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Article

Conversion of Oil-Containing Residue from Waste Oil Recycling Plant into Porous Carbon Materials by the Activation Method with Phosphoric Acid

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Abstract: In the waste oil recycling industry, large amounts of oil-containing sludge were still generated, thus posing a resource-depleted issue if it was disposed of or incinerated without energy recovery or residual oil utilization. In this work, the chemical activation experiments by using phosphoric acid (H_3PO_4) were performed at a lower temperature (600°C) for holding 30 min to produce the porous carbon products. From the results of the pore property analysis, it showed an increasing trend with impregnation ratio from 0.5 to 2.0. Based on the Brunauer–Emmett–Teller (BET) model, the maximal BET surface area was about 70 m²/g, which was indicative of the hysteresis loop and the type IV isotherms in the resulting carbon product. In addition, the enhancement in the pore properties of carbon products by acid-washing was superior to those by water-washing and without post-washing. By the observations of using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), the carbon product featured its porous structure and inherent magnetism due to its richness of iron oxides. In this regard, it can be used as an efficient adsorbents or catalyst supports due to its simple recovery (or separation) if exhausted.

Keywords: oily sludge; chemical activation; phosphoric acid; washing modification; pore analysis

1. Introduction

With the rapid development of the industrial & commercial activities and the increase in population, the energy demand and the environmental issues are becoming more and more serious. Recycling all kinds of waste oil has attracted significant attention in recent years [1]. These oil sources include engine oil (or mineral engine oil), lubricating oil, cutting oil, tank bottom oil, and so on. For example, the so-called waste engine oil refers to the engine oil that has been mixed with water, dust, metal-containing power produced from mechanical wear and tear like iron (Fe), lead (Pb), zinc (Zn), and magnesium (Mn) [2]. Without waste oil collection and reuse by recycling into oil-related or oil-derived products, it can pose adverse environmental and health impacts due to its contents of petroleum-based components, heavy metals and other contaminants [3]. Although the production of alternative fuels from waste oils can decline the consumption of petroleum-based fuels and thus reduce greenhouse gas (GHG) emissions [4], the waste oil refining process still generates large amounts of oil-containing residue. Based on the current situation, the conversion of oil-containing residue from waste oil recycling plant into valuable products not only provided the total solutions in the waste oil recycling industry, but also made additional profits for these recycling enterprises.

In recent years, many researches have reviewed on different thermal, chemical and physical technologies to convert oil-containing residue or oily sludge into a variety of products [5–9]. In brief, these studies focused on the recovery of oils (or residual oils) by adopting solvent extraction and ultrasonication, and the energy recovery by using thermal treatment and thermochemical processes like pyrolysis and gasification. Regarding the production of porous carbon-rich materials from oily sludge by activation process, only few studies performed the cases from the waste oil recycling plants [10,11], not those from the oil (petroleum) refinery plants like oil tanks (at the bottom of the tanks) [12–28]. Furthermore, most of these researches adopted the chemical activation by using potassium hydroxide (KOH), less cases by using zinc chloride ($ZnCl_2$). Exceptionally, Li *et al.* prepared the de-ashed char at 700°C and post-washing with hydrogen fluoride (HF) solution for 24 h to remove inorganic impurities [18]. The authors used phosphoric acid (H_3PO_4) as an activating agent to promote the pore properties of the above-mentioned resulting char with different H_3PO_4/char ratios of 2:1, 2.5:1, and 3:1 at 400 °C for 1 h under a nitrogen flow [18]. To obtain the highly porous carbon products, the crude products were washed with plenty of deionized (D.I.) water and then dried at 105°C for 24 h. In the previous studies [10,11], the pore properties of the resulting carbon products prepared from oil-containing residue by physical activation of carbon dioxide (CO_2) at 850°C for 0.5-1.5 h showed a decreasing trend [11]. The maximal Brunauer–Emmett–Teller (BET) surface area only had 21.59 m^2/g. In addition, the data on the BET surface area can be enhanced to 40.53 m^2/g due to the acid-washing of the crude carbon products [10].

Based on the results of the previous studies [10,11], it showed a feasible approach to prepare the carbon products from the residual sludge of waste oil recycling plant, even if the pore properties were not significant. In this work, we carried out the chemical activation experiments by using H_3PO_4 at a lower temperature (600°C). To enhance the pore properties by removing residual H_3PO_4 and inherent inorganic minerals, the post-washing of the crude carbon products were further performed by using deionized water and dilute acid. In this regard, the pore properties of the resulting carbon products were determined by the surface area and porosity analyzer based on the nitrogen isotherms (- 196°C). Their porous textures and elemental compositions on the surface were viewed by the scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), respectively.

2. Materials and Methods

2.1. Materials

The starting precursor for producing carbon product was derived from a waste oil recycling plant, located in Neipu Industrial Park (Pingtung county, Taiwan). According to the official definition, the as-received oil-containing sludge in the form of dark and sticky slurry is a non-hazardous waste. The sample was analyzed to get the information about the thermochemical data on proximate analysis, calorific value, elemental content and thermogravimetric analysis (TGA). To perform the chemical activation experiments with phosphoric acid (or *ortho*-phosphoric acid), the concentration of ACS-grade activation agent from Merck KGaA (Darmstadt, Germany) was 85 wt%.

2.2. Thermochemical Properties of Oil-Containing Sludge

The baseline information about the thermochemical properties (including proximate analysis, calorific value and TGA) of the oil-containing sludge were first determined to get the thermal decomposition behavior and the potential for preparing carbon materials. Based on the official standard methods (i.e., "Standard Method for Determining Moisture Content of Industrial Waste" and "Standard Method for Determining Combustible and Ash Contents of Industrial Waste", coded as NIEA R203.02C and NIEA R205.01C, respectively) in Taiwan, the proximate analysis of as-received sludge sample was performed to assess the quality of the precursor. Combustible is the component remaining after the determination of moisture and ash contents. Therefore, it is a measure of the solid combustible fraction. Calorific value is the energy content per unit mass of the sample (dry basis), which was indicative of the heat energy released while completely burning it by an adiabatic bomb calorimeter (Model: CALORIMETER ASSY 6200; Parr Co., Moline, IL, USA) in

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triplicate. It should be noted that the determined value represents <u>gross calorific value</u> or higher calorific value because it contains the latent heat of combustion product water vaporization. On the other hand, the TGA was performed by a precision instrument (Model: TGA-51; Shimadzu Co., Kyoto, Japan). The dried sludge sample was uniformly heated at four rates (5, 10, 15, and 20°C/min) under nitrogen gas (flowrate set by 50 cm^3/min) up to 900°C. In addition, the main elemental contents (including carbon, oxygen, alkali metals, alkaline earth metals, silicon, and other main elements) on the surface of dried sludge sample were determined by using an energy-dispersive X-ray spectroscopy (Model: 7021-H; HORIBA Co., Kyoto, Japan).

2.3. Phosphoric Acid Activation Experiments

Chemical activation is a low energy-consumption process for producing porous carbon materials because it generally performed at lower temperatures (400–800°C) as compared to physical activation process at higher temperatures (700–1000°C) [29]. In the former process, phosphoric acid is a commonly used activator acted as a dehydrating agent. According to the preliminary data on the pore properties of resulting carbon products prepared at 600-900°C for holding 30-60 min by a higher impregnation ratio of 2.0 (the mass ratio of phosphoric acid to oil-containing sludge), it only showed non-regular variations on specific surface area (BET model) ranging from 50.7 to 59.3 m^2/g. Therefore, the chemical activation experiments were designed at a lower temperature (600°C) by different impregnation ratios (i.e., 0.0, 0.5, 1.0, 1.5, and 2.0) in the present study. To carbonize the residual sludge, the inert atmosphere was carried out by purging nitrogen gas with a flowrate of 500 cm^3/g during all activation experiments. In order to evaluate the enhancement of the pore properties for the resulting carbon products, the post-washing treatment by deionized water and dilute acid solution (0.25 M HCl) were performed on a hot-plate at about 75°C for 30 min. The detailed procedures can refer to the previous studies [11,30,31]. In this work, the resulting carbon products were stated as the specific code. For example, C-05-SL-600-30, C-05-SL-600-30-W and C-05-SL-600-30-A represent the carbon products (C) prepared from the sludge (SL) at 600°C for 30 min without washing, water-washing and acid-washing, respectively. To reduce the use of phosphoric acid, two acid-washing experiments with the impregnation ratios of 0.0 and 0.5 were carried out in the present study. That is, the resulting carbon products are C-0-SL-600-30-A and C-05-SL-600-30-A.

2.4. Characterization of Carbon Products

The nitrogen adsorption/desorption isotherm at –196°C were commonly used for determining the pore properties of a carbon material (or product), including specific surface area, pore volume, average pore size and pore size distribution [32,33]. An accelerated surface area & porosimeter (Model: ASAP 2020; Micromeritics Instrument Co., Norcross, GA, USA) was adopted for all pore property analyses. Prior to the determinations of pore properties, the degassed steps were performed under vacuum condition (1.33 Pa) at high temperature (200°C) for holding 10 h. Regarding the specific surface area, the Brunauer-Emmett-Teller (BET) surface area (S_{BET}) should be the most commonly used one, which is expressed in units of area per mass of sample (m^2/g). By comparison with the adsorption isotherm of a nonporous reference material, the data on micropore (pore size < 2.0 nm) volume (V_{micro}) and micropore surface area (S_{micro}) can be calculated by using the "*t*-plot" method [33]. Herein, the *t*-plot method was used to estimate the surface area and pore volume with micropores (pore diameter or width: < 2.0 nm) based on the Harkins-Jura equation. The data on total pore volume (V_t) were estimated by assuming that all pores are filled with liquid adsorbate (i.e., nitrogen). Therefore, total nitrogen gas adsorbed at a saturated relative pressure (*ca.* 0.995) was converted to liquid nitrogen volume by using its density at –196°C (i.e., 0.807 cm^3/g). By assuming uniform cylindrical pores, the following equation was generally used to calculate average pore diameter (D_{av}) of a porous sample for a given total pore volume and BET surface area.

$$D_{av} = (V_t*4)/S_{BET}$$

On the other hand, the pore size distribution of a porous material was based on the Barrett–Joyner–Halenda (BJH) method, which can be represented both in differential and cumulative models

[33]. It should be noted that the BJH method was limited to display the pore size distributions in the range of mesopore (2.0 - 50.0 nm) to macropore (> 50.0 nm). In order to image the porous structures of the resulting carbon products, the scanning electron microscopy (SEM) (Model: S-3000N; Hitachi Co., Tokyo, Japan) was applied under an accelerating voltage of 15.0 kV. Prior to the SEM observations, the non-conductive carbon products were coated by a gold film in an ion sputter (Model: E1010; Hitachi Co., Tokyo, Japan).

3. Results and Discussion

3.1. Thermochemical Characterization of Oil-Containing Sludge

Table 1 listed the data on proximate analysis and calorific value of oil-containing sludge, which were used to evaluate the potential for the production of carbon products in the chemical activation process. Obviously, the as-received sample still contained large non-combustible fractions, including moisture content (65.44 wt%) and ash content (24.98 wt%). It showed high separation efficiency of residual oil in the waste oil recycling plant, resulting in only about 10 wt% of combustible component remained in the oil-containing sludge. Using the preliminary analysis by EDS, Figure 1 showed the elemental compositions on the surface of the dried oil-containing sludge, indicating high carbon and oxygen contents (38.81 wt% and 29.03 wt%, respectively) and other inorganic elements like iron (19.45 wt%), silicon (6.93 wt%), magnesium (4.50 wt%) and sulfur (1.28 wt%). In this regard, the origin of oil-containing sludge could be derived from the waste oil at the bottom of iron-made storage tank in the petroleum refinery plants. As seen in Figure 1, the unidentified peaks at around 2.1 keV are assigned to the gold (Au) because this element was used to provide a conductive film on the surface by an ion sputter. Furthermore, the calorific value of dried oil-containing sludge only had 13.06 MJ/kg. This value was significantly lower than those of coal and petroleum-based fuels [34,35]. Although the oil-containing sludge can be treated by combustion method, the emissions of particulates and sulfur oxides (SOx) from the incineration plants or industrial boilers should be controlled by air pollution control systems like baghouse and flue gas desulfurization (FGD).

**Table 1.** Proximate analysis and calorific value of oil-containing sludge.

Property [a]	Value
Proximate analysis [b]	
Moisture (wt%)	65.44 ± 0.34
Ash (wt%)	24.98 ± 0.47
Combustible (wt%)	9.58 ± 0.35
Calorific value (MJ/kg) [c]	13.06 ± 0.92

[a] The mean ± standard deviation for three determinations. [b] As-received sample. [c] Dry basis.
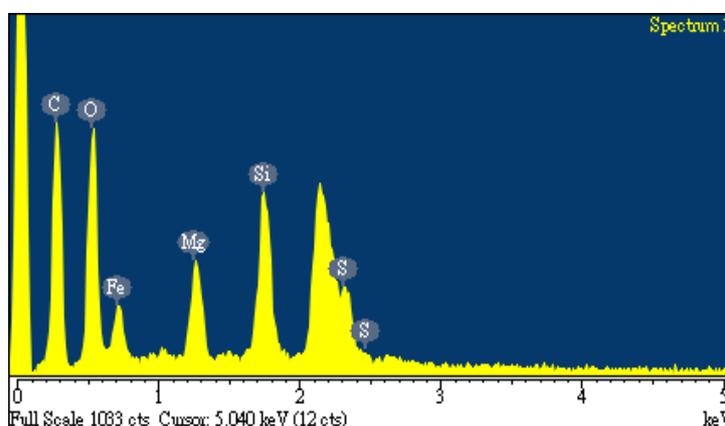
Figure 1. EDS spectra of oil-containing sludge.

Figure 2 depicted the results of thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) for the dried oil-containing sludge in the temperature range of 25°C to 900°C at four heating rates (5, 10, 15 and 20°C/min) under the inert nitrogen atmosphere. These curves have been normalized by the initial sample mass. Obviously, the significant weight loss of about 25-30% was observed in the temperature range of 200°C to 500°C. It can be attributed to the evaporation loss of residual heavy oil fractions still contained in the dried sludge. This value was close to the data on proximate analysis in Table 1 (9.58 wt%/(1 - 0.6544) = 27.7 wt%). The weight loss at high temperatures (> 900°C) may be caused by the evaporation loss of inorganic fractions (or minerals) with low melting points.
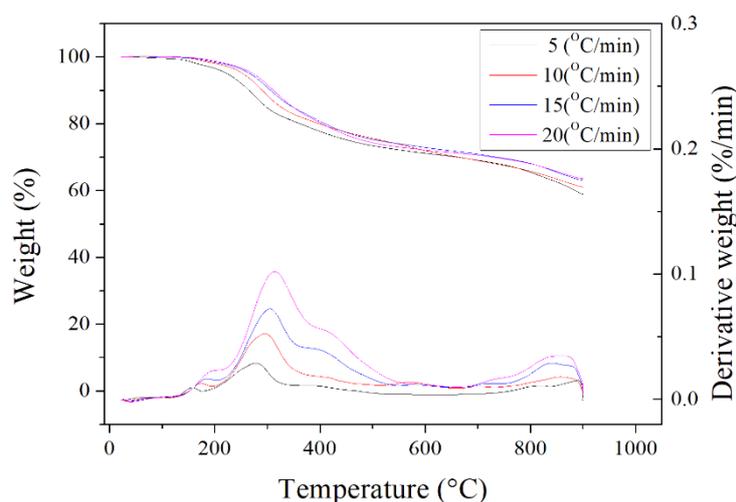
Figure 2. Thermogravimetric analysis (upper, referred to the vertical coordinate at the left side) and derivative thermogravimetry (lower, referred to the vertical coordinate at the left side) curves of dried oil-containing sludge.

3.2. Characterization of Resulting Carbon Products

The data on the pore properties of the resulting carbon products, including BET surface area (S_{BET}), micropore surface area (S_{micro}), external surface area (S_{ext}), total pore volume (V_t), micropore volume (V_{micro}) and average pore diameter (D_{av}), were summarized in Table 2. Using BET surface area values as a porosity criterion, the main results can be concluded as follows:

1. The H_3PO_4 impregnation ratio had a positive impact on the pore properties of resulting carbon products. The BET surface area indicated a slight increasing trend with impregnation ratio increased. As compared to the carbon product without impregnation by H_3PO_4 (i.e., C-0-SL-600-30), this enhancement of pore development seemed to be not significant, thus showing that its BET surface area was slightly higher than that of carbon product (i.e., C-05-SL-600-30).

2.   The pore properties of carbon products can be enhanced by post-washing by water and dilute acid solution; that is, 50.799 and 49.462 m²/g (C-0-SL-600-30 and C-05-SL-600-30, respectively), 58.980 and 57.832 m²/g (C-0-SL-600-30-W and C-05-SL-600-30-W, respectively), 63.132 and 69.132 m²/g (C-0-SL-600-30-A and C-05-SL-600-30-A, respectively). On the other hand, the enhancement by acid-washing showed better pore properties than those by water-washing possibly due to more dissolution (leaching-off) of inorganic minerals and more pore developed and formed [36–38].

3. As compared to the previous studies on the production of carbon products from oil-containing sludge [10,11], the results of H_3PO_4 chemical activation at 600°C in this work were superior to those by CO_2 physical activation at 850°C for holding same time (30 min). The maximal BET surface area value (69.13 m²/g, seen in Table 2) for the carbon product (C-05-SL-600-30-A) was larger than that (40.53 m²/g) by CO_2 physical activation and post-acid washing [10].

Table 2. Pore properties of resulting carbon products [a].

Code of carbon product	S_{BET} [b] (m²/g)	S_{micro} [c] (m²/g)	S_{ext} [d] (m²/g)	V_t [e] (cm³/g)	V_{micro} [c] (cm³/g)	D_{av} [f] (nm)
C-0-SL-600-30	50.799	24.947	25.852	0.0769	0.0130	6.053
C-05-SL-600-30	49.462	29.524	19.938	0.0657	0.0148	5.314
C-10-SL-600-30	51.610	31.352	20.258	0.0613	0.0163	4.751
C-15-SL-600-30	54.563	39.245	15.318	0.0566	0.0197	4.147
C-20-SL-600-30	58.611	38.529	20.082	0.0590	0.0195	4.028
C-0-SL-600-30-W	58.980	31.315	27.665	0.0796	0.0157	5.399
C-05-SL-600-30-W	57.832	29.589	25.243	0.0760	0.0598	5.256
C-10-SL-600-30-W	60.168	36.468	23.700	0.0674	0.0190	4.478
C-15-SL-600-30-W	57.255	37.268	19.987	0.0584	0.0187	4.083
C-20-SL-600-30-W	59.296	37.800	21.496	0.0686	0.0197	4.629
C-0-SL-600-30-A	63.132	26.641	36.6889	0.0979	0.0138	6.185
C-05-SL-600-30-A	69.132	31.152	37.980	0.1100	0.0155	6.365

[a] The carbon products were produced from oil-containing sludge (SL) with different impregnation ratios (H_3PO_4/SL) at 600°C for holding 30 min. [b] BET surface area was correlated in a relative pressure range of 0.06-0.30. [c] By the *t*-plot method. [d] By deducting micropore surface area (S_{micro}) from BET surface area (S_{BET}). [e] Total pore volume was obtained at relative pressure of 0.995. [f] By the ratio of the total pore volume (V_t) to the BET surface area (S_{BET}) (i.e., Average pore width = $4 \times V_t/S_{BET}$).

Figure 3 and Figure 4 showed the N_2 adsorption & desorption isotherms and the pore size distributions for the carbon products without H_3PO_4 impregnation and with H_3PO_4 impregnation (using the lowest mass ratio of 0.5), respectively. Based on the classification of the International Union of Pure and Applied Chemistry (IUPAC) [32,33], the isotherms featured the hysteresis loop and the type IV, indicating mesoporous structures. As seen in Figure 4, the mesopore size range concentrated on 3.0 to 4.5 nm, which was obtained by using the data on the branch of desorption isotherms and the Barrett-Joyner-Halenda (BJH) model [33].
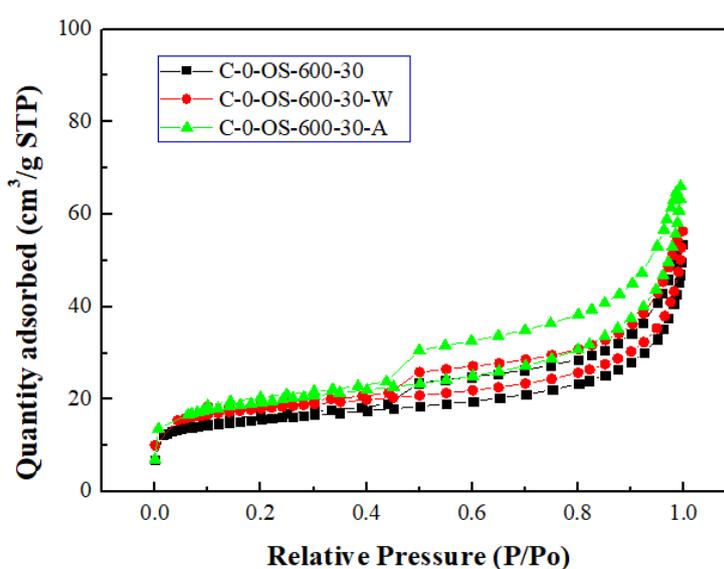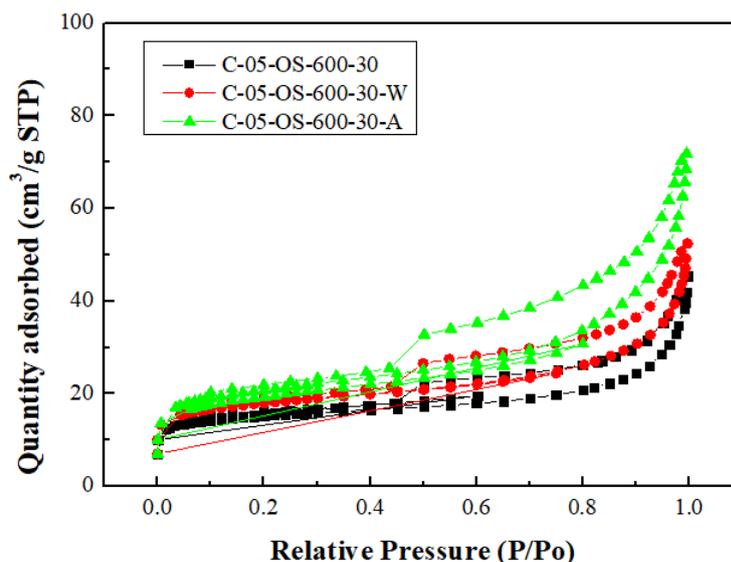
Figure 3. Nitrogen adsorption-desorption isotherms of carbon products. Upper images for no impregnation by H_3PO_4, Lower images for impregnation ratio of 0.5.
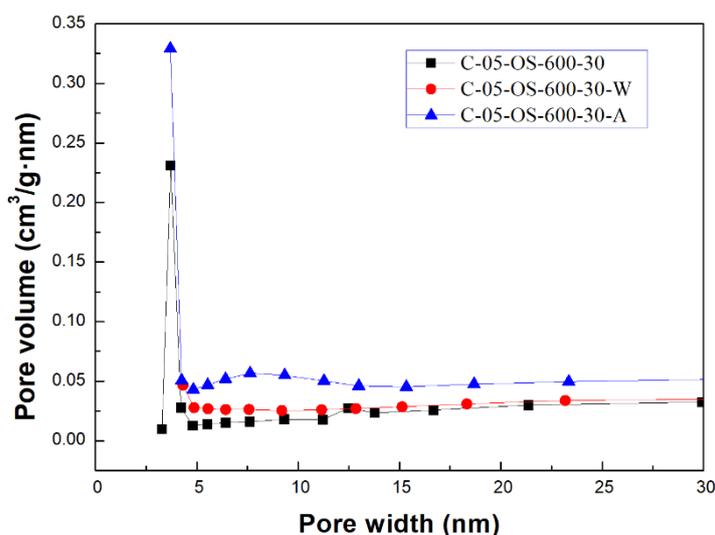

Figure 4. Pore size distributions of carbon products for impregnation ratio of 0.5.

The SEM images of the dried oil-containing sludge (SL) and the optimal carbon product (i.e., C-05-SL-600-30-A) were shown in Figure 5. The former seemed to be non-porous and heterogeneous (Figure 5(a)) due to its low BET surface area (3.795 m^2/g). By contrast, the carbon product (Figure 5(b)) indicated a porous texture on the surface, thus having higher BET surface area. In addition, the elemental compositions on the surface of the carbon products (i.e., C-05-SL-600-30-A) can be seen in Figure 6. Herein, the significant peak on the far right is a background gold (Au) for providing a conductive film on the surface. The contents of carbon, oxygen, silicon, magnesium and iron were 24.22, 15.84, 5.04, 2.27 and 52.64 wt%, respectively. These results were consistent with the previous study [10]. In comparison with the EDS data on the starting sludge (Sec. 3.1), the contents of carbon, silicon and magnesium were slightly reduced, the iron content was concentrated by increasing from 19.45 wt% to 52.64 wt%. As mentioned above, the carbon product with having mesoporous and magnetic properties may be used as an efficient adsorbents or catalyst supports. When it was disposed of or exhausted, it can be easily collected or separated by external magnets applied [39,40].
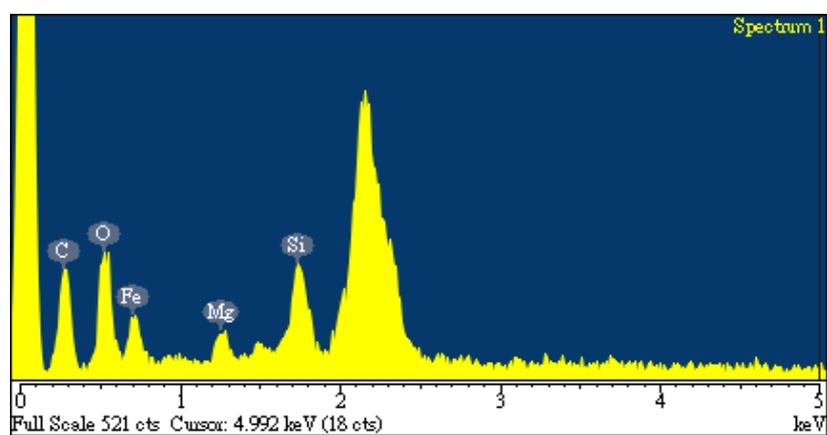
(a)SL
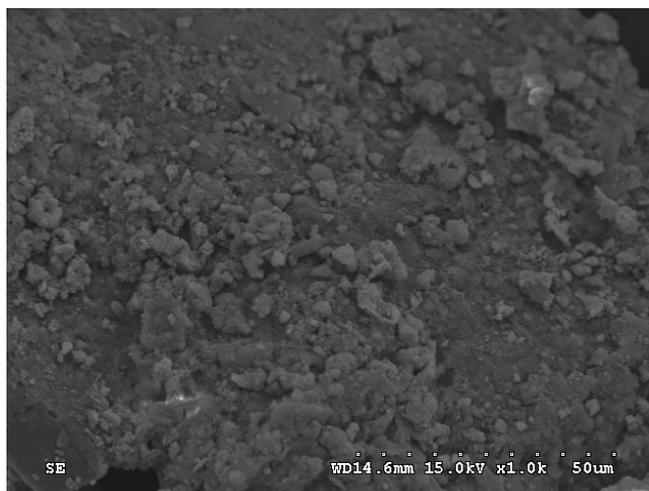
(b) C-05-SL-600-30-A
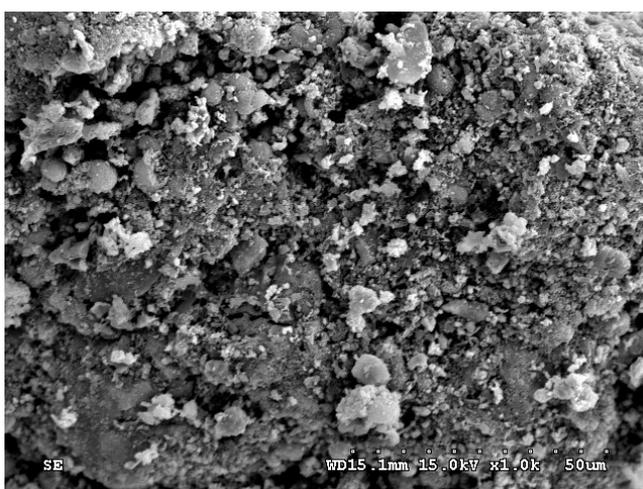
Figure 5. SEM images (×1,000) of (a) oil-containing sludge (SL) and (b) resulting carbon product (C-05-SL-600-30-A).

Figure 6. EDS spectra of resulting carbon product (C-05-SL-600-30-A).

4. Conclusions

The waste oil recycling plants still generated large amounts of residual sludge with containing oils and inorganic minerals (e.g., iron oxides), which was used to produce porous carbon products by phosphoric acid (H_3PO_4) activation method in the present study. From the data on the pore properties, it was found that the H_3PO_4 impregnation ratio had a positive impact on the pore development or formation. The higher impregnation ratios, the larger pore properties. As predicted, the enhancement in the pore properties of resulting carbon products by acid-washing was superior to those by water-washing and without post-washing. It could be ascribed to the leaching removal of residual H_3PO_4 and inherent minerals. The carbon product with a maximal BET surface area (69.132 m^2/g) can be produced at a lower temperature (600°C). More significantly, the resulting carbon product was a mesoporous and magnetic material, suggesting that it can be used as an efficient adsorbents or catalyst supports due to its simple recovery (or separation) if exhausted.

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