PRE-TREATMENT OF PALM OIL MILL EFFLUENT (POME): A COMPARISON STUDY USING CHITOSAN AND ALUM

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Abstract: Chitosan is a natural organic polyelectrolyte of high molecular weight and charge density; obtained from deacetylation of chitin. This study explored the potential and effectiveness of applying chitosan as a primary coagulant and flocculent, in comparison with aluminium sulphate (alum) for pre-treatment of palm oil mill effluent (POME). A series of batch coagulation and flocculation processes with chitosan and alum under different conditions, i.e. dosage and pH were conducted, in order to determine their optimum conditions. The performance was assessed in terms of turbidity, total suspended solids (TSS) and chemical oxygen demand (COD) reductions. Chitosan showed better parameter reductions with much lower dosage consumption, compared to alum, even at the original pH of POME, i.e. 4.5. At pH 6, the optimum chitosan's dosage of 400 mg/L was able to reduce turbidity, TSS and COD levels by 99.90%, 99.15% and 60.73% respectively. At this pH, the coagulation of POME by chitosan was brought by the combination of charge neutralization and polymer bridging mechanism. As for alum, the optimum dosage was 8 g/L at pH 7 which result in reductions of turbidity, TSS and COD by 99.45%, 98.60% and 49.24%, respectively. Combinations of chitosan and alum, showed very little increment in efficiency, compared to using chitosan alone. It can be suggested that polymer bridging mechanism by chitosan is more dominant than alum and the dosage of alum can also be reduced.

Keywords: *Chitosan; Alum; Coagulation; Palm oil mill effluent; Wastewater Treatment*

Abstrak: Kitosan adalah polielektrolit organik semulajadi yang berjisim molekul dan berketumpatan caj yang tinggi, diperoleh dari deasetilasi kitin. Kajian ini meneroka potensi dan keberkesanan kitosan sebagai pengental utama dan flokulan, dibandingkan dengan aluminium sulfat (alum), untuk rawatan awal sisa kilang kelapa sawit (POME). Siri ujian pengentalan dan flokulasi kelompok telah dikendalikan di bawah keadaan yang berbeza seperti dos dan pH untuk menentukan keadaan optimal bagi pengental kitosan dan alum. Prestasi diuji berdasarkan penurunan nilai kekeruhan, kandungan pepejal terampai (TSS) dan keperluan oksigen kimia (COD). Kitosan menunjukkan penurunan parameter yang lebih baik dengan keperluan dos yang lebih rendah berbanding alum, walaupun pada pH sampel yang asal, iaitu 4.5. Pada pH 6, dos optimal kitosan pada 400 mg/L mampu menurunkan nilai kekeruhan, kandungan pepejal terampai (TSS) dan keperluan oksigen kimia (COD) sebanyak 99.90%, 99.15% dan 60.73%

masing-masing. Pada pH ini, pengentalan POME oleh kitosan dibawa oleh kombinasi mekanisme peneutralan cas dan titian polimer. Alum merekodkan dos optimal pada 8 g/L dan pH optimal pada pH 7 dengan penurunan nilai kekeruhan, kandungan pepejal terampai (TSS) dan keperluan oksigen kimia (COD) sebanyak 99.45%, 98.60% dan 49.24% masing-masing. Kombinasi kitosan dan alum menunjukkan peningkatan kecekapan yang amat kecil dibandingkan dengan menggunakan kitosan sendirian. Daripada keputusan yang diperolehi, dapat dicadangkan bahawa mekanisme titian polimer oleh kitosan adalah lebih dominant berbanding alum dan dos alum juga dapat dikurangkan.

Kata kunci: *Kitosan; Alum; Sisa Kilang Kelapa Sawit; Rawatan Sisa Air*

1.0   Introduction

Palm oil production is one of the major industries in Malaysia. During the period between 1990 and 2002, palm oil production was nearly doubled from 6.094,622 to 11,880,000 (MT) per year, making Malaysia the biggest palm oil producer worldwide (Vijayaraghavan *et al*, 2007). The improvement of processing technology will lead to further increase in world's palm oil supply. However, the rapid development of the industry has had serious consequences on the natural environment, which mainly related to water pollution due to a large discharge of untreated or partially treated palm oil mill effluent (POME) into watercourses. In the year 2004, more than 40 million tonnes of POME was generated from 372 mills in Malaysia (Yacob *et al*, 2006). Therefore, the palm oil mill industry in Malaysia is identified as the one that produces the largest pollution load into the rivers throughout the country (Hwang *et al,* 1978).

Fresh POME is a colloidal suspension containing about 95% water, 0.6-0.7% oil, and 4-5% total solids including 2-4% suspended solids that are mainly debris from palm fruit (Ahmad *et al*, 2005). It is acidic with pH 4-5 and discharged at temperature about 80-90°C. Although the effluent is non toxic, it has a very high concentration of biochemical oxygen demand (BOD) (i.e. 25 000 mg/L) which becomes a serious threat to aquatic life when discharged in relatively large quantities into watercourses. Furthermore, POME contributes 83% of the industrial organic pollution load in Malaysia (Vigneswaran *et al*, 1999).

The most common practice for POME treatment nowadays is by biological processes in which based on anaerobic and aerobic ponding system. However, biological treatment systems need proper maintenance and monitoring as the processes rely solely on microorganisms to break down the pollutants. Many palm oil mills which apply the biological treatment system failed to comply with the Department of Environment (DOE) standard discharge limits. Therefore, the pre-treatment of POME using coagulation and flocculation processes has become an important feature, in order to efficiently reduce the organic load prior to subsequent treatment processes. Aluminium sulphate (alum), an inorganic salt, is the most widely used coagulant in wastewater treatment, due to its proven performance, cost-effectiveness and availability. However, the used of aluminium-based coagulant has become under scrutiny. Besides the large amount of sludge produced, high level of aluminium remained in the treated

water has raised concern on public health (Driscoll and Letterman, 1995). Previous research have pointed out that intake of large amount of aluminium salt may contribute to the development of neurodegenerative diseases, including Alzheimer disease (Pontius, 2000). Alternatively, an environmental friendly coagulant such as chitosan can be developed and used nowadays.

Chitosan, known as poly[β-(1→4)-2-amino-2-deoxy-D-glucopyranose], is a cellulose like biopolymer of high molecular weight obtained from deacetylation of chitin. Chitin, a linear chain polysaccharides, is the second most abundant organic material after cellulose, which is the major structural component of invertebrate exoskeleton, particularly in crustacean, mollusks and insects, as well as the principal fibrillar polymer in the cell wall of certain fungi (Roberts, 1992). Besides the reactive primary and secondary hydroxyl groups, chitosan's versatility as an adsorbent is a function of its highly reactive amino group at the C(2) position (Savant and Torres, 2000). The protonation of the chitosan amino groups (NH_2) in solution makes the chitosan positively charged (exhibit as cationic polyelectrolytes) and thereby very attractive for flocculation and different kind of binding application, by allowing the molecule to bind to negatively charged surface via ionic or hydrogen bonding (Gamage, 2003).

Chitosan offers a broad range of applications favour by unique properties of chitin and chitosan, such as biocompatibility, biodegradation, biological activity, non-toxicity, non-allergenic and ability for fiber and film formation. In water and wastewater treatment applications, chitosan has been used to synthesize membrane, used as an absorbent as well as primary coagulant or flocculent. Chitosan is recognized as excellent metal ligands, forming complexes with many metal ions, thus enhance the removal of toxic metals from industrial wastewater. It has been shown to effectively remove metals such as molybdenum, arsenic, gold, cadmium, vanadium, chromium, lead, cobalt, iron, manganese, silver, copper, nickel, mercury, and zinc from aqueous solutions (Evans *et al*, 2002). In addition, it has been proved that chitosan could coagulate and flocculate a variety of suspensions or wastewaters including mash and lauter wastewater of brewery (Cheng *et al*, 2005), fish-meal factories (Guerrero *et al*, 1998), mineral colloids (Huang and Chen, 1996), river silt (Divakaran and Pillai, 2002), latex particles (Ashmore and Hearn, 2000), microorganisms (Strand *et al*, 2003) and POME (Ahmad *et al*, 2006).

In this study, the effectiveness of chitosan as a coagulant for pre-treatment of POME was assessed, in comparison with alum. A series of batch coagulation test was conducted to obtain the optimum dosage and pH for both coagulants, by evaluating the parameter reduction such as turbidity, total suspended solids (TSS) and chemical oxygen demand (COD). Finally, this study aimed at combining chitosan and alum, in an effort to determine their effectiveness. Thus, the pre-treatment of POME could be improved in a more economically and environmentally manner.

2.0   Experimental

2.1   Materials

Samples of POME were collected from a FELDA palm oil mill in Kulai, Johor. The samples were then placed in a thermal resistant plastic container, sealed tight and labeled, before being transported to the laboratory. For preservation, samples were refrigerated at about 4°C in order to prevent the wastewater from undergoing biodegradation due to microbial action. A portion of the samples was analyzed for its characteristic.

Chitosan was purchased from Acros Organic, New Jersey in the form of white fine powder. For the experimental purpose, chitosan stock solution was prepared as follows: 1.5 g of chitosan powder was dissolved in 150 mL of 0.1M HCl solution and agitated at approximately 100 rpm with a magnetic stirrer until the solution was completely dissolved. It was further diluted with 150 mL of distilled water to yield a solution containing 5.0 mg chitosan per mL of solution. For consistency, the solutions were prepared fresh before each set of experiments. Alum, $Al_2 (SO_4)_3.18H_2O$, was purchased from GCE Laboratory Chemicals with molecular weight of 666.42 g/mol.

2.2   Jar Test

A conventional jar test apparatus (Phipps and Bird stirrer, USA) was used in the experiments to coagulate POME with the coagulants. It was carried out as a batch test, accommodating a series of six beakers together with six-spindle steel paddles. The POME samples were mix homogeneously before fractionated into beakers containing 500 mL of suspension each. Prior to the test, the samples were measured for turbidity, TSS and COD for representing an initial concentration. After the desired amount of coagulant was added to the suspension, the beakers were agitated at various mixing times and speeds, which consist of rapid mixing (250 rpm) for 3 minutes and slow mixing (30 rpm) for 30 minutes. After the agitation stopped, the suspension was allowed to settle for 30 minutes. A sample was withdrawn using a pipette from the top inch of supernatant for turbidity, TSS and COD measurements, representing the final concentration. The pH was controlled by adding either strong acid (5M HCl) or strong base (5M NaOH). All tests were performed at an ambient temperature in the range of 26-30°C.

2.2   Analytical analysis

Turbidity was measured using HACH Ratio/XR Turbiditimeter (HACH Company, USA). The measurement is based on the light-transmitting properties of water. A gravimetric method was used to determine the TSS, with the aid of vacuum filtration apparatus. The weight of solids retained on a filter paper was determined after heating. The COD test was performed by colorimetric method using Spectrophotometer HACH Model DR/2000 (HACH Company, USA). It measures the amount of oxygen (O_2)

required for complete oxidation of organic matter using strong oxidation agent, i.e. dichromate ion ($Cr_2O_7^{2-}$).

3.0 Results And Discussion

3.1 *Effect of dosage on chitosan and alum performances*

Effect of different coagulant dosage for chitosan and alum on the destabilization of POME was analyzed. The tests were carried out at original pH of POME sample, i.e. 4.5. Chitosan, in this case, acts as a primary coagulant to destabilize, coagulate and further flocculate the suspension. The results are presented in Figures 1 (a) and 1 (b) for chitosan and alum, respectively. These figures show that the increases of coagulant dosage for both chitosan and alum lead to better coagulation performances. The trends for all parameters are almost identical. Chitosan recorded the highest reduction of parameters for the applied dosage of 400 mg/L, which are the reduction of 99.59 %, 99.11 % and 59.47 % for turbidity, TSS and COD, respectively. On the other hand, alum seems to require much higher dosage, i.e. 8 g/L to achieve the best turbidity, TSS and COD reductions, which are 99.90 %, 95.80 % and 47.70 %, respectively. Thus, chitosan was far better than conventional alum for POME coagulation, since it provides better parameter reductions with 20 times much lesser dosage. These results are in agreement with the study by Ahmad *et al*, (2006), which also proved that chitosan is a better coagulant even at lower dosage to remove suspended solids of POME, compared to alum and PAC, which needed much higher dosage.

This phenomenon could be explained based on charge density. Chitosan has a high charge density compared to the other coagulants (Ahmad *et al*, 2006). Moreover, polymer adsorption increased as the charge density of the polymer increased (Ariffin *et al*, 2005). Therefore, this signifies the rapid destabilization of the particles; and can also be concluded that the amount of the coagulant required to destabilize the particles is less for a coagulant of higher charge density, i.e. chitosan.

On top of that, the operating pH of 4.5 could influence the chitosan behavior. In acid solution the amino groups of chitosan are protonated and under these conditions chitosan would be expected to exhibit behavior typical of a polyelectrolyte (Roberts, 1992). The protonation of amino groups of chitosan in solution makes chitosan positively charged (act as cationic polyelectrolytes) and since the particles in POME suspension is negatively charged, chitosan is very attractive as coagulant by allowing the molecule to bind to negatively charged surface via ionic or hydrogen bonding (Gamage, 2003). This will further reduce or neutralize the particles surface charge. Therefore, the particles destabilization by chitosan could be explained by charge neutralization mechanism.

However, overdosing of chitosan beyond the optimal state causes e a slight decrease in the removal efficiencies, as illustrated in Figure 1 (a). This could be due to reversal of surface charge as well as the restabilization of coagulated particles. Once the chitosan dosage exceeds the saturation of polymer bridging, surplus chitosan has a tendency to destroy the polymer bridging between particles, thereby exhibiting an increase in
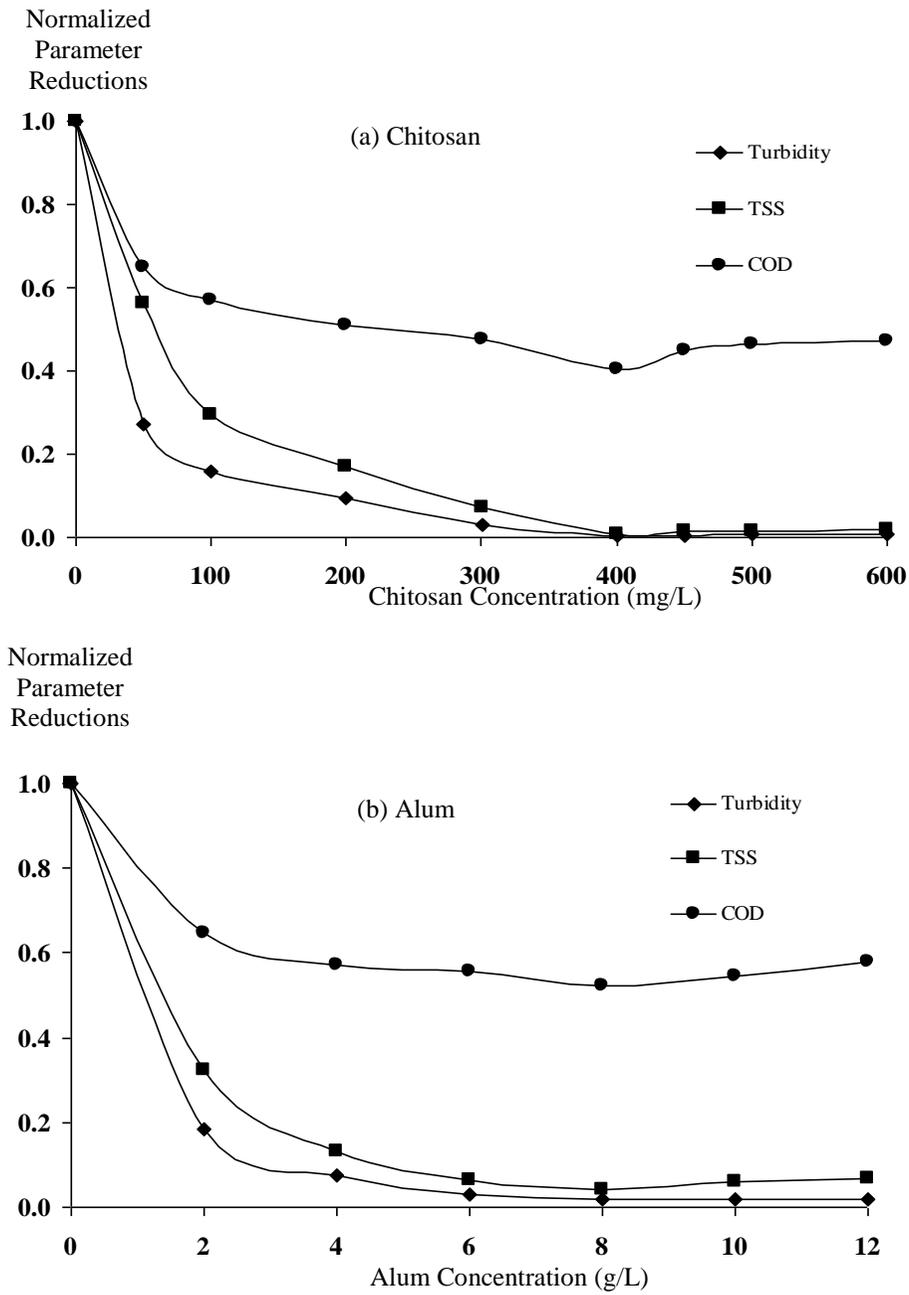
Figure 1: Effect of dosage on parameter reductions for: (a) Chitosan; and (b) Alum

residual turbidity. Weber (1972) indicated that polymer overdosing produces restabilized particles, due to unavailable site for the formation of bridges, resulting in the steric repulsion.

The same trend of restablization of coagulated particles can also be seen in Figure 1 (b) for alum, although not too significant. The excess concentration of alum beyond its optimum dosage has the possibility to get a charge reversal, which led to particles restabilization and a decreased in coagulation performance.

3.2   *Effect of pH*

The study of pH is essential to determine the optimum pH condition of a treatment system. The pH will not only affect the surface charge of coagulants, but also affects the stabilization of the suspension. The study was conducted by adjusting the pH from 2 to 9, using the optimized dosage of each coagulant, i.e. 400 mg/L of chitosan and 8 g/L of alum.

3.2.1   *Effect of pH on chitosan performance*

The parameter reductions for chitosan coagulation at different pH are shown in Figure 2. By analyzing every curve in Figures 2 (a), (b) and (c) for turbidity, TSS and COD reductions, respectively; it can be stated that the pH of POME has an influence on coagulation using chitosan. The trends for all parameters are almost identical. The figure demonstrates that over 99 % turbidity reduction can be achieved at pH 4.5, 6 and 7; of these the optimum is pH 6. At pH 6, the removal of turbidity, TSS and COD are 99.90 %, 99.15 % and 60.73 %, respectively. Nevertheless in pH < 4.5 and > 7, the turbidity, TSS and COD values increased. Therefore, chitosan demonstrates the best result of POME destabilization in slightly acidic condition, while portrays poorer efficiencies in strongly acidic and alkaline condition.

The cationic nature of chitosan, which is affected by the behavior of its functional amino group, is strongly influenced by pH. Equation (1) describes the equilibrium reaction for amino group.

$$- NH_3^+ + H_2O \leftrightarrow - NH_2 + H_3O^+ \qquad\qquad \text{Equation (1)}$$

The reaction shifts to the left as the concentration of H^+ ions increase. Ashmore and Hearn (2000) pointed out that the equilibrium lies predominantly (99.97 %) to the left at pH 3. It is known that strong acidic led to very strong cationic charge on chitosan. This situation is believed to create more possibility for particles restabilization due to reversal of surface charge, compared to at a higher pH. Besides that, at very low pH value, chitosan is very soluble and incapable of producing floc (Divakaran and Pillai, 2004). According to Schmuhl *et al.* (2001), chitosan is unstable at pH 2. Therefore, it can be concluded that at pH below 4.5, the given concentration of chitosan causes the charge reversal of POME; and charge neutralization is the principal mechanism at low pH.
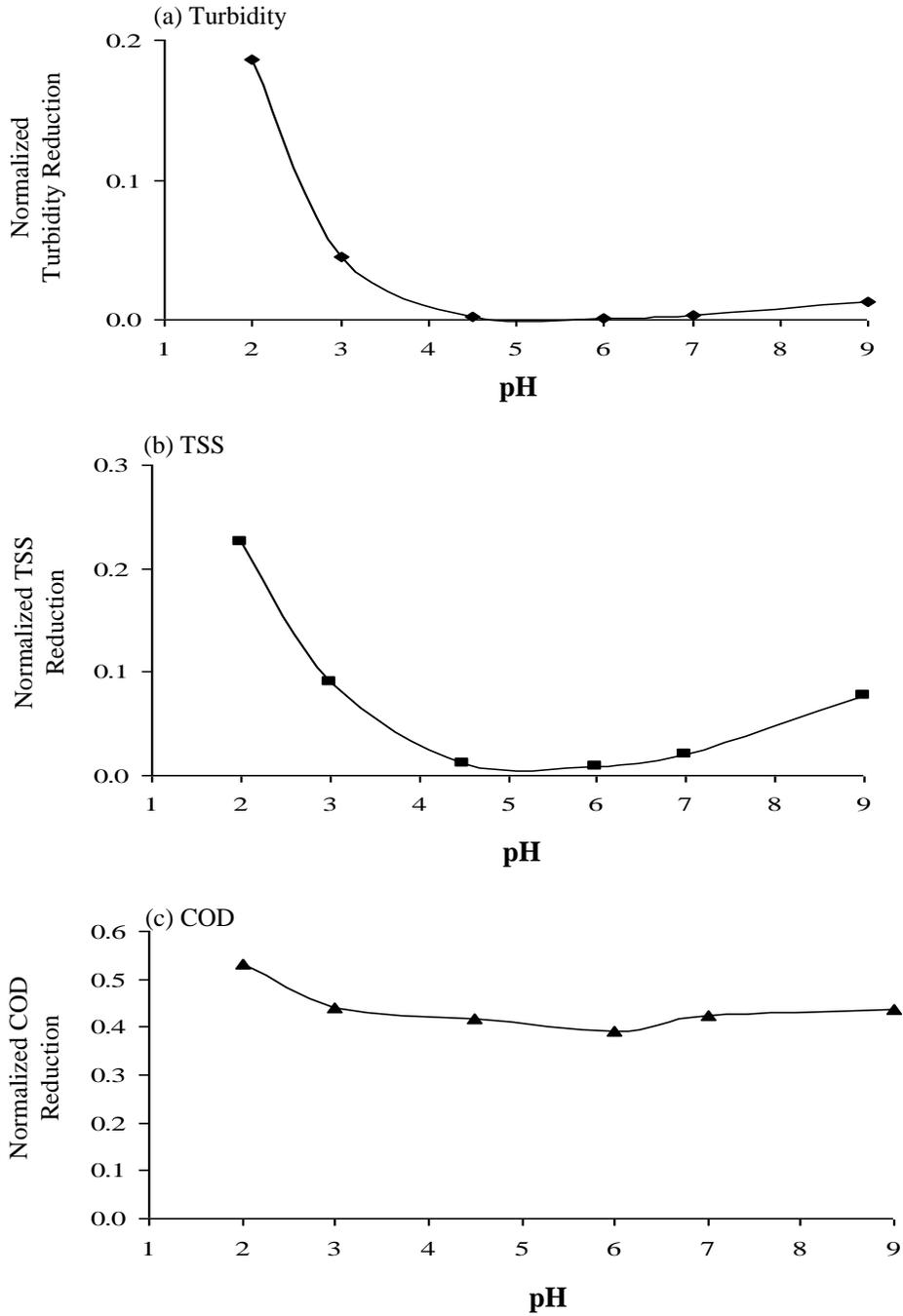
Figure 2: The effect of pH on chitosan performance for the reduction of : (a) Turbidity; (b) TSS; and (c) COD.

Although the differences between the plots at pH 4.5, 6 and 7 in Figure 2 are not very significant, but if based on the parameters' value, pH 6 provides the optimum removals compared to the other pH. It is agreed in the previous discussion that charge neutralization plays an important part for POME destabilization at pH 4.5. Domard *et al.* (1989) pointed out that there are 90% of the functional group of NH_2 on chitosan surface has been protonated at pH 4, and gradually reduced to about 50% as pH increased to 6. Therefore, the positive charges on the chitosan surface will significantly decrease as solution pH increased, so the contribution by the charge neutralization of the chitosan to destabilize the particles becomes less important as pH increased. The properties of chitosan, including its cationic behavior and molecular weight, may be used both for charge neutralization (coagulating effect for anionic compounds) and for particle entrapment (flocculating effect) (Roussy *et al.*, 2005). Therefore, it is suggested that at optimum pH (i.e. pH 6), the coagulation of POME by chitosan is brought by the combination of charge neutralization and polymer bridging mechanism. Moreover, based on observation, the floc produced by chitosan appears rapidly and form a larger size, which can be easily settled, indicating the polymer bridge is formed.

On the contrary, the efficiency of chitosan drops at pH 9, as shown in Figure 2. From the study of Huang and Chen (1996), the isoelectric point of chitosan is about pH 8.7. Above this pH, chitosan loses its cationic nature, in other word positive charge on chitosan surface reduced significantly. Thus, bridging mechanism dominated the particles removal in this region. However, it is not strong enough to efficiently destabilize particles. Roussy *et al.* (2005) also proved that chitosan at alkaline pH (i.e. pH 9) shows very low efficiency and required high concentration of chitosan to achieve the required treatment levels. This confirmed that, at least partial protonation of chitosan amino group was required to achieve efficient coagulation of these organic suspensions. Besides the nature of chitosan, in alkaline condition, the surface of colloidal material has a higher negative charge density due to the deprotonation of carboxylic or phenolic functional groups, so the particles become more stable (Cheng *et al.*, 2005).

3.2.2   *Effect of pH on alum performance*

The parameter reductions for alum coagulation at different pH for (a) turbidity; (b) TSS and (c) COD, are demonstrated in Figure 3. The trends for all parameters are almost identical. It can be seen that alum produced the maximum efficiency at pH 7. About 99.45% turbidity, 98.60% TSS and 49.24% COD reductions were achieved at this pH. Nevertheless, at a low pH range, the efficiencies drop significantly, and slightly drop at alkaline condition. Therefore, the interactions involved for alum to destabilize particles are strongly dependent on pH.

The hydroxide of very low solubility and an amorphous precipitate can be formed at intermediate pH values (Duan and Gregory, 2003). This is of practical significance in the action of these materials as coagulants, which favours the particles removal by sweep floc mechanism. At neutral pH range, large alum hydroxide floc were formed, and as these floc settled, they sweep through the water containing colloidal particles. Thus, the colloidal particles became enmeshed in the floc and settled together. As a
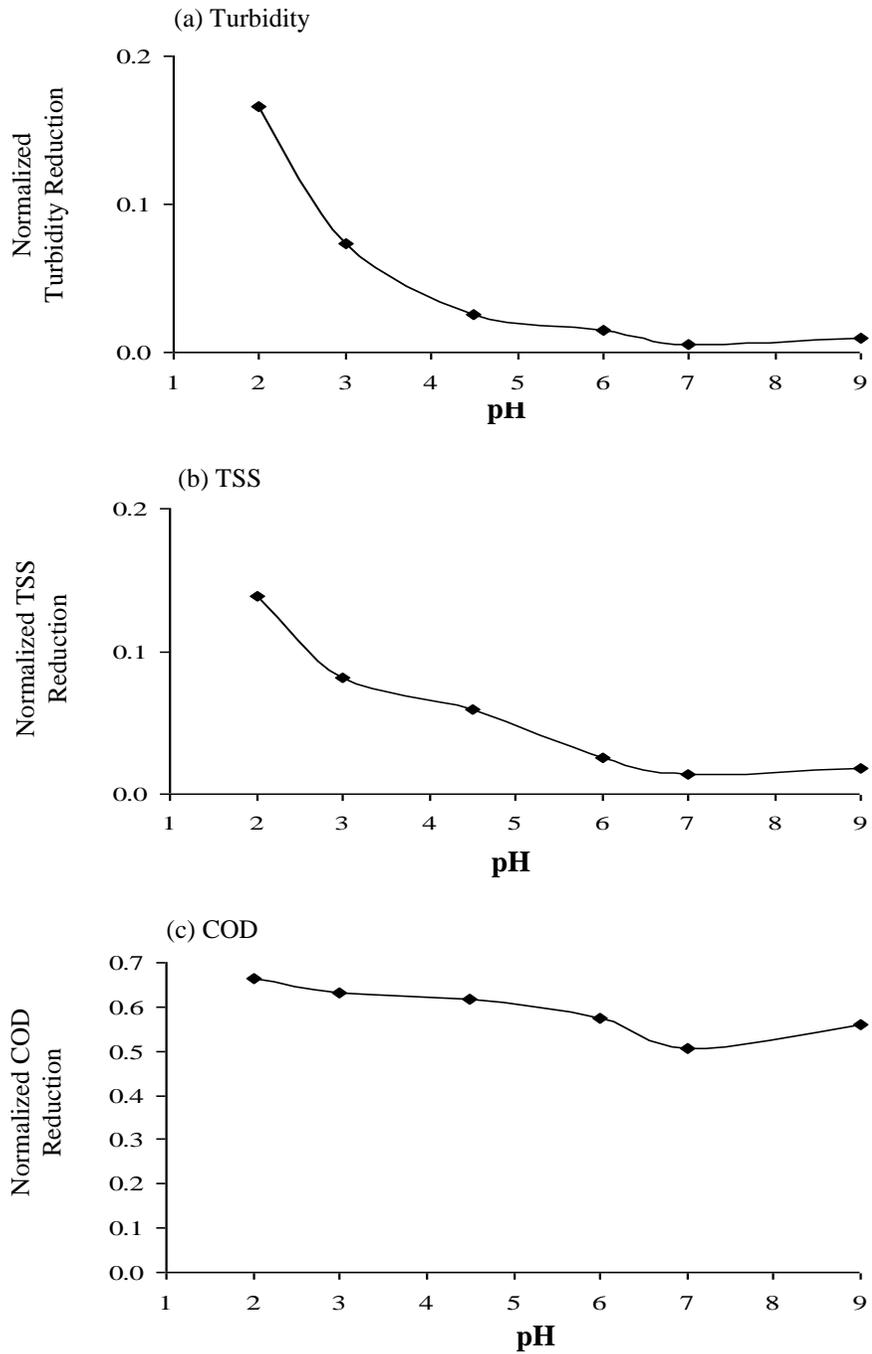
(a) Turbidity

(b) TSS

(c) COD

Figure 3: The effect of pH on alum performance for the reduction of: (a) Turbidity; (b) TSS; and (c) COD.

result, the parameter reductions were improved when the pH were shifted to the neutral condition as depicted in Figure 3. Unfortunately, in acidic conditions, significant amount of non-hydrolyzed Al^{3+} can be found. They are very soluble and not effective as hydroxide precipitate. However, at pH 9, the soluble anionic form of aluminate ion $(Al(OH)_4^-)$ becomes dominant and the decrease of efficiency was also observed.

By comparing the influence of pH for chitosan and alum, chitosan has wider pH range (i.e. 4.5 to 6) to achieve 99% turbidity reduction, whereas, the range is quite narrow for alum. Through observations from jar testing, the chitosan floc size is larger than alum, signifies its rapid settling, but the amount of sludge produced by alum is larger than chitosan.

3.3   *Performance of combination alum and chitosan*

Polyelectrolyes are often successfully used with inorganic coagulants. In many cases, the result of using alum or an iron salt in combination with polyelectrolyte is more beneficial than using either the inorganic salt or the organic polymer alone. Therefore, the final experiment is aimed at combining alum and chitosan. In this case, alum acts as coagulant while chitosan as a flocculent. Alum was added during rapid mixing and chitosan was added during slow mixing. Other than searching for better particles removal, the combination also aims to reduce the alum consumption efficiently. For this reason, the concentration of alum was varied, i.e. 1, 2, 3, 4, 6 and 8 g/L; while the optimized dosages of chitosan, i.e. 0.4 g/L, were fixed for every combinations. By considering the fact that the optimum pH of chitosan is 6 and 7 for alum, as well as they have shown a good efficiency at neutral pH, the operating pH for the combinations were done at pH 7.

Table 1: The performance of alum and chitosan combination for reducing turbidity, TSS and COD in POME

Alum and chitosan concentration	Percentage of Reduction (%)		
	Turbidity	TSS	**COD**
1 g/L alum + 400 mg/L chitosan	99.89	98.47	57.16
2 g/L alum + 400 mg/L chitosan	99.97	98.77	60.36
3 g/L alum + 400 mg/L chitosan	99.98	99.08	61.00
4 g/L alum + 400 mg/L chitosan	99.96	98.58	59.97
6 g/L alum + 400 mg/L chitosan	99.89	98.39	59.85
8 g/L alum + 400 mg/L chitosan	99.88	98.39	56.52

All the combination achieved excellent parameter reductions   (Table 1). The parameter reductions are 99% for turbidity, 98 % for TSS and 55% for COD. Of these, although not very significant, the best results are reported for 3 g/L alum with 0.4 g/L chitosan combination. Reductions of 99.98%, 99.08 % and 61 % of turbidity, TSS and COD, respectively were achieved. The largest turbidity reduction observed was from 9700 NTU to 1.8 NTU.

Even though the differences on the parameter reduction of the combinations and by using chitosan alone are not large, it is evident that a large quantity of alum can be reduced if used in combination with chitosan. During the addition of chitosan in the slow mixing region, a large floc was formed rapidly. This suggests that the polymer bridge mechanism by chitosan is the dominating mechanism of the combinations to destabilize POME.

In this study, the highest reduction of COD obtained was only 61% (Table 1). COD value is associated with the amount or strength of the organic matter in wastewater. Since POME is highly organic and its suspended solids are mainly associated with organic matter, chitosan and alum can effectively remove most of the colloidal and suspended organic matter contents, but is less effective in removing of dissolve organic matter. According to Cheng *et al.*, (2005), poor COD removal from organic suspension may be due to the behavior of the functional groups or the small molecular weight fraction of the dissolved organic matter.

4.0   Conclusion

This study assessed the feasibility of chitosan for the coagulation of colloidal particles found in POME, in comparison with alum. It was found that chitosan was far better than conventional alum for POME coagulation, in term of effluent quality and coagulant dosage. Beside promoting excellent parameter reductions (i.e. turbidity, TSS and COD), chitosan only required 400 mg/L of dosage, compared to 8 g/L for alum, to achieve the best efficiency. Moreover, it is found that the pH of POME has an influence on the coagulation using chitosan and alum. The optimum pH for chitosan and alum are 6 and 7, respectively. As the best pH is obtained in a slightly acidic region, it is recommended that the coagulation by chitosan is performed by the combination of charge neutralization and polymer bridging mechanism, and the latter become significant at higher pH value. For the combination study, all the combination achieved excellent parameter reductions at the adjusted pH 7 and the best results are reported for 3 g/L alum with 400 mg/L chitosan combination. However, combinations of chitosan and alum, showed very little increment in efficiency, compared to using chitosan alone. Through combination, polymer bridge mechanism by chitosan is the dominating mechanism and large amount of alum can be reduced. This study also revealed that chitosan and alum can remove most of the colloidal and suspended form organic matter in POME, but less effective in removing dissolving organic matter.

5.0 Acknowledgement

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