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Engagement of Calcium Hydroxide onto Sulphate Calamity in Palm Oil Mill Effluent: pH optimization

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KEYWORDS

Sulphate
Palm oil mill effluent
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pH optimization

ABSTRACT

In this paper, the investigation of the inadequate quality of palm oil mill effluent (POME) due to the excessive sulphate that contributed to endanger aquatic life and production of hydrogen sulphide (H_2S) was conducted with the approaches such as coagulation-flocculation (C-F) using calcium hydroxide coagulant, $Ca(OH)_2$. Then, the optimization of the parameter such as pH need to be achieved. Then, the optimization was determined by optimal sulphate removal percentage (%). From the research, the optimized parameter obtained were pH (8) with optimal sulphate removal of 85.4 %. From these results, it can be concluded that this study accredited C-F and $Ca(OH)_2$ as an auspicious natural source for sulphate removal in POME.

1. INTRODUCTION

Malaysia had dedicated to oil palm cultivation, producing million tonnes of crude palm oil (CPO) annually. CPO production is related to the generation of palm oil mill effluent (POME). For every ton of CPO produced, approximately 0.87 to 3.5 m^3 of POME is generated, depending on the processing and efficiency of the mills [1]. About 95–96% water, 0.6-7.7% oil, and 4-5 percent total solids (including 2-4 percent suspended particles) were presented in the mill's untreated POME [2]. POME is characterized as a harmful effluent by high levels of chemical oxygen demand (COD), which can reach up to 100 g/L [3]. According to records, there was a high sulphate content up to 1,032.93 mg/L in the POME sample [4].

Then, a guideline towards sulphate of maximum 500 mg/L (all class of water hardness and chloride < 5 mg/L) was set by Illinois Environmental Protection Agency (EPA), both for aquatic life protection [5]. The increasing sulphate in various environments affecting ecological systems in the matter of ecosystem disruption [6] and contributes to the formation of hydrogen sulphide gas (H_2S) [7]. Meanwhile, most of the contaminant removal involving POME focused on the constituents of COD [8] and solids [9]. However , there is still lacking of sulphate removal in POME [9]. Hence, this study intended to remove sulphate in POME as the pre-treatment for conventional treatment system in mill.

Then, considering other research onto sulphate removal in effluent, 98.7% sulphate removal has been achieved by electro-coagulation (EC) [10], meanwhile 60% by ion exchange resin [11] and 58.3% by adsorption [12]. Although EC can be described as the promising method for sulphate removal, however, EC process is influenced by electrode material and current density. This complexity can lead to inconsistent results. In comparison, coagulation-flocculation processes are generally more straightforward and easier to control [13]. Recently, researches have been using various type of chemical coagulant such as aluminium, ferric chloride and natural coagulant such as minerals and plant-based coagulants. However, chemical coagulants resulted in the generation of sludge that often contain hazardous materials [14]. Hence, coagulant from natural material has been widely introduced by researches and industries and gained much attention towards future perspective of wastewater treatment.

Overall, there is lacking of investigation towards sulphate removal in POME and utilizing coagulation-flocculation (C-F). Thus, this study intended to investigate on the effect of pH for the removal of sulphate in POME by using natural coagulant such as calcium hydroxide from limestone. The efficiency of this regime was determined by the optimum sulphate removal percentage (%) with the optimization of pH.

2. EXPERIMENTAL PROCEDURE

Raw POME was collected from a palm oil mill operated in Pulau Pinang, Malaysia. Initial characterization such as COD, BOD_5, pH, temperature and sulphate were determined by American Public Health Association (APHA) method as in Table 1. Next, limestone ($CaCO_3$) powder, was collected from a limestone quarry located in Perak, Malaysia. Analysis of X-ray Fluorescence (XRF) was performed to obtain the composition of $CaCO_3$ powder. From XRF, the $CaCO_3$ powder had high percentage (%) mass of calcium oxide (CaO) of more than 90 %. $CaCO_3$ powder was ignited in a furnace for

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calcination as expressed in Equation (1) [15]. Then, the quicklime (CaO) underwent exothermic and produced an activated coagulant which was $Ca(OH)_2$ as expressed in Equation (2) [16]. Then, the prepared paste was readily used as coagulant.

$$CaCO_3 \longrightarrow CaO + CO_2 \tag{1}$$
$$CaO + H_2O \longrightarrow Ca(OH)_2 + heat \tag{2}$$

The experimental setup of C-F comprised of a method of Jar-test. Fixed parameters set up during C-F were working volume (200 ml), room temperature (37°C), jar test operation speed of 250 rpm for 2 minutes (rapid mixing), operation speed of 100 rpm for 15 minutes (slow mixing) and settling time (45 minutes) for pH optimization among 2-10. Afterwards, all filtrates obtained were investigated with analytical measurement and the removal percentage (%) of sulphate content was assessed through Equation (3) [17]:

$$SO_4^{2-} \text{ removal } (\%) = (C_0 - Ce)/C_0 \times 100 \tag{3}$$

where C_0 and Ce represented initial and final sulphate content (mg/L), respectively.

2.1 Analysis

The determination of sulphate in POME solutions abode method of Turbidimetric method (APHA 4500-SO_4^{2-}-E) and measured by HACH DR3000 spectrophotometer.

3. RESULTS AND DISCUSSION

Table 1 Initial characteristics of POME

Parameter	Characteristics
COD (mg/L)	38, 540
BOD_5 (mg/L)	24, 652
pH	3 - 4
Temperature (°C)	70 - 80
Sulphate (mg/L)	12, 965

It can be concluded that sulphate in raw POME sample obtained was 12,965 mg/L, which was higher than sulphate content in previous researches [4]. Then, the removal of sulphate in POME was conducted by C-F using $Ca(OH)_2$ coagulant in various range of pH and achieved optimized pH of 8, final sulphate of 1,893 mg/L and optimum sulphate removal (%) of 85.4 %, as illustrated in Figure 1. The effective condition for sulphate removal occurred in alkaline condition of pH 8 can be affected by the destabilization of sulphate by Ca^{2+} and OH^- from coagulant, as these cations neutralized anion compound such as sulphate in alkaline condition and formed insoluble precipitation or the slurry [18].

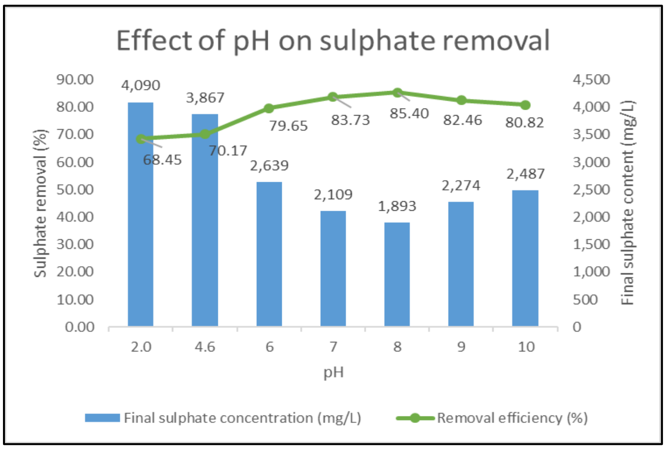

Figure 1. Effect of pH onto sulphate removal.

On top of that, high CaO content as determined in XRF analysis was an effective compound for insoluble precipitation such as gypsum or ettringite formations [19]. Thereby, in alkaline conditions, the solubility of many metal hydroxides decreased, leading to the formation of insoluble precipitate such as calcium sulphate in this study. This explained after pH of 7 and above, sulphate removal % were only differed in 3% but still higher than 80% sulphate removal, compared to acidic condition of pH 2 and 4.6. In acidic conditions, the availability of OH^-, which is crucial for forming insoluble precipitates, was reduced. This led to lower formation rates of precipitates like metal hydroxides, which was essential for removing sulphate from POME.

In the meantime, to achieve final sulphate concentration of 500 mg/L and below, the removal of sulphate should achieve at least 96.14%. Therefore, an improvement should be introduced to mitigate the insufficient of sulphate removal % for meeting the allowable limit before final discharge. This occurrence can be improved with the addition of coagulant dosage, investigation on the effect of initial sulphate content and increasing settling time for more time spent towards destabilization of sulphate.

4. CONCLUSION

The aim of this study was to assess the efficacy of $Ca(OH)_2$ and C-F method for sulphate removal in POME and to provide a wider knowledge onto POME pre-treatment. The relevance of 85.4% removal of SO_4^{2-} from raw POME was clearly supported by the optimized pH of 8. XRF quantified characteristics of calcite in limestone that demonstrated high CaO content and contributed to successive sulphate entrapment as insoluble precipitation and flocs. Overall, pre-treatment of POME potentially be conducted by C-F and $Ca(OH)_2$ coagulant.

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