DEVELOPMENT OF NEW HYBRID ADSORPTION COAGULATION METHOD FOR PALM OIL MILL WASTEWATER TREATMENT

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Abstract

Activated carbon has been using as an adsorbent for wastewater treatment for decades. It has also been reported that use of fly ash to adsorb impurities in waste water treatment .The main objective of this study is to optimize hybrid adsorption-coagulation method for removal of color, BOD, COD, TDS, TSS and Turbiditypresence in palm oil mill effluent (POME).Mango pit is a natural environmental friendly coagulant and have many advantages over commercially available aluminum and ferric salts used for water and wastewater treatment. Fly ash has the proficiency to be recycled and used various times. This study further investigates the combination of fly ash with mango pit. Three sets of experiments were performed using jar test method namely; only adsorption using fly ash and the second is using mango pit as coagulant and the third one is using fly ash in combination with mango pit in hybrid adsorption-coagulation system. In the first set of experiments only adsorption process was studied using fly ash as an adsorbent by varying particle size and weight. Samples of 300ml wastewater were used with variable fly ash particle size ranging from 355µm and 500µm and operated at 200rpm. Results showed that with decrease in particle size the amount of pollutant adsorbed increased, therefore process was optimized using 355 µm granule size and 90g of dose producedresults in color reduction as 91%, COD 82%, BOD_5 83%, TDS 74%, TSS 78% and turbidity 93% respectively. In second set of experiment mango pit was proved to be an excellent coagulant to be used for wastewater treatment which gave reduction of pollutants up to 70%. Further in the third set of experiments equal amount of wastewater samples were investigated using hybrid adsorption-coagulation method by varying concentration and pH of adsorbent-coagulant as (50g-0.6ml, 70g-0.8ml, 90g-1.2ml). When applying hybrid method an improved trend was recorded comparing with previous resultsin reduction of Color from 91% to 97%, COD from 82% to 89%, BOD from 83% to 94%, TDS from 84% to 93% and TSS from 88% to 96% respectively. Hybrid coagulation-Adsorption method has not only positive impact on reduction of wastewater quality parameters but also very cost effective and environmental friendly process. Other advantages include low sludge production and the less amount of coagulants used.

Key words: POME, Hybrid, Fly ash, Coagulation, Adsorption

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Nomenclature

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POME	Palm oil mill Effluent
POBFA	Palm oil mill boiler fly ash
COD	Chemical Oxygen Demand
BOD	Biological oxygen demand
TDS	Total dissolved solid
TSS	Total suspended solid
FFB	Fresh fruit bunches.
CPO	Crude palm oil

1. INTRODUCTION

1.1 Research Background

The extraction and purification processes generate different kinds of waste generally known as palm oil mill effluent (POME). The environmental impact of POME cannot be over emphasized; hence the need for treatment measures to reduce these impacts before discharge. Among the waste generated in Palm oil Industry, palm oil mill effluent (POME) is considered the most harmful for the environment if discharged untreated. POME is a thick brownish liquid that contains high solids, oil and grease, COD and BOD values. Since the direct discharge of POME adversely affects the environment, several treatment technologies have been used for POME treatment which sometimes are not cost effective or generate solid waste which requires another capital to be treated. The cost for wastewater treatment could be reduced either by reducing the wastewater generation or enhance the treatment efficiency. The concept of introducing the kind of ingredients which not only reduces the risks of environment but can also seem more appealing and cost-effective. Adsorption- coagulation using in a hybrid system can reduce the amount of ingredients used by decreasing the individual concentration. Mango kernel extract used was proved to be one of best organic biodegradable coagulant. Palm oil mill boiler fly ash is produced in the mill by burning empty fruit bunches in the boiler, that was found very useful adsorbent by many researchers. Hybrid Adsorption-Coagulation techniques were successfully used for the dye removal from textile mill effluent. Using the same technique for POME was done in this study to reduce the overall impact of POME to the environment before discharge and reduce the operating cost for effluent treatment.

1.2 Brief introduction to Palm oil wet extraction production process

Wet extracting of crude palm oil from palm fruits generates large quantities of wastewater. To treat wastewater it is very important to find out the source from where wastewater is generating. Raw Palm Oil Mill Effluent (POME) can be considered as one of the highest industrial polluting sources having BOD, COD and TDS values as high as 26,000, 67,000 and 72,000 mg/lit respectively. Detail of palm oil production process and the source of wastewater were reviewed to find out the characteristics of wastewater and suggest a better method to treat POME.

Before going for processing ripe fresh fruit bunches (FFB) are harvested in the oil palm plantations and transported as soon as possible to the palm oil mills for immediate processing.

Following steps are involved in the production of palm oil.

1.2.1Sterilization

After loading into the sterilizer cages, the FFB (fresh fruit bunches) is subjected to steam-heat treatment in horizontal sterilizers. Saturated steam at a pressure of 3 kg/cm^2 and a temperature of 140^oC is used as the heating medium. The FFB is usually steamed for 75 to 90 minutes. The main objectives of sterilization are as follows:

- Prevent further formation of free fatty acids due to enzyme action;
- Facilitate stripping of the fruits from the spikelets;
- Prepare the fruit mesocarp for subsequent processing by coagulating the Mucilaginous material which facilitates the breaking of the oil cells; and
- Pre-conditioning of the nuts to minimize kernel breakage during pressing and nut cracking.

The sterilization cycles, times and patterns vary from mill to mill. Three-peak sterilization pattern is normally used. This is because of the compactness of the FFB that was brought aboutby the weevil pollination introduced in the early 1980s. The steam condensate is discharged aswastewater and referred to as sterilizer condensate, this is the first source of wastewater generation.

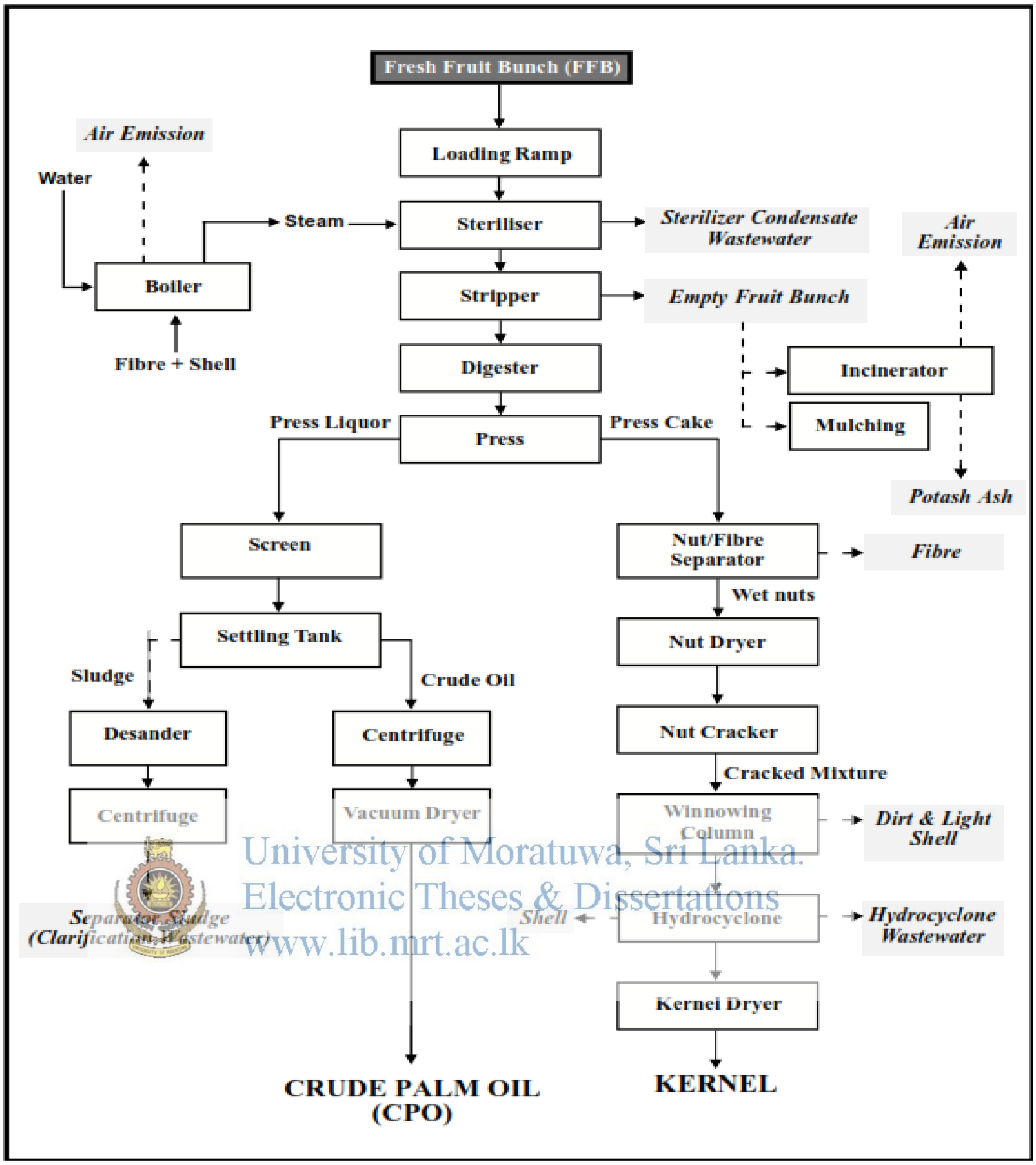


Figure 1.1 Conventional Palm Oil Extraction Process and Sources of Waste Generation

Source: Ir. Dr. Ma Ah Ngan et al (1999)

1.2.2Striping

After sterilization, the FFB are fed to a rotary drum-stripper where the fruits are separated from the spikelets or bunch stalks. As the drum-stripper rotates, the bunches are lifted up and then dropped again repeatedly as the bunches travel along the stripper. The fruits are knocked off the bunch by this action. The detached fruits pass through the bar screen of the stripper and are collected below by a bucket conveyor before being discharged into the digester. The empty bunch stalks pass out at the end of the stripper continuously and are collected and handled separately.

1.2.3 Digestion

Digestion involves mashing of the palm fruits under steam heated conditions. Heating can be either by steam jacket around the digester or by direct live steam injection. The digester consists of a vertically arranged cylindrical vessel fitted with a rotating shaft carrying a number of stirring arms. The fruits are mashed by the rotating arms. This mashing of the fruits under heating breaks the oil-bearing cells of the mesocarp. Thus, some palm oil is released and is collected in the crude oil tank together with the pressed oil described below. In order to have good digestion of the fruits, it is important to maintain the digester full all the time at about 90^{o}C.

1.2.4 Crude Palm Oil Extraction

Twin screw presses are generally used to press out the oil from the digested mash of fruits under high pressure. Hot water is added to enhance the flow of the oils. The crude oil slurry is fed to a clarification system for oil separation and purification. The fibre and nut (press cake) are conveyed to a depericarper for separation.

Ideally, the press should be operated at a high enough pressure to press out all the oil in the mesocarp without breaking any nuts. However, this can never be achieved in practice. Higher pressing pressure will obviously result in lower oil loss in the fibre but will cause higher nut breakage or vice versa. Therefore, this is more of a compromised operation.

It is undesirable to have high nut breakage as it will result in high broken kernel and subsequently higher kernel loss in the recovery process. Furthermore, the palm oil will be “contaminated” by the “kernel oil”.It is possible to reduce the nut breakage by employing double pressing. This is being practiced by a number of palm oil mills. As the name implies, it consists of two pressing operations. The first pressing presses the mashed fruits at a lower pressure. A practical set of operating conditions has to be obtained to reduce the nut breakage to an acceptable minimum. The fibre, after separating from the nut, is sent for second pressing at a higher pressure to recover the residual oil from the fibre.

1.2.5 Clarification and Purification of the Crude Palm Oil

The crude palm oil (CPO) from the presses consists of a mixture of palm oil (35%-45%), water (45%-55%) and fibrous materials in varying proportions. It is pumped to a horizontal or vertical clarification tank for oil separation. The temperature of the clarification tank content is maintained at about 90^{o}C to enhance oil separation. The clarified oil is continuously skimmed-off from the top of the clarification tank. It is then passed through a high speed centrifuge and a vacuum dryer before it is sent to the storage tanks. The oil at this stage has a moisture and dirt content of below 0.1% and 0.01%, respectively. The underflow from the clarification tank still contains some oil and this is recovered by passing the underflow through a sludge separator. The recovered oil is returned to the clarification tank. The other stream consisting of water and fibrous debris is discharged as wastewater, which is generally referred to as separator sludge or clarification wastewater.

1.2.6 Depericarping and Nut Fibre Separation

The press cake discharged from the screw press consists of moisture, oily fibre and nuts (including broken ones and kernels), and these are conveyed to a depericarper for nut and fibre separation. The conveyor is fitted with paddles which breakup the press cake on the way to the depericarper. The fibre and nuts are separated by a strong air current induced by a suction fan. The fibre is sent to the boiler house and is used as boiler fuel. The nuts are sent to a rotating drum where any remaining fibre is removed before they are sent to a nut cracker.

Figure 1.2 Shell and fibre are used as boiler fuel

The air velocity has to be accurately determined for efficient nut and fibre separation. Conversely, if the air velocity is too low, blocking of the separation duct and cyclone can occur. Such occurrence will affect the throughput of the palm oil mill.

1.2.7. Nut Cracking

Nuts coming from the nut fibre separator are usually still warm, and a large number may have the kernels sticking to the shell. Cracking of the nut at this stage, by the conventional centrifugal-type nut-cracker, will result in the splitting of the nuts and any kernels sticking to the broken shell will be lost. Thus, cooling of the nuts to loosen the kernels before cracking will result in better cracking efficiency and kernel recovery. Moreover, warm nuts are more difficult to crack as the shells are more elastic. However, with the introduction of the ripple mill for nut-cracking, drying of the nuts is no longer necessary, especially if the FFB have been effectively sterilized.

1.2.8 Separation of Kernels and Shells

The methods employed to separate the kernels and shells are based on the difference in specific gravity (SG) between the kernels and the shells. Undried kernels and shells have a SG of about 1.07 and 1.15-1.25, respectively. Thus, a separation medium consisting of clay suspension or salt solution with a SG of 1.12 will effectively separate the kernels and the shells. The choice of which depends on the availability, costs and maintenance of the materials and equipment. Presently, the most popular separator is the hydrocyclone which is much easier to operate and maintain. The discharge from this process constitutes the last source of wastewater stream, i.e. hydrocyclone wastewater.

1.2.9. Palm Kernel Drying

The palm kernels have to be dried to below 7% moisture in order to prevent the growth of mould and permit a longer storage time. The growth of mould on kernels not only spoils their appearance but also promotes the hydrolysis of the palm kernel oil. Palm kernels are commonly dried in a silo dryer. Drying is achieved by blowing a current of warm air through the kernels in the silo. In a large silo, it is important to avoid over-heating or over-drying in order to prevent the palm kernel oil from being pre-maturely "liberated".The dried kernels are traditionally bagged for sale. As a recent practice, palm oil mills have built kernel bunkers and the kernels are transported in bulk instead of in bags. The kernels are normally sold to palm kernel crushers for palm kernel oil production.

1.3 Sources of wastewater

Large quantities of water are used during the extraction of crude palm oil from the fresh fruit bunch. About 50% of the water results in palm oil mill effluent (POME), the other 50% being lost as steam, mainly through sterilizer exhaust, piping leakages, as well as wash waters.

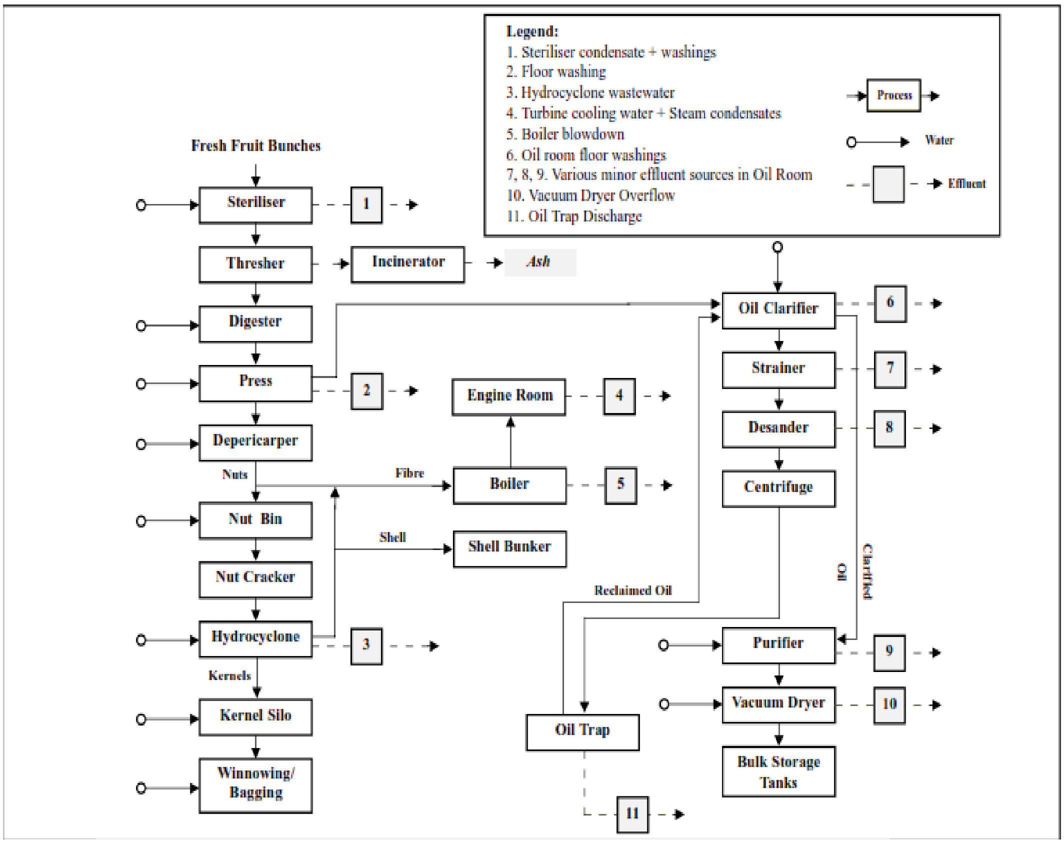


Figure 1.3Sources of Effluent (POME) Legend:
Source:Ir. Dr. Ma Ah Ngan et al (1999)

The POME comprises a combination of the wastewaters which are principally generated and discharged from the following major processing operations as show in Figure 1.2:

- Sterilization of FFB - sterilizer condensate is about 36% of total POME;
- Clarification of the extracted crude palm oil - clarification wastewater is about 60% of total POME; and
- Hydrocyclone separation of cracked mixture of kernel and shell – hydrocyclone wastewater is about 4% of total POME.

1.4 Palm oil mill effluent (POME) treatment process

POME is a colloidal suspension, which is 95 – 96 % water, 0.600.7 % oil, and 405 % total solids including 204 % suspended solids originating in the mixing of sterilizer condensate, clarifier and hydro cyclone wastewater (Ma, 2000). The POME coming out of processing unit is a thick brownish in color liquid and discharged at temperature between 80 to 90° , which contains high range off color , BOD,COD, TDS,TSS, Bacteria, Phosphate, ammonia, organic matters, inorganic metals and turbidity. Biological treatment method is currently being applied in most of the industries to minimize these pollutants before discharging to the river of in land areas. It was indicated that Water coming out of aeration process in biological treatment plant still contains of high values of color index, BOD,COD, TDS,TSS and turbidity which are well above the standard values and need to be regularize before discharging to the river. Detail of selected palm oil mill with POME treatment facility for current study is given below. Furthermore, the selected point of sampling after aeration process is also mentioned to suggest post treatment plant.

1.4.1 Tank digestion and mechanical aeration

This method consists of cooling/acidification ponds, an anaerobic digestion tank and an aeration pond.

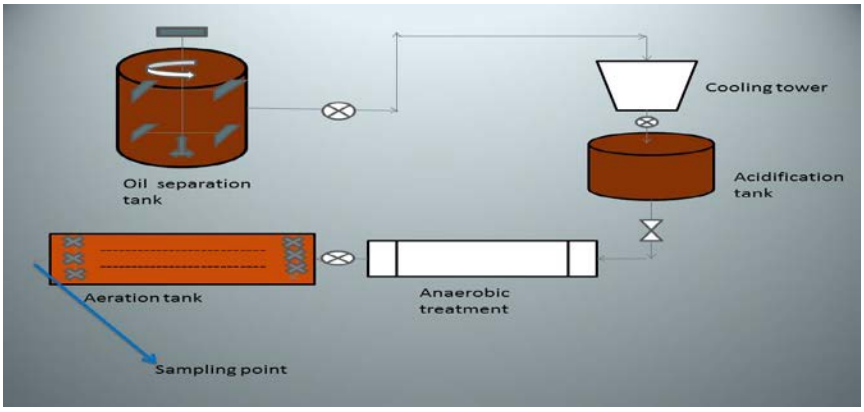


Figure 1.4 Biological treatment process with fat separation.

Raw effluent after oil trapping is pumped to the acidification pond through a cooling tower and retained for one to two days. It is then mixed with an equal volume of liquid from the anaerobic digester before it is fed back to the digester and the achievement recorded indicates that the effluent water has been treated. The hydraulic retention time of the digester is about twenty days. The digested liquid is discharged to an aeration pond with two floating aerators. The liquid is aerated for twenty days before it is discharged. The below figure 1.5 shows the color quality of POME after aeration process.

Figure 1.5 Water sample collection point after aeration

1.5 Characteristics of Palm oil mill effluent (POME)

A part from Being a sign of famous crop into global trade market Palm oil is the tremendous economic and social importance in Sri Lanka.Beside this the Palm oil mill Effluent (POME) generated from Palm oil mill contains many organic and inorganic impurities in it which need to be treated before discharging to the river or sea or to be used in irrigation purpose. Most of the time the color of POME cannot be removed after initial biological treatments sometimes it contains still higher range of other parameters as BOD5,COD, TDS,TSS,Turbidity and color respectively.

1.6Palm oil mill boiler fly ash (PMBFA)

"Palm oil mill boiler fly ash (POBFA) which is produced in palm oil mills from the burning of the fiber and shell in the boiler as a fuel"(Igwe et al 2010). "Every tone of

POBFA produces about 4kg to 6 kg of boiler ash. This porous ash, which is contains about 0.28% -1.33% phosphorous, 1.2% to 4.31% potassium, 0.39% -3.24% calcium and 0.29% - 2.60% magnesium" given by Rusnani et al (1999). Fly ash produced in palm oil industry by burning solid remains, pressed bunches etc. was practiced to treat wastewater. "Earlier studies have indicated that the possibility of using boiler fly ash to adsorb impurities and color in POME treatment" by Igwe et al (2010). Mostly the POBFA obtained is thrown as a waste or otherwise used as a fertilizer .The use of POBFA for wastewater treatment can reduce the harmful environmental impact of this fly ash meanwhile can reduce the operating cost.

1.7 Mango Pit as Coagulant

Coagulants are widely used for the removal of colloidal and suspended materials in the form of turbidity. Aluminum and ferric salts are the mainly used coagulants for the treatment of water and wastewater. These inorganic coagulants are not safe from health point of view. In the past research was focused on developing bio-coagulant either from plant residue or animal tissues. These coagulants are biodegradable and are presumed to be harmless for human health and generate less quantity of sludge (Qureshi et al 2014).

Mango Kernel on the other hand was proved to be a good alternative coagulant enriched natural ingredient. It is generally accepted that Mango kernel works as a coagulant due to positively charged, water soluble proteins, which bind with negatively charged particles (salt, clay, bacteria, toxins etc.) allowing the resulting "flocs" to settle to the bottom or to be removed by filtration. In this study the efficiency of mango pit to reduce the color, COD, BOD, TS, TDS and turbidity are enhanced by using with fly ash as adsorbent in hybrid system.

1.8 Hybrid Adsorption-Coagulant Process

Using POBFA and mango pit coagulant at once has been used in this research work to optimize the % removal of pollutants and minimize the environmental risks and capital cost. "A combined coagulation/ carbon adsorption process for the treatment of reactive dyes in the synthetic wastewater" was proposed by Papic et al(2008). COD and color including turbidity were reduced from textile industry effluent, study were performed by Karadag et al, (2006) and Shah et al, (2013).

1.9 Research Problem

Palm Oil Mill Effluent (POME) generated from palm oil mill contains many organic and inorganic impurities which need to be treated before discharging to the river or sea or to be used in irrigation purpose. Mostly the color of POME cannot be removed after initial biological treatments and it also contains still higher range of other parameters as BOD5, COD, TDS, TSS, Turbidity and color respectively. Palm oil mill boiler fly ash (POBFA) is produced in palm oil mills by burning of the fiber and shell in the boiler as a fuel Shah et al., 2013. Most of the time the POBFA obtained is thrown as a waste or otherwise used as a fertilizer. The use of POBFA for wastewater treatment can reduce the harmful environmental impact and meanwhile it can reduce the overall operational cost of industry. Mango Kernel on the other hand was proved to be a good alternative coagulant enriched with natural ingredients. It is generally accepted that Mango kernel works as a coagulant due to positively charged, water soluble proteins, which bind with negatively charged particles (salt, clay, bacteria, toxins etc.) allowing the resulting "flocs" to settle to the bottom or to be removed by filtration. .A combine coagulation/ carbon adsorption process for the treatment of reactive dyes in the synthetic wastewater was proposed by Papic et al., 2004.

1.10 Objectives

The major objective of this research is to develop new treatment strategy for Palm oil mill wastewater treatment. This research aims to develop a new treatment method for palm oil mill effluent (POME). There are three specific objectives in order to meet the goal:

1. To study the effect of variable size and weight of fly ash as an adsorbent on percentage removal of contaminants.

2. To investigate and increase the efficiency of naturally biodegradable coagulant Mango pit for the treatment of Palm oil mill effluent (POME).
3. To optimize the hybrid Coagulation-adsorption process for the removal of Color, BOD, COD, TDS, TSS and turbidity present in POME.

1.11. Outline of the Thesis

This thesis consists of five chapters. In the first chapter, Introduction, research objectives and outlines are given. Literature related with the study is given in second chapter and materials and Methods of the study is given in chapter Three.

Results and Discussion is given in chapter Four. Conclusions and recommendations are given in chapter Sixth. Published research paper and data sheets are given in annexure.

2. LITERATURE REVIEW

The main focus of the first section of this literature review is to identify alternative coagulant low cost, biodegradable and environmental friendly for Palm oil mill effluent (POME) treatment. In the second part of review the focus is to find the way to activate and make Palm oil mill boiler fly ash as an alternate to activated carbon for the adsorption process. Finally seeking a Hybrid system where coagulation and adsorption processes are brought together in one system to improve overall efficiency of the system.

2.1. Introduction

Palm oil is one of the two most important vegetable oils in the world's oil and fats market. Oil palm was introduced to Sri Lanka from Malaysia in late nineteen sixties. Approximately following three and a half decades, it has spreaded over 10,000 acres of the southern part of the Island. Watawala, Namunukula, Agalawatta and Elpitiya are the four key companies that share oil palm plantations, which are distributed mainly in the Galle District (Weerasekara, 2006). Palm oil is an edible vegetable oil derived from the mesocarp (reddish pulp) of the fruit of the oil palm. It is found naturally reddish in color due to presence of high beta-carotene content present. Palm kernel oil is derived from the kernel of the same fruit. The differences are in color (raw palm kernel oil lacks carotenoids and is not red), and in saturated fat content. Palm mesocarp oil is 41% saturated, while palm kernel oil is 81% saturated (Albert and Morrison et al 2013). The extraction and purification process of palm oil generate different kinds of waste water generally known as the palm oil mill Effluent (POME) (Igwe et al, 2000).The solid waste produced from palm oil mill industry has been found increasing annually and are producing adverse effects on environment beside their use as a fertilizer. Different treatment methods have applied to recycle that solid waste, most of them rather need a huge investment otherwise cannot utilize such quantity waste.

2.2 Palm oil mill Effluent (POME) treatment

Palm oil mill effluent (POME) is generated mainly from oil extraction, washing and cleaning processes in the mill.POME is a colloidal suspension originating from mixture of sterilizer condensate, separator sludge and hydro cyclone wastewater in a ratio of 9:15:1 respectively (Wu et al. 2010). According to Borja & Bank (1994); Ma & Ong (1985), about 2.5-3.0 tonnes of POME per tonnes of produced crude oil is obtained in the extraction processes. The processing of fresh fruit bunches of oil palm results in the generation of different types of residue. Among the waste generated, palm oil mill effluent (POME) is considered the most harmful waste for the environment if discharged untreated. Palm oil mill effluent is a thick brownish liquid that contains high solids, oil and grease, COD and BOD values. Several treatment technologies have been used for POME treatment, since the direct discharge of POME adversely affects the environment (Othman et al, 2008). POME cannot be discharged prior to specific treatment due to its acidic nature and very high biochemical oxygen demand (BOD).Many treatment methods have been applied to treat POME before discharging to the river to irrigational purpose.Boilogical treatment method is the most commonly method used but it has been observed that effluent obtain after biological treatment still contains color and high COD values.

Table 2.1: Typical Characteristics of Palm oil Mill Effluent.
Source: Othman et al 2008

Parameters	Range	Average value
Temperature (oC)	75 - 90	80
pH	4.0 – 4.8	4.5
Suspended solid, SS (mg/L)	11,500 – 22,000	17,927
Total Solid, TS (mg/L)	36,500 – 42,600	39,470
Chemical Oxygen Demand, COD (mg/L)	30,000 – 50,400	40,200
Biological Oxygen Demand,BOD (mg/L)	14190-42250	30800
Oil and Grease (mg/L)	1,300 – 4,700	2,658
Total Kjeldahl Nitrogen, TKN (mg/L)	660 - 890	800

2.3 Commonly used treatment methods

Land application of palm oil mill effluent (POME) is one of the disposal alternatives. Various researches indicated that discharging the POME on the land may results in clogging and water logging of the soil and kills the vegetation on contact. However, Wood et al., 1979 reported that these problems could be overcome by the controlled application of small quantities of POME at a time. The cheapest way of discharging of POME is to release it into the river; since it is believed by POME is a nontoxic oily waste. But discharge of effluent into water bodies cause water depletion and results in aquatic pollution. Therefore, these problems make it essential to study the effect different types of treatments on POME quality and environment. Several researchers have studied the various aspects of palm oil mill effluent treatment (Ahmed et al., 20002; Fakhrul et al., 1999). Physical pretreatment of POME consist of stages such as screening, sedimentation and oil removal prior to the secondary treatment in biological treatment system. According to Hojjat and Salleh., 2009 the combination of two processes of acidification pond and flocculation treatment is a developed pretreatment process. Hojjat and Salleh., 2009in his study showed that by applying both centrifugation and coagulation gave different pretreatment quality which was reported to be better than that of pretreatment by filtration method. Apart from this process, different chemicals are used in flocculation such as alum, aluminium chlorohydrate, aluminium sulfate etc. There are some natural products used as coagulant such as chitosan (poly D- glucosamine that have been used in flocculation. Chitosan is a natural organic polyelectrolyte of high molecular weight and charge density; obtained from DE acetylation of chitin. As the suspended solids in POME are mainly associated with its organic matter, therefore chitosan can effectively remove most of the colloidal and suspended organic matter contents, but is found to be less efficient in removing of dissolved organic matterby Nawawi et al., 2008. Solvent extraction method was used by Hameed et al., 2003 for removal of residual oil from POME as a pretreatment process. Hameed et al., 2003 reported that the percentage extraction of oil from POME increased with the increase of mixing time, solvent/feed ratio and mixing rate for all solvents.

According to Perez et al.,2001, anaerobic process is a suitable treatment method due to the organic characteristic of POME. Therefore ponding system is the most conventional method for treating POME. The pond systems have been applied in Malaysia for POME treatment since 1982 and they are classified as waste stabilization pond. More than 85% of palm oil mills exclusively use ponding systems due to their low costs . Ponding systems are easy operating systems but they have some disadvantages such as occupying a vast amount of land mass, relatively long hydraulic retention time (HRT) of 45-60 d for the effective performance, bad odor and difficulty in maintaining the liquor distribution and biogas collection which results harmful effect on the environment. In the oil palm mill, the ponding system of POME treatment is the main source of environment pollution. Huge amount of the strong greenhouse gas methane with the biogas is emitted by the anaerobic ponds and the effluent of the ponds holds the nutrients accountable for surface and ground water pollution (Schuchardt et al., 2007). Every ton of crude palm oil produced is responsible for the emission of 46 m3 (32.9 kg) of methane, corresponding 384 m3 (756 kg) CO2 equivalent (Schuchardt et al., 2007).

There is a possibility of improvement of POME treatment by other processes such as aerobic and anaerobic digestions, physicochemical treatments and membrane filtration (Wu et al., 2009). The organic substance of POME is generally biodegradable; therefore treatment by biodegradable process could be suitable, which are based on anaerobic, aerobic and facultative processes (Sethupathi et al., 2004). Anaerobic process or biological treatment has considerable advantages over other processes such as less energy demands, minimum sludge formation, no unpleasant odor and production of methane due to efficient break down of organic substances by anaerobic bacteria. According to Linke et al ., 2007 the anaerobic digestion process has great potential for rapid disintegration of organic matter to generate biogas that can be used in electricity generation and save fossil energy. However, such biological practices are only applicable in the palm oil mills which acquire large area of lands. According to Ahmad et al., 2005 the treatment process that is based mainly on biological treatment is quite inefficient in treatment of POME, which may lead to several environmental pollution issues. This is largely due to the high BOD load and low pH of POME, together with the colloidal nature of the suspended solids, which renders POME treatments by environmental methods difficult.

Several researchers have used the composting technology for managing the liquid waste coming from agro industries. In order to attain adequate physical conditions for the earthworms' life and growth, the liquid waste coming from agro industries are required to be blended with ligno-cellulosic material (Macci et al., 2009).Macci et al., 2009 carried out vermicomposting of olive oil mill wastewaters (OOMW) by absorbing them on ligno-cellulosic solid matrix. According to Macci et al., 2009 the vermicomposting process could be an alternative and suitable technology for the management of OOMW. Even though OOMW are resistant to biological degradation, the joint action of earthworms and micro-organisms enhances its biodegradability and transformation into a non-toxic and value-added product that is useful for agricultural purposes (Macci et al., 2009).This new approach can be used for the management of POME using the ligno-cellulosic material like empty fruit bunch (EFB), EFB fiber generated in huge amount during the process of extraction of palm oil from oil palm fruit.

2.4 Coagulation

Coagulation refers to the addition of chemical to an aqueous solution to combine small dispersed particles into large agglomerates which can be removed by some other methods such as sedimentation, air flotation, or filtration. Most coagulation operations are intended to lower the suspended solids level of a wastewater, although additional benefits are often obtained by precipitation formation to remove some soluble compounds such as phosphates as expressed by Lee et al., (2007).

Coagulation is a chemical process to remove turbidity and color producing material that are mostly colloidal particles (1 to 200 millimicrons) such as algae, bacteria, organic and inorganic substances, and clay particles. Most colloidal solids in water and wastewater are negatively charged. The mechanisms of chemical coagulation involve the zeta potential derived from double-layer compression, neutralization by opposite charge; inter particle bridging, and precipitation. Destabilization of colloid particles is influenced by the Van der Waals forceof attraction and Brownian movement. While many advances have been made in the development of new coagulants, the design of facilities to use these chemicals is an art as well as a science. Pilot plant information is still needed to determine coagulation times and concentration of chemicalspublished in Donald et al, (1979).The potential applications of this process in treating wastewater are:

(1) direct coagulation of organic matter present mostly as colloidal particles in wastewater; (2) the removal of colloidal substances prior to such tertiary treatment processes as ion exchange, carbon adsorption, and sand filtration; (3) the removal of colloidal precipitates formed in phosphate precipitation processes; and (4) the removal of dispersed microorganisms after a brief bio oxidation process Donald W et al ,(1979). The majority of colloids in domestic wastewater or in organic wastes are of a hydrophilic nature; that is, they have an affinity for water. The affinity of hydrophilic particles for water results from the presence of certain polar groups such as −COOH and $-NH_2$ on the surface of the particles. These groups are water-soluble and, as such, attract and hold a sheath of water firmly around the particle. The primary charge on hydrophilic colloidal particles may arise from ionization of the chemical groups present at the surface of the particles, e.g., carboxyl, amino, sulfate, and hydroxyl. This charge is dependent upon the extent to which these surface groups ionize, and thus the particle charge depends upon the pH (Metcalf and Eddy. 2003).

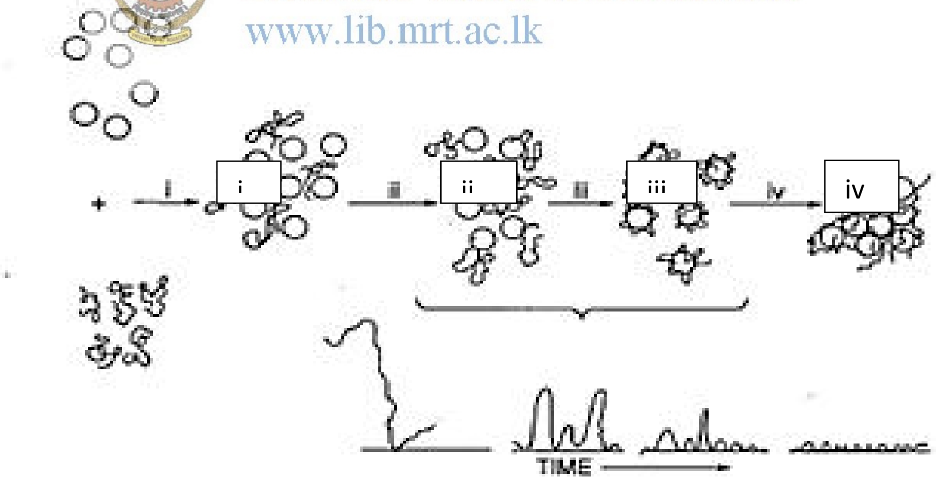


Figure 2.1 Stages in the bridging mechanism: (**i)** Dispersion; (ii) Adsorption; (iii) Compression or settling down (Polymeric coagulation)

2.4.1 Coagulants, their characteristics and applications

Use of advanced water treatment processes in conjunction with coagulation process hasOften been found to improve the overall removal efficiency of trace organic contaminant in both laboratory investigations and operational drinking water treatment plants (Bundy et al, 2007;Choi, 2006; Huerta-Fontela, 2008; Lefebvre et al., 2010; Ternes, 2002). Coagulants are widely used for the treatment of wastewater and solid waste management application due to their affinity to eliminate the unwanted pollutants from domestic an industrial wastewater. The properties of coagulant to act as a water purification ingredient is the ability of binding small particles present in the water together into larger, and work by creating a chemical reaction and eliminating the negative charges that cause particles to repel each other and as a result heavier clumps will settle out relatively quickly. The larger particles produced are known as floc. Properly formed floc will settle out of water quickly in the sedimentation basin or at the base of beaker, which tends to remove the majority of the water's turbidity. Many coagulants are being used commercially, the commonly used metal coagulants fall into two general categories: those based on aluminum and those based on iron. The aluminum coagulants include aluminum sulfate, aluminum chloride and sodium aluminate. The iron coagulants include ferric sulfate, ferrous sulfate, ferric chloride and ferric chloride sulfate. Other chemicals used as coagulants include hydrated lime and magnesium carbonate. The effectiveness of aluminum and iron coagulants arises principally from their ability to form multi-charged polynuclear complexes with enhanced adsorption characteristics. The nature of the complexes formed may be controlled by the pH of the system. When these metal coagulants are added to water the metal ions (Al and Fe) hydrolyze rapidly but in a somewhat uncontrolled manner, forming a series of metal hydrolysis species. The efficiency of rapid mixing, the pH, and the coagulant dosage determine which hydrolysis species is effective for treatment (Donald., 1979).

2.4.2 Natural coagulants

Researchers are working from a long time to search alternative coagulants which are more reliable, environmental friendly and cost effective.Abdelaal, (2004) in his work mentioned that a prime concern of the environmental engineer today, is how to lower the coagulants and flocculants cost and at the same time to improve the characteristics of the produced sludge to be safely utilized. During their work they found a number of alternative natural biodegradable coagulant produced from plant and their seeds. In certain areas of the developing world natural coagulants have been used for centuries within traditional water treatment practices (J.P. Sutherland et al 1994).In recent years, natural polyelectrolytes of plant origin (i.e., Moringa oleifera seeds, Cactus latifaria, nirmali seed, mesquite bean, etc.) have been applied to treat industrial effluents as coagulants.(Beltrán-Heredia et al, 2004),(Zhang et al, 2008), (Raghuwanshi et al, 2007). Zalina Othman et al (2008) revealed that Moringa oleiferaseeds after oil extraction (MOAE) have the potential to become new source of environmentally friendly and natural coagulant for POME pretreatment. Researchers have also worked on natural / biodegradable coagulants from Acacia mearnsii (Beltran-Heredia et al., 2011), Chestnut, Acorn (Šćiban et al., 2009), Jatropha curcas, Guar gum (Pritchard et al., 2009), chitosan (S et al., 2009), Nirmali Seed (Jingdong et al., 2006), cactus (Meyssami and Kasaeian A, 2005), , Cassia Angustifolia (Pramod Kumar et al., 2002) Cactus Latifaria, Prosopis juliflora (Diaz et al., 1999), seeds of Moringa Oleifera (Ndabigengesere et al., 1995) and different leguminous species (Rashmi et al., 2002).

In another study the coagulation performance of the natural coagulants has shown similar efficiencies as commercial coagulants in the clarification of wastewater (J. Zhang et al 2008). Natural coagulants have the significant advantages over the commercial ones as they are available in abundance, cheaper, environmental friendly, multifunction, and biodegrades naturally in water purification (M. Sciban et al, 2002).Mango pit (Mango seed kernel) was investigated first time for the purification of turbid water by (K.Qureshi et al, 2014).

2.4.3 Characteristics of mango pit as a Coagulant

Mango pit contains protein which works as a binding agent in coagulation i.e Proteins becomes fully charged in strong base as well as in strong acidic medium, charged proteins pull the molecules toward its center and form agglomerates hence agglomerates settle down due to attraction of gravity (K.Qureshi et al, 2014).The average content of mango kernel comprises carbohydrates (69.22%-79.78%), fat (8.35%-16.13%), protein (5.6%-9.5%), starch constitutes about 92% and a fair amount of fiber (0.14%-2.95%) and ash content from 0.35% to 3.66% (Dhingra and Kapoor , 1985).Coagulant generates an electron charge, which results coalescence of the oppositely charged particles. It was observed due to neutralization of the charges particles. Inorganic coagulants are mineral salts i.e. Aluminum Sulfate $Al_2(SO_4)_3$, Magnesium chloride $MgCl_2$, Calcium Chloride $CaCl_2$ and Ferric Chloride $FeCl_3$ (Edzwald & Van Benschoten,1990; Crittenden et al., 2005).Many researchers revealed that mango seed kernel contains tannins. Tannins are a group of polyphenols which form insoluble complexes with protein and inhibit several enzymes (Bressani et al.,1983).

2.5. Adsorption

Adsorption process is one of the promising approaches for the removal of organics in water and wastewater. Previous studies show that adsorption is efficient method used for the removal of wide range of organic compounds, different type of adsorbents have been applied to remove pollutants from potable water and industrial effluent.

Adsorption is the accumulation of a substance at the interface between two phases. Although the process can occur at any interface between two phases. The material adsorb is called the adsorbate or solute (pollutant present in wastewater) and the adsorbing phase is the adsorbent (Fly ash).Adsorbent made of oil palm empty fruit bunches was used by Igwe et al, (2010) to remove COD, colour and turbidity with combination of other treatment process as pretreatment with efficiency 89%, 97.9% and 98.9%, respectively from biologically treated POME. While (Aber and Sheydaei., 2004) removed COD from dying factory with efficiency 75% using activated carbon fibre. (Kutty et al, 2010) used microwave incinerated rice husk ash (MIRHA)to adsorb anaerobically treated POME and found 41% of COD removalefficiency. Igwe. et al, (2010) used boiler fly ash to remove TSS from palm oil mill effluent.

2.5.1 Adsorbents and their characteristics

Different types of adsorbents are used for the treatment of water and wastewater. Different types of adsorbents are classified into natural adsorbents and synthetic adsorbents. Natural adsorbents include charcoal, clays, clay minerals, zeolites, and ores. These natural materials, in many instances are relatively cheap, abundant in supply and have significant potential for modification and ultimately enhancement of their adsorption capabilities. Synthetic adsorbents are adsorbents prepared from Agricultural products and wastes, house hold wastes, Industrial wastes, sewage sludge and polymeric adsorbents. Each adsorbent has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces. Many waste materials used include fruit wastes, coconut shell, scrap tyres, bark and other tannin-rich materials, sawdust, rice husk, petroleum wastes, fertilizer wastes, fly ash, sugar industry wastes blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss, clays, red mud, zeolites, sediment and soil, ore minerals etc (Metcalf and Eddy., 2003) .When selecting an adsorbent the most important factors arethe adsorbent rate and pre requisites for adsorption process. The most important attributes of an adsorbent for any application are: capacity, selectivity, regenerability, kinetics, compatibility, and cost. Single adsorbent be optimal rarely in all these respects.

2.5.2 Characteristics of fly ash as adsorbent

Fly ash is the commonly ash content that remains after burning the dry solid part of palm fruit that is basically utilized to produce steam in the boiler. Different type of ash is produced from the boiler andaccording to Yoshizaki et al.(2012) theyare top fly ash and bottom ash. Generally, all fly ash contains the same basic chemical elements, but only in different proportions (Cho et al.2005). It was found that 80% of waste material generated from oil palm cultivation and processing, such as empty fruit bunch (EFB), palm mesocarp fiber (PMF), and palm kernel shell (PKS), are either utilized for plantation nutrients recycling (Fertilizer) or burnt inefficiently as a fuel to produce steam in the mills. Palm oil boiler mill fly ash (POBFA) contain high amounts of alumina, calcium, potassium, and silica that could be utilized to synthesize active compounds that are responsible for sorption of pollutant gasses into the absorbent (Mohamed et al.2006; Zainudin et al.2005).The general characteristics are mentioned in table 2.2. Thus it is possible to assume that these similar compounds could also be used for the adsorption of heavy metals in aqueous solution. According to Foo and Hameed (2009), oil palm ash is characterized by a spongy and porous structure that has a large surface area and pore volume.

Figure: 2.2 Remain solid palm fruit Figure 2.3 Dry palm fruit solids
feeding Bunches to be used as fuel boiler fuel

Table 2.2: Chemical analysis of POFA.
Reference:J.C Igwe et al, 2007

Chemical Composition	**(%)**
Silicon Dioxide (SiO2)	49.2
Aluminum Oxide (Al203)	5.45
Ferric Oxide (Fe2O3)	5.73
Calcium Oxide (CaO)	7.5
Magnesium Oxide (MgO)	3.93
Sulphur Trioxide (SO3)	1.73
Sodium Oxide (Na2O)	0.9
Potassium Oxide (K2O)	5.3
Phosphorus Pent oxide (P2O5)	6.41
Loss on Ignition (LOI)	13.85

2.5.3 Application of POBFAin wastewater treatment

Adsorptions of heavy metals and dissolved pollutants using common commercialized activated carbon have been widely used in many applications due to its high surface area and adsorption capacity. However, the high cost of the activation process limits its use in the wastewater treatment applications (Babel and Kurniawan 2003; Demirbas 2008; Sud et al.2008). Realizing the complications of the situation, a large number of agricultural lignocellulosic by-products have been utilized in order to develop cheaper and more effective adsorbents for the removal of various pollutants from wastewater (Demirbas 2008;Han et al.2010).These lignocellulosic by-products possess various advantages, such as eco-friendly nature, renewability, low cost, and abundant availability, as compared to commercial adsorbents (Han et al.2010). The application of oil palm biomass (that remain after extracting oil component) as commercialized adsorbents is still in research phase. Therefore, It was found that in order to enhance the value of this material, palm oil boiler mill fly ash (POBFA) could be developed into a natural low-cost absorbent for the removal of heavy metals and other pollutants in the industrial wastewater, needed to be explored and further investigated. Several investigators (Johnson et al., 1965; Peloso et al., 1983; Kumar et al., 1987; Mott and Weber, 1992; Viraraghavan and Alfaro, 1994; Banerjee et al., 1995, 1997; Ackerman and Zardkoohi, 1996; Gupta, 1998; Aksu and Yener, 1999; Gupta et al., 2000; Kao et al., 2000; Sakellaridis and Albanis, 2000; Gupta and Ali, 2001; Ricou-Hoeffer et al., 2001; Nollet et al., 2002) explored the use of fly ash as an adsorbent for the treatment of wastewater to remove a variety of organic compounds and color. They concluded that fly ash has a significant adsorption capacity for the removal of organic compounds from aqueous solutions. On top of that, the rich and cheap source of the biomass materials will further authenticate its use in the wastewater treatment industry (Ahmad et al.2011; Chowdhury et al. 2011; Foo and Hameed 2009).

2.5.4.Use of POBFA for Palm oil wastewater treatment

Different studies have been conducted to investigate the performance and characteristics of POFA as a natural low-cost adsorbent for removal of heavy metals, Color, COD, BOD, TDS, TSS, Turbidity and toxic pathogens from aqueous solutions and POME. Researchers have also worked on fly ash characteristics as an adsorbent to be used for POME treatment and developed model for isotherm studies. Research by Ofomaja (2010) reported that palm kernel fibre can be utilized effectively in removing copper ions from wastewater. The sorption process is endothermic in nature and there is high affinity of the adsorbent towards the sorbate.By using fly ash for POME treatment Igwe et al (2013) found that Fly ash obtained from palm oil mill boiler can be activated and used as an adsorbent which proves to remove Color up to 90 % and Remove BOD, COD, and turbidity more than any other adsorbent or coagulant. Furthermore, he also developed thermal equilibrium model for this purpose.

2.6. Introduction to Hybrid Adsorption- coagulation

At present, different wastewater treatment technologies are available, includingconventional methods such as chemical precipitation, coagulation, reverse osmosis, ion exchange, membrane filtration, oxidation, air stripping, sedimentation, and adsorption (Foo and Hameed 2009; Naiya et al.2009; Salam et al.2011; Wang et al.2010 ; Aziz et al 2010). Ammir et al. (2009) evaluated optimization of coagulation process using ferrous sulphate as a coagulant for removal of COD, color and turbidity. A properly designed coagulation-flocculation unit can efficiently remove suspended solids and can thereby enhance the performance of a subsequent activated carbon adsorption unit by reducing competitive adsorption (Hai et al., 2007).Gandhimathi et al. (2013) carried out a combined process of chemical coagulation and adsorption as a pretreatment for stabilized landfill leachate. They used ferric chloride and aluminum sulphate as coagulant and fly ash as adsorbent. In his recent research work Motling et al ., (2014) investigated and examined the efficiency of combined coagulation- flocculation and adsorption process using alum, PAC, ferric chloride as coagulants and commercial grade activated carbon for employing physico-chemical treatment of leachate.

2.6.1 Application of Hybrid Coagulation-Adsorption process in wastewater treatment

The first study on the treatability of raw wastewater by physical-chemical processes was reported by Rudolfs and Trubnick in 1935. In this study, solids were removed by chemical coagulation with ferric chloride followed by absorption of dissolved impurities with activated carbon (Rudolf et al, 1935). Study was conducted by Aryadasa where organic coagulation and adsorption by non-ion exchange processes were coupled and combined treatment process was tested to remove PFOS from synthetic wastewater.

Research studies were conducted on wastewater to minimize different parameters, such that G.M Ayoub et al., (2011) in his study foundthat the removal results for both the apparent color and the turbidity were practically identical. Very high removals, amounting to an average of 99.5±0.58% for the coagulation process and about 100±0% for the combined coagulation–adsorption process were recorded. He also concluded that the effect of adsorption alone has been relatively effective in reducing the concentrations of the parameters by values that averaged about 56±6.8% and 47±10.1% for COD and BOD, respectively. Highest removals were recorded with the combined treatment of coagulation and adsorption which averaged about 72±2.4% and a maximum of 75% for COD and 57±5.0% and maximum of 64% for BOD. Coagulation followed by adsorption was reported to produce effluent of reuse standard, while reducing the coagulant consumption by 50%, hence lowering the volume of sludge formed, in comparison to coagulation only (Papic et al., 2004). Hybrid Coagulation-Adsorption not only remove TDS or TSS, the tendency of the process can eliminate heay metals and removing organic contaminants as well, Bundy et al (2006); Choi (2006); Temes (2002) in their work proved that coagulation and flocculation flowed by filtration with granular activated carbon (GAC) be very effective in removing certain organic contaminants during drinking water treatment. GAC post treatment has been found to significantly enhance the removal efficiency to almost complete removal of caffeine, trivoflaxin mesylate and estradiol (Bundy, 2007), carbamazepine, bezafibrate and diclofenac (Ternes, 2002), cocaine, 3,4-Methylene dioxy methamphetamine (MDMA) and benzoylecgonine (Huerta-Fontela, 2008). Activated carbon following coagulation has also been reported to be reasonably effective in removing certain tetracycline antibiotics (Choi et al., 2008).Hwang et al (2010) concluded by conducting various experiments that carbon black in combination with coagulants might be a potentially useful technology to remove high concentrations of Natural organic matter (NOM) from raw water. Tomaszewska et al. (2004) investigated the removal efficiency of humic acid and phenol by coagulation and adsorption (powdered activated carbon, PAC) and revealed that in comparison to coagulation alone, the integrated adsorption-coagulation system is effective in removing phenol. Zhang et al. (2011) reported an enhanced phenol removal in a process involving combined application of the common coagulant aluminum chloride and manganese dioxide formed in situ. Nanotechnology has appeared as a very promising new way to remove organics from water (Matilainen et al., 2010).Nanomaterials have exceptional adsorption properties and they are able to entrap diverse organic molecules, including those in trace concentrations (Joseph et al., 2011; Upadhyayula et al., 2009). Analysis of the mode of action of such adsorbents may be beneficial while carrying out fundamental research on development of high performance coagulants. H. Wang et al (2010) indicated that the addition of alum resulted in substantial Natural organic matter removal even at very low coagulant doses ofalum increased the removal to above 90% when added along with Powdered Activated carbon.

2.7 Settling / Sedimentation

Sedimentation is a solid–liquid separation by gravitational settling. There are four types of sedimentation: discrete particle settling (type 1); flocculants settling (type 2); hindered settling (type 3); and compression settling (type 4). Sedimentation theories for the four types are discussed in elsewhere (Gregory and Zabel, 1990).To get the best output product settle ability parameters play a vital role after coagulation / adsorption treatment. Z.Othman et al. (2008) worked on natural coagulant settle ability parameters found that the high stirring speed of solution only have a decrease in sedimentation and highest settling velocity. She observed that It therefore seems that, although the effect is only moderate, longer mixing times lead to breaking of the flocs, with a reduction in settling velocity and a rise in sediment percentage and residual conductivity. She observed from her experiments that the settling velocity increased with an increase of the coagulant dosage. The residual conductivity was reduced with further addition of the coagulant. With a high coagulant dosage, sweep floc mechanism of coagulation process prevailed and resulted in the reduction of the floc growth rate.

2.8 Filtration

Most of the time in water clarification or softening processes where coagulation and precipitation occur, at least a portion of the clarified water is filtered after settling. Clarifier effluents of 2-10 NTU may be improved to 0.1-1.0 NTU by conventional sand filtration. Filtration is capable to ensure acceptable suspended solids concentrations in the finished water even when upsets occur in the clarification processes. Normally to retain small amount of flocs or dissolved particles of fly ash rapid sand filter was used as an efficient filtration technique. Some of the design size range with specific gravity is given in table 1.3.

Table 2.3Media used in multilayer filtration.
Source : http://www.gewater.com/handbook/ext_treatment/ch_6_filteration.jsp

Media	Effective size, mm (in.)	Specific gravity
Anthracite	0.7-1.7 (0.03-0.07)	1.4
Sand	0.3-0.7 (0.01-0.03)	2.6
Garnet	0.4-0.6 (0.016-0.024)	3.8
Magnetite	0.3-0.5 (0.01-0.02)	4.9

2.9. Summary and objectives of the study

Overview of this literature survey indicates that efficiency of hybrid system was verified by different researchers from time to time, looking into their outcomes and the worth of their work it seems that hybrid process of wastewater treatment is very useful if applied in practice. Different researchers have worked on hybrid adsorption-coagulation method using activated carbon and alum as coagulant for the treatment of textile effluent and dyes and pigments wastewater treatment.A variety of coagulants has been studied to assess their ability to destabilize the POME suspension and to flocculate the particulate matter. The conditions that would allow for optimal use of the respective chemicals were noted especially for suspended solid removal. However, the magnitudes of the increase in the removal rate by the application of the coagulants are still vague as there is currently no published information on the use of natural biodegradable coagulants together with POBFA as adsorbent in POME treatment for BOD, COD, TDS, TSS and color removal. Most studies performed did not carry out chemical cost analysis which is equally important so as to determine the most cost effective process. Natural coagulant was proven to be an excellent ingredient for the removal of pollutants from wastewater.

The main objective of this study is to use hybrid adsorption-coagulation process for the first time for the removal of color, BOD, COD, TDS, TSS and turbidity presence in POME.Mango pit was used as biodegradable coagulant and POBFA was utilized as adsorbent to get better quality wastewater.

3. MATERIALS AND METHODS

Hybrid process in the presence of adsorbent and coagulant may require a number of physical and chemical steps to achieve good quality water.The porosity and adsorption capacity of adsorbent was improved by physic-chemical treatment (A.K.Shah et. Al, 2013). In this study Chemical treatment is required to accomplish the adsorption and coagulation phenomena, whereas the physical treatment is required to further retain the “flocs”, sludge and any other contaminant present before getting the final product.

Overall procedure comprises of three stages

1. Preparation of Coagulant
2. Preparation of activated fly ash
3. Experimental procedure (Chemical and physical treatment)

To go further towards experimental part the POME obtained from Palm oil mill was characterized to fine out the exact efficiency of the process by considering the characteristics of POME as initial point.

3.1. Characterization of POME

In order to compare the results with initial concentrations of pollutants wastewater sample taken from palm oil mill after aeration process was characterized and results are shown in Table 3.1. The characteristics values shows that palm oil mill effluent after biological treatment may still contains high organic and inorganic contaminants in terms of color, BOD,COD,TDS and TSS that still need to be removed.

Table 3.1: Characteristics of POME after aeration

Parameters	values
Color(Pt-Co)	3560
TDS(mg/l)	5400
TSS(mg/l)	700
BOD(mg/l)	560

COD(mg/l)	890
TURBIDITY(FAU)	1275

3.2. Preparation of Coagulant

Mango pit commonly known as (kernel, seed or embryo) (K.Qureshi et al 2014), Collected from fruit juice industry were processed through a number of steps in order to extract high amount of coagulant. These steps consists of, collection of mango pit, de-shelling, washing, drying, crushing, extracting and finally preparing the coagulant active extract. Initially mango pit obtained were washed and dried for their shell to be removed easily. Dried mango pit shell was removed and the kernel present inside were de skinned and cut down into small pieces figure 3.1 in order to achieve higher rate of drying. After cutting down into small pieces, the kernels were washed with distilled water and dried at 130^{o}C for 1hour in the "Remi, laboratory oven" capacity 0-300 ^{o}C. Dried mango seeds were cooled and crushed using ball mill to extract its coagulant enriched protein component. Ground mango kernel was sieved to particle size 0.44mm using "Endecotts test sieve ltd sieve shaker". The sieved mango kernel granules were dissolved in distilled water (50g/liter of water) and the suspension was stirred for 10 min using a magnetic stirrer to extract the coagulation active species,after proper stirring the coagulant active species were filtered using Whitman filter paper to separate the solid contents present." Suggested by K.Qureshi, et al 2014. The final product obtained was kept refrigerated at below 15 ^{o}C Figure 3.2.

Figure 3.1. Mango kernels

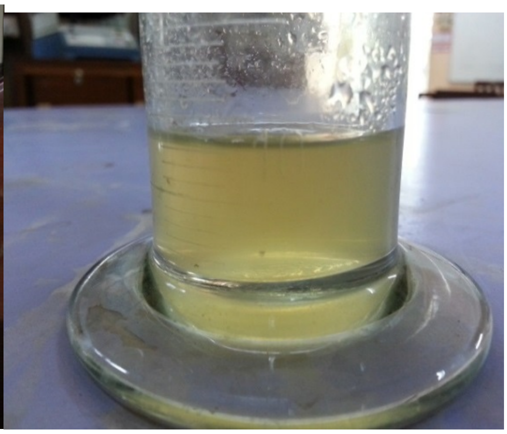


Figure 3.2 Mango kernel coagulants

3.3. Preparation of activated boiler fly ash

Palm oil boiler Fly ash (POBFA) was directly collected from the boiler at AEN palm oil Processing unit, located in Muhameddi estate, Sri Lanka. The large particles of POBFA obtained are ground and sieved in order to reduce the particle sizes up to 355 and 500µm respectively for future comparison. Ground POBFA obtained after sieving was washed with warm distilled water and activated by soaking with 3% v/v Nitric acid solution for 24 hours. In order to obtain highly activated fly ash without any contaminant or soluble component, samples of fly ash were soaked with different concentration of acid to obtain an optimum condition for activation but knowing the fact that excess use of acid can dissolve all adsorbent and can be washed off. Using Low concentration of acid with warm distilled water was practiced one of the good method to minimize the loss in weight of fly ash. It was noted that after soaking with Nitric acid higher concentration Leads to 15 – 20% loss in total weight. Loss can be minimized by direct washing and using low concentration of acid. After soaking, fly ash was washed three times with warm distilled water shown inFigure 3.3. Activated granules were then air dried. After activation samples of fly ash of different granule sizes were visually compared using high efficiency electron microscope, the infinity analyzer capture can be seen as shown in (figure 3.4 to 3.7).It can be seen that the pores were become open when activation applied and the porosity of the granules increased when checked usually. Different particles of 355 µm and 500 µm are visible by magnifying their structures.

Finally highly activated POBFA obtained was kept under dry condition till further use.

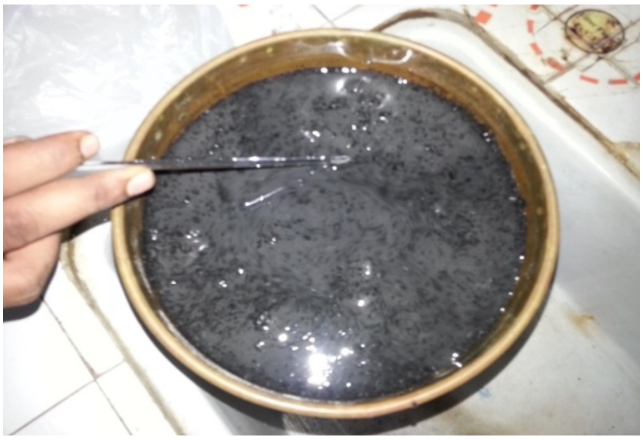
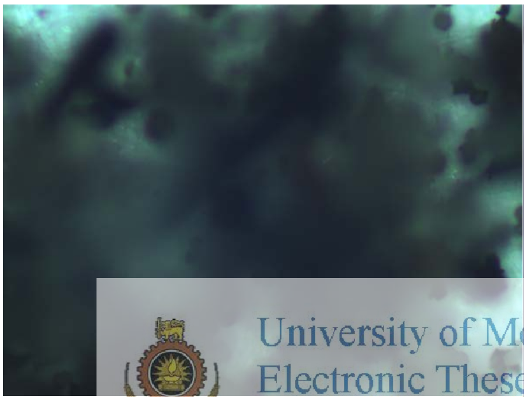


Figure 3.3 Cleaning of fly ash after activation



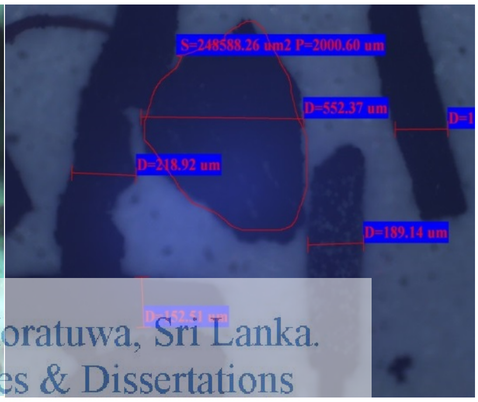


Figure 3.4 500µm size particles

Figure 3.5 500 µm activated using 2%v/vHNO_3

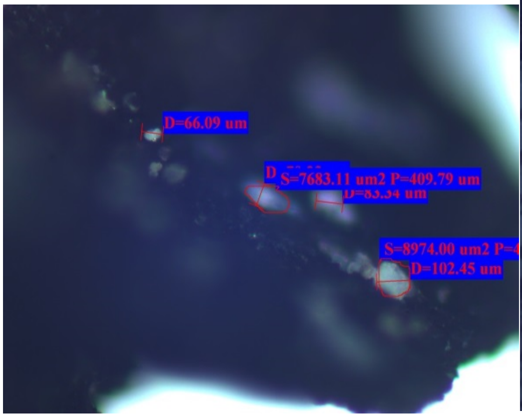


Figure 3.6 355 µm granules after activation

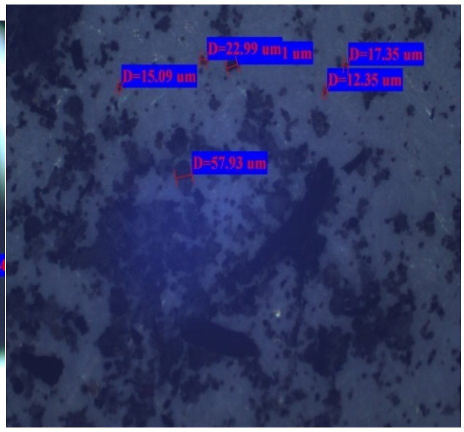


Figure 3.7 355 µm Granule before activation

Figure 3.8High efficiency electron microscope and the infinity analyzer

3.4. Experimental procedure

Experimental procedure in this study composed of following two treatment methods in order to achieve the required standard of finally treated wastewater.

1. Chemical treatment
2. Physical treatment

3.4.1. Chemical Treatment

Chemical treatment process in wastewater treatment generally composed of different techniques i.e. Coagulation, Adsorption, Biological treatment, sludge treatment (Biogas production). Hybrid Adsorption-coagulation technique was applied in this research with alternative coagulant and POBFA as adsorbent to get the optimum results based on the variable parameters are initialConcentration, initial pH, mixing rpm, filtration media to achieve more reliable, effective and environmental friendly process outputs. Three sets of experiments were performed in chemical treatment section. These are,

- Using 100 % POBFA with variable particle size and weight.
- Using different initial concentration of 100 % mango coagulant only.
- Hybrid Coagulation-Adsorption process

3.4.1.1 Experiments using 100% POBFA

Jar test method was applied for chemical treatment of the waste water. Initially tests were performed using 355 µm and 500 µmparticle size of POBFA. 300ml Samples of wastewater were taken into the beaker along with variable weight of POFA (80, 90,100g/300ml of sample) as shown in (table 3.4)to check the effect of weight and particle size on percentage removal of pollutants.

Table 3.2 Parameters of Fly ash and wastewater samples at initial pH 4 and 200rpm

Samples	Particle size		Weight of POBFA g/ 300ml of wastewater sample
Sample 1	355 µm	500 µm	80
Sample 2	355 µm	500 µm	90
Sample 3	355 µm	500 µm	100

Prepared samples were adjusted to initial pH 4 which was optimizedbased on the various trial experiments on different pH.

Figure 3.9. Performing Jar test using ISCO Teeni Amanda Jar test Apparatus

3.4.1.2 Experiments using Mango Pit Coagulant only

Using jar test method, experiments were performed by taking 300ml samples of wastewater into the beaker and keep different concentration (2, 3, 4mg/lit) of Mango kernel extract as coagulant into it. Parameters such as temperature, rpm, settling time) were kept constant during the process and pH of the solution was adjusted to 4. During coagulation Best Result was achieved at pH 3 which is maximum value in acidic medium (K.Qureshi et.al, 2014). Prepared Wastewater solutions were agitated at 80rpm for 40minutes and kept for settling for 30 minutes after that. Clear water from the surface was then used for physical treatment.

3.4.1.3 Experiments using Hybrid Coagulation-Adsorption method

300ml samples of wastewater were taken into the beaker and appropriate amount of coagulant (2, 2.67,3mg/lit) were added into it, after few minutes interval different weight of adsorbent (POBFA) 60, 90, 120g were added into the solution and the pH was adjusted to 4.After mixing and settling, the treated solution was taken for physical treatment. Similarly Second experiment was performed to check the impact of pH on the rate of reduction in impurities present in water. The pH of different solutions were adjusted to, 4, 5, 6 respectively. The initial concentration of coagulant- adsorbent were adjusted to (4ml/lit, 300g/lit), mixing rate was adjusted at 200rpm for 1 hour. Treated samples were kept for settling for 40 minutes.

3.4.2. Physical Treatment

Physical treatment is a pre requisite in this Physico-Chemical treatment process to get the final water quality required. Filtration is used in both water treatment and wastewater treatment in final stage as a separation process, which has the capability to remove fine inorganic and organic particles from the wastewater. Sand filters are often used in treatment of water and wastewater to remove fine particles, which are not possible to be economically removed by only sedimentation process. Sand filtration is a type of granular mediumfiltration, in which the filtering medium consists of granular material such as sand, anthracite, activated carbon or other grains. The main applications in water treatment are rapid sand filtration and slow sand filtration.

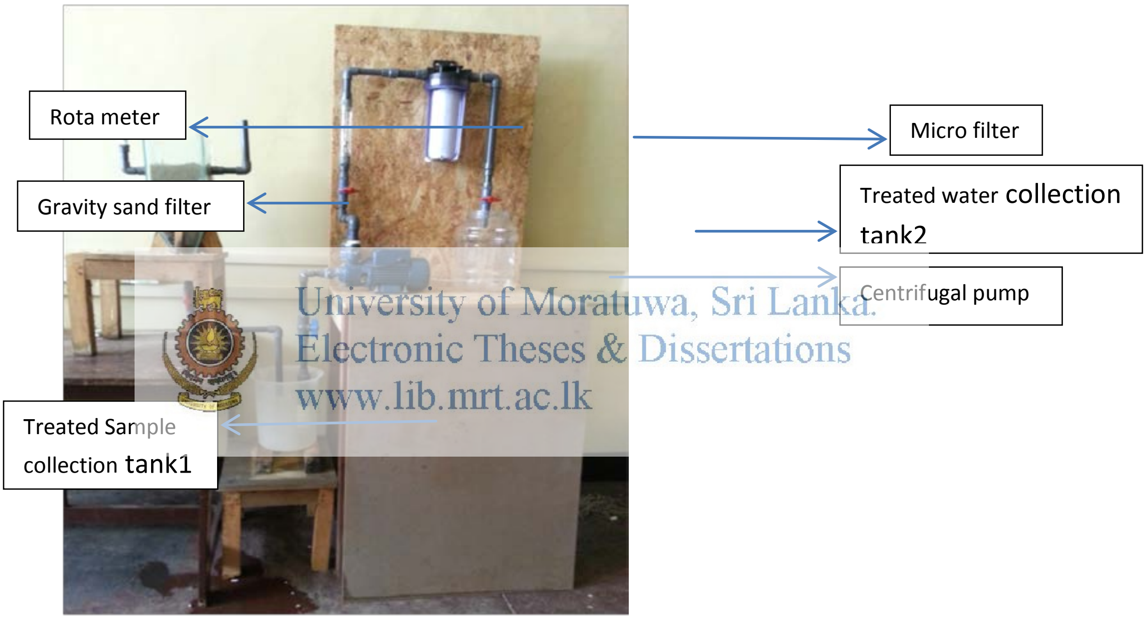


Figure 3.10 Experimental set up for physical treatment of POME

Pilot plant was designed and builtas shown in Figure 3.10and was installed with filters, valves, pumps, and flow meter. A well designed rapid gravity sand filter unit for filtration was also included in the process to treat the solution samples obtained after chemical treatment jar tests to remove sludge produced.

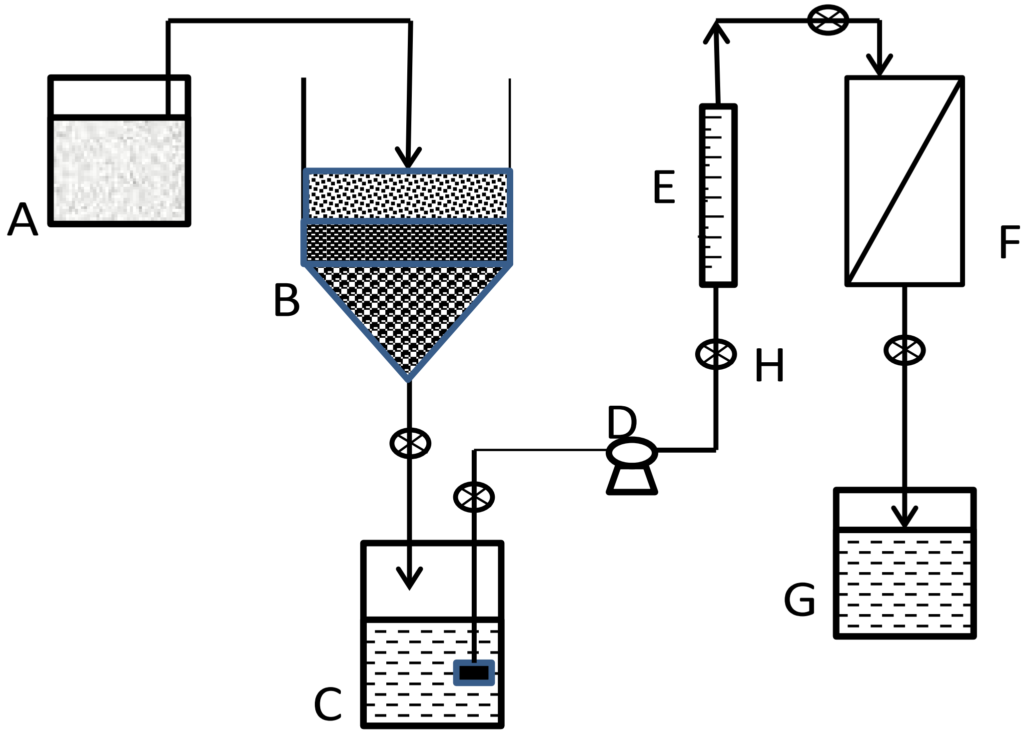


Figure 3.11: Schematic diagram of physical treatment system developed in this study : (A) Solution obtained after jar test chemical treatment ; (B) dual media gravity filter ; (C) Water collection tank after gravity filter ; (D) Centrifugal pump of 0.5hp ; (E) Rota meter to adjust the exit flow rate ; (F) Micro filter ; (G) Product collection tank ; (H) Valves

Two different filtration units were installed to compare the results as well as to check the reliability of filtration systems and to minimize the cost of filtration by comparing different techniques and using the best one with economically proven background. Dual media sand and gravel gravity filtration unit was designed with 1mm sand and gravels of different sizes were put into conical type glass tank. Filter clothes were placed in between these gravel distributions to achieve better results. Water once filtered out through gravel filter was pumped (Centrifugal pump 0.5 hp) to micro filter unit through a flow meter (Rota meter) ranging 1-7 lit/min to check the rate of filtration on different flow rates. End product was obtained at point G as shown in Figure 3.10; further samples were also taken from Point C, to check the efficiency of Dual media sand filter.

Due to a batch process and low amount of wastewater sample used at very small scale no head loss was calculated. Pressure drop was not measured and the effectiveness of the filter media was checked by output water quality and contaminants. Velocity variation was also checked after some interval to check the efficiency of the filter media or whether it is blocked or particles are contaminating other samples. To avoid this, intermittent cleaning was performed. Sand filter was designed on the basis of velocity of wastewater filtered. The parameters which were measured are.

- Volume of sand and gravel
- Particle size of sand
- Filter cloth type
- Thickness of the filter bed
- Total volume of the tank

Rapid sand filter was used in this study and effective particle size suggested was in between 0.4 and 0.8mm, which is larger than in slow sand filters. This was only done due to low quantity of water samples used. The performance of sand filter is not only retaining used carbon particles / sludge or flocs it can also retain trace of organic contaminants that left during chemical treatment. Three different layers were made layer 1 of sand with particle size 1mm and the thickness of the bed 200mm, Layer 2 of small gravels of silica stone with particle size 20mm and thickness of the bed was 120mm and finally the layer of gravels of biggest particle size with thickness of the bed 200mm.Filter clothes type Polypropylene woven filter cloth of size 50µm were placed in between each layer for better performance. Due to small amount of filter media used washing was performed after every batch of 5 samples filtration. Sands and gravels were removed washed and placed again. For large scale, the, more convenient and method applied is the backwash cleaning method which is more reliable, less time consuming, and not much human work is involved.

3.5 Experimental Analysis

In order to obtain the results and comparison of the same with current and previously conducted work number of analysis were performed to calculate the water quality of the product water. The methods applied for different analysis are

- BOD Incubation test
- COD test using digester and titration method
- Color and Turbidity using colorimeter
- TDS and TSS using filter paper and petri dish

3.5.1 Biological Oxygen Demand (BOD) Analysis

BOD test was performed using incubator machine (Aqualytic Leibherr Incubator) as shown in (Figure 3).

Figure 3.12 BOD Incubation apparatus with scales shown

The methodology applied to perform BOD measurement was BOD incubation test. The required quantity to be obtained is given in (Table 3.6). The required volume of sample was poured into different sample bottles specifically provided for this test according to adopted scale Table 3.1 measured by graduated cylinder. Magnetic stirrer used for continues mixing. A small container, located under bottle cap was filled with alkali for carbon dioxide absorption (Scales of Potassium hydroxide or Pallets of sodium hydroxide) enough to avoid losses through the holes on walls. Bottles were placed into their location in the BOD apparatus and the caps were screwed tightly. Scales were placed into their position (In relative to their sample volume).Instrument was placed into refrigerated and incubation temperature was set to 20 ^{o}C.Magnetic stirrers were connected to mains introducing the plug into the socket. After 30-40 minutes, when samples and apparatus become in thermal equilibrium, the caps were closed and the manometers were set to zero scales by moving them to make zero notches correspond to mercury meniscus. Clamp was screwed tight and scale was fixed. BOD_5 method was selected in this analysis where the sample was kept inside incubator for five days with 20 ^oC steady state temperature. Reading was obtained on daily basis just to check the trend and that the sample is correctly placed and the cap is tightened properly.

Table 3.3 Scales versus the volume of sample

Sample Volume(ml)	Scale (mg O2/l)
100	1000
150	600
250	250
400	90

3.5.2 Chemical oxygen Demand (COD) Analysis

COD test was conducted using "Redox titration" method. The test is performed with the digestion vessel with holes to fit the culture tubes. Borosilicate culture tubes, 16 * 100mm with TFE-lined screw caps were taken and washed clearly. Solution samples were prepared according to the reagent volume to be used given in **Table 3.2**.

Table 3.4 Amount of reagents used for COD

Digestion Vessel	**Sample (ml)**	**Digestion Solution (ml)**	**Sulfuric acid Reagent (ml)**	**Total Final Volume**
16 * 100mm Culture tubes	2.5	1.5	3.5	7.5

Solution samples were placed in culture tube after adding digestion solution; caps were closed tightly and mixed well by inverting them various times. Tubes were placed in block digester which was already preheated to temperature 150 ^oC and refluxed for 2 hours. After 2 hours' time samples were cooled to room temperature and titrated against 0.1M standard FAS (Ferrous ammonium Sulfate) after adding 1 or 2 drops of ferroin indicator. During titration end point was a sharp color changed from blue green to reddish brown where the final reading was noted. Formula guess between was used to calculate COD value.

$$COD\ as\ mg\ O2/L\ =\ (A-B)\ *\ M\ *8000/\ mL\ sample$$

Where

A = ml FAS used for blank

B = ml FAS used for Sample

M = Molarity of FAS

8000 = Milliequavalent weight of oxygen * 1000ml/l

3.5.3 Color and Turbidity Analysis

Color and turbidity tests were performed using DR /890 Colorimeter shown in (Figure 3.11). The program number selected were 19 for turbidity and 95 for Color, The measurement units were Color (Pt-Co) and for turbidity FAU which is the same as NTU. The measured values were obtained against distilled water as standard.

3.5.4. Total dissolved solid and total suspended solid Analysis

Total dissolved solids and total suspended solids were measured using filter paper (glass fiber filters; 47mm; Whitman934AH) and oven (Remi laboratory oven range 0-300 ^{o}C) for drying. Calculation was done by obtaining the initial and final weight of the sample with filter paper and petri dish before and after drying.

3.6. Recycling of POBFA

Recycling part of the POBFA was done by using thermal cleaning in order to best utilize the ingredient. Sludge retained after physical treatment contain heavy amount of used Fly ash, flocs, organic and inorganic contaminants. Sludge was then washed with normal distilled water at normal temperature and kept soaked in 2% v/v nitric acid for 1 hour and later washed using warm distilled water. The same procedure was repeated after every batch of experiment. This is recorded as the total capacity of POBFA and the number of times to be recycled.

4. RESULTS AND DISCUSSION

This chapter includes the discussion on the results obtained by varying different parameters. Detailed experimental variations and key factors that effecting results are also included. Graphical representation shows the trend towards the targeted value and the factors that helped to achieve that target are discussed in this chapter. Finally, results are compared with previously conducted research studies.

4.1. Effect of Fly ash (POBFA) on water quality

Activated POBFA was checked for its efficiency for percentage reduction in Color, BOD, COD, TDS, TSS and turbidity. In two different experiments variable granule size and variable weight of POBFA were checked and optimized. The results were further compared with previously done research studies using the same ingredient for the wastewater treatment.

4.1.1 Effect of particle size

To check the effect of particle size on % contaminants removal, particle size of the fly ash used were 355 µm and 500 µm at initial pH: 4. First experiment was conducted with particle size 355µm with variable weight of adsorbent and the initial pH of the solution was set to 4.This was due to the use of POBFA in hybrid system along with coagulant at same ph. The effect of percentage reduction was noted and the same experiment was performed using 500µm. At the end both results were compared.

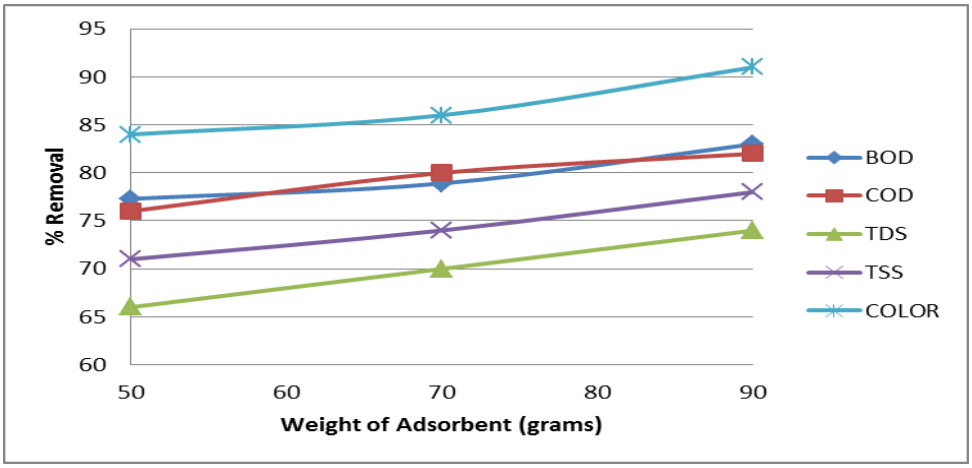


Figure 4. 1 Weight (grams) of 355 µm Adsorbent against the % removal of BOD, COD, TDS, TSS and color.

Following first set of experiments the results are shown in(Figure 4.1). This Indicate that when using 100 % pure fly ash as adsorbent (355 µm particle sizes and 90gram of weight) gives reduction in color up to 91%, BOD 83%, COD 82%, TDS 74% and TSS 78% respectively. To further investigate the effect of granule size on the rate of adsorption, experiment was conducted using 500µm adsorbent.(Figure 4.2) Shows that using 500µm and same amount of adsorbent, the percentage reduction is lower than using smaller particle size. This can be explained by increase of surface area due to small particle size and thereby enhancing adsorption process. Rate of adsorption increases when particle size is decreased this can be seen from previous studies conducted The particle size of 425µm gave higher sorption capacity than particle size of 850µm.(Igwe et al,2008). Adsorption rate is very much dependent on the total surface provided for sorption and the capacity of adsorbent till equilibrium state.

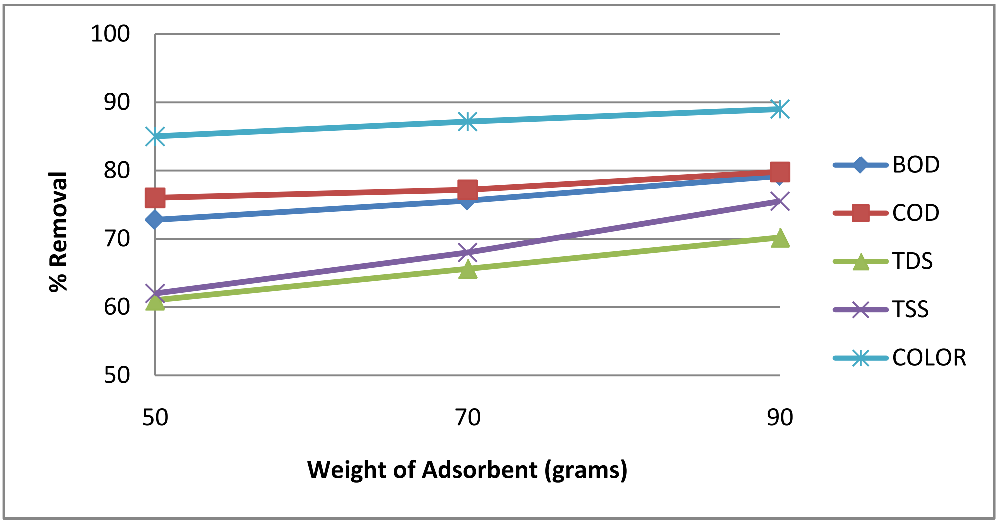


Figure 4.2: Weight of Adsorbent 500 µm (grams) against the % removal of BOD, COD, TDS, TSS and color.

4.1.2 Effect of weight

From (figure 4.1 and 4.2) it can be seen that, when the weight of POBFA was increased the % reduction of Color,BOD,COD,TDS, TSS and Turbidity was also increased.

4.2. Effect of Mango Pit (Coagulant)

Effect of coagulant was checked and optimized according to variable concentration and pH. Two sets of experiments were performed using variable pH and other using variable concentration to find the optimum values in terms of pH and concentration for the percentage reduction of Color, BOD, COD, TDS, TSS and turbidity. Furthermore, experiments were performed to check which concentration and pH to be used when combining with adsorption.

4.2.1 Effect of Coagulant concentration

The effect of concentration (2.3, 3, 4, 5.3mg/lit) on rate of reduction in color, BOD, COD, TDS, TSS and Turbidity is shown in (figure 4.3).

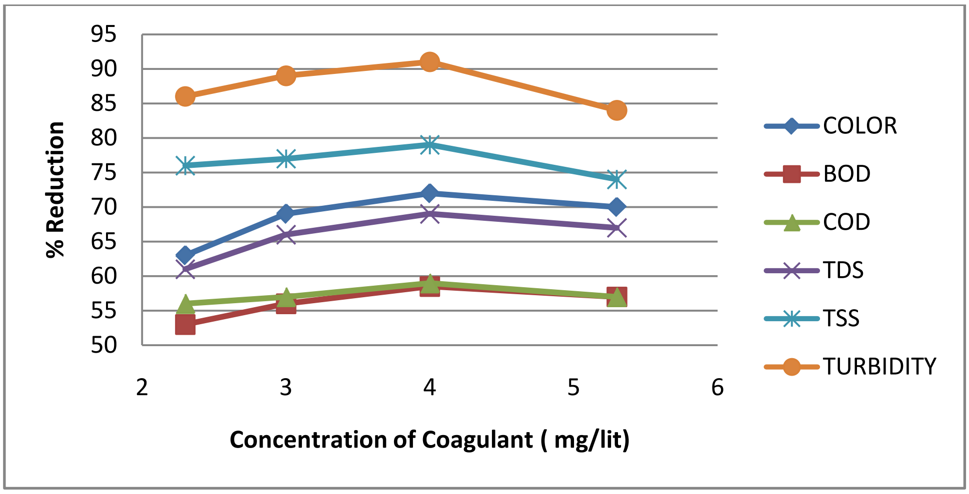


Figure 4.3 Concentration (mg/lit) of coagulant vs the percentage reduction in Color, BOD, COD, TDS, TSS and turbidity.

when concentration of coagulant increases the percentage reduction will also increase , But at certain concentration it is possible that a higher rate of reduction can be achieved after that the coagulant particles will become destabilized which is seen at concentration 1.6ml, thus the optimum concentration for percentage removal of coagulant is 4mg/lit or between 3 and 4mg/lit.It can also be observed that the effect of coagulant on reduction of turbidity is higher i.e. 91% when comparing with Color,BOD,COD,TDS and TSS 71, 58.5,59,69 and 79% respectively. Moreover these variations can vary when mixed or followed by adsorption process.

4.2.2 Effect of pH

In this experiment concentration of the coagulant was kept constant at 3mg/lit which was obtained from previous experiment. There was an adverse effect on percentage reduction of pollutants with the increase in pH as observed in Figure 4.4.Therefore pH was reduced to level 4 which gives the highest results in terms of percentage reduction in Color 72% ,BOD 59%,COD 57%, TDS 68%, TSS 74% and turbidity 91% respectively. This is due to Proteins becomes fully charged in strong base as well as in strong acidic medium. Charged proteins pull the molecules toward its center and form agglomerates hence agglomerates settle down due to attraction of gravity (K.Qureshi et al, 2014).Concentration of the coagulant was kept constant at

3mg/lit(obtained from previous experiment) while changing pH. In order to obtain a better pH value the rest of all parameters (rpm, settling time, temperature) were also kept constant. Again it is shown in Figure 4.4 that the removal of turbidity is highest amongst all the other parameters. The same is the case when pH is decreased. This is shown in Figure 4.4 that when the pHis decreased the amount of turbidity and Color is reduced and slight reduction in terms of COD, BOD, TDS and TSS was also reported. This results show that the effect of coagulant is towards more on reduction of turbidity and color.

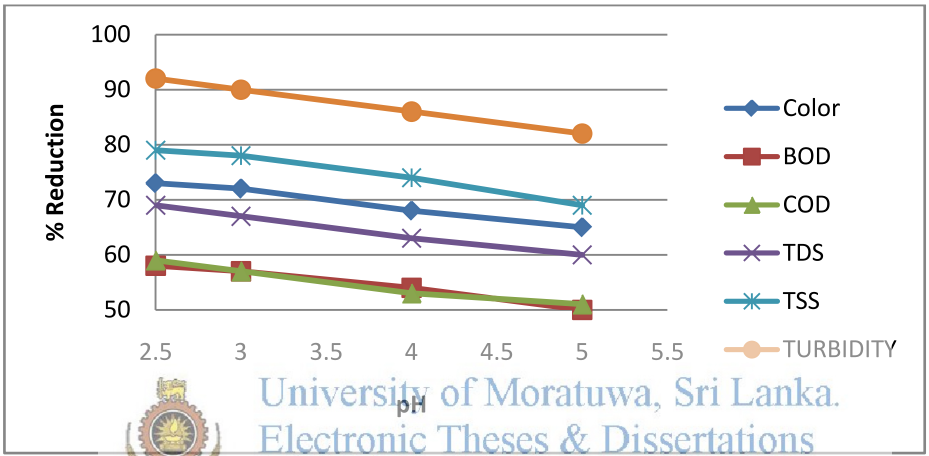


Figure 4.4 Effect of Coagulant concentration (mg/lit) vs initial pH

4.3. Hybrid Coagulation-Adsorption method

When adsorbent and coagulants were applied in a Hybrid Coagulation-Adsorbent system a better trend was observed towards the percentage reduction in contaminants. Also it has indicated that using hybrid system reduces the amount of coagulant used. When using coagulation separately optimum value was obtained at concentration 4mg/lit while doing in hybrid system it has reduced to 3mg/lit. Similarly in terms of POBFA, the concentration was optimized at 110g/lit when used separately and once used with coagulant in hybrid system it was reduced to 300g/lit.

4.3.1 Effect of concentration of Adsorbent-coagulant

The effect of adsorbent – coagulant concentration on the removal of TDS, TSS, Color, BOD, COD and Turbidity was investigated by varying the amount of adsorbent-coagulant used. Other parameters such as pH, agitation speed, timewere kept constant. It was observed that the addition of adsorbent into the course of coagulant can not only increase the floc size but can also robust the settling time of flocs . Using only coagulant results in 50-70% reduction in contaminants whereas when a specific optimum amount of coagulant was mixed with POBFA gives a rapid improvement towards the reduction.Varius concentrations of adsorbents were used with an specific amount of coagulant to find out the optimum solution concentration. (3mg/lit of coagulant and 300g/lit of adsorbent) gives the best result in % reduction of contaminants similarly (200, 233, 300g/lit) give results slight lower than the previous one. It can be seen from Figure 4.5 that with increase in the concentration of adsorbent the percentage reduction in Color, BOD, COD, TDS, and TSS has increase. Further it can also be seen from Figure 3.5 that percentage reduction in pollutants increase when comparing results with other experiments where POBFA or Coagulants were used as adsorbent or coagulant separately. The results shown in Figure 3.5 when compared with the previous results shows that the reduction in color from 92 to 97%, BOD from 88 to 94.64%, COD 84 to 89%, TDS 85 to 93%, TSS 89 to 96%, Turbidity 94 to 98.8% respectively. These results can clearly indicate that hybrid coagulation and adsorption process is more efficient method to be used. Moreover amount of coagulant consumed is lower when combined with adsorption.

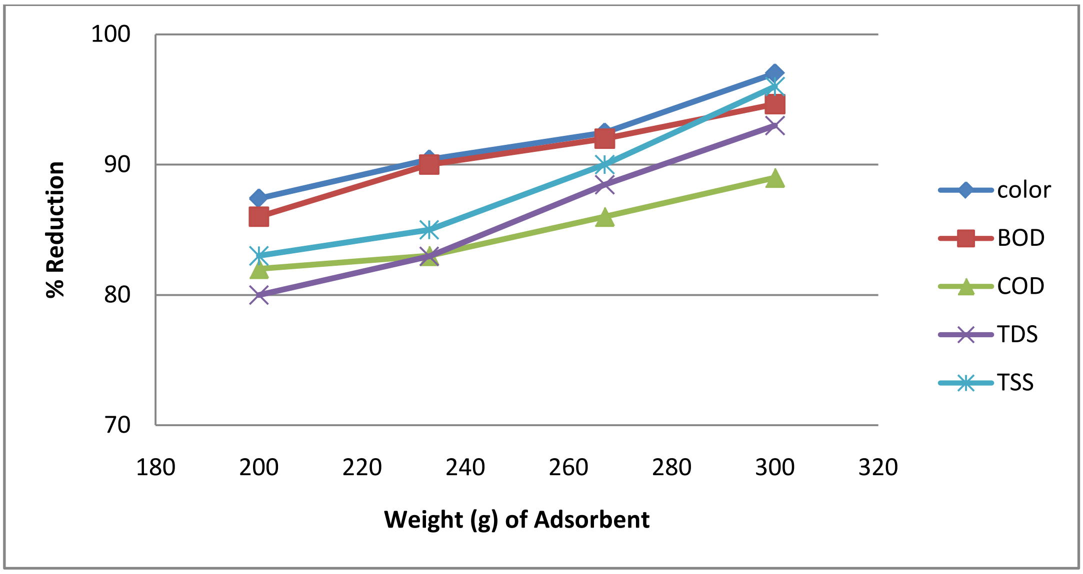


Figure 4.5 Weight (g) of fly ash adsorbent against the % removal of BOD, COD, TDS, TSS, and Color at constant pH and coagulant (3mg/lit).

4.3.2. Effect of pH

Effect of pH on percentage reduction was observed in coagulation and adsorption separately. When reducing the pH towards acidic medium the rate of coagulation increased and similar trend was observed when applying in adsorption process.

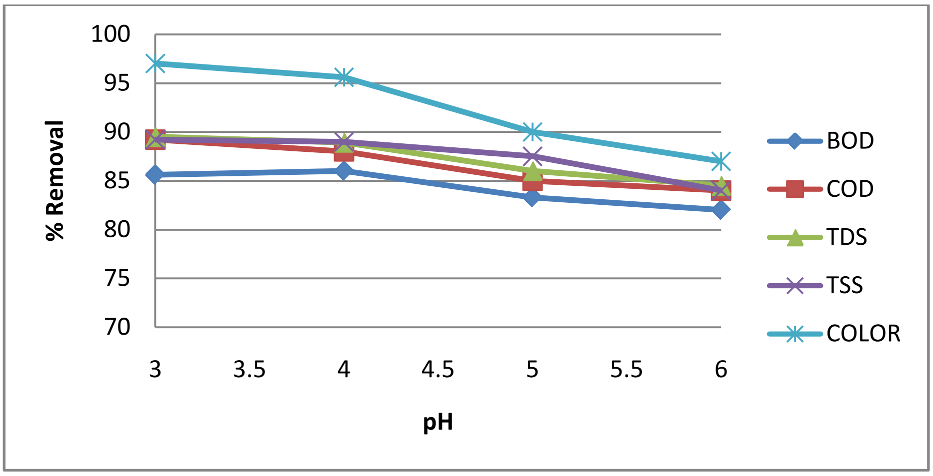


Figure 4.6: pH against the % removal of BOD, COD, TDS, TSS, and Color.

Trend lines in Figure. 4.6 show that with the decrease in pH the amount of color, BOD_5, COD, TDS and TSS. At pH: 4 highest reductions in color 96%, BOD 89%, COD 87%, TDS %90 and TSS 88% respectively.

Table 4.1. A summary of results with standard values

Parameters	***Sri Lankan standards***	***Wastewater before treatment***	***After treatment***			***% Reduction (based on hybrid system)***
			(Using Hybrid method)	***(using fly ash only)***	***(Using Mango pit only)***	
COLOR(Pt-Co)	*250Pt-Co*	*3560*	*97*	*156*	*260*	***97.27***
COD(ppm)	*250-400*	*890*	*96*	*128*	*224*	***89.21***
BOD(ppm)	*30-250*	*560*	*64.5*	*90*	*150*	***94***
TDS(ppm)	*850-2100*	*5400*	*566*	*400*	*890*	***93***
TSS(ppm)	*50*	*700*	*600*	*3600*	*3900*	***96***
TURBIDITY (FAU)	*3-50*	*1275*	*16*	*82*	*164*	***98.74***

4.4 Comparisons of results with previous studies

Many studies have been performed for the treatment of POME including pre and post treatments. The most common methods usedwere Coagulation, adsorption, sedimentation and filtration. The key focus of this study is to use alternative methods by applying same methods with different environmental friendly and cost effective ingredients.

Mango kernel as a natural biodegradable coagulant for water treatment was successfully studied by K.Qureshi et al (2014).This work was focused on the removal or turbidity from turbid water. Thus successfully managed to get positive trends. 95.85 % reduction in turbidity was achieved at pH 3 which is the maximum value in acidic medium, pH 2 (77.1%) produced lower conversion effect than pH 3.Similarly at pH 4 (78.33 %) and at pH 5 (73 %) also produced lower conversion efficiencies , At the neutral pH of turbid water the efficiency of removal of turbidity by applying natural coagulant decreased. It was found that coagulant, extracted from the mango kernel removed the turbidity of water up to the 98% at an optimized dose of 0.5ml/liter (K.Qureshi et al).Coagulation activity of mango pit was (98%) higher than other natural (organic) coagulant such as Chestnut (80 %) [Marina Sciban 2009], Moringa Oliefera; (86 %), Acorn; (70 %) [Marina Sciban 2009] but similar to inorganic coagulant Alum (99 %) (K.Qureshi et al, 2014)

Table 4.2: Comparison of Water quality with previous study (Coagulation vs Hybrid Coagulation Adsorption)

Parameters	**% Reduction**			
	D.Karadag (Combine Ads-Coag) (Textile Mill effluent)	**A.K.Sahah Hybrid Ads-coag(Dyes and pigments wastewater)**	**K.Qureshi et al(Mango pit) (Turbid water)**	**Current research study(Hybrid) (POME)**
Turbidity	--------	90	98.65	98.74
Color	98.21	89	------	97
COD	97.11	54	-------	89.21
BOD	-------	------	-------	94
TDS	-------	------	-------	93
TSS	--------	98	-------	96

From table 4.2 the comparison between current study and previous studies on mango pit can show that mango pit not only clean turbid water but can also play a vital role when combine with adsorbent fly ash to minimize the Color, COD,BOD,TDS and TSS present in wastewater. In comparison with other natural (organic) coagulant such as chestnut gives in turbidity reduction 80% (marina sciban 2009), Moringa oliefera 86%, Acorn 70% (marina sciban 2009), and the efficiency of natural coagulants vary according to the protein contents. Previous studies have not applied mango pit as coagulant for the color removal of POME.Mango pit has maximum protein content and showed maximum efficiency as compared to other organic coagulants. Although Alum has higher efficiency of 99% in reduction of turbidity, it is harmful due to its hazardous effects on health of human being as well as on environment.

Further if it can be seen that towards the maximum reduction in Color, BOD, COD, TDS, Turbidity and TSS achieved is lower than current values obtained, where the mode of treatment was adsorption. Further, in table 4.2 When comparing the current study results with results obtained by using only fly ash as an adsorbent the slight improvement was observed towards the reduction in Color, TSS,TDS, COD, BOD, and turbidity. Further the same fly ash once used was recycled three times with almost the same efficiency. In experiments conducted by D.Karadag(2014) on textile mill wastewater, improved results were obtained towards removal of Color 98% and COD 97%, ferric chloride was used as coagulant and Zeolite as adsorbent in combine coagulation – adsorption process. These ingredients are not much environmental friendly and cost effective.

5. CONCLUSION

Based on the above mentioned mechanism and the results of the present research study; it could be concluded that

- The Mango kernel coagulant has a high potential of coagulation of turbid as well as wastewater; and that the protein associations inside the mango kernels are responsible for coagulation activity.
- Mango kernelcoagulant was indicated as an excellent natural coagulant for waste water treatment, its efficiency was found good when compared with other proven natural coagulants.
- The efficiency of mango kernel for the removal of COD, BOD, TDS and TSS was not found excellent when comparing with fly ash.
- POBFA has also proved to be a best adsorbent for wastewater treatment.
- Using simple adsorption or coagulation processes separately were not found much effective for the treatment of color, BOD, COD, TDS and TSS present in POME.
- Combine coagulation-adsorption processes is the most effective for the color removal of POME in particular and BOD5, COD, TSS, TDS in general at effective cost.

- Hybrid process gave overall removal rate more than90% for the color, TSS, BOD_5, TDS and COD respectively.
- Environmental pollution problems related to fly ash and POME can be solved by processing fly ash in hybrid system.
- Sludge produced from hybrid process can be further utilized as a fertilizer. Moreover Coagulation-adsorption process gives best results when followed by gravity sand filter of different granule size.
- It is necessary to filter out the flocs and sludge before getting the final product for better results.

6. FUTURE WORK

- Further studies can be made to apply the same technology for the removal of heavy metals from brackish and wastewater.
- Hybrid Adsorption- coagulation method can be applied industrially specially in the industries where solid fuel is used as a fuel so that they can easily manufacture activated carbon and use for wastewater treatment applications.

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