Synthesis of alumina nanoparticles by sol-gel method and their applications in the removal of copper ions (Cu\textsuperscript{2+}) from the solution

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Abstract. Two different phases of alumina (Al\textsubscript{2}O\textsubscript{3}) nanoparticles (γ-alumina and α-alumina) have successfully been synthesized by using a sol-gel method. During the process a mixture of aluminum nitrate and citric acid (C/N=0.5) was heated at 60°C followed by 80°C until a gel was formed. The amorphous gel structure then was dried and sintered from 600°C to 1200°C. From the X-ray diffraction (XRD) analysis, crystalline structure of γ-alumina started to form at 800°C with average crystallite size of 11.5 nm, followed by the formation of the mixture phase of γ-alumina and α-alumina at 1000°C. The transformation from γ- to α-alumina occurred at 1100°C of sintering temperature and above with the average crystallite size of 49 nm. The efficiency of the synthesized alumina nanoparticles as an adsorbents was tested by immersing the powder into the copper ions solution. The percentage of the copper removal was measured by using atomic absorption spectroscopy (AAS). It was found that, the efficiency of the alumina nanoparticles as an adsorbent was not depending on their phases, but might due to the increased of the particle size at higher sintering temperature. The highest percentage of removal 82.1% was obtained when using the alumina sintered at 1200°C.

1 Introduction

Alumina (Al\textsubscript{2}O\textsubscript{3}) has been used in different applications because of its various importance and beneficial properties. The chemical compound of alumina composed of aluminum and oxygen and most widely used ceramic materials among others ceramic material such as aluminum nitride, zirconia, silicon carbide, etc. Various applications that used alumina are as a biomedical implants, catalyst support and absorbents, fire retardants, polymer matrix composite, insulator and in clinical field, electronic fields, etc. [1-6]. The reason of alumina most widely attractive used material in many application is due to its greater properties such

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as chemical and thermal stability, relatively good strength, good wear resistance, high hardness, high melting points, and good electrical and chemical resistance [7].

Alumina can be synthesized into different phases including alpha, beta, gamma, and delta. All of these phases can be attained at different temperature during synthesizing of alumina. Each phase have its own features which are different for application used. However, among these phases the alpha alumina is most stable structure and popular among researchers due to its superior properties such as high hardness, high stability, high insulation and transparency [8]. The basic unit cell structure of alpha-alumina is hexagonal. While internal crystal structure of alpha-alumina for oxygen is in close packed hexagonal with aluminum in 2/3 of octahedral sites.

The synthesis of alumina nanoparticle can be used by using variety of methods such as, vapor phase reaction, mechanical milling, sol-gel, hydrothermal, combustion and, precipitation method. The synthesis of alumina by using mechanical milling are easily introduces contaminations. The preparation of alumina via vapor phase reaction demand high temperature above 1200°C. The precipitation method need long washing and aging time which are contribute to long time consuming. Hydrothermal process needs high pressure and temperature that can cause the increasing in cost. While, alumina powders that yield via combustion method contains nano sized primary particles. Sol gel is a method ordinarily use precursor that good control over stoichiometry and morphology of nanoparticles. Thus, among these methods sol gel are the most favorable and mostly investigated because it produces high purity and high specific surface area of solid particles [9].

Waste water treatment are quite challenging due to the development of the industrial activities. For example, heavy metal ion is the one material content in the waste water include copper (Cu²⁺), cadmium (Cd²⁺), zinc (Zn²⁺). These hazardous materials are come from the waste product industry activity such as electroplating, galvanizing and mine drainage. Therefore, several of treatments have been done in order to overcome this problem. This include by using the metal oxide as an adsorbent metal through adsorption process instead of filtering the metal ion. Alumina is one of the effective metal oxide which it can be as adsorbent material [10].

2 Experimental

The reagents that were applied during the experiments were aluminum nitrate (Al(NO₃)₃·9H₂O, Merck) citric acid (C₆H₈O₇H₂O, Sigma-Aldrich) and deionized water. All the materials were used as-received without further purification.

2.1 Synthesis of alumina nanoparticles

Alumina nanoparticles were synthesized by using a sol-gel method. About 18.76 g of aluminum nitrate was dissolved with citric acid in the deionized water. The molar ratio of the citrate/nitrate (C/N) was 0.5. The solution was stirred continuously for several hours at 60°C until it turned into a yellowish sol. Then, the solution was heated up to 80°C under constant stirring until the transparent gel was formed. The gel was dried at 90°C in the oven for 12 hours. The dried gel was ground and sintered at 600°C, labeled as Sample A.

The synthesis of alumina nanoparticles was repeated by using the same process as described above and were sintered at temperature of 700°C, 800°C, 900°C, 1000°C, 1100°C, and 1200°C, labelled as Sample B, Sample C, Sample D, Sample E, Sample F, and Sample G, respectively.
2.2 Characterization of the materials

The phases of the synthesized sample were determined by using X-ray diffraction (XRD) model Shimadzu XRD-6000 at room temperature. The X-ray copper (Cu) tube was used with radiation wavelength of $\lambda = 1.54\text{Å}$ in the range of $2\theta = 10^\circ-80^\circ$ at scanning speed of 30 kV and 10 mA. The average crystallite size of alumina nanoparticles was calculated according to the Scherrer equation as shown in Eq. (1) by using the FWHM data of each phase after correcting the instrumental broadening.

\[
t = \frac{0.9 \lambda}{B \cos \theta}
\]  

where,
- $t$ = estimate of the crystallite size
- $\lambda$ = X-ray wavelength of the source material
- $\theta$ = Bragg angle.
- $B$ = spectral breadth due to the crystallite size effect.

The morphology and elemental analysis of the alumina nanoparticles were identified by using a scanning electron microscopy (SEM) JOEL-JSM 6460 LA with an energy dispersive analyzer (EDX).

2.3 Application of the synthesized alumina particles in adsorption of copper ions (Cu$^{2+}$)

For the adsorption of Cu$^{2+}$, about 1 g of alumina nanoparticles (Sample A) was added into the 100 ml of 150 mg/L copper sulphate (CuSO$_4$) solution. The mixture was mixed for 60 minutes by using an orbital shaker at the speed of 200 rpm. Then, the solution was filtered by using a Whatmann No.1 filter paper, followed by the Cu analysis of the filtrate by using an atomic absorption spectrometry (AAS). For the analysis, the filtrate was dissolved in 25 ml of hydrochloric acid and few drops of nitric acid, followed by the dilution with 1L of deionized water in the volumetric flask. The presence of residual alumina in filtrate was also identified by using AAS to ensure the minimum leaks of alumina from the samples into the filtrate. The adsorption process was repeated by using sample B-G.

3 Results and discussion

Alumina nanoparticles is expected to be physically white after the sintering process. However, from Fig.1 only samples E, F and G turned into white powders, which were sintered at 1000°C, 1100°C and 1200°C respectively. Sintering at temperature below than 1000°C resulted in the black powders. The black appearance of the powder is expected due to the existence of the residual carbon inherited from the sol that was not fully burnout during sintering below 1000°C [11].
Fig. 1. The sintered samples at different temperature (A) 600°C (B) 700°C (C) 800°C (D) 900°C (E) 1000°C (F) 1100°C and (G) 1200°C.

Fig. 2 shows XRD pattern of the phases formed after the sintering process. The amorphous structures are observed for the powder sintered at 600°C and 700°C. When the sintering temperature was increased to 800°C, there are peaks appeared at 2θ values, 61.3°(440) and 46.7° (400), which reflects to the γ-alumina peaks that indicates the transition of amorphous structure into γ-alumina phase. The formation of γ-alumina becomes stronger at 900°C where additional of γ-alumina peak at 38.5°(222) appeared. At 1000°C there are peaks of α-alumina started to grow at 44.3°(113), 35.1°(104) and 26.4°(012). Transformation of γ-alumina into α-alumina completely occured at 1100°C. At sintering temperature of 1200°C, the α-alumina phase is remain unchanged.

Fig.2. XRD pattern of the synthesized sample and heat treated at (a) 1200°C, (b) 1100°C, (c) 1000°C, (d) 900°C, (e) 800°C, (f) 700°C, (g) 600°C.

The crystallite size for α- and γ-alumina nanoparticles were calculated from few most intense XRD peaks by using a Scherrer equation. The average of the crystallite size is presented in Table 1. At sintering temperature 600°C and 700°C, since the structure was
amorphous, no crystallite size can be determined. For Sample C, which is sintered at 800°C, the average crystallite size is 11.5 nm. When the temperature was increased to 900°C, the crystallite growth is up to 15.5 nm in average and this value is not far difference with Sample E which consist of mixture phases of alumina. The obvious crystallite growth can be seen when the sintering temperature was raised to 1100°C and 1200°C where the average crystallite size are 46.6 nm and 49.1 nm, respectively. The rapid growth of the crystallite due to particles coarsening of α-alumina at higher temperature [12].

Table 1. The crystallite size and phase structure of the synthesized Al₂O₃ sintered at different temperatures.

| Sample | Sintering temperature (°C) | Crystallite size (nm) | Phase structure  |
|--------|---------------------------|----------------------|-----------------|
| A      | 600°C                     | -                    | Amorphous       |
| B      | 700°C                     | -                    | Amorphous       |
| C      | 800°C                     | 11.5                 | γ-alumina       |
| D      | 900°C                     | 15.5                 | γ-alumina       |
| E      | 1000°C                    | 19.2                 | α- + γ-alumina  |
| F      | 1100°C                    | 46.6                 | α-alumina       |
| G      | 1200°C                    | 49.1                 | α-alumina       |

Fig. 3 shows the morphology of the alumina nanoparticles before and after sintering. The images were captured under 2000x of magnification. It can clearly be observed the big agglomeration of alumina nanoparticles, thus the particle size cannot be calculated. This might due to no surfactant added during the sol-gel synthesis [13]. The EDX analysis also was conducted for sample A, D and G. From Fig. 4, the percentage of carbon decreased as the sintering temperature increased. The weight percent of carbon at 600°C was 15.4 and then decreased to 13.40 at 900°C and the carbon peak disappeared at 1200°C. The present of residual carbon in the alumina nanoparticles is due to the citric acid used during the experimental work. At 1200°C the carbon was fully burnout resulted in white color powder. Additionally, since the sample was coated by platinum before the SEM analysis in order to make the sample conductive, the small amount of element Pt also has been detected. Nevertheless, percent of element Al still has the highest amount of percentage among the samples.
Fig. 3. SEM micrographs of alumina nanoparticles sintered at different temperature (a) 0°C, (b) 600°C (c) 700°C (d) 800°C (e) 900°C (f) 1000°C (g) 1100°C and (h) 1200°C.
The efficiency of the synthesized alumina nanoparticles as an adsorbents for the removal of copper ions (Cu$^{2+}$) from the solution was tested. From the results, the amorphous samples (sintered at 600°C and 700°C), about 70.4% and 71.6% of copper ions can be removed, respectively. The percentage of the copper ion removal increased for the crystalline alumina. For the γ-alumina nanoparticles which was formed at 800°C and 900°C, about 76.7% and 78.4% of copper ions can be removed from the solution. The percentage of the copper ions removal was increased as the sintering temperature increased with maximum of the removal about 82.1%. From Table 1, the sintering temperature caused the crystallite size to grow. A particle may made up from several crystallites except for the single crystal [14]. For this case, the synthesized alumina is not a single crystal and it is expected that their particle size consist of several crystallites. Thus, it is expected that as the crystallite size growth, the particle size also becomes bigger. Based on this results, the increased of the percentage of the copper removal might not depending on the phase of alumina, but might due to the particle size since the bigger the size, the higher the surface area for the absorption to occur. However, not 100% of copper ions can be removed from the solution. This situation might due to the several factors that affected the adsorption process including the heavy metal ion concentration, adsorbent dosage, pH of the solution, temperature, etc. [15].

4 Conclusion

Alumina nanoparticles was successfully synthesized via the sol-gel method by using a citric precursor derived from aluminum nitrate and citric acid (C/N=0.5) mixed solution. Sintering at 800°C change the amorphous structure into crystalline γ-alumina with the average crystallite size of 11.5 nm. The γ-alumina continue to growth at higher sintering temperature.
until the white powder of α-alumina formed at 1100°C and 1200°C with rapid growth of the crystallite size about 48 nm in average. For the application as an adsorbent, the efficiency of the copper ions removal from the solution is not depending on the alumina phases, but might due to the increased of particle size at higher sintering temperature. The highest percentage of removal 82.1% was obtained when using the alumina sintered at 1200°C.

This work was financially supported by the Fundamental Research Grant Scheme FRGS/1/2014/TK04/UNIMAP/02/2 from Ministry of Education Malaysia (MOE). The supports from School of Materials Engineering, Universiti Malaysia Perlis are greatly acknowledged.

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