DOI: 10.21776/ub.jpacr.2019.008.03.477 *J. Pure App. Chem. Res.*, **2019**, 8 (3), 232-238
12 December 2019

The Effect of Acidity and Aging Time in The Synthesis of $Al(OH)_3$ from The Anodized-Waste with A Sol-Gel Method

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Received 12 May 2019; Accepted 12 December 2019

ABSTRACT

Synthesis of alumina has been carried out by utilizing anodized waste as raw material. Anodized waste is a by-product of metal anodizing processes such as aluminium. This study aims to determine the effect of acidity (pH) and aging time on the mass of $Al(OH)_3$ and the property of $Al(OH)_3$ as well as Al_2O_3 that produced. Anodized waste was deposited into $Al(OH)_3$ and then purified. Alumina synthesized by the sol-gel method with pH variations of 7, 8, 9, and 10 and aging times of 24, 48, and 72 hours. The $Al(OH)_3$, which has been produced, was characterized by PSA and powder XRD spectrophotometer. The results showed that the synthesis of $Al(OH)_3$ was influenced by pH and aging time. It affects the yield and particle size of $Al(OH)_3$. The optimum condition of the synthesis was pH 7 and aging time of 24 hours with yield of 1.85 grams. Characterization by PSA at a current diameter of 90% indicate that higher pH value and longer aging time produces smaller particle size. Characterization by powder XRD shows that the $Al(OH)_3$ has *gibbsite* crystal phase with *d* values of 3.360, 3.217, 2.252, 2.029, and 1.649 Å.

Keyword: alumina, sol-gel method, characteristic, waste

INTRODUCTION

Anodization is the process of electrolysis of the formation of an oxide layer in metals by reacting a metal, one of which is aluminum with oxygen from an electrolyte solution as a medium [1]. Anodized liquid waste contains a lot of dangerous heavy metals [2]. According to Naziruddin et al. [3], the metals contained in anodized wastes was Al, Cu, Ni, and Zn. Aluminum content in about 3.6-6.0 mg/L of water can cause hardness of water, and endangers the human health [4]. Finding the way for reducing the negative impact of anodized waste to the environment and also to human is important stage [5]. And applying this waste as source for $Al(OH)_3$ [6-7] and for calcined alumina [8-9] is an alternative.

Alumina is one type of oxide ceramic which is widely applied in the fields of electronics, thermal, catalyst and mechanical chemistry. Alumina has a superior strength and hardness properties, was often used as material in engineering, such as for aircraft constructing materials. In addition, alumina has a very low electrical conductivity, that is commonly applied as an electrical insulator material [10]. In other report, applying alumina for textile coating material. It is used for finishing process of textile, due to form a transparent thin layer on the textiles. The process applying it on the surface by sol-gel technique [11]. Following the alumina crystal structure, it has a very stable form, namely α-Al_2O_3. But also has metastable crystal structures, namely γ-Al_2O_3, θ-Al_2O_3, δ-Al_2O_3, κ-Al_2O_3, and χ-Al_2O_3

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p-ISSN : 2302 – 4690 | e-ISSN : 2541 – 0733

[12]. The general method applied to prepare γ-alumina is sol-gel technique. The sol-gel process is a phase change from colloidal (sol) suspension to form a continuous liquid phase (gel) based on hydrolysis and condensation reactions on alkoxide or metalloid transition metal compounds [11]. The sol gel method is a good method because it can produce particles with a large surface area, high purity, good thermal stability, and high mechanical stability [12]. The parameters influence the sol-gel method include acidity or pH condition during synthesis and also the aging time. In the sol-gel process, pH affects the hydrolysis and condensation during gel formation. Moreover, the pH also affects the particle size and the purity of the product [13]. According to Meirawati et al. [14] and Mardiana et al. [15], the particle size of the synthesized gel was greater, when the aging time was extended. Gel tissues formation surrounded outer side causes the size increment, and also the gel afforded stronger.

EXPERIMENT

Chemicals and instrumentation

Chemical used for research i.e. sodium hydroxide (Merck), hydrochloric acid (37%, Merck), ammonia (Merck, distillated water, pH indicator universal. While some equipment applied for analysis such as particle size analyzer (PSA 1090-Cilas) and X-ray diffraction spectrometer (PanAnalytical type Expert).

Reaction Procedures

Sample preparation was done by firstly filtering off the liquid anodized waste samples from macro impurity, and the filtrate was used for synthesis. Aluminium extraction from anodized waste was undergone by taking a 50 mL of liquid anodizing waste. And then, it was added with 4.0 M NaOH solution until the waste pH was 10. This mixture was further filtered off. The precipitate was dried at 100 °C for 5 hours and weighed until a constant mass was reached. This a dried precipitate, then, was added with a NaOH solution until pH of 14. The mixture was filtered off and the filtrate was used for further step.

Synthesis of $Al(OH)_3$ with the sol-gel method was taken placed by neutralizing the filrtrate solution with 2.0 M hydrochloric acid solution until pH 7. During which in a cloudy gel was formed after several hours of aging. The effect of final pH (7, 8, 9, and 10) and aging time during gelling process was studied by varying the aging time (24, 48, and 72 hours) at room temperature. The formed gel then filtered off and washed with distilled water several times. Finally, the gel was dried in an oven for 24 hours at 100 °C. The product was then weighed to constant mass. The dried solids were further characterized by powder X-ray diffraction spectrometer and particle size analyzer.

RESULT AND DISCUSSION

Extraction of Al from Anodized Waste

Anodized liquid waste is cloudy yellow, has a strong odor, and pH 1. The addition of NaOH (strong base) to the anodized waste aims to form $Al(OH)_3$ precipitate. The reaction process following equation 1 [16]. The mass of $Al(OH)_3$ obtained from 100 mL of the anodized waste was 6.03 ± 0.71 g. Based on Munawarti et al. [17], $Al(OH)_3$ was produced at this stage contains a high quantity of impurities. Purification can be done by dissolving of $Al(OH)_3$ with sodium hydroxide solution until pH 14, to produce the sodium aluminate. The formation reaction of sodium aluminate is presented in equation 2 [17]. The by product as impurities for the reaction as reported [18] was iron(III) hydroxide. The presence of this impurities produces an orange suspension of $Fe(OH)_{3(s)}$ [19]. Separation by filter paper resulting in orange deposits and a clear yellow filtrate.

$$Al^{3+}_{(aq)} + 3OH^{-}_{(aq)} \rightarrow Al(OH)_{3(s)} \quad (1)$$

$$(2Al(OH)_{3(s)} + impurities) + 2NaOH_{(aq)} \rightarrow Na_2Al_2O_{4(aq)} + 4H_2O_{(l)} + impurities_{(s)} \quad (2)$$

$$Na_2Al_2O_{4(aq)} + 6HCl_{(aq)} \rightarrow 2AlCl_{3(aq)} + 2H_2O_{(l)} + 2NaOH_{(aq)} \quad (3)$$

$$2AlCl_{3(aq)} + 6H_2O_{(l)} + 6NH_{3(l)} \rightarrow 2Al(OH)_{3(s)} + 6NH_4Cl_{(aq)} \quad (4)$$

Synthesis of $Al(OH)_3$ by the Sol Gel method
The effect of pH conditions

Mixing of sodium aluminate with hydrochloric acid solution, produces aqueous of aluminium chloride or $AlCl_{3(aq)}$ (equation 3). Addition of 25% ammonia solution to pH 7 filtrate was carried out to study the effect of pH (8, 9, and 10) on the synthesis of $Al(OH)_3$. The reaction between $AlCl_3$ and NH_3 is presented in equation 4. The addition of 25% ammonia solution aims to form sol in an alkaline condition. The sol was stand at room temperature with aging times of 24, 48, and 72 hours to form a gel of $Al(OH)_3$.

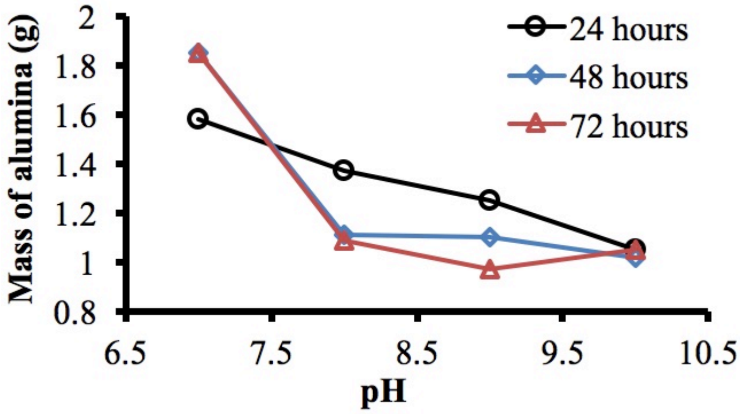

Figure 1. Effect of pH synthesis on the mass of $Al(OH)_3$ produced

Figure 1, is depicted the yield of $Al(OH)_3$ at various pH. The pH condition varies into several value, from pH 7 to pH 10. The reaction was undergone in room temperature and stood for 24, 48, and 72 hours. It shows that pH affects the yield of $Al(OH)_3$ with optimum pH of 7. The increment of pH solution, decrease the mass of $Al(OH)_3$ formed. The highest $Al(OH)_3$ mass was produced at pH 7.0 in both 48 and 72 hours. The process affords $Al(OH)_3$ in about 1.85 g, however, it gives 1.62 g of $Al(OH)_3$ for 24 hours. The yield drops to almost 1.0 g at pH of 10. It was predicted that acidity decrease or pH value above 8.0 was able to dissolve the aluminium hydroxide [20].

Effect of Aging Time on the mass of $Al(OH)_3$

Figure 2 shows that aging time affects the mass of $Al(OH)_3$. The highest mass of $Al(OH)_3$ occurs at aging 48, and 72 hours at pH 7. However, at pH 8, 9 and 10, the longer the aging time the less mass of $Al(OH)_3$ is formed. This is probably caused by the dissolution of $Al(OH)_3$ at pH 8, 9, and 10 with longer aging times. $Al(OH)_3$ dissolves to form aluminate ions when there is a strong base [16,21] as in the reaction equations 5 and 6.

$$2Al_{(s)} + 2OH^-_{(aq)} + 6H_2O_{(l)} \rightarrow 2[Al(OH)_4]^-_{(aq)} + 3H_{2(g)} \quad (5)$$

$$Al(OH)_{3(s)} + OH^-_{(aq)} \rightarrow [Al(OH)_4]^-_{(aq)} \quad (6)$$

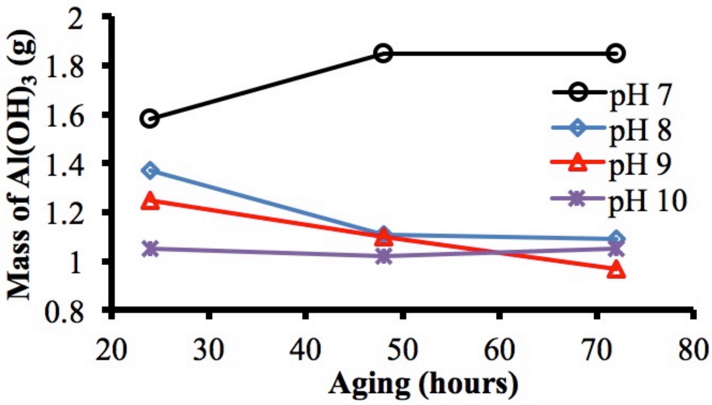

Figure 2. Effect of aging time on the synthesis of $Al(OH)_3$

Table 1. Results of characterization of PSA $Al(OH)_3$ pH 7

Aging times (hours)	Diameter $Al(OH)_3$ particle (µm)		
	10%	**50%**	**90%**
24	11.65	124. 52	419.83
48	16.19	128.78	406.58
72	14.57	120.17	402.04

Table 2. Results of characterization of PSA $Al(OH)_3$ in various pH

pH condition	Diameter of $Al(OH)_3$ particle (µm)		
	10%	**50%**	**90%**
7	11.65	124.52	419.83
8	13.10	117.97	397.76
9	17.56	122.49	389.94
10	3.55	51.22	146.83

Characterization with Particle Size Analyzer (PSA)

Analysis of the particle size of $Al(OH)_3$ gel is summarized in Tables 1 and 2. In overall, the mean that aging time is getting longer then the particle size is getting smaller and the pH is getting higher than the size gets smaller too. The crystal core is formed during aging. The longer the aging time, the more the crystal core is formed so that the smaller the crystal size. This is in accordance with the literature [22], increasing pH can cause smaller particle size. pH affects the solubility of the precursor and the ratio of ion configurations that dissolve and settle.

Characterization of $Al(OH)_3$ with XRD

The diffractogram of produced $Al(OH)_3$ gel at pH 7 with aging time 48 hours is depicted in Figure 3. A sharp peak and clean diffractogram is afforded. It indicates a high crystalline of $Al(OH)_3$ was formed. The d(Å) value recorded are 3.360; 3.217; 2.252; 2.029; and 1.649. Summary is tabulated in Table 3, and the d(Å) value of aluminum hydroxide synthesized were compared with data from reference [23]. The d(Å) value of synthesized $Al(OH)_3$ corresponds to polymorphic gibbsite d(Å) $Al(OH)_3$.

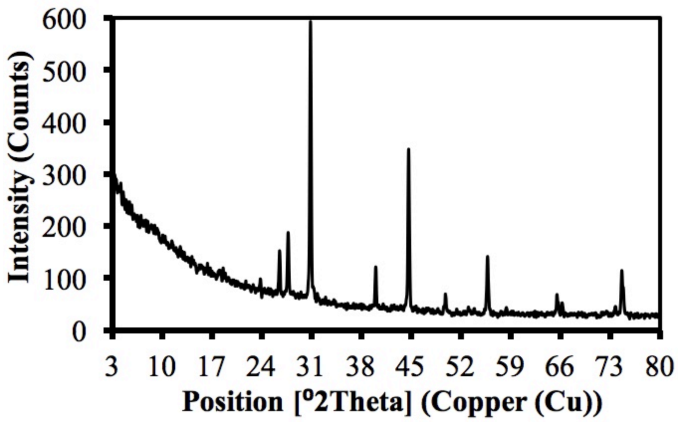

Figure 3. Diffractogram of $Al(OH)_3$ pH 7

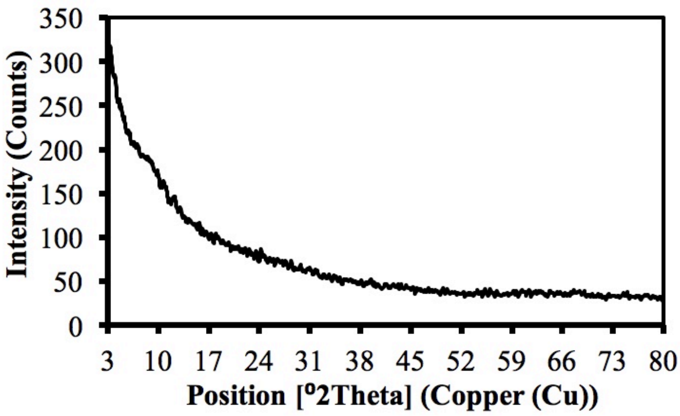

Figure 4. Diffractogram of $Al(OH)_3$ pH 10

Moreover, the diffractogram of $Al(OH)_3$ produced from pH 10 is displayed in Figure 4. The aging for 72 hours at this pH provide the characteristics of $Al(OH)_3$ with poor crystallinity or amorphous form. Amorphous form of $Al(OH)_3$ is influenced by pH which is high and long aging time, so the crystallinity of $Al(OH)_3$ is damaged or dissolved when reacting with strong bases as in equation 6. Aluminum hydroxide crystals react with excess hydroxide ions. This reaction causes the crystallinity of aluminum hydroxide to decrease and form amorphous aluminum hydroxide which then dissolves in an alkaline solution.

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Table 3. Data of d (Å) and intensity (%) of $Al(OH)_3$

$Al(OH)_3$ produced by sol-gel (pH 7 and aging 48 h)		Gibbsite (γ-$Al(OH)_3$) from literature [23]	
d Å	**Intensity (%)**	**d Å**	**Intensity (%)**
4.766	4	4.848	100
3.360	16	3.359	17
3.218	22	3.182	25
2.252	16	2.385	55
2.042	4	2.048	40
2.029	66	2.023	3
1.837	3	1.804	30
1.649	24	1.684	30
1.425	10	1.457	30
1.411	7	1.411	19
1.285	4	1.299	3

CONCLUSION

The yield of $Al(OH)_3$ is influenced by pH and aging time. The optimum condition is pH 7 and aging time of 48 hours. In this condition, 1.85 g of $Al(OH)_3$ was obtained. The size of $Al(OH)_3$ particles is smaller as pH and aging time increased. Characterization of $Al(OH)_3$ with XRD shows that the obtained $Al(OH)_3$ is Gibbsite.

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