Article

Product Characteristics of Sludge Pyrolysis and Adsorption Performance of Metals by Char

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Abstract: The microwave heating system was used for sludge pyrolysis. The raw sludge and KOH-immersed sludge were pyrolyzed and their product characteristics were determined. The research results are advantageous to understand the influence of KOH activation on characteristics of pyrolysis products and the adsorption performance of metals in char. In the case of a high temperature and high KOH dose, most of the lost mass from sludge pyrolysis was converted into gaseous products instead of oil. The heat values of liquid oils were 40.86–41.39 MJ kg^{−1}, which has the potential for use as fuels. The use of a higher KOH dose for sludge pyrolysis is beneficial to the porosity development and generates a mesopore structure. The results from adsorption tests indicate that precipitation could be the dominant adsorption mechanism due to the binding between alkaline anion and carbonate and metal ions with a strong chemical affinity. The high KOH dose sludge adsorbent has a remarkable adsorption performance and can be used as adsorbent for the removal of the studied metals.

Keywords: sludge; potassium hydroxide (KOH); mesopore; precipitation

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1. Introduction

Waste disposal is an important issue in industrialized countries, especially in urban areas. Public concerns focus on the release of contaminants into the environment and ecological systems, which can pose serious risks to human health and the environment. Therefore, the development of reuse procedures is important work for the safe disposal of waste. Bio-sludge, which has a high organic content, is a product of wastewater treatment facilities. Waste sludge disposal can account for a high fraction of the operating costs of wastewater treatment plants (WWTPs) [1]. Due to its rapidly increasing amount and potential risks for the environment and human health, the sludge issue has raised significant public concerns. Reduce, recycle, and reuse are important concepts for sludge disposal [2].

Sludge from the biological treatment of wastewater can be considered a biomass resource due to its high organic content (lipids or fats, carbohydrates, and proteins) [3,4]. The organic fraction of sludge can be a source of oil and gas fuels for energy or for use in valuable chemical products after suitable treatment [5–8]. The thermochemical processes of sludge, such as pyrolysis, gasification, and combustion, have been reviewed in detail in terms of process enhancements and the recovery of energy and resources from sludge [9]. The pyrolysis technique for sludge disposal offers many advantages, including inhibiting heavy metal vaporization due to a decrease of the pyrolysis temperature, reducing the leaching of heavy metals from the pyrolysis carbonaceous residue [10], and offering

relatively low pollution control cost compared to combustion techniques [11,12]. Due to the high moisture content of the sludge, microwave systems may be used for drying and pyrolysis to improve the energy efficiency of the process.

Some biomass materials, such as evergreen oak, bamboo, and coconut shells, can be used as raw materials for activated carbon [13]. Biomass reuse should be considered for the sustainable preservation and protection of the environment. There are two activation methods for biomass materials to develop porous structures: (1) physical activation, such as steam or carbon dioxide, for gasification and carbonization to produce char; and (2) chemical activation with a chemical reagent, such as zinc chloride, phosphoric acid, or potassium hydroxide. Specifically, chemical activation has the obvious advantages of a shorter processing time, lower pyrolysis temperature, lower energy consumption, and larger specific surface area [14], so it may be suitable for the development of sludge-based adsorbents.

One drawback of ZnCl_2 activation, compared with alkaline and phosphoric acid activation, is that zinc is a heavy metal, which can pollute the environment. Catalysts KOH, KOH/AC, and KOH/CaO can conduct the trans-esterification reaction with sludge under alkaline conditions and produce high-quality stable bio-oil [15]. In addition, the alkaline catalysts react with the fatty acids of sludge, and reaction mixtures can be easily separated, thereby simplifying the operating conditions for recycling materials and reducing environmental pollution [16–18]. KOH activation can enhance various materials (such as tires [19], peel [20], and sludge [15,21]) to be adsorbents for the removal of pollutants from various media. For sludge-based adsorbents, KOH was regarded as an effective activation reagent, producing sludge adsorbents with a high specific surface area [22,23].

Heavy metals, such as cadmium, chromium, copper, lead, mercury, nickel, and zinc, are of concern because of their toxicity and longevity in the environment and their health effects on human [21,23]. Many studies have reported that sludge-derived adsorbents can be applied for the removal of heavy metals under various conditions [21]. Sludge-based adsorbents prepared by KOH activation showed the highest surface area with Brunauer–Emmett–Teller (BET) theory [24] and were used for the removal of Cu(II) and Pb(II) from liquid solutions [25]. The physicochemical characteristics (such as surface area, porosity, pH, surface charge, functional groups, and mineral contents) of biochar could affect its sorption capacity of metals [26]. For biochar, the removal mechanisms of heavy metals from aqueous solutions could be chemical interaction, physical sorption on surface sites, surface precipitation and complexation, and ion exchange (e.g., Na^+ , Ca^{2+} , and Mg^{2+}) [27–29]. In any case, the use of KOH as a sludge pyrolysis activator still requires careful evaluation in terms of the operating conditions and product characteristics, because this is related to the suitability and safety in the use of the derived oil and char.

In this work, microwave pyrolysis technology was employed to treat sludge from a petrochemical wastewater treatment plant. The raw sludge and KOH-immersed sludge were pyrolyzed and their mass fraction distributions of the products were determined. The characteristics of oil and char, and pore development in char were analyzed, for which the influence of KOH activation was also compared. The adsorption capacities of Cd(II), Pb(II), Zn(II), and Ni(II) on sludge-derived adsorbents were measured, and the possible adsorption mechanism was explored.

2. Experimental

2.1. Materials

Sludge samples were obtained from the wastewater treatment plant of a petrochemical industry in southern Taiwan. Sludge cake obtained from an activated sludge process after the mechanical dewatering process and the biosludge contains microorganisms. The moisture content was determined at $105 \pm 5^\circ\text{C}$ by ASTM D3173-02 [30] and the ash content was determined at $800 \pm 20^\circ\text{C}$ and followed the method ASTM D3174-02 [31]. Volatile matter was determined by using the method ASTM D3175-02 [32]. The fixed carbon is a calculated value. It is the resultant of the summation of percentage moisture,

ash, and volatile matter subtracted from 100. The raw sludge cakes contained 81 ± 4 wt.% water, 6.8 ± 0.5 wt.% ash, 11.6 ± 0.8 wt.% volatile matter, and 0.7 ± 0.06 wt.% fixed carbon. Before pyrolysis, the sludge was stored at 4 °C.

2.2. Sludge Microwave Pyrolysis

A multi-mode microwave oven was used for sludge drying and pyrolysis in a single process. The microwave oven can be operated with a maximum input power of 900 W at a frequency of 2450 MHz. First, 100 g of sludge sample were put into a quartz tube reactor (length 25 cm, inner diameter 5.5 cm, outer diameter 9 cm), outside of which was a quartz container, and placed in the microwave oven. During the period of sludge pyrolysis, N₂ gas was introduced and passed through the tube reactor at a rate of 200 mL/min to maintain an oxygen-free state. A rubber-silicon-ring and stainless-steel cap were selected to seal the tube reactor. A thermocouple (0–1000 °C) was installed in the reactor and connected to a temperature controller. The gas emitted during the experiment was cooled by an ice-water bath condenser, and the condensable vapor was collected by a liquid collector. The liquid oil was separated from the primary pyrolysis liquid product by distillation at 120 °C (20 °C min^{-1}) for 10 min to remove water. The oil was weighed to determine the yield of liquid oil. Microwave pyrolysis was conducted on three replicate samples for each pyrolysis temperature.

2.3. Sludge-Derived Adsorbent

The raw sludge was immersed and mixed with KOH at mass ratios (KOH:dried sludge, by weight) of 0.25:1 (low KOH dose) and 0.5:1 (high KOH dose). Before microwave pyrolysis, the mixture (added KOH in sludge) was heated in a separate oven at 80 °C for 4 h. With microwave heating, the sludge sample was heated to 135 °C and held for 3 min for dehydration. Then, it was continuously heated to the desired temperature and held for 30 min. The raw sludge and KOH-immersed sludge were pyrolyzed at 400, 500, and 600 °C for 30 min. The pyrolysis residues (char) were leached with 0.2 M HCl solution and then washed with distilled water to remove the KOH and impurities, until the rinsed water reached a pH of 6.8 ± 0.2 and the electrical conductivity was close to distilled water. After that, the washed char was dried in an oven at 105 °C for 48 h and weighed to determine the yield of solid product. The final adsorbent derived from pyrolysis char was transferred to a desiccator until use for the analysis and adsorption test.

2.4. Elemental Constituents

An element analyzer (Heraeus CHN-O Rapid Element analyzer, Heraeus Incorporated, Yardley, PA, USA) was employed to determine the major element contents, including carbon, hydrogen, and nitrogen, in the dried raw sludge and pyrolysis oil. Sulfur and chloride concentrations were measured with a Tacussel Coloumax 78 (USA) automatic coulometric titrator. The oxygen content of the dried raw sludge was calculated by subtracting the summation of N, H, C, S, and ash content from 100%. The oxygen content of the oil was calculated in the same way, but the ash content can be ignored. Sulfanilic acid and 1-chloro-2, 4-dinitrobenzene were selected as standards of the elemental analyzer.

X-ray fluorescence analysis was used to determine the content of trace elements in dry raw sludge and sludge-derived adsorbents. An instrument (SPECTRO model 300T Benchtop Multi-Channel analyzer) equipped with a titanium (Ti) target X-ray tube and a high-resolution detector (ASOMA Instruments Inc., Austin, TX, USA) was used. Samples were ground and sieved to ensure a uniform sludge particle size before analysis.

2.5. Organic Constituents of Liquid Oil

The organic constituents of liquid oil were detected using a gas chromatograph equipped with a DB-5 column (Agilent J&W) with 30 m length, 0.25 mm internal diameter, 0.25 µm film thickness, and a mass detector (GC-MS, model QP-2010; Shimadzu, Japan). The temperature program of the GC oven was set to increase at a rate of 5 °C min^{-1} from

60 (the initial time 10 min) to 325 °C. Helium was used as the carrier gas with a flow rate of 2 mL min^{−1}. For each peak, compounds were identified by comparing the mass spectra with those of the reference compounds available in the library. The relative contents of the liquid constituents were expressed as the percentage of area under the curve for each peak.

2.6. Pore Characteristics of Sludge-Derived Adsorbents

After pyrolysis, the sludge-derived adsorbents were analyzed to determine their physical characteristics, including the specific surface area, pore volume distribution, and pore diameter, using N₂ (gas) adsorption (in liquid N₂ condition at 77K) in an ASAP 2010 micropore analyzer. The BET method [24] and Barrett–Jovner–Halenda (BJH) method [33] were selected to determine the surface area and pore volume distribution, respectively. Silica-alumina, alumina, and molecular sieves were purchased from Micrometrics and used in quality assurance and quality control procedures to determine the pore characteristics of sludge-derived adsorbents.

2.7. Metal Adsorption

Cd(II), Pb(II), Ni(II), and Zn(II) were selected to evaluate the adsorption capacity of sludge-derived adsorbents. The Cd(II) stock solution was prepared by dissolving cadmium nitrate tetrahydrate (Cd(NO₃)₂·4H₂O) Merck KGaA, Darmstadt, Germany) in 2% nitric acid. Pb(II), Ni(II), and Zn(II) standard nitrate solutions (Merck KGaA, Darmstadt, Germany) were used as the stock solutions of lead, nickel, and zinc, respectively. An atomic absorption spectrometer (AA, Perkin Elmer model 3110) was employed to determine the metal content in the solution. The individual standard solution of the studied metal ions was prepared by dilution from stock solution (each of 1000 mg/L). The calibration curves (included 5 standard solutions with distinct concentrations) were established using the single standard solution of Cd(II), Pb(II), Ni(II), and Zn(II), respectively.

The adsorption of a single metal ion was conducted for the adsorption isotherm of each metal ion. A preliminary experiment showed that the adsorption of the four metal ions (200 mg L^{−1}; liquid: solid = 1 L: 0.2 g) on sludge-derived adsorbents reached equilibrium within 24 h. Therefore, the adsorption isotherms experiments were conducted with a duration time of 24 h. For each metal ion, the ion solutions were in the concentration range of 50–800 mg/L and the pH was regulated to 6.0 with diluted HCl and NaOH aqueous solution. Sludge-derived adsorbent particles (0.1 g) were put into a 50 mL metal solution under a 25 ± 1 °C water bath with a 100 rpm vibrator for 24 h. Then, the mixture was filtered through a 0.45 µm filter and the filtrate was collected. The ion concentration in the solution was determined, and the adsorption capacity of sludge-derived adsorbents was calculated by the difference between the initial and final equilibrium ion concentration.

2.8. Data Analysis

The Langmuir model was selected to describe the metal ion adsorption isotherms as the following equation:

$$q = q_m K C_e / (1 + K C_e) \quad (1)$$

where q (mg g^{−1}) is the adsorption capacity, q_m (mg g^{−1}) is the maximum adsorption capacity of the monolayer, K (L mg^{−1}) is the constant related to the affinity, and C_e (mg L^{−1}) is the ion concentration at equilibrium. The Langmuir model explains adsorption by assuming monolayer adsorption onto a surface with homogenous adsorption sites without ion interaction with each other. Equation (1) can be rewritten to linear form as follows:

$$1/q = (1/q_m K) 1/C_e + 1/q_m \quad (2)$$

According to Equation (2), the Langmuir model was applied to fit the experimental data (including all three replicate tests), and the statistical parameters (q_m and K) were estimated using the linear regression approach in an SPSS statistical package (version 19.0.0;

IBM Corp., Armonk, NY, USA). The optimum values of the parameters were selected with the least-square method.

One-way analysis of variance (ANOVA) was used to analyze results for pyrolysis temperatures and KOH doses associated with product data, element data, organic constituent data for oil, and pore characteristic data. Where appropriate, the *t*-test was used for pairwise comparisons of means. The ANOVA and *t*-test (version 19.0.0; IBM Corp., Armonk, NY, USA) were both performed at $\alpha = 0.05$.

3. Results and Discussion

3.1. Sludge Pyrolysis and Mass Distribution

As described in Section 2, the yields of both liquid oil and char (referred to as sludge-derived adsorbent) were determined, and then the yield of gas was calculated by the difference. As seen in all cases of Table 1, a higher pyrolysis temperature reduces the yield of char and increases the yields of both liquid oil and gas. With an increasing pyrolysis temperature from 500 to 600 °C, for the KOH-immersed sludge, the increment of gas yield (32–41 wt.%) is much higher than the increment of oil yield (13–14 wt.%).

Table 1. Major elemental composition in liquid oils and mass fraction of products after pyrolyzing raw sludge and KOH-immersed sludge at different temperatures.

KOH/Sludge Ratio	0			0.25			0.5		
Temperature °C	400	500	600	400	500	600	400	500	600
Mass fraction									
Char (wt.%)	69 ± 3.5	63 ± 2.9	59 ± 2.1	64 ± 3.8	60 ± 3.2	54 ± 3.4	62 ± 4.2	55 ± 3.5	45 ± 3.1
Liquid oil (wt.%)	16 ± 1.4	17 ± 1.3	20 ± 1.6	14 ± 1.2	16 ± 1.5	17 ± 1.3	8.0 ± 0.6	13 ± 1.1	14 ± 1.2
Gas (wt.%)	15 ± 1.2	20 ± 1.7	21 ± 1.8	22 ± 1.6	24 ± 2.2	29 ± 2.3	30 ± 2.3	32 ± 2.5	41 ± 3.4
Major element in oil									
N (wt.%)	2.1 ± 0.15	2.0 ± 0.12	1.7 ± 0.11	1.5 ± 0.09	1.4 ± 0.09	1.2 ± 0.08	2.1 ± 0.10	1.2 ± 0.06	1.1 ± 0.05
C (wt.%)	80.7 ± 4.26	81.6 ± 5.05	77.1 ± 4.45	73.7 ± 3.83	74.3 ± 4.11	70.4 ± 3.77	77.9 ± 3.18	74.1 ± 3.32	66.5 ± 3.47
S (wt.%)	3.8 ± 0.12	1.5 ± 0.10	1.3 ± 0.09	0.9 ± 0.07	0.8 ± 0.06	0.9 ± 0.06	0.7 ± 0.04	0.8 ± 0.05	0.8 ± 0.06
H (wt.%)	3.9 ± 0.18	4.5 ± 0.28	4.2 ± 0.24	3.8 ± 0.27	3.6 ± 0.25	4.3 ± 0.22	4.1 ± 0.23	3.4 ± 0.21	3.9 ± 0.26

Furthermore, the pyrolysis products from raw sludge were 15–21 wt.% in the gas phase, 16–20 wt.% in the liquid oil phase, and 69–59 wt.% in char at temperatures of 400–600 °C (shown in Table 1). The mass fractions of pyrolysis products were expressed on the dried raw sludge base. Due to the addition of KOH, the yields of both char and liquid oil were reduced, while the yield of gas was increased. Higher KOH doses resulted in the same tendency and the effect of KOH activation was more significant. The results suggest that the mass loss of KOH-immersed sludge tends to produce lighter molecules, under high-temperature pyrolysis conditions, without being condensed and collected as liquid oil. KOH immersion seems to improve the decomposition of large molecular intermediates and forms small molecules as reported by the literature [34]. Especially at high temperatures, most of the lost mass was converted into gaseous products instead of liquid oil.

3.2. Elemental and Organic Constituents of Liquid Oil

The major element contents of the dried raw sludge (105 ± 5 °C, overnight) were 32.8% carbon, 6.1% hydrogen, 2.6% nitrogen, and 3.9% sulphur. The chlorine content was less than 0.01 wt.%. At pyrolysis temperatures of 400–600 °C, the dominant element components in liquid oil from raw sludge were carbon (77–81 wt.%), hydrogen (3.9–4.5 wt.%), nitrogen (1.7–2.1 wt.%), and sulfur (1.3–3.8 wt.%) (shown in Table 1). The carbon, sulfur, and nitrogen contents decreased in liquid oil due to the addition of KOH. However, the hydrogen content in liquid oil was slightly affected by KOH.

For raw sludge pyrolysis at 400 °C, the dominant constituents of the oil were monoethyl toluene (C9) (6.9%), trimethyl benzene (C9) (5.7%), diethyl benzene (C10) (5.8%), mo-

noethyl xylene (C10) (5.5%), tetramethyl benzene (C10) (5.5%), 1+2+3-methylindene (C10) (7.6%), naphthalene (C10) (8.8%), 1-methylnaphthalene (C11) (8.8%), 2-methylnaphthalene (C11) (6.0%), and dimethyl naphthalene (C12) (11.5%) (shown as Table 2). Some cases of these compounds, such as diethyl benzene, tetramethyl benzene, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, and dimethyl naphthalene, significantly decreased in their contents at high temperatures (up to 600 °C). Most of the identifiable species were aromatics, which could come from the cracking of the raw material itself or formation by restructuring of organic compounds with the pyrolysis process. A previous study indicated that KOH first reacts with active oxygen-containing substances under the process of biomass pyrolysis, which can remove most of the oxygen-containing groups, thereby releasing a large amount of free radicals. A certain amount of KOH and free radicals can react with pyrolysis intermediates to promote deoxygenation and aromatization reactions (introducing high aromatic species in oil). These processes also release many gaseous products. In addition, certain free radicals can also be directly converted into gaseous products. These processes lead to a large reduction in bio-oil and a sharp increase in gaseous products [35]. As shown in Table 2, for the KOH-immersed sludge pyrolysis (KOH/sludge ratio: 0.5), monoethyl toluene, trimethyl benzene, and dicyclopentadiene (C10) cannot be detected at 400–600 °C. At temperature of 600 °C, diethyl benzene, monoethyl xylene, and tetramethyl benzene also disappear further. Different from the pyrolysis of raw sludge, some intermediate products are easily decomposed into gaseous substances due to the addition of KOH, and some major organic components cannot be found in the oil.

Table 2. Liquid oil constituents for raw sludge and KOH-immersed sludge after various pyrolytic temperatures.

Compounds	Formula	KOH/Sludge Ratio: 0			KOH/Sludge Ratio: 0.5		
		400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
Monoethyl toluene mixture	C ₉ H ₁₂	6.87 ± 0.27	4.11 ± 0.21	5.68 ± 0.17	*nd	*nd	*nd
Trimethylbenzene mixture	C ₉ H ₁₂	5.38 ± 0.27	4.63 ± 0.32	5.71 ± 0.29	*nd	*nd	*nd
Dicyclopentadiene	C ₁₀ H ₁₂	3.47 ± 0.10	1.47 ± 0.04	1.77 ± 0.07	*nd	*nd	*nd
Indene	C ₉ H ₈	2.45 ± 0.15	2.72 ± 0.11	3.36 ± 0.24	2.18 ± 0.17	3.05 ± 0.27	3.37 ± 0.34
Diethylbenzene mixture	C ₁₀ H ₁₄	5.77 ± 0.23	2.26 ± 0.14	2.47 ± 0.21	2.41 ± 0.14	3.24 ± 0.16	*nd
Monoethyl xylene mixture	C ₁₀ H ₁₄	5.45 ± 0.27	5.46 ± 0.27	5.01 ± 0.32	6.23 ± 0.56	10.17 ± 0.71	*nd
Pyrindan	C ₈ H ₉ N	*nd	*nd	*nd	*nd	*nd	3.26 ± 0.39
Indolene	C ₈ H ₉ N	*nd	*nd	*nd	*nd	*nd	2.29 ± 0.21
Tetramethyl benzene mixture	C ₁₀ H ₁₄	5.54 ± 0.33	3.75 ± 0.15	3.84 ± 0.31	4.44 ± 0.36	5.01 ± 0.32	*nd
1+2+3-Methylindene	C ₁₀ H ₁₀	7.64 ± 0.23	6.26 ± 0.38	7.37 ± 0.52	6.51 ± 0.33	8.21 ± 0.74	6.45 ± 0.45
Naphthalene	C ₁₀ H ₈	8.75 ± 0.35	6.23 ± 0.19	6.37 ± 0.33	6.42 ± 0.51	8.41 ± 0.34	12.40 ± 0.62
1-Methylnaphthalene	C ₁₁ H ₁₀	8.76 ± 0.53	5.54 ± 0.33	5.32 ± 0.21	9.95 ± 0.63	11.20 ± 0.22	5.39 ± 0.43
2-Methylnaphthalene	C ₁₁ H ₁₀	5.95 ± 0.30	4.20 ± 0.13	3.92 ± 0.24	7.37 ± 0.52	7.82 ± 0.63	9.26 ± 1.02
4-Phenylbutyronitrile	C ₁₀ H ₁₁ N	*nd	*nd	*nd	*nd	*nd	3.19 ± 0.29
Biphenyl	C ₁₂ H ₁₀	1.74 ± 0.07	1.81 ± 0.07	1.66 ± 0.13	1.91 ± 0.17	1.93 ± 0.13	3.48 ± 0.21
1+2-Ethyl naphthalene	C ₁₂ H ₁₂	*nd	*nd	*nd	3.52 ± 0.32	3.02 ± 0.12	1.28 ± 0.12
Dimethylnaphthalene mixture	C ₁₂ H ₁₂	11.53 ± 0.69	10.24 ± 0.51	7.74 ± 0.23	10.11 ± 0.71	10.56 ± 0.95	3.05 ± 0.15
Biphenylene	C ₁₂ H ₈	*nd	*nd	*nd	2.37 ± 0.12	2.30 ± 0.25	*nd
2+3+4-Phenyltoluene	C ₁₃ H ₁₂	2.81 ± 0.20	2.95 ± 0.15	2.53 ± 0.18	4.16 ± 0.33	3.74 ± 0.37	5.32 ± 0.21
Trimethylnaphthalene mixture	C ₁₃ H ₁₄	1.78 ± 0.05	2.77 ± 0.19	1.89 ± 0.08	0.94 ± 0.07	0.73 ± 0.04	*nd
1,3-Diphenylpropane	C ₁₅ H ₁₆	*nd	*nd	*nd	*nd	*nd	10.85 ± 0.87
Phenanthrene	C ₁₄ H ₁₀	1.11 ± 0.06	2.24 ± 0.09	1.97 ± 0.16	3.74 ± 0.34	3.37 ± 0.27	0.93 ± 0.07
Sum (%)		84.90 ± 4.25	66.64 ± 4.66	66.61 ± 3.83	72.26 ± 6.48	82.76 ± 7.97	70.88 ± 6.74

*nd: not detectable.

In addition, some species (e.g., monoethyl xylene, 1-methylnaphthalene, and 2-methylnaphthalene) increase in their contents significantly due to the addition of KOH, at 400–500 °C. As mentioned previously, the addition of KOH causes a large number of free radicals (e.g., O-CH₃, H, OH, etc.) to be generated, which suggests that some radicals could react to the primary oil compositions with aromatic substitution and consequently increase the production of some species in oil. Higher temperature (600 °C) could more significantly enhance the reactions between free radicals and oil compositions, leading

to a decrease of certain species, and meanwhile an increase of other species. As a result, a high content of 1,3-diphenylpropane (C15) (10.8%) can be found only at 600 °C under pyrolysis of KOH-immersed sludge (shown in Table 2). However, the influence of KOH on the pyrolysis chemical reactions is very complicated, and the effects from the distinct raw material, temperature, and heating method still need to be further studied.

3.3. Potential Use for Pyrolysis Char

The higher heating values of raw sludge, pyrolysis char, and oil were determined by a bomb calorimeter (IKA C-200). The heat value of dried sludge was about 15.68 MJ kg^{−1}. The heat values of liquid oils were 40.86–41.39 MJ kg^{−1} after raw sludge pyrolysis at 400–600 °C (shown as Table 3), which was close to the values obtained with water emulsion diesel fuel [36,37]. For KOH-immersed sludge, the liquid oil has a lower heat value (30.01–39.38 MJ kg^{−1}), and more KOH addition results in a significant decrease in the heat value. The char's heat values was also determined to assess the energy recovery. As seen in Table 3, more KOH addition and a high pyrolysis temperature resulted in a significant decrease in energy recoveries. Especially at 600 °C, the energy recovery of char was low at 27% in the case of high KOH dose. As a result, this type of char may not be suitable for energy recycling, and it is better to develop other valuable material, such as adsorbent. In a previous study [38], a similar microwave heating system was also applied to sludge pyrolysis. The results indicated that a high temperature increases the energy consumption in microwave power and reduces the produced energy from pyrolysis residue (char) and oil. Therefore, lower energy consumption and higher energy recovery efficiency could be achieved at a lower pyrolysis temperature.

Table 3. Heat values and energy recoveries for liquid oil and char of raw sludge and KOH-immersed sludge after various pyrolytic temperatures.

KOH/Sludge Ratio	Temperature (°C)	Heat Value (MJ kg ^{−1})		Energy Content (MJ kg-drb ^{−1} *)		Energy Recovery (%)	
		Oil	Char	Oil	Char	Oil+Char	Char
0	400	41.39 ± 2.48	12.15 ± 1.34	6.62 ± 0.86	8.38 ± 0.75	95 ± 7.6	53 ± 7.4
	500	40.93 ± 3.27	11.58 ± 1.39	6.96 ± 0.57	7.29 ± 1.02	90 ± 4.5	46 ± 5.1
	600	40.86 ± 2.04	11.07 ± 0.77	8.17 ± 0.98	6.64 ± 0.53	94 ± 8.5	42 ± 3.8
0.25	400	39.38 ± 4.33	11.93 ± 0.72	5.51 ± 0.72	7.63 ± 0.96	84 ± 10.1	49 ± 2.9
	500	36.05 ± 1.85	11.03 ± 1.43	5.76 ± 0.63	6.62 ± 0.73	79 ± 4.7	42 ± 5.2
	600	30.03 ± 2.14	10.63 ± 0.53	5.12 ± 0.36	5.74 ± 0.52	69 ± 7.6	37 ± 3.3
0.5	400	37.32 ± 4.48	10.83 ± 1.32	2.98 ± 0.33	6.71 ± 1.02	62 ± 5.6	43 ± 5.6
	500	34.05 ± 3.06	9.93 ± 0.89	4.43 ± 0.42	5.46 ± 0.65	66 ± 7.3	35 ± 4.9
	600	30.01 ± 3.88	9.43 ± 0.67	4.02 ± 0.48	4.24 ± 0.63	53 ± 6.4	27 ± 2.4

The heat value multiplied by yield to obtain energy content on a dried raw sludge base (drb*); the energy content was divided by 15.68 MJ kg^{−1} (heat value of dried raw sludge) to obtain the recovery %.

3.4. Characteristics of Sludge-Derived Adsorbents

Ca was the predominant trace element with several percent in dried raw sludge. All of the trace elements have a slightly higher content in char (data not shown) as compared to dried raw sludge. If the content was expressed on the dried raw sludge base (mg kg-drb^{−1}), it was found that a small amount of trace elements would be lost during the pyrolysis process. The washing process is an important step in the preparation of adsorbents through chemical activation [39]. When the activation temperature is lower than the boiling point of the activator, the char should be washed to release the compounds remaining in the carbon network to improve the porous structure. In addition, some inorganic residues and elemental metals need to be removed. After high acid washing, the contents of seven hazardous elements in sludge adsorbent and high KOH dose sludge adsorbent (KOH/sludge ratio: 0.5) were much lower as compared to dried raw sludge (as shown in

Table 4). The contents of Ni and Zn were relatively high, and the content of Zn was much higher than other hazardous elements. However, the content of hazardous elements was slightly changed with increasing pyrolysis temperature.

Table 4. Trace element contents (mg kg⁻¹) in dried raw sludge and sludge-derived adsorbents.

KOH/Sludge Ratio	Temperature (°C)	Ni	Cu	Zn	As	Cd	Cr	Pb
	Dried Raw Sludge	616.7 ± 45.9	124.3 ± 6.1	2859.4 ± 217.9	16.6 ± 2.2	15.5 ± 1.9	168.2 ± 21.2	174.8 ± 7.2
0 (acid washing)								
	400 °C	357.9 ± 27.4	86.3 ± 10.2	1148.9 ± 60.3	12.4 ± 0.8	8.2 ± 0.4	122.2 ± 7.2	135.7 ± 7.4
	500 °C	393.7 ± 23.5	93.2 ± 3.9	1202.6 ± 78.5	13.3 ± 0.9	8.8 ± 0.8	131.5 ± 9.5	139.2 ± 10.2
	600 °C	388.5 ± 27.6	99.8 ± 12.2	1280.3 ± 116.4	14.5 ± 1.2	9.1 ± 0.7	138.6 ± 17.7	144.6 ± 16.3
0.5 (acid washing)								
	400 °C	263.4 ± 33.5	93.4 ± 5.7	923.2 ± 104.7	13.7 ± 0.7	9.3 ± 1.1	115.1 ± 13.1	123.5 ± 15.7
	500 °C	302.5 ± 24.8	102.7 ± 6.4	939.6 ± 101.8	14.5 ± 1.1	9.7 ± 1.3	119.4 ± 8.6	128.7 ± 7.4
	600 °C	311.7 ± 14.3	110.5 ± 8.1	1006.5 ± 84.3	15.5 ± 1.3	10.3 ± 0.8	123.7 ± 15.3	133.4 ± 5.8

As shown in a previous study [40], the heavy metals in sludge and char samples were sequentially extracted, and the fractions of heavy metals can be divided into four groups. F1 and F2 are soluble in water and weak acid and easily leach out. F3 is merely released under high acid and oxidized conditions. F4 is a fixed fraction and is difficult to leach out. The authors also indicated that some amounts of F4 of Ni, Zn, Cr, and Mn were further converted into F3 due to the addition of KOH. Meanwhile, Cd was transformed a large part of F3 to F4 [40]. In this work, high acid was used in the washing of adsorbents, thus the elements of F1, F2, and F3 could be released. The contents of the seven elements in the sludge adsorbents decreased by about 22–60% as compared to dried raw sludge (as shown in Table 4). This loss could include exchangeable and carbonate-associated fractions (F1), oxides fraction (F2), and organics-associated fraction (F3), which was leached out by using strong acid. As compared to sludge adsorbents, the contents of Ni, Zn, Cr, and Pb in high KOH dose sludge adsorbents still decreased by about 8–26%, which showed that F3 could increase and can be released under high acid conditions. In contrary, the contents of Cu, As, and Cd in high KOH dose adsorbents increased by about 7–13% as compared to sludge adsorbents. This could be due to an increase in the fixed fraction (F4) of Cu, As, and Cd.

Table 5 shows the pore characteristics of the specific surface area, total pore volume (TPV), and micropore volume (MV) of the adsorbents. The results indicate that the sludge adsorbents have few micropores, with a low contribution to the total pore volume. When the pyrolytic temperature was higher than 400 °C, the total pore volume increased at temperatures up to 600 °C, although the micropore (pore diameter (PD) < 20 Å) volume decreased (seen in Table 5). This suggests that the increase of the total pore volume resulted from the increase in mesopores (20–500 Å). As a result, the specific surface area of the sludge adsorbents increased with an increase in the temperature, with the BET surface areas close to 25 m² g⁻¹ at 600 °C. The activated effect was not significant with the addition of low dose KOH. The low KOH dose sludge adsorbents have similar specific surface areas and total pore volume as compared with the sludge adsorbents. With the KOH dose increase, pore development resulted in an increase in the specific surface area. For the high KOH dose sludge adsorbents, the BET surface area increased 6.3–7.5 times, and the total pore volume increased 3.2–4.2 times compared with the sludge adsorbents at 400–600 °C. As described in previous studies, the KOH activation of materials high in carbon (such as sludge) could result in the formation of K₂CO₃ and K₂O and subsequently carbonaceous materials were etched by KOH, K₂CO₃, and K₂O. At high temperatures, K₂CO₃ was reduced by carbons to form K₂O, CO, and CO₂, and K₂O could be further reduced by carbons to form vapor of metallic K atoms (>762 °C). Meanwhile, the gaseous products caused by gasification were emitted so that more pores were formed. Additionally,

K atoms intercalated into the internal structure of carbonaceous materials, leading to an increase in the surface areas [23,41].

Table 5. Pore characteristics of dried raw sludge and KOH-immersed sludge after various pyrolytic temperatures.

KOH/Sludge Ratio	Temperature °C	BET Surface Area (m ² g ^{−1})	TPV (cm ³ g ^{−1}) × 10 ²	MV (cm ³ g ^{−1}) × 10 ³	PD (Å)
0	400	8.43 ± 0.75	5.36 ± 0.21	1.67 ± 0.05	254.14 ± 14.63
	500	16.12 ± 0.58	9.75 ± 0.83	1.02 ± 0.04	241.82 ± 17.09
	600	25.11 ± 1.49	10.89 ± 0.61	0.56 ± 0.05	173.52 ± 9.27
0.25	400	11.22 ± 0.56	7.68 ± 0.73	0.10 ± 0.01	273.83 ± 25.17
	500	12.89 ± 0.94	8.19 ± 0.37	0.14 ± 0.01	254.46 ± 22.89
	600	22.29 ± 1.52	12.21 ± 0.53	0.20 ± 0.01	219.16 ± 10.95
0.5	400	63.42 ± 2.78	22.62 ± 0.97	1.18 ± 0.08	142.65 ± 5.35
	500	101.26 ± 4.42	31.09 ± 2.10	1.52 ± 0.07	122.83 ± 6.63
	600	174.71 ± 10.29	39.27 ± 2.21	2.05 ± 0.09	89.91 ± 7.19

Due to the pore creation and new pore formation under the activation process, the average pore diameter decreased with an increase in the KOH dose. Compared with sludge adsorbents, the high KOH dose sludge adsorbent had a higher total pore volume and higher micropore volume at 400–600 °C (shown as Table 5 and Figure 1). However, the increment of the total pore volume was several hundred times larger than the increment of the micropore volume. This also suggests that the high KOH dose sludge adsorbent significantly increases the volume of mesopores but slightly increases the volume of micropores. As a result, for the high KOH dose sludge adsorbents, the BET surface area and total pore volume were 174.7 m² g^{−1} and 0.39 cm³ g^{−1} at 600 °C, respectively (seen in Table 5). The temperature range of this study is 400–600 °C (<762 °C), thus decreasing the reduction of K₂CO₃ and K₂O in carbonaceous materials and the penetration of potassium metal into the internal structure of the carbon lattice. It is reasonable to infer that at a temperature higher than 762 °C, the development of pores may tend to increase the micropore volume and expand the specific surface area.

Figure 1. Cont.

Figure 1. Pore size distribution of sludge adsorbent and KOH-immersed sludge adsorbent. (a) Sludge adsorbent; (b) Low KOH dose sludge adsorbent; (c) High KOH dose sludge adsorbent.

3.5. Metal Adsorption Capacity

The adsorbents derived at 600 °C have high surface area and pore volume, which is suitable for evaluating the removal effect of heavy metals in water. The Cd(II), Pb(II), Ni(II), and Zn(II) adsorption isotherms were investigated at different initial metal concentrations ranging from 50 to 800 mg L⁻¹ (shown in Figure 2). The fitting parameters and coefficients of determination (r^2) for Cd(II), Pb(II), Ni(II), and Zn(II) onto distinct adsorbents obtained from the Langmuir model are shown in Table 6. The coefficients of determination indicate that the Langmuir model is suitable for description of the adsorption isotherms, with r^2 from 0.956 to 0.997. The experimental values are in good agreement with the calculated

values as shown in Figure 2. The adsorption isotherms of metal ions on the high KOH dose sludge adsorbent showed a sharp increase in adsorption capacity, leading to most of the metal ions' removal at low equilibrium concentrations (Figure 2c). When the equilibrium concentrations of metal ions exceed 100 mg L^{-1} , almost no additional metal ions are removed. This phenomenon suggested that precipitation was the dominant adsorption mechanism due to the release of alkaline anion, such as carbonate, that could precipitate metal ions with strong chemical affinity [42].

Figure 2. Cont.

Figure 2. Metal adsorption isotherms of sludge adsorbent and KOH-immersed sludge adsorbent. The experimental and calculated values were plotted as points and lines, respectively. The Langmuir parameters were estimated with the linear regression method by using Equation (2) and the q_e was calculated from Equation (1). (a) Sludge adsorbent; (b) Low KOH dose sludge adsorbent; (c) High KOH dose sludge adsorbent.

Table 6. Parameters of metal ions adsorption isotherms fitted with the Langmuir model for the adsorbents at pyrolytic temperatures of 600 °C.

KOH/Sludge Ratio	Metal Solution	K (L mmol ⁻¹)	q_m (mmol g ⁻¹)	r^2
0	Cd(II)	0.607	0.395	0.969
	Pb(II)	1.580	0.309	0.964
	Ni(II)	0.353	0.673	0.975
	Zn(II)	0.362	0.478	0.973
0.25	Cd(II)	0.704	0.423	0.967
	Pb(II)	1.668	0.367	0.956
	Ni(II)	0.449	0.772	0.988
	Zn(II)	0.430	0.514	0.983
0.5	Cd(II)	4.439	1.774	0.982
	Pb(II)	4.307	1.068	0.985
	Ni(II)	8.473	3.962	0.995
	Zn(II)	6.128	3.472	0.997

As mentioned earlier, the raw sludge in this study contains several percentages of calcium. After acid washing, the three test adsorbents contained about 1.6–2.9% of calcium, thus calcium carbonate may be a source of carbonate in the adsorbents. The potassium was about 0.3–1.2% for the two KOH activation adsorbents. A low KOH dose causes a lower activation effect and less K_2CO_3 and K_2O in char, and poor development of porosity. When compared to raw sludge adsorbent, the adsorption capacities of KOH-immersed sludge adsorbents increased for each ion, but no significant change was found for the case of the low KOH dose. In other words, besides precipitation, there should be another important

adsorption mechanism for the raw sludge adsorbent and low KOH dose sludge adsorbent. The adsorption isotherm of metal ions on the sludge adsorbent showed that the adsorption capacity increased slowly with the increase of the equilibrium concentration, and a small amount of metal ions were continuously removed at a higher equilibrium concentration (Figure 2a). This phenomenon could be explained by the presence of adsorption with weaker affinity, such as the exchange between H^+ and metal ions through deprotonating on aromatic [43] and carboxylic groups. The initial pH of the solution added with the sludge adsorbent was about 6.0. As part of the metal ions used at low concentration were consumed by the alkaline anions, the H^+ exchange capacity was reduced, so the equilibrium pH slightly dropped to 5.8. At the high concentration, the relatively high H^+ release caused the equilibrium pH to drop to 5.5. Although a similar pH drop can also be found when using a low KOH dose sludge adsorbent, this drop is not sufficient to explain the difference in the adsorption capacity between the sludge and the low KOH dose sludge adsorbent (Figure 2a,b). Therefore, for the low KOH dose sludge, the exchange of metal ions with Ca^{+2} and K^{+1} on the carbon material surface may be more important. In addition, when using high KOH dose sludge adsorbent, it was found that low-concentration solutions caused an increase in equilibrium pH (about 6.8), while high-concentration solutions slightly decreased (about 5.6). This is consistent with previous observations that at low concentration, almost all metal ions are precipitated, and excess alkaline anions cause the pH to rise. At a high concentration, metal ions can consume all available alkaline anions in the solution, so additional ion exchange occurs (H^+ release), which leads to a slight drop in pH. The results also indicated that a high KOH dose significantly enhanced pore development during the pyrolysis process and consequently increased the metal adsorption. The high KOH dose sludge adsorbent was mesoporous carbon material, which avoided the adsorption sites from being shielded or the pore channel blocked to a certain extent, and promoted the adsorption capacity.

The parameter K is related to the affinity of the adsorption sites to the metal ion. Among the studied adsorbents, the high KOH dose significantly improved the affinity of the adsorbent, and the highest K values can be found for the high KOH dose sludge adsorbent to each metal ion (seen in Table 6). For the low KOH dose sludge adsorbent, the q_m increased slightly as compared with the sludge adsorbent. For high KOH dose sludge adsorbent, the q_m increased to 3.5–7.3 times the sludge adsorbent for different metal ions (221.33 mgg^{-1} for Pb(II), 199.45 mgg^{-1} Cd(II), 227.04 mgg^{-1} Zn(II), and 232.53 mgg^{-1} Ni(II)). The unit of maximum adsorption capacities (q_m) was converted to $mmolg^{-1}$, which allowed a comparison of the adsorptive sites of the distinct adsorbents to a single ion. The q_m of sludge adsorbents was 0.309 $mmolg^{-1}$ for Pb(II), 0.395 $mmolg^{-1}$ Cd(II), 0.478 $mmolg^{-1}$ Zn(II), and 0.673 $mmolg^{-1}$ Ni(II) (shown in Table 6). The high KOH dose sludge adsorbent has the highest q_m values for an individual metal ion, which differs with the following order: Ni(II) (3.962 $mmolg^{-1}$) > Zn(II) (3.472 $mmolg^{-1}$) > Cd(II) (1.774 $mmolg^{-1}$) > Pb(II) (1.068 $mmolg^{-1}$). A previous study reported that the adsorption increased as the ionic radius decreased [44]. In this work, the ionic radius of the metals varied in the following order: Ni(II) < Zn(II) < Cd(II) < Pb(II), and the q_m was in the order: Ni(II) > Zn(II) > Cd(II) > Pb(II). This result agrees with the previous research report. However, the detailed reasons for this phenomenon are not clear and need to be further studied. Direct comparisons with other published results are not appropriate due to changes in parameters and experimental conditions. The adsorption capacities of the biochar produced from *Sida hermaphrodita* were respectively 48.08 and 35.71 mgg^{-1} for Zn(II) and Cd(II) [45]. The adsorption capacity was 53.6 mgg^{-1} of Pb(II) on hickory wood biochar using alkali modification [46]. However, compared to the above-mentioned biochar, the high KOH dose sludge adsorbent (pyrolyzed at 600 °C) has a higher adsorption capacity.

4. Conclusions

The microwave heating system used for sludge pyrolysis can integrate dehydration and carbonization steps, which simplify the operating procedures and are cost-effective. With pyrolysis by KOH activation, under a high temperature and high KOH dose, most of the lost mass from sludge was transformed into gaseous products instead of liquid oil. The heat values of liquid oils were 40.86–41.39 MJ kg^{−1}, which suggests their potential for use as fuels after distillation. The energy recovery of char was low at 27% in the case of sludge pyrolysis with a high KOH dose. This type of char may not be suitable for energy recycling, and it is more suited for development to be an adsorbent. The pyrolysis of sludge by KOH activation is beneficial to the porosity development and generates a mesopore structure. A high KOH dose could be necessary to enhance the development of the pore structure. The adsorption mechanism of the adsorbent tested in this study may mainly include precipitation and two types of ion exchange (referred to as replacement of H⁺, and replacement of Ca⁺² and K⁺). However, for the studied adsorbents, the precipitation could be the dominant adsorption mechanism due to the binding between alkaline anions, such as carbonate, and metal ions with strong chemical affinity. The high KOH dose sludge adsorbent has remarkable adsorption performance and can be used as adsorbents for the removal of the studied metals.

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