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Preparation and characterization of nano porous bentonite for regeneration of semi-treated waste engine oil: Applied aspects for enhanced recovery

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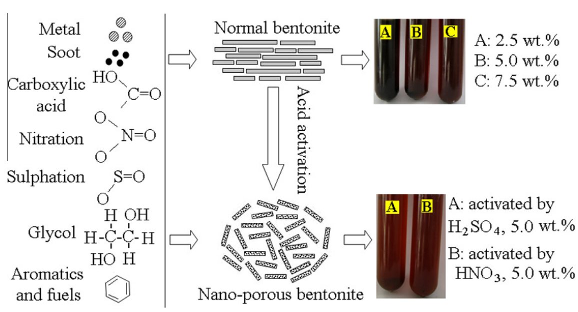
HIGHLIGHTS

- The nano porous bentonite is a powerful powder in recovery waste engine oil.
- The nano pores were successfully extended to decrease the adsorbent content.
- The methylene blue titration was applied to quantify powder ability.
- The relationship between powder characteristics and oil recovery was determined.
- The used method for waste oil regeneration can be useful from applied aspect.

GRAPHICAL ABSTRACT



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ABSTRACT

The present investigation studies the regeneration of waste engine oil by active Ca-bentonite powder. The porous adsorbents were prepared by acidification in the presence of nitric and sulfuric acid solutions at different residence times. The methylene blue adsorption test was applied to evaluate the acidification. The characteristics of normal and treated powders were also characterized by ICP, XRD, FTIR and BET techniques. The optimum condition was determined in which the methylene blue adsorption reached the maximum value. In this condition, the specific surface area of clays activated in the presence of nitric and sulfuric acids were determined to be 109.0 and 89.0 $m^2 g^{-1}$, respectively. The change in specific surface area was found to be due to formation of new nano-pores in the range of 10–12 nm, according the N_2 adsorption isotherms. The feasibility of active powders for removal of contaminants from waste oil has been studied in the next part. The modified powders had higher adsorption capacity for removal of contaminants from waste oil. It was demonstrated that the adsorption of methylene blue by active clay yields the valuable information about minimizing the powder content in recovery of waste oil by semi-treated process.

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1. Introduction

Bentonite, which is an aluminosilicate, normally contains fine clay minerals mainly montmorillonite and other crystals such as quartz, cristobalite and opal-CT [1]. The isomorphic substitution in montmorillonite structure is substantially observed [2] and Na^+ and Ca^{2+} can be exchanged with the other ions easily without affecting the mineral structure [3]. When cations are exclusively exchanged in the structure, the interlayer swelling occurs when it is exposed to water or other liquids [4]. The unsaturated edge sites possess high reactivity and adsorption can occur at the edge and internal sites. The large specific surface area, chemical stability and high cation exchange capacity, CEC, have made bentonite as an excellent adsorbent. Bentonite powder plays an important role in the regeneration and clarifying of wastes [5]. The edges and faces of bentonite particles can adsorb cations, non-ionic and polar contaminants from environment [6].

The treatment of bentonite powder with inorganic acids is known as activation [7]. The exchangeable cations can be replaced by H^+ ions. While the SiO_4 groups are largely intact in the acid environment, Al^{3+} and Mg^{2+} escape out of octahedral sites [8]. This process generally increases the specific surface area and acidity of clay minerals, along with the elimination of several impurities such as calcite and partial dissolution of the external layers. The changes in specific surface area and structure of powder depend on type of clay and non-clay minerals existing in the starting powder, type of acid, temperature, residence time and other environmental factors such as pH [7,9]. The decomposition of octahedral layer is related to the individual resistance to acid attack [10,11]. It has been reported that the acid activation followed by thermal treatment increases the adsorption capacity [12].

The waste engine oil content increases steadily due to plentiful automotive traffic in the countries. The physico-chemical characteristics of motor oils change as a result of their exploitation. The extreme operating conditions lead to soot, dust and fuel accumulation in the oil. Also, different wear metals particles and corrosion products ultimately deteriorate the quality of engine oil. From the environmental point of view, the waste engine oil has a high hazardous potential and the small amount of the waste can pollute the surface water, groundwater and soil [13]. Also, some of oil contaminants like poly-aromatic hydrocarbons are poisonous or carcinogenic materials. The regeneration was found as the best option for the disposal of waste oil [14]. By applying highly complex processes such as vacuum distillation, extraction and solvent treatment, adsorption and filtration, it is possible to manufacture the high quality lubricant oil. The regeneration plants makes use of waste as raw material, decreases the amount of harmful discharges and improves the environmental situation in preventing disposal of waste.

The most commonly used process for refining waste engine oil in the small to medium scale is the acid-clay process [15]. The insoluble sludge, asphalt, is formed in the reactor [16,17]. Thereafter, the product is neutralized with lime or caustic soda. The main drawback of acid treatment is the produced sludge which creates the environmental problems. An adsorption unit is considered for decolorizing semi-treated oil by clay powder. Finally, the refined oil can be obtained by filtration of stream exiting adsorption unit. The refining cost of waste is relatively low compared to its production from crude oil [15]. The semi-treatment process is the best technique to achieve the oil with high quality and is much cheaper than the extraction [16,18].

The adsorption operation depends on oil/clay ratio [19]. The treated powders by hydrochloric [20] or sulfuric [21,22] acids provide attractive opportunities for refining waste oil. The uptake of contaminants from distillated oil by treated clays is affected by acid treatment condition. The acid type and concentration are two important factors that influence the oil regeneration process [23]. The type of recovery process in treatment of waste lubricant oil should be considered in manufacturing modified powder to minimize the disposal of hazardous materials in the environment.

To our knowledge, most studies on regeneration of waste engine oil have been focused on recovery techniques and a few studies have been considered the role of activation agent on adsorption process. In order to manufacture the applicable adsorbent for acid–clay process, it is necessary to optimize acidification factors for reaching the suitable adsorption capacity. Acid type, concentration and residence time significantly affect the size and morphology of clay structures [24]. Therefore, the aim of the present work is to increase the knowledge on the absorbent characteristics for regeneration semi-treated oil. This evaluation is important to assess the technical feasibility of activation as a route to reduce the powder content for recycling waste engine oil. Understanding relationship between the acid type, concentration and residence time with the chemical and crystalline changes, specific surface area and porous structure of modified powders is the first aim of present study. The removal efficiency of contaminants as a function of mentioned factors is another goal of investigation to identify the optimum condition for manufacturing active powder which promises minimizing adsorbent content in recovery of semi treated engine oil.

2. Materials and methods

2.1. Materials and activation

The bentonite used in this study was collected from Soltaniyeh region, south-western of Zanjan in Iran. The raw material was dry milled industrially and the obtained powder was screened by 200 mesh sieve. Nitric, 65.0 wt.%, and sulfuric, 98.0 wt.%, acids both as received, were used for the acidification. The acid solutions were prepared with concentrations of 0.06, 0.13, 0.25, 0.50 and 1.00 mol l^{-1}. In order to minimize the dead time, the solutions were heated up to process temperature, 80 °C, in a baker before mixing with starting powder. The experimental setup consisted of a 1000 ml three necks flask equipped by a condenser and thermometer. 80 g of dry powder and 500 ml of hot acid solution were mixed in each run. The suspension was heated by a laboratory water bath and the suspension temperature was controlled by thermometer about 80 ± 1 °C. The suspensions were mixed during the activation by propeller mixer. The zero time was considered when suspension temperature reached to desired temperature. In order to evaluate the effect of residence time, activation process was carried out during 10, 30, 60, 120 and 180 min. The activated samples were filtered and the precipitates were washed with deionized water until the obtained cakes were free from ions. The wet cakes were dried at 60 °C in a laboratory oven and then the dry samples were ground in a milling equipment to obtain a particle size less than 75 μm.

It possible to quantify the absorption ratio by measuring the content of MB needed to cover the total external and internal surface of the particles. This testing technique was carried out based on the chemical reactions between the negative charges in the clay particles and the released MB cations in water. Furthermore, the absorption ratio is a function of minerals found in the material. MB powder, Merck 6045 Germany, has been used to determine the adsorption ratio of activated clays respect to normal powder. The molecular weight of MB is 355.9 g mol^{-1}. It is important to highlight that the technique is done in water, thus extensive minerals can expose all available surface. The MB solution was prepared by mixing 1.0 g of dry powder in 200 ml of deionized water. The clay suspensions were obtained by addition of 2.0 g