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COMPARISON ON THE EFFECTIVENESS OF HYDRATED ALUMUNIUM SULFATE AND FERRIC CHLORIDE AS A COAGULANT IN BREWERY WASTEWATER TREATMENT. THE CASE OF WALIA BREWERY, HEINEKEN ETHIOPIA

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Abstract: Reclamation of process wastewater is a key to water resources conservation and sustainability. Since brewery is inherently associated with the use of considerable amount of water, this study was undertaken to investigate the appropriate dosage of ferric chloride and alum for the wastewater generated by Heineken (Wallia) brewery. For this work, samples of wastewater were collected and characterized. Series of jar test experiments were conducted in which the efficiencies of ferric chloride and alum were compared with in a coagulation/flocculation process at discharge pH.. The results showed that 20 mg/l of ferric chloride was enough for removal of both turbidity and COD where as in the case of hydrated aluminum sulfate, 40 mg/l of hydrated aluminum sulfate was found to be sufficient for the removal of both turbidity and COD. Both demonstrated the ability to coagulate colloidal particles in the brewery wastewater. Overall, hydrated aluminum sulfate was found to be a more preferable coagulant at a dosage of 40mg/l.

Keywords: coagulation, flocculation, ferric chloride, hydrated aluminum sulfate

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1. Introduction

In the food industry, the brewing sector holds a strategic economic position with the annual world beer production exceeding 1.34 billion hectoliters in 2002 (Au and Lechevallier, 2004). Beer is the fifth most consumed beverage in the world behind tea, carbonates, milk and coffee and it still continues to be a popular drink all over the world (Braeken, et al, 2004). This beverage is obtained through alcoholic fermentation, using selected yeast of genera Saccharomyces, malt cereals (mainly barley), and other sugar based raw material, to which hop, and adequate water is added. Brewers are very concerned that the techniques they use are the best in terms of product quality and cost effectiveness. During production, beer alternately goes through four chemical and biochemical reactions (mashing, boiling, fermentation and maturation) and three solid–liquid separations (wort separation, wort clarification and rough beer clarification) (Goldammer, 2008). Consequently water management and waste disposal have become a significant cost factors and an important aspect in the running of a brewery operation (Harrison, 2009).Every brewery tries to keep waste disposal costs as low as possible whereas the legislation imposed for waste disposal by the authorities becomes more and more stringent.

Though this brewing industry is faced by a number of problems, now a day's their most critical concerns are water usage – its quality and scarcity - and the subsequent wastewater generated from its operations. The industry requires the use of large quantity of clean water in its beer production. The main water consuming areas of a typical brewery are brew house, cellars, packaging and general water use (van der Merwe, Friend, 2002). Specifically, of the water consumed, about two-thirds are used in the process and the rest in the cleaning operations (Fillaudeau et al, 2006). As revealed in literature survey by Simate (Simate et al, 2012), it is estimated that about 3-10 liters of water is required to produce 1 liter of beer. As a result, a large quantity of wastewater is produced. Consequently, water and wastewater management in breweries remains a critical practical problem.

Currently the ever increasing need for clean, but scarce water in the brewing industry has continued to motivate the need to find alternative sources of water. One alternative that requires attention is wastewater reclamation and reuse. Wastewater reclamation and reuse has been an important option since industrialization accelerated pollution in water environment, making it a limited resource for production activities (Seo et al, 1996). When properly treated and recycled, wastewater can be an alternative water source which can reduce the demand for fresh water. Recycled wastewater can reduce stress on the environment as well. However, the removal of contaminants from wastewater completely remains a big challenge.

There have shown that a good number of brewery wastewater treatment methods are either in operation, being piloted or under evaluation. These treatment processes are selective depending on the purpose of water and the water quality required, and wastewater characteristics (Chung et al, 1997). Furthermore, each method has its advantages and disadvantages, and the removal of contaminants using these technologies can be complex and costy.

Breweries in Ethiopia mostly use groundwater as a raw material as seen in Heineken, Meta and also in other breweries in the country for their beer production because of its constant and good quality. This exert a tremendous pressure on the ground water resource of the country and plus the high quantity of waste water they generate exert pollution load on the environment resulting in surface and graund water pollution. Due to this, we must start looking for alternative water resources and ways of wastewater treatment to prevent pollution. In this context, coagulation/flocculation followed by sedimentation might be a solution to treat the waste water so that it could be reused. This paper investigates the suitability of using Alum and ferric chloride coagulants and flocculants in the treatment of brewery wastewater. Ferric chloride and Alum were chosen among other inorganic coagulants because they are effectiveness over a wider pH range, easily accessible and the floc they form is heavier than others, thus improving settling characteristics in view of recycling in order to decrease the amount of fresh water needed and wastewater generated. The quality standards for the regenerated waste water depend on the application (Simate et al, 2012).

2. Methodology

2.1. Jar test

The coagulation and flocculation potential of ferric chloride and alum were evaluated using the standard jar tests at discharge pH. For each jar test, the procedure followed is as given below. According to the APHA, the standard method for conducting Jar test for brewery wastewater consists of a three-phase mixing process of rapid mix, gentle mix, and no mix. The rapid mix phase consists of 1 minute of stirring at a speed of 100 rpm. The mixing speed was then reduced over the next 30 seconds to 40 rpm, and left to mix at this speed for the next 20 minutes during the slow mix phase. In the no mix phase, the samples settled for 15 additional minutes, after which turbidity, pH, and other measurements were

GSJ: Volume 7, Issue 5, May 2019
ISSN 2320-9186

taken to quantify changes induced by coagulation and settling. (APHA, 1995).

2.2. Raw water and treated water quality analysis

The quality of raw water is one of the fundamental variables in water treatment. The parameters that define the quality of water can be categorized as physical, chemical and biological (Peavy et al, 1985). Physical parameters define those characteristics of water that respond to the senses of sight, touch, taste, or smell. Suspended solids, turbidity, color, taste, odors, and temperature fall into this category. On the other hand, total dissolved solids, alkalinity, fluorides, hardness, metals, organics, and nutrients are chemical parameters of concern in water quality management. The majority of analytical methods listed in this sub-section follow the standard methods for the examination of water and wastewater.

COD analysis

Among the parameters, the most important parameter for recycling water or required to be measured is the COD.COD is a measure of the oxygen equivalent of the organic and inorganic matter content of a sample that is susceptible to oxidation by a strong oxidant (Braeken, et al, 2004). The COD is considered an appropriate index for showing the amount of organic and inorganic in water (Mansourpanah, 2006), (Ince, et al, 2000).It mainly represents the biodegradable and non biodegradable organic components, although inorganic compounds may be significant in certain cases (Ince, et al, 2000). However, in general, brewery effluents are easily biodegradable with BOD/COD ratio in the range 0.6–0.7 (Cronin,T.V.Lo, 1998). The organic components in the brewery effluent (expressed as COD) consist of sugars, soluble starch, ethanol, volatile fatty acids, etc (Braeken, et al, 2004).

Total Phosphorus – analysis

Phosphorous concentration determines the level of Eutrophication, slime formation and microbial growth (increased plant and algal growth due to an excess of nutrients such as phosphorous) (Crittenden & Harza, 2005) and fouling effect (EPA, 1992).

Ammonium – analysis

Measurement of ammonia concentration in waters could be done by the Nessler method – based on the yellow to brown color produced by the chemical reaction between the Nessler reagent and ammonia. The Nessler's reagent is an aqueous solution consisting of HgI_2, KI and NaOH. The color is absorbed over a wide range of wavelengths (λ= 400-500 nm). After adding the Nessler's reagent to the sample, the sample was mixed by shaking and waited for 30 minutes before colorimetric measurement in spectrophotometer takes place. (APHA, 1995)

Total nitrogen analysis

The total nitrogen analysis concentration determines the level of Eutrophication, slime formation and microbial growth (increased plant and algal growth due to an excess of nutrients such as nitrates) (Crittenden & Harza, 2005) and fouling effect (EPA, 1992), (APHA, 1995).

pH – analysis

pH value of water was determined by the relative concentrations of H^+ ion and OH^- ion. pH analysis was carried out using pH meter. Put the sensor of pH meter into sample, open pH meter, and wait for some time when the reading was stable, read the result. (APHA, 1995)

Turbidity analysis

Turbidity is a measure of the extent to which light is either absorbed or scattered by suspended materials in water (EPA, 1992). Turbidity was measured using a turbidity meter. It is measured photo metrically by determining the percentage of light of a given intensity that is either absorbed or scattered. In the absorption mode, a photometer measures the light intensity on the side of the vial opposite the light source, while in the scattering mode a photometer measures the light intensity at a 90° angle from the light source (EPA, 1993). In this study the Hatch turbid meter was used following the scattering principle with NTU as unit of measure.

Conductivity analysis

Conductivity is a measure of electrical conductance of water or the mineral content of water. It gives a qualitative measure of the total dissolved solids in water. It is important to measure conductivity of water in order to know the likelihood of the water becoming corrosive (EPA, 1992). Conductivity was measured in milli Siemens per centimeter (mS/cm) using Conductivity meter.

2.3. Data Analysis

Statistical analysis was performed with the help of Microsoft Excel program .Descriptive data analyses using graphs were made using Microsoft Excel program. Results obtained by experiment were compared with the specified industrial discharge limit values. The statistical significance of the experimental results was analyzed by the Student's *t*-test.

Removal efficiencies of treatment system were calculated based on the following formula (Boonsong and Chansiri, 2008).

$$\%\ \text{Removal Efficiency} = \frac{Cinf - Ceff}{Cinf}$$

Where *Cinf* is initial parameter concentration, *Ceff* is final parameter concentration.

3. RESULT AND DISCUSSION

GSJ: Volume 7, Issue 5, May 2019
ISSN 2320-9186

3.1. Origin of waste water

The brewery waste water was obtained from a Heineken brewery (Kilinto, Addis Ababa, Ethiopia).This brewery consumes 6 liters of water per liter of beer. Wastewater was originated at different places in the production process. In this factory three different types of wastewater: (the bottle rinsing water, the rinsing water of the bright beer reservoir and the rinsing water of the brewing room) were collected and treated by the biologically treatment and released to the nearby river when the discharge limits are adhered. The wastewater which is treated by biological treatment and discharged has a low organic load, an intermediate conductivity, a more or less constant composition (in terms of e.g. COD and turbidity) and contains bacteria.

3.2. Characterization of the brewery wastewater

The table below illustrates physicochemical characteristics of Brewery wastewater from the discharge point of biological treatment plant in Heineken Brewery in Ethiopia. This experimental result is also in the same range with that of the last 6 months record of the factory.

Table 3.1 characterization of brewery wastewater

Parameters	Mean	Range
pH	7.70	7 - 8
COD(mg/l)	89.33	75 - 110
Turbidity(NTU)	55.11	47 - 75
Total nitrogen (mg/l)	4.4	4 - 5
Total ammonia(mg/l)	1.06	0.6 – 1.6
Total phosphorus(mg/l)	4.3	3 - 4
Conductivity(Scm^{-1})	1.92	1.5 - 2

The characterization result showed that the pH level range was 7 to 8. It was influenced by the amount and type of chemicals used in cleaning and sanitizing operations(e.g, caustic soda, phosphoric acid, nitric acid, sulphonic acid). The Nitrogen and phosphorus levels range from 4-5 mg/l and 3-4mg/l and their concentration mainly dependent on the handling of raw material and the amount of yeast present in the effluent .Whereas the ammonia level range from 0.6 – 1.6 which is generated mainly from the CO_2 room. The electrical conductivity was also in a range of 1.5 – 2 Scm^{-1} as can be seen from table 3.1.

Figure 3.1. Heineken brewery wastewater

3.3. Coagulants dosage determination

The optimum dosages of ferric chloride and alum (hydrated aluminum sulfate) was determined following the jar tests using American Public Health Association (APHA) standard procedures. In generally, the following procedures were followed. Exactly 500 mL of brewery wastewater will be measured into each jar test beaker. The pH neutrality will be checked before addition of various dosages of the coagulant. Here since the pH is already adjusted before the wastewater enters into the biological treatment plant for the wellbeing of the microorganisms in UASB reactor, the final effluent pH is always kept in between 7–8 as can be seen from the characterization of the effluent of the factory. The mixture will then rapidly mix at 100 rpm for 1 min followed by slow mixing at 40 rpm for 15 min. Finally it will be allowed to settle for 20 minute supernatant will then be collected and analyses for turbidity and COD.

3.3.1 Determination of Ferric chloride dosage

The ferric chloride dosage was determined following the APHA standard procedures.

Figure 3.2 Jar test to determine ferric chloride dosage

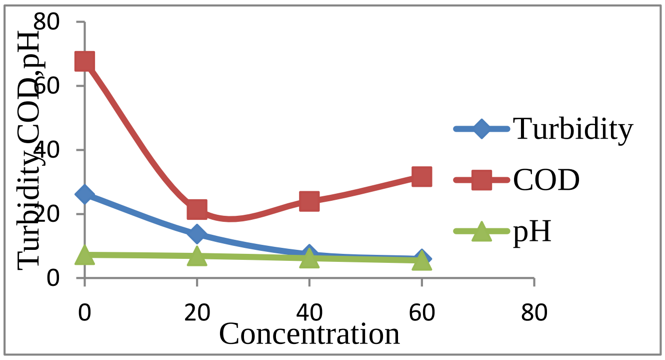

Figure 3.3 Ferric chloride effect on removal of COD, turbidity and pH

As can been seen from figure 3.3, ferric COD removal efficiency were high at 20mg/l and then it decreased with the concentration of the ferric chloride increased. This is mainly due to the formation of ferric salt and HCl during the coagulation process. So it is wise to keep the concentration of ferric at optimum level otherwise there will be a need to counter act its increases effect on COD.

Whereas the turbidity removal efficiency increased as the concentration increases and maximum removal were achieved at 40mg/l and remained almost constant then after. Finally the pH decrease with increase in concentration of ferric even enters into acidic condition. This is mainly due to the formation of HCl after the dissociation of ferric chloride.

In general the optimum amount of ferric chloride concentration for the treatment of brewery waste water was found to be 20mg/l because, the COD removal was higher and the pH was in desired level

GSJ: Volume 7, Issue 5, May 2019
ISSN 2320-9186

(almost neutral) even though the turbidity removal is lower than at 60mg/l at discharge pH of the wastewater.

3.3.2. Determination of Hydrated alimunium sulfate dosage

The optimum dosages of hydrated aluminum sulfate were also determined using APHA standard.

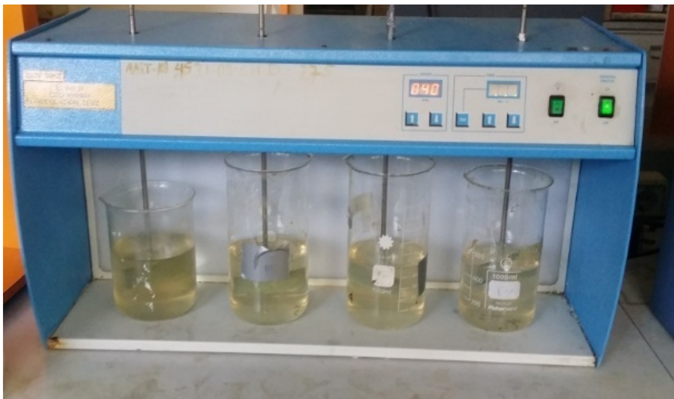

Figure 3.4 Jar test to determine hydrated aluminum sulfate dosage

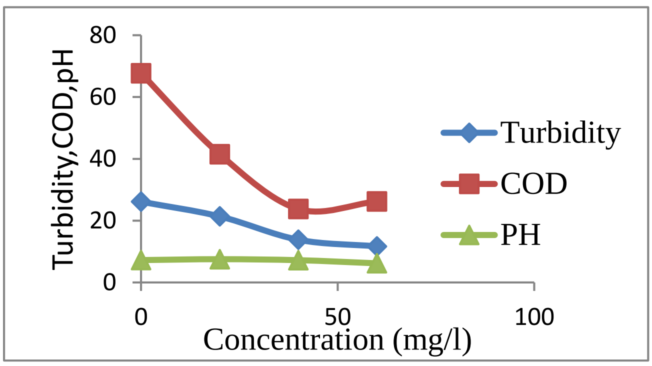

Figure 3.5 Hydrated aluminum sulfate effects on removal of COD, turbidity and pH

As can been seen from figure 3.5, Alum COD removal efficiency increased until 40mg/l and then remained almost constant after wards until it reached 60mg/l. This was mainly due to the formation of soluble forms of Al compounds.

With the concentration of the alum increases, the turbidity removal efficiency also increases. The maximum removal was achieved at 60mg/l. This was mainly due to the effect of coagulation, flocculation and sedimentation mechanisms which are double ion compression, Adsorption and charge neutralization, Adsorption and inter-particle bridging.

Finally the pH decreased a bit or remained almost in a constant range (6.2 – 7.2) with increase in concentration of alum. This was mainly due to the soluble alum compound formed counter act the effect of sulfate salt formed. In general alum concentration for the treatment of brewery waste water was found to be 40mg/l because, the COD removal is higher, the pH is in desired level(almost neutral) even though the turbidity removal was lower than 60mg/l at discharge pH of the wastewater.

In summary, the results showed that an optimum concentration of 40 mg/l of hydrated aluminum sulfate was found to be sufficient for the removal of both turbidity and COD.

3.4. Comparison of hydrated aluminum sulfate and ferric chloride

The suitability of using Alum coagulants and flocculants in the treatment of brewery wastewater was compared with ferric chloride. Ferric chloride and Alum were chosen among other inorganic coagulants because they are effectiveness over a wider pH range, easily accessible and the floc they form is heavier than others, thus improving settling characteristics (Simate et al, 2012).

Figures below shows a comparison of the effectiveness of Alum and ferric chloride in removing turbidity and COD from brewery wastewater and pH condition they result in. The wastewater discharged into the environment was always in neutral condition due to discharge regulations set by appropriate authorities and most importantly it was adjusted before it enters into biological treatment system (not to harm the microorganisms in the biological treatment plant).

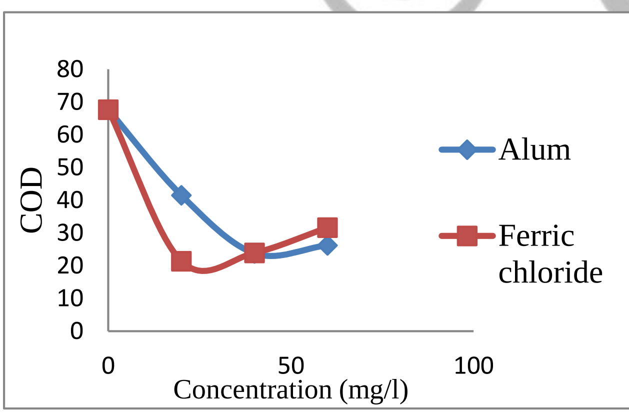

Figure 3.6 Comparison of Alum and ferric chloride on removal of COD

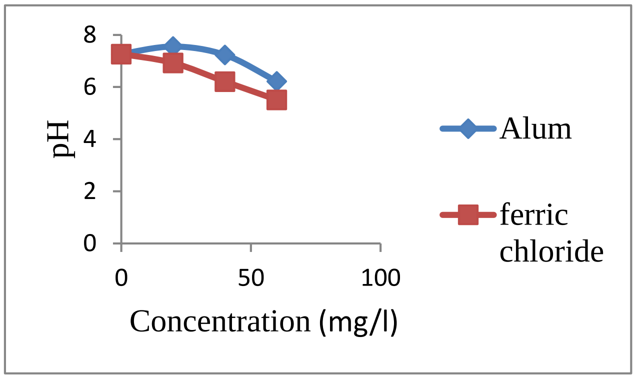

Figure 3.7 Comparison of Alum and ferric chloride effect on final pH

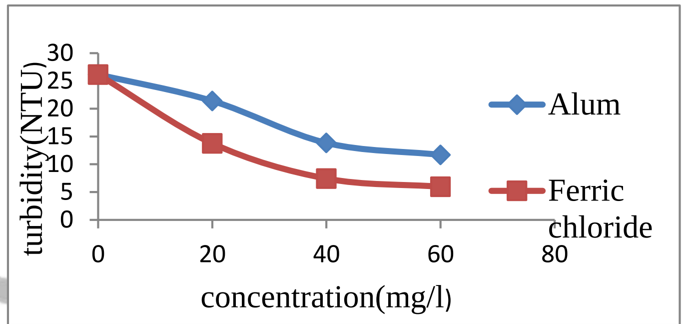

Figure 3.8 Comparison of Alum and ferric chloride on removal of turbidity.

An overview of the figures above shows that both coagulants were able to remove turbidity to a larger extent. This may be attributed to the fact that several flocculation mechanisms may have been simultaneously involved when they are used, i.e., (1) adsorption/ charge neutralization, and (2) sweep-floc coagulation (or enmeshment). Sweep-floc coagulation was significant and more likely to have predominated. In sweep-floc coagulation, metal hydroxide precipitates promote coagulation by increasing the antiparticle collision rate and enmeshing suspended particles (Peavy et al, 1985).

However, ferric chloride was found to display

GSJ: Volume 7, Issue 5, May 2019
ISSN 2320-9186

higher efficiency than hydrated aluminum sulfate for the coagulation/flocculation of colloidal matter in brewery wastewater due to its ability to form heavier flocs especially in turbidity removal at lower concentration. However, it was seen that the pH droped to acidic range as the concentration increased. This was mainly due to hydrolysis reaction taking place (Peavy et al, 1985). The following reactions show main reasons for drop of pH in the coagulation /flocculation test for both coagulants. (Peavy et al, 1985)

$$Al(H_2O)_6^{3+} \longrightarrow (Al(H_2O)_5OH)^{2+} + H$$

$$Al(H_2O)_5OH)^{2+} \longrightarrow Al(H_2O)_4(OH)_2)^{+} + H^{+}$$

$$Al(H_2O)_4(OH)_2)^{+} \longrightarrow \downarrow (Al\ (H_2O)_3(OH)_3) + H^{+}$$

$$(Al(H_2O)_3(OH)_3) \longrightarrow (Al(H_2O)_2(OH)_4)^{-} + H^{+}$$

$$Fe^{3+} + 3H_2O \longrightarrow \downarrow Fe\ (OH)_3 + 3H^{+}$$

When the H^+ ions formed react with the sulfate, it resulted in pH drop but it's not that much as that of the ferric because its effect was countered by the soluble salt formed as seen in the above Equation, whereas for ferric chloride the same type of reaction (hydrolysis reactions) take place,followed by the reaction of the H^+ ions with the Cl^- resulting in the formation of HCl which is the root cause for the lowering of pH of the solution.

In general, even though ferric chloride posses' higher COD and turbidity removal than alum, it was aluminum sulphate that was chosen as a coagulant for coagulation/flocculation because;

1) Alum is widely available and produces in Ethiopia, whereas ferric chloride is imported from abroad, as a result it is too costy.
2) The pH drop and rise in COD due to the use of ferric chloride may finally result in need of additional treatment and affect the performance of the filtration system.

4. Conclusion

The Brewery wastewater which is discharged from Heineken brewery contains organic and inorganic pollutants .specifically it contains NH_4, nitrogen, phosphorus and relatively larger COD.The addition of ferric chloride and alum to the coagulation/flocculation tanks at discharge pH resulted in better turbidity and COD removal. Even though ferric chloride was effective at lower dosage than alum, alum was chosen due to its easy accessibility in our country and it results of neutral pH at the end of the operation.

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GSJ: Volume 7, Issue 5, May 2019
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