

Article



# Chlorine Gas Removal by H<sub>2</sub> Treated Red Mud for the Potential Application in Waste Plastic Pyrolysis Process

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**Abstract:** In the process of pyrolyzing waste plastics, the generation of Cl<sub>2</sub> gas can pose a problem. During the pyrolysis processing, incomplete combustion of organic compounds containing chlorine can lead to the formation of toxic chemicals, which can cause issues in subsequent processing stages. Therefore, an adsorbent plays an important role in removing Cl<sub>2</sub> in the dechlorination process, and alkaline adsorbents and metal oxides are generally used. Waste red mud is composed of Fe metal oxide and alkaline components, so it is intended to be used as a Cl<sub>2</sub> adsorbent. The Cl<sub>2</sub> removal ability of red mud with different redox status of iron oxides was assessed. Hydrogen treatment was performed at various temperatures to control the reduction potential of the Fe in the metal oxides, and phase changes in the Fe oxide component of red mud were confirmed. In the case of red mud hydrogenated at 700 °C, most of the Fe<sub>2</sub>O<sub>3</sub> structure could be converted to the Fe<sub>3</sub>O<sub>4</sub> structure. As a result, red mud at an H<sub>2</sub> treatment temperature of 700 °C showed about three times higher Cl<sub>2</sub> adsorption compared to red mud without H<sub>2</sub> treatment.

Keywords: red mud; H2-treatment; dechlorination; waste plastic; pyrolysis

## 1. Introduction

In 2020, 367 million tons of plastic were produced worldwide, and demand for use is expected to quadruple by 2050 due to its lightweight, affordability, and versatility [1–4]. According to European Plastics, most of the plastics in 2020 were used for packaging (40.5%), which generally has a short life span and rapidly enters the waste stream. These are mainly used in various forms of polyethylene (Low Density Polyethylene; LDPE and High Density Polyethylene; HDPE), Polypropylene (PP), Polystyrene (PS), Polyvinyl Chloride (PVC), and Polyethylene Terephthalate (PET). The main components of these plastics were PP (19.7%), LDPE (17.4%), HDPE (12.9%), PVC (9.6%) PET (8.4%), and Polyurethane (PUR) (7.8%). Plastics have been used in large quantities since 1950, and the current global plastic waste is estimated at 6.3 billion tons, of which 79% accumulates in landfills and the environment, causing environmental pollution and resource waste [5,6]. Landfill or incineration to dispose of waste plastic affects air, water, and soil due to the release of chlorine and dioxin. To alleviate these problems, many countries are trying to recycle waste plastic in various ways.

Common recycling methods include mechanical recycling, thermal recycling, and chemical recycling [7,8]. Mechanical recycling involves physical processes like washing, shredding, melting, and blending to recycle plastics into solid fuels or fibers. While it's

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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/license s/by/4.0/). widely used, accounting for over 90% of recycling, it has economic drawbacks and limitations due to contamination and degradation of material properties [9,10]. Thermal recycling leverages the heat generated from incinerating waste plastics, but the harmful emissions contribute to environmental pollution. Chemical recycling, on the other hand, involves breaking down plastics through chemical processes to revert them back to their raw or polymer forms. Pyrolysis oil produced from high-temperature decomposition of waste plastics is a prime example of chemical recycling [11,12]. It is seen as a key recycling method for its ability to recycle plastics without quality or functionality loss, and for its ability to handle a variety of plastics, reducing recycling costs and increasing the volume of recyclable materials. Among waste plastic recycling methods, the waste plastic treatment process using pyrolysis can reduce CO<sub>2</sub> emitted from the process compared to other recycling methods [13].

The liquid produced by the thermal decomposition of waste plastic represents a complex mixture of various types of aromatic compounds, alkanes, and alkenes [14–16]. However, waste plastic, which is the feedstock for the pyrolysis oil process, also contains PVC, so the pyrolysis oil produced in the process contains both inorganic and organic chlorinated compounds. Challenges in the industrial application of pyrolysis oil include its high chlorine content and waxy, semi-solid characteristics, necessitating complex physicochemical treatments. PVC releases various chemicals during the pyrolysis process, one of which is chlorine gas. When PVC is heated at high temperatures during the thermal decomposition process, the chlorine present in PVC can form chlorine gas Cl<sub>2</sub> through various chemical reactions, a highly toxic and corrosive oxidizer that needs to be removed [17–20]. Therefore, Cl must be treated in the waste plastic pyrolysis process.

Typically, it has been reported that chlorine is adsorbed by using alkaline adsorbents and metal oxides, which immobilize chlorine in the form of metal chlorides. These include substances such as CaO, Ca(OH)<sup>2</sup>, CaCO<sup>3</sup>, and Fe<sub>3</sub>O<sub>4</sub> [21–24]. These materials effectively capture chlorine, preventing it from being released into the environment. Red mud, an industrial waste generated during aluminum production, poses significant environmental and disposal challenges. Millions of tons of red mud are produced globally each year, with most being landfilled due to a lack of proper disposal methods. In South Korea, KC Co., Ltd. (Seoul, Republic of Korea) produces over 300,000 tons annually [25]. Red mud consists of various metal ions and inorganic contents such as Fe, Al, Na, Ca, Ti, and Si. It has a high surface it suitable adsorption properties, making it a potential candidate for use in adsorbents, ion-exchangers, catalysts, and cement materials [26]. Red mud as an adsorbent can offer both environmental and economic benefits. However, its actual application in commercial settings is limited, necessitating further research in utilizing various industrial by-products for the removal of atmospheric and water pollutants.

Many Studies have been conducted to remove Cl components generated from waste plastic pyrolysis oil using Fe-based adsorbents, and have been found to have an excellent effect on Cl removal [27,28]. Red mud, which is discarded as a waste resource every year, mainly consists of Fe, so it can be used to remove Cl generated from waste plastic pyrolysis oil, and we aim to use it more effectively. Red mud is suitable to be used as an adsorbent, but there is little research on Cl<sub>2</sub> gas adsorption performance depending on the reduction state of red mud. In this study, we examine the use of red mud as an adsorbent for Cl2 gas from the pyrolysis of waste plastics. For the utilization of red mud as a Cl<sub>2</sub> adsorbent, it was subjected to hydrogen treatment at various temperatures. It was designed to alter the degree of reduction in iron oxide within the red mud based on the temperature of the hydrogen treatment. Additionally, this study compared the Cl<sub>2</sub> adsorption capacity of the red mud adsorbents used. Most papers compare the Cl content in pyrolysis oil and do not compare the adsorption capacity of the adsorbent used, so the adsorption capacity is checked to suggest the optimal amount of adsorbent used. We examined the Cl<sub>2</sub> adsorption performance in relation to the different reduction states of iron oxide in red mud. The H2-treated red mud was analyzed using X-ray Diffraction (XRD), Brunauer-EmmettTeller method (BET) analysis, scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS), and X-ray Fluorescence (XRF).

### 2. Materials and Methods

## 2.1. Material Synthesis

Figure 1 shows the process of extrusion molding red mud to fabricate adsorbent. The basis for each adsorbent sample is 10 g. Distilled water is added to the red mud for physical mixing to create a slurry. The adsorbent is then formed into a 0.1 mm diameter using an extrusion technique via a syringe. The calcined adsorbent is cut into 5 mm particle sizes, resembling pellets, to complete the RM adsorbent. The adsorbent is calcined at 550 °C for 5 h in an air atmosphere, with a heating rate of 10 °C/min. The H<sub>2</sub>-treatment step is carried out at a rate of 5 °C/min to temperatures of 400 °C, 550 °C, and 700 °C for 2 h under a flow of 100 mL/min (H<sub>2</sub> 10 vol%, N<sub>2</sub> balanced). The samples are named RM\_X, where X denotes the temperature of the H<sub>2</sub>-treatment.



Figure 1. The schematic diagram of extrusion molding red mud samples.

#### 2.2. Material Characterization

X-ray Fluorescence (XRF, SHIMADZU, XRF-1700, Kyoto, Japan) was conducted for basic component analysis of red mud. N<sub>2</sub> adsorption-desorption at –196 °C experiments were performed using a Micromeritics ASAP 2020 apparatus (Norcross, GA, USA) prior to the adsorption measurements, the samples were purged at 300 °C for 5 h to measure textural properties such as specific surface area, pore volume, and average pore size. The average pore size was determined using the Barrett–Joyner–Halenda (BJH) method. The crystal structure of red mud was analyzed using a Cu K $\alpha$  radiation source ( $\lambda$  = 1.5406 Å) in a Phillips X'PERT X-ray diffractometer (XRD) at the Korea Basic Institute in Daegu. The morphology and crystalline phase of red mud, as well as Cl-adsorbed on the surface, were examined using Field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4800, Tokyo, Japan) with EDS (Oxford Instruments, Oxford, UK). H<sub>2</sub>-TPR analysis was performed to confirm the reduction characteristics of RM. RM samples (~17 mg) were heated in an alumina crucible from 30 °C to 900 °C at a rate of 10 °C/min. A total of 10% H<sub>2</sub> was used as a carrier gas at a flow rate of 30 mL/min.

## 2.3. Cl<sub>2</sub> Adsorption Test

In this study, a fixed-bed reactor was used for the Cl<sub>2</sub> adsorption experiments. A schematic of the apparatus is shown in Figure 2. The reactor utilized a 1/2-inch diameter quartz tube, and the temperature inside the reactor was controlled using a Proportional–integral– derivative (PID) controller and a Chromel–Alumel thermocouple sensor. The reactor was placed in an electric furnace at atmospheric pressure. The Cl<sub>2</sub> adsorption reaction was conducted at a furnace temperature of 350 °C until the breakthrough point, using a gas flow of 100 mL/min (Cl<sub>2</sub> 100 ppm and N<sub>2</sub> balance). The flow was regulated using a Mass Flow Controller (MFC, Brooks, AB, Canada, 5859E). All experiments used 0.3 g of red mud adsorbent, and ceramic wool was used to fix the catalyst layer within the reactor. During the experiments, any Cl<sub>2</sub> gas that passed through the sorbent was dissolved in 500 mL of distilled water. The amount of Cl<sub>2</sub> dissolved in distilled water was measured to compare the Cl<sub>2</sub> adsorption performance of the adsorbents. Ion Chromatography (IC) is a type of liquid chromatography that separates ionizable samples dissolved in water using an ion exchange column. However, IC is costly due to its inability for real-time measurement and the need for manual sample collection with a per-sample analysis fee. To overcome these drawbacks, an ion sensor (AT-500) was used for real-time measurement of Cl content in the solution. This was five times cheaper than IC equipment, allowing for more economical experiments. The outlet gases from the reactor were analyzed automatically every 1 min using an ion sensor equipped with an autosampler. Figure S1 presents the results of a blank experiment conducted to verify the correlation between the Ion Chromatograph analysis and the real-time measurement device.

As a result of the chromatographic analysis and the calibration curve of the real-time device, the same Cl ion concentration was detected.

The dechlorination efficiency at each time interval of inlet gas is given by Equation (1)

Dechlorination efficiency (%) = 
$$1 - \frac{M_{Cl,t}}{M_{Cl,blank}} \times 100$$
 (1)

where  $M_{Cl,t}$  is the total molar amount of chlorine in the outlet gas and  $M_{Cl,blank}$  is the total molar amount of chlorine in the blank experiment



Figure 2. The schematic diagram of experimental apparatus.

# 3. Results

## 3.1. Screening of Iron Oxide Phases for Dechlorination Capacity

The dechlorination capacity was conducted to compare the Cl<sub>2</sub> adsorption performance depending on the iron oxide phases. Figure 3 exhibits the dechlorination capacity of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> in the presence of 100 ppm Cl<sub>2</sub> at 350 °C for 60 min. The dechlorination efficiency of Fe<sub>2</sub>O<sub>3</sub> is almost 100% during the 11 min with an adsorption capacity of 1.06 mgc<sub>1</sub>/g and then slowly decreases to 81% at the time of 11–60 min. In contrast, the dechlorination efficiency of Fe<sub>3</sub>O<sub>4</sub> shows 100% for the 25 min with an adsorption capacity of 2.65 mgc<sub>1</sub>/g and decreases to 82% in the time range of 25–60 min. The Fe<sub>3</sub>O<sub>4</sub> phase showed more than twice the Cl<sub>2</sub> adsorption capacity compared to the Fe<sub>2</sub>O<sub>3</sub> phase. These results suggest that the Fe<sub>3</sub>O<sub>4</sub> phase has a more critical influence on the dechlorination capacity than the Fe<sub>2</sub>O<sub>3</sub> phase.



Figure 3. The dechlorination capacity of Fe2O3 and Fe3O4 in the presence of 100 ppm Cl2 at 350 °C.

Figure 4 shows the XRD patterns of iron oxide in fresh and after Cl<sub>2</sub> adsorption. The peaks of Fe<sub>2</sub>O<sub>3</sub> (JCPDS No. 89–8103) and Fe<sub>3</sub>O<sub>4</sub> (JCPDS No. 75–0449) were observed in the fresh state. After Cl<sub>2</sub> adsorption, the peak of iron oxide remained and the iron chloride phase did not appear. It might be difficult to observe the phase change of iron oxide after Cl<sub>2</sub> adsorption under the conditions of this experiment. In addition, the dechlorination effects of the iron oxide phases are confirmed by the SEM–EDS results in Figure 5. It revealed that while no Cl ions were adsorbed on Fe<sub>2</sub>O<sub>3</sub>, 0.3 wt% of Cl ions were observed on Fe<sub>3</sub>O<sub>4</sub>. This confirms that the Cl<sub>2</sub> adsorption capacity varies with the structural form of iron oxide. Since the red mud component is mainly formed in the Fe<sub>2</sub>O<sub>3</sub> structure, it is necessary to investigate the effect of Cl<sub>2</sub> gas adsorption capacity according to H<sub>2</sub> treatment.



Figure 4. XRD patterns of iron oxide (a) fresh and (b) after Cl<sub>2</sub> adsorption at 350 °C: (•) Fe<sub>2</sub>O<sub>3</sub>, (■) Fe<sub>3</sub>O<sub>4</sub>.



**Figure 5.** SEM images and corresponding EDS analyses of the (**a**) Fe<sub>2</sub>O<sub>3</sub> and (**b**) Fe<sub>3</sub>O<sub>4</sub> after Cl<sub>2</sub> adsorption at 350 °C.

## 3.2. Characterization of the H<sub>2</sub>-Treated Red Mud

The chemical compositions of red mud were analyzed by X-ray fluorescence, as listed in Table S1. Here, it can be seen that the main components of red mud include Fe, Al, Na, Ca, Si, and Ti. Among the components, Fe has the highest content at 73.75%. The

red mud used in this study had a high Fe ratio, and the alkaline components Na and Ca were found to be distributed in small amounts at 5.63 and 3.74%, respectively.

Figure 6 shows the H<sub>2</sub>-TPR profiles of the red mud under 10% H<sub>2</sub> at a temperature range from 30 °C to 850 °C with a temperature ramp rate of 10 °C/min after pretreatment with N<sub>2</sub> at 200 °C for 1 h. The H<sub>2</sub>-TPR curve of the red mud displayed two peaks at 430–520 °C and 630–800 °C, which are ascribed to the reduction in different iron oxides. The peak between 430 °C and 520 °C can be assigned to the reduction from Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub>, and the high-temperature peaks at 630–800 °C correspond to the reduction from Fe<sub>3</sub>O<sub>4</sub> to FeO and included FeO to Fe metal [29–31]. Based on H<sub>2</sub>-TPR analysis, the H<sub>2</sub> treatment temperature was set to 400 °C, 550 °C, and 700 °C to control the Fe oxide phase on red mud.



**Figure 6.** H<sub>2</sub>-TPR profile of red mud under 10% H<sub>2</sub> conditions from 30 °C to 850 °C at a temperature ramp rate of 10 °C/min.

The physicochemical properties of H<sub>2</sub>-treated red muds were analyzed. As listed in Table 1, the BET surface area, pore volume, and average pore size of RM were 37.8 m<sup>2</sup>/g, 0.22 cm<sup>3</sup>/g, and 3.82 nm, respectively. In general, heat treatment reduces the specific surface area of red mud [32]. However, in the case of heat treatment using H<sub>2</sub>, there is no significant change in specific surface area, pore volume, and average pore size. It might be that the specific surface area is maintained as some of the Fe<sub>2</sub>O<sub>3</sub> is reduced during the H<sub>2</sub> treatment process.

Sample	BET Surface Area (m²/g)	Pore Volume (cm <sup>3</sup> /g)	Average Pore Size (nm)
RM	37.8	0.22	3.82
RM 400	42.8	0.21	3.41
RM 550	32.0	0.18	3.05
RM 700	36.5	0.18	3.14

Table 1. Texture properties of RM, RM 400, RM 550, and RM 700.

Figure 7 shows the XRD patterns of red mud in fresh and H<sub>2</sub>-treatment with various temperatures. For the red mud, the peak of Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> (JCPDS No. 65–5714), CaTiO<sub>3</sub> (JCPDS No. 02–0907), and Na<sub>8</sub>(AlSiO<sub>4</sub>)<sub>6</sub>(CO<sub>3</sub>) (JCPDS No. 89–8103) were observed in the fresh state. After H<sub>2</sub> treatment at 400 °C, there was no phase change in the Fe<sub>2</sub>O<sub>3</sub> peak and CaCO<sub>3</sub> (JCPDS No. 86–2334) was observed as Ca in the red mud reacted with the release of CO<sub>2</sub> from the decomposition of some Na<sub>8</sub>(AlSiO<sub>4</sub>)<sub>6</sub>(CO<sub>3</sub>). The amount of Na<sub>8</sub>(AlSiO<sub>4</sub>)<sub>6</sub>(CO<sub>3</sub>) gradually decreased as the H<sub>2</sub> treatment temperature increased. After the H<sub>2</sub> treatment at 550 °C, it was confirmed that Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> structures were formed together. In the case of H<sub>2</sub> treatment at 550 °C, unlike the H<sub>2</sub>-TPR results, it is difficult to

completely reduce the Fe<sub>2</sub>O<sub>3</sub> structure to the Fe<sub>3</sub>O<sub>4</sub> structure. Finally, when the H<sub>2</sub> treatment temperature reaches 700 °C, the peak of Fe<sub>2</sub>O<sub>3</sub> decreased significantly, while the peak of Fe<sub>3</sub>O<sub>4</sub> was exhibited. Therefore, in order to convert the Fe<sub>2</sub>O<sub>3</sub> of red mud into the Fe<sub>3</sub>O<sub>4</sub> structure, it is judged that hydrogen treatment must be performed at a temperature range of at least 700 °C. The peak of CaCO<sub>3</sub> was not confirmed due to the release of CO<sub>2</sub> from the decomposition of CaCO<sub>3</sub> at 700 °C.



**Figure 7.** XRD patterns of RM, RM 400, RM 550 and RM 700: (●) Fe<sub>2</sub>O<sub>3</sub>, (■) Fe<sub>3</sub>O<sub>4</sub>, (�) CaCO<sub>3</sub>, (♦) TiO<sub>2</sub>, (□) SiO<sub>2</sub>, (▲) Na<sub>8</sub>(AlSiO<sub>4</sub>)<sub>6</sub>(CO<sub>3</sub>).

## 3.3. Dechlorination Capacity of the H2-Treated Red Mud

Figure 8 shows the dechlorination capacity of red mud with various H<sub>2</sub> treatment temperatures. The dechlorination performances of the H2-treated red mud increase in the order of RM (10 min) < RM 400 and RM 550 (15 min) < RM 700 (29 min). In the 100% Dechlorination capacity range, the Cl2 adsorption capacity of RM, RM 400, RM 550, and RM 700 was 1.06, 1.58, 1.58, and 3.06 mgci2/g, respectively. There is a significant difference between the dechlorination performances of RM without H<sub>2</sub> treatment and RM with H<sub>2</sub> treatment, indicating that the changes in phase of iron oxide on red mud by H<sub>2</sub> treatment affect the reaction of the red mud with Cl<sub>2</sub>. Especially, the dechlorination performances change significantly when the treatment temperature is further increased from 550 to 700 °C. When comparing the treatment temperature in the XRD results, it is believed that this is because most of the Fe<sub>2</sub>O<sub>3</sub> structure was transferred to the Fe<sub>3</sub>O<sub>4</sub> structure under 700 °C. During the chlorination of hematite ( $Fe_2O_3 + 3Cl_2 = 2FeCl_3 + 3/2O_2$ ) or magnetite ( $3Fe_3O_4 + 3/2O_2$ )  $3/2Cl_2 = FeCl_3 + 4Fe_2O_3$ ), the oxygen may be consumed to produce higher oxides, thus affecting the subsequent chlorination behavior. As demonstrated in Section 3.1, the Fe<sub>3</sub>O<sub>4</sub> phase has a critical influence on the dechlorination capacity rather than the Fe<sub>2</sub>O<sub>3</sub> phase. Consequently, it was observed that the Cl<sub>2</sub> gas adsorption capacity of red mud varies depending on the H2 pretreatment conditions. Accordingly, red mud at H2 treatment temperature of 700 °C showed about three times higher Cl<sub>2</sub> adsorption compared to red mud without H2 treatment.



**Figure 8.** The dechlorination capacity of RM, RM 400, RM 550, and RM 700 in the presence of 100 ppm Cl<sub>2</sub> at 350 °C.

Figure 9 shows the XRD patterns of red mud with various H<sub>2</sub> treatment temperatures after Cl<sub>2</sub> adsorption. In the case of TiO<sub>2</sub> and SiO<sub>2</sub> peaks in all samples, no change was observed even after the Cl<sub>2</sub> adsorption experiment. Therefore, it is judged that the TiO<sub>2</sub> and SiO<sub>2</sub> structures have no effect on Cl<sub>2</sub> adsorption. The peak of Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub> (JCPDS No. 35-0755), Ca(ClO<sub>3</sub>)<sub>2</sub> (JCPDS No. 01-0716), and NaClO<sub>3</sub> (JCPDS No. 73-0145) was observed in red mud without H<sub>2</sub> treatment after Cl<sub>2</sub> adsorption. In the case of H<sub>2</sub>-treated red mud, the NaClO<sub>3</sub> peak was relatively small after the Cl<sub>2</sub> adsorption reaction, and it was confirmed that the Ca(ClO<sub>3</sub>)<sub>2</sub> peak mainly increased. As the temperature of the H<sub>2</sub> treatment process increases, the Na<sub>2</sub>CO<sub>3</sub> structure relatively decreases because CO<sub>2</sub> is desorbed, and the stable CaCO<sub>3</sub> structure increases at high temperatures, so it is assumed that the Ca(ClO<sub>3</sub>)<sub>2</sub> peak relatively increases after Cl<sub>2</sub> adsorption. However, as shown in Figure 7, at the H<sub>2</sub> treatment temperature of 700 °C, CO<sub>2</sub> in the CaCO<sub>3</sub> structure was desorbed and the CaCO<sub>3</sub> peak almost disappeared, resulting in a tendency for the Ca(ClO<sub>3</sub>)<sub>2</sub> peak to decrease after Cl<sub>2</sub> adsorption. These results indicate that the presence of Na and Ca in the elemental composition has a decisive influence on the dechlorination capacity of the red mud. For the H2-treated red mud above 550 °C, the Fe3O4 peak relatively decreased and the FeCl<sub>3</sub> peak was confirmed after the Cl<sub>2</sub> adsorption, which is believed to have changed the Fe<sub>3</sub>O<sub>4</sub> structure to the FeCl<sub>3</sub> structure during the Cl<sub>2</sub> adsorption. After Cl<sub>2</sub> adsorption (Figure 10), the SEM-EDS analysis results showed that the Cl ion concentration was approximately 0.26% for the red mud without H<sub>2</sub> treatment, and for the red mud with H<sub>2</sub> treatment at 700 °C, the Cl ion concentration was confirmed to be 0.61%. Although the  $Nas(AlSiO_4)_6(CO_3)$  structure was relatively reduced by the H<sub>2</sub> treatment, when the Fe<sub>2</sub>O<sub>3</sub> structure was converted to the Fe<sub>3</sub>O<sub>4</sub> structure, it was relatively suitable for adsorbing Cl<sub>2</sub>.

Previously, authors have used adsorbents either in-situ or ex-situ and reported a decrease in Cl content in pyrolysis oil when using adsorbents [18,21–24]. This study used red mud containing Fe<sub>3</sub>O<sub>4</sub>, which is used as a Cl adsorbent, to confirm the Cl adsorption capacity of red mud. Red mud components with dechlorination activity include Na in the form of Na<sub>8</sub>(AlSiO<sub>4</sub>)<sub>6</sub>(CO<sub>3</sub>) and Ca in the form of CaCO<sub>3</sub>. During the H<sub>2</sub> treatment of red mud, the forms of Na<sub>8</sub>(AlSiO<sub>4</sub>)<sub>6</sub>(CO<sub>3</sub>) and CaCO<sub>3</sub>, which have dechlorination activity, are reduced. However, the Cl adsorption capacity improved as the Fe<sub>3</sub>O<sub>4</sub> form with high dechlorination activity increased from the Fe<sub>2</sub>O<sub>3</sub> form with low dechlorination activity.



**Figure 9.** XRD patterns of RM, RM 400, RM 550 and RM 700 after Cl<sub>2</sub> adsorption at 350 °C: (•) Fe<sub>2</sub>O<sub>3</sub>, ( $\blacksquare$ ) Fe<sub>3</sub>O<sub>4</sub>, ( $\blacklozenge$ ) TiO<sub>2</sub>, ( $\square$ ) SiO<sub>2</sub>, ( $\blacktriangle$ ) Na<sub>8</sub>(AlSiO<sub>4</sub>)<sub>6</sub>(CO<sub>3</sub>), ( $\triangle$ ) NaClO<sub>3</sub>, ( $\triangle$ ) Na<sub>4</sub>Al<sub>3</sub>Si<sub>9</sub>O<sub>24</sub>Cl, ( $\nabla$ ) Ca(ClO<sub>3</sub>)<sub>2</sub>, ( $\square$ ) FeCl<sub>3</sub>.



Figure 10. SEM images and corresponding EDS analyses of the (a) RM and (b) RM 700 after Cl<sub>2</sub> adsorption at 350  $^{\circ}$ C

## 4. Conclusions

This study demonstrates that the development of a red mud-based adsorbent can play a significant role in both removing Cl<sub>2</sub> gas generated during the pyrolysis of waste plastics and in addressing the environmental issues associated with red mud. Furthermore, recycling red mud in this study can reduce the post-processing costs of plastic pyrolysis technology and help preserve the environment. We intend to use Fe oxide, the main component of red mud, as a Cl<sub>2</sub> adsorption source. Cl<sub>2</sub> adsorption experiments according to the Fe oxide structure were investigated, and it was confirmed that the Fe<sub>3</sub>O<sub>4</sub> structure had higher Cl<sub>2</sub> adsorption than the Fe<sub>2</sub>O<sub>3</sub> structure. In the case of Fe oxide in red mud, it has a Fe<sub>2</sub>O<sub>3</sub> structure, so we tried to change the structure through the H<sub>2</sub> treatment process to change it to a Fe<sub>3</sub>O<sub>4</sub> structure. At an H<sub>2</sub> treatment temperature of 700 °C, most Fe<sub>2</sub>O<sub>3</sub> structures in red mud can be converted to Fe<sub>3</sub>O<sub>4</sub> structure. After the Cl<sub>2</sub> adsorption experiment, the Ca(ClO<sub>3</sub>)<sub>2</sub>, NaClO<sub>3</sub>, and FeCl<sub>3</sub> structures were confirmed. In the case of red mud at an H<sub>2</sub> treatment temperature of 700 °C, the ratio of Ca(ClO<sub>3</sub>)<sub>2</sub> and NaClO<sub>3</sub> structures was relatively reduced, but it was confirmed to have higher Cl<sub>2</sub> adsorption performance. Converting the Fe<sub>2</sub>O<sub>3</sub> structure to the Fe<sub>3</sub>O<sub>4</sub> structure through the H<sub>2</sub> treatment process appears to have a higher Cl<sub>2</sub> absorption capacity compared to the alkaline structure without the H<sub>2</sub> treatment state. As a result, through the H<sub>2</sub> treatment process, we were able to obtain a Cl<sub>2</sub> adsorption capacity that was about three times higher than that of red mud that was not H<sub>2</sub> treated.

Although H<sub>2</sub>-treated red mud exhibits higher Cl<sub>2</sub> adsorption performance than red mud without H<sub>2</sub> treatment, the manufacturing cost increases relatively as high calcination temperature is required. To improve this, future research will be conducted to enable the reduction in iron oxide in red mud at lower temperatures.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su16031137/s1, Figure S1: Calibration curve for Cl<sub>2</sub> between the Ion Chromatograph analysis and the real-time measurement; Table S1: Chemical Compositions of the red mud, as analyzed by XRF.

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