SURFACE ACTIVATION OF FULLER'S EARTH (BENTONITE CLAY) USING ORGANIC ACIDS

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ABSTRACT: *Specific properties of bentonite clay have made them a valuable material in different process industries. Easy availability, low price and their effectiveness are the major factors which made fuller's earth, an adsorbent in cooking oil manufacturing industry. Textural characteristics of fuller's earth play an important role in its performance. These characteristics can be modified by treatment with organic acids, which is the safest method for enhancing the properties of fuller's earth. Major motivation of this research is to increase the adsorption capacity of fuller's earth by modification in its properties by organic acid treatment. Organic acid treatment assures the safety of equipment and safety of the labor as well. Four organic acids are used which are recommended best for activation. These acids are acetic acid, phosphoric acid, citric acid and oxalic acid. Clay is treated with all of these four acids and the acid which generates more active sites in clay is the best recommended acid for activation.*

INTRODUCTION

Due to abundance of clay minerals and adsorptive properties, fuller's earth is used as an adsorbent in cooking oil industry [1]. Refining is a major step for cooking oil production. There are basically two types of refining processes available in cooking oil industry namely physical and chemical refining [2]. These methods differ from each other in method of removing free fatty acids and type of chemical used [3]. There are four major steps in refining i.e. bleaching, deodorization, degumming and neutralization [4]. Among these four stages bleaching is the most important step because it helps in improving the appearance of cooking oil. In bleaching stage color, flavor and taste of oil is improved by contacting it with the surface active material which remove unwanted particles from the oil through adsorption [5]. Adsorbent along with adsorbed particles are filtered off and required color of the oil is achieved. In bleaching process there are three methods which are mostly used. These methods are bleaching through heat, oxidation through chemical reaction and bleaching by adsorption [2]. Among these methods the most famous and applicable method is bleaching by adsorption. Adsorption bleaching involves removal of coloring materials from the oil. This material is either present in colloidal form or dissolved in the oil [6].

Fuller's earth is preferred due to its high adsorption capacity and low purchasing cost. It decolorizes the oil by tint reduction to a light shade without alteration in chemical properties of oil [1]. It also removes other impurities like some aromatic compounds, traces of metal, oxidized products and phospholipids [7]. Both the natural and activated fuller's earth can be used commercially but the latter is most preferred because it possesses higher adsorption capacity than natural fuller's earth. For enhancing the properties of fuller's earth activation by inorganic acid is most commonly technique used but there is a disadvantage associated with that technique [5]. Due to fumes of inorganic acids mostly HCL and H_2SO_4, safety of the equipment and labors is compromised and results in great loss to the material and human life. In order to avoid this great loss instead of inorganic acids, organic acids can be used for activation. This technique is the main objective and motivation of this research work. During the activation, structure and textural characteristics of fuller's earth are altered in such a way to enhance the specific properties of fuller's earth [8]. Specific surface area and pore volume enhance the adsorption capacity of clay for metallic impurities and coloring material. Therefore porous structure and surface chemistry has a great impact on the performance of fuller's earth [9].

Application of fuller's earth for cooking oil purification has some problems such as filtration and oil losses. If the amount of fuller's earth used is greater than its required quantity then oil loss will be more due to the oil retention properties of fuller's earth [10]. The pore size distribution and type of clay has greater impact on filtration efficiency. Greater will be the pore size distribution more efficient will be the process of filtration and vice versa [11]. Similarly if greater amount of fuller's earth increases the land disposal cost which ultimately lead the environmental problems. Due to above mentioned problems researches have been carried out to improve the efficiency of fuller's earth in recent years [8]. These researches based on the technique of modification of textural and surface properties of fuller's earth for improving the adsorption capacity of fuller's earth. Those parameters are carefully studied which effects the activation treatment of fuller's earth. The characteristics such as surface area, and pore volume play important role in fuller's earth performance. These two properties can be improved by modifying the structure of clay minerals by some techniques [12]. As mentioned earlier, acids are used for changing the structure and composition of clay material. The main objective of this research is to enhance these characteristics through safe technique (using organic acids) [13]
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MATERIAL AND METHODS

Sample preparation and Acid activation

According to Hussin et al 1N solution of organic acids is best for activation [6]. In literature suitable organic acids for activation are oxalic acid, citric acid, acetic acid and phosphoric acid. 1N solution of each of these acids is prepared according to standard calculation procedure given in literature [11]. 100 gram sample of raw clay is taken for treatment with each organo acid solution. Reaction between clay and organo acid solution is carried out. After 24 hours residence time organo acid clay sample is collected through filtration. After collection each clay sample is dried to 200^0C for four hours to ensure maximum removal of moisture. Then these activated samples are ground to fine size.

Method of Characterization

Fourier Transform Infrared Spectroscopy (FTIR) is performed for structural changes in clay structure, its crystalline properties and the expansion of basal spacing after the reaction with organic acid solution. Infrared spectroscopy is preferred over other testing techniques because infrared spectrum provides a rich array of absorption band which provide a wealth of structural information of clay sample [14]. It covers the electromagnetic range from 500 cm^{-1} to 4000 cm^{-1}(mostly used). FTIR analysis may simply involve the characterization of material with respect to the presence or absence of a specific group frequency associated with one or more fundamental modes of vibration. The spectral data is also used to measure one or more complex compounds in a simple or complex structure [10].

RESULTS AND DISCUSSIONS

Clay analysis before treatment

Figure 1 shows that at lower wave numbers (from 600 to 1200 cm^{-1}) larger peaks formed which shows wide gap between the layers of clay structure but when the wave number is increased gaps become narrower and small peaks are formed. But between the range of 3600 to 3800 cm^{-1} peaks become wider little bit. At initial wave number range wider gaps are present due to presence of straight chain aliphatic hydrocarbons and alkyl halides.

The spectrum range in raw clay analysis shows that there is lesser number of functional groups of unsaturated hydrocarbons and greater amount of straight chain hydrocarbons. Lesser amount of unsaturated hydrocarbons shows lower adsorption capacity.

Clay analysis after treatment

Figure 2 shows the spectrum range of clay after treating with acetic acid. In this analysis peaks are reduced as compared to untreated clay. If acetic acid results are compared with phosphoric acid treatment (fig.3), more sharp peaks are produced but the result is same if compared with untreated clay analysis. Citric acid analysis (fig.4) shows same results but between the ranges (1600 to 2400 cm^{-1}) more sharp peaks are formed which shows more unsaturated esters and saturated aliphatic hydrocarbons. Oxalic acid analysis (fig.5), shows the wide range of aromatics and phenolic groups more sharp peaks are formed between the ranges (2000 to 3800 cm^{-1}). Oxalic acid analysis shows that more unsaturated organic functional groups are formed

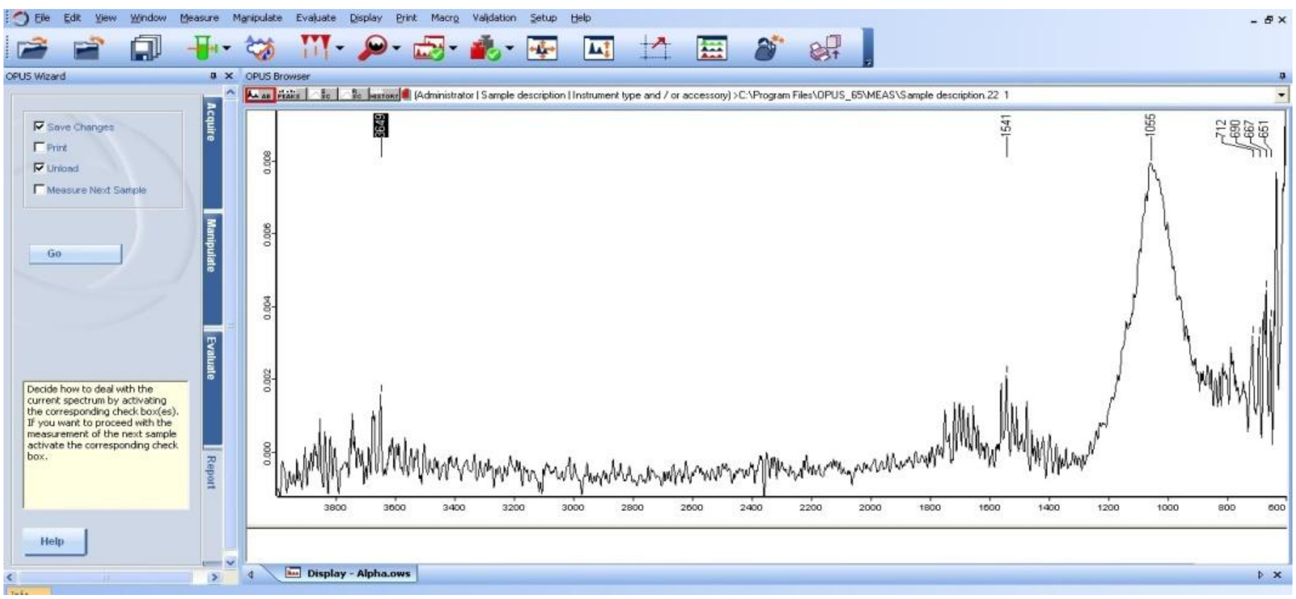

Figure 1: FT-IR analysis of untreated raw clay

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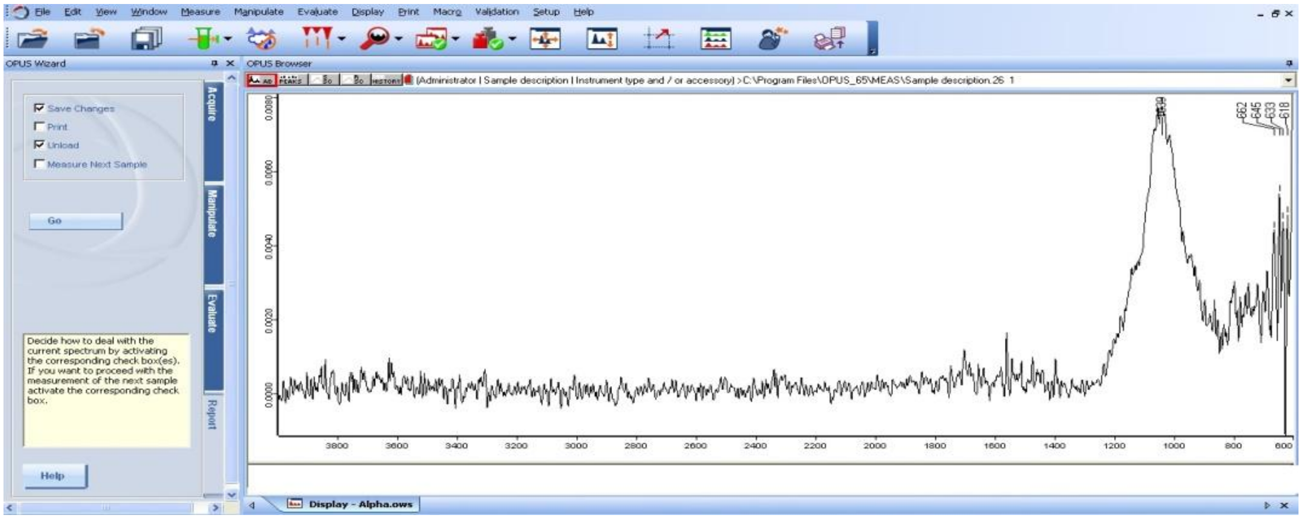

Figure 2: FT-IR analysis of acetic acid treated clay

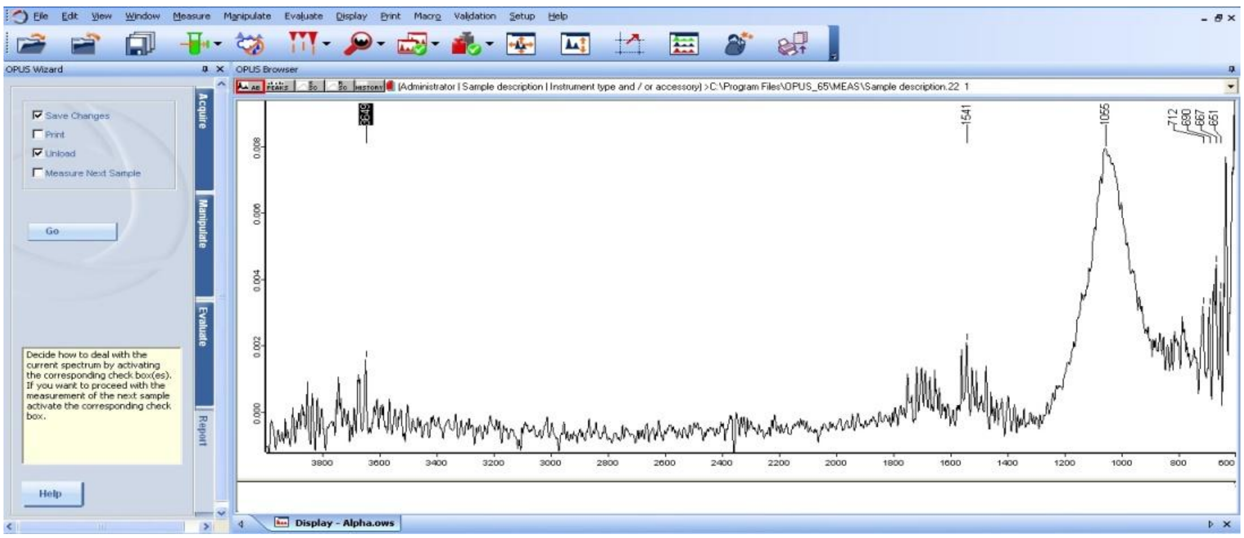

Figure 3: FT-IR analysis of phosphoric acid treated clay

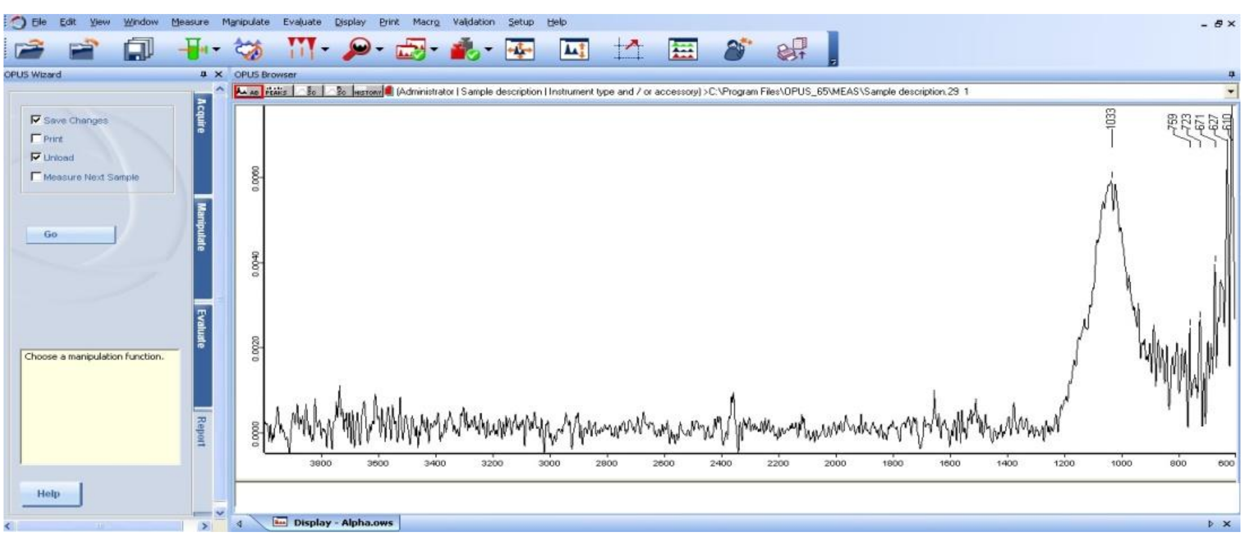

Figure 4: FT-IR analysis of citric acid treated clay

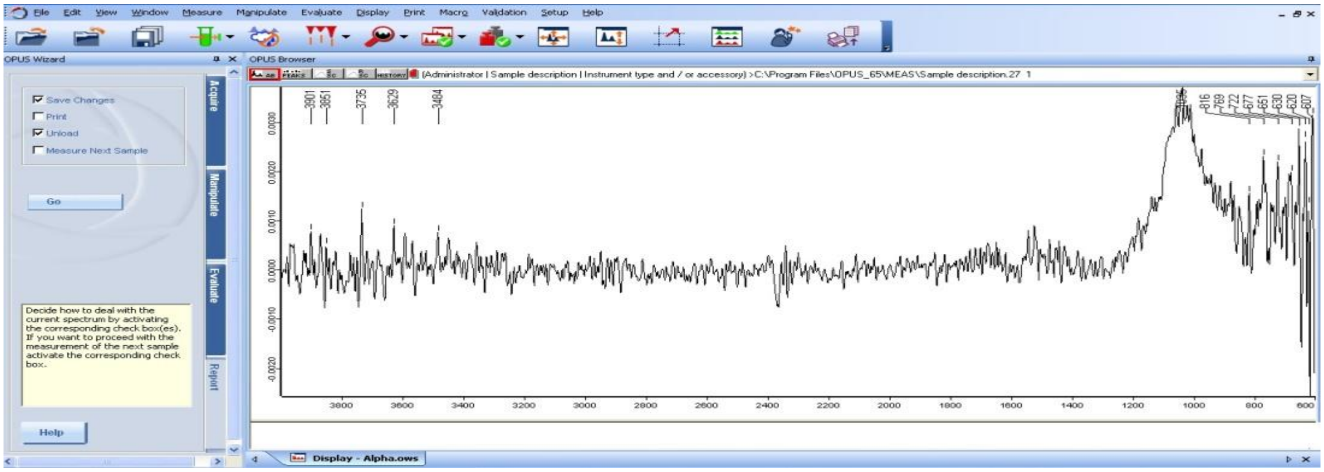

Figure 5: FT-IR analysis of oxalic acid treated clay

CONCLUSION

Organic acid treatment is the safest mode for surface activation of clay. Among four organic acids the best acid which showed good and satisfactory results is oxalic acid. Oxalic acid creates more unsaturated organic functional groups in bentonite clay (fuller's earth). Aromatic and phenolic functional groups are highly unsaturated functional groups which show the higher degree of adsorption capacity. Compared to other organic acids, Oxalic acid treatment modified the clay properties more effectively and enhanced the adsorptive properties of clay. So among these four organic acids oxalic acid is recommended acid for improving the adsorption properties of fuller's earth .Organic acid treated fuller's earth is also recommended for treatment of used lube oil. Because used lube oil can be regenerated by organic acid activated fuller's earth and it is very economical treatment method as compared to other conventional techniques.

REFERENCES

[1] F. Hussin, M. K. Aroua, and W. M. A. W. Daud, "Textural characteristics, surface chemistry and activation of bleaching earth: A review," *Chemical Engineering Journal*, vol. 170, pp. 90-106, 2011.

[2] F. Kooli and L. Yan, "Chemical and thermal properties of organoclays derived from highly stable bentonite in sulfuric acid," *Applied Clay Science*, vol. 83, pp. 349-356, 2013.

[3] H. Bayram, M. Önal, H. Yılmaz, and Y. Sarıkaya, "Thermal analysis of a white calcium bentonite," *Journal of thermal analysis and calorimetry*, vol. 101, pp. 873-879, 2010.

[4] H. Noyan, M. Önal, and Y. Sarıkaya, "The effect of sulphuric acid activation on the crystallinity, surface area, porosity, surface acidity, and bleaching power of a bentonite," *Food chemistry*, vol. 105, pp. 156-163, 2007.

[5] Z. Wu, C. Li, X. Sun, X. Xu, B. Dai, J. e. Li, *et al.*, "Characterization, acid activation and bleaching performance of bentonite from Xinjiang," *Chinese Journal of Chemical Engineering*, vol. 14, pp. 253-258, 2006.

[6] M. Usman, V. Ekwueme, T. Alaje, and A. Mohammed, "Characterization, acid activation, and bleaching performance of Ibeshe clay, Lagos, Nigeria," *ISRN Ceramics*, vol. 2012, 2012.

[7] H. He, Y. Ma, J. Zhu, P. Yuan, and Y. Qing, "Organoclays prepared from montmorillonites with different cation exchange capacity and surfactant configuration," *Applied clay science*, vol. 48, pp. 67-72, 2010.

[8] F. Kooli, Y. Z. Khimyak, S. F. Alshahateet, and F. Chen, "Effect of the acid activation levels of montmorillonite clay on the cetyltrimethylammonium cations adsorption," *Langmuir*, vol. 21, pp. 8717-8723, 2005.

[9] F. Kooli, P. C. Hian, Q. Weirong, S. F. Alshahateet, and F. Chen, "Effect of the acid-activated clays on the properties of porous clay heterostructures," *Journal of Porous Materials*, vol. 13, pp. 319-324, 2006.

[10] B. Tyagi, C. D. Chudasama, and R. V. Jasra, "Determination of structural modification in acid activated montmorillonite clay by FT-IR spectroscopy," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 64, pp. 273-278, 2006.

[11] M. Rossi, M. Gianazza, C. Alamprese, and F. Stanga, "The role of bleaching clays and synthetic silica in palm oil physical refining," *Food Chemistry*, vol. 82, pp. 291-296, 2003.

[12] J. Nguetnkam, R. Kamga, F. Villiéras, G. Ekodeck, and J. Yvon, "Assessing the bleaching capacity of some Cameroonian clays on vegetable oils," *Applied Clay Science*, vol. 39, pp. 113-121, 2008.

[13] P. C. Wei, C. Y. May, M. Ngan, and C. C. Hock, "Degumming and bleaching: effect on selected constituents of palm oil," *J. Oil Palm Res*, vol. 16, pp. 57-63, 2004.

[14] G. A. Lomić, E. E. Kiš, E. B. Dimić, and R. S. Romanić, "Investigation of activated Al-pillared clay efficiency in vegetable oil purification," *Acta periodica technologica*, pp. 31-36, 2004.