Obtaining zeolite A from filtrate of zeolite LSX and its influence on the removal of heavy metals and organic pollutants in spent lubricating oil

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Abstract

Zeolites A was synthesized from alternate sources such as filtrate from synthesized zeolite LSX and aluminate solution extracted from bauxite which produced a very good yield. The synthesized zeolite type was characterized by X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX). The synthesized product showed a high degree of crystallinity from the XRD results. When applied to a spent lubricating oil, the efficiency in removing the heavy metals was: 23.4% Fe, 96.8% Zn, 19.0% Cu, and 12.0% Cr. The saturates in the regenerated oil were 80% carbon, 4% residue, and 16% aromatics as compared to that of a commercial virgin oil that contained 84% saturates, 3% carbon residue, and 13% aromatics. This indicated that the spent oil can be reused.

Keywords: zeolites, saturates, aromatics, lubricating oil, synthesis.

INTRODUCTION

Zeolites are hydrated aluminosilicates materials that are formed under hydrothermal conditions by condensation polymerization [1]. Zeolites LSX and A are mostly synthesized using a basic medium of various sources of silica and aluminum compositions [2]. These zeolite type has many applications. They are used for purification [3], ion exchange [4], gas adsorption [5], and even thermal energy storage [6]. Currently, the interest in the field of synthesis and preparation of synthetic zeolites has increased in three main directions [7]: the first one is the treatment of natural zeolites, so as to preserve their initial crystalline structure [8]; secondly is by natural clay minerals, and thirdly by conventional hydrothermal synthesis [9]. In all these processes the main problem faced by researchers is cost and availability of raw materials. Zeolite LSX is mostly synthesized from kaolin in combination with NaOH [10]. The filtrate produced from this reaction is mostly discarded. Zeolites are used in many applications such as improving the hydration properties of cement paste [11], in cements for composite coating designs [12], and removal of pollutant dyes in wastewater [13]. They can also be used as nanocomposites for dye degradation [14], inhibition of antimicrobial activities, and in microalgal-immobilized biocomposites [15]. Zeolites can also be applied to co-contaminated soils for heavy metal removal [16]. They are also used in removing heavy metals from wastewater [17]. Zeolites are also used in treating spent lubricants [10].

Spent lubricants are lubricating oils that have lost their lubricating properties after being used to minimize friction, wear and tear between interacting surfaces in internal combustion engines after some time period [18]. A virgin lubricant is composed of base oil (mostly 90%), mineral oils, and additives that are less than 10%. When the additives added to the lubrication oil break down, this leads to the production of halogenated hydrocarbons, polycyclic aromatic hydrocarbons, and metals from wear and tear which all accumulate in the oil [19]. When these spent lubricants are improperly disposed of, this leads to the pollution of the environment. Due to the high stability of chemical compounds contained in the base oil of lubrication oils, they are not much affected by the accumulation of these impurities, hence the oil can be regenerated [20].

In this paper, the authors report a frugal approach of synthesizing zeolite A from an untapped source such as filtrates from already synthesized zeolite LSX [10] and aluminate solution extracted from bauxite obtained from Awaso, in the western region of Ghana. This process produced zeolite A with a very good yield. The synthesized zeolite A was confirmed using X-ray diffractometry, scanning electron microscopy, and Fourier transform infrared spectroscopy. The synthesized zeolites together with sulfuric acid were then used to purify and regenerate spent lubricating oil that can be reused with the addition of a few additives.

MATERIALS AND METHODS

The bauxite was obtained from Awaso in the western region of Ghana. NaOH pellets and sulfuric acid were obtained from Aldrich Chem. with 99% purity. The spent or used oil samples (Quartz 20W50, Total) were collected from a service station in Ho, in the Volta Region of Ghana: 10 L of used oil were collected.

Zeolite A synthesis: a filtrate was obtained from the

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former synthesized samples of zeolite LSX [10] and analyzed using X-ray fluorescence spectroscopy (XRF). Aluminate solution was extracted from bauxite using NaOH pellets. The two mixtures were then mixed in the ratio of 20 to 10 mL to form the hydrogels. These hydrogel mixtures were then transferred into 100 mL Teflon bottles. The procedure was repeated for four other samples and they were all kept in Teflon bottles. The samples were then aged for 5, 10, 15, 20, and 25 h at room temperature in the Teflon bottles. They were then crystallized in an oven set at 100 °C for 4 h. The post-synthesis treatment involved quenching of the samples after the stipulated time in the water, washing off the excess NaOH from the samples with distilled water to a pH 10, and dried at 100 °C for 15 h. The dried samples were then ground in a mortar to a very fine powder, weighed, and kept in plastic bags for characterization. The samples were characterized using the following techniques: X-ray diffractometry (XRD), scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX), and Fourier transform infrared spectroscopy (FTIR).

Regeneration of the used oil: the collected used oil was first filtered to remove impurities using a centrifuge set at 1000 rpm for 20 min and allowed to settle for 24 h. The decanted oil was preheated to degrade some of the additives. 500 mL of the pre-heated oil was treated with 50 mL of 98% sulfuric acid. The mixture in the beaker was thoroughly mixed to ensure that there was a homogenous mixture between the acid and the oil at 50 °C. Afterward, the mixture was allowed to cool, held for 24 h, and then poured gently into a separate beaker. Each mass of 5, 10, 15, and 20 g of the zeolite A was mixed with 100 mL of the acid-treated oil and well stirred on a hot plate magnetic stirrer for 20 min. The process yielded refined oils with some dark in color and others very bright. This method was then repeated and the 10 g of the zeolite A treated with 100 mL of the treated acid oil mixture produced the maximum yield and best color. The regenerated oil was then obtained for physicochemical analysis as shown in Fig. 1.

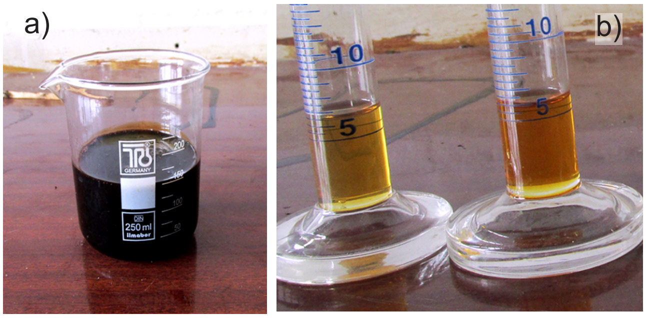

Figure 1: Images of: a) spent oil; b) commercial virgin oil (left) and treated oil (right).

RESULTS AND DISCUSSION

XRF results of filtrate: the chemical composition of the starting material, filtrate formed from zeolite LSX was $Na_2Al_2O_3.2SiO_2.4H_2O$ (Table I). According to the quantitative determination of SiO_2 and Al_2O_3, the $[SiO_2]/[Al_2O_3]$ molar ratio was 1:2. This was an indication that the filtrate can be converted to a zeolite. The sodium-aluminosilicate content in the filtrate was enhanced by the addition of aluminate solution obtained from the dissolution of bauxite ($Al_2O_3.3H_2O$) in sodium hydroxide as shown by the reaction:

$$Al_2O_3.2H_2O_{(s)} + 2NaOH_{(aq)} \rightarrow 2NaAlO_2 + 3H_2O \qquad (A)$$

This was done to alter the alumina to silica ratio in the filtrate. The final product involved the mixing of sodium aluminate solution prepared from the bauxite and the sodium-aluminosilicate filtrate to form sodium zeolite A. The general formula for most zeolites is represented by the equation $xM^{n+}_{2/n}O.xAl_2O_3.ySiO_2.zH_2O$ [4] and hence sodium zeolite could be represented as $Na_2O.xAl_2O_3.ySiO_2.zH_2O$ where x, y, and z are the moles of Al_2O_3, SiO_2, and H_2O, respectively.

Table I - XRF results (wt%) of filtrate.

SiO_2	Al_2O_3	Na_2O	CO_2	Cu_2O	SO_3
46.56	39.83	12.43	0.51	0.38	0.29

XRD characterization: the XRD pattern of zeolite A is presented in Fig. 2. Various crystalline peaks present in the sample were identified with the aid of collections of simulated XRD powder pattern for zeolite A [8]. The synthesized samples aged at 15, 20, and 24 h revealed different peak intensity/count. In contrast, the samples aged at 5 and 10 h and crystallized under the same condition showed no zeolite peaks. The synthesized samples with aging times of 15 and 24 h showed a relative presence of zeolite A peaks, in relation to those with 20 h of aging, which exhibited most of the peaks with 100% crystallinity of type A zeolite. The first four peaks were distinct. This implied the importance of aging as a contributory factor in zeolite synthesis.

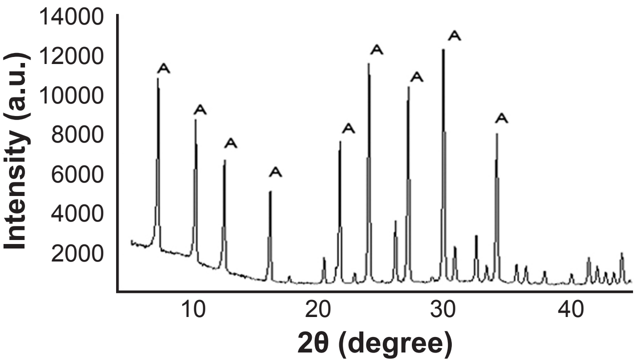

Figure 2: XRD pattern of synthesized zeolite A.

SEM characterization: Fig. 3 shows the morphology of the 20 h aged sample of a synthesized zeolite A product, as examined under a scanning electron microscope. The synthesized sample revealed the presence of a cubic crystal.

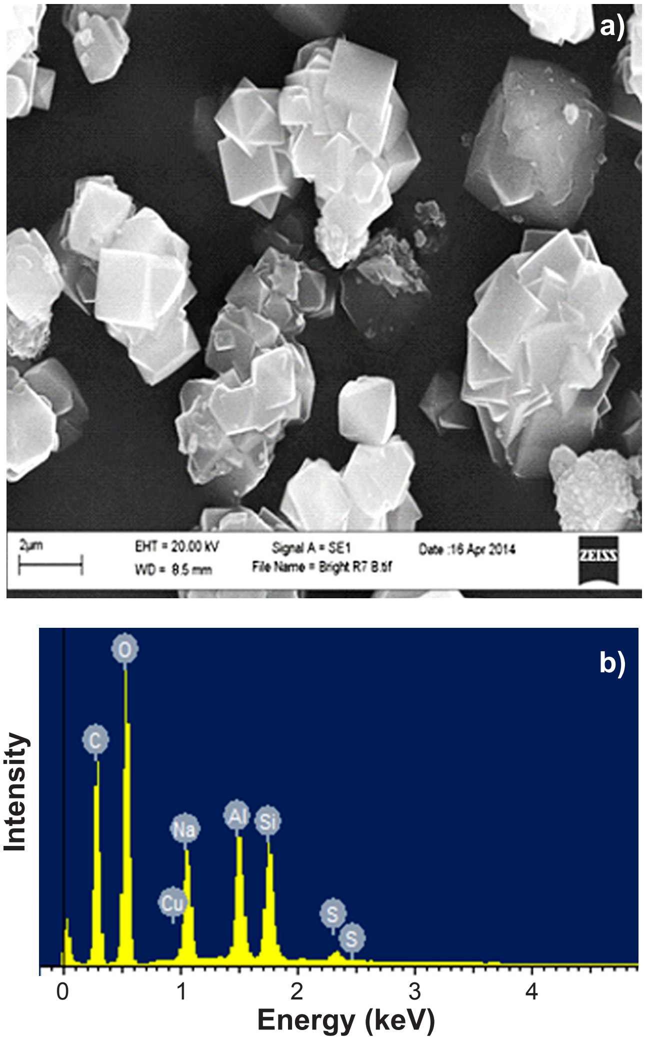

Figure 3: SEM image showing the morphology (a) and EDX spectrum (b) of the synthesized zeolite A.

FTIR spectrum of zeolite: Fig. 4 shows the FTIR spectra of the synthesized zeolite A sample. Based on [20], the peak of transmittance frequency at 966.2 cm^{-1} corresponded to internal tetrahedron asymmetrical stretch vibration found in zeolites, and 667.2 cm^{-1} peak corresponded to linkage due to symmetric stretch also found in zeolites. The peak at 560.2 cm^{-1} was related to the existence of a double ring in the framework structure of zeolites. These peaks suggested the synthesized sample to be zeolite in the class of zeolite A.

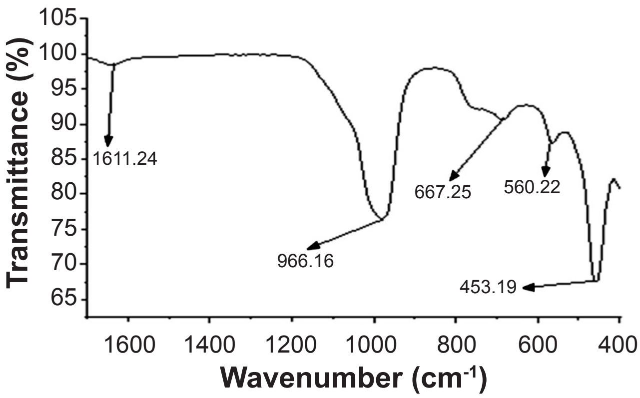

Figure 4: FTIR spectrum of synthesized zeolite A.

Physicochemical properties of spent, treated, and virgin oils. *Physical properties*: as depicted in Table II, the flash point for the regenerated oil was low compared to the virgin and used oils, although the value was acceptable. The importance of flash point of an engine oil shows how the oil is tainting. The flash point of the recycled oil was highly affected by the addition of sulfuric acid, which reacted with the additives in the oil [21]. The flash point of the virgin oil (Quartz 20W50, Total) and used oil were high because they contained many different additives which contributed to improving their flash points. Accordingly, the flash point of the spent engine oil was 231 °C. This decrease in flash point was a result of contamination with fuel and oxidation products. Since the flash point is also an aid in establishing the identity of a particular petroleum product, it increases with the increasing molecular mass of the oil, and hence oxidation would also result in the formation of volatile compounds that leads to a decrease in the flash point in the used oil [22]. The impact of the pour point is on the lubricating oil's viscosity. Henceforth, lubricating oils with high viscosity are described as having high pour points [23]. As the lubricant is used, the long aliphatic chains attached to the aromatic ring are separated and cracked as a result of oxidation. The oxidation products such as aldehydes and ketones produced have a low pour point [24]. Table II also shows the pour point values of the virgin, used, and recycled oil samples. The pour point of the recycled oil was not notably affected. There was a small change in the average pour points of around 2 °C. It is obvious that recycling the used oil with sulfuric acid combined with zeolite A gave remarkable results (-18 °C), higher than that of the virgin oil. It is speculated that the additives present in the virgin oil may have affected its pour point.

Viscosity index demonstrates the impact of changes in temperature on the viscosity of lubricating oil. When the viscosity index is high, there is a little change in the thickness of the oil with temperature. This implies better protection of an engine that works under profound temperature changes [21]. A high viscosity index is due to the non-appearance of aromatic and volatile compounds. It additionally implies great warm strength and low-temperature flow processes [25]. In Table II, the average viscosity index of the recycled oil was 123 °C. This was higher than the used oil, which had 91 °C, and even better than the virgin oil. Clearly, the zeolite had a very good effect on the viscosity index of the recycled oil. The viscosity index of all the recycled oil was high, hence there would be no need to add additives to improve its viscosity. The specific gravity of lubricating oil is mainly influenced by its chemical composition as shown in Table II. When there is an increase in the number of aromatic compounds in lubricating oil, this results in an increase in its specific gravity. When there is an increase in the saturated compounds, it results in a decrease in the specific gravity of the oil [21]. The average specific gravity of the used oil increased due to the presence of increasing amounts of solids accumulated in it; 1 wt% of solids in the sample can raise the specific gravity by 0.007 [26]. Used engine oil was contaminated with oxidized and condensed

Table II - Physical properties of oil samples.

Sample	Flash point (°C)	Pour point (°C)	Viscosity index (°C)	Specific gravity
Spent engine oil	231	-20	91	0.834
Regenerated engine oil	130	-18	123	0.653
Virgin engine oil	265	-19	119	0.693

Table III - Chemical properties of oil samples.

Property		Spent engine oil	Zeolite A-sulfuric acid treated oil	Virgin engine oil
Metallic content (wt%)	Cr^{2+}	0.0740	0.0034	0.0049
	Cu^{2+}	0.0025	0.0014	0.0012
	Zn^{2+}	0.0590	0.0013	0.0427
	Fe^{2+}	0.0690	0.0042	0.0053
Total acid No. (mgKOH/g)		10.51	3.02	5.20
Saturates (%)		42.8	80.0	84.0
Carbon residue (%)		17.7	4.0	3.0
Aromatic content (%)		39.5	16.0	13.0

products rich in carbon. In Table II, the specific gravity of the regenerated oil was 0.653 at room temperature, without any additives. These values were low as compared to that of the used engine oil of average specific gravity of 0.834. The high value of the average specific gravity of the used engine oil was due to the presence of oxidation products and metal contaminants.

Chemical properties: an engine block consists of aluminum (Al), iron (Fe), and lead (Pb) together with some other metals. When fuel is burning in an engine there is wear of some of these metals which are all stored in the lubricating oil. Corrosion also takes place when fuel is diluted with water together with bad piston rings [24]. Many lubricating oils contain metals that are added to upgrade the oil's efficiency. Therefore, metals that contaminate engine oils must be reduced to acceptable levels. Table III shows the average zinc concentration in virgin oil at 0.0427 wt%. This was added to the base oil as part of multi-functional additives for improving the oils' performance. Other metals also found in the virgin oil were Fe with an average concentration of 0.0053 wt%, copper with an average concentration of 0.0012 wt%, and chromium with an average concentration of 0.0049 wt%. After the virgin oil had been used for the stipulated period, there was an increase in the average concentrations of the entire metals: iron to 0.069 wt%, zinc to 0.059 wt%, copper to 0.0025wt%, and chromium to 0.074 wt%. After the spent oil was recycled using the sulfuric acid-zeolite A method (Table III), the average concentrations of iron and chromium decreased to 0.0042 and 0.0034 wt%, respectively. The average concentration of zinc was also reduced to 0.0013 wt% and that of copper to 0.0014 wt%. Comparing some of the regenerated oil characteristics with the used and virgin oils, Table III shows petroleum products contained acidic constituents present as additives or as degraded products. The used oil was found to have an average acid number of 10.51 mgKOH/g. After recycling the used oil, the average acid number value decreased to 3.02 mgKOH/g. The virgin oil had an acid number of 5.20 mgKOH/g. These results showed that the organic and inorganic acids, esters, phenolic compounds, water, and corrosive materials, which resulted from the oxidation process occurring in the engine at high temperatures, have been successfully reduced. From Table III, the number of saturated compounds left in the used oil was 42.8% and the rest were aromatics and residual compounds. After recycling the spent oil with zeolite A (acid-clay method), the saturated compounds increased to 80%. This increase in the saturated compounds after the recycling process was due to the fact that most of the aromatic hydrocarbons were left behind in the zeolite.

FTIR of oil samples: the FTIR spectrum of the spent engine oil is shown in Fig. 5a. Medium new bands at 1705 and 1635 cm^{-1} indicate the presence of short-chained compounds in carbonyl groups from esters, ketones, or acids. The formation of these compounds in engine oils is mainly due to the oxidation processes that occur in the oil. Spent engine oil has a reported band at 1168 cm^{-1}, which indicates the presence of peroxide compounds. Unsaturated additives have bands that are located at 704 and 1603 cm^{-1}. The presence of bands at 1235, 1356 and 1470 cm^{-1} are due to the hydrocarbon compounds mixing with small chain lengths and C-H vibrations within C-H groups contained in the spent oil [21]. The presence of aromatics and polyaromatic hydrocarbons (PAHs) in the used oil can be identified by new bands that occur at 810, 850, and 1630 cm^{-1}, which represent the hydrocarbons in aromatic rings. There is also an indication of degradation of the oil as a result of absorption of water at the band of 900 cm^{-1} and fuel from the engine at 1200 cm^{-1} [21]. The FTIR results of the recycled and virgin oils in Figs. 5b and 5c, respectively, showed no peaks of degradation as compared to that of the used oil. All the above results show no oxidation, nitration, and sulfation components. Hence the sulfuric acid-

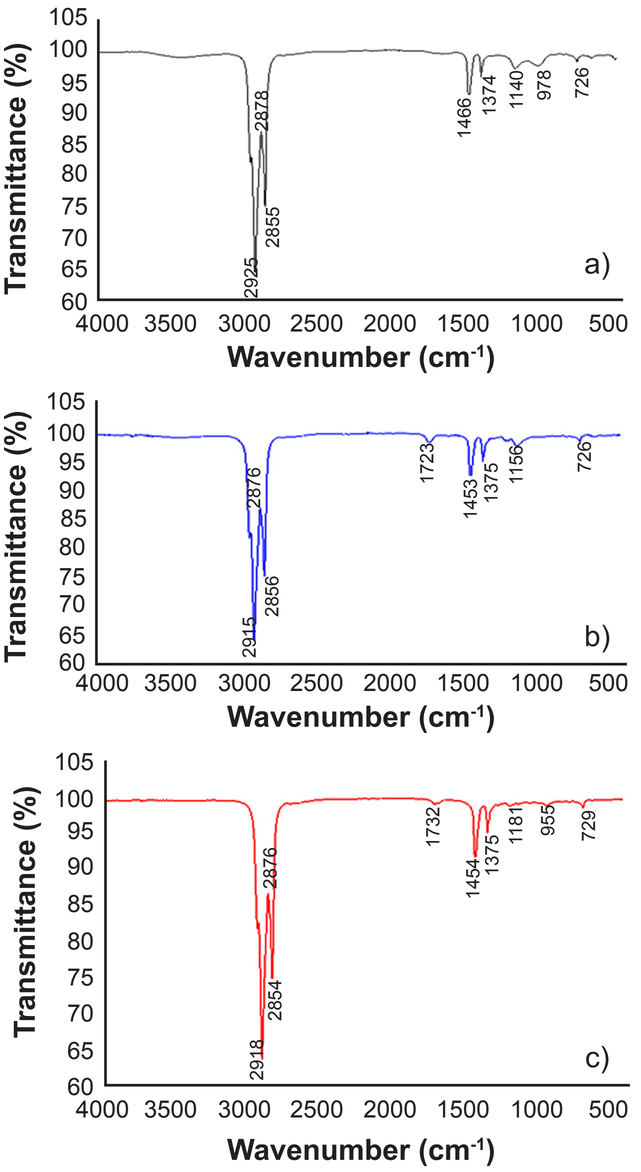

Figure 5: FTIR spectra of used (a), zeolite A-treated (b), and virgin (c) oils.

zeolite A was able to remove the degraded products from the spent engine oil.

CONCLUSIONS

Zeolite A was successfully synthesized from an alternate source such as the combination of the filtrate of synthesized zeolite LSX and aluminate solution extracted from bauxite. The yield from this synthesis route was very good and highly crystalline. The synthesized zeolite together with sulfuric acid was then used in regenerating a spent lubricating oil. Heavy metals in the spent oil were reduced to acceptable ranges and organic pollutants in the spent oil were successfully removed. Hence, with the addition of a few additives to the regenerated oil, this regenerated lubricating oil can possibly be reused.

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