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Treatment of Waste Water from Li-ion Batteries Cathode Material Production: Selection of adsorbents

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ABSTRACT: Batteries become determining factor in the sustainability of NREs as their boundaries are pushed beyond its limits. The development of batteries can be trace back to its discovery by Volta. A hundred years later, the energy and power density of batteries has increased significantly. The production of cathode materials is performed using the hydrometallurgical method followed by high-temperature metal processing and involving large amounts of waste water. The processing of cathode material precursors also involves a hydrometallurgical process and also produce significant amount of wastewater. In addition, the recycling of end-of-life LIBs are also using a hydrometallurgical method which generates waste water. To improve the eco-friendliness of LIBs technology, wastewater treatments of LIBs production from upstream and downstream industries should be considered. The wastewater from LIBs production is unavoidable; thus, proper wastewater treatment is necessary to assure the sustainability of the technology. The adsorption of inorganic pollutants is considered a win-win solution. The selection of adsorbents such as silica (SiO_2), titania (TiO_2), alumina (Al_2O_3), activated carbon, and zeolites offer different characteristics. The processing of these types of material is discussed and most of them require precursors that can be obtained from another source of waste. This means the waste treatment is not only reducing one type of pollutant but also another type of pollutant during the synthesis of adsorbents.

Keywords: Li-ion battery, cathode, waste water, adsorbents.

1. Introduction

Recently, the G20 nations have declared to fight climate change to have a sustainable ecosystem. Based on the event, the acceleration of energy transition from fossil fuel to new and renewable energy (NRE) will be implemented by the nation to achieve net zero emissions by 2060. The journey toward NRE implementation has major challenges such as their feasibility, availability, economical aspect, and technological key factors. NRE have been established since the 20th century, however, efforts on improving their sustainability and efficiency are continuously performed up until today. New and renewable energy such as wind and solar energy become more efficient with the invention of energy storage devices such as batteries. Batteries become determining factor in the sustainability of NREs as their boundaries are pushed beyond its limits. The development of batteries can be trace back to its discovery by Volta. A hundred years later, the energy and power density of batteries has increased significantly. In the late 20th century, Li-ion batteries (LIBs) have been commercially produced offering high energy density, high power, and long cycle life. Due to this fact, several types of research have been developed to decrease the production cost by selecting cheaper and more abundant materials. In the span of fewer than two decades, the cobalt-based LIBs are successfully substituted by economically attractive and more sustainable nickel-based LIBs. Nowadays, most electric vehicles and energy storage systems have been utilizing this type of battery [1].

The rising demand of Li-ion batteries promotes the production of their active materials. Around 40% of batteries consist of cathode materials. The production of cathode materials is performed using the hydrometallurgical method followed by high-temperature metal processing and involving large amounts of waste water. The processing of cathode material precursors also involves a hydrometallurgical process and also produce significant amount of wastewater. In addition, the recycling of end-of-life LIBs are also using a hydrometallurgical method which generates waste water. To improve the eco-friendliness of LIBs technology, wastewater treatments of LIBs production from upstream and downstream industries should be considered. There are lots of method to treat wastewater containing inorganic compounds such as ultra-filtrations, reverse osmosis, coagulation and flocculation, and adsorption. Ultra-filtration and reverse osmosis require expensive membranes and polymers with a complex regeneration process. Meanwhile, coagulation and flocculation techniques are not effective when the pollutant concentration is too small. On the other hand, adsorption using cheap adsorbent is considered as an effective approach to treating wastewater. There are numerous types of adsorbents, however abundant, large adsorption capacity and inexpensive adsorbents should be prioritized to assure the overall economic potential of the process [2].

This review offers understanding of the promising type of adsorbents to treat LIBs waste water. The characteristics, synthesis method, advantages, and disadvantages are deeply discussed. The review only focuses on silica, titania, alumina, activated carbon, and zeolites due to their availability, eco-friendliness and economic value. State-of-the-art adsorbents such as nanoparticles from transitional metal oxides, nanodots, and other morphologically controlled materials are not discussed and are out of the scope of this review.

2. TYPES OF ADSORBENTS

2.1 Activated Carbon

The use of activated carbon as an adsorbent in various aspects of research has increased very rapidly from year to year [3].Activated carbon as an absorbent is no longer foreign to our lives, we can find the use of activated carbon starting from the smallest things in household life, in the world of health, and also in large industries both in separation and for gas storage. The magnitude of the need for the use of activated carbon as an absorbent is not accompanied by activated carbon production in this country. We still rely on foreign countries as suppliers of activated carbon needs, while the availability of basic materials for the manufacture of activated carbon in Indonesia is very abundant and untouchable at all [4].

Activated carbon can be defined as a carbon material with an amorphous structure and a large internal surface area with a high degree of porosity. Activated carbon has both microcrystalline and non-graphite forms of carbon. The non-graphite form means that it contains a small amount of hydrogen or a large amount of oxygen in its structure. Activated carbon has high performance in electrical conductivity, good thermal stability, and surface reactivity which are the main reasons it has been used in recent years [5].

Activated carbon can adsorb certain gases and chemical compounds or its adsorption properties are selective, depending on the size or volume of the pores and surface area. Activated carbon can be used in various fields such as the medicine and food industries for filtering, deodorizing, and tasting. Petroleum chemical industry, water purification, shrimp farming, sugar industry, gas purification, catalyst, and fertilizer processing [6].

2.1.1. Type of ACs

Activated carbon contains micropores, mesoporous and macropores in its structure. This structure has an important role in determining the performance of activated carbon as an adsorbent. Activated carbon is categorized as non-graphite carbon because it has a low density and porous structure. Activated carbon can be produced from materials that contain carbon, one of which is from agricultural waste such as oil palm shells, fruit peels, shells, roots, stems, bark, flowers, leaves, and fruit peels. Some of the criteria for selecting raw materials for making activated carbon are high carbon content, low inorganic substance content so that the ash yield is low, abundant so that the cost is low, low degradation rate on storage, and the possibility of producing activated carbon with a high percentage yield [6]. Activated carbon has been recognized as one of the most popular adsorbents and is widely used in water and wastewater treatment worldwide. The specific adsorptive property of charcoal was first discovered by Scheele in 1773 for gas treatment followed by decolorization in water in 1786. Activated carbon has an abundant porous structure and strong adsorption capacity, widely used in various industries, including in separation, removal dyes and pollutants from wastewater, and water purification processes. There are three main forms of activated carbon as follows [7]:

a. **Granular activated carbon**
   Irregularly shaped with a particle size of 0.2 to 5 mm. This type of activated carbon is used in both applications, namely the liquid and gas phases [8].
b. **Powder Activated Carbon (PAC)**
   It is activated carbon that has been crushed so that it has a size smaller than 0.18 mm (US mess 80). This type of activated carbon is usually used in liquid phase applications and filtering of flue gases [9].
c. **Activated carbon in the form of pellets**
   Pellet-shaped activated carbon is made through an extruding process and is cylindrical in shape with a diameter of 0.8 to 5 mm. Pellet-shaped activated carbon is usually used for applications in the gas phase because of its low-pressure drop value, high mechanical strength, and low ash content [7].
d. **L-Carbon (L-AC)**
   Activated carbon made by oxidizing at a temperature of 300-400^{0}C using air or chemical oxidation of L-AC is very suitable for adsorbing dissolved ions of basic heavy metals such as Pb2+, Cn2+, Cd2+, its surface character which is acidic will interact with basic metals. Regeneration of L-AC can be carried out using acids or salts such as NaCl which are almost the same as ion exchange [10].
e. **H-Carbon (H-AC)**
   The activated carbon produced from the cooking process at a temperature of 800-1000^{0}C is then cooled in an inertial atmosphere. H-AC has an alkaline surface so it is not effective in adsorbing alkaline heavy metals in an aqueous solution but is very efficient in adsorbing organic chemicals, hydrolytic particulates, and chemical compounds that have low solubility in water, however, H-AC can be modified by increase acidity. A neutral

surface will result in ineffectiveness in reducing and adsorbing chemicals [11].

2.1.2. Synthesis of ACs

a. Carbonization

Making activated carbon through the stages of carbonization and activation. The carbonization process is a phase for enriching the carbon content by removing non-carbon species using thermal decomposition. Although the initial porosity of charcoal is still relatively low, it can be developed at this stage before experiencing further development in the activation process. In the production process, organic matter is first carbonized at a temperature of 600–700°C and releases most of the volatile components which are the result of the breakdown of cellulose, hemicellulose, and lignin. The product of the carbonization step is a solid with a high carbon content, usually in the range of 25-50% calculated by mass, depending on the starting material and process parameters used [12].

b. Carbon Activation

The activation process aims to increase the pore volume, enlarge the pore diameter and increase the porosity of the activated carbon. The activation process can be done by three methods. Physical activation, chemical activation, and Physico-chemical activation. Physical activation usually uses steam or CO_2. For physical activation, steam is more effective than CO_2, because it can produce activated carbon with a relatively larger surface area. The activation process is divided into two, namely physical and chemical activation [13].

2.1.2.2.1. Physics activation process

Physical activation uses steam or CO_2 as an activating agent. The purpose of the activation process is to enlarge the pore distribution and enlarge the pores, especially for mesopores and micro-pores so that it will increase the surface area of activated carbon by incomplete combustion (partial combustion) [14].

2.1.2.2.2. Chemical activation process

In chemical activation activating agents, such as $ZnCl_2$, KOH, NaOH, and H_3PO, are used to activate the carbon. The procedure is simple: the solution containing the chemical activation agent permeates the surface of the biomass, is dried in the oven, and finally activated in the furnace for 1 to 4 hours. The advantages of using the chemical activation method are higher final carbon yields, one-step process, generally lower activation temperature, and easier adjustment of porosity. The carbonization and activation steps can be carried out in two different ways, in a two-stage process, where the carbonization and activation steps are separated in time, or in a single-stage process, where the carbonization and activation are carried out sequentially in the same reactor [14].

c. Active Carbon Characteristics

The adsorption properties of activated carbon are highly dependent on the porosity of its surface, but in the industrial field, the characterization of activated carbon is more focused on adsorption properties than on its pore structure. Pore shapes vary, namely in the form of cylinders, rectangles, and other irregular shapes. Quality requirements for activated carbon can be seen in the following table [15]:

Table 1. Active Carbon Characteristics

No.	Description	Unit	Remark	
			Grain	Powder
1	The missing part is heating 950^{o}C	%	Max 15	Max 25
2	Water content	%	Max 4.5	Max 15
3	Ash content	%	Max 2.5	Max 10
4	Solvent absorption I_2	Mg/g	Min 750	Min 750
5	Pure Activated Carbon	%	Min 80	Min 65

2.1.2.3.1. Water Content

The water content increases with the higher activator concentration. This is due to the better dissolution of the pyrolysis process of residues and organic minerals on the activated carbon surface with increasing activator concentrations. Increasing the concentration of the activator will increase the number and volume of pores and surface area, which causes an increase in the performance of activated carbon to absorb water from the air [15].

The water content of activated activated charcoal is greater than that of unactivated charcoal. The hygroscopic nature causes activated charcoal under certain conditions and humidity to reach a balance of water content, this balance of water content is a measure of hygroscopicity. The moisture content is strongly influenced by the amount of water vapor in the air, the length of the cooling process, and the hygroscopic nature of the charcoal [16].

2.1.2.3.2. Volatile Content

Volatile content is the content of volatile compounds other than water in activated charcoal. The level of volatile matter shown by activated charcoal is greater than that of non-activated charcoal. The difference in the levels of volatile matter between activated charcoal and charcoal, can be caused by the formation of functional groups when activated using phosphoric acid. The increase in the levels of volatile substances is thought to be due to the breaking of atomic bonds such as oxygen, nitrogen and hydrogen in the groups that are formed and evaporate due to the heating given.

Volatile levels decreased with increasing activator concentration. This is because the addition of activator causes changes in the structure and absorption properties of activated carbon. H_3PO_4 activator causes degradation of organic matter which weakens the surface structure of activated carbon. At higher temperatures, more volatile matter will be released, causing less carbon to form. This is due to the higher pyrolysis temperature, so that the decomposition of components contained in raw materials such as water, tar and volatile matter is also higher [14]

2.1.2.3.3. Ash Content

Ash content has an influential role in affecting the quality of the activated carbon produced. Excessive ash content can cause clogged pores in activated carbon so that the surface area of activated carbon is reduced. The ash content increased with increasing activator concentration so that the organic compounds of activated carbon decreased, but the inorganic content of the compounds remained relatively constant. Interactions in the reactor during the pyrolysis process cause inorganic compounds to trigger the formation of metal oxides. Increasing the amount of metal oxide causes the ash content in activated carbon to increase, especially with increasing temperature. An activator concentration that is too high can also cause damage to the activated carbon structure, which results in an increase in the ash content.

Activated charcoal made from natural ingredients not only contains carbon compounds, but also contains several minerals. The ash content will indicate the mineral content contained in the activated charcoal. Activated charcoal has a lower total ash content than unactivated charcoal. The ash content is related to the content of minerals such as metals in activated charcoal. Kosting and Conrad (1931) reported that phosphoric acid can corrode metals. Based on this, the metal contained in the charcoal will experience corrosion during activation using phosphoric acid, causing the ash content of activated charcoal to be lower than that of non-activated charcoal [17].

2.1.2.3.4. Carbon Content

The value of the fixed carbon content produced fluctuates with increasing pyrolysis temperature. The fixed carbon content is also affected by the content of cellulose and lignin which can be converted into carbon atoms. At 250 °C there is a decrease in fixed carbon caused by the breakdown of the activated carbon structure by high temperature or carbon combustion. Carbon reduction can also be caused by the reaction between carbon and activator at high concentrations, which can damage the micropores on the carbon surface [17].

2.1.2.3.5. Methylene Blue Absorption

Determination of the absorption capacity of methylene blue aims to determine the surface area of activated charcoal and its ability to absorb colored solutions [18]. The determination of the absorption capacity of methylene blue is to determine the ability of activated charcoal to absorb colored solutions with a molecular size of less than 15 Å or 1.5 nm [19].

2.1.2.3.6. Iodine Absorption

Determination of iodine absorption aims to determine the adsorption capacity of activated charcoal [18]. The determination of the absorption of iodine aims to determine the ability of activated charcoal to absorb colored solutions with a molecular size of less than 10 Å or 1 nm. Iodine absorption capacity of activated charcoal activated with 15% phosphoric acid meets the quality standard of iodine absorption capacity [19]. Activated charcoal has a greater absorption of iodine than unactivated charcoal. Increased absorption of meylene blue and iodine from activated charcoal can occur because activation using phosphoric acid activator (H_3PO_4) can clean the pores and expand the surface of the charcoal and provide active groups so as to increase the absorption of charcoal.

2.1.3. Advantages and Disadvantages of Activated Carbon

Some of the advantages of using activated carbon to treat liquid waste include, namely, the costs used are cheaper. The main raw materials used as activated carbon are organic materials with a high carbon content. There have been many studies on activated carbon materials with cheap and widely available ingredients such as coconut shell, hazelnut shell and wood fiber. Activated carbon can be made yourself from the raw materials mentioned earlier, while the process includes dehydration, carbonation and activation. The equipment used to treat liquid waste with activated carbon is also simple, because only a filter with activated carbon is needed to remove organic compounds that cannot be decomposed. Weaknesses of using activated carbon in adsorbing liquid waste include; the use of activated carbon is limited to liquid waste containing several compounds and several types of heavy metals. Its use is limited and cannot be applied to all types of industrial wastewater [20]

2.2 Silica

Silica gel is amorphous silica (irregular atomic arrangement) which can be used as an adsorbent. Silica gel is an inorganic solid that has active sites on the surface of silanol groups (Si-OH) and siloxane (Si-O-Si) as well as physical properties such as mechanical stability, porosity and surface area. The presence of –OH groups which are capable of forming hydrogen bonds with the same groups of other molecules causes silica to be used as a desiccant and stationary phase in column chromatography or adsorbents for organic compounds [21]

Silica is widely used in various applications including as an absorbent and catalyst support. Silica gel is one of the synthetic silica compounds and can be synthesized through the sol-gel process, in solid form and is widely used as an adsorbent. Its properties as an adsorbent are also called adsorptive properties due to the presence of active sites on the surface, but silica also has a weakness, namely the active site is only a silanol group (-SiOH) which has low acidity and has oxygen as a donor atom which is weak in nature so it is less able to applied as an adsorbent for certain metal ions. One way to increase the ability of silica to adsorb is to modify the silica surface by adding certain materials. The added material has properties that can bind with one or more metal ions so as to increase adsorption power [21], [22].

Adsorption is one method that can be used to overcome the dangers of dye wastewater, because it is cheaper and easier to obtain, which is an absorption process that occurs on a surface. There are several factors that affect adsorption, namely the physical and chemical properties of the adsorbent and adsorbate; liquid phase properties (pH and temperature); gas phase properties (temperature and pressure); adsorbate concentration; contact time of adsorbent and adsorbate. It is hoped that this wastewater treatment can reduce pollution and the dangers of wastewater for the environment and living things. Silica is a mineral whose main constituent is silicon dioxide (SiO_2). Silica is composed of two elements consisting of silicon (Si) and oxygen (O_2), both of which are the most abundant elements in nature. It is estimated that 60% of the earth's crust is composed of silica. Silica that is on earth is usually found in the form of silicates [23].

Silicon dioxide or silica is one of the most common chemical compounds. Pure silica exists in two forms, namely quartz and cristobalite. Silicon is always tetrahedrally bonded to four oxygen atoms, but the bonds are quite ionic in nature. In cristobalite, the silicon atoms are positioned much like the carbon atoms are in diamond with the oxygen atoms in the center of each pair. In quartz there is a helix so that enantiomorphic crystals are formed. Quartz and cristobalite are interchangeable when heated. This process is slow because it requires the breaking and reforming of bonds and the activation energy is high. Silica is relatively unreactive to Cl_2, H_2, acids and most metals at 25^oC or higher, but can be attacked by F_2, HF aqua, alkaline hydroxides and carbonate melts [24].

Silica is relatively unreactive to Cl_2, H_2, acids and most metals at 25^{o}C or higher, but can be attacked by F_2, HF aqua, alkaline hydroxides and carbonate melts. Silica forms constitute some of the important crystal structures not only because silica is an abundant and useful substance, but because its structure

Based on the molecular structure of silica is divided into two parts, namely:

The synthetic compound is amorphous. Synthetically, silica compounds can be prepared from silicate solutions or from silane reagents [26].

Synthetic silica gel, made by going through processes and processing using machines. Where there is a change in form and type of material into finished goods. With the basic ingredients of quartz sand and soda ash, silica gel (SiO_3) is made. In its development there are two types of synthetic silica gel, namely: Silica Gel White is a synthetic silica gel in the form of white/clear granules. Blue Silica Gel is a modified synthetic silica gel with the addition of a blue indicator. The color indicator changes to brick red when saturated. This material contains cobalt chloride which has carcinogenic side effects and causes respiratory irritation. It is better to avoid using blue silica gel in food products. Natural silica gel is made from natural silica gel, such as zeolite stone and other substances containing silica compounds, such as shell ash and palm fiber, which are processed through an activation and screening process [27].

2.2.2 Silica Synthesis

The chemical properties of silica (SiO_2), namely:

Silica minerals have various chemical properties, including the following:

a. Acid reaction

Silica is relatively unreactive with acids except for hydrofluoric acid and phosphoric acid.

(SiO_4) is the fundamental unit in most minerals [25].

2.2.1 Type of SiO_2

a. Crystalline Silica
b. Microcrystalline Silica
c. Vitreous Silica (Supercooled Liquid Glasses)
d. Amorf Silica

$zSiO_2(s) + 4HF(aq) \rightarrow SiF_4(aq) + 2H_2O(l)$ [28]

In excess of acid the reaction is:

$SiO_2 + 6HF \rightarrow H_2[SiF_6](aq) + 2H2O(l)$ [28]

b. Base reaction

Silica can react with bases, especially with strong bases, such as with alkaline hydroxides.

$SiO_2(s) + 2NaOH(aq) \rightarrow Na_2SiO_3 + H_2O$ [28]

Commercially, silica is prepared by mixing sodium silicate solution with a mineral acid. This reaction produces a concentrated dispersion which eventually separates particles from the hydrated silica, known as silica hydrosol or silicic acid which is then dried at 110°C to form silica gel. The reaction happened:

$Na_2SiO_3(aq) + 2HCl(aq) \rightarrow H_2SiO_3(l) + 2NaCl(aq)$ [28]

$H_2SiO_3(s) \rightarrow SiO_2.H_2O(s)$ [28]

The chemical compound silicon dioxide, also known as silica (from the Latin silex), is an oxide of silicon with the chemical formula SiO2. It has been known since ancient times for its hardness. Silica is most often found in nature as sand or quartz, as well as in the cell walls of diatoms. Silica is produced in several forms including fused quartz, crystals, irritated silica (or pyrogenic silica, trademarks Aerosil or Cab-O-Sil), colloidal silica, silica gel, and air-gel.

1.1.1. Characteristics of SiO_2

Silica gel is a chemical substance in solid form which is widely used as an adsorbent. This is due to the ease of production and also several other advantages, namely: very inert, hydrophilic, has high thermal and mechanical stability and relatively does not swell in organic solvents when compared to solid organic polymer resins. Quality related to its utilization is determined by various factors, namely internal structure, particle size, porosity, surface area, resistance and polarity [29].

Although it has many advantages, it turns out that silica gel also has several weaknesses. This weakness is because in silica gel the type of active site is only in the form of silanol (-SiOH) and siloxane (Si-O-Si) groups. This silanol group has low acidity, besides having oxygen as a donor atom which is weak. The existence of this weakness can be overcome by means of surface modification. In this modification, it is hoped that the type of active site will change so that it becomes a wider field of utilization [30].

1.2. Nano-Alumina

Alumina is found in bauxite minerals which contain aluminum in the hydroxide form, namely boehmite (γ-AlO(OH)) and gibbsite $Al(OH)_3$, with levels of around 30-54%. As a natural mineral, besides aluminum, bauxite also contains various impurities, such as iron oxide, silica and clay minerals. Because of this composition, to obtain pure alumina, bauxite must be processed, and one of the processing methods is the Bayer process [31].

Nano alumina is developed in several ways to produce alumina with different methods and are categorized in physical methods and chemical methods. Physical methods include mechanical milling, laser ablation, and flame spray. Chemical methods include sol–gel processing, solution combustion decomposition and vapor deposition. Most of the physical methods above apply only to certain materials and the size of nanoparticles cannot be controlled properly, so chemical methods are considered better in producing products with high homogeneity, even though they require relatively more expensive costs [32].

Regarding the use of nano catalysts in Indonesia, it is still minimal because this is still a new thing. Its use is only limited to the reactions of making alternative energy and has not been attempted in reactions which are the main source of energy. In addition, the method for making nano catalysts currently being developed in Indonesia is not economical and efficient enough if we look at the aspect that product achievement must be easy, cheap, and efficient [33].

1.2.1. Type of Alumina

2.3.1.1. Alumina

Aluminum oxide is a chemical compound of aluminum and oxygen, with the chemical formula Al_2O_3. The name of the mineral is alumina, and in mining, ceramics and engineering materials this compound is more commonly referred to as alumina. Aluminum oxide is a good thermal and electrical insulator. Generally, Al_2O_3 exists in a crystalline form called corundum or α-aluminum oxide. Al_2O_3 is used as an abrasive and as a component in cutting tools, because of its hardness. Aluminum oxide plays an important role in the resistance of aluminum metal to corrosion by air. Aluminum metal is very easy to react with oxygen in the air. Aluminum reacts with oxygen to form aluminum oxide, which forms a thin film that quickly covers the aluminum surface. This layer protects the aluminum metal from further oxidation. The thickness of this layer can be increased through an anodizing process. Some alloys, such as aluminum bronze, take advantage of this property by adding aluminum to the alloy to increase its corrosion resistance [34].

In nature, alumina is found in bauxite minerals that contain aluminum in the hydroxide form, namely boehmite (γ-AlO(OH)) and gibbsite $Al(OH)_3$, with levels of around 30-54%. As a natural mineral, besides aluminum, bauxite also contains various impurities, such as iron oxide, silica, and clay minerals. Because of this composition, to obtain pure alumina, bauxite must be processed, and one of the processing methods is the Bayer process [35].

2.3.1.2. Gamma Alumina (γ-Al_2O_3)

Gamma alumina (γ-Al_2O_3) is a transition alumina in the form of an amorphous solid. Gamma alumina is widely used as a catalyst and adsorbent, for example as a substrate-catalyst catalyst in the automotive and petroleum industries, structural compositions for aerospace and friction and heat or abrasion, and thermal protective clothing. This is because the gamma alumina catalyst has a large surface area (150-300 m^2/g), and a large pore volume (3-12 nm). In addition, γ-Al2O3 is stable in the catalytic process and at high temperatures, easy to form in the manufacturing process, and inexpensive. Gamma alumina (γ-Al_2O_3) is formed by heating at a temperature of 500-800^{0}C. Heating $Al(OH)_3$ causes $Al(OH)_3$ to decompose into an oxide with a microporous system and a large surface area [36]

2.3.1.3. Nano Alumina

Nano catalysts are defined as dispersed particulates or solid particles with particle sizes ranging from 1-100 nm. Nano catalysts have attracted a lot of interest from researchers because nano catalyst materials exhibit different physical and chemical properties from their bulk materials, such properties as mechanical, electronic, magnetic, thermal, catalytic, and optical stability. Two main things make nano catalysts different from similar materials in bulk, namely:

1. Due to their small size, nano catalysts have a greater ratio between surface area and volume than similar large-sized particles. This makes the nano catalyst more reactive. The reactivity of a material is determined by the atoms on the surface because only those atoms are in direct contact with other materials.
2. When the particle size reaches the nanometer order, the applicable laws of physics are more dominated by the laws of quantum physics. These properties can be an advantage of nano catalysts compared to similar particles in the bulk state.

nano catalysts has a large surface area and the ratios of atoms are evenly distributed on its surface. This property is advantageous for mass transfer within the pores and also contributes to a large interfacial interface for adsorption and catalytic reactions. In addition, nano catalysts have been widely used as catalysts to produce fuels and chemicals and to deal with environmental pollution [32].

Another development in the field of alumina that is currently being researched is the utilization of nano-alumina, along with the development of nanotechnology. In general, nanomaterials are materials with a particle size of 1-100 nm, and therefore have many advantages over macro-sized materials. The advantages of nano alumina include having a greater ratio between surface area and volume compared to similar large-sized particles. This makes the nanoparticles more reactive, for example, as a reactant to produce other products or as a catalyst. Nano-alumina is also widely used as a very mild abrasive and surface finish [33].

1.2.2. Synthesis of Alumina

Chemical methods include sol–gel processing, solution combustion decomposition, and vapor deposition. Most of the physical methods above apply only to certain materials and the size of nanoparticles cannot be controlled properly, so chemical methods are considered better for producing products with high homogeneity.

2.3.2.1. Sol-Gel Method

The process of the sol-gel method in this study began by preparing a solution by mixing 0.5 M aluminum nitrate with aluminum isopropoxide gradually until the molar ratio of aluminum isopropoxide and aluminum nitrate reached 3, then the mixture was stirred until homogeneous. The solution formed was stirred at different times, 24, 36, 48, and 60 hours, after which Sodium bis-2ethylhexyl sulfosuccinate and Sodium sulfonate dodecylbenzene (SDBS) was added, then the solution was stirred for 1 hour. The solution was heated to 60°C and stirred continuously during the evaporation process to form a gel. The gel was then heated at 90 °C for 8 hours. The dried gel was then calcined at a temperature range of 1000-1200°C, and ground using a mortar and paste. The alumina samples obtained from the sol-gel method were characterized using XRD, TGA, DSC, FTIR, TEM, and SEM. The XRD results show that the most stable phase of alpha alumina is at 1200°C. TGA results show that there is a decrease in weight at temperatures below 400°C by 3-4% and at temperatures of 400-750°C by 1%. DSC results show that the gamma alumina phase begins to form at 420°C, and the alpha alumina phase begins to form at 1035°C. The FTIR results show that the two surfactants are adsorbed by the nano alumina. TEM results show that the difference in stirring time affects the size and shape of the particles. Increasing the stirring time from 24 to 48 hours can reduce the size of the particles, but at 60 hours of stirring time, the formation of aggregation occurs. The size of the α-alumina particles formed is around 20-30 nm at 48 hours of stirring. The SEM results show that the more surfactant used, the smaller the resulting alumina particle size [37].

2.3.2.2. Flame Spray Method

The process of making alumina using the flame spray method begins with injecting $AlCl_3$ powder into the gun using a nitrogen gas chamber heating to a temperature of 300°C. Pyrolysis was carried out at a temperature below 2000°C to obtain nano alumina, which was then calcined at 1100°C for 2 hours gradually with an increase in temperature of 10°C/minute to remove water and turn the alumina into a perfect crystal. The resulting alumina was characterized using DSC, XRD, and TEM. Characterization with DSC showed that at 760°C there was a phase change from γ-Al_2O_3 to α-Al_2O_3.

The results also show that to convert all γ-Al_2O_3 into α-Al_2O_3 the sample needs to be calcined at temperatures above 1000°C. Characterization of the sample by XRD showed that before calcination the sample consisted of a mixture of α-Al_2O_3 and γ-Al_2O_3 and after calcination at 1100°C, the XRD results showed that the sample was pure α-Al_2O_3, in the sense that it did not contain any more γ-Al_2O_3. Characterization by TEM showed that the sample before calcination had a particle size of 10-30 nm, while after calcination at 1100°C, the sample size became 50-100 nm. This change in particle size indicated that three and four grains grew into one alpha alumina phase particle after calcination and the shape of the particles became more spherical than before calcination [38].

2.3.2.3. Laser ablation Method

The process of the laser ablation method begins by preparing an irradiated corundum crystal target having dimensions of 10 mm × 10 mm × 4 mm with a purity of 99.9%. All ablation experiments were performed at room temperature at atmospheric pressure in distilled water, using a Low Power Thermal Sensor (Ophir; Model 7Z01560) laser beam generator equipped with a laser power meter (Ophir Vega Model). The crystal target is placed in a container containing 20 ml of distilled water and equipped with an electric centrifuge with a rotational speed of 0-100 rpm. In the experiment, the rotational speed used was 40 rpm. The purpose of the rotation is to ensure the sample is irradiated uniformly and to move the water to promote the diffusion of the resulting alumina particles. The laser beam hits the target at an angle that is set using glass, and irradiation lasts for 1-2 hours. After the tools and materials are ready, the laser power measurement is carried out. This measurement was carried out before and after the experiment and the measurement point was under the lens after being exposed to laser light. This measurement is made to ascertain the amount of laser power colliding with a target which is different from the amount of laser power emitted from the source because the laser beam has previously hit mirrors and air or dust. The alumina samples obtained were characterized using XRD, TEM, and SEM.

The results of characterization by XRD and TEM showed that the resulting product was α-Al2O3 with a particle size of 9.3 nm. While the SEM results show that the sintering treatment affects the sample size and particle shape of the resulting alumina samples, the higher the sintering temperature, the larger the particle size and the more spherical shape [39].

2.3.2.4. Combustion Synthesis Method

The process of making alumina with this method begins by making a mother liquor consisting of a mixture of aluminum nitrate solution and citric acid, then the mixture is neutralized (pH 7) using ammonia. For the experiment, solutions were made from the mother liquor with different pH, namely 2, 4, 6, and 10 by adding ammonia solution or nitric acid solution. Then the solution that has been formed is heated to dryness using infrared light, which is directed from the top of the solution until a dry black gel is obtained, and finally, it turns into alumina in the form of fine powder in a foam-like form. The alumina samples formed by this method were characterized using TEM, XRD, and TGA. The results of the analysis with TEM showed that the alumina sample obtained had a particle size of 1 μm. From the results of the characterization using XRD, it is known that the sample which was calcined at 700oC formed delta and gamma alumina phases, and at 1200oC it formed a single phase of alpha alumina. The results of the analysis with TGA showed that the endothermic peak appeared at 300oC and the exothermic peak appeared at 470° [40].

1.3. Zeolite

Zeolite is a mineral resource that is widespread in Indonesia and its development has not been optimal. Zeolite is defined as an alumina-silica hydrate with a three-dimensional framework structure. The zeolite structure consists of tetrahedral alumina (AlOf) and silica (S_1O_4ha), and the cavities are filled with alkaline/alkaline earth metal ions and surrounded by water. The zeolite crystal shape is relatively regular, with cavities interconnected in all directions, and the very large surface area of zeolite makes it an excellent adsorbent [41].

Zeolites have a very complex structure, and their skeletal structure contains intercrystallite channels or interconnected cavities occupied by cations and water molecules. Cations are mobile and usually undergo ion exchange. On the other hand, water can be removed reversibly by applying heat. The intracrystalline channels or cavities can be one-dimensional, two-dimensional, or three-dimensional. The proper dimension for promoting intracrystalline diffusion in adsorption and catalytic applications is 3 dimensions. Chemically, the molecular formula of zeolite is:

$$M_{2/n}O \cdot Al_2O_3 \cdot y\ SiO_2 \cdot w\ H_2O$$

Where y is 2 to 100, n is the valence of the cation and w is the water content in the zeolite shell chamber [42].Zeolite is classified into 4 types [43], namely:

1. Small porous material, having pore holes composed of 6, 8, or 9 tetrahedral (6-, 8- and 9-member rings),
2. The material is medium porous, has 10-member rings,
3. Large porous material, having 12-member rings,
4. Ultra-large porous material, having 14-, 18- or 20-member rings.

1.3.1. Types of Zeolite

Zeolite consists of 2 types, namely natural and synthetic zeolite. Synthetic zeolite is purer when compared to natural zeolite. Natural zeolite obtained by open pit mining can be found mechanically in Indonesia.

2.4.1.1. Natural Zeolite

1.3.1.1.1. Modernite

The Si/Al ratios of the natural and synthetic forms of zeolite mordenite are usually around 5.0 but the aluminum content in the cross-sectional structures can be reduced substantially by acid leaching without loss of crystallinity. The channel structure of mordenite is composed of a 12-membered oxygen ring, having a nominal free diameter of about 6.7–7 A. However, natural mordenite is like a zeolite with small pores, and even small molecules such as methane and ethane are adsorbed very slowly. Large porous mordenite can also be prepared synthetically where channels can be freed from clogging and has the diffusion properties expected of a 12-ringed sieve.

The presence of small amounts of impurities in the crystals has a very large effect on the adsorption ability of mordenite, whereas such amounts have relatively little effect on zeolites A, X, and Y. For similar reasons, the one-dimensional structure makes mordenite unsuitable for applications where there is a possibility of adsorption of hydrocarbons. which results in the formation of carbon/coke in the crystal. The application of mordenite as an adsorbent is limited to relatively clean non-hydrocarbon gases [44]

1.3.1.1.2. Pentasil

The pentasil zeolite comprises a group of silica-rich zeolites with a structure based on a double five-ring. By arranging the sections in different orders, different variations and structures can be obtained. In the ZSM−5 and ZSM−11 zeolites, the channel-channel system is distinguished by a 10-oxygen ring with a free diameter of about 6 A, which is the intermediate product of a small porous sieve with 8-ring channels and a large porous sieve with 12-ring channels. This zeolite has a Si/Al ratio of about 30 but other variations are possible and structures can be prepared in the aluminum-free form. The aluminum-free form of ZSM−5 is often referred to as silicalite [45].

1.3.1.1.3. Clinoptilolite

Clinoptilolite zeolite is one of the zeolites that is often found in nature which has a very high silica content with a Si/Al ratio between 7−18. Natural clinoptilolite zeolite at a temperature of 25 °C and a pressure of 2.6666 kPa its adsorption capacity for H_2O can reach 16 grams of H_2O/100 grams [46].

2.4.1.2. Synthesis Zeolite

Synthetic zeolite can be grouped according to the ratio of the content of Al and Si components in the zeolite into:

2.4.1.2.1. Low Si Zeolite

Zeolite with low Si content is often rich in Al. This type of zeolite contains a lot of Al, is porous, and has high economic value because it is effective for large-capacity separations. The pore volume can reach 0.5 cm3 per cm3 of zeolite volume. Examples of low Si zeolite are zeolite A and X [47].

2.4.1.2.2. Medium Si Zeolite

Zeolite Si content is moderate. This type of modern zeolite has a very stable Si/Al = 5 ratio, so efforts are made to make zeolite with a Si content higher than 1 which is then obtained Y zeolite with a ratio of Si/Al = 1 − 3. An example of this type of synthetic zeolite is omega zeolite [48].

2.4.1.2.3. High Si Content Zeolite

This type of zeolite is very hygroscopic and absorbs non-polar molecules so it is good for use as an acid catalyst for hydrocarbons. This type of zeolite is for example zeolite ZSM−5, ZSM−11, ZSM−21, and ZSM−24 [49].

2.4.1.2.4. Zeolite Si

If the high Si zeolite still contains Al even if only a little, but this Si zeolite does not contain Al at all or has no cation side at all. The nature of this type of zeolite is very hydrophilic-hydrophobic so it can remove or separate an organic molecule from a water mixture. An example of silica zeolite is silicalite [50].

1.3.2. Synthesis of Zeolite

2.4.2.1. Sol-Gel

Zeolites can be synthesized from silica and alumina solutions containing alkaline hydroxides or organic bases to achieve high pH. Alumina silica gel is formed by a condensation reaction. If the silica content of the zeolite is low, the product can often crystallize at 70-100°C, and if the zeolite is rich in silica, most of the hydrothermal product is a gel. In this case, the gel was placed in an autoclave for several days. Zeolite products with a specific structure are formed at temperatures between 100 and 350°C. Variables that determine the type of product include the composition of the initial solution, pH, temperature, aging conditions, and speed of agitation and mixing [51].

2.4.2.2. Hydrothermal Synthesis

Most zeolites are prepared by hydrothermal synthesis. Synthesis conditions depend on the desired material composition, particle size, morphology, and so on. The synthesis process is sensitive to several variables such as impurity (impurities), mixing and washing time, temperature, pH, silica and alumina sources, type of alkaline cation, and reaction time as well as surfactants.

An example of the application of hydrothermal synthesis is in the manufacture of zeolite with rice husks. Sodium silicate solution was prepared from 2.94 g SiO2 from rice husk ash mixed with 16.264 g NaOH and 50 mL of distilled water. The mixture was heated at 50°C for 3 hours accompanied by stirring with a magnetic stirrer. Sodium aluminate solution was prepared from 4.7503 g Al2O3 mixed with 16.264 g NaOH and 50 mL of distilled water. The mixture was heated at 50°C for 1 hour accompanied by stirring with a magnetic stirrer. Zeolite synthesis was carried out by the hydrothermal method using an autoclave based on Nur's procedure. The sodium silicate solution is mixed with the sodium aluminate solution accompanied by stirring using a magnetic stirrer for 1 hour. The mixture was put in the autoclave and heated in an oven at 160°C for 7 hours. The precipitate is washed until the pH is neutral, then dried in an oven for 1 hour at 105ºC. The precipitate was calcined in a furnace at 400ºC for 1 hour. Weigh the weight of the zeolite obtained. The resulting zeolite was tested for its characteristics using FT-IR and XRD [52].

2.4.2.3. Microwave Technic

The technology that was introduced was the use of microwaves. Although not yet fully successful, this technology provides good prospects in improving zeolite synthesis techniques whereby zeolite can be made in a very short time. Several researchers reported that with this technique, zeolite can be synthesized within 20 minutes, after the solution mixing process. The principle of microwave application is to utilize electromagnetic waves with a frequency of 300 MHz–300 GHz to mix aluminate and silicate solutions until a homogeneous mixture is formed. The process of making zeolite is carried out using a microwave at various temperatures and times. Temperature variations are adjusted according to the settings in the microwave, namely low, medium low, and medium conditions. So far, this technique is relatively better when compared to the hydrothermal technique, because it is faster in synthesis and not a lot of chemicals are wasted [53].

1.3.3. Zeolite Characteristic

Characteristics of natural zeolite include increased acidity, crystallinity, specific surface area and Si/Al ratio, and loss of impurities. Zeolite has chemical properties, including:

2.4.3.1. Dehydration

Dehydration of zeolite affects its adsorption properties. The uniqueness of zeolite lies in its unique pore structure. Natural zeolite has cations or water molecules in its pores. Zeolite leaves empty pores when cations or water molecules are removed from the pores by several treatments [54].

2.4.3.2. Absorption

Under normal circumstances, the cavity of the zeolite crystal is filled with water molecules surrounding the cations. Water escapes when the zeolite is heated. The heated zeolite can act as a gas or liquid absorbent [55].

2.4.3.3. Ion Exchange

The ions in the voids help maintain the neutrality of the zeolite. Because these ions are free to move, the ion exchange that occurs depends on the size and charge, as well as the type of zeolite. The properties of zeolite as an ion exchanger depend on the type of cation, temperature, and type of anion [56].

2.4.3.4. Catalyst

Zeolite as a catalyst can increase the difference in the molecular pathways of the reaction so that it only affects the reaction rate without affecting the reaction balance. Porous catalysts with very small pores contain small molecules, but prevent the entry of large molecules. This molecular selectivity is called molecular sieves which are found in natural zeolite materials [57].

2.4.3.5. Filter/Separation

Zeolite as a filter or molecule separator is based on differences in the shape, size, and polarity of the molecules being filtered. This property is because the zeolite has a large enough vacuum. Molecules smaller than the vacuum can pass, but molecules larger than the vacuum are compressed [58].

4. Conclusion

The wastewater from LIBs production is unavoidable; thus, proper wastewater treatment is necessary to assure the sustainability of the technology. The adsorption of inorganic pollutants is considered a win-win solution. The selection of adsorbents such as silica (SiO_2), titania (TiO_2), alumina (Al_2O_3), activated carbon, and zeolites offer different characteristics. The processing of these types of material is discussed and most of them require precursors that can be obtained from another source of waste. This means the waste treatment is not only reducing one type of pollutant but also another type of pollutant during the synthesis of adsorbents. In the end, we believe that the adsorption of pollutants is cost-effective and eco-friendly based on the production process and the implementation.

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