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Ultrasonic-assisted Hydrothermal Synthesis of Zeolite Y Adsorbent from Natural Kaolin for the Recycling of Waste Engine Oil

Hanan A. Ahmed [1,*], Sameh A. Elbanna [1], Ramadan Khalil [2], A. Tayel [3], A. B. El Basaty [3]

[1] *Egyptian Petroleum Research Institute, Nasr City, Cairo 11727, Egypt*

[2] *Used Oil Department, Petrotrade Company, Ministry of Petroleum & Mineral Resources, Cairo 11727, Egypt*

[3] *Basic Science Department, Faculty of Technology and Education, Helwan University, Cairo 11727, Egypt*

Abstract

Waste lubricating engine oils are categorized as one of the most dangerous hazardous wastes. Herein, zeolite Y was synthesized from natural kaolin via the ultrasonic-assisted hydrothermal technique for the first time. The natural kaolin and the synthesized zeolite Y were characterized by x-ray diffraction, Fourier transformed infrared spectroscopy and scanning electron microscopy. The synthesized zeolite is then applied for the recycling of the waste lubricant engine oil. The recycled engine oil parameters such as flashpoint, dynamic viscosity, kinematic viscosity, viscosity index, pour point, sulfur content, heavy metals content, sulfur content, ash content and carbon residue were analyzed and compared to those of the virgin and waste oils. The results reveal that zeolite Y adsorbent efficiently removed heavy metals, particularly chrome, copper, iron, lead, and zinc that were in the waste engine oil. A removal efficiency of 35.71% Cr^{3+}, 66.67 % Cu^{2+}, 92.17 % Fe^{2+}, 63.02 % Pb^{2+} and 95.24 % Zn^{2+} were obtained for Zeolite Y at 25 ºC whilst 47.14 % Cr^{3+}, 76.19 % Cu^{2+}, 92.93 % Fe^{2+}, 70.70 % Pb^{2+} and 96.31 % Zn^{2+} are obtained for Zeolite Y at 40 ºC. The viscosity index of the waste oil treated with zeolite Y was reduced to 327 as compared to the viscosity index of the virgin and waste oils which were 326 and 336, respectively. These results showed that the waste engine oil can be recycled using the synthesized low-grade zeolite Y adsorbent. Additionally, the physical properties of the recycled oil indicate that it has good efficiency and can be reused.

Keywords: Kaolin; Zeolite Y; Ultrasonic-assisted hydrothermal; Waste engine oil; Recycling efficiency

1. Introduction

Zeolites are inorganic alumino-silicate materials open framework structure constructed from linked tetrahedral TO_4 (T = Al, Si) units with a different order, resulting in various types of framework topologies [1, 2]. The channel- or cage-like system of the zeolite three-dimensional structure acts as an entrance for molecules with specific sizes and shapes [3]. Zeolites have been applied in various reactions such as oil refining, esterification, alkylation, adsorption, fuel production and catalysis [4-9]. Zeolites are having extra negative charges on their surfaces arising from the partial replacing of silicon by aluminum atoms in its crystal lattice structure which can easily attract heavy metals and cationic dyes [10-12]. These surface negative charges are balanced by the surrounding cations, like Na^+, K^+, Ca^{2+}, and Mg^{2+} that may be exchanged by other cations in the contact solution [10]. The widespread activity of zeolites can be ascribed to their fascinating characteristics such as high ion-exchange capacity, excellent chemical and thermal stability and low cost [13, 14]. Zeolites are conventionally produced by using expensive pure chemicals as starting materials

*Corresponding author e-mail: drhananepri@yahoo.com.; (Hanan A. Ahmed).

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which restrict their applications. Therefore, there is still a continuous search on lowering the production cost by replacing the conventional chemicals with cheap raw materials to meet the requirement of growing demand in the commercial market [15-17]. In this regard, the cost-effective synthesis of zeolite from low-cost silica-alumina sources has become increasingly interesting. Many attempts have been made on the synthesis of zeolite from low-cost sources such as kaolin [18, 19], diatomite [20], oil shale ash [16] and blast furnace slag [21]. Among the mentioned cheap raw materials, natural kaolin has been widely used for this purpose [22]. Kaolin is a clay in which its major constituent is kaolinite, $Al_2Si_2O_5$ $(OH)_4$, a dioctahedral layered hydrated alumino-silicate of the 1:1 type with two distinct interlayer surfaces which is ideally suited for zeolites synthesis [23, 24]. The utilization of kaolin waste for the production of zeolite has both economic and environmental advantages over chemical reagents used in processes to obtain zeolites [25]. Much attention has been paid to the synthesis of zeolites as adsorbents using the naturally abundant Egyptian kaolin. This is due to its wide availability in the Egyptian lands and low cost as it's a green precursor of silica and alumina [26]. The crystalline kaolin cannot be used directly as a source to synthesize zeolite y due to its chemical inertness. The crystalline phase of kaolin has to be converted into the amorphous and reactive metakaolin phase via its thermal activation at high temperatures that is usually in the range of 600–1100 ^{o}C. This is followed by the hydrothermal synthesis step, which typically involves the hydrothermal reaction of metakaolin with an aqueous alkali medium at proper reaction temperatures. Over the years, successful efforts of implementing ultrasonic hydrothermal synthesis technique have been proven as a potential technique in shortening the zeolite crystallization time and producing zeolites with smaller crystal sizes compared to the conventional methods [27]. Nga et al. reported the successful synthesis of highly crystalline zeolite RHO by applying the ultrasonic-assisted hydrothermal synthesis method [2]. They found that increasing the ultrasonication time for 120 minutes resulted in the formation of zeolite RHO with higher crystallinity and the synthesis duration has been reduced compared to the conventional synthesis methods. Among different types of zeolites, zeolite Y is one of the most interesting zeolites in terms of the volume of research activity and the scale of commercial use. It can be a good candidate considering its unique chemical-physical and morphological properties. Zeolite Y has been utilized in various applications having environmental, industrial or medical concerns, like reduction of nitrophenols [28], preparation of nanosized spinels [28], removal of heavy metals and organic pollutants from waters [23] and petrochemical and refinery [29].

Lubricating oils (LOs) are one of the most important petroleum fractions that are used in almost all vehicles and machines to reduce the rubbing between surfaces in moving parts [30]. During the application of LOs in internal combustion engines, they lost their greasing properties due to the oxidative degradation of base oil components, decomposition of oil and its additives and contamination with water, metals, etc resulting in the generation of serious pollutants [31, 32]. These pollutants contain acidic-, phenolic- and aldehydic- compounds, salts, water, toxic heavy metals, and other compounds which have harmful concerns on the environment and human health [33]. Thus, the obtained waste engine oil becomes difficult to handle and undesirable for use due to its toxicity [34]. Increasing the yearly consumption volume of lubricating engine oils by increasing the number of vehicles has led to an increase in the annually produced amounts of fresh and waste lubricating engine oils. Mostly, huge quantities of these waste oils are used in ways that are harmful to the environment such as throwing them into landfills, gutters and running waters [35]. Also, they may penetrate the ground and cause serious destruction to aquatic life or may cause ground water contamination [36]. Additionally, the burning of these waste oils resulted in the production of carcinogens and ashes which creates a lot of problems in the environment such as air pollution [30, 37]. Therefore, recycling the waste lubricating oils not only provides an efficient way for reducing the environmental pollution concerns related to their disposal but also adds value to the waste lubricant via restoring its properties [38]. In this regard, facile synthesis of zeolite Y adsorbent from natural kaolin via the ultrasonic-assisted hydrothermal method was examined for the first time. The cost of zeolite Y synthesis was reduced by using the naturally available Egyptian kaolin as alumina and silica sources instead of pure chemicals. The natural kaolin and the synthesized zeolite Y adsorbent were characterized by Fourier transformed infrared spectroscopy, x-ray diffraction and scanning electron

microscopy. The effect of zeolite Y addition on the recycling efficiency of waste lubricant engine oil was studied. Additionally, the recycled engine oil parameters such as flashpoint, dynamic viscosity, kinematic viscosity, viscosity index, pour point, sulfur content, heavy metals content, specific gravity sulfur content, ash content and carbon residue were measured and compared to those of the virgin and waste oils.

2. Materials and Methods

2.1. Materials

The naturally available Egyptian kaolin was collected from South Sinai Governorate, Egypt and utilized for the synthesis of zeolite Y. Sodium hydroxide and sulfuric acid were purchased from Merck Chemical Co. and used as received. Virgin lubricant engine oil was obtained from the Total oil service station while the waste engine oil was collected from a mechanical shop after using it for 4 months in vehicles by commercial drivers and purified before recycling.

2.2. Methods

2.2.1. Ultrasonic-assisted hydrothermal synthesis of zeolite Y adsorbent

Zeolite Y adsorbent is synthesized from the natural kaolin by the ultrasonic-assisted hydrothermal method adapted from previous works [2, 39] with some modifications. Firstly, the Egyptian natural kaolin; the alumino-silicate source was grounded and sieved to obtain particles with the grain size of < 75 μm. Then, it was subjected to calcination at 850 °C for 3 h followed by activation with H_2SO_4 (4 mol/L) at 90 °C for 2 h, drying and calcination at 550 °C for 2 h which resulted in the formation of metakaolin; amorphous alumino-silicate ($Al_2Si_2O_7$). Secondly, the obtained alumino-silicate precursor was mixed with an alkaline solution of sodium hydroxide (3 mol/L) by the ratio of (1/9) followed by aging under stirring (700 rpm) at 60 °C for 12 h. After that, the obtained mixture was ultrasonicated in an ultrasonic bath for 120 min. Then, the hydrothermal crystallization was performed by transferring the obtained mixture into a Teflon-lined stainless steel autoclave which was sealed and heated at 98 °C for 10 h. After that, the autoclave was cooled down to room temperature; the obtained solid was collected by centrifugation, washed multiple times with distilled water until reaching a neutral pH. Finally, the collected zeolite Y adsorbent was dried overnight at 90 °C, crushed into a fine powder and stored for further analysis.

2.3. Characterization of natural kaolin and zeolite Y

The natural kaolin and the synthesized zeolite Y samples were characterized by various techniques. The chemical structures of the samples were confirmed by Fourier transform infrared (Nicolet IS-10 FTIR). The KBr pressed disk technique was used to record IR spectra in transmittance mode in the range of 400-4000 cm^{-1}. X-ray diffraction (XRD) patterns were recorded by using PANalytical X'Pert PRO diffractometer with Cu Ka = 1.54, 18 A˚ over the angular range from 4º to 64º with a scanning rate of 4º/min. The surface morphology of the samples was examined by scanning electron microscope (SEM) model (ZEISS, Gemini, Sigma 300 VP, Germany).

2.4. Purification of waste engine oil (WEO)

The waste engine oil (WEO) collected from commercial vehicles after using it for 4 months was vacuum-filtered to remove the impurities such as sand, metal chips and micro impurities. The filtered waste oil was then allowed to settle down for 12 h, filtered again by centrifugation at 8000 rpm for 15 min to allow the suspended particles in the oil to settle down at the bottom and the liquid portion was decanted.

2.5. Removal of heavy metal ions from WEO using zeolite Y adsorbent

100 ml of the obtained decanted liquid oil was placed into a beaker and mixed with 0.5 g of zeolite Y. The mixture was magnetically stirred at 25 °C for 120 min to study the effect of zeolite Y adsorbent addition on the removal of Cr^{3+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} heavy metal ions from the waste engine oil. Another experiment was performed by the mentioned method but with increasing the temperature to 40 °C. After completing each experiment, the mixture was centrifuged and the concentration of the remaining metal ions in the recycled WEO was analyzed using the Agilent 5100 Synchronous Vertical Dual View (SVDV) ICP-OES, with Agilent Vapor Generation Accessory VGA 77. The concentrations of Cr^{3+}, Cu^{2+}, Fe^{2+}, Pb^{2+}, and Zn^{2+} ions in the virgin and waste oils were also measured for comparison.

The removal efficiency of the adsorbed metal ions was calculated from Eq. (1) [40-42].

$$\text{Removal efficiency } \% = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \qquad (1)$$

2.6. Physico-chemical characteristics of the virgin, waste and recycled oils

The physico-chemical characteristics of the recycled oil after treatment with zeolite Y as compared with those of the virgin oil and waste engine oil were analyzed. The following characteristics were determined: dynamic viscosity, kinematic viscosity, viscosity index, flash point, pour point [43], carbon residue, density, sulfur content, heavy metals content and ash content using ASTM standards [44]. Prior to the measurements, 100 ml of the WEO was placed into a beaker and mixed with 0.5 g of zeolite Y and magnetically stirred for 120 min at different temperatures; 25 ºC, 65 ºC and 100 ºC. The obtained samples were named zeolite Y25, zeolite Y65 and zeolite Y100, respectively. The dynamic and kinematic viscosities were measured at 40 ºC and 100 ºC following the ASTM D 445 procedure [45]. The viscosity index was calculated from the kinematic viscosity at 40 ºC and 100 ºC and following the ASTM D 2270 procedure.

3. Results and Discussion

3.1. Structural analysis of natural kaolin and zeolite Y adsorbent

Various structural characterizations were performed for the natural kaolin and the synthesized zeolite Y.

3.1.1. FTIR spectroscopy

The FTIR spectra of the natural kaolin and the synthesized Zeolite Y are illustrated in Fig. 1. The FTIR spectrum of natural kaolin showed that its characteristic absorption bands are well identified. The two broad bands centered at 3640 cm^{-1} and 3762 cm^{-1} are due to the –OH stretching vibrations of the Al-OH and Si-OH groups of kaolin clay. The existence of these groups proved the hydrophilic nature of kaolin [46, 47]. As stated by Tunega et al. [48], kaolinite -OH groups are very flexible and able to act as proton donors or acceptors in the interactions with polar molecules and capable to form hydrogen bonds. The two broad bands observed at 438 cm^{-1} and 602 cm^{-1} represent the deformational vibration of Si–O bonds and symmetric vibration of Mg-Al-OH, respectively [49]. The FTIR bands observed at 752 cm^{-1} and 1280 cm^{-1} could be assigned to the vibrations of Si-O-Al bonds in the TO_4 tetrahedra while that band recorded at 1095 cm^{-1} is due to the Si-O bonds.

For the synthesized zeolite Y sample, there is an obvious change in its FTIR spectrum relative to that of the natural kaolin. Briefly, the two -OH vibration bands recorded in the FTIR spectrum of kaolin are replaced by a single broad band in the range of 3000-3640 cm^{-1} in the spectrum of zeolite Y. The intensity of the Si-O bands is increased in the zeolite Y spectrum with a clear shift to 414 cm^{-1} and 1048 cm^{-1} than those appeared in the spectrum of kaolin. Also, the presence of a new band recorded at 528 cm^{-1} is typically ascribed to the double six-member rings in the zeolite Y structure [50]. Additionally, another two new bands are recorded at 748 and 890 cm^{-1} in zeolite Y spectrum related to Si-O-Al bonds in the TO_4 tetrahedra which indicate the formation of zeolite Y structure [51]. The band at 890 cm^{-1} could represent the crystallization of zeolite Y with double rings [52]. All the mentioned changes indicated the presence of primary and secondary structural building units of zeolite Y structure confirming its successful formation.

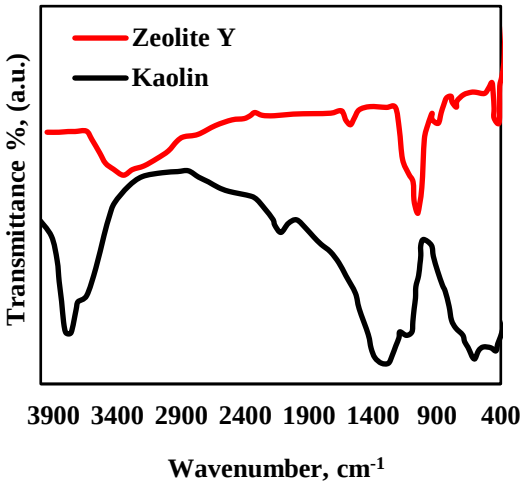

Fig. 1 FTIR spectra of natural kaolin and zeolite Y

3.1.2. XRD analysis

The XRD patterns of natural kaolin and zeolite Y were depicted in Fig. 2. The X-ray diffraction peaks of natural kaolin showed the appearance of strong peaks characteristic of kaolin crystalline structure and low intense peaks characteristics of quartz which recorded at 2θ values of 9.75°, 18.35°, 25.09°, 26.60°, 37.37°, 38.69°, 41.49°, 42.52° and 61.61° [53, 54].

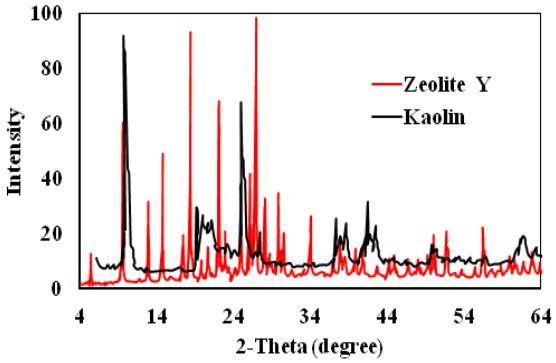

Fig. 2 XRD patterns of natural kaolin and zeolite Y

The XRD patterns of zeolite Y exhibits significant changes in comparison to the patterns of natural kaolin. It showed the standard phase of zeolite Y with diffraction peaks at the 2θ values of 5.45°, 9.45°, 12.94°, 14.83°, 17.47°, 20.71°, 22.13°, 25.35°, 26.96°, 27.02°, 29.82°, 29.86°, 34.08°, and others, suggesting the successful formation of well-ordered highly crystalline zeolite Y structure [55].

3.1.3. SEM analysis

The surface morphology of natural kaolin and the synthesized zeolite Y adsorbent are examined by SEM analysis as shown in Fig. 3a and b. The SEM image of kaolin showed that it has an unstructured nature, irregular shape with uneven edge agglomerates and porous surface [56]. Figure 3a also validated that the natural kaolin clay layers are in the form of books tells that the particles are not fully dispersed into individual layers [55]. For zeolite Y adsorbent (Fig. 3b), there is a clear difference in its morphology relative to that of the natural kaolin. SEM image of zeolite Y showed the existence of a more ordered structure with porous nature on the surface and the particles are of cubic morphology.

3.2. Characterization of virgin-, waste- and zeolite Y-treated waste engine oils

3.2.1. Physico-chemical characteristics

The physico-chemical characteristics of the recycled engine oil by zeolite Y25, zeolite Y65 and zeolite Y100 as compared with those of the virgin and waste oils and the ASTM specifications are represented in Table 1. It can be seen that the properties of the recycled oil by zeolite Y samples are better than those of the waste oil and the recycled oil by zeolite Y100 has the best performance. It is clear that the values of dynamic and kinematic viscosities measured at 40 ºC and 100 ºC for the recycled oil by zeolite Y25, zeolite Y65 and zeolite Y100 were reduced to lower values as compared with those of the waste oils indicating the decrease in contamination after treatment with zeolite Y adsorbent. Pour point is defined as the lowest temperature at which the oil will stop to flow [57, 58].

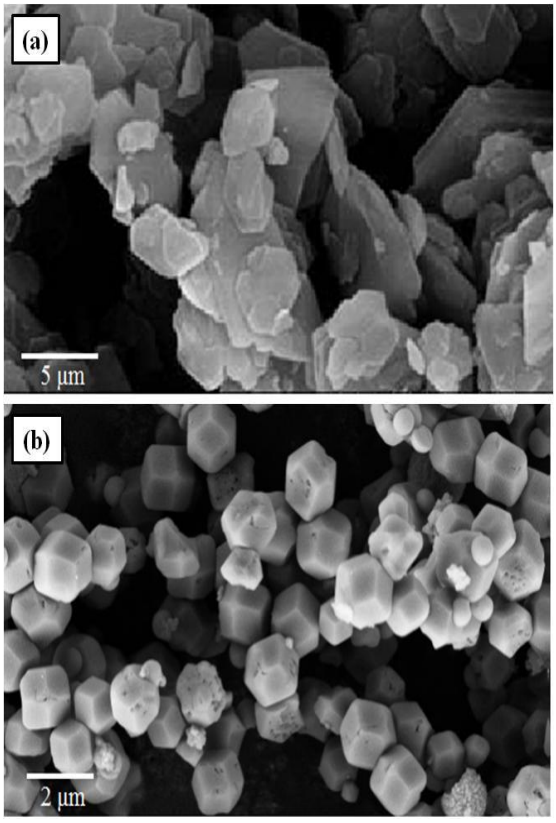

Fig. 2 SEM of (a) natural kaolin and (b) Zeolite Y

The results in Table 2 show that the pour point value of waste engine oil (-15 ºC) was reduced to -21 ºC, -21 ºC and -24 for the recycled oil by zeolite Y25, zeolite Y65 and zeolite Y100, respectively. This decrease in pour point is because of degradations of additives, which were present in virgin oil as pour point depressants. These results show that the three recycling samples are comparatively efficient for treatment. Also, the results reveal that the specific gravity, viscosity index, flash point, ash content, carbon residue and sulfur content were enhanced to reasonable values relative to those of the waste oil. Based on the mentioned discussions, it can be concluded that the WEO can be recycled using the synthesized low-grade zeolite Y adsorbent and its properties indicate that it has good efficiency and can be reused.

Table 1 Physico-chemical characteristics of the recycled oil with zeolite Y

Test	Method	Virgin oil	Waste oil	Recycled oil by zeolite Y25	Recycled oil by zeolite Y65	Recycled oil by zeolite Y100
Dynamic viscosity @40 °C	ASTM D 2196-18	142.1	155.0	142.3	142.3	142.2
Dynamic viscosity @100 °C	ASTM D 2196-18	40.1	45.1	40.7	40.5	40.2
Specific Gravity @20 °C**, g/m^3**	ASTM D 1298	0.8734	0.8825	0.8785	0.8763	0.8761
Pour Point, °C	ASTM D 97-02	-15	-15	-21	-21	-24
Kinematic viscosity @40 °C	ASTM D445-18	162.697	175.645	161.980	162.387	162.310
Kinematic viscosity @100 °C	ASTM D445-18	45.912	51.107	46.328	46.217	45.885
Viscosity Index	ASTM D2270	326	336	330	328	327
Flash Point	ASTM D 92	195	117	138	165	192
Carbon residue, %	ASTM D 524	0.56	1.08	0.89	0.68	0.58
Sulfur content, %	ASTM D4294	0.1	0.98	0.31	0.28	0.18
Ash content, %	ASTM D2584	0.01	1.89	0.23	0.09	0.05

3.2.1.Recycling of WEO through heavy metal ions removal with zeolite adsorbent

Removal of hazardous heavy metal ions contaminants from the WEO by using zeolite Y can help in restoring the properties of the oil as well as minimizing the waste by-products. The effect of zeolite Y adsorbent addition on the removal efficiency of Cr^{3+}, Cu^{2+}, Fe^{2+}, Pb and Zn^{2+} toxic heavy metal ions from WEO was investigated and the results are summarized in Table 2. The metallic content (ppm) of the mentioned ions in the recycled engine oil by zeolite Y at 25 Cº and 40 Cº after stirring for 120 min as compared to their initial content in the virgin and waste engine oils is also presented in Table 2. There was a clear reduction in the metallic content of all ions in the recycled oil after treatment with zeolite Y at the mentioned temperatures as compared to that of the waste oil. A removal efficiency of 35.71% Cr^{3+}, 66.67 % Cu^{2+}, 92.17 % Fe^{2+}, 63.02 % Pb^{2+} and 95.24 % Zn^{2+} was obtained for Zeolite Y at 25 ºC whilst 47.14 % Cr^{3+}, 76.19 % Cu^{2+}, 92.93 % Fe^{2+}, 70.70 % Pb^{2+} and 96.31 % Zn^{2+} was obtained for Zeolite Y at 40 ºC. The ion adsorption behaviour of zeolite Y arises from the acid-base surface hydroxyl groups. The protonation and deprotonation of these surface hydroxyl groups affect the oxide surface to develop an electrical charge promoting adsorption. The cation and anion exchange takes place at the acid (-OH) and the base (-OH) hydroxyl sites. The abovementioned results indicate that the synthesized zeolite Y adsorbent efficiently removed heavy metals from the waste engine oil and the mentioned oil can be efficiently recycled using the low-grade zeolite Y adsorbent.

4. Conclusion

Zeolite Y adsorbent was synthesized from natural kaolin via the ultrasonic-assisted hydrothermal technique and examined in the recycling of waste lubricant engine oil for the first time in the current research. The produced adsorbent (Zeolite Y) was characterized by various techniques which confirm new structural and morphological properties relative to that of the natural kaolin. These new properties indicated the existence of zeolite Y primary and secondary structural building units and confirmed the successful formation of well-ordered highly crystalline zeolite Y structure with particles of cubic morphology. The outcome of recycling waste lubricating engine oil using the synthesized Zeolite Y adsorbent gave recycled oil with quality comparable to that of the virgin lubrication oil.

Table 2 Effect of Zeolite Y adsorbent addition on the removal efficiency of toxic heavy metal ions from WEO

Sample Name	Metallic content (ppm)				
	Cr^{3+}	Cu^{2+}	Fe^{2+}	Pb^{2+}	Zn^{2+}
Virgin engine oil	0.006	0.001	0.0058	0.0360	0.0622
Waste engine oil (WEO)	0.007	0.0021	0.0651	0.0430	0.0651
Recycled engine oil by Zeolite Y @ 25 °C after 120 min stirring	0.0045	0.0007	0.0051	0.0159	0.0031
Recycled engine oil by Zeolite Y @ 40 °C after 120 min stirring	0.0037	0.0005	0.0046	0.0126	0.0024
Efficiency by Zeolite Y @ 25 °C after 120 min stirring	35.71	66.67	92.17	63.02	95.24
Efficiency by Zeolite Y @ 40 °C after 120 min stirring	47.14	76.19	92.93	70.70	96.31

Although the results show that the three recycling samples zeolite Y25, zeolite Y65 and zeolite Y100 were comparatively efficient for waste engine oil treatment, the physico-chemical properties of the recycled oil by zeolite Y100 has the best performance and can be reused. Also, the results revealed that the treatment of waste engine oil with zeolite Y adsorbent resulted in an obvious reduction in the metallic content of heavy metals contamination. A maximum removal efficiency of 47.14 % Cr^{3+}, 76.19 % Cu^{2+}, 92.93 % Fe^{2+}, 70.70 % Pb^{2+} and 96.31 % Zn^{2+} was obtained for Zeolite Y. Thus, the synthesized low-grade zeolite Y can be applied as a viable and alternative adsorbent for the recycling of waste engine oil through the efficient removal of contaminants and returning the waste oil to a quality nearly equivalent to oils produced by fresh lubricant oil stocks.

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