ENERGY ENVIRONMENT
Sustain Conference 2015, Bali
DOI: 10.24910/jsustain/5.2/210

International Journal
Sustainable Future for Human Security
J-SustaiN Vol. 5 No. 2 (2017) 2-10
http://www.j-sustain.com

Water Recovery of Black Liquor from Alkaline Pretreatment of Bioethanol Production from Oil Palm Empty Fruit Bunch by Coagulation and Flocculation Method

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Received: September 30, 2015 / Accepted: June 14, 2017

Abstract

Black liquor from the pretreatment process for bioethanol production from oil palm empty fruit bunch was treated using the coagulation-flocculation process with several coagulants/flocculants under various conditions. Decolorization, total suspended solid (TSS), final pH, and sludge volume were analyzed. The aim of this study was to investigate which coagulant and flocculants, concentration, and optimum pH would be the most effective for water recovery. Alum, PAC, ferrous sulphate, cationic and anionic polyacrylamide acted both as coagulant and flocculants with various combinations and condition. The result showed that the combination of PAC and cationic polyacrylamide with ratio combination of 3:1 and optimum pH of 6.5 was the most effective coagulant/flocculants for treating the black liquor. The combination gave 93.14% decolorization, final pH of 7.2, 40% sludge volume formation and 79.64% TSS decreased percentage.

Keywords:*black liquor; decolorization; TSS; coagulation-flocculation; alum; PAC; $FeSO_4.7H_2O$; cationic polyacrylamide; anionic polyacrylamide*

1. Introduction

The chemical pretreatment for bioethanol production from oil palm empty fruit bunch releases black liquor as waste. The major components of black liquor are water, lignin, hemicellulose, NaOH and some byproducts. Black liquor exudes a rotten odor and has unappealing color. The black color is formed by lignocellulose degradation. Lignin, which is the major content of the waste water, affects the intensity of the color and foam production. The greater the amount, the darker the water and the more foam generated [1]. The color is not only undesirable but also disrupts the aquatic biosphere, in regards to reduction of sunlight penetration and dissolved oxygen concentration. In addition, colored water is frequently not suitable for reuse [2].The NaOH content of black liquor contributes to high pH. The high content of total suspended solids (TSS) and chemical oxygen demand (COD) (see Table 1) also adds more complexity which means that this black liquor is not allowed to be discharged directly to the environment or for reuse [3]. However, the high amount of water content (73% of black liquor) means it has high potential for water recovery.

Lignin, the major content of black liquor, has a negatively charged surface in water [2]. The similar electrical charges lead to the stabilization of the black liquor. The addition of some chemicals, followed by precipitation of dissolved materials, can change the surface property which leads to the separation of solids by gravity or filtration [4].

Several methods including physical, chemical and biological modifications are used to treat wastewater. However, standard biological methods cannot decompose lignin. Due to its low efficiency, anaerobic treatment is not suitable for the purpose. Activated sludge plants have several problems, including poor settling characteristics, toxicity and inability to degrade lignin. Ozonation, Fenton's reagent and membrane technology are useful but expensive [5].

On the other hand, coagulation has an economic benefit due to its low capital cost, simple procedure and high efficiency [6]. The coagulation process decreases or neutralizes the negative charges of suspended solids which allows microfloc formation by van der Waals force [7], while flocculation helps the flocs interact with each other and form larger aggregates (macroflocs) [8].

Several factors affect the coagulation/flocculation, including type and dosage of coagulant/flocculant, pH, mixing condition, temperature and retention time [9]. A suitable combination of these factors could result in a highly efficient treatment [10]. This study involved three of these factors: type and dosage of coagulant/flocculants and pH.

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For coagulants, alum, PAC and $FeSO_4$ (aluminium and iron salts) are widely used. The mechanisms of their action are charge neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous hydroxide precipitate [11]. Polyelectrolytes of various structures, such as polyacrylamide, are usually used as coagulant aids or flocculants to enhance the formation of larger floc in order to improve the rate of sedimentation. Polyacrylamide (PAM) can also be used to produce good settling performance at relatively low cost [12].Table 2 shows the comparison of alum, PAC, $FeSO_4.7H_2O$, cationic polyacrylamide and anionic polyacrylamide.

The use of coagulant dosage varies across a wide range of concentrations which aim for maximum removal efficiency of contaminants using minimum doses at optimum pH [13] because maximum dosage does not mean maximum removal since excessive dosage can give charge reversal and re-stabilisation of colloids. Among other similar tests, the jar test is the most reliable method to determine both the effective type of coagulant and their proper dosage [14].

Coagulant dosage is also related with pH. The role of pH is particularly significant as it determines the electrical charge of organic and inorganic colloids at the same time and it is a major factor in the hydrolysis of aluminium salts. pH control improves soluble matter removal [15]. Highly alkaline water, such as black liquor, may require an excessive coagulant addition to decrease pH to values favourable for coagulation. The pH at which coagulation occurs is the most important parameter for proper coagulation performance as it affects the surface of colloids, charge of contaminant functional groups, charge of dissolved-phase coagulant species, surface charge of floc particles and coagulant stability [14].

The goal of this study was to investigate the most effective coagulant/flocculants and the optimum pH for treating black liquor from pre-treatment process of bioethanol from oil palm empty fruit bunch for water recovery with decolourization, total suspended solid (TSS), final pH, and sludge volume as the evaluated parameters.

2. Materials and Method

Black liquor (Figure 1) from chemical pre-treatment of oil palm empty fruit bunch was obtained from bioethanol pilot plant at Research Centre for Chemistry, Indonesian Institute of Sciences. Table 1 showed the characteristics of the black liquor. The COD value was measured according to Indonesian National Standard (SNI) method (SNI-06-6989.2-2009).

Samples were diluted by a ratio of 1:1 with distilled water. The selected coagulants and flocculants for this study were alum, PAC, ferrous sulphate, cationic and anionic polyacrylamide. These coagulants were all of technical grade and purchased from local merchant, except for ferrous sulphate (Merck). All of the coagulants/flocculants were in solution form (diluted with distilled water) to ensure homogeneity when mixed with black liquor. pH was adjusted using H_2SO_4 72% and NaOH 10%. The value was measured using a digital pH meter (Seven Easy pH, Mettler Toledo AG, Switzerland).

Table 1 The characteristics of black liquor

Parameters	Value
pH	13.09
TSS	36,550 ppm
COD	145,000 ppm
Color	Shiny black
Odor	Rotten
Temperature	Ambient

Source: Measurement

Figure 1 Black liquor, waste from chemical pre-treatment for bioethanol production from oil palm empty fruit bunch

A series of jar test experiments with a conventional flocculator was conducted at 300 rpm for 3 minutes, 50 rpm for 8 minutes and 24 hour settling. We selected different speeds for coagulation and flocculation because when solid surfaces were brought close enough together (e.g. 0.01 microns or less) the London-van der Waals forces overpowered the repulsion forces. Agitation of a suspension causes particles to come close or even collide, allowing natural coagulation to occur. Excessive agitation will cause floc breakdown since the bonding forces are relatively weak [16].

A jar test procedure comprising of five 500-ml beaker glasses was set up at a room temperature for each experiments. Each of the beakers contained 150 ml of black liquor and coagulant/flocculants solution. Figure 2 showed the steps of coagulation process. This study was preceded by a preliminary test. The objective of the preliminary test was to set the concentration boundary that would be employed in the experiments and also to avoid overdose which led to re-stabilization. All coagulants were tested individually. During the test, no chemical was added to control the pH. Table 3 showed coagulant and flocculants used in the preliminary test and coagulation test.

Table 3 Coagulant and Flocculants used in this research

Coagulants
Preliminary Test
Alum
PAC
Ferrous sulphate
Polyacrylamide cationic
Polyacrylamide anionic
Combination
Alum & PAC
Alum & Ferrous sulphate
Alum & Polyacrylamide cationic
Alum & Polyacrylamide anionic
PAC & Alum
PAC & Ferrous sulphate
PAC & Polyacrylamide cationic
PAC & Polyacrylamide anionic
Ferrous sulphate & Alum
Ferrous sulphate & PAC
Ferrous sulphate & Polyacrylamide cationic
Ferrous sulphate & Polyacrylamide anionic

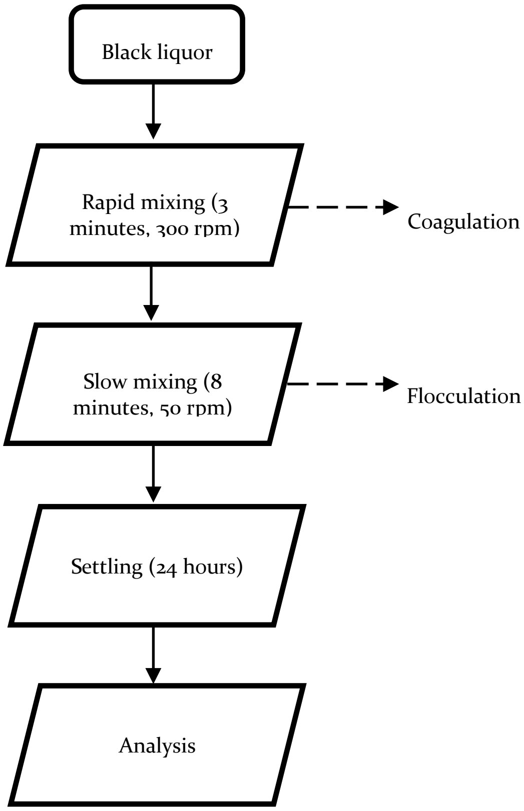

Figure 2 Procedure of coagulation process

Final pH was measured by pH meter after filtration for TSS measurement followed by decolourization measurement. SNI standard method (SNI 06-6989.3-2004) was used as reference method to measure TSS value[17].

$$mg\ TSS\ per\ liter = \frac{(A-B)\ x\ 1000}{Sample\ volume, mL} \quad (1)$$

Where A was the weight of filter paper (Glass Microfiber Filters 934-AH™, 0.45 μm) plus the weight of dry residue (mg) and B was the weight of filter paper, mg.

Decolourization was measured with a single beam UV-Vis spectrophotometer (UV-2120, Optizen, South Korea). The change in absorbance of black liquor was determined at 400 nm. All samples were diluted in the range of 2 – 20 times. AG medium only containing black liquor was used as a control. The percentage of decolorization was calculated as folows:

$$Decolorization\ (\%) = \left(\frac{C_c - C_s}{C_c}\right) x100\% \quad (2)$$

where C_c was the initial concentration of untreated black liquor and Cs was the final concentration of treated black liquor.

Table 2 Comparison of alum, PAC, $FeSO_4.7H_2O$, cationic polyacrylamide and anionic polyacrylamide as coagulant[18]–[25]

Parameters	Alum ($Al_2(SO)_3.18H_2O$	PAC	Ferrous sulphate ($FeSO_4.7H_2O$)	cationic polyacrylamide	anionic polyacrylamide
Cost	Low cost	Low cost	Expensive	The most expensive	More expensive
pH	Narrow pH range (5.5 – 6.5)	Wide pH range 5.0 to 8.0. Less dependent of temperature and pH	Wide pH range	Wider pH range	Wider pH range
Residual	Residual aluminium levels in the treated water often exceeded acceptable limits	Low level of residual aluminium in the treated water	High soluble iron concentration	Low residual	Low residual
Floc	Resultant alum floc was fragile	Quick formation of flocs, big floc formation and rapid precipitation	Mildly corrosive	Larger, stronger and more rapidly formed floc	Larger, stronger and more rapidly formed floc
Sludge	More superior regarding the removal of humic and fulvic color constituent than PAC (due to enhanced coagulation)	Less sludge compared to alum at equivalent dosage and more impact than alum	Less sludge compared to alum at equivalent dosage	Less sludge compared to aluminium and iron-based coagulant	Less sludge compared to aluminium and iron-based coagulant
Dosage	More effective, compared to ferric,at low dose	Lower dosage compared to alum	Lower dosage compared to alum	Lower dosage (typically 1% on dry weight basis)	Lower dosage (typically 1% on dry weight basis)
Toxicity	Presumably induce Alzheimer's disease	NA	NA	Generally low toxicity, but slightly more toxic than anionic polyacrylamide	Not toxic
Reaction to alkalinity	Needed supplemental addition of alkalis to achieve optimum coagulation pH	Required less alkalis than alum	Required more alkalis and tended to decline pH of the dosed water more dramatically	Less susceptible to pH	Less susceptible to pH
Settling time	Slower than PAC	Faster than alum	Rapid settlement	Showed significant increase when added with PAC and ferric sulphate	Showed significant increase when added with PAC and ferric sulphate
Solubility	Readily soluble	Wide-range adaptability for different-temperature of source water and good solubility	Less soluble	Soluble at least 40 %(w/v) in water	Soluble at least 40% (w/v) in water

3. Results and Discussion

Preliminary result

Recycled water needs to be adequately treated to ensure the quality. General quality requirements for discharged water aimed for in this study were having neutral pH (7 – 8), decolourization above 90%, TSS reduction above 75%, and sludge volume percentage below 50%**.** Neutral pH was considered safe to use for any chemical or physical reaction and living things. One of the problems with chemical precipitation was the increased sludge volume which caused poor settling, dewatering and disposing of generated sludge and the high concentration of residual cautions left in the supernatant [23], [26], thus the formation of sludge volume as low as it could was also included in this study's evaluation priorities. From this preliminary test, ratios of 3:1 and 3:2 and pH ranging from 6 to 8 at room temperature in various combinations were set.

Coagulation and Flocculation

pH effect

A preliminary test was conducted for all five coagulants individually. The range of concentration was 1-3%. Changes were shown directly for ferrous sulphate after mixing from concentration of 1%. For both alum and PAC, changes were seen from concentration of 2% but none for cationic and anionic polyacrylamide. Therefore, in this study, cationic and anionic polyacrylamides were not used as coagulants but as flocculants. Figure 3 shows the relationship between concentration of each coagulant (1, 2 and 3%) with pH and decolourization (%).

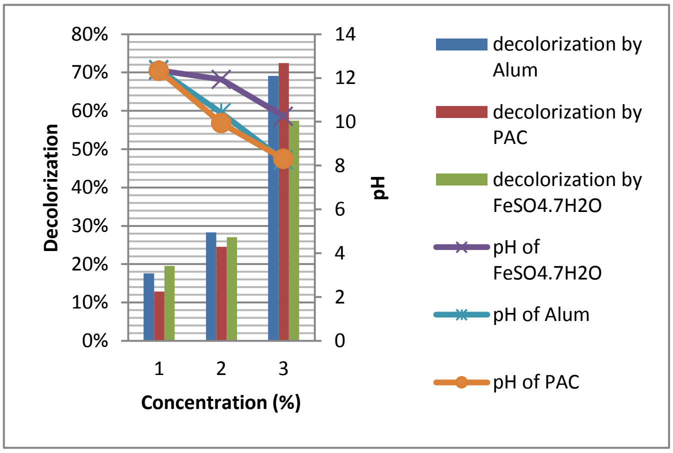

Figure 3 Relationship between concentration with pH and decolourization of Alum, PAC and $FeSO_4.7H_2O$[27]

From Figure 3, it is clearly shown that the concentration of coagulants affected pH. Metal coagulants are acidic, therefore addition of the coagulants reduced alkalinity [29].The more coagulants added to the black liquor, the lower the pH and in turn the higher resulting decolourization percentage. Among the coagulants, PAC showed a great impact on both pH and decolourization. With concentration of 3%, PAC alone decreased the pH from 12.47 to 8.3 and achieved decolourization around 72%. The decreased pH occurring in black liquor could be explained from the chemical reactions below.

Alum[23]:

$$Al_2(SO_4)_3.18H_2O \rightarrow 2Al^{3+} + 3SO_4^{2-} + 18H_2O \rightarrow 2Al(OH)_3 + 6H^+ + 3SO_4^{2-} + 12H_2O \quad (3)$$

PAC[20]:

$$Al_2(OH)_3Cl_3 \rightarrow Al_2(OH)_3^{3+} + 3Cl^- + 3H_2O \rightarrow 2Al(OH)_3 + 3H^+ + 3Cl^- \quad (4)$$

$FeSO_4.7H_2O$:

Reaction of ferrous sulphate in water in the presence of natural alkalinity [30],

$$FeSO_4 + 2HCO_3^- \rightarrow Fe(OH)_2 + SO_4^{2-} + 2CO_2 \quad (6)$$

The chemical reactions above (3–6) are the hydrolysis reaction between coagulants followed by the formation of metal hydroxide floc as well as hydrogen ions. The hydrogen ion will react with alkalinity of the water and in the process, decreasing the pH of the water. Although from the reaction alum released more hydrogen ions ($6H^+$) than PAC, but from the experiments, it was PAC, with $3H^+$ that decreased pH more and thus increased the decolourization higher than with alum.

Sludge volume (SV)

The sludge produced in the coagulation and flocculation process is formed because of the removal of organic matter in the wastewater [31]. The species formed from the use of coagulants also become part of the sludge. The result of the sludge formation showed in Table 4.

The low sludge detected as a result of alum, PAC and $FeSO_4.7H_2O$ coagulation with concentration of 1 and 2% (see Table 3) did not mean that it successfully formed less sludge, but was caused by incomplete coagulation. The concentration of the coagulants was so low that the pH still beyond the optimum, and therefore, the hydrolysis could not fully occur and neither did the coagulation.

Visually speaking, the appearance of ferrous sulphate supernatant and floc was different compared with that of alum and PAC. The coagulation using ferrous sulphate gave a brown-orange-greenish floc and light brown liquid, while alum and PAC gave a brown-yellowish floc and clear yellow liquid. From this study, we could say that the amount and characteristic of the sludge generated during coagulation/flocculation were varied by the type of coagulant and the condition of the process (pH)[32].

Table 4 Comparison of sludge volume formation between alum, PAC and $FeSO_4.7H_2O$

Coagulants	Concentration (%w/v)	Final pH	Sludge Volume Formation (%)
Alum	1	12.38	-
	2	10.34	13.33
	3	8.21	66.67
PAC	1	12.33	20
	2	10.1	33.33
	3	8.37	66.67
$FeSO_4.7H_2O$	1	12.32	33.33
	2	11.9	73.33
	3	10.04	73.33

Total Suspended Solids

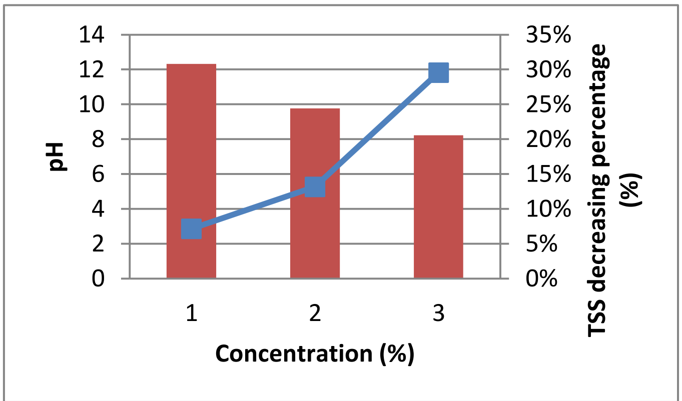

Figure 4 Relation of concentration (PAC) with pH and TSS decreasing percentage (%)

From the preliminary study, it was found that the lower the pH the greater the TSS decreases. PAC was the best candidate in removing TSS content. But, as the study involved optimum pH, it was difficult to see the trend line of the resultant TSS decrease (Figure 4).

3.1 Alum as coagulant

The best result that alum could provide as a coagulant was when it was combined with anionic polyacrylamide. With a concentration ratio of 3:1 and optimum pH 6 for alum and 6.5 for anionic polyacrylamide, the combination could achieve neutral pH of 7.23, decolourization of 90.04%, TSS decreasing percentage of 68.48% and sludge volume formation percentage of 54.55%. With regards to decolourization, the combination of alum and PAC gave a better result (95.38%). However, a higher volume of sludge formed as a result. The combination of alum and ferrous sulphate did not show any good results for all responses (data not shown). It was observed that low sludge was always achieved using polyacrylamide as flocculants, especially cationic polyacrylamide. Table 5 showed the best results for alum as coagulant.

From this study, it was found that the best concentration for alum combined with other flocculants (either PAC or polyacrylamide) was 3% at pH 6 - 6.5.

The chemistry of aluminium in the coagulation process is complex because various reaction pathways are feasible. The mechanism by which aluminium functions relies on which aluminium species react to remove the dissolved or colloidal pollutant [33]. When alum is introduced to water, it rapidly undergoes hydrolysis reaction to form other dissolved Al species or Al-hydroxide precipitates, including monomeric Al species $Al(OH)^{2+}$, $Al(OH)^{+}_2$ and $Al(OH)_4^-$, dimmer $(Al_2(OH)_2^{4+}$, trimer $(Al_3(OH)_4^{5+}$, tridecamer $(Al_{13}O_4(OH)_{24}^{7+}$ and amorphous precipitate $Al(OH)_{3(am)}$ [34]. The dissolved species can be removed by adsorption or aluminium precipitation [33]. If coagulation occurs at pH>7, a high fraction of dissolved Al is present as $Al(OH)_4^-$. Hence, at high pH there would be a small fraction of positively charged Al species available to form a complex with the contaminant and neutralize its negative charges. At pH<5, $Al(OH)^{2+}$ and Al^{3+} dominate and Al complexes with the contaminant were formed, neutralizing the negative charges and leading to direct solid precipitation. Generally, coagulation at low pH could result in high concentration of dissolved Al in the treated water [35].

Table 5 The best results of Alum as coagulant

Combination of Coagulants/Flocculants	Conc. %w/v	Optimum pH	Final pH	Decolorization (%)	TSS Decreasing Percentage (%)	SV Formation (%)
Alum and PAC	3:2	None	6.58	95.38	52.08	86.67
Alum and cationic polyacrylamide	3:1	6.5 for both	6.69	91.59	51.74	36.36
Alum and anionic polyacrylamide	3:1	6 for alum and 6.5 for anionic polyacrylamide	7.23	90.04	68.48	54.55

3.2 PAC as coagulant

As a coagulant, PAC showed the best performance with good results for decolourization (four of the good results showed high decolourization above 90%) and neutral pH. Since the preliminary test, PAC had already shown to be a potential candidate. Although the combination with anionic polyacrylamide gave a better result for decolourization and TSS decrease, PAC proved to be more suitable when combined with cationic polyacrylamide. The combination showed the best result for four responses (neutral pH, high decolourization, high TSS decrease and low sludge volume formation). This superior response of PAC may be related to the highly positive charged polycation content that is highly effective in neutralizing the negative charge of colloidal particles, therefore resulting in increased colloidal destabilization [36]. After being introduced to water, PAC rapidly undergo hydrolysis reactions to form other dissolved Al species or Al-hydroxide precipitates. At low concentration, aluminium hydroxide precipitation was minimal. Charge neutralization was the mechanism used to explain the precipitation. The positive charge of aluminium interacts electrostatically with negative charge from the contaminant particles and form insoluble neutral products. When the concentration of PAC was high enough to cause rapid precipitation of $Al(OH)_3$, contaminants could be removed by surface adsorption. Further, a small portion of Al reacted with contaminants to form a complex between Al-contaminant [37]. $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ has been shown to dominate the species [14]. Table 6 shows the best results for four responses of PAC as coagulant.

Table 6 The best results of PAC as coagulant

Combination of Coagulants/Flocculants	Conc. %w/v	Optimum pH	Final pH	Decolorization (%)	TSS Decreasing Percentage (%)	SV Formation (%)
PAC and alum	3:2	6 for both	3.99	97.39	79.64	56
PAC and anionic polyacrylamide	3:1	6 for PAC and 6.5 for anionic polyacrylamide	7.21	95.68	67.61	61.54
PAC and anionic polyacrylamide	3:1	6.5 for both	7.14	93.94	67.06	71.43
PAC and cationic polyacrylamide	3:1	6.5 for both	7.2	93.14	79.64	40

From this study, we found that the best concentration for combination of PAC with other flocculants was 3% and like alum, its optimum pH was also in the range of 6 – 6.5.

3.3 $FeSO_4.7H_2O$ as coagulant

Neither as coagulant nor flocculants, the coagulation using ferrous sulphate resulted any good result for the four responses. From this study we could conclude that ferrous sulphate, at the concentration tested, was not suitable for treating the black liquor from alkaline pre-treatment of bioethanol production from oil palm empty fruit bunch. However, higher dosage and a wider range of pH might be needed in order for this coagulant to perform better. However, the nature of ferrous sulphate, which is corrosive, and the use of H_2SO_4 for pH adjustment made it not environmentally friendly.

3.4 Cationic and Anionic Polyacrylamide as flocculants

From the study, cationic polyacrylamide showed the best performance combining with the coagulants, except $FeSO_4.7H_2O$. Actually, both of the polyacrylamide (cationic and anionic) resulted in good responses, however, cationic polyacrylamide produced less sludge volume than anionic polyacrylamide (see Table 6). Generally, polymers flocculants generate less sludge than aluminium or ferric salt because they did not increase weight [13].

Generally, polymers are characterized by their molecular weight and the ionic charges. Bridging and electrostatic patch were potentially the best mechanisms to describe the effect of polymer molecular weight on flocculation. When the system was predominated by bridging regardless of the charges, increase in molecular weight also improved flocculation. At higher molecular weight, as the polymer was being absorbed, it could extend further away from the particle surface and was slower to reach equilibrium. This, therefore, increased the particle radius and collision number which led to an increase in flocculation rate[4].

In flocculation, the long chain polymers attach at a relatively few site of the particles, leaving long loops and tails who stretch out into the surrounding water. In order for the bridging flocculants to work, the distance between the particles must be small enough for the loops and tails to connect two particles[33], [38]. The polymer molecules thus attached themselves forming a bridge[7], [39], [27]. Therefore, in order to get a more effective flocculation, polymer with higher molecular weight was required. Compared with anionic polyacrylamide, cationic polyacrylamide had higher molecular weight (see Table 7), and it could explain the reason why cationic polyacrylamide more effective.

Table 7 Characteristic properties of different type of polyacrylamide (PAM)[40]

Ionic type	Molecular Weight (g/mole)	Charge density (c/g)	Percentage charge monomer
Anionic	$5.5 - 7 \times 10^6$	-260	30.0
Cationic	$6.0 - 7 \times 10^6$	+150	19.0
Non-ionic	5.0×10^6	-1.07	-

Table 8 Comparison of the best result of alum and PAC as coagulant

Combination Coagulants/Flocculants	Conc. %w/v	Optimum pH	Final pH	Decolorization (%)	TSS Decreasing Percentage (%)	SV Formation (%)
Alum as coagulant : Alum and Cationic Polyacrylamide	3:1	6 for alum and 6.5 for cationic polyacrylamide	6.69	91.59	51.74	36
PAC as coagulant : PAC and cationic polyacrylamide	3:1	6.5 for both	7.2	93.14	79.64	40

From the study, it was found that the pH adjustment for coagulation and flocculation had a strong positive effect on decolourization and final pH. As for the TSS decrease percentage, pH adjustment for the coagulant and flocculant combination did not result in a clear trend line. Nevertheless, in general from all of the combinations between PAC, alum, ferrous sulphate, anionic and cationic polyacrylamide, the most suitable coagulants were alum, PAC and polyacrylamide (cationic and anionic) as flocculants. It was also found that adsorptive coagulation using cationic or anionic polyacrylamide as coagulant aid (bridging flocculation) showed better results than sweep coagulation using alum, PAC and ferrous sulphate as flocculants.

Water recovery of black liquor from bioethanol production via coagulation is one of the most efficient method for water treatment. The treated black liquor has neutral pH which can be discharged directly to the water way or reused for the pre-treatment process of the bioethanol production. Intensive decolourization and high TSS decrease percentage which were represented from the slightly clear water was safe for aquatic biosphere. Low sludge volume means low sedimentation which can further reduce the risk of flood. Thus, both economic and environmental aspects were achieved and could support sustainability for a better earth.

Conclusion

Four parameters were evaluated in this study to investigate the most effective coagulants and its condition for treating black liquor wastewater in bioethanol process from oil palm empty fruit bunch. The result showed that decolourization was greatly influenced by pH. Adding aluminium-based (alum and PAC) and iron-based coagulant (ferrous sulphate) decreased the pH of the black liquor, and therefore increased the decolourization. Changes in pH also affected TSS content and final pH, while sludge volume formation depended on the type of coagulant/flocculants. From all the concentration combinations and pH, we found that the combination of PAC and cationic polyacrylamide with ratio combination of 3:1 and optimum pH of 6.5 was the most effective coagulant/flocculants for treating the black liquor. The combination gave 93.14% decolourization, final pH of 7.2, 40% sludge volume formation and 79.64% TSS decreased percentage.

Acknowledgements

This research was supported by Insentif Riset SINAS 2015-Ministry of Research & Technology.

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