Synthesis, Characterization and Efficiency of Alum Produced from Waste Aluminium Cans for Wastewater Treatment

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Abstract

Herein, the synthesis, characterization and efficiency test of alum obtained from waste aluminium cans were investigated for wastewater treatment. Prior to the synthesis of the alum, the cans were subjected to physical treatments such as communition (size reduction), plastic components removal, colour label removal, cleaning, pulverization etc. The physically treated waste aluminium cans were later chemically and step wisely converted to alum-a viable double salt. The process economy was found to be 99.37%. The synthesized alum and purchased alum were analyzed both qualitatively and quantitatively. The two samples exhibit similar coagulation performance.

Keywords: Alum; communition; process economy; coagulation performance

1. Introduction

Aluminum is one of the most important metals used by modern societies. The combination of the physical properties of aluminium results in its use in a wide variety of products, many of which are indispensable to modern life. Partly to this reason, the global production of aluminium in 2005 rose to 31.9 million tonnes, and the world aluminum consumption, which was 45.3 Mt in 2006, is estimated to be 59 Mt in 2015, 92 Mt in 2020, and 120 Mt in 2025 (Menzie et al., 2010). For instance aluminium has a light weight, high corrosion resistance, good formability, and is non-toxic. These qualities have made aluminium the fastest-growing metallic material in the past 100 years (Boin, 2005). Aluminium has found application in transportation, packaging and construction company (EAA, 2012), household use, alloy (World coin news, 1992 and Skachkov, 2014). For the sake of brevity, the detailed chemistry of the aluminium can be found in most basic inorganic chemistry books and related publications.

Nonetheless, aluminium is found in combined state in over 270 different minerals (Ugwekar et al., 2012). The chief ore being bauxite (Al_2O_3) requires 780 kJ for the production of 1 mole of aluminium (Shakhashir, 2008). This amount is on a high side in terms of energy requirement and on a debit side in terms of cost for a product that will be eventually be discarded as waste even indiscriminately most of the time. For instance, with a global primary metal use of 27.4 million tonnes, a recycled aluminum production from purchased and tolled scrap of approximately 13.1 million tonnes in 2003, aluminium has taken the top position of all the non-ferrous metals (Boin, 2005). Though, recycling of aluminum saves considerable energy (26 kJ/mol) (Shakhashir, 2008) of aluminium but considering, the huge amount of aluminium to be recycled, this option seems energy and cost consuming in a country with a developing economy. Another viable option is to convert the waste aluminium into other aluminium compounds such as alum ($KAl(SO_4)_2 \cdot 12H_2O$), an important and common double

salt while simultaneously producing hydrogen gas.

Alum is a widely used chemical in industry, playing an important role in the production of many products used in the home and industry. The pulp and paper industry alone consumes 70 % of more than one million tonnes of alum produced annually in the United State of America. The second largest use is in the purification of water for human and industrial consumption (Ugwekar et al., 2012; Rice, 1957). Other uses include soaps, greases, fire extinguisher compounds, textiles, leather, synthetic rubber, drugs, cosmetics, cement, plastics, and pickles (Birni-Yauri, 2014). Alum's anti-perspirant and anti-bacterial properties (Ugwekar et al., 2012 and Aguilar et al., 1956) contribute to its traditional use as an underarm deodorant. Other uses of alum include its waterproofing agent and accelerator in concrete, as a clarifier for fats and oils and as a foaming agent in fire foams (Kanlayavattanakul et al., 2011), and finally, alum is the major adjuvant used to increase the efficacy of vaccines, and has been used since the 1920s (Mbow et al., 2011; Marrack et al., 2009). Alum has also been found to stop bleeding in cases of hemorrhagic cystitis (Kennedy, 1984). Hydrogen gas on the other hand has a great potential use as a fuel. Limited reports have been found on the synthesis of alum- a vital product from waste aluminium using local and cheap resources. In this report however, the aim is to synthesize a common aluminium compound called alum from aluminium waste to complement the existing waste aluminium waste management processes and also to make alum more readily available to the growing water treatment industries.

Recent product synthesis studies have shown the importance of process economy in the justification of such synthesis especially on a large scale basis (David *et al.,* 2006). A number of metrics have been proposed almost a decade ago to make chemist's aware of the need to change the practice of chemical synthesis so that they become less wasteful, (David et al., 2006). Hudlicky et al., 1999 proposed a metric known as effective mass yield (Eq. 1.0) that is defined as the percentage of the mass of desired product relative to the mass of all non-benign materials used in its synthesis.

$$\text{Effective mass yield} = \frac{\text{mass of product}}{\text{mass of non-benign reagent}} \times 100 \quad (1)$$

Sheldon 1992 also proposed a metric known as E-factor which is defined as:

$$E\ factor = \frac{Total\ waste\ (kg)}{kg\ product} \quad (2)$$

Curzons et al., 2001 similarly proposed a metric known as

$$Mass\ Intensity = \frac{Total\ mass\ used\ in\ a\ process\ or\ process\ step\ (Kg)}{mass\ of\ product\ (kg)} \quad (3)$$

Other metrics (Eq. 4-5) developed and explored by GlaxoSmithKline both in U.S.A and U.K are

$$Reaction\ Mass\ Efficiency = \frac{mass\ of\ product}{mass\ of\ reactant} \times 100 \quad (4)$$

$$Atom\ Economy = \frac{molecular\ weight\ of\ desired\ product}{molecular\ weights\ of\ all\ the\ reactants\ or\ products} \quad (5)$$

Wang *et al*., (2011) also described and proposed another concept called real atom economy or effective atom economy (Eq. 6).

$$Real\ Atom\ Economy = \frac{Actual\ weight\ of\ desired\ product(kg)}{Total\ weight\ of\ all\ raw\ materials\ in\ the\ product(kg)} \quad (6)$$

Secondly, and to the best of our knowledge, no study has reported prior to this, the characterization or parameterization of the process economy of the aluminium waste management process the case of which is being considered in this study.

2. Materials and Reagents

Aluminium beverage cans were collected from domestic homes in Olorunkemi area, Oke-baale, Osogbo, Osun State, Nigeria longitude and latitude 7.7667° N, 4.5667° E, Distilled water, KOH, H_2SO_4, NaCl, $BaCl_2$, glycerol were obtained from Zayo-Sigma (Germany) while C_2H_5OH, HCl, isopropane and $NH_{3(aq)}$ were obtained from Sigma-Aldrich (USA). All reagents were used as received.

2.1 Methods

2.1.1. Synthesis of Alum

The recent method of Birni-Yauri 2014 was adopted herein for the synthesis of the alum. Empty aluminium beverage cans were broken into small pieces. Plastic coatings over the cans were removed using sand paper. 1.0 g of clean aluminium pieces was weighed and transferred into 250 ml beaker and placed in a fume cupboard. 50 ml of 1.4 M KOH solution was slowly added till there is evidence of effervescence.

During the reaction, the initially colourless mixture was turned to dark grey and black. The cold black solution formed was filtered. The filtrate was a clear and colourless solution. The clear filtrate was transferred into a clean beaker, cooled by placing the beaker in a cooling bath of cold water. Slowly and carefully, (with a graduated cylinder) and stirring quickly with care, 20.0 mL of 9.0 M solution of H_2SO_4 was added to the cooled and colourless solution till the solution get warm. Initially, a thick, white, gelatinous precipitate was formed, as more acid was added. The solution was boiled to evaporate excess water. The final solution contains potassium ions (K^+), (from potassium hydroxide KOH used), aluminium ion (Al^{3+}), and sulfate ions (SO_4^{2-}). Reaction beaker was kept into the ice-water bath to chill. The mixture was allowed to chill for 15 minutes, and as the solution cools, solid alum precipitated out forming alum crystals. Finally, the alum crystal was removed from the solution after 24 hours by filtration and washed with a mixture of 20 % v/v aqueous ethanol i.e. 20 ml of absolute ethanol and with 20 ml of water in a 50 ml graduated cylinder. This serves to wash the isolated crystal as it dries. The crystal was placed on filter paper and allowed to dry overnight and then re-weighed. The synthesized alum crystal was analyzed against purchased alum.

2.2 Qualitative Analysis

The following basic qualitative analyses were carried out on the synthesized Alum crystal**.**

2.2.1. Analysis for sulphate ion (SO_4^{2-}) in the synthesized alum crystal

1.5 g of the dried Alum crystals was pulverized. A spatula tip full of the pulverized alum powder was added into a test tube filled half way with distilled water and the solution was stirred with a stirring rod until dissolution is complete. Two drops of aqueous barium chloride ($BaCl_2$) solution was added to the mixture. A white precipitate formed, which was insoluble indicated the presence of sulfate ion (SO_4^{2-}) in the synthesized alum crystals.

2.2.2. Analysis for Potassium ion (K+) in the synthesized alum crystal

Flame test was used to test for the presence of potassium ion in the synthesized alum. The crystal was held in the flame for 20 seconds until the solid glows. Potassium was volatilized and red flame turned to pale purple flame which indicates the presence of potassium ion (K^+) in the synthesized alum crystals.

2.2.3. Analysis for Aluminium ion (Al3+) in the synthesized alum crystal

The method of Birnin-yuri and Musa (2014) was adopted for the analysis of aluminium ion in the synthesized alum crystal. Two drops of diluted 1.4M KOH was added to the dissolved alum solution. Sulfuric acid (H_2SO_4) in drop and in excess was also added to the alum solution. A thick, white gelatinous precipitate was formed, insoluble in drop but soluble in excess which indicates the presence of aluminium ion (Al^{3+}) in the synthesized alum crystals.

2.2.4. Melting Point of the synthesized alum crystal

0.5g of dry pulverized alum was packed into a melting point capillary tube. The tube was fastened to a thermometer. The alum was leveled with the bulb of the thermometer and a universal clamp and cork stopper was used to fasten the thermometer to a ring stand. The bottom of the capillary tube and thermometer was immersed in the beaker of water and heated. The water was stirred to maintain an even distribution of temperature.

2.3 Quantitative analysis

The following quantitative analyses were carried out on the ions present in the synthesized alum crystal using flame photometry and Atomic Absorption Spectroscopy (AAS) respectively.

2.3.1. Analysis for Potassium ion (K^+) in the synthesized alum crystal Using Flame Photometry.

0.5 g of alum sample was dissolved in distilled water in 50 ml volumetric flask. Few drops of concentrated hydrochloric acid was added**.** A blank and potassium calibration standards was prepared in stepped amount in a reasonable ranges. Emission intensity was determined at 766.5 nm. Calibration curve was constructed from the potassium standards. Potassium concentration of sample was determined from the calibration curve.

2.3.2. Analysis for Sulfate ion (SO_4^{2-}) in the Synthesized Alum crystal using Atomic Absorption spectroscopy (AAS)

0.5 g of alum sample was dissolved in 50 ml distilled water. 2.0 ml of the diluted sample was then added to 1.0 ml of conditioning reagent. Standard solution was prepared at 5.0 mg/L sulphate range. The absorbance measurements were mark on spectrophotometer at wavelength of 425.0 nm and it was used to prepare calibration curve.

2.4 Coagulation Analysis

2.4.1.Acidity /Alkalinity and colour of the synthesized alum

The pH meter electrodes were immersed in the water sample and equilibrium was established between electrodes and sample by stirring sample to ensure homogeneity. Thereafter, the pH was read and recorded. The colour was determined by visual comparison of the sample.

2.4.2. Turbidity

Turbidometer was used for sampling a well mixed sample and the readings were taken. Results from nephelometric measurements are expressed as nepholometric turbidity units (NTU)

2.4.3.Total Solids

20.0 ml of a well-mixed alum sample was evaporated in a weighed dish and dried to constant weight in an oven at 105 ^{0}C for 24 hours. It was then cooled in a desiccator, weighed and recorded. The total solids are expressed as:

$$Total\ \text{Solids,mg}/L = \frac{(W_2 - W_1)\times 1000}{\text{Sample volume,ml}}$$

where:

W_1 = Weight of dish, mg and

W_2 = Weight of dried residue + dish, mg

2.4.4. Total Dissolved Solids

20.0 ml of a well-mixed sample was filtered under vacuum through a standard glass fiber filter, and the filtrate was evaporated to dryness in a weighed dish and dried to constant weight at 180 ^{0}C for 1hour. It was then cooled in a desiccator, weighed and recorded. The drying was repeated until a constant weight is obtained. The total dissolved solid is expressed as:

$$Total\ \text{Filterable Residue, mg}/L = \frac{(A - B)\times 1000}{C}$$

Where:

A = Weight of dried residue + dish

B = Weight of dish

C = mL of filtrate used

2.4.5.Total Suspended Solids

20.0 ml of a well-mixed sample was filtered through a weighed standard glass-fiber filter. The residue retained on the filter paper was dried to a constant weight at 103 to 105 ^{0}C. The increase in weight of the filter represents the total suspended solids. To obtain an estimate of total suspended solids, the difference between the total dissolved solids and total solids was calculated. Therefore total suspended solids can be calculated thus:

$$Total\ \text{Suspended Solids,mg/L} = \frac{(A - B)\times 1000}{\text{ml sample}}$$

where:

A = Weight of filter + dried residue, mg, and

B = Weight of filter, mg.

3. Results and Discussion

The qualitative analysis of the synthesized alum crystal is reported in Table 1. The potassium, aluminium and sulphate ions were positively tested as expected. The purchased alum similarly responded positively to the same qualitative analyses.

Quantitative analysis were carried out on the synthesized crystal to know the amount of each ions present in the crystal. The results of both the synthesized alum crystal and purchased alum crystal are shown in Table 2. Flame photometry and Atomic absorption spectroscopy (AAS) were used respectively to quantify the ions present in both the synthesized solid crystal and the purchased alum crystal. The result of the analysis shows that the synthesized solid crystal contained potassium and sulphate with concentration (ppm) 1524.930 ± 0.016 and 16.581 ± 0.000 and the purchased alum crystal contained potassium and sulphate with concentration (ppm) 1518.050 ±

0.017 and 12.571 ± 0.000. In general, it is observed that quantitative analysis of the synthesized solid crystal contain both potassium and sulphate and the concentration (ppm) are in close range with that of the original purchased alum. Potassium and sulphate ions in the synthesized alum crystal were higher compared to the purchased alum. This may be due to the presence of potassium hydroxide (KOH) and sulphuric acid H_2SO_4 used in synthesizing the alum crystal.

Table 1: Qualitative analysis of ions present in the synthesized alum crystal

Test	Observation	Inference
Alum solution + Aqueous $BaCl_2$ Solution	White Precipitate formed, and insoluble (After 20 hours)	SO_4^{2-} Confirmed
Solid Alum Crystal + heat (10 minutes)	Red flame turned to lavender (pale purple) flame color	K^+ Confirmed
Aluminate ion Solution + $H_2SO_{4(aq)}$ in drop and in Excess	Thick, white gelatinous precipitate formed insoluble in drop but soluble in excess	Al^{3+} Confirmed

Table 2: Quantitative analysis of ions present in synthesized and purchased Alum crystal.

Ions	Conc. (ppm) Mean ± SD	Method
K^+	[a]1524.930 / [b]1518.050	Flame photometry
SO_4^{2-}	[a]16.581 /[b]12.571	AAS

[a] Synthesized alum crystal [b] Purchased alum crystal

Coagulation Performance

The effectiveness of the two alum samples (i.e synthesized and the purchased one) was carried out. An initial experiment was performed to determine the initial characteristics of the raw wastewater for monitoring the effectiveness of the alum samples. 1.0 g each of alum crystal was applied to the waste water for coagulation purpose. The characteristics of the wastewater with purchased and synthesized alum before and after coagulation are summarized in Table 3. The appearance of the wastewater was initially muddy but after coagulation it became clear and colourless, and the wastewater was also very turbid initially but after coagulating with the synthesized alum it became less turbid. It can also be observed that the synthesized alum crystal performed slightly more coagulation action than that of purchased alum crystal. The summary of calculated values is shown in Table 4.

Table 3: Result for test of Coagulation action of synthesized and Purchased Alum crystal

Parameters	Test tube A (Before Coagulation)	Test tube B (After coagulation)
Volume of wastewater (ml)	[a,b] 20.00	[a,b] 20.00
pH of muddy water	[a,b]11.76	[a]4.47 / [b]4.88
Appearance of water	[a,b] muddy	[a,b] clear and colourless
Turbidity (NTU)	[a,b]1.58	[a]2.92/ [b]2.98
Total solids (mg)	[a,b] 2.50	[a,b] 1.50
Total dissolved solids (mg)	[a,b] 4.00	[a,b] 2.00
Total suspended solids (mg)	[a,b]1.50	[a,b] 0.50

[a] Synthesized alum crystal [b] Purchased alum crystal

Table 4: Summary of calculated values

Parameter	Calculated value
Melting point of Alum	^{0}C 92
Mass of Alum obtained	10.020 g
Number of mole of Aluminium used	0.0434 mol
Number of mole of Alum	0.680 mol
Theoretical yield of Alum	322.592 g
Percentage yield of Alum	3.161%
Number of mole of water of crystallization	12.255
Mass Conc. (ppm) of SO_4^{2-}	16.581 ± 0.000
Mass Conc. (ppm) of K	1524.930 ± 0.016

The above parameters were calculated to know the mass of synthesized alum obtained from the chemical process, theoretical yield of alum and the percentage yield of the alum. The following values were calculated in other to know the effectiveness of these chemical

recovery methods. The melting point of the synthesized alum crystal is 92 ^{0}C. The chemical recovery method is thereby found to be effective and efficient because 1.17g of aluminium can was used to produce 10.020g of alum. Similarly the atom economy of the process has been found through eq. (5) as 99.37%.

4. Conclusion

The synthesis of alum from aluminum related waste is feasible. Apart from ridding the environment off discarded items, demands of the growing water treating industries is also being met. The synthesis is therefore a better waste aluminium management practice. Similarly, it has a high atom economy which is a current trend in the green and sustainable chemistry. The economical feasibility of the process is outside the scope of the present study and therefore recommended for future studies.

References

Aguilar, T. N., Blaug, S.M. and Zopf, L.C., 1956. A study of the antibacterial activity of some complex aluminum salts, Journal of the American Pharmaceutical Association, 45, pp. 498–500.

Birnin-Yauri, A.U. and Musa, A., 2014. Synthesis and Analysis of Potassium Aluminium Sulphate (Alum) from Waste Aluminium Can, International Journal of Advanced Research in Chemical Science, 1, pp. 1-6.

Boin, U.M.J. and Bertram, M., 2005. Melting Standardized Aluminum Scrap: A Mass Balance Model for Europe, overview, 2005.

Curzons, A.D, Constable, D.J.C. Mortimer and Cunningham, V. L., 2001. Green Chemistry, 3, pp. 1–6.

David J. C. C, Alan D. C and Virginia L. C., 2002. Metrics to 'green' chemistry—which are the best? Green Chemistry, 4, pp. 521–527.

Etuaful, R.K. Production of Alum from Bauxite Waste from Awaso mine, 2013. M.Sc Thesis, Kwame Nkrumah University of Science and Technology, Ghana.

European Aluminium Association (EAA), 2012. Sustainability of Aluminium in Buildings Retrieved 13 October, 2015.

Hetherington, L. E., 2007. World Mineral Production. British Geological Survey, ISBN 978-0-85272-592-4.

Hudlicky,T., Frey, D.A., Koroniak, L., Claeboe, C.D., Brammer, L.E., 1999. Green Chemistry, pp. 57–59.

Kanlayavattanakul, M.and Lourith, N., 2011. "Body malodours and their topical treatment agents". International Journal of Cosmetic Science, 33, pp. 298–311.

Kennedy, C., Snell, M.E. and Witherow, R.E., 1984. Use of Alum to Control Intractable Vesical Haemorrhage, British Journal of Urology, 56, pp. 673–675.

Marrack, P., McKee, A. S. and Munks, M.W., 2009. Towards an understanding of the adjuvant action of aluminium, Nature Reviews Immunology, 9, pp. 282–7.

Mbow, M L. De Gregorio, E., and Ulmer, J. B., 2011. Alum's adjuvant action: grease is the word, Nature Medicine, 17, pp. 415–416.

Menzie, W.D., Barry, J.J, Bleiwas, D.I., Bray, E.L., Goonan, T.G. and Matos, G., 2010. The Global Flow of Aluminum from 2006 through 2025.

Rice, J. K., 1975. The use of organic flocculants and flocculating aids in the treatment of industrial water and industrial waste water, Symposium on Industrial Water and Industrial Waste Water (ASTM International), 207, pp. 41–51.

Skachkov, V. M., Pasechnik, L. A., Yatsenko, S.P., 2014. Introduction of scandium, zirconium and hafnium into aluminum alloys. Dispersion hardening of intermetallic compounds with nanodimensional particles, Nanosystems: physics, chemistry, mathematics, 5, pp. 4.

Shakhashiri, B. Z., 2008. Chemical of the Week: Aluminum SciFun.org. University of Wisconsin, Retrieved 13 October 2015.

Sheldon R A. E., 2008. Factors, green chemistry and catalysis: an odyssey, Chemical Communications, 29, pp. 3352–3365.

Sheldon, R.A. (1992). Chemical Industry, London, 903–906..
Ugwekar R.P. and Lakhawat, G.P., 2012. Potash Alum from Waste and Medicinal Foil, 2012. IOSR Journal of Engineering, 2, pp. 62-64.

Wang, W., Lu, J., Zhang, L, and Li, Z., 2011. Real atom economy and its application for evaluation the green degree of a process, Frontiers of Chemical Science and Engineering, 5, pp. 349-354.

Whitten, K. W., Davis, R. E., and Peck, L., 1996. General Chemistry, 5th Ed., Saunders College Publishing, Philadelphia.

World Coin News (WCN), (1992. World's coinage uses 24 chemical elements, Part 1.

World Coin News (WCN), 1992. World's coinage uses 24 chemical elements, Part 2.