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Conversion of Anodizing Sludge into Aluminum Sulphate for Use in Waste Water Treatment

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Abstract:
During the process of aluminium surface treatment, a large quantity of aluminum-rich sludge is generated and its disposal is a great challenge to the respective industry. The main objective of this study was to investigate the potential of environmental pollution reduction by recovery of aluminum from the anodizing sludge in the form of alum for use in waste water treatment. Both waste water and dumped sludge from various sampling locations in the plant were characterized. Waste water effluents were analyzed for temperature, pH, total suspended solids, total dissolved solids, turbidity, dissolved oxygen, biological oxygen demand and chemical oxygen demand. The final effluent temperature was 28.7±5.8°C which was within permitted levels while the pH was 5.8±0.4. The total suspended and dissolved solids were significantly high at 690.6±183.7 and 4619.8±0.23mg/L respectively. The sludge from the dumpsite had solids content ranging from 13.73% to 16.80%. Recovery of aluminium from sludges obtained from the dumpsite, wastewater treatment plant and from mixed effluent emanating from process tanks were 87.1%, 77.4% and 64.26% respectively. The prepared alum had higher content aluminium metal and coagulation performance of the prepared alum compared well with that of the commercial alum. Jar tests gave reduction in waste water pollution and the optimum settling dosage, pH, temperature and time were 8g/L, 6.5, 40°C and 20 minutes respectively.

Keywords*: Aluminum anodizing, anodizing sludge, alum*

1. General Introduction

During aluminum anodizing, the metal is coated in a controlled manner with a thickness of aluminum oxide, (Stepniowski et al. 2012,). This treatment produces a metal which has longer life with resistance to corrosion and abrasion. Anodized metal is then used in architectural building construction, as well as in engineering fabrication which supports very many economic sectors including transportation, construction, electrical application as well as mechanical equipment. (Frie, 1972 Xie et al., 2006). Anodized aluminum has unique properties which include corrosion resistance, good electrical and thermal conductivity, light weight, workability and ease of recycling (Fan and Kerrich, 1997). These processes however produce large amounts of wastes which include acidic and alkaline aluminium-containing solutions.

One of the major challenges encountered by anodizing plants is the disposal of the sludge produced since the cost of disposal which mainly includes transportation very high. The sludge's are dumped on a land fill in the plant site where they still pose environmental problems. The process also generates large amounts of effluents which are treated before discharge. This has made the recycling of anodizing waste of great importance to both anodizing industries and the environmental regulatory agency.

2. Literature Review

Aluminium anodizing involves a series of processes that change the surface of the metal to get specific properties. The process is done in well-defined stages which include pretreatment, etching, anodizing, coloring and sealing. Rinsing schedules are then used to remove residual solution after every stage. Waste water from the rinse tanks is discharged to a treatment plant facility. Apart from the wastewater, anodizing produces a large amount of sludge. This process is shown schematically.

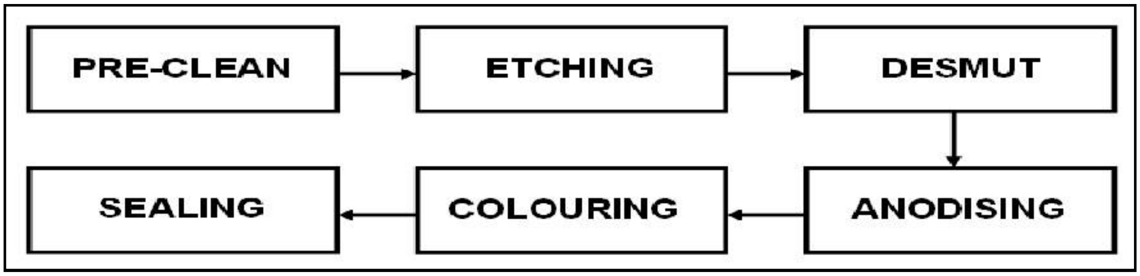

Figure 1: Anodizing process flow diagram (Patel, 2008)

Pre-treatment removes grease or lubricants from aluminium surface and it uses alkaline degreasers, of soda, tri-sodium phosphate and sodium carbonate (Andreazza, 2001). In some cases, acid cleaners have been used. The Etching Process is done using either alkaline or acidic etch formulations. A typical alkaline etch formulation consists of sodium hydroxide, mixed with sequestering agents as well as surfactants. Usually, there is buildup of aluminium precipitates in the etch solution. Acidic etching is done using concentrated acids at 100^{o}C. Anodizing process is done in an acidic electrolyte made of acids such as sulphuric acid, phosphoric acid or chromic acid (Furnea, 1996). Aluminium ions dissolve in the electrolyte and its concentration is controlled to a maximum level. Alum or potassium aluminium sulfate is used in waste water treatment and it works through the coagulation process (Corriea A. Chambino, 2005). Alum made from aluminium waste of an anodizing plant can be used to coagulate suspended solids in waste waters from the same plant. (Metcalf and Eddy, 2003). It provides a very high efficiency removal of different parameters, which include COD, BOD, suspended solids, turbidity, color and micro-organisms. Turbidity measurements represent an experimental procedure for the determination of the stability of colloidal suspensions. As aggregation occurs and colloids settle out of solution, turbidity decreases.

2.1. Procedure

Extraction of aluminum and making alum from anodizing sludge and its crystallization can be done as per the following equation (Pansward and Charmnan, 1992)

$$2Al_{(s)} + 2KOH_{(aq)} + 4H_2SO_{4\,(aq)} + 22H2O\ (l) \rightarrow 2KAl\,(SO_4)_2.12H_2O\ (aq) + 3H_2\ (g)$$

2.2. Characterization of Sludge

The five types of sludge sampled from company premises were characterized for moisture, solids and the metal ions. They were labeled as indicated in Table.

2.3. Moisture Content in the Sludge

After heating the sludge for 72 hours at 105^{o}C, its moisture content was determined from the weight loss is shown in Table 1.

Sludge Sample	Initial sludge mass (g)	Mass after heating at 105ºC for 72hrs (g)	Mass of Water (g)	% sludge moisture
A	35.973	27.237	8.736	24.28
B	39.372	29.417	9.9553	25.26
C	32.105	25.912	5.974	18.61
D	32.791	26.942	5.8493	17.84
E	36.425	29.841	6.584	18.07

Table 1: Sludge moisture as a percentage of the initial sludge

The percentage water contents of settled sludge of the rinse effluent mixture (Sludge A) and wastewater entering the treatment plant (Sludge B) were 24.28%, and 25.26 % respectively. The sludge collected from the dumping site had least amount of moisture content with an average of 18.07%. The results show that the sludge produced by the anodizing process contains high water content which increases the cost of alum production.

The water in the sludge could be reduced by using some mechanical dewatering technology like the press filter which is already in use at the plant. These techniques have various advantages one of which is in the reduction of the cost of disposal through reducing the amount of bulk water in the sludge produced. The dewatered sludge can then be processed into alum. Some other mechanical methods which have been used are belt press, centrifugation technology, plate and frame filter press (Patel 2005).

2.4. Volatile Content of the Sludge
After ashing the sludge for 4hours at 500°C, the volatile content was determined from the weight loss and is shown in Table 2 below.

Sludge Sample	mass of dry sludge after heating at 105°C in (g)	Mass after Heating 500°C for 4 Hours	Mass of Volatile matter (g)	% Volatile matter of dry sludge
A	27.237	21.421	5.816	16.17%
B	29.417	22.803	6.614	16.80%
C	25.912	21.504	4.408	13.73%
D	26.942	22.270	4.671	14.24%
E	29.841	24.310	5.531	14.60%

Table 2: Volatile content of sludge as a percentage of the initial sludge

Non-volatile components of Sludge A which was from the mixture of effluent was found to be 16 .17% of its dry weight, while that of Sludge B obtained from the treatment plant was 16.80 % of dry weight. Sludge C obtained from the etching tank contained 13.73%, non-volatile components, while D and E sampled from two different sections of the dumping site had 14.24% and 14.60%.

2.5. Alum from ashed Sludge Cakes
About 40g of sludge was weighed in a dry porcelain dish which was then placed in an oven at 105°C for 24hours. The dish and its contents were then further heated at 500°C to constant weight (Patel, 2005). The difference in weight of the porcelain dish and its contents before and after drying at 500°C was taken as the weight of the non-volatile solids (ash). Aluminum extraction was done using a 2L beaker which was wrapped in aluminium foil and covered with a watch glass cover. The ashed sludge was put in the beaker and it was placed on a laboratory hot plate maintained at temperature of between 50°C and 90°C. To each sample, 50ml of 2M sulphuric acid was added. This amount was in excess of the stoichiometric ratio 1 mole Al to 1.5 moles acid i.e. 1g aluminum per 5.44g acid. A stirring glass rod was used to mix the contents. To the solution prepared, a calculated amount of potassium sulphate was added whereby 1g of Al required 3.2g of potassium sulphate. The details of amount added are shown in Table 3. The solution was warmed and stirred at 30°C for 15 minutes and the contents of the beaker were allowed to cool and then filtered to remove any undissolved material.

Sludge	A	B	C	D	E
Amount of ashed Sludge (g)	21.421	22.421	21.507	22.270	24.310
2M H_2SO_4 added (ml)	50	50	50	50	50
K_2SO_4 added (g)	23.715	24.822	23.808	24.656	26.915

Table 3: Preparation of Alum from sludge's

The filtrate was crystallized and the crystals formed were separated from mother liquor by filtration through a piece of clean filter paper. They were washed with ethanol and dried at 30°C in an oven for 1 hour. The dried sludge alum crystals were weighed and stored in a clean glass bottle. Percentage yield of the product was calculated as follows:

% yield = 100(Mass of alum obtained (g) / Theoretical mass of alum expected.

2.6. The Quality and Performance of Alum Made from the Sludge
Some experiments were done to test quality and performance of the product alum and they include; Solubility of sludge alum, Coagulation of effluent and synthetic waste water, Pollution removal using sludge slum and the effect of alum addition on sedimentation rate.

3. Results and Discussion

3.1. Preparation of Alum
Five different sludge samples were used in alum preparation. The results obtained are presented in Table 4.6 below.

	Sludge A	Sludge B	Sludge C	Sludge D	Sludge E
Sludge ashes obtained at 500°C(g)	21.421	22.803	21.504	22.270	24.310
22M H_2SO_4 Acid (ml)	50.0	50.0	50.0	50.0	50.0
K_2SO_4 used (g)	23.715	24.822	23.808	24.656	26.915
product (g)	101.68	85.244	95.210	108.178	136.021
Theoretical yield (g)	129.734	138.114	130.246	134.885	147.241
Alum recovery %	78.38	61.72	73.10	80.20	92.39

Table 4: Preparation of Alum from sludges

The percentage recovery aluminium as alum for sludge A was 78.32%. The effluent sludge A had high water content and needed drying before it could be put into use, otherwise the water could cause heat production during the reaction. The aluminum content recovered was quite low compared to the other sludge samples.

The sludge cake B collected from the treatment plant had high moisture and hence had a low percentage aluminium recovery of 61.72%. Aluminium recovery from sludge C collected from the etching tank was 73.10%. The ashes from sludges D and E sampled from two different sections of the dumping site gave the higher recoveries of 80.2% and 92.38% respectively. These two ashes were used in subsequent experiments.

3.2. Solubility of the Alum

The data for the solubility of sludge and commercial alum is shown in Figure 4.3. Solubility of the sludge alum in water is presented in Figure 4.2. The increase in solubility of alum with increase in temperature is in agreement with that observed by Graham (1884) for potassium aluminium sulphate, $KAlSO_4.12H_2O$ as shown in Fig. 4.3.

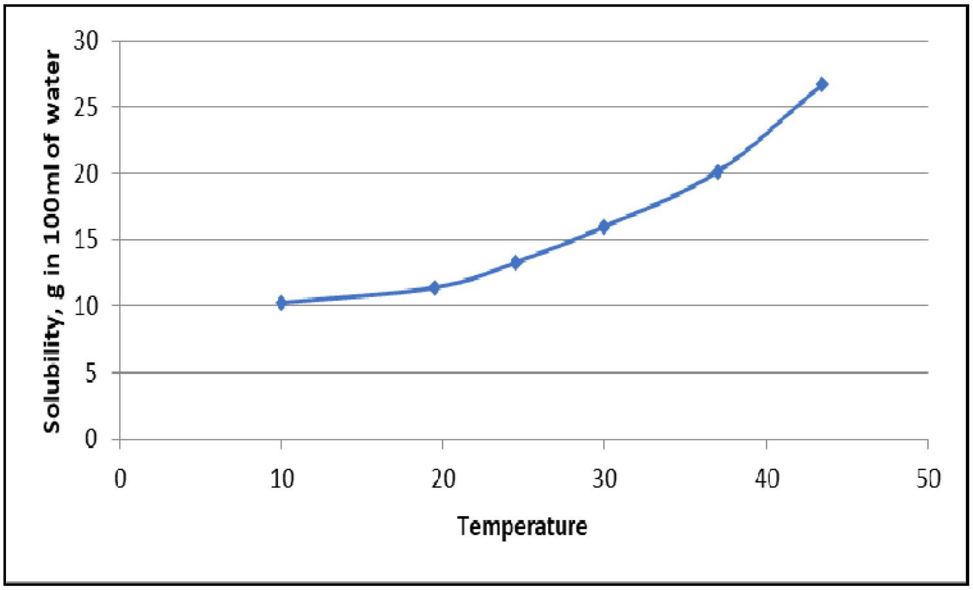

Figure 1: Solubility of prepared sludge alum in water Coagulant Dose

Results for the effect of alum dose on coagulation are presented in Figure 2.

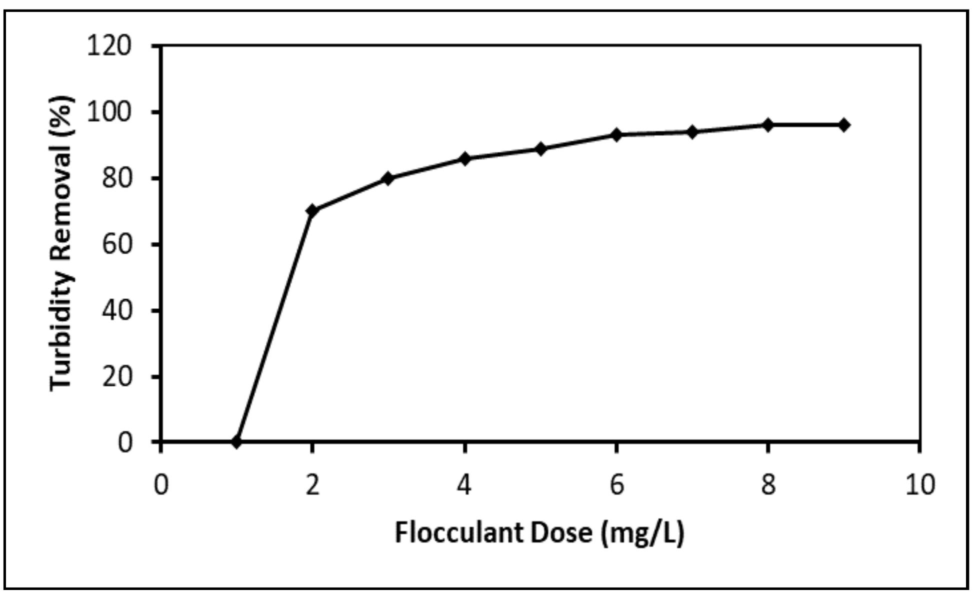

Figure 2: Turbidity Removal with Flocculants Dose

Turbidity removal increased quite rapidly with increase in flocculants dose and was in the range of 70% to 86% (Figure 4.4). At 4g/l alum, 80% removal was achieved.

3.3. The effect of Alum Addition on Sedimentation Rate

After addition of 0.6mg/l of the commercial alum and 0.6mg/l prepared sludge alum at a pH 7.0, the mixture was allowed to settle. The results are shown in Table D-2. The minimum volume of settled sludge was 29.1% for commercial alum and 34.3% for sludge alum after 11 minutes. Further sludge volume reduction occurred on settling the system for a longer time of one hour.

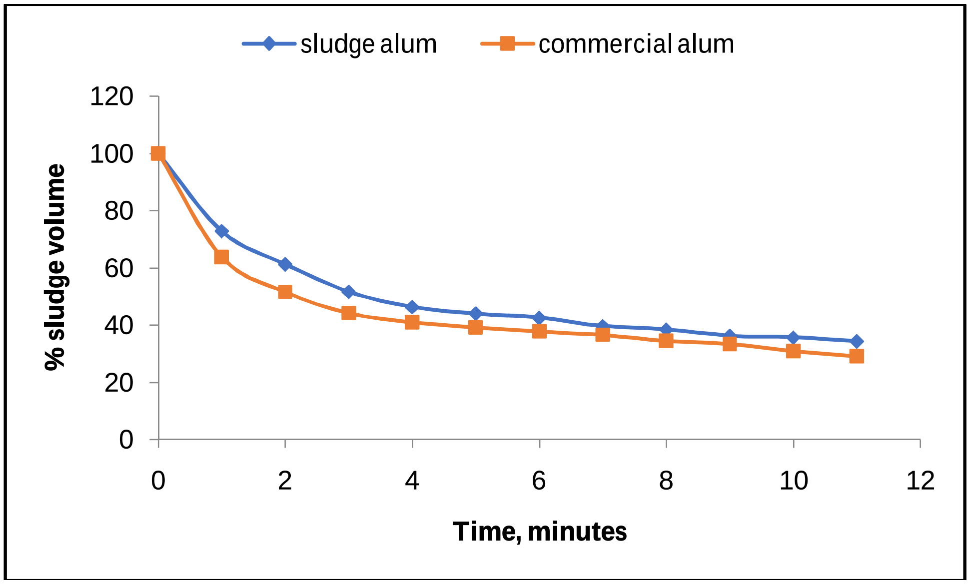

Figure 3: Settled sludge volume after addition of 0.6mg/l commercial alum and sludge alum

3.4. Pollution Removal using Sludge Slum

Sludge alum was used to treat both industrial waste water and synthetic effluent. Results of the main physical chemical characteristics of the two effluents before and after treatment using 0.6mg/l sludge alum are shown in Figures 4 to 7. It is quite clear that the prepared alum was effective in reduction of total suspended and dissolved solids, turbidity, BOD and COD.

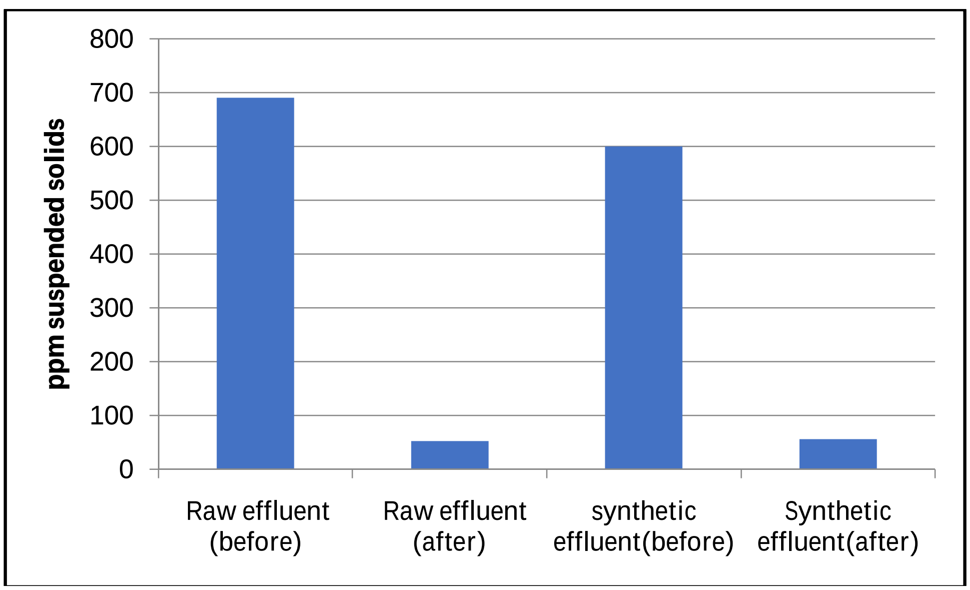

Figure 4: Removal of suspended solids in raw and synthetic effluent

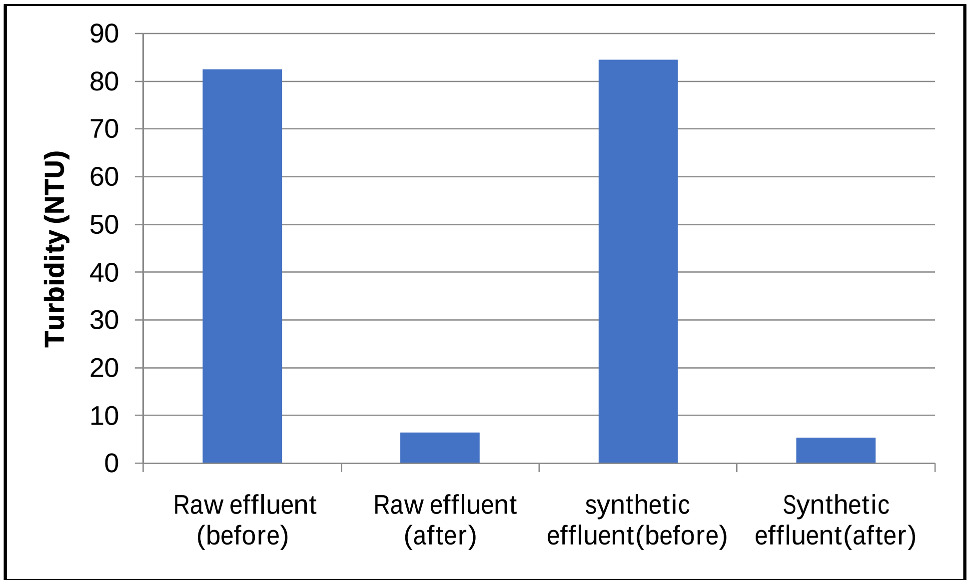

Figure 5: Removal of turbidity in raw and synthetic effluent

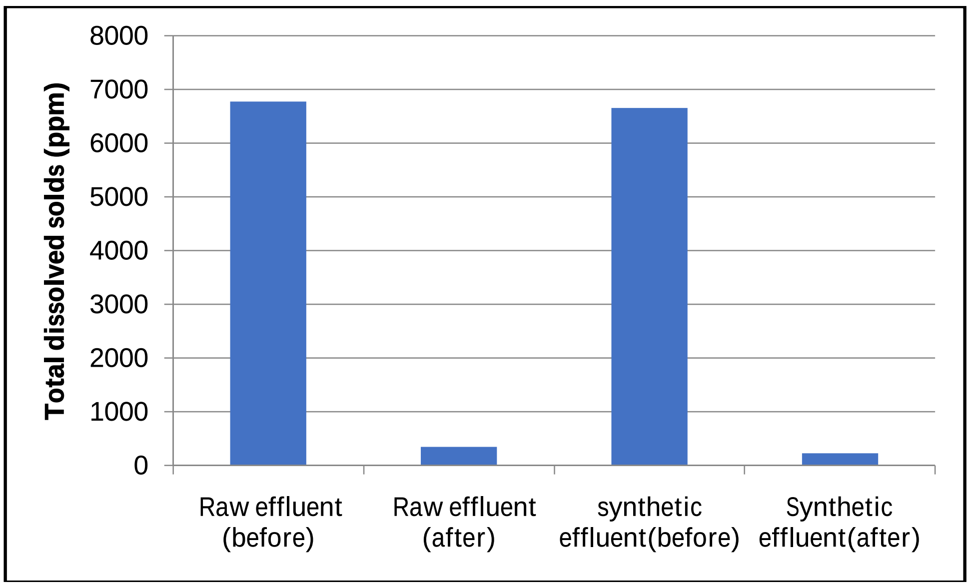

Figure 6: Removal of dissolved solids in raw and synthetic effluent

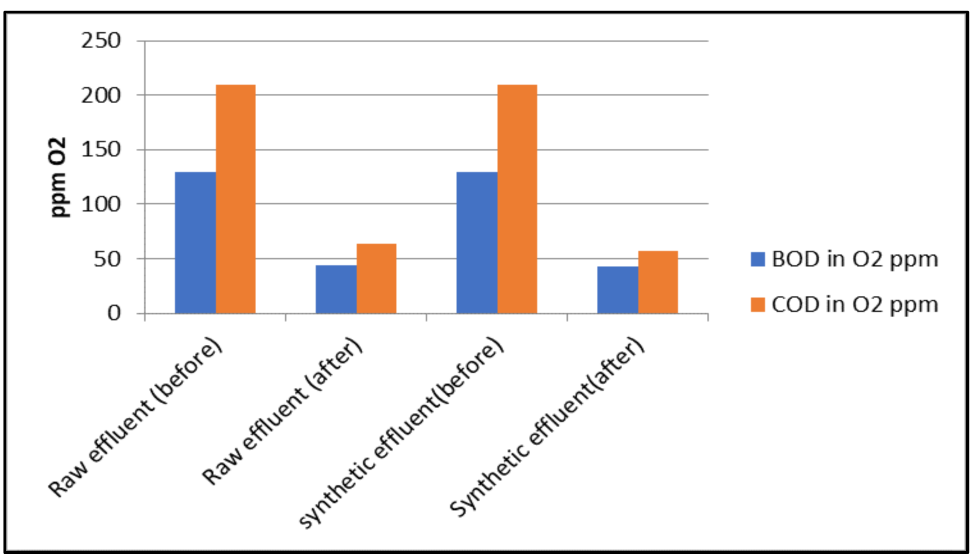

Figure 7: Removal of BOD and COD from raw and synthetic effluents

The process of water treatment using alum occurs by coagulation and flocculation. These processes are researched by executing the jar test, whereby coagulation and floc formation is stimulated. Waste water under test had high BOD_5 and COD of 130mg/L and 210mg/L respectively and the content of suspended solid matter of was 690.6mg/l. Addition of 0.6mg/l of alum decreased the values of the three parameters as indicated in Figures 4.6 to 4.9 and Table D-3 in Appendix D. The flocs formed were quite visible and settled rapidly and therefore coagulation process was effective. The waste water used in the flocculation experiment had high turbidity of 82.5 NTU for industrial effluent and 84.5 NTU for the synthetic effluent. This was also decreased to 6.4 NTU and 5.3 NTU respectively making a turbidity reduction greater than 80%. Total dissolved solids in the two effluents were very high at 6777.1 ppm for industrial effluent and 6650.2 ppm for synthetic effluents. After addition of 0.6g sludge alum they were reduced to 345.2 ppm and 223.2 ppm respectively.

4. Conclusions and Recommendations

In this study where, anodizing sludge was characterized its potential as a source of alum was investigated, various outcomes were obtained. The sludge produced by the anodizing plant was found to contain high amounts of water. The company could decrease the cost of disposal by reducing the amount of water. This reduction was done by settling the sludge at an optimized pH followed by decantation. The amount of aluminum in the dried sludge was anticipated to be very high compared to other elements. Its recovery from the sludge and use as alum raw material was investigated. Preparation of alum and its crystallization was carried out and its performance in wastewater treatment was tested and compared to that of commercial alum. Alum prepared from the industrial sludge was found to be effective in coagulation and flocculation of plant and synthetic waste water and its performance compared well with that of commercial alum. Coagulation was better at elevated temperatures and therefore, the alum could be used with hot plant effluents. This study therefore recommends that pilot studies be carried out to investigate the economic viability of the process.

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