Production of Industrial Coagulant (Poly Aluminium Chloride) From Used Beverage Cans

H Deena1, P Khadeeja1, PK Fahmi Leena1, JS Lekshmi1 and N Sreekumar2*
1Department of Biotechnology, Sree Chitra Thirunal College of Engineering, Trivandrum, Kerala, India
2School of Bio and Chemical Engineering, Kalasalingam Academy of Research and Education (KARE), Anand Nagar, Krishnankoil-626126, Tamil Nadu, India

Received 10 August 2018; revised 25 March 2019; accepted 03 June 2019

Because of the positive contribution of aluminium products to modern living, their demands are growing steadily. The second most widely used metal is aluminium and the most recycled consumer product in the world is aluminium can. Aluminium (Al) manufacture and expenditure are considered to be two sides of a coin and both are increasing. In this work, a novel method for the reuse of aluminium scrap is proposed. The used aluminium cans are crushed into fine powders and converted to aluminium chloride (AlCl3). The prepared AlCl3 was used to produce poly aluminium chloride (PAC), a coagulant. This study also includes an investigation of the effect of different varying parameters such as coagulant dosage, pH of the solution, temperature and mixing speed. Using the predetermined optimal conditions coagulation-flocculation of industrial effluent was carried out, and the COD removal efficiency was calculated; and compared with that of commercially available flocculants. The cost analysis for the production of 1L of synthesised PAC and commercially available PAC is also included in this work.

Keywords: Aluminium, poly aluminium chloride, coagulation, COD, flocculant dosage, recycle

Introduction
The industrial and technological development over the last few decades has been phenomenal but has caused depletion of natural resources at an unprecedented rate1, 2. Development of sustainable wastewater treatment and reuse technology is essential in our generations’ battle to conserve natural resources 3, 4. Globally, the aluminium industry produces 100.5 billion cans, or 1.5 million tonnes. About 60% of used beverage containers are processed back again into aluminium cans by aluminium recycling 5. However, they can also be used in the synthesis of aluminium based coagulants like alum, poly aluminium chloride etc. 6, 7. The process newly proposed is helpful to recycle wasted resources and protect the environment, and also can reduce production cost by lowering the cost of purchasing raw materials. It will help to reduce the toxicity and hazardous nature of industrial effluents to a greater extent 8, 9.

Materials and methods

Materials
The industrial effluent from HLL Lifecare limited, Peroorkkada (8°31’40.7”N 76°58’03.9”E) was used as the sample wastewater. Used beverage cans were collected from APM Restaurant, Pappanamcode (8°28’13.8”N 76°58’50.2”E) and crushed in a Metal workshop in Industrial Estate, Pappanamcode. Potassium antimonyl tartrate, Ammonium molybdate, Ascorbic acid, Sodium salicylate, Aluminium chloride, Aluminium sulphate and all other required chemicals were purchased from SRL Chemicals, Chennai.

Methods

Extraction of aluminium chloride from used beverage cans
Initially, 20 used beverage cans were taken. The lid portion was cut off, and the paint on the cans was removed manually by scrubbing. Then, they were crushed into fine powder using can crusher. The powder was collected and then subjected to sieve analysis to determine the average particle size. Aluminium solution was prepared by dissolving 30g of can powder (to be added in portions to preheated (65–70°C) HCl solution with constant stirring) in 105 ml of commercial HCl (38%). The following reaction takes place:

\[ 2\text{Al} + 6\text{HCl} \rightarrow 2\text{AlCl}_3 + 3\text{H}_2 \]

Preparation of poly aluminium chloride (PAC)
100ml of 0.25M aluminium chloride (3.33g) (from can aluminium + pure hydrochloric acid...
38 - 35%) solution were placed in 500ml glass beaker. Then, the solution was heated to 85°C in a water bath. After 20 minutes, 240ml of 0.25M Sodium hydroxide solution (2.4g) was added slowly under continuous stirring and accurate temperature control 70°C to yield the required flocculant, i.e., poly aluminium chloride.

**Characterization of industrial effluent**

The physical and chemical characteristics of industrial effluent like pH, TSS, amount of phosphates, sulphates, ammonia, nitrates etc. are calculated. All the methods were performed according to Standard Method for The Examination of Water and Wastewater (20th Ed)

**Determination of total suspended solids**

The total suspended solids (TSS) are the retained materials on a filter after filtration of a well-mixed sample. The well-mixed sample was filtered through a weighed Whatman filter paper and the residue retained on the filter was dried at 100°C. The increase in weight of the filter represents the total suspended solids.

**Determination of total dissolved solids**

A well-mixed sample was filtered through a filter paper, and the filtrate was evaporated to dryness in a weighed dish at 100°C. The increase in dish weight represents the total dissolved solids.

**Determination of chemical oxygen demand**

20ml of industrial effluent was taken in a conical flask. 10ml of 0.25N Potassium dichromate and 30ml of dilute sulphuric acid (50% v/v) were also added to it. The solution was refluxed for 1.5 hours in the presence of a trace amount of silver sulphate and allowed to cool down to room temperature. The unreacted potassium dichromate is then titrated against 0.025N Mohr’s salt solution by adding Ferroin indicator. Ferroin gives a colour change from blue-green to red-brown at the endpoint. The same procedure was followed to determine the chemical oxygen demand of untreated industrial effluent and also that of the industrial effluent treated with commercial PAC.

**Estimation of phosphates**

**Preparation of Phosphate Standards**

1000ppm of standard phosphate solution was prepared by weighing 1.43g of potassium dihydrogen orthophosphate and diluting to1000ml in a standard volumetric flask using distilled water. 0.1ml, 0.2ml, 0.3ml, 0.4ml, 0.5ml and 0.6ml of the standard phosphate solutions were pipetted into a 100ml volumetric flask, equivalent to 1-6ppm.

**Preparation of Combined Reagent**

0.27g of potassium antimonyl tartrate was diluted with 100ml distilled water to prepare potassium antimonyl tartrate solution. Ammonium molybdate solution was prepared by dissolving 4g of ammonium molybdate in 100 ml water. 1.76 g of ascorbic acid was dissolved in 100ml to get ascorbic acid solution. Combined reagent was prepared by mixing 50ml of 5N sulphuric acid, 5ml potassium antimonyl tartrate solution, 15ml ammonium molybdate solution, and 30ml of the ascorbic acid solution.

**Phosphate Analysis**

10ml of each of the standards, blank and samples were measured into a test tube. 2ml of combined reagent was added to the standards, blanks and samples. One drop of phenolphthalein indicator was added to the solutions. A pink colour was developed. In order to dissolve the colour, sulphuric acid (5N) was added. After ten minutes, the absorbance of each solution was measured at 620nm using colorimeter.

**Estimation of ammonia**

Initially, the burette was filled with 0.1N NaOH solution. Then, 10 ml of the sample was pipetted into a beaker. Two drops of phenolphthalein indicator were added to the content of the beaker. The sample in the beaker was titrated against the standard alkali in the burette until it is just pink. Take the reading of the burette (R1). To the contents of the beaker, 2 ml of 40% formaldehyde was added. The pink colour disappeared. It was again titrated with the standard alkali until the pink colour just reappears. Take the burette reading (R2). The difference between the second and first reading (R2-R1) is the volume of standard alkali (R) equivalent to the ammonia content of 10ml of the sample.

Amount of ammonia in the sample (in mg/ml) = \( \left( \frac{R2-R1}{0.17} \right) \)

**Estimation of nitrates**

The effluent sample was treated with sodium salicylate in an acid medium (pH around 5), the mixture was made alkaline (pH 8) and the yellow colour obtained was measured using a colorimeter at 420 nm. A blank (without sample) with all the reagents and distilled water was also conducted. A calibration curve is determined with standard nitrate solution.
Nitrate nitrogen (as N) mg/L = w/v
Where, w = weight in mg of nitrogen (as N) as read from the curve, and v = volume in mL of the sample taken for the test.

Study of the effect of various parameters on flocculation
Effect of flocculant dosage
1, 2, 3, 4 and 5ml of poly aluminium chloride was added respectively to 5ml of the sample. One tube was taken as zero flocculant control. Water was added to give a total liquid volume of 10ml in each tube. Samples were mixed thoroughly by inverting the tubes 20 times and centrifuged at 1000rpm, to remove suspended solids, if any. Optical density was recorded at 600nm for the top 2ml of the supernatant, including control. The flocculant volume corresponding to which optical density was identified, and optimum flocculant dosage was determined.

Effect of pH
The adjustment of pH was conducted from 2 to 10 with 0.1M HCl and 0.1M NaOH solution. For optimal pH selection, constant dose of poly aluminium chloride (30 mg/ml) was added to the sample and flocculation was carried out at various pH. The best output corresponding to maximum removal was selected as optimum pH.

Effect of temperature
The influence of temperature variation on coagulation-flocculation was analysed at temperatures ranging from 20°C to 60°C with intervals of 10°C. For the determination of optimal temperature, constant dose of poly aluminium chloride was added to the sample and flocculation was carried out at a fixed pH of 6.

Effect of mixing speed
Experiments were performed at constant pH of 6 and temperature of 35°C with optimum flocculant dosage. In each experiment, speed was varied from 40 to 200rpm with an increment of 40rpm while mixing time of 3 minutes was used.

Comparison of PAC with other coagulants
Three commercial coagulants, namely, aluminium chloride, aluminium sulphate (alum) and ferric chloride, were selected for comparing with PAC. The optimum pH, temperature and mixing speed was obtained from the literature. Reports show that Ferric chloride, alum and aluminium chloride has optimum mixing speed of 120, 140 and 140rpm at pH 4, 4 and 6 at 35°C. Flocculation of latex effluent was carried out using each coagulant separately at their optimum conditions.

Results and Discussion
Preparation of poly aluminium chloride (PAC)
From 20 cans, 190 g of aluminium powder was obtained after grinding. On sieving, this 190g of aluminium powder using a sieve shaker apparatus, particles of different sizes were retained in sieves of different mesh sizes. By studying the particle size distribution, it was found that the maximum amount of particles retained was on the sieve of mesh size 90µm, and the amount of aluminium obtained was 112g. Using 30g of aluminium and 105ml of Hydrochloric acid, 90ml of aluminium chloride was obtained. This 90ml is then made up to 100ml aluminium chloride using 0.25M sodium hydroxide. Then 340ml of poly aluminium chloride was prepared by treating 240ml of sodium hydroxide with 100ml of aluminium chloride.

Characterization of latex effluent
Wastewater collected from the latex industry was characterised for their pollution characteristics (Table 1). The parameters analysed were pH, COD, total suspended solids (TSS), Dissolved solids (DS), ammonia, nitrates and phosphate contents. Results of the analysis show that the COD, TSS and DS were 3216mg/ml, 2420mg/ml and 995mg/ml respectively. These values show that the wastewater has pollution potentials and so need to be treated before discharge into the environment. The values for ammonia, nitrate and phosphate were 2.49mg/ml, 1.36mg/ml and 1.32mg/ml respectively.

Study of the effect of various parameters on coagulation-flocculation
Effect of temperature
Results showed that as the temperature rises from 20°C to 60°C, efficiency for COD reduction lowers from 31.8% to 27.98% Figure 1. This means that high

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>10</td>
</tr>
<tr>
<td>COD (mg/ml)</td>
<td>3216</td>
</tr>
<tr>
<td>Total suspended solids (mg/ml)</td>
<td>2420</td>
</tr>
<tr>
<td>Dissolved solids (mg/ml)</td>
<td>995</td>
</tr>
<tr>
<td>Ammonia (mg/ml)</td>
<td>2.49</td>
</tr>
<tr>
<td>Nitrate (mg/ml)</td>
<td>1.36</td>
</tr>
<tr>
<td>Phosphate (mg/ml)</td>
<td>1.32</td>
</tr>
</tbody>
</table>
temperatures have adverse effects on settling condition. It can be due to the reduction in viscosity and consequently, bio-flocculation reduction and settling. The maximum COD removal was obtained at 20°C.

Effect of pH
The pH not only affects the surface charge of PAC but also affects the stabilisation of suspension. As the pH was varied from 2 to 10, first there was an increase, and then a decrease in coagulation efficiency. The reduction in COD was observed to be good at pH 6 to 8, with a maximum of 31.592%. The results are presented in Figure 1, which shows the effect of pH on COD level reduction.

Effect of mixing speed
Mixing speed is one of the important factors in achieving higher flocculation efficiency during the coagulation-flocculation process\textsuperscript{15}. Figure 1 shows that, at a lower mixing speed of 40rpm, the COD of the effluent was 2490mg/ml, showing a removal efficiency of 22.57%. Also, at a higher mixing speed of 200rpm, the value of COD was 2660 mg/ml, thus suggesting a decrease in the efficiency of the coagulant to 17.28%. The best result of the mixing speed was at 120rpm, with 35.38% removal efficiency. Hence, it was observed that, at lower mixing speeds (below 80rpm), the collisions between the flocculant and suspended particles are low and lead to the lower flocculation rate while at higher mixing speed (above 160rpm), the flocculate chains tend to break and limiting the size of the flocs formed. The small size flocs are not dense to settle down in wastewater and thus, indirectly cause the sample to be turbid again.

Effect of flocculant dosage
To determine the optimum condition of PAC in coagulation and flocculation, dosage was one of the most important parameters considered. The insufficient dosage or overdosing would result in the poor performance in flocculation. It was a crucial task to determine the optimum dosage of PAC in treatment. The effect of dosage was measured at pH 7, room temperature and 120 rpm of mixing speed. The optimum flocculant dosage was obtained as 30% (v/v). The results are represented in Figure 2.

Comparison of PAC with other coagulants
The objective of this step was to compare PAC with other commercially available coagulants, namely Aluminium chloride, Aluminium sulphate (alum) and ferric chloride that can be used to coagulate the suspension particles in the latex wastewater. It was understood from the literature survey that the behaviour of coagulant according to many factors including pH, temperature, mixing speed and the characteristics of wastewater. So, the coagulation was carried out at their optimal conditions and a constant coagulant dosage.

Out of the four coagulants, Ferric chloride was found to have maximum COD removal efficiency, i.e., 43.65%. Poly aluminium chloride synthesised also had a comparable efficiency of 36.97% Figure 3. The least efficiency was observed for alum and aluminium chloride. Ferric chloride is highly acidic and hence is corrosive such that it needs to be stored, pumped and conveyed in synthetic corrosion-resistant materials. However, PAC works exceptionally well at low raw water temperatures and is non-corrosive.

Process economics
Comparison of the performance and efficiency of PAC with other commercially available coagulants was studied and was found that ferric chloride has a removal efficiency of 43.65%. Also, PAC synthesised has a comparable removal efficiency of 36.97%. In this context, it is important to note that this study
was aimed to compare the operating costs of the PAC synthesised and the commercially available PAC. Thus, a preliminary economic evaluation has been carried out. The operating costs involve the costs related to the price of the coagulant reagents and the energy consumption required for the production of PAC in coagulation and flocculation processes. To estimate the energy costs, one must take into account that the prices of electricity are highly dependent on the particular country (in our case Kerala, India). The present unitary electricity cost for industrial use in India is Rs.5.50 per kWh (Table 2). The process economics was analysed, and the total cost required for the production of 1 litre of PAC from waste aluminium cans was found out.

The cost of synthesised and commercial PAC for 1 litre is obtained as follows:

Cost of production of synthesised PAC= Rs.11 per litre

Cost of commercial PAC= Rs.42 per litre

From the comparison study made between the cost of production of synthesised PAC and commercially available PAC, it can be concluded that the cost of production of synthesised PAC is less than that of the commercially available PAC. Moreover, the PAC was synthesised from waste aluminium beverage cans such that the cost of raw material for synthesising PAC is negligible and that this method is beneficial in lowering environmental pollution. So, the proposed method for the synthesis of PAC is not only economic but also a step towards a clean environment.

**Conclusion**

Removal of turbidity from water is an essential step in the treatment of industrial effluent. This is achieved by coagulation-flocculation using some chemicals like alum salts and polymers. One of the important inorganic polymers used is the poly aluminium chloride (PAC) which found to be very effective in removing the turbidity from water. In this work, PAC was produced by using the waste aluminium beverage cans. The recycling of aluminium cans for production of PAC will lower the cost of PAC production and helps in cleaning and protecting the environment. The removal of turbidity using PAC solutions was initially attempted and gave good results. The optimisation experiments for coagulation using PAC was carried out, and the optimum conditions for the coagulant dosage of 30 mg/ml was pH 8, 30°C temperature, 120 rpm mixing speed. It was observed that flocculation efficiency decreased when the pH was changed from the optimum range. On the other hand, the temperature had a very negligible effect on flocculation, even though high temperature slightly reduced the stability of flocs formed. At lower mixing speeds, the collisions between the flocculant and suspended particles are low and lead to the lower flocculation rate while at higher mixing speed, the flocculate chains tend to break and limiting the size of the flocs formed. The synthesised coagulant was also compared with ferric chloride, alum and aluminium chloride, in which, ferric chloride was found to be more efficient, followed by PAC, alum and aluminium chloride. However, from the comparison study made between the cost of production of synthesised PAC and commercially available PAC, it can be concluded that the cost of production of synthesised PAC is less than that of the commercially available PAC.

**Table 2 — Cost analysis for the production of 1L PAC**

<table>
<thead>
<tr>
<th>Material / equipment</th>
<th>Specification</th>
<th>Cost (in rs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating Mantle</td>
<td>1000ml, 350W</td>
<td>0.437</td>
</tr>
<tr>
<td>Sieve Shaker</td>
<td>3kg, 180W</td>
<td>0.3</td>
</tr>
<tr>
<td>Can Crusher</td>
<td>200-300kw/hr., 7.5 kw</td>
<td>0.003</td>
</tr>
<tr>
<td>HCl</td>
<td>38%</td>
<td>6.684</td>
</tr>
<tr>
<td>NaOH</td>
<td>Solid form</td>
<td>3.57</td>
</tr>
<tr>
<td>Total cost</td>
<td></td>
<td>11</td>
</tr>
</tbody>
</table>

![Fig. 2 — Absorbance v/s Flocculant dosage graph](image1)

![Fig. 3 — Comparison of PAC with other coagulants](image2)
available PAC. This technique of treating wastewater is beneficial in lowering environmental pollution and thus can be studied upon further to be considered as an effective method of wastewater treatment.

Acknowledgement
The authors thank the Department of Biotechnology and biochemical engineering, SCT College of Engineering for the continuous support provided throughout the work. The authors declare that no external funding was used in the work. There is no conflict of interest whatsoever.

References