sulphuric acid.

Table 1. Chemical contents of Goshica`s natural bentonite before and after treatment in sulphuric acid

| Bentoniti | SiO ₂ % | TiO ₂ % | Al ₂ O ₃ % | Fe ₂ O ₃ % | MgO % | CaO % | Na ₂ O % | K ₂ O % | Ratio SiO ₂ /Σ M _x O |
|--------------|--------------------|--------------------|----------------------------------|----------------------------------|-------|-------|---------------------|--------------------|--------------------------------------------|
| Untreated | 38.5 | 0.46 | 10.54 | 3.99 | 2.72 | 18.93 | 0.63 | 2.16 | 2.23 |
| Goshica 10 % | 43.52 | 0.55 | 12.38 | 4.28 | 3.17 | 14.51 | 0.61 | 2.52 | 2.20 |
| Goshica 20 % | 51.8 | 0.67 | 13.19 | 4.88 | 3.73 | 7.71 | 0.71 | 2.88 | 2.38 |
| Goshica 30 % | 60.59 | 0.8 | 14.11 | 5.76 | 2.82 | 1.12 | 0.73 | 2.96 | 2.67 |

Table 1. Chemical contents of Karaqevë`s natural bentonite before and after acid treatment

| Bentoniti | SiO ₂ % | TiO ₂ % | Al ₂ O ₃ % | Fe ₂ O ₃ % | MgO % | CaO % | Na ₂ O % | K ₂ O % | Ratio SiO ₂ /Σ |
|---------------|--------------------|--------------------|----------------------------------|----------------------------------|-------|-------|---------------------|--------------------|---------------------------|
| Untreated | 59.48 | 0.51 | 12.50 | 5.03 | 2.49 | 3.44 | 0.50 | 1.68 | 2.35 |
| Karaqevë 10 % | 62.37 | 0.57 | 12.55 | 2.60 | 3.17 | 4.97 | 0.54 | 1.38 | 4.57 |
| Karaqevë 20 % | 64.80 | 0.77 | 13.01 | 2.10 | 2.47 | 3.16 | 0.65 | 1.65 | 4.61 |
| Karaqevë 30 % | 61.05 | 0.84 | 12.97 | 3.10 | 2.88 | 2.71 | 0.70 | 1.96 | 5.10 |

Figure 2 contains the chemical changes on bentonite compounds that occur as a function of various concentrations of sulphuric acid. As is evident from the change in chemical composition, acid activation modifies the chemistry of bentonite. The process as such is seen to result in a material that has larger silicates amount and smaller quantities of oxides. Chemical changes that occur in the bentonite look by the way of changing the ratio SiO₂ / ΣM_xO. Table 3 shows the experimental results on the characteristics of motor oil, before and after treatment with activated bentonite with sulphuric acid 20%.

Table 3. Characterization of used motor oil before and after treatment with activated Bentonite from two different regions of Kosovo

| Parameters tested | Unused motor oil | Used motor oil | Recycled oil with activated bentonite of Goshicë | Recycled oil with activated bentonite of Karaqevë |
|----------------------------------|------------------|----------------|--------------------------------------------------|---------------------------------------------------|
| Specific gravity (ρ) | 0.8819 | 0.9241 | 0.8776 | 0.8821 |
| Kinematic viscosity@ 40 °C (cst) | 194.53 | 133.6 | 80.10 | 80.25 |
| Kinematic viscosity@ 100°C (cst) | 18 | 13 | 9 | 8 |
| Viscosity index | 100.973 | 89.04 | 82.759 | 71.489 |
| Water content (mL) | 0 | 2.2 | 0.5 | 0.3 |
| Water and Sediment (mL) | 0 | 12 | 0.9 | 0.7 |
| Pour point °C | -20 | -6 | -11 | -9 |
| Flash point °C | 230 | 144 | 191 | 186 |
| Carbon residue (Wt %) | 0.67 | 2.97 | 1.20 | 1.34 |
| (TAN) mg KOH/g (sample) | 0.04 | 4.2 | 1.2 | 1.4 |
| (TBN) mg KOH / g (sample) | 3.45 | 2.8 | 0.12 | 0.14 |

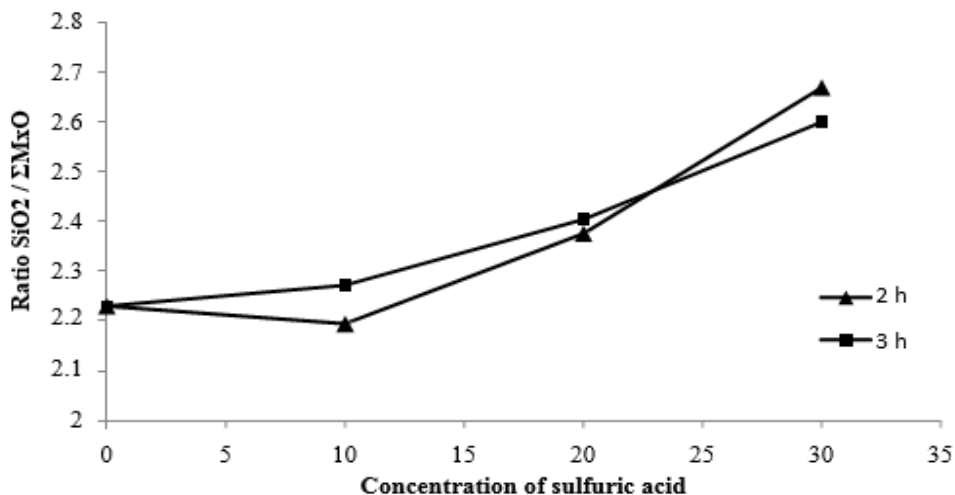


Figure 2. Dependency ratio of SiO₂/ΣM_xO from concentration of sulphuric acid for different activation time

Discussion of Results

To the report of SiO₂ / ΣM_xO are taken into account only the amount ΣM_xO oxides TiO₂, Al₂O₃, Fe₂O₃ and MgO because only these are oxides which are found in the structure of clay and not be dissolved in water in the space between its layers. This ratio increases with the concentration of sulfuric acid in addition to 10% clay of Goshicë where we have a slight decline it.

For surface characterization of untreated bentonite and treated samples with acid, shows that chemical analysis and the performed measurements we have changing of chemical composition, specific surface and pore volume with increasing cumulative concentration of acid (Sadiku, 2005).

During treatment with acid in the two types of bentonite note that is not decreased but increased slightly the proportion of oxides of Na and K in clay. It is known that these ions are not part of the structure of the bentonite but found in the space between the layers of clay. This fact shows that treatment with acid is not a kind cation exchangeable between H⁺ ions and Na⁺ and K⁺ ions, but a true chemical interaction with tetrahedron structure of the first layer of clay. Ions of Na⁺ and K⁺ remain inside the clay after acid treatment.

Selection of bentonites from Karaqevë and Goshicë is done because of earlier studies have shown bleaching activity and high adsorption capacity because of their large specific surface (Kola, 1986). But acid activation has been shown effective in the treatment of motor oils precisely because of the complex changes in the acidic clay mineral, also modified the surface characteristics resulting in increased specific surface ore, production of finely dispersed particles of silicon oxide from the destruction of the structure of the ore, leaving the Al amorphous or silicon compounds, the occupation of the surface pores or interlaminar space, the formation of cracks and voids in the surface.

Flash point of engine oil is the lowest temperature to which the oil should be heated under defined conditions to release enough vapour to form a mixture with air that can be spontaneously flammable from a certain flame (Lenoir, 1975). Table 3 shows a flash point value of different samples. Flash point of new oil is 230 °C because it contains many different additives which contribute to the improvement of its ignition point. In contrast, the measured ignition point for used motor oil is 144 °C. On the other hand it is shown slightly smaller with the Karaqevë's bentonite (186 °C), indicating that the Goshicë's Bentonite slightly raises more to 191.

Pour point of motor oil is the lowest temperature at which the oil will remain in a fluid state. Most motor oils that contain wax and paraffin freeze in cold temperature (Riazi *et al.*, 1987). Motor oils with high content of wax and paraffin will have a higher pour point. Table 3 shows the values of different pour point samples treated with activated bentonite. There has been a slight change in the pour point of about 3 °C, the treatment of oil with Karaqevë's bentonite but the treatment of oil with Goshicë's bentonite showed that gives a increased value of 5 °C. So it is clear that the recycling of used oil with Goshicë's activated bentonite gave satisfactory results (-11 °C).

The viscosity index is exactly an empirical number and shows the effect of changes in temperature on the viscosity. Table 3 shows that the index is increased, and it shows that increasing the viscosity index is due to the removal of aromatic and easily volatile compounds. This also means good thermal stability and flow properties at low temperatures (ASTM D2270, 2004).

Used motor oils increase the specific gravity of the growing presence of the amount of solid substances into used motor oils. One percent of the weight of solid substances in the sample can increase specific gravity of 0.007 (ASTM D1298, 2004). Used motor oil is contaminated with products rich oxidized and carbon condensates. If used motor oil was spotted due to dilution by fuel and/or water originating from fuel combustion in the engine and eventually from accidental contamination from rain, its gravity will be lower than that of lubricating fresh oil. Table 3 shows that the specific gravity was improved by comparing its values with the non-used oil, concretely more improved is shown oil that is treated Goshicë's bentonite to a very small nuance, which shows that there are adsorbed contaminating substances of used oil.

Total Acid Number (TAN) is considered to be an important indicator of the quality of motor oil, especially with regard to the determination of the oxidation state. Oil during engine operation on time and under high temperatures, oxidation products form polymerize leading to precipitate formation of sludge which reduces the efficiency of the engine oil and cause excessive wear (Fox *et al*, 1991). As shown in Table 3, TAN of used motor oil is much higher than the TAN of new motor oil unused. This shows that as a result of used oil treatment with activated Goshicë's bentonite the presence of organic compounds, inorganic chemicals, heavy metals, ammonium salts, resins, water and corrosive materials is removed, a part of the evaporative effect, the adsorption effect of Bentonite and the rest with deposit of heavy layer of sludge, which means that this decrease TAN is evident.

Conclusions

In conclusion the chemical changes of clay we need to talk about a clear separation between its calcite part represented by calcium oxide CaO and its bentonite part that is represented by all other oxides. So when we talk about changing the ratio $\text{SiO}_2/\Sigma\text{M}_x\text{O}$ that shows changes in chemical composition of bentonite should note that the amount of CaO is not involved in the discussion. During the acid treatment it is expected that CaCO_3 to be digested by acid, giving ion of CO_2 and Ca^{+2} .

For activation of two hours, specific surface and cumulative volume of pore has steadily increased with the increasing concentration of sulphuric acid. This shows that with increasing concentration up to 30% do not have limits or the optimal amount of acid concentration that it takes to obtain a specific surface area as large. For activation of three hours these parameters enabled rise to acid samples of 10% and 20% whereas the activated samples with 30% of acid concentration we have decreased their values.

Acid treatment dissolves also impurities such as calcite and replaces the exchangeable cations with hydrogen ions. Acid treatment also opens stratified roads and therefore from all these changes the surface and pore diameter increased.

The decline in flash point is a result of contamination by fuel and oxidation products (Lenoir, 1975).

In connection with the point of leakage results show that treatment with bentonite oil does not damage his fluency parameters, provided by the presence of additives in the base oil.

Products polymerized oxidized and dissolved and suspended in the oil can cause an increase in viscosity of the oil, while reductions in engine oil viscosity indicate contamination of the fuel, which is thought to be the main factor affecting this parameter. This reduction means the removal of additives which are used to increase the viscosity.

The high value of the specific gravity of used motor oil is due to the presence of oxidation products, metals and contaminants.

Increased TAN values caused by the presence of organic compounds, inorganic salts of heavy metals, ammonia, resin, water and corrosive materials resulting from the oxidation process occurring at high temperatures in the engine.

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