

Coagulation of residue oil and suspended solid in palm oil mill effluent by chitosan, alum and PAC

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Abstract

Aluminum sulphate (alum) and polyaluminum chloride (PAC) are types of commonly used coagulants in wastewater treatments. However, these coagulants produce activated sludge which is very hazardous. Hence, it is suggested that a biodegradable coagulant can be a better alternative. Coagulation of residue oil and suspended solid from palm oil mill effluent (POME) an oily effluent using a biodegradable biopolymer, i.e. chitosan was explored in this study using a flocculator. Chitosan is a cationic biodegradable biopolymer produced by the extensive deacetylation of chitin obtained from shrimp shell wastes. The performance of chitosan was compared to alum and PAC. POME contains about 10,000 mg/l of suspended solid and 2000 mg/l of residue oil. The results obtained proved that chitosan was comparatively more efficient and economical to alum and PAC. At the defined optimum experimental conditions (dosage: 0.5 g/l, contact time: 15 min, mixing rate: 100 rpm, sedimentation time: 20 min and pH 4) chitosan showed more than 95% of suspended solid and residue oil removal. For alum and PAC the optimum dosages were 8.0 and 6.0 g/l, respectively, 30 min of mixing time at 100 rpm, 50 and 60 min of settling, respectively, and pH of 4.5 to obtain the same percentage of removal as performed by chitosan.

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Keywords: Chitosan; Alum; Polyaluminum chloride; Suspended solid; Residue oil; Palm oil mill effluent

1. Introduction

Vegetable oil processing plants, such as sunflower, olive and palm normally discharge large volumes of oily wastewater. These wastes contain very high volumes of oil-in-water emulsions as their basic contaminant. This emulsified oil droplets are sheltered from spontaneous coalescence into larger flocs, thus making oil separation by simple gravity a difficult and time consuming process [1]. Reducing the environmental loading from oily wastes, decreasing processing costs and other products which utilize residue are strong drives for oily waste treatments. Thus, numerous methods have been used to remove residue from wastewaters such as adsorption, coagulation, flocculation, electro-coagulation and flotation [2].

In Malaysia, palm oil-processing mills are the most prominent vegetable oil industry which discharges large volumes of oily and colloidal wastewater. The environmental issues of palm

oil industry are primarily related to the water pollution due to indiscriminate discharge of untreated or partially treated palm oil mill effluent (POME) into public watercourses. POME is a colloidal suspension containing 95–96% water, 0.6–0.7% of oil and grease and 4–5% of total solids. It is a thick, brownish in color liquid with a discharged temperature of between 80 and 90 °C, being fairly acidic with a pH value in the range of 4.0–5.0. Table 1 shows the typical characteristics of raw POME [3,4].

POME contains about 4000–6000 mg/l of oil and grease. The oil droplets of POME can be found in two phases, being either suspended in the solids or floating in the supernatant. Approximately 2000 mg/l of residue oil is present in an emulsified form in the supernatant of POME [5]. These residue oil droplets are solvent extractable. The extract of the oil droplets consist of 84 wt% neutral lipids and 16 wt% of complex lipids. POME also possesses high concentrations of surface active compounds such as phospholipids (10 wt%) and glycolipids (6 wt%) [6]. These natural surfactants stabilizes the oil droplets, hence make it impossible to recover the oil from the sludge as a homogeneous phase [7]. The maximum allowable limit set by the Malaysian

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Table 1
Characteristics of palm oil mill effluent

| Parameter | Concentration (mg/l) | Element | Concentration (mg/l) |
|---------------------------|----------------------|------------|----------------------|
| Oil and grease | 4000–6000 | Phosphorus | 180 |
| Biochemical oxygen demand | 25000 | Potassium | 2270 |
| Chemical oxygen demand | 50000 | Calcium | 439 |
| Total solids | 40500 | Boron | 7.6 |
| Suspended solids | 18000 | Iron | 46.5 |
| Total volatile solids | 34000 | Manganese | 2.0 |
| Ammoniacals nitrogen | 35 | Copper | 0.89 |
| Total nitrogen | 750 | Magnesium | 615 |
| | | Zinc | 2.3 |

Department of Environment (DOE) is 50 mg/l for oil and grease and 200 mg/l for suspended [8]. Therefore, the challenge of balancing the oily effluent of palm oil mills into a more environmental friendly waste requires sound and efficient treatment and disposal approach.

Coagulation method is widely used in water and wastewater treatments and well known for its capability of destabilizing and aggregating colloids. There are number of different mechanisms involved in a coagulation process, including ionic layer compression, adsorption and charge neutralization, inter-particle bridging, and sweep coagulation [9]. These mechanisms are very important in forming flocs of residue oil and suspended solid which could be easily settled and finally removed. Numerous researches have reported the treatment of oily mill effluents using coagulation, filtration and settling procedure [10–12]. A pilot plant study of POME treatment using a series of process such as coagulation, sedimentation, solvent extraction, membrane filtration and adsorption was also found to be very successful by Ahmad et al. [13].

In conventional wastewater treatment systems, coagulants such as aluminum chloride, ferrous sulphate, aluminum sulphate, ferric chloride and hydrated lime are the most widely used. This is because of their effectiveness, cheap, easy to handle and availability [14]. Among the available coagulants, aluminum sulphate (alum) and poly-aluminum chloride (PAC) are the most extensively used coagulant for sludge conditioning and dewatering coagulation processes [15,16]. The most significant usage of aluminum coagulants are usually overdosed in order to ensure coagulation efficiency [17,18]. They are more effective at lower temperatures, a broader pH range and forms positive charged Al species that adsorb to negatively charged natural particles resulting in charge neutralization [19]. Destabilizing oil droplets and destroying emulsions via addition of alum and PAC; polyelectrolytes have been shown to be effective as a pretreatment coagulant to separate oil and grease [20]. However, the usage of this coagulant has been questioned. These coagulants create hazardous activated sludge which contains residual aluminum which may cause side effects when discharged into the open water course [21]. It has been pointed out that intake of large amount of aluminum salt may cause Alzheimer's disease [21]. Thus, it has become a necessity to develop a more efficient, environmental friendly coagulant which has similar potential as aluminum coagulants with an enhanced economic profile. Hence, in this study, a natural polyelectrolyte, i.e. chitosan has

been tried to coagulate the residue oil and suspended solid in POME.

Chitosan (*N*-acetyl-D-glucosamine) is a cellulose-like polyelectrolyte biopolymer which is derived from the deacetylation of chitin. Chitin is widely distributed in marine nature, occurring in the insects, yeasts, fungi and exoskeletons of crustaceans [22]. Chitosan has been recommended as a suitable coagulant resource material because of its excellent properties such as biodegradability, biocompatibility, adsorption property, flocculating ability, polyelectrolyticity and its possibilities of regeneration in number of applications [23]. It is a non-toxic, linear cationic polymer with high molecular weight, charge density and readily to be soluble in acidic solution [24]. Chitosan has been used for various applications such as; coagulation of colloidal particles [18], as a coagulant for suspended solids in food processing plants [25], peatland water treatment [26], rubber factory effluent treatment [27], as a chelator of heavy metals [28] and flocculation of food emulsion waste and river silt [29,30]. Chitosan is not a health threatening material because it is a biodegradable and biopolymeric material. Furthermore, chitosan enhances the recycling of marine waste into value added item. Chitosan chain structure has positively charged amine (NH₂) functional groups which are responsible for the polyelectrolyte behavior. Chitosan could coagulate negatively charged material with its positively charged functional group to give electric neutrality [25].

The objective of this research work was to investigate the potential and effectiveness of chitosan compared to alum and PAC as a coagulant to coagulate suspended solid and residue oil from POME. Experiments were done in a batch coagulation system. Thus, the optimum dosage of coagulant needed to achieve maximum removal of suspended solid and residue oil was determined. The best mixing time and sedimentation time was analyzed. The influence of pH on the coagulation of residue oil and suspended solid was also observed.

2. Materials and method

2.1. Experimental materials

Samples of POME were collected from United Palm Oil Mill, Sungai Kechil, Nibong Tebal, at a temperature ranging from 80 to 90 °C. Samples may vary day to day depending on the discharge limit of the factory, climate and condition of the palm

oil processing. Before the samples are dispensed into the batch system, the samples were cooled to room temperature and let to sediment to remove the total solid. Portions of this suspension were withdrawn and analyzed for their initial residue oil content and pH properties.

Chitosan were supplied by a local manufacturer, Hunza Pharmaceutical Sdn. Bhd., Malaysia in the form of a fine off-white powder with mesh size less than 120. This chitosan was soluble in 1% diluted acetic acid with a 90% degree of deacetylation. Alum and PAC were obtained from Quicklab Sdn. Bhd., Malaysia. Both Alum and PAC were in powder form with mesh size less than 80 and 120, respectively.

Distilled water was used to dilute hydrochloric acid solution (Merck, Germany) and dissolve sodium hydroxide pellets (Merck) to obtain solutions of 5 M. These solutions were then used for pH adjustment during the treatment process, *n*-hexane (Merck) was used as the solvent for oil extraction in the oil and grease analysis.

2.2. Procedure

POME was allowed to sediment for 1 h with the supernatant being analyzed for its residue oil content before and after sedimentation. A conventional jar apparatus (Stuart Science Flocculator model (SW1)) was used to coagulate the samples of POME with chitosan. This apparatus could accommodate six beakers. The contents of each beaker can be simultaneously stirred at the same speed with six-spindle of steel paddles. Each beaker was filled with 1 l of POME. After adding the coagulants into the suspension, the beakers were rapidly mixed at various mixing time (5–60 min) and for different doses of chitosan (0.08–0.8 g/l), alum (0.5–5 g/l) and PAC (0.5–5 g/l). The effect of sedimentation time was analyzed from 5 to 60 min. pH adjustment (3–6) was done to obtain the best pH condition to remove residue oil and suspended solid from POME.

2.3. Analysis

The residue oil content was measured using the oil and grease method recommended by APHA Standard Method of Examination of Water and Wastewater [31], with *n*-hexane being used as the oil-extraction solvent. The oil and grease content in the suspension was determined for each sample of POME both before and after experiment. Three replicates of each test were undertaken with the mean value obtained for residual oil content being calculated from the replicates. All tests were carried out at an ambient temperature of 26–30 °C.

3. Results and discussion

3.1. Relationship between suspended solid of POME and turbidity

Determination of suspended solid concentration (in mg/l) gravimetrically gives a linear relationship with turbidity in NTU, as shown in Fig. 1.

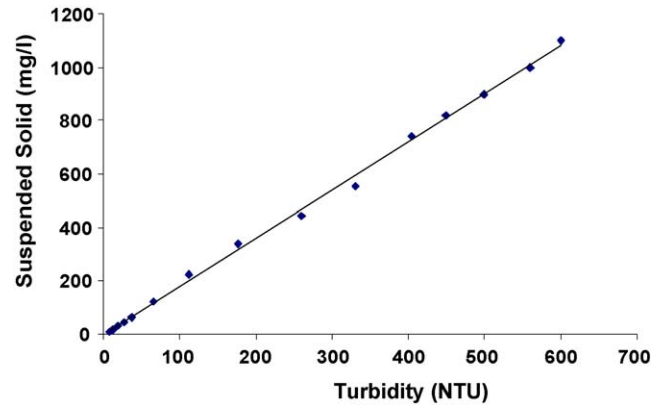


Fig. 1. Calibration curve of suspended solid (mg/l) vs. turbidity (NTU) content.

3.2. Effect of coagulant dosage

The effect of coagulant dosage was analyzed by varying the weight dosage of coagulant with 100 rpm of mixing rate, 1 h of mixing time and 1 h of sedimentation time at pH 4.5. The initial concentration of residue oil in POME is 2.0 ± 0.5 g/l. Fig. 2 shows the comparative of weight dosage against different coagulants and percentage of residue oil removal. It was noticed that 0.5 g/l of chitosan was needed to remove 99% of residue oil from a liter of POME. For alum and PAC it takes about 8.0 and 6.0 g/l, respectively, to remove the same amount of residue oil from POME.

The dosages needed by the synthetic coagulants were 10 times more than chitosan. Furthermore, chitosan proved to be a better coagulant even at lower dosage; 0.3 g/l of chitosan dosage could remove about 70% of residue oil from POME. These results can be explained based on charge density. Chitosan has a high charge density [23] compared to the other coagulants. Therefore, it requires lower dosage to destabilize the residue oil. This proves that chitosan is a very effective coagulant to remove the residue oil content in POME compared to alum and PAC. PAC shows moderately good removal of residue oil compared to alum. The use of polymerized forms of aluminum-like PAC has become more common because of its high charge density compared to alum. PAC and polyaluminum sulphate (PAS) often results in a decrease of coagulant doses and associated solid's

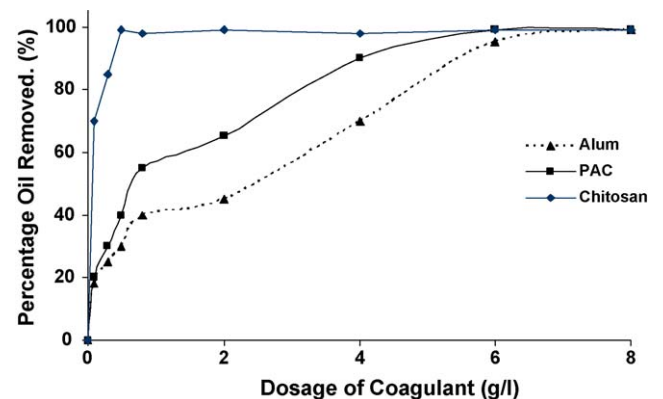


Fig. 2. Percentage of residue oil removed vs. dosage of chitosan, alum and PAC.

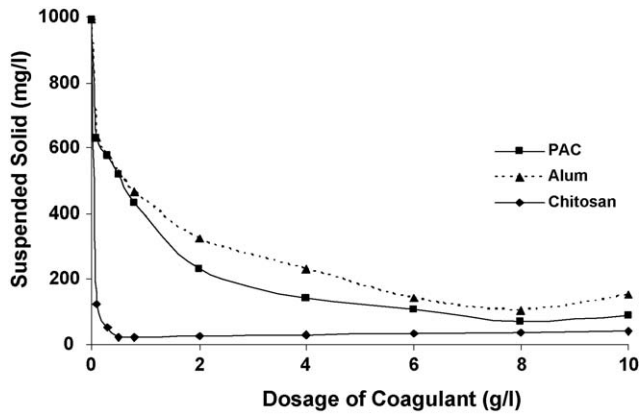


Fig. 3. Suspended solid removal vs. dosage of chitosan, alum and PAC.

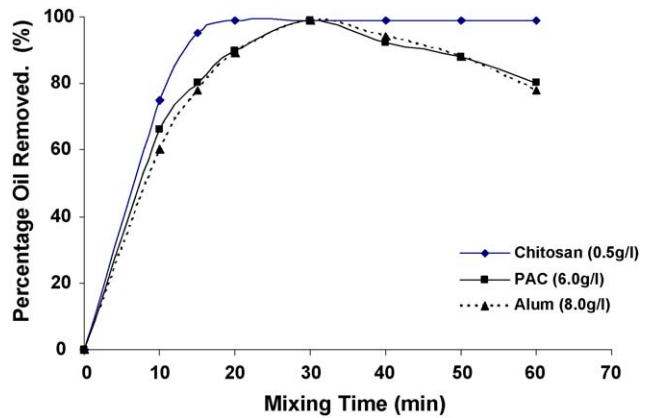


Fig. 4. Percentage of residue oil removed vs. mixing time for chitosan, alum and PAC.

production [19]. This proves why PAC showed a better removal of residue oil at lower dosage compared to alum. This concludes that alum is the poorest coagulant compared to chitosan and PAC in coagulating the residue oil in POME.

Chitosan is a positively charged linear polyelectrolyte at acidic conditions. POME is naturally an acidic suspended effluent. Therefore, this condition could easily stimulate chitosan to coagulate the residue oil from POME. Chitosan destabilizes the negatively charged colloids of residue oil and emulsion from POME by charge neutralization mechanism [18]. Amine functional group of chitosan which attracts anionic ions to bind and bridge [32] helps to coagulate and adsorb the residue oil which is negatively charged in POME.

Fig. 3 demonstrates the suspended solid removal of POME. Turbidity analysis represents the suspended solid removal in POME. The initial turbidity of POME is 550 NTU (1:10) and if this value is compared to the turbidity-suspended solid calibration curve in Fig. 1 it is equivalent to about 990 mg/l (1:10) of suspended solid. Chitosan shows the lowest suspended solid reading. 0.5 g/l of chitosan was needed to reach a minimum suspended solid reading of 23 mg/l. For alum at 8.0 g/l and PAC at 6 g/l to reach a minimum suspended solid reading of 107 and 70 mg/l, respectively. Alum can be classified as a poor choice of coagulant to coagulate POME compared to PAC and chitosan. Chitosan proved to be the best coagulant to remove suspended solid of POME at lower dosages compared to alum and PAC which needed much higher dosages.

The flocs produced by chitosan appear rapidly and grows very fast to form a larger size which can be easily sedimentated. The flocs are fibrous and forms large entangled mass resembling cobwebs. This might due to the bridging mechanism. This proves that chitosan is a successful coagulant to coagulate suspended solid in POME compared to the widely used industrial coagulant alum and PAC. Almost 99% of the suspended solid has been coagulated by chitosan coagulation.

Nevertheless in Fig. 3, it was also noticed that when the applied dosage was higher than the optimum amount, the suspended solid value increased. This shows restabilization of POME. At 0.8 g/l of chitosan and 10 g/l of alum and PAC there was an increase in suspended solid reading. At high doses of coagulant, a sufficient degree of over-saturation occurs to pro-

duce a rapid precipitation of large quantity of coagulant. A number of works on restabilization of colloidal suspensions due to excessive treatment with polyelectrolytes have been done [25].

3.3. Effect of mixing time

The effect of mixing time was conducted by varying the mixing time at 100 rpm of mixing rate. The sample was then let to settle for 1 h. Dosage of chitosan, alum and PAC was fixed at their optimum values which were analyzed earlier in Section 3.2. Fig. 4 shows that the mixing time allocated to mix the chitosan, alum and PAC with POME suspension is very crucial in coagulating the oil content. Fig. 5 shows that a complete 15 min of mixing at 100 rpm with 0.5 g/l of chitosan could coagulate about 99% of residue oil in POME.

It was also observed that alum and PAC needs about 30 min of mixing to achieve 99% of residue oil removal. Chitosan reacts faster to the residue oil compared to alum and PAC. It was observed that when the mixing time was increased to 1 h for alum and PAC, the residue oil was introduced again in the suspension. For chitosan it was still the same without any changes. This is because chitosan not only agglomerates the residue oil suspended in the POME but adsorbs the residue oil due to its amine functional groups. For alum and PAC just agglomerates and bridges the residue oil. They do not adsorb the residue oil.

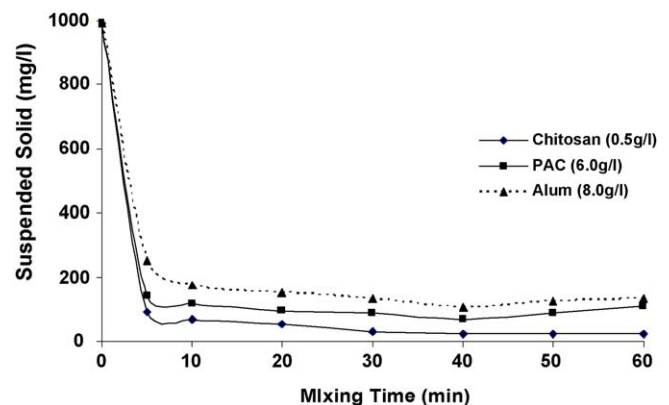


Fig. 5. Suspended solid removal vs. mixing time for chitosan, alum and PAC.

Hence, when the mixing time was prolonged the flocs tend to break and release again the residue oil into the supernatant of POME.

Therefore by analyzing the destabilization of residue oil in Fig. 4 and suspended solid in Fig. 5 the predominant proposed mechanism for chitosan, alum and PAC will be adsorption, chemical forces and electrostatic attractions [33]. At a shorter time of mixing, it was observed that the percentage of residue oil removal was low for all the coagulants. This is because the chances of the oil molecules and coagulant particles to meet were low causing the rate of removal inadequate. At longer time of mixing, breakage of the oil droplets are enhanced thus reduces the diameter of the oil droplets (emulsification) resulting in larger interfacial area available for the coagulation and adsorption to happen [34].

Fig. 5 shows the suspended solid reading of POME after coagulation with coagulants at different mixing time. Alum and PAC shows higher suspended solid values after 30 min of mixing. For chitosan the changes was very small compared to alum and PAC. This proves that chitosan bridges the flocs more firmly and tightly than alum and PAC. After 40 min of mixing alum's and PAC's turbidity reading increased from 107 to 125 mg/l and from 70 to 90 mg/l, respectively. The flocs that have been formed by alum and PAC seemed to be easily dispersed in the sample if the mixing time was prolonged. The breakage of the flocs causes the sample to be turbid again. This indirectly causes the suspended solid to disperse in the sample. Therefore, it is clearly noticed that alum and PAC acts only as a coagulant which flocs the residue oil and suspended solid in POME and settle it by gravity settling. PAC and alum does not adsorb the residue oil nor bind the flocs strongly.

3.4. Effect of sedimentation time

Effect of sedimentation was analyzed at different sedimentation time at optimum dosage of chitosan, alum and PAC with 30 min of mixing time and 100 rpm of mixing rate. Residue oil and suspended solid treated with the optimum dosage of chitosan were clarified immediately, once the suspension finishes coagulation. The settling mechanism of chitosan was faster compared to alum and PAC. Chitosan coagulated POME produces flocs of better quality, namely larger flocs with faster settling velocity.

Fig. 6 shows that the settling time needed for the maximum removal of residue oil in POME suspension. 20 min of sedimentation can remove about 99% of residue oil. While alum and PAC needs about 60 and 50 min, respectively, of settling to achieve the same percentage as chitosan. Chitosan shows a much faster sedimentation. Ten minute of sedimentation shows almost 90% of oil has been removed from the POME suspension. Whereby, for alum; 60% and PAC; 65% of residue oil has been removed. This proves that the oil droplets attached to the flocs formed by alum and PAC takes longer time to settle causes the percentage of residue oil removal unfavorable at earlier stage. The time needed for the flocs to settlement is very important in removing the coagulated residue oil faster and more effective. Chitosan promotes the faster aggregation of colloids, by the formation of bridges between the dispersed oil droplets, and the formation of

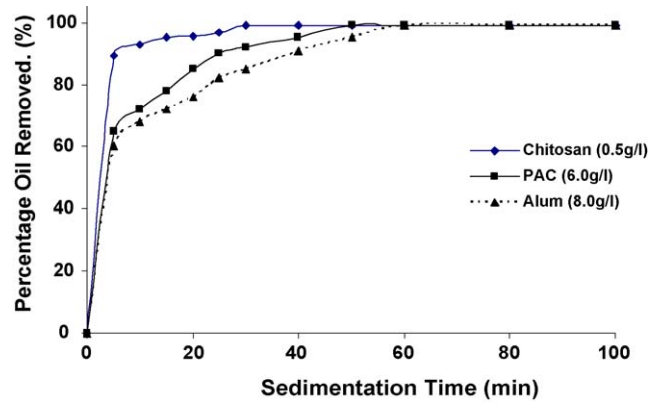


Fig. 6. Percentage of residue oil removed vs. sedimentation time of chitosan, alum and PAC.

particles of sufficient size which can be settled faster and easily.

The turbidity of the coagulated sample depends on the sedimentation effect. Fig. 7 shows that there is a drastic reduction in suspended solid reading once the sample is left to settle for more than 1 h. Chitosan shows the best and fastest sedimentation rate. It needs only about 20 min to reach the minimum suspended solid reading of 23 mg/l. Alum and PAC needs about 50 min to achieve the minimum suspended solid values of 107 and 70 mg/l, respectively. Suspended solid values gets lower as the bridged particles and flocs starts to settle to the bottom of the beaker and this effect is mainly affected by the gravitational force. The flocs formed by chitosan are larger and denser causing the suspended solid to settle faster.

3.5. Effect of pH

Emulsion breaking is usually brought about by changing the samples pH value or inorganic coagulants [35]. Therefore, pH adjustment was done to study the effect of removing the residue oil using chitosan, alum and PAC by coagulation. The effect of pH was conducted by adjusting the pH from 3 to 6 and using the optimum dosage of chitosan, alum and PAC with 30 min of mixing time and 100 rpm of mixing rate. The sample was then let to settle for 1 h. POME is an acidic suspension, therefore pH adjust-

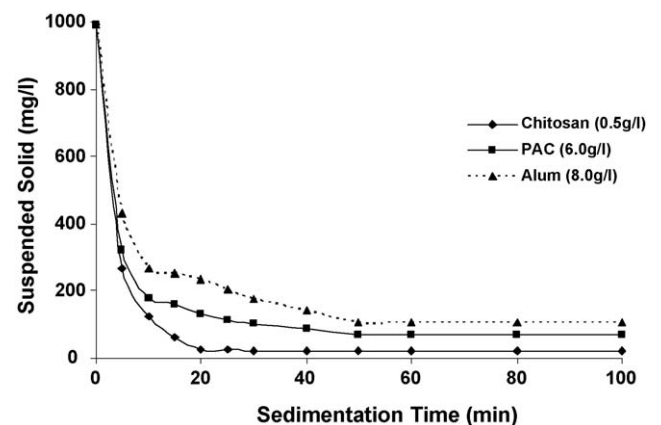


Fig. 7. Suspended solid removal vs. sedimentation time for chitosan, alum and PAC.

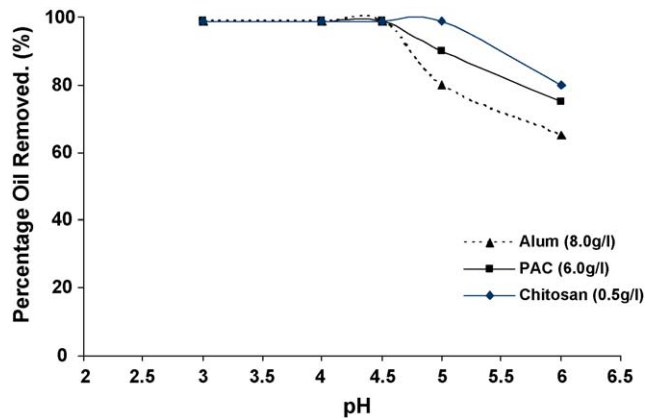


Fig. 8. Percentage of residue oil removed using chitosan, alum and PAC vs. different pH of POME.

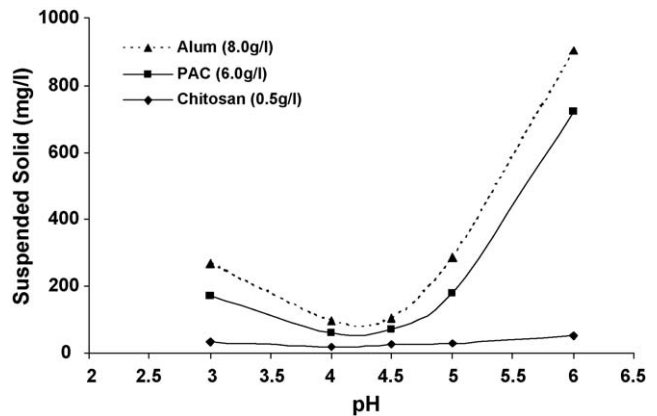


Fig. 9. Suspended solid removal using chitosan, alum and PAC vs. different pH of POME.

ments were only done between pH 3 and 6. The removal was more than 95% at pH 4 for all the coagulants. These results can be clearly seen in Fig. 8. The acidic condition of POME incites the residue oil removal. The original pH of POME was more or less 4.5 and from Fig. 8 it was observed that the residue oil removal was very satisfying at this pH. Nearly 95% of removal could be achieved at this initial pH. All the coagulants showed a good potential of residue oil removal at initial pH value. This encouraging fact could bring to a conclusion that pH adjustment on POME in the real treatment system can be discarded in order to remove the residue oil by using any of these coagulants. When the pH was adjusted to a higher value to about pH 5 and above, the residue oil removal was poorer compared to the acidic condition.

Strong acidic condition aggravates POME to break oil droplets and destabilization of suspended solid in the suspension. Thus, enhances the coagulation of residue oil in POME. In acidic condition chitosan provokes physico-chemical effect, apparently serving to demulsify and increase the droplet size and enhance the adsorption of oil and grease. More protons will be available to protonate amine groups of chitosan molecules to form -NH_3^+ groups [36]. Therefore, the electrostatic attractions between residue oil molecules and adsorption site increase and indirectly increases the adsorption of residue oil onto chitosan. For alum and PAC at acidic pH, the Al^{3+} exist in significant amount; therefore the coagulation of residue oil was good.

Fig. 9 shows that chitosan, alum and PAC have a good removal of suspended solid at acidic pH. Chitosan was still the best and shows almost similar trend with a very minor change. The suspended solid reading of chitosan was low as 23 mg/l when the pH value of the suspension was around 4. For PAC and alum it was 61 and 97 mg/l, respectively, at pH 4. The suspended solid value of initial POME at pH 4.5 without the addition of coagulant was higher compared to the one with pH 3. This shows the destabilization of suspended solid in acidic condition. At pH more than 5.0 the turbidity value was higher and increased quite drastically for alum and PAC compared to chitosan. When the pH value was more than pH 5 it leads to a dissolution of precipitate formed by $\text{Al}(\text{OH})_4^-$ [25], which indirectly introduces the turbid and increases the suspended solid values. pH 6 shows the poorest

removal efficiency for all the three coagulants proposed. This may due to the destabilization of the coagulants itself at weaker acid conditions.

As a conclusion we could say that chitosan performed exceptionally well to coagulant and remove the suspended solid and residue oil from POME compared to alum and PAC. The destabilization of suspended solid and residue oil in POME were successfully performed by applying coagulation process which shows a synergistic enhancement for effective agglomeration, adsorption and coagulation. The results showed that coagulation with chitosan was an effective and health risk free treatment technique for palm oil mill effluent wastewater compared to alum and PAC which creates hazardous waste. Even though the performance of alum and PAC was at par under certain conditions but the side effects caused by these synthetic coagulants is not negotiable. Chitosan is a natural and environment friendly biopolymer therefore it can be disposed easily but alum and PAC creates residual aluminum which has to be treated further carefully before being discharged into the watercourse. Furthermore results prove that chitosan was more economical to be used. Coagulation of POME using chitosan resulted higher than 99% of residue oil and suspended solid reduction. The suspended solid value was a low as 23 mg/l in the supernatant of POME. In order to achieve 99% of residue oil and suspended solid reduction from an influent with 2.0 g/l of initial residue oil and 990 mg/l (1:10) of initial suspended solid, the following optimum parameters should be considered: chitosan dosage of 0.5 g/l, pH 4, 15 min of mixing at 100 rpm and 20 min of settling. For alum and PAC the dosages are 8.0 and 6.0 g/l, respectively, 30 min of mixing time, 50 min and 60 min of settling at 100 rpm and at a pH of 4.5. Since the optimal condition of coagulation is around pH 4.0–5.0, pH adjustment can be neglected for POME, thus keeping the treatment cost lower and the quality of treated waste better compared to the conventional coagulation.

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