International Journal of Engineering Management
2018; 2(3): 67-75
http://www.sciencepublishinggroup.com/j/ijem
doi: 10.11648/j.ijem.20180203.13
ISSN: 2640-1525 (Print); ISSN: 2640-1568 (Online)

Wastewater Treatment Using Alum, the Combinations of Alum-Ferric Chloride, Alum-Chitosan, Alum-Zeolite and Alum- *Moringa Oleifera* as Adsorbent and Coagulant

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To cite this article:

Ahmad Hussaini Jagaba, Sule Abubakar, Ibrahim Mohammed Lawal, Ab Aziz Abdul Latiff, Ibrahim Umaru. Wastewater Treatment Using Alum, the Combinations of Alum-Ferric Chloride, Alum-Chitosan, Alum-Zeolite and Alum- *Moringa Oleifera* as Adsorbent and Coagulant. *International Journal of Engineering Management.* Vol. 2, No. 3, 2018, pp. 67-75. doi: 10.11648/j.ijem.20180203.13

Received: October 30, 2018; **Accepted**: November 19, 2018; **Published**: December 17, 2018

Abstract: 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 use of aluminium-based coagulant has become under scrutiny. Besides the large amount of sludge produced, high level of aluminium remaining in the treated water has raised concern on public health. Previous research has pointed out that the intake of large amount of aluminium salt may contribute to the development of neurodegenerative diseases. To reduce the large intake of aluminium salt in the treatment of palm oil mill effluent (POME), this research examined the comparative suitability of alum and combinations of alum as the primary coagulant with other coagulants (ferric chloride, zeolite, chitosan and *moringa oleifera*) for the treatment of (POME) at optimum conditions of both coagulants. It also ascertain which combined coagulants with alum and an anionic polymer has the potential for higher pollutants removal. Results obtained revealed that, addition of 1 g/L of ferric chloride, 0.4 g/L chitosan and 1 g/L zeolite each to different dose of alum, were able to reduce alum dose from 4 g/L to 2 g/L, 3 g/L and 2 g/L. However, 2 g/L *moringa oleifera* addition could not reduce alum dose as high removal efficiencies for most parameters were obtained at 4 g/L alum + 2 g/L *moringa oleifera.*

Keywords: Aluminium Sulphate, Coagulation, Flocculation, Heavy Metals, Wastewater

1. Introduction

In spite of a relatively positive environmental record, Malaysia faces problems which can be attributed to deforestation, discharge of pollutants into rivers, lands and air, overfishing and coral reef destruction, along with air and water pollution thereby making the environment unhealthy for living organisms. Malaysia has enjoyed one of the least polluted urban environments in Asia. However, with the massive industrial development of recent years, and an increase in urbanisation that attributed to increase in agricultural practices and vehicular use resulting to various types of pollutants such as solid waste, hazardous waste, toxic and liquid waste, water and air pollution are of growing concern [1].

Water pollution still poses a serious threat in certain parts of Malaysia. Studies show that the major contributors to water pollution are agriculture, agro-based industries such as palm oil processing industries, rubber processing industries, food and beverage processing plants, textile and leather tanneries, and electronic hardware factories, many of which discharge effluents directly into rivers. Uncontrolled release of the pollutants into the air during manufacturing processes of palm oil has led to an unstable environmental threat [2]. Some negative effects of these pollutants worldwide are depletion of ozone layer, global warming and significant raise of ocean level.

Malaysia, like other developing countries had achieved an

outstanding performance of economic growth since implementing mass industrial revolution. One of big and outstanding industries in Malaysia is agricultural based oil palm industry. The production of palm oil generates large amounts of polluted wastewater known as palm oil mill effluent (POME). Palm oil industries worldwide are facing significant challenges in meeting the increasingly stringent environmental regulations on the disposal of POME. The raw or partially treated POME has an extremely high content of degradable organic matter, which is due in part to the presence of unrecovered palm oil. This highly polluting wastewater can, therefore, cause pollution of waterways due to oxygen depletion and other related effects as reported by [3]. Thus, while enjoying a most profitable commodity, the adverse environmental impact from the palm oil industry cannot be ignored.

Palm oil industry produces palm oil mill effluent (POME) which becomes one of the major sources of water pollution containing toxic substances, harmful bacteria and unwanted solid waste which can be classified as organic or inorganic. To mitigate the effect of these effluents and also balance economic growth with environmental protection, the Malaysian government enact the Environment Quality Act, 1974 under the Department of Environment (DOE) which is a comprehensive law on environmental management in Malaysia and specific regulations for palm oil mill effluent in 1975. This act was later amended to [4]. Under this act, it is mandatory for all palm oil mills to treat their wastewaters on site to an acceptable level or convert them into by-products with added value before they are allowed to be discharged into water ways [5].

The enactment of the environment regulations in 1975, concerted and intensive research and development programs initiated by both the public and private sectors to find cost-effective solutions in minimizing the environmental impact of the palm oil industry. Wastewater treatment capability is one of the most important components in the palm oil production. This capability is normally used to treat a large volume of POME generated during the production of CPO before the effluent is safely discharged to the surrounding environment through water canal or river which affects the natural environment and creates a major ecological problem throughout the world [6].

Most of industrial wastewater can lead to severe problems in different treatment stages, current methods for such wastewater treatment include coagulation-flocculation, sedimentation, filtration, membrane and biological processes. Each one of these methods has its advantages and disadvantages. Among the current methods, coagulation-flocculation process is one of the most effective methods widely used in wastewater treatment [7].

Treatment of POME by coagulation-flocculation within a short period of time without involving a vast area of land may offer a cost-effective solution to negative environmental impacts as a result of untreated POME discharged to the environment. The use of chemicals, herbs, seafood, and some geological materials in the treatment of wastewaters has been reported to be successful by many researchers [8].

In order to reduce the negative effects of inorganic salts during and after the treatment of POME, aluminium sulphate (alum) would be partially replaced by zeolite, ferric chloride, *moringa oleifera* and chitosan. The capability of alum and its partial replacement with these other coagulants in POME treatment via coagulation-flocculation process would then be investigated.

1.1. Comparison Between Commercial Coagulants (Alum & $FeCl_3$) in Terms of Parameter Removal

Coagulation by hydrolysing metal salts, typically of iron (Fe) or aluminium (Al), is the main reaction stage that drives the removal of natural organic matter (NOM) and other contaminants in potable water treatment [9]. The species distribution of Al(III) and Fe(III) in aluminum coagulants and iron coagulants has significant effects on its coagulation efficiency, floc properties, and contaminant removal efficiency. Previous research has indicated that Al has been the most effective polymeric Al species in water and wastewater treatment, the separation and purification of which mainly includes the SO_4/Ba^{2+} deposition-replacement method, ethanol–acetone precipitation method, the ultra-filtration method and column chromatography method. Aluminium sulphate [$Al_2(SO_4)_3.16H_2O$] with a molecular weight of 598.4 g/mol and Ferric chloride [$FeCl_3$] with a molecular weight of 162 g/mol are commonly used coagulants and were used in this study where the reduction efficiency of turbidity, COD, TSS, NH_3-N, oil and grease. colour, and heavy metals (Fe, Pb, Cu, Mn, Cd and Zn) were the main evaluating parameters.

1.2. Comparison between Natural Coagulants (Chitosan, Zeolite and Moringa Oleifera) in Terms of Parameter Removal

In recent years, chitosan and *moringa oleifera* have been applied as coagulants in water treatment [10]. Chitosan is a partially deacetylated polymer obtained from the alkaline deacetylation of chitin, a biopolymer extracted from shellfish sources. Chitosan with a molecular weight of 1,526.454 g/mol exhibits a variety of physico-chemical and biological properties resulting in numerous applications in fields such as cosmetics, biomedical engineering, pharmaceuticals, ophthalmology, biotechnology, agriculture, textiles, oenology, food processing and nutrition. This amino-biopolymer has also received a great deal of attention in the last decades in water treatment processes for the removal of particulate and dissolved contaminants. In particular, the development of chitosan-based materials as useful coagulants and flocculants is an expanding field in the area of water and wastewater treatment. Their coagulation and flocculation properties can be used to remove particulate inorganic or organic suspensions, and also dissolved organic substances [11].

The protonization of amino groups in solution makes chitosan positively charged, and thereby very attractive for

flocculation and different kinds of binding applications. Since most natural colloidal particles including bacteria and macromolecules, are negatively charged, attractive electrostatic interactions may lead to flocculation [12]. The main parameters influencing the characteristics and properties of chitosan are its molecular weight (MW), degree of deacetylation (DD), representing the molar fraction of deacetylated units, and crystallinity. These parameters are determined by the conditions set during preparation [13].

Natural macromolecular coagulants extracted from plants such as *moringa oleifera* seed, Jatropha curcas, copra and Cactus etc. are promising and have attracted a lot of attention due to their advantages such as abundant source, low toxicity, multi-purposeness and bio-degradability [14]. In particular, Moringa oleifera seed has been regarded as one of the best natural products for water treatment. It has been reported that *moringa oleifera* seed can be used to remove many pollutants including turbidity, heavy metals, Escherichia coli, algae, surfactants from water [15]. The cationic proteins in *moringa oleifera* seed have been proved to be the active components for water treatment [16]. Adsorption and neutralization of charges are the main mechanisms of coagulation. It is possible to extract an edible vegetable oil from the *moringa* seeds before using as the coagulant. In coagulation, *moringa* hardly affects the pH and conductivity. Therefore, the application of *moringa oleifera* seeds in wastewater treatment can reduce the cost of chemicals used for pH adjustment. The volume of sludge produced using *Moringa* as coagulant is considerably less compare to alum and do not offer any disposal problem [17].

The use of clay mineral has undoubtedly become more popular and widely used as an adsorbent and ion exchange for water and wastewater treatment applications especially for removing heavy metal, organic pollutants, and nutrients [18]. Clay minerals, such as bentonite and zeolite, are some of the potential alternatives, as they have large specific surface areas with a net negative charge, which can be electrically compensated for by inorganic and organic cations from the environment compared to polyaluminium chloride. Their sorption capabilities come from their high surface areas and exchange capacities. It is a highly effective natural clay mineral, especially in granular form, used for the purification of wastewater and sludge dewatering [19]. Zeolite used in this study has a molecular weight of 2190 g/mol.

2. Materials and Method

2.1. Materials

Raw palm oil mill effluent was collected from Pertubuhan Peladang Negeri Johor (PPNJ) Oil Palm Mill, Kahang, Johor Darul Takzim, Malaysia. Alum ($Al_2(SO_4)_3 \cdot 18H_2O$), ferric chloride, chitosan, zeolite and *moringa oleifera* were used without any further modifications. Distilled water was used to dilute hydrochloric acid and dissolve sodium hydroxide pellets to obtain solutions with a concentration of 1 mol/L. The prepared acid and base solutions were used to adjust the initial pH of treatment process.

2.2. Characterization of POME

The POME used in this study was obtained from Pertubuhan Peladang Negeri Johor (PPNJ) Oil Palm Mill, Kahag, Johor, Malaysia. Table 1 shows the concentration of all parameters obtained during the characterization of Palm oil mill effluent from PPNJ given a pH of 4.50 which fell within the range of 4.39–4.60 reported by [20] with an average temperature of 49.5°C. The average values of BOD_3 and COD were 24367 mg/L and 74686 mg/L respectively, and the ratio of BOD_3/COD of raw POME was about 0.33.

Table 1. *Initial Characteristics of Raw POME.*

Parameter	Conc	Parameter	Conc.	Parameter	Conc.
pH	4.50	COD	7223	Mn (mg/L)	8.216
Temperature °C	49.5	BOD_3/COD	0.33	Fe (mg/L)	63.14
TDS (mg/L)	4595	Colour (Pt. Co)	8021	Al (mg/L)	7.933
TSS (mg/L)	2673	NH_3-N (mg/L)	520.6	Cu (mg/L)	0.823
Turbidity (NTU)	2658	Oil & Grease (mg/L)	7310	Pb (mg/L)	0.026
BOD_3 (mg/L)	2387	Zn (mg/L)	3.554	Cd (mg/L)	0.007

2.3. Analytical Method

Analysis of chemical oxygen demand (COD), ammoniacal nitrogen, oil and grease, turbidity, colour, total suspended solids (TSS) and heavy metals (Pb, Mn, Fe, Cu, Zn) removal following standard methods [21] was carried out on the wastewater.

2.3.1. Chemical Oxygen Demand (COD) (USEPA Method 8000)

In this study, Chemical Oxygen Demand (COD) was analyzed using HACH Method. Four HACH test tubes were prepared consisting of concentrated sulphuric acid, potassium dichromate and distilled water. The first test tube was used as blank while the other three were used as sample run repetition. The samples were diluted with a dilution factor of 50. 2 mL of distilled water would be added into the first test tubes as blank and 2 mL of diluted sample would be added into each of the three test tubes. The mixture of each four test tube would then be refluxed for 2 hours after which the oxidant used up by the organic and inorganic substances in the sample would be determined by colorimetric measurements. The COD content of the sample in mg/L would be read directly using DR 6000 Spectrophotometer. Hence, the COD reduction efficiency was determined by:

COD reduction efficiency (%) = COD final discharge POME – COD after treatment x 100 %

COD final discharge POME

2.3.2. Turbidity (Standard Method 2130B)

The turbidity measurement was carried out on wastewater sample (POME) using DR/2010 Portable Data logging Spectrophotometer at 750 nm. The measurement was based on the light-transmitting properties of the wastewater. For blank, distilled water were used in a 25 mL sample cell and first inserted into the spectrophotometer to calibrate. The same volume of wastewater sample in another sample cell was inserted into DR/2010 Portable Datalogging Spectrophotometer and read at 860 nm. This analysis was made before and after each treatment. Turbidity removal efficiency was then determined by:

Turbidity removal (%) = Turbidity final discharge POME – Turbidity after treatment x 100 %

Turbidity final discharge POME

2.3.3. pH (APHA Standard Method 4500)

Initial and subsequent pH tests were carried out according to the Standard Method [21]. HQ440d HACH pH meter was used to determine the pH of the POME sample before and after the treatment. For the determination of initial pH for the coagulation process, sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH) solutions were used to get the desired pH value.

2.3.4. Total Suspended Solid (TSS) (Standard Method 2540D)

The experiment began by preparing the GAST DOA-P404-BN filtration apparatus. 5 mL of the raw POME sample was used for the filtration. Suction of the effluent also began and followed by stirring of the sample with a magnetic stirrer at a speed that would shear larger particles. Stopwatch was used to measure the amount of time it takes for the sample water to flow through the filter. The filter was then carefully removed from the filtration apparatus, dried for at least 1 hour at 103 to 105°C in an oven, cooled in a desiccator to balance the temperature and was finally transferred to the aluminium weighing dish for weighing.

The concentration of total suspended solids in the sample was be obtained by the given formula below:

$$\text{Total suspended solids, mg/L} = \frac{(\text{A} - \text{B}) \text{ x } 1000}{(\text{Sample vol.mL})}$$

Where:

A= Sample and filter weight, mg

B= Filter weight, mg

2.3.5. Ammoniacal Nitrogen (Nessler Method, USEPA Method 8038)

Ammoniacal nitrogen in mg/L present in the effluent was determined by Nessler's method, using DR 6000 HACH spectrophotometer. Distilled water was be used as a blank for ammonia measurements. The experiment began by filling a graduated cylinder with 25 mL of the wastewater sample after dilution. Another graduated cylinder was also be filled with 25mL of distilled water in another mixing graduated cylinder as the blank. Three drops of Mineral Stabilizer would be added to each cylinder and put upside down several times to mix. Three drops of Polyvinyl Alcohol Dispersing Agent was also added to each cylinder by holding the dropping bottle vertically and mixed them. 1.0 mL of Nessler reagent was then be pipetted into each cylinder and mixed several times. Each solution was poured into a sample cell and the results were taken by DR 6000.

2.3.6. Oil and Grease (Hexane Extractable Gravimetric Method, USEPA Method 10056)

An experiment was conducted to evaluate the performance of petroleum ether in the extraction of residual oil from POME. The original and treated POME samples were transferred to a separating funnel and 30 mL of petroleum ether was introduced into the separating funnel. The contents were shaken vigorously for 2 min and allowed to separate into layers for 5 min. The aqueous layer was then drip drained into a conical flask. Extractions were repeated twice with two more portions of 30 mL petroleum ether. The solvent layer was then drained through a funnel containing filter paper and 2 g of anhydrous sodium sulphate, both of which had been solvent-rinsed, into a clean conical flask. The solvent was distilled off using the rotary evaporator. The drying was completed in the oven at 103^{o}C for 5 to 10 minutes. The flask was cooled in a desiccator for about 30 min and weighed. The drying and cooling steps were repeated until the weight becomes constant to calculate the concentration of residual oil extracted. The concentration of residual oil extracted with petroleum ether was used for the analysis.

2.3.7. Colour (USEPA, Method 8025)

The colour of raw POME for both the influent and effluent were measured by the standard platinum-cobalt method using DR 6000 HACH spectrophotometer. For testing colour, two test tubes were prepared, deionised water was poured in one test tube and used as control while the diluted wastewater sample was poured in the other test tube. The Hach method program number 125 corresponding to colour measurement at wavelength 465 nm was then selected after inserting each of the test tubes in the cell holder followed by pressing zero to get 0 Pt. Co for the control and pressing read for the colour measurement of the second test tube containing wastewater.

2.3.8. Heavy Metals

The determination of heavy metals concentration in POME was carried out using an Atomic Absorption Spectrometer (AAS) and Inductively Coupled Plasma (ICP). To begin the AAS analysis, substance were first dissolved in a liquid, dried and then atomized to vaporize the substance into gas atoms. Sample were prepared by adding 5% of nitric acid and refluxed at 95°C for 15 minutes. Samples were then filtered with a filter paper. Standard solutions were prepared for Al, Zn, Fe, Cd, Pb, Cu and Mn all based on the permissible limit concentration.

2.3.9. Sludge Volume Percentage

The sludge volume percentage was determined by measuring the sludge height after each electrocoagulation

process which is 30 minutes of settling time. The recorded sludge heights then were determined by doing simple calculation to get the percentages of sludge volume. The diameter of the beaker which is 11 cm were taken into account as well as the height of the sample after being poured into the beaker at the beginning of the process which is also 11 cm.

$$\% \text{ Sludge Volume} = \frac{\text{A x H1 x}}{\text{A x H2}} \times 100\%$$

Where;
A = Cross sectional area of the 1L beaker
$= (\pi d^2)/4$; d = diameter of the beaker = 11 cm
H_1 = Height of sludge after 30 minutes settling time
H_2 = Height of POME sample in the 1L beaker (11 cm)

3. Result Analysis and Discussions

3.1. Settleability of Raw POME

Palm oil mill effluent from PPNJ was found to contain high values of TSS and TDS which implies that the sample is capable of producing high sludge. Hence, this study investigated the setleability of the raw sample at different time interval thereby measuring sludge height and calculating the percentage sludge volume as in Figure 1. Raw POME was kept to settle for several minutes where readings of the supernatant were taken to mark the sludge height at an interval of 60 minutes. It was observed that sludge volume decreases as the minute's increases and was almost constant at 240 minutes.

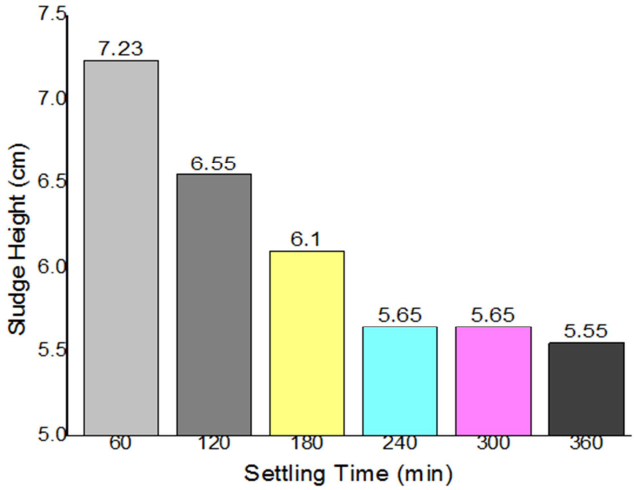
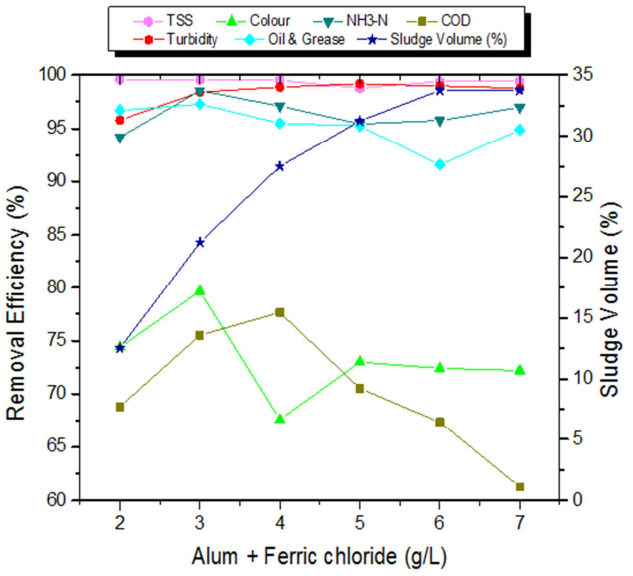


Figure 1. *Settleability of raw POME*

3.2. Optimization for Various Combinations

3.2.1. Optimum dose of ALUM + $FeCl_3$

Combination of different doses of Alum with 1 g/L dose of ferric chloride showed significant in pollutants load reduction in POME as can be seen Figure 2, 2 g/L alum + 1 g/L $Fecl_3$ provides the highest removal percentages of colour, NH_3-N, oil & grease, Pb, Cd and Zn as 79.67%, 98.54%, 97.28%, 95.95%, 95.39% and 92.10% respectively while 77.65% COD removal was reached at 3 g/L alum + 1 g/L $FeCl_3$ with not much variance compared to 75.52% obtained at 2 g/L alum + 1 g/L $FeCl_3$. 99.59%, 86.05% and 92.19% removals were achieved for TSS, Cu and Mn respectively at combination dose of 1 g/L alum + 1 g/L $FeCl_3$. Turbidity removal was best at 4 g/L alum + 1 g/L $FeCl_3$ with an efficiency of 99.18%. 2 g/L alum + 1 g/L $FeCl_3$ combination dose with 21.25% as the percentage sludge volume is chosen as the optimum combination dose since most parameters performed better at the dose.



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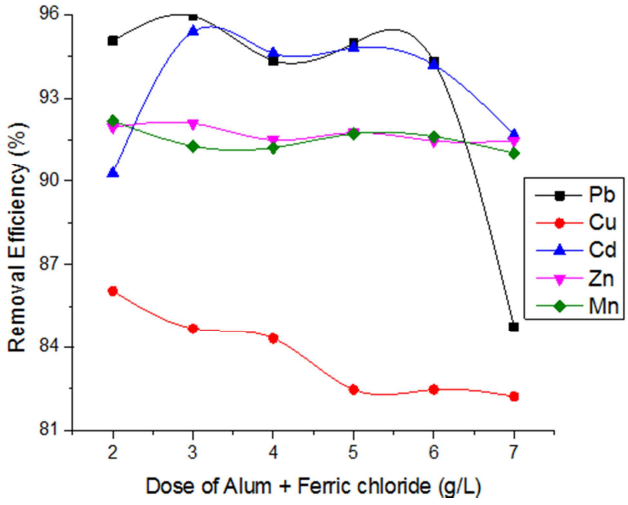


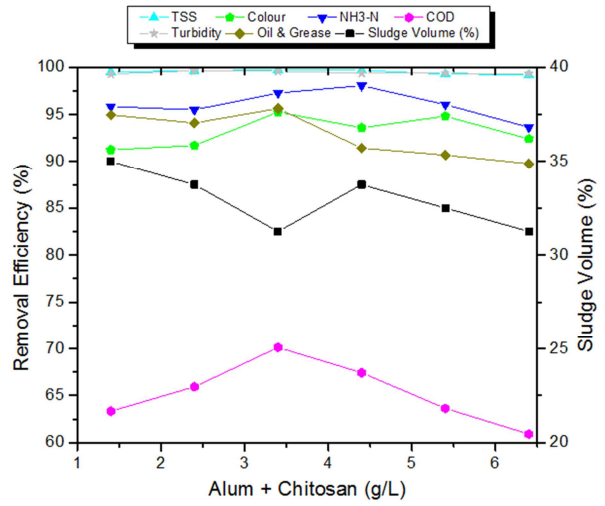
(b)

Figure 2. *Removal percentage of (a) TSS, turbidity, oil & grease, colour, COD and NH_3-N as well as sludge volume percentage and (b) Pb, Cu, Cd, Zn and Mn for 1 g/L – 6 g/L dose of alum incorporating 1 g/L of $FeCl_3$ to each dose at pH 4.51, 250 rpm rapid mixing speed for 3 minutes, 30 rpm slow mixing speed for 30 minutes and 60 minutes settling time.*

3.2.2. Optimum dose of Alum + Chitosan

Results seen in Figure 3 proved that the combination of alum + chitosan at variable doses increases the removal

efficiency until the optimum dose was reached where the removal efficiency start to decrease. 3 g/L alum + 0.4 g/L chitosan as reported by [22] also provides the highest removal percentages of TSS, colour, oil & grease, COD, Pb, Cu, Cd and Fe as 99.69%, 95.24%, 95.63%, 70.12%, 97.65%, 83.95%, 95.00% and 92.23% while 98.04% NH_3-N removal was reached at 4 g/L alum + 0.4 g/L chitosan even though 97.26% was at 3 g/L alum + 0.4 g/L chitosan. Therefore 97.26% would be considered since it has the lower dose. Turbidity and Zn with removal efficiencies of 99.61% and 91.57% were best at 2 g/L alum + 0.4 g/L chitosan. However, Mn removal efficiency continuously increases as combination dose is being increased up to the last dose of 6 g/L alum + 0.4 g/L chitosan which obtained 93.45% removal. More so, least percentage sludge volume of 31.25% was achieved at 3 g/L alum + 0.4 g/L chitosan, hence it becomes the optimum combination dose.



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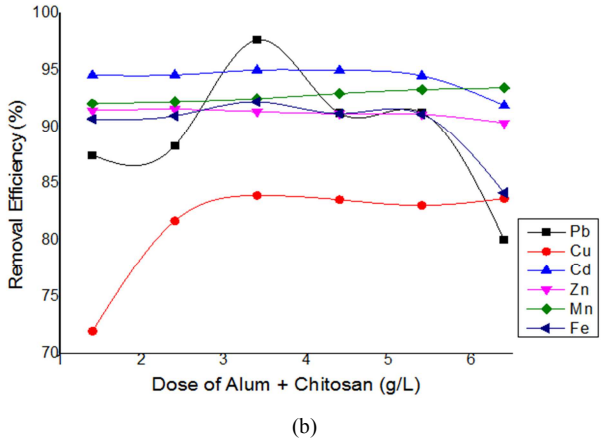
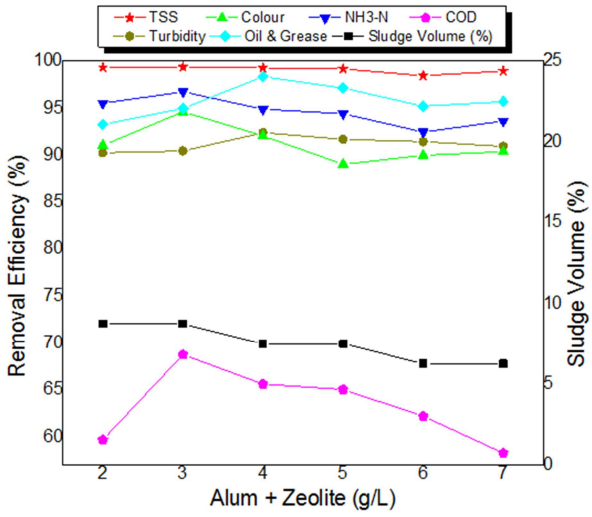


(b)

Figure 3. *Removal percentage of (a) TSS, turbidity, oil & grease, colour, COD and NH_3-N as well as sludge volume percentage and (b) Pb, Cu, Cd, Zn, Mn and Fe for 1 g/L – 6 g/L dose of alum incorporating 0.4 g/L of chitosan to each dose at pH 4.51, 250 rpm rapid mixing speed for 3 minutes, 30 rpm slow mixing speed for 30 minutes and 60 minutes settling time.*

3.2.3. Optimum dose of Alum + Zeolite

Combination of different doses of alum with 1 g/L dose of zeolite showed removal efficiencies of TSS, turbidity, oil & grease, colour, NH_3-N, COD, Pb, Cd, Cu, Zn Fe and Mn as well as sludge volume percentage in the POME as can be seen in Figure 4. 2 g/L alum + 1 g/L zeolite provides the highest removal percentages of TSS, colour, NH_3-N, COD, Pb, Cd and Mn as 99.33%, 94.62%, 96.73%, 68.72%, 78.88%, 93.07% and 91.69% respectively with 92.41% and 98.32% removal at 3 g/L alum + 1 g/L zeolite for oil & grease and turbidity respectively. Cu removal efficiency was found to be increasing as combination dose is being increased up to the 5th combination dose of 5 g/L alum + 1 g/L zeolite which obtained 89.14% removal where 91.68% and 87.75% removals for Zn and Fe were obtained at the 1st combination dose of 1 g/L alum + 1 g/L zeolite and continue to decrease as the dose is being increased indicating that the combination dose is not suitable for their removal. Hence, 2 g/L alum + 1 g/L zeolite with 8.75% as percentage sludge volume is found to be the optimum combination dose for this experiment.



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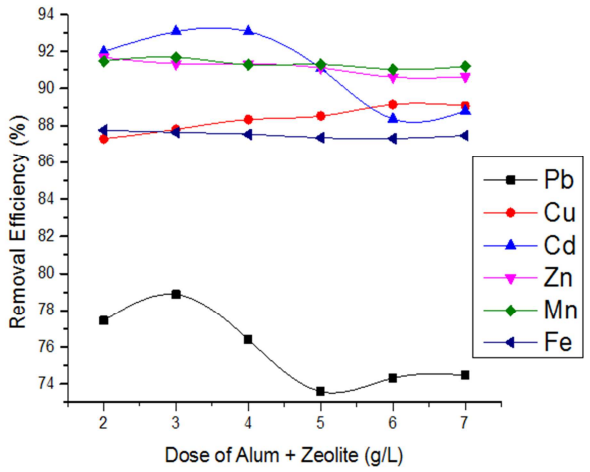
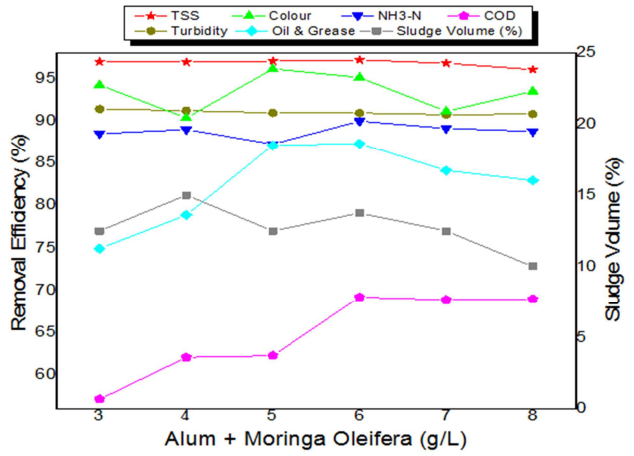


(b)

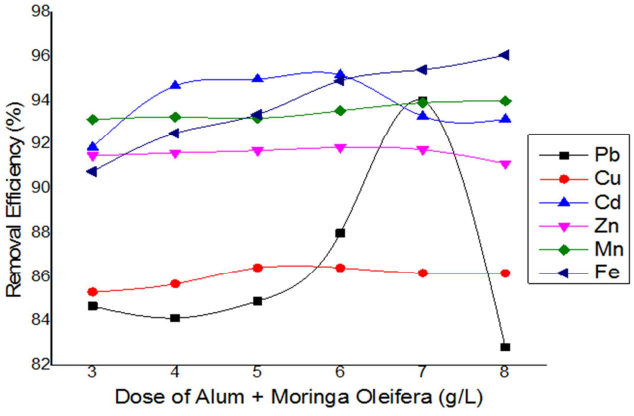
Figure 4. *Removal percentage of (a) TSS, turbidity, oil & grease, colour, COD and NH_3-N as well as sludge volume percentage and (b) Pb, Cu, Cd, Zn, Mn and Fe for 1 g/L – 6 g/L dose of alum incorporating 1 g/L of zeolite to each dose at pH 4.51, 250 rpm rapid mixing speed for 3 minutes, 30 rpm slow mixing speed for 30 minutes and 60 minutes settling time.*

3.2.4. Optimum dose of Alum + Moringa Oleifera

Results shown in Figure 5 indicates that the combination of alum + *moringa oleifera* at variable doses of alum increases the removal efficiency until the optimum dose was reached where the removal efficiency start to decrease. 4 g/L alum + 2 g/L *moringa oleifera* provides the highest removal percentages of TSS, NH_3-N, oil & grease, COD, Cu, Cd and Zn as 97.19%, 89.98%, 87.32%, 69.17%, 86.42%, 95.16%, 91.85% respectively. 96.13% and 93.98% removal at 3 g/L alum + 2 g/L *moringa oleifera* and 5 g/L alum + 2 g/L *moringa oleifera* were achieved for colour and Pb respectively. Mn and Fe with 93.98% and 96.06% removals respectively were obtained at the last combination dose signifying that they require higher combination dose for effective removal while 91.40% turbidity removal was achieved at the initial combination dose. Thus, it can be concluded that alum + *moringa oleifera* combination is not suitable for turbidity removal. From the results obtained for this experiment, it can be concluded that 4 g/L alum + 2 g/L *moringa oleifera* with 13.75% as percentage sludge volume is the optimum combination dose.



(a)

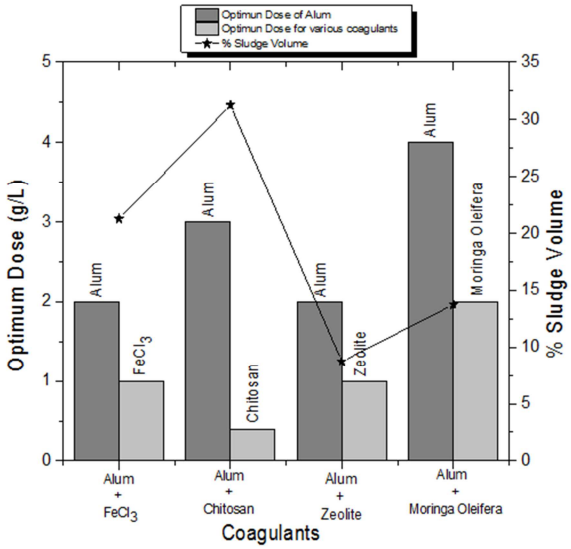


(b)

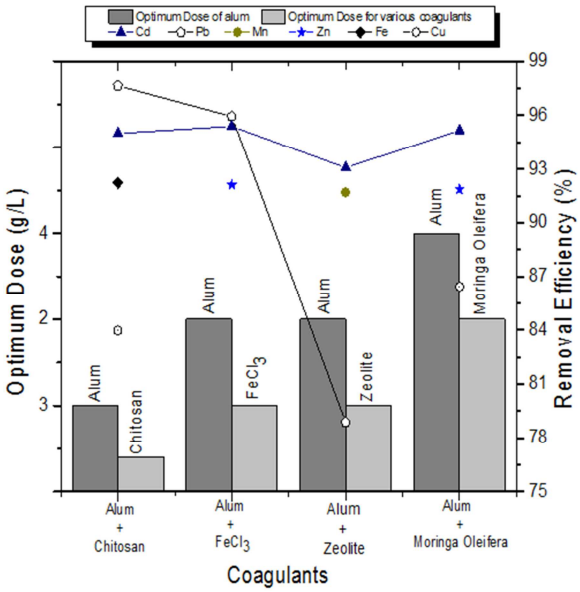
Figure 5. *Removal percentage of (a) TSS, turbidity, oil & grease, colour, COD and NH_3-N as well as sludge volume percentage and (b) Pb, Cu, Cd, Zn, Mn and Fe for 1 g/L – 6 g/L dose of alum incorporating 2 g/L of moringa oleifera to each dose at pH 4.51, 250 rpm rapid mixing speed for 3 minutes, 30 rpm slow mixing speed for 30 minutes and 60 minutes settling time.*

3.2.5. Comparison of Optimum dose for Various Coagulants Combinations

Results obtained from laboratory experiments proved that addition of 1 g/L of ferric chloride, 0.4 g/L chitosan and 1 g/L zeolite each to different dose of alum, were able to reduce alum dose from 4 g/L to 2 g/L, 3 g/L and 2 g/L respectively. However, 2 g/L *moringa oleifera* addition could not reduce alum dose as high removal efficiencies for most parameters was obtained at 4 g/L alum + 2 g/L *moringa oleifera*. On the sludge volume reduction, Figure 6a indicates that zeolite is the best in sludge reduction with the least sludge volume of 11.25% followed by alum with 12.50% and it was further reduced to 8.75% by a combination of 2 g/L alum + 1 g/L zeolite.



(a)



(b)

Figure 6. *Comparison of optimum dose combinations for optimum removal of (a) TSS, turbidity, oil & grease, colour, COD and NH_3-N alongside (b) some heavy metals of Pb, Cu, Cd, Mn, Zn and Fe with sludge volume percentage.*

The performance of heavy metals reduction improved when alum was combined with various coagulants as shown below in Figure 6b where 2 g/L alum + 1 g/L $FeCl_3$ obtain 95.95%, 95.39% and 92.10% as highest removals for Pd, Cd and Zn respectively. Combined coagulants dose of 3 g/L alum + 0.4 g/L chitosan removed Pb, Cu, Cd and Fe at efficiencies of 97.65%, 83.95%, 95.00% and 92.23% respectively. When 2 g/L alum was combined with 1 g/L zeolite, three metals (Pb, Cd and Mn with 78.88%, 93.07% and 91.69%) recorded high performance compared to when zeolite was used alone with two metals achieving high removals. The use of an anionic polymer as a flocculent together with the combination of 4 g/L alum and 2 g/L *moringa oleifera* has greatly improved the performance of *moringa oleifera* in the coagulation of POME as 86.42%, 95.16% and 91.85% removals were obtained for Cu, Cd and Zn respectively.

Tables 2 and Table 3 shows that 3 g/L alum + 0.4 g/L chitosan combination achieved excellent parameter reductions and as well the highest for Pb, TSS and turbidity as 97.65%, 99.69% and 99.61% respectively. The parameter reductions of 95.39%, 92.10%, 98.04% and 77.65% were achieved for Cd, Zn, NH_3-N and COD when 2 g/L alum + 1 g/L $FeCl_3$ were combined. Combined dose of 2 g/L alum + 1 g/L zeolite gave the highest Cu and oil & grease removal of 89.14% and 98.32% while 4 g/L alum + 2 g/L *moringa oleifera* was the best Mn, Fe and colour removal at efficiencies of 93.98%, 96.06% and 96.13% respectively.

Table 2. *Parameters removal for various coagulant combination.*

Coagulants	Parameters removal efficiency (%)					
	TSS	Turbidity	NH_3-N	COD	Colour	Oil & Grease
Alum + Chitosan	99.69	99.61	98.04	70.12	95.24	95.63
Alum + M. O.	97.19	91.40	89.98	69.17	96.13	87.32
Alum + FeCl3	99.59	99.18	98.54	77.65	79.67	97.28
Alum + Zeolite	99.33	92.41	96.73	68.72	94.62	98.32

Table 3. *Heavy metals removal for various coagulant combination.*

Coagulants	Parameters removal efficiency (%)					
	Pb	Cu	Cd	Zn	Mn	Fe
Alum + Chitosan	97.65	83.95	95.0	91.6	93.5	92.2
Alum + M. O.	93.98	86.42	95.2	91.9	94.0	96.1
Alum + $FeCl_3$	95.95	86.05	95.4	92.1	92.2	-
Alum + Zeolite	78.88	89.14	93.1	91.7	91.7	87.8

4. Conclusion

This study was aimed at alum dose reduction in the treatment of POME because of its numerous effects to human and aquatic life. Thus, coagulation-flocculation method was used to examine the effectiveness alum and a combination of alum with ferric chloride, chitosan, zeolite and *moringa oleifera*. Series of Jar test were carried out and the comparison of coagulants under optimised conditions indicates that the best coagulant combination in terms of sludge volume reduction was alum + zeolite as the sludge volume was reduced from 12.50% to 8.75% by a combination of 2 g/L alum + 1 g/L zeolite. The performance of heavy metals reduction was also improved when alum was combined with various coagulants. Alum combination with other coagulants gave higher reductions for turbidity, oil & grease, TSS, NH_3-N, COD, Zn, Pb, Cu, Mn and Fe as 99.61%, 98.32%, 99.69%, 98.54%, 77.65%, 92.10%, 97.65%, 89.14%, 93.98% and 96.06% respectively. However, all combinations were not successful in high colour and Cd removals as 96.44% for colour was obtained using chitosan alone while 95.75% for Cd using alum alone. From these obtained results, it can be concluded that treatment of POME by coagulant-flocculation technique through the combination of alum with other coagulants is effective in high effluent removal.

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