Process Intensification of Anaerobically digested Palm Oil Mill Effluent (AAD-POME) Treatment Using Combined Chitosan Coagulation, Hydrogen Peroxide (H_2O_2) and Fenton's Oxidation

Shridharan Parthasarathy[a, b], Rachel L Gomes[b] and Sivakumar Manickam[a,*]

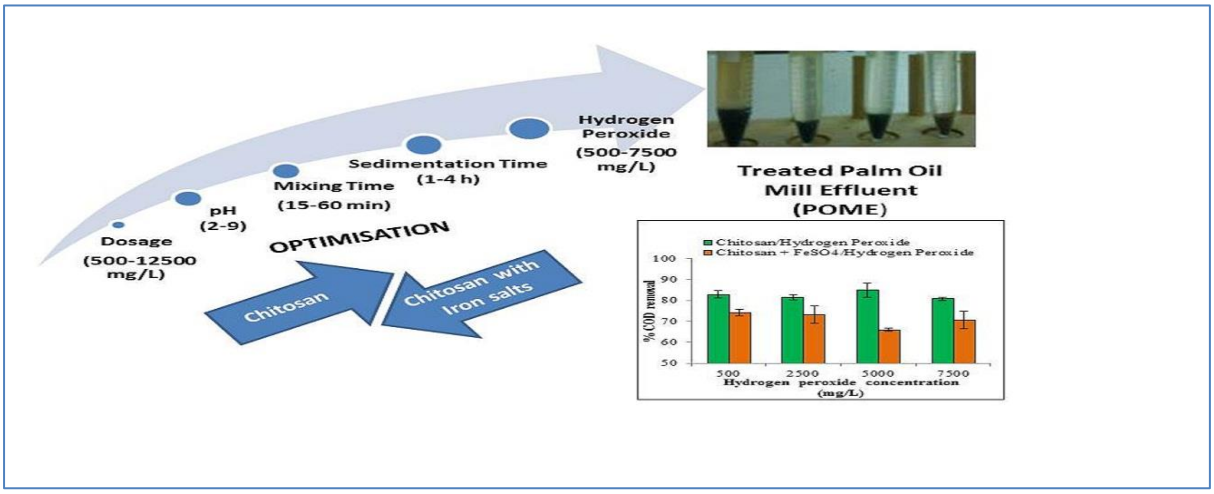
[a]Manufacturing and Industrial Processes Research Division, Faculty of Engineering, University of Nottingham Malaysia campus, 43500 Semenyih, Selangor, Malaysia.

[b]Manufacturing and Process Technologies Research Division, Faculty of Engineering, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom.

*Corresponding author E-mail address: Sivakumar.Manickam@nottingham.edu.my (Sivakumar Manickam)

Tel: +6 (03) 8924 8156; Fax: +6 (03) 8924 8017

Graphical Abstract



Highlights

- An eco-friendly green processing method for Anaerobically digested POME treatment has been investigated.
- Combined chitosan coagulation with AOPs was utilised.
- Higher COD (82.82±1.71%) removal for chitosan/H_2O_2 compared to chitosan-Fenton oxidation was observed.
- Chitosan-Fenton oxidation was found to be favourable for higher TSS removal but not for COD removal.
- Comparison of performance with other technologies has been reported with economic analysis.

Research significance

Industrial wastewater treatment exploiting advanced oxidation processes (AOPs) involves generation of hydroxyl radicals ($OH^{\cdot}$) to degrade the organic components and is a well-documented approach. In the present study, natural biomaterial Chitosan as a coagulant combined with various AOP's have been investigated for the anaerobically digested palm oil mill effluent (AAD-POME) treatment. Research investigations to-date on the post-treatment of POME is very limited and the lacking of lab-scale study could be the major reason for the failing industrial plant trials. Hence the current study explores the possibility and reports in detail on an alternative eco-friendly green processing technique for POME treatment. The objectives of present investigation focuses on the post-treatment of AAD-POME primarily by coagulation using (a) chitosan (b) chitosan with $FeSO_4$ (c) chitosan with H_2O_2 and (d) chitosan with Fenton oxidation. The results conclude that chitosan with H_2O_2 proved to be the most promising alternative for POME treatment compared to chitosan with Fenton oxidation.

Abstract

The present study investigates the removal efficiency of chemical oxygen demand (COD) and total suspended solids (TSS) of anaerobically digested palm oil mill effluent (AAD-POME) in batch studies through the following 4 strategies: coagulation by chitosan, addition of ferrous sulphate ($FeSO_4$), chitosan with hydrogen peroxide (H_2O_2) and chitosan with Fenton oxidation. The parameters tested were: chitosan dosage (500-12500 mg/L), $FeSO_4$ dosage (500-12500 mg/L), mixing time (15-60 min), sedimentation time (1-4 h), initial pH (2-9) and H_2O_2 (500–7500 mg/L). Coagulation only by using chitosan (2500 mg/L) achieved the maximum COD and TSS removal of 70.22±0.23% and 85.59±0.13% respectively. An increase in the TSS removal (98.7±0.06 %) but with a reduction in the COD removal (62.61±2.41%) was observed when $FeSO_4$ (2500 mg/L) was added along with chitosan (2500 mg/L). Alternatively, an improvement in the COD (82.82±1.71%) and TSS (89.92±0.48 %) removal efficiencies was observed when chitosan was coupled with H_2O_2 (500 mg/L). Finally chitosan (2500mg/L) integrated with Fenton oxidation ($FeSO_4$ of 2500 mg/L and H_2O_2 of 500 mg/L) resulted in 100% TSS and 73.08±4.11% COD removals. Overall chitosan with H_2O_2 proved to be the most promising alternative for POME treatment compared to chitosan with Fenton oxidation.

Keywords: Palm oil mill effluent, POME, Treatment, Chitosan, Hydrogen peroxide, Coagulation, Chemical oxygen demand, Total suspended solids.

1 Introduction

The palm oil industry is one of the fastest growing agro based industries in Malaysia (Wu et al. 2009). The major downside of this industry is the large volume of wastewater, commonly termed as palm oil mill effluent (POME), generated from the palm oil milling process (Faisal and Unno 2001; Chungsiriporn et al. 2006; Al-Shorgani et al. 2012). Palm oil mill effluent contains 95-96% water, 0.6-0.7% oil, 2-5% solids and possesses a very high chemical oxygen demand (COD) (45000-75000 mg/L) and biochemical oxygen demand (11000-45000 mg/L) (Bhatia et al. 2007).

Anaerobic digestion of POME followed by aerobic post-treatment by ponding system is commonly practiced in palm oil mills mainly because of the low equipment cost and simple operational control to achieve the discharge limit standards (Chaiprapat and Laklam 2011; Zinatizadeh et al. 2007). Table 1 shows the Environmental Quality Act (EQA) 1974 for POME discharge (Zinatizadeh et al. 2007).

Table 1 POME discharge standards set by Department of Environment (Malaysia) under the Environmental Quality Act 1974

Parameters^{a}	**Discharge Limits**
Biochemical Oxygen Demand	100
Chemical Oxygen Demand	Not legislated
Total Suspended Solids	400
Total Nitrogen	200
Oil & Grease	50
pH	5 - 9

a: All parameters are in mg/L except pH

However the disadvantages of this biological treatment include long hydraulic retention time (HRT) (75-120 days), huge investment in the land for ponds and digesters and problems associated with the methane gas collection which have been identified to be the most important reasons for the greenhouse effect on the environment (Ahmad et al. 2009; Igwe and Onyegbado 2007). Even after aerobic ponding, many mills are not able to achieve the discharge limits due to poor operational design of the existing aerobic ponding system. Moreover, the chemical components from the finally treated effluent after anaerbobic treatment become difficult to treat further biologically (Bhatia et al. 2007).

Research studies dealing with the post-treatment of anaerobically digested POME (AAD-POME) are limited with the most dealing with biological approaches for the treatment. Vijayaraghavan et al. 2007 used an activated sludge reactor for the post-treatment of AAD-POME. However the treated effluents failed to meet the discharge limits, in addition to their high operational cost. A sequential batch reactor (SBR) was proposed to treat AAD-POME by Chan et al. 2010, where a maximum COD (95–96%), BOD (97–98%) and TSS (98–99%) removal were obtained and met the standard discharge limits. Even though the earlier treatment methods delivered promising results, their operational costs were neither cheap nor an easy route to commercialise industrially. The disadvantages of the current biological methods necessitate looking for alternative and efficient technologies to treat POME.

Coagulation is a process by which agglomeration and hence destabilization of colloidal particles occur due to chemical aids (coagulants) and the resulting agglomerates could be removed by flocculation, sedimenatation and filtration (Chan et al. 2010; Aboulhassan et al. 2006; Abood et al. 2013). In flocculation, the destabilised colloidal particles further conglomerate into larger agglomerates, referred as flocs, which are easily settled down (Jiang and Graham 1998; Bolto and Greory 2007). Chitosan is a poly N-acetyl-glucosamine, a non-toxic biopolymer and a cationic polyelectrolyte and environmentally safe (Roussy et al. 2004). It is produced by the acetylation of chitin and has a wide range of applications in pulp and paper, food, agriculture as well as in the industrial effluent treatments (Roussy et al. 2004; Chi and Cheng 2006; Meyssami and Kasaeian 2005). For a majority of the applications, the following characteristics of chitosan are considered i.e. molecular weight, pH, degree of deacetylation and basicity (Meyssami and Kasaeian 2005; Bratskaya et al. 2006). Since chitosan is positively charged and hydrophilic in nature, the electrostatic interactions between chitosan and other negatively charged compounds could be easily achieved resulting into charge neutralisation. This is a very unique feature of this biopolymer (Roussy et al. 2005). In addition, its use eases the sludge handling abilities. Application of chitosan has been reported for the following wastewater treatments i.e. brewery wastewater (Cheng et al. 2005), river silt (Divakaran and Pillai 2001) and raw POME (Ahmad et al. 2006). However, its use for post-treatment of AAD-POME has yet to be explored.

Ferrous sulphate ($FeSO_4$) is a commercially available and a cheaper inorganic coagulant when compared with synthetic polyelectrolytes and hence widely used for the municipal and industrial wastewater treatment to control odour, to thicken sludge and as a dewatering agent (Tang and Chen 1996). Since it is positively charged in nature, it can attract the negatively charged counter ions present in the colloidal suspensions to form small flocs. Coupling $FeSO_4$ with chitosan has never been investigated to treat POME and the reasons to employ both of them in the present study are due to: (1) chitosan acts both as a destabiliser and as a bridge (2) $FeSO_4$ acts as a coagulant aid and improves the destabilisation efficiency.

Industrial wastewater treatment exploiting advanced oxidation processes (AOPs) involves generation of hydroxyl radicals ($OH^{\cdot}$) to degrade the organic components and is a well-documented approach (Oller et al. 2011; Klavarioti et al. 2009; Pera-Titus et al. 2004; Sekaran et al. 2013). Hydrogen peroxide (H_2O_2) is a well-known and a promising oxidant (Raffellini et al. 2011) and owing to its performance and ease of operation, many studies utilise this oxidant (Chu et al. 2012; Kestioğlu et al. 2005; Szpyrkowicz et al. 2001; Cailean et al. 2014). However, it has been previously reported that when H_2O_2 was used alone it was not effective for certain complex organic components due to kinetic limitations at reasonable peroxide concentrations (Kestioğlu et al. 2005; Chen et al. 2014). Taking into account of its oxidant capability, H_2O_2 has been considered along with chitosan as a hybrid system so that process intensification and hence an improvement in the efficiency could be achieved. The main idea behind this hybrid approach is to apply AOP for POME and optimising the concentration of H_2O_2 required to form the intermediate by-products thereby improving the performance of subsequent coagulation using chitosan. Such a coupled operation of chitosan with H_2O_2 for the post-treatment of AAD-POME has yet to be attempted. H_2O_2 with an iron salt known as Fenton's reagent generates hydroxyl radicals is another promising oxidation process for industrial wastewater treatment (Szpyrkowicz et al. 2001). Pre-treatment of organic compounds using Fenton's oxidation has been reported earlier (Szpyrkowicz et al. 2001; Tang and Chen 1996; Rizzo et al. 2008). Fenton oxidation is a simple AOP technique utilized to generate hydroxyl radical (HO•) (Gernjak et al. 2006). HO• is generated through the reaction between ferrous (Fe^{2+}) and hydrogen peroxide (H_2O_2) at acidic condition is shown in equation (1).

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + HO^{\bullet} + OH^{-} \qquad (1)$$

Numerous studies on the applications of Fenton oxidation process with different pollutants and wastewaters have been reported (Szpyrkowicz et al. 2001; Tang and Chen 1996; Rizzo et al. 2008). In addition, Fenton oxidation is also capable of removing pollutants via coagulation (Kuo, 1992; Lin and Lo, 1997; Kang and Hwang, 2000). A study was conducted by Aris et al. 2008 to determine the feasibility of Fenton oxidation process in treating biologically treated palm oil mill effluent. It was reported that the highest removals of COD (75.2%) and color (92.4%) for were achieved by Fenton oxidation. Also, it was reported that Fenton oxidation is capable of removing COD and color from the POME and thus a viable treatment option. However the effectiveness of chitosan coupled with Fenton oxidation has never been explored for POME.

Thus, the objectives of present investigation focus on the post-treatment of AAD-POME primarily by coagulation using (a) chitosan (b) chitosan with $FeSO_4$ (c) chitosan with H_2O_2 and (d) chitosan with Fenton oxidation. Besides, the investigation also looked into evaluating and optimising the suitable process conditions such as dosage, mixing time, sedimentation time and pH for the effective treatment of AAD-POME.

2 Experimental

2.1 Materials

Anaerobically digested POME (AAD-POME) was collected from Ulu Kanchong Oil Palm Mill, Rantau, Malaysia. The collected POME samples were at a temperature of 27.5±2.5 °C and the characteristics of samples differed based upon the processing of palm oil, climate and operating conditions during the sampling period. The COD and TSS of the samples were 15290±855 mg/L and 14950±2400 mg/L respectively. Chitosan, a white fine powder with a molecular weight of 350 kDa with 95% deactylation was obtained from Chitin-Chitosan Research Centre of Universiti Kebangsaan Malaysia. $FeSO_4$ was purchased from R&M chemicals, (NJ, USA). Distilled water was used for diluting 37 % fuming H_2O_2 (Merck, Germany) and sodium hydroxide pellets (R&M chemicals, NJ, USA) to prepare 5M solution for pH adjustment.

2.2 Methods

The experiments were carried out in a conventional jar-tester (Loviband water testing, model ET720, Germany) which accommodates six glass reactors at a time and all the reactors were simultaneously mixed at the same speed using the stainless steel paddles. Each reactor was filled with 200 ml of POME and the coagulant was added into POME and mixed rapidly for various periods (15-60 min) with different doses of chitosan and ferrous sulphate (500-12500 mg/L). The effect of sedimentation time (1-4 h) and the effect of pH (2-9) were also investigated. The role of hydrogen peroxide (500–7500 mg/L) in the treatment was also considered. At the end of the treatment, the samples were taken from the clarified supernatant layer to determine the COD, TSS and Zeta potential (ζ).

2.3 Analysis

The COD test was carried out using COD vials (HR 20-1500 mg/L) following the American Public Health Association (APHA) standard method 8000 using a spectrophotometer (HACH model DRB 2000). TSS was measured by following the APHA standard method 8006 using a spectrophotometer (HACH model DR 2800) by filling 10 ml of sample in a specially designed glass bottle. Zeta potential was calculated using Zetasizer (Malvern 2000, UK) and pH was tested using a pH meter (Martini Instruments, NC, USA).

3 Results and discussion

3.1 Effect of dosage

Fig. 1 shows the effect of chitosan dosage (500-12500 mg/L) on the COD (%) and TSS (%) removal of POME.

At an initial dose of 500 mg/L, 67.34 ± 3.76 % (**Fig. 1 (a)**) and 85.68 ± 0.81 % (**Fig. 1 (b)**) of COD and TSS removals were observed. A further increase in the dose to 2500 mg/L improved the COD removal to 70.22 ± 0.23 %, whereas the removal of TSS remained the same (85.59 ± 0.13 %). A decrease in the COD (66.57 ± 7.13%) was observed when the dosage was finally increased to 12500 mg/L which may be probably due to overdosing of chitosan. Similar observations were noticed by Zhu et al. **2011** during the coagulation process by employing polymeric aluminium ferric sulphate (PAFS). It has been observed that when the dosage was increased more than the optimum, restabilisation of colloidal particles of POME occurs, decreasing the COD and TSS removal efficiencies. From the results it is evident that optimising the chitosan dose is important for the increased removal of COD and TSS.

The obtained results could be explained by three different mechanisms i.e. charge neutralisation, patch flocculation and micro-bridging. Charge neutralisation of the colloidal particles is normally achieved by the addition of coagulant aids of opposite charges (Zhu et al. **2011**; Assaad et al. **2007**). The organic molecules in POME are normally negatively charged and the coagulant aids are positively charged in nature. Thus, when these coagulant aids are introduced to the effluent, attraction of oppositely charged ions occurs owing to Van der Waals forces resulting in neutralisation of charges and hence the formation of larger agglomerates (Wu et al. **2008**; Crini and Badot **2008**; Gérente et al. **2007**). The bridging of colloidal particles is achieved by the addition of polyelectrolytes and is very similar to the charge neutralisation by the coagulant aids. The colloidal particles are attracted to the long polymer chains of these polyelectrolytes forming a bridge resulting in the agglomeration and coagulation (Varma et al. **2004**; No and Mayers **2000**). POME contains various types of colloidal particulates including organic components and is negatively charged. Chitosan is a linear polyelectrolyte and has a positive charge at acidic conditions and thus attracts the negatively charged colloidal particles of POME and destabilizes them resulting in agglomeration (Ravi Kumar **2000**). Besides, amine functional groups of chitosan help to adsorb components of POME into larger agglomerates thereby achieving the maximum COD removal at lower dosages of chitosan (Ravi Kumar 2000). The obtained results using chitosan could be compared with the previous results for olive oil wastewater where it was observed that increasing the chitosan dosage achieved the maximum TSS removal (Rizzo et al. 2008). Based on this study, the optimised chitosan dosage of 2500 mg/L was used for further investigation to treat POME using $FeSO_4$.

The effect of dosage of $FeSO_4$ was studied in the range of 500-12500 mg/L. Maximum COD removal of 62.61 ± 2.41 % (**Fig. 2 (a)**) and TSS removal of 98.7 ± 0.06 % (**Fig. 2 (b)**) were achieved for 2500 mg/L of $FeSO_4$. Further it was observed that with the addition of $FeSO_4$ to chitosan, TSS removal increased from 85.59 ± 0.13 % (2500 mg/L of chitosan alone) to 98.7 ± 0.06 % (2500 mg/L of chitosan with 2500 mg/L of $FeSO_4$) whereas the COD removal was decreased from 70.22% (2500 mg/L of chitosan alone) to 62.61 ± 2.41 % (2500 mg/L of chitosan with 2500 mg/L of $FeSO_4$). Similar observations were earlier reported by Ginos et al. 2006 while using $FeSO_4$ coupled with poly-electrolytes where a maximum TSS removal of 95-98% with the lower COD removal of 22-28% was noticed for olive mill wastewater treatment. This observation clearly indicates that addition of $FeSO_4$ is favourable for TSS removal but not for COD removal. The obtained results could be further supported by analysing the zeta potential. **Fig. 3** shows the zeta potential measurements using different doses of chitosan and chitosan with $FeSO_4$.

Zeta potential (ζ) is defined as the electrical potential difference between the colloidal particles and the solution and it is an indirect way of measuring the charge of colloidal particles. Isoelectric point is defined as the condition where the colloidal particles have enough counter ions so that they can be electrically neutral and zeta potential is zero. The highest degree of agglomeration is achieved at this isoelectric point (Ariffin et al. 2012). It was observed that increasing the chitosan dosage increased the ζ value nearing the isoelectric point (mV=0). Similar observations were earlier reported by Ariffin et al. for the paper and pulp mill wastewaters using a hybrid flocculant system of PolyDADMAC and polyacrylamide (Ariffin et al. 2012). The observed ζ values were -0.9 mV for 2500 mg/L of chitosan and 0.07 mV for 2500 mg/L of chitosan with 2500 mg/L of $FeSO_4$ which were very close to the isoelectric point. Thus, a consistency in the results was observed in this range of dosage with COD and TSS removal. Hence at the end of this study, 2500 mg/L of chitosan and 2500 mg/L of $FeSO_4$ were selected for further investigation.

3.2 Effect of mixing time

The effect of mixing time (15-60 min) was studied for the optimised chitosan and chitosan with $FeSO_4$ dosages at a mixing speed of 100 rpm and the observed results have been shown in **Fig. 4**. In the case of chitosan after an initial mixing time of 15 min, the COD and TSS removal efficiencies were 82.11 ± 0.23 % (**Fig. 4 (a)**) and 89.61 ± 0.43 % (**Fig. 4 (b)**) respectively. But after 15 min of mixing time, no significant improvement in the COD and TSS removal was observed. Thus 15 min of mixing time was found to be the optimum condition for chitosan. The zeta potential values were also observed within the range of -0.805 to 1.37 mV (**Fig. 5**) which are close to near zero or isoelectric point proving the role of chitosan as a coagulant that causes charge neutralisation.

For coagulation processes, two kinds of mixing were followed i.e. rapid mixing (up to 700 rpm for 5 min) and slow mixing (150 rpm for 30 min). Rapid mixing focused on the coagulant dispersion for the destabilisation of colloidal system whereas the slow mixing concentrated on the propagation of growth of floc by limiting the breakdown of aggregates. When the mixing speed was very rapid and mixing time was longer, the COD and TSS removal efficiencies were decreased, even though it was assumed that the longer mixing time and higher mixing speed would indirectly increase the collision frequency of the flocs. The disruption of flocs to smaller particles occurs with the higher shear rate, thereby inhibiting the flocs to settle down and decreasing the COD, TSS removal efficiencies. On the other hand when the mixing time was very short, the flocs would not have been formed due to the inadequate contact of the coagulants with the components of the effluent.

For chitosan with $FeSO_4$, the maximum COD and TSS removal efficiencies were 69.06 ± 0.27 % (**Fig. 4 (a)**) and 98.01 ± 1.26 % (**Fig. 4 (b)**) respectively after 15 min of mixing. However at the end of 60 min, the COD and TSS removal efficiencies were 65.59 ± 0.36 % and 97.60 ± 0.77% respectively. The zeta potential (**Fig. 5**) was 0.0414 mV for chitosan with $FeSO_4$ after 15 min of mixing time which clearly proves that the surface charge was very close to zero or to the isoelectric point improving the coagulation performance of POME treatment. Thus, 15 min was considered as the optimised mixing time for chitosan and chitosan with ferrous sulphate.

3.3 Effect of sedimentation time

Using the optimised conditions of dosage and mixing time from the previous studies, optimisation of sedimentation time was investigated both for chitosan and chitosan with $FeSO_4$ without aeration and the obtained results have been presented in **Fig. 6** and **Fig.7**. For chitosan, after 1 h of sedimentation time, the COD and TSS removal efficiencies were 85.70 ± 3.09% (**Fig. 6 (a)**) and 90.06 ± 4.36% (**Fig. 6 (b)**) respectively with a surface charge of 0.0015 mV (**Fig.7**). Since no aeration was employed, the chances of oxidation of $FeSO_4$ to $Fe_2(SO_4)_3$ is not possible and hence the possibility of its precipitaton is negligible.

Whereas, after 4 h of sedimentation, the COD and TSS removal efficiencies were 87.18±4.06 % and 91.84 ± 2.61% respectively, along with a surface charge of 0.093 mV. Thus with an increase in sedimentation time no significant change in the COD and TSS removal efficiencies was observed. Chitosan shows a faster agglomeration of organic compounds forming larger flocs and hence a higher settling velocity (Divakaran and Pillai **2001**). In the case of chitosan with $FeSO_4$, after 1 h of sedimentation time, COD and TSS removal efficiencies were found to be 67.06 ± 3.37% (**Fig. 6 (a)**) and 98.32±0.24% (**Fig. 6 (b)**) respectively with a surface charge of 0.0545 mV. But at the end of 4 h of sedimentation time, COD and TSS removal efficiencies were 66.38 ± 5.64 % and 91.84 ± 2.61% respectively with a surface charge of -0.883mV.

Chitosan shows predominant effects as compared to chitosan with $FeSO_4$ for the COD removal. But maximum TSS removal was achieved when chitosan was coupled with $FeSO_4$ as compared to using chitosan alone. This effect is mainly because of iron salts which act as destabilisers for the POME colloidal suspension, whereas chitosan acts as a neutraliser and bridger that promotes faster agglomeration of organic particulates and resulted in faster settling of the formed flocs thereby reducing the TSS of POME. Based on this investigation, 1 h was considered to be the optimised sedimentation time to achieve the maximum removal of COD and TSS.

3.4 Effect of pH

In the case of coagulation-flocculation process, pH acts as a crucial parameter since the performance of coagulant aids is always observed to be in a specific range of pH. Hence the effect of initial pH of POME was studied using the optimised dosage of coagulant, mixing time and sedimentation time in reducing the COD and TSS.

Fig. 8 shows the effect of initial pH on the COD and TSS removal efficiencies. From the results, a very similar trend in the COD reduction could be observed for chitosan and chitosan with $FeSO_4$. As the pH increased from 2 to 7 there was a substantial increase in the COD removal for chitosan and chitosan with $FeSO_4$. For chitosan, the COD removal increased from 69.39 ± 1.38 % at pH 2 to 82.66 ± 0.18 % at pH 7 (**Fig. 8 (a)**). Similarly for chitosan with $FeSO_4$, the COD removal increased from 38.65 ± 0.83 % to 67.49 ± 1.20 % (**Fig. 8 (a)**). There was also a decrease in the COD removal at pH 9. This could be due to the hydrolysis of coagulant at a higher alkaline environment resulting in the inhibition of bridging flocculation or particle aggregation (Divakaran and Pillai 2001). The highest TSS removal for chitosan was observed at pH 2; also with an increase in pH there was a substantial reduction in the TSS removal from 95.37 ± 1.01% at pH 2 to 91.43% at pH 9 (**Fig. 8 (b)**). **Fig. 9** shows the zeta potential measurements at various pH.

The highest degree of agglomeration is achieved at the isoelectric point. The surface charges increase when the pH increased from 2 to 5 for both the coagulants whereas there was a decrease in the surface charge at neutral pH 7. The surface charge of POME gets decreased due to the charge neutralisation mechanism at neutral pH indirectly improving the coagulation efficiency and hence the COD and TSS removals. At an alkaline pH, an increase in the surface charge decreases the coagulation efficiency. This trend was very similar to the observations as reported by Zhu et al. 2011. At the end of this study, pH 7 was chosen to be the optimum pH which is also the pH after the aerobic digestion of POME and which resulted in the COD and TSS removals.

3.5 Effect of hydrogen peroxide

The effect of hydrogen peroxide (500-7500 mg/L) on the COD and TSS removals was investigated and the results have been shown in **Fig. 10**, whereas **Fig. 11** shows the surface charge measurements.

For chitosan, it was observed that at the lowest H_2O_2 concentration (500 mg/L), COD and TSS removal efficiencies were 82.82 ±1.71 % (**Fig. 10(a)**) and 89.92 ±0.48 % (**Fig. 10(b)**) respectively along with a zeta potential of 0.175 mV (**Fig. 11**). The reason for introducing H_2O_2 was to increase the generation of hydroxyl radicals ($OH^{\cdot}$) thereby improving oxidation and hence the removal of chemical components of POME. H_2O_2 is widely used in the advanced oxidation processes (AOPs) for wastewater treatment. When this AOP is coupled with chemical coagulation, an increase in the removal of chemical components of POME could be expected. It was evident from the observation that the COD removal efficiency was increased from 66.59 ± 7.13 % (for 2500 mg/L chitosan without H_2O_2) to 82.82 ± 1.71 % (for 2500 mg/L chitosan with 500 mg/L H_2O_2); for TSS, the removal efficiency was improved from 85.15 ± 0.47 % (for 2500 mg/L chitosan without H_2O_2) to 89.92 ± 0.48 (for 2500 mg/L chitosan with 500 mg/L H_2O_2). When the concentration of H_2O_2 was further increased to 5000 mg/L, a maximum removal of 91.80 ± 1.30% in the TSS and 84.95 ± 3.32% in the COD was achieved. Hence an external addition of H_2O_2 improves the removal of chemical components of POME by oxidation due to the abundant availability of $OH^{\cdot}$ radicals. This confirms that the radical attack is the main pathway for the POME degradation which significantly increases the performance of chitosan coagulation. Whereas, when the concentration of H_2O_2 was further increased to 7500 mg/L there was a reduction in the removal efficiency of both the COD as well as TSS. This observation could be explained due to the over abundant generation of hydroxyl radicals, which in turn results in the formation of hydrogen peroxide and finally reduces the oxidation as hydrogen peroxide is relatively a weak oxidising agent as compared to $OH^{\cdot}$ radicals (Harish Prashanth and

Tharanathan 2007; Chu et al. 2012). a possibility of oxidation of $FeSO_4$ by H_2O_2 into $Fe_2(SO_4)_3$ at pH 7 as well as oxidation of chitosan by H_2O_2 must

Thus an optimum concentration of H_2O_2 (500 mg/L) is found to be suitable for POME treatment. Apart from this, the effect of Fenton oxidation was also investigated using ferrous sulphate. The mechanism involved in the Fenton oxidation has been shown in the following equations (2-10) (Sychev and Isak 1995):

$$HO^{*} + H_2O_2 \longrightarrow H_2O + HO_2^{*} \tag{2}$$

$$HO^{*} + Fe^{2+} \longrightarrow Fe^{3+} + OH^{-} \tag{3}$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + H^{*} + HO_2^{*} \tag{4}$$

$$HO^{*} + HO^{*} \longrightarrow H_2O_2 \tag{5}$$

$$H_2O^{*} + H_2O_2 \longrightarrow O_2 + H_2O + HO^{*} \tag{6}$$

$$Fe^{3+} + HO_2^{*} \longrightarrow Fe^{2+} + O_2 + H^{+} \tag{7}$$

In the presence of organic substrate (XH), the primary product of the oxidation would be the organic radical, X•, which possesses mainly reducing properties and may be consumed through the reactions with H_2O_2 and Fe^{3+}.

$$HO^{*} + XH \longrightarrow H_2O + X^{*} \tag{8}$$

$$X^{*} + H_2O_2 \longrightarrow XOH + HO^{*} \tag{9}$$

$$X^{*} + Fe^{3+} \longrightarrow Fe^{2+} + H^{+} + \text{Product} \tag{10}$$

It was also observed that chitosan with Fenton oxidation reduced the COD removal from 82.82 ± 1.71 % (for 2500 mg/L chitosan with 500 mg/L H_2O_2) to 73.08 ± 4.11% (for 2500 mg/L chitosan with 2500 mg/L $FeSO_4$ and 500 mg/L H_2O_2). Thus, chitosan with Fenton oxidation does not show any favourable result for the COD removal and it could be concluded that the chitosan with H_2O_2 proves to be producing better results for POME as compared to chitosan with Fenton oxidation.

3.6 Economic analysis and performance comparison with other technologies

The chitosan coagulation coupled with H_2O_2 as a POME treatment method has been compared to other reported work to evaluate its performances and has been shown in Table 2.

Table 2 Comparison of the current chitosan coagulation coupled with H_2O_2 treatment process with other reported work for POME treatment

Treatment Process	Operational Conditions		Overall COD reduction (%)	Overall TSS reduction (%)	References
	Temperature (°C)	pH			
2.5 g/L chitosan + 0.5 g/L H_2O_2	25-30	7	89.92	82.82	Current Study
8 g/L alum	26-30	4.5	-	89	Ahmad et al. 2006
6 g/L alum	30	5	66	89	Bhatia et al. 2007
6 g/L MOA	30	5	52.2	95	Bhatia et al. 2007
0.1 g/L Magnafloc LT22 polymer + 0.3 g/L $FeCl_3$	25	5	49	92	Karim and Hie 1987
4 g/L MOAE + 7 g/L flocculant NALCO 7751	70	5	42	98	Bhatia et al. 2007
6 g/L polyaluminum chloride	26-30	4.5	-	93	Ahmad et al. 2006

Among the other POME treatment methods reviewed above; it is observed that the chitosan coagulation coupled with H_2O_2 is appeared to be a suitable alternative for POME treatment. Table 3 shows the operational costs estimation calculation for the POME treatment.

The optimum dosage for the POME treatment was found to be 2500 mg/L from the previous lab scale optimisation studies. If the price of chitosan used is 162.30 MYR/kg, then for the treatment of 400 tonnes of POME, 1 tonne of chitosan is required. The chemical cost for treating $1m^3$ of POME under optimum conditions is MYR/m^3 163575. The treatment needs an electricity usage of 144000 KWh. The total operation cost of anaerobically digested POME treatment using chitosan coagulation was found to be 1.96 MYR/thousand gallon. The operation cost of using chitosan coagulation for the treatment of anaerobically digested POME is still seems to be acceptable for commercial feasibility. It has been reported that the open digesting tank for POME treatment without land application, the capital cost quoted (Gopal et al. 1986) for a palm oil mill processing 30 tons FFB/h is MYR 750,000. Also, the capital cost for a membrane system in POME treatment for a palm oil mill processing 36 tons FFB/h at MYR 3,950,000 (Chong, 2007).

Table 3 Operational costs estimation

Item	**Notes**	**Cost in MYR**
Energy	Average power of installation-25 kW Average unit price of electrical energy MYR 0.345/kwh	49680
Labour	Three shift work. Costs MYR 6/hr	345600
Chemical Costs	Prices calculated for local market Chitosan: MYR 162.3/kg Ferrous sulphate: MYR 0.685/kg Hydrogen Peroxide: MYR 1.275/kg	65704000
Land cost		1235927
Taxes and Insurance		66522.77
Maintenance		133045.55
Total O&M Cost		**67534775.33**

4 Conclusions

The effectiveness of chitosan, $FeSO_4$, combined chitosan with H_2O_2 and combined chitosan with Fenton oxidation were evaluated for the AAD-POME. From the results it could be concluded that chitosan has been identified as an effective coagulant for maximum COD removal. Also, $FeSO_4$ addition to chitosan is favourable for TSS removal but not for COD removal. The TSS removal was improved from 66.59 % (2500 mg/L of chitosan without any H_2O_2) to 82.82 % (2500 mg/L of chitosan with 500 mg/L H_2O_2) whereas the COD removal was improved from 85.15 % (2500 mg/L chitosan without any H_2O_2) to 89.92 % (2500 mg/L chitosan with 500 mg/L H_2O_2). The optimum parameters were: chitosan dose of 2500 mg/L; 500 mg/L of H_2O_2; 15 min of mixing time; 1 h of sedimentation time; and a pH of 7. It could be concluded that chitosan coagulation coupled with H_2O_2 proves to be a better alternative for the post-treatment of anaerobically digested POME due to its improved performance, safe handling and availability.

Acknowledgements

The authors gratefully acknowledge the Inter-campus PhD studentship funding awarded by the University of Nottingham (Malaysia and United Kingdom) campuses. Author Authors would like to thank Fundamental Research Grants Scheme (FRGS) for the funding support (FRGS/1/2013/SG05/UNIM/01/1).

References

1. Abood A, Bao J, Abudi Z, Zheng D, Gao C (2013) Pretreatment of nonbiodegradable landfill leachate by air stripping coupled with agitation as ammonia stripping and coagulation–flocculation processes Clean Technol Environ Policy 15**:** 1069-1076
2. Aboulhassan MA, Souabi S, Yaacoubi A, Baudu M (2006) Improvement of paint effluents coagulation using natural and synthetic coagulants aids. J Hazard Mater 138: 40–45
3. Ahmad AL, Chong MF, Bhatia S (2009) A comparative study on the membrane based palm oil mill effluent (POME) treatment plant. J Hazard Mater 171: 166-174
4. Ahmad AL, Sumathi S, Hameed BH (2006) Coagulation of residue oil and suspended solid in palm oil mill effluent by chitosan, alum and PAC. Chem Eng J 118: 99-105
5. Al-Shorgani N, Kalil M, Ali E, Hamid A, Yusoff, W (2012) The use of pretreated palm oil mill effluent for acetone–butanol–ethanol fermentation by Clostridium saccharoperbutylacetonicum N1-4. Clean Technol Environ Policy 14**:** 879-887
6. Andreozzi R, Caprio V, Insola A, Marotta R (1999) Advanced Oxidation Processes (AOP) for water purification and recovery. Catalysis Today 53: 51-59
7. Ariffin A, Razali MAA, Ahmad Z (2012) PolyDADMAC and polyacrylamide as a hybrid flocculation system in the treatment of pulp and paper mills waste water. Chem Eng J 179: 107-111
8. Assaad E, Azzouz A, Nistor D, Ursu AV, Sajin T, Miron DN (2007) Metal removal through synergic coagulation–flocculation using an optimised chitosan-montmorillonite system. Appl Clay Sci 37: 258–274
9. Bhatia S, Othman Z, Ahmad AL (2007) Coagulation and flocculation process for POME treatment using Moringa oleifera seeds extract: Optimization studies. Chem Eng J 133: 205-212
10. Bhatia S, Othman Z, Ahmad AL (2007) Pretreatment of palm oil mill effluent (POME) using Moringa oleifera seeds as natural coagulant. J Hazard Mater 145: 120–126
11. Bolto B, Gregory J (2007) Organic polyelectrolytes in water treatment. Water Res 41: 2301-2324

12. Bratskaya SY, Avramenko VA, Schwarz S, Philippova I (2006) Enhanced flocculation of oil-in-water emulsions by hydrophobically modified chitosan derivatives. Colloids Surf A 275: 168–176
13. Cailean D, Teodosiu C, Friedl A (2014) Integrated Sono-Fenton ultrafiltration process for 4-chlorophenol removal from aqueous effluents: assessment of operational parameters (Part 1). Clean Technol Environ Policy 16**:** 1145-1160
14. Chaiprapat S, Laklam T (2011) Enhancing digestion efficiency of POME in anaerobic sequencing batch reactor with ozonation pretreatment and cycle time reduction. Bioresource Technol 102: 4061-4068
15. Chan YJ, Chong MF, Law CL (2010) Biological treatment of anaerobically digested palm oil mill effluent (POME) using a Lab-Scale Sequencing Batch Reactor (SBR). J Environ Manage 91: 1738-1746
16. Chen Y, Liu C, Nie J, Wu S, Wang D (2014) Removal of COD and decolorizing from landfill leachate by Fenton's reagent advanced oxidation. Clean Technol Environ Policy 16**:** 189-193
17. Cheng WP, Chi FH, Yu RF, Lee YC (2005) Using chitosan as a coagulant in recovery of organic matters from the mash and lauter wastewater of brewery. J Polym Environ 13: 383–388
18. Chi FH, Cheng WP (2006) Use of chitosan as coagulant to treat wastewater from milk processing plant. J Polym Environ 14: 411–417
19. Chong MF (2007) Simulation and design of membrane based palm oil mill effluent (POME) treatment plant from pilot plant studies .PhD. Thesis. Universiti Sains Malaysia
20. Chu L, Wang J, Dong J, Liu H, Sun X (2012) Treatment of coking wastewater by an advanced Fenton oxidation process using iron powder and hydrogen peroxide. Chemosphere 86: 409-414
21. Chu L, Wang J, Dong J, Liu H, Sun X (2012) Treatment of coking wastewater by an advanced Fenton oxidation process using iron powder and hydrogen peroxide. Chemosphere 86: 409-414
22. Chungsiriporn J, Prasertsan S, Bunyakan C (2006) Minimization of water consumption and process optimization of palm oil mills. Clean Technol Environ Policy 8**:** 151-158
23. Crini G, Badot PM (2008) Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: a review of recent literature. Prog Polym Sci 33: 399–447
24. Divakaran R, Pillai VNS (2001) Flocculation of kaolinite suspensions in water by chitosan. Water Res 35: 3904–3908

25. Dovletoglou O, Philippopoulos C, Grigoropoulou H (2002) Coagulation for treatment of paint industry wastewater. J Environ Sci Heal A 37: 1361–1377

26. Faisal M, Unno H (2001) Kinetic analysis of palm oil mill wastewater treatment by a modified anaerobic baffled reactor. Biochem Eng J 9: 25–31

27. Fernandez M, Fox PF (1997) Fractionation of cheese nitrogen using chitosan. Food Chem 58: 319–322

28. Gérente C, Lee VKC, Le Cloirec P, McKay G (2007) Application of chitosan for the removal of metals from wastewaters by adsorption— mechanisms and model review. Crit Rev Env Sci Tec 37: 41–127.

29. Gernjak W, Fuerhacker M, Fernandez-Ibanez P, Blanco J, Malato S (2006) Solar photo-Fenton treatment - process parameters and process control. Appl. Catal. B 64: 121-130

30. Ginos A, Manios T, Mantzavinos D (2006) Treatment of olive mill effluents by coagulation–flocculation–hydrogen peroxide oxidation and effect on phytotoxicity. J Hazard Mater 133: 135-142

31. Gopal G, Ma, AN (1986) The comparative economics of palm oil mill effluent treatment and resource recovery systems. National Workshop on Recent Developments in Palm Oil Milling Technology & Pollution Control

32. Harish Prashanth KV, Tharanathan RN (2007) Chitin/chitosan: modifications and their unlimited application—an overview. Trends Food Sci Tech 18: 117-131

33. Igwe JC, Onyegbado CC (2007) Review of Palm Oil Mill Effluent (POME) Water Treatment. Global J. Environ. Res 1 (2): 54-62

34. Jiang JQ, Graham NJD (1998) Pre-polymerized inorganic coagulants and phosphorus removal by coagulation – a review. Water SA 24: 237–244

35. Kang YW, Hwang KY (2000) Effects of reaction conditions on the oxidation efficiency in the Fenton process. Water Research 34: 2786-2790

36. Karim MIA, Hie LL, (1987) The use of coagulating and polymeric flocculating agents in the treatment of palm oil mill effluent (POME). Biol Wastes 22: 209-218.

37. Kestioğlu K, Yonar T, Azbar N (2005) Feasibility of physico-chemical treatment and Advanced Oxidation Processes (AOPs) as a means of pretreatment of olive mill effluent (OME). Process Biochem 40: 2409-2416

38. Klavarioti M, Mantzavinos D, Kassinos D (2009) Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. Environ Int 35: 402-417

39. Kuo WG (1992) Decolourizing dye wastewater with Fenton's Reagent. Water Research 26: 881-886

40. Lin SH, Lo CC (1997) Fenton process for treatment of desizing wastewater. Water Research 31: 2050-2056

41. Meyssami B, Kasaeian AB (2005) Use of coagulants in treatment of olive oil wastewater model solutions by induced air flotation. Bioresource Technol 96: 303–307

42. No HK, Meyers SP (2000) Application of chitosan for treatment of wastewaters. Rev Environ Contam 163: 1–28

43. Oller I, Malato S, Sánchez-Pérez JA (2011) Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination—A review. Sci Total Environ 409: 4141-4166

44. Pera-Titus M, García-Molina V, Baños MA, Giménez J, Esplugas S (2004) Degradation of chlorophenols by means of advanced oxidation processes: a general review. Appl Catal B. 47: 219-256

45. Raffellini S, Schenk M, Guerrero S, Alzamora SM (2011) Kinetics of Escherichia coli inactivation employing hydrogen peroxide at varying temperatures, pH and concentrations. Food Control 22: 920-932

46. Ravi Kumar MNV (2000) A review of chitin and chitosan applications. React Funct Polym. 46: 1–27

47. Rizzo L, Lofrano G, Grassi M, Belgiorno V (2008) Pre-treatment of olive mill wastewater by chitosan coagulation and advanced oxidation processes. Sep Purif Technol 63: 648-653

48. Roussy J, Van Vooren M, Guibal E (2004) Chitosan for the coagulation and flocculation of mineral colloids. J Disper Sci Technol 25: 663–677

49. Roussy J, Van Vooren M, Guibal E (2005) Influence of chitosan characteristics on coagulation and flocculation of organic suspensions. J Appl Polym Sci 98: 2070–2079

50. Sekaran G, Karthikeyan S, Evvie C, Boopathy R, Maharaja P (2013) Oxidation of refractory organics by heterogeneous Fenton to reduce organic load in tannery wastewater. Clean Technol Environ Policy 15**:** 245-253

51. Sychev AY, Isak VG (1995) Iron compounds and the mechanisms of the homogeneous catalysis of the activation of O2 and H2O2 and of the oxidation of organic substrates. Russ Chem Rev 64: 1105-1129

52. Szpyrkowicz L, Juzzolino C, Kaul SN (2001) A Comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and fenton reagent. Water Res 35: 2129-2136

53. Tang WZ, Chen RZ (1996) Decolorization kinetics and mechanisms of commercial dyes by H2O2/iron powder system. Chemosphere 32: 947-958

54. Varma AJ, Deshpande SV, Kennedy JF (2004) Metal complexation by chitosan and its derivatives: a review. Carbohydr Polym 55: 77–93

55. Vijayaraghavan K, Ahmad D, Ezani Abdul Aziz M (2007) Aerobic treatment of palm oil mill effluent. J Environ Manage 82(1): 24-31

56. Wu TY, Mohammad AW, Jahim JM, Anuar N (2009) A holistic approach to managing palm oil mill effluent (POME): Biotechnological advances in the sustainable reuse of POME. Biotechnol Adv 27: 40-52

57. Wu ZB, Ni WM, Guan BH (2008) Application of chitosan as flocculant for coprecipitation of Mn (II) and suspended solids from dual-alkali FGD regenerating process. J Hazard Mater 152: 757–764

58. Zhu G, Zheng H, Zhang Z, Tshukudu T, Zhang P, Xiang X (2011) Characterization and coagulation-flocculation behavior of polymeric aluminum ferric sulfate (PAFS). Chem Eng J 178: 50-59

59. Zinatizadeh AAL, Mohamed AR, Mashitah MD, Abdullah AZ, Isa MH (2007) Optimization of pre-treated palm oil mill effluent digestion in an up-flow anaerobic sludge fixed film bioreactor: A comparative study. Biochem Eng J 35: 226-237

Figure Captions

Figure1 Effect of chitosan dosage on the removal (%) of (a) CODand (b) TSS

Figure 2 Effect of $FeSO_4$ dosagewithchitosan (2500 mg/L) on the removal (%) of (a) COD and (b) TSS

Figure 3 Zeta potential at different dosages of chitosan andchitosan(2500 mg/L)with $FeSO_4$

Figure 4 Effect of mixing time by employing chitosan (2500 mg/L) and chitosan (2500 mg/L) with $FeSO_4$ (2500 mg/L) on the removal (%) of a) COD and (b) TSS

Figure 5 Zeta potential measurements at different mixing time for chitosan (2500 mg/L)and chitosan (2500 mg/L) withFeSO4 (2500 mg/L)

Figure 6 Effect of sedimentation time using chitosan(2500 mg/L) and chitosan (2500 mg/L) with $FeSO_4$ (2500 mg/L) on the removal (%) of a) COD and (b) TSS

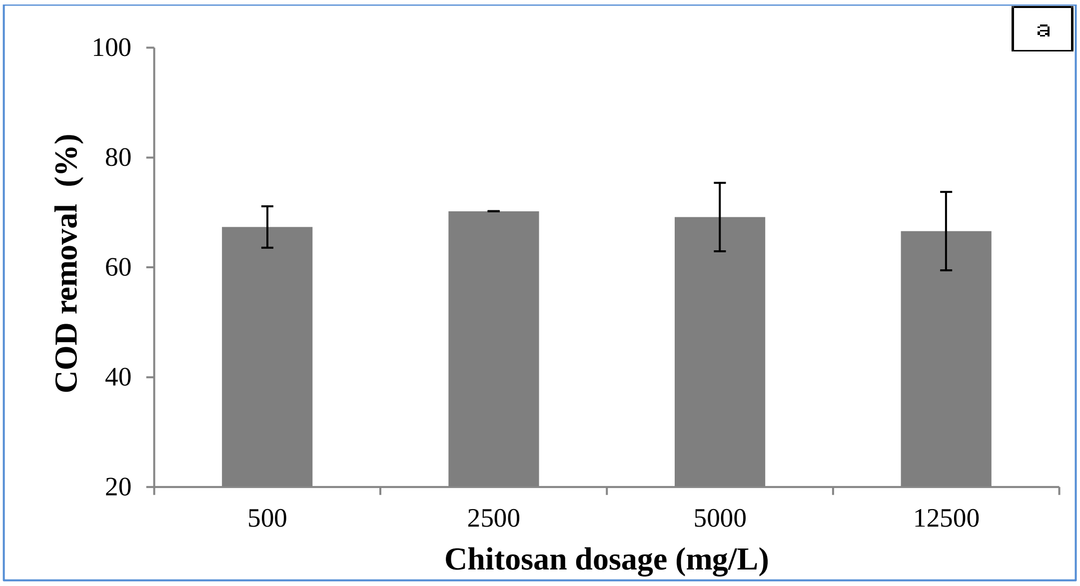
Figure 7 Zeta potential measurements at different sedimentation time for chitosan (2500 mg/L) and chitosan(2500 mg/L) with FeSO4 (2500 mg/)

Figure 8 Effect of pH of chitosan (2500 mg/L) and chitosan (2500 mg/L) with$FeSO_4$ (2500 mg/L) on the removal (%) of a) COD and (b) TSS

Figure 9*Zeta* potential measurements at different pH for chitosan (2500 mg/L) andchitosan (2500 mg/) with$FeSO_4$ (2500 mg/)

Figure10 Effect of hydrogen peroxide with chitosan (2500 mg/L) andchitosan (2500 mg/L) with $FeSO_4$ (2500 mg/L) on the removal (%) of a) COD and (b) TSS

Figure 11 Zeta potential measurements at different hydrogen peroxide concentrations for chitosan (2500 mg/L) and chitosan (2500 mg/L) with $FeSO_4$ (2500 mg/L)


a
COD removal (%)
100
80
60
40
20
500
2500
5000
12500
Chitosan dosage (mg/L)

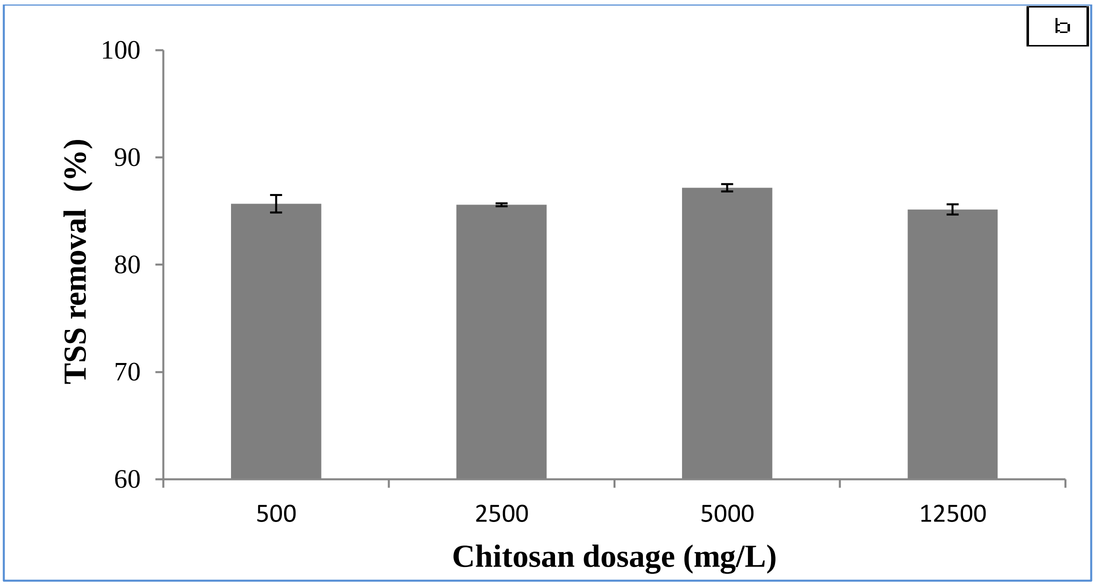

b
TSS removal (%)
100
90
80
70
60
500
2500
5000
12500
Chitosan dosage (mg/L)

Fig. 1

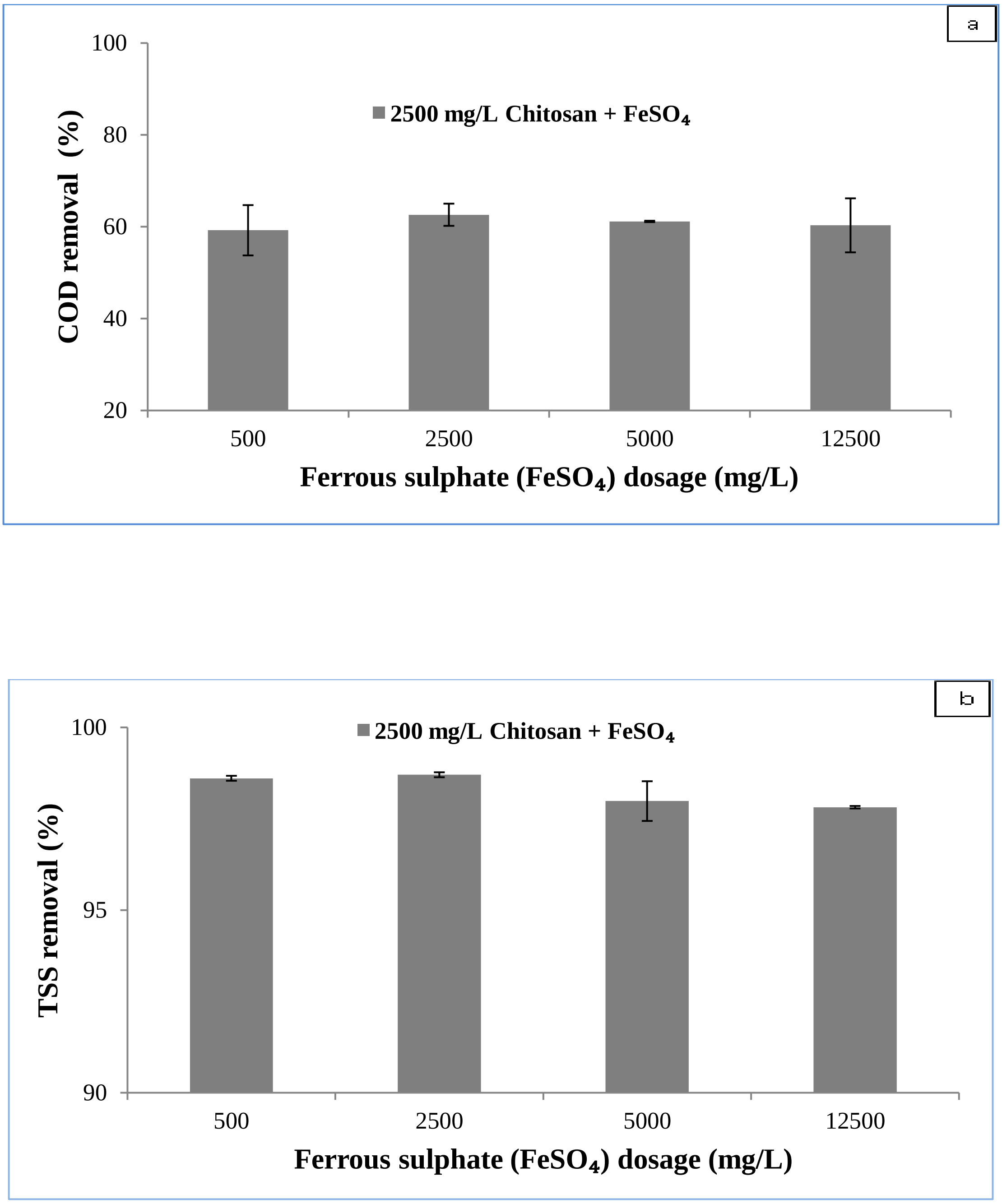

a
100
80
60
40
20
COD removal (%)
2500 mg/L Chitosan + FeSO4
500
2500
5000
12500
Ferrous sulphate (FeSO4) dosage (mg/L)
b
100
95
90
TSS removal (%)
2500 mg/L Chitosan + FeSO4
500
2500
5000
12500
Ferrous sulphate (FeSO4) dosage (mg/L)

Fig.2

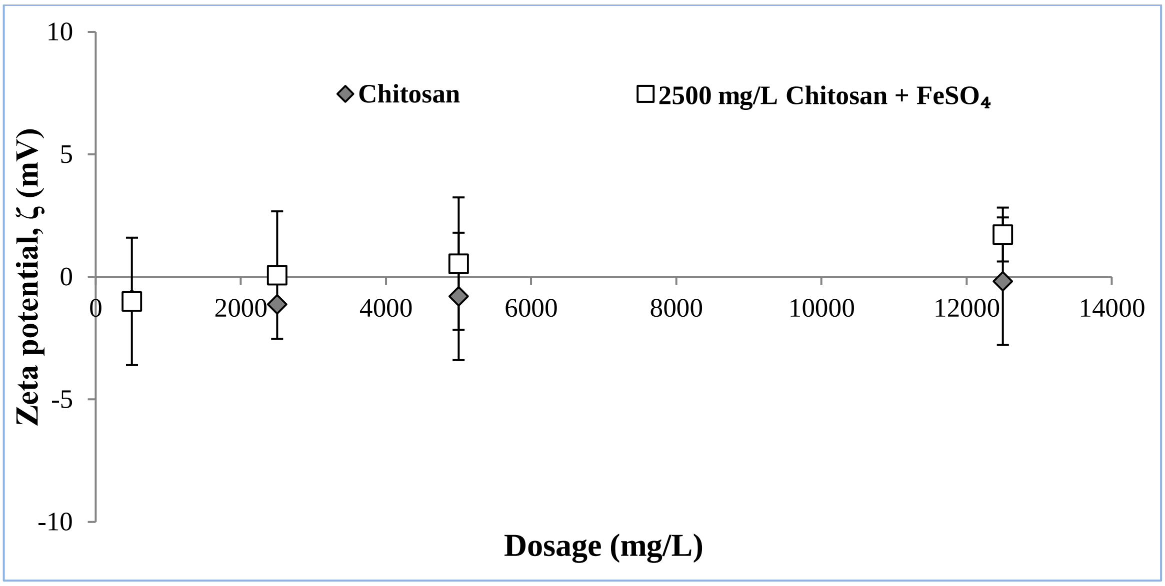

Zeta potential, ζ (mV)
Dosage (mg/L)
◆ Chitosan
☐ 2500 mg/L Chitosan + $FeSO_4$
10
5
0
-5
-10
0
2000
4000
6000
8000
10000
12000
14000

Fig.3

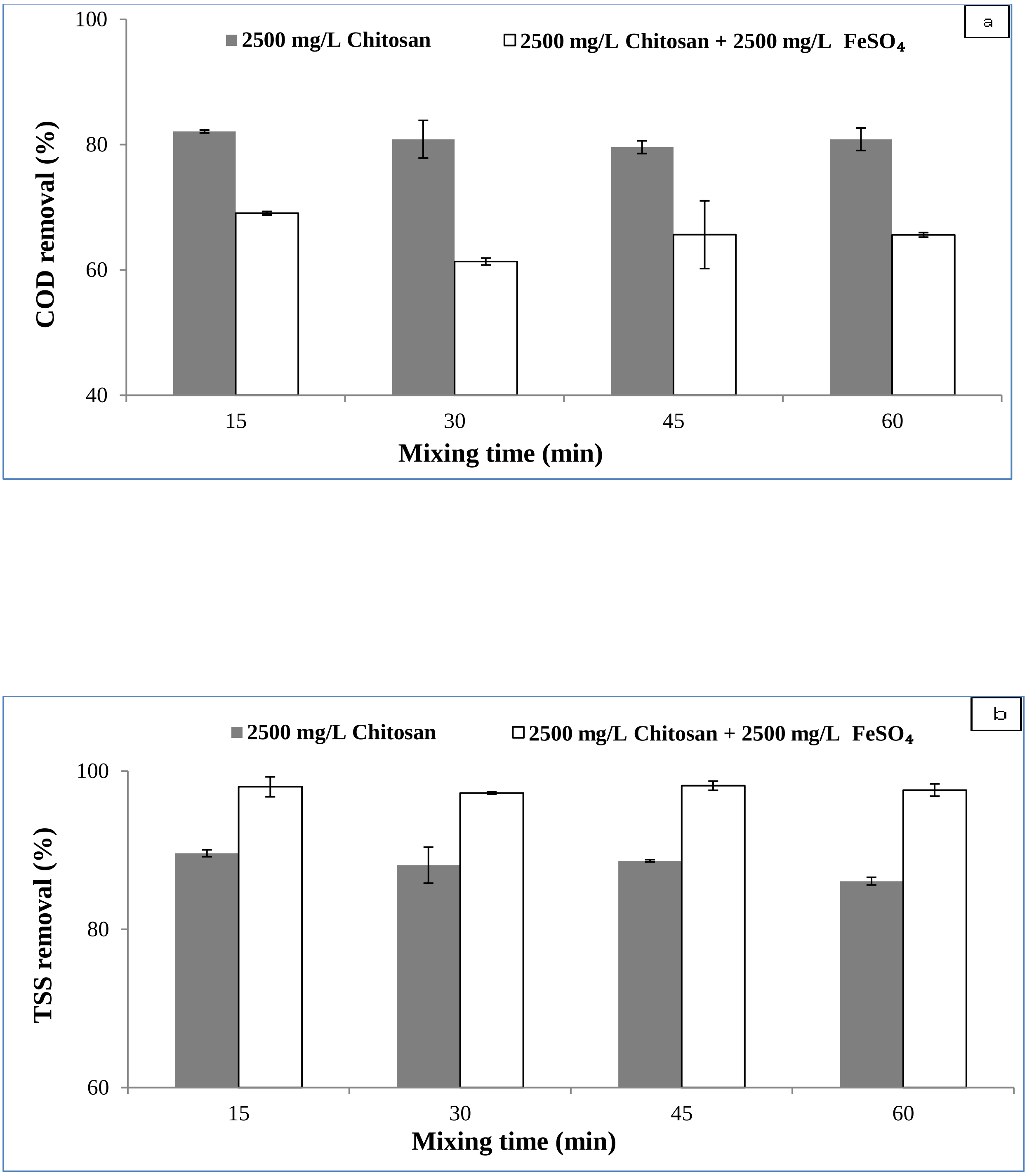

a
■ 2500 mg/L Chitosan
☐ 2500 mg/L Chitosan + 2500 mg/L FeSO$_4$
COD removal (%)
100
80
60
40
15
30
45
60
Mixing time (min)
b
■ 2500 mg/L Chitosan
☐ 2500 mg/L Chitosan + 2500 mg/L FeSO$_4$
TSS removal (%)
100
80
60
15
30
45
60
Mixing time (min)

Fig. 4

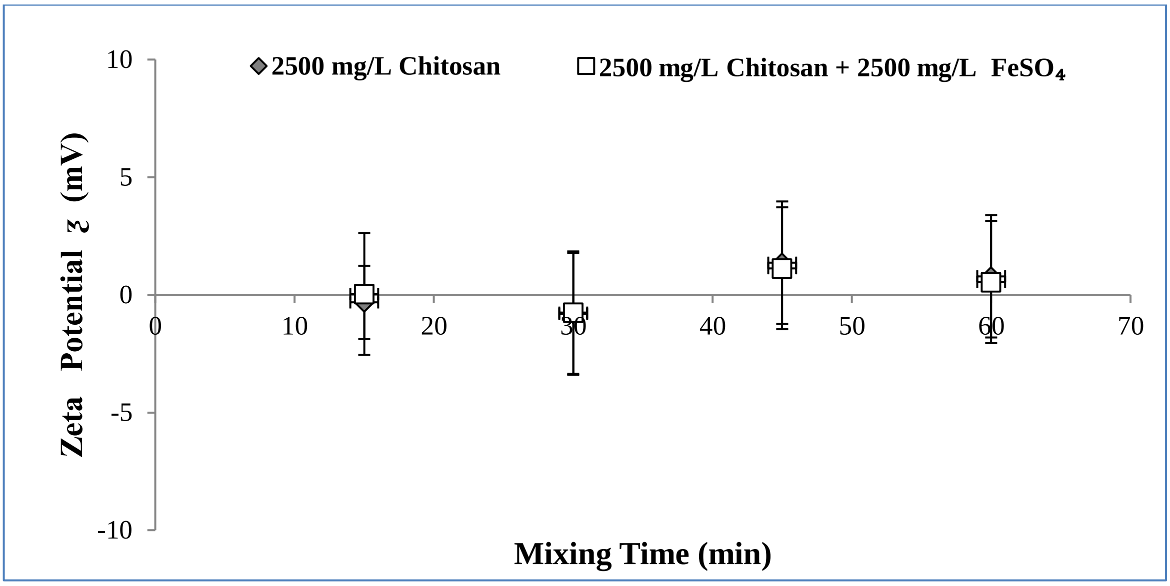

◆2500 mg/L Chitosan
☐2500 mg/L Chitosan + 2500 mg/L FeSO₄
Zeta Potential ƺ (mV)
10
5
0
-5
-10
0
10
20
30
40
50
60
70
Mixing Time (min)

Fig.5

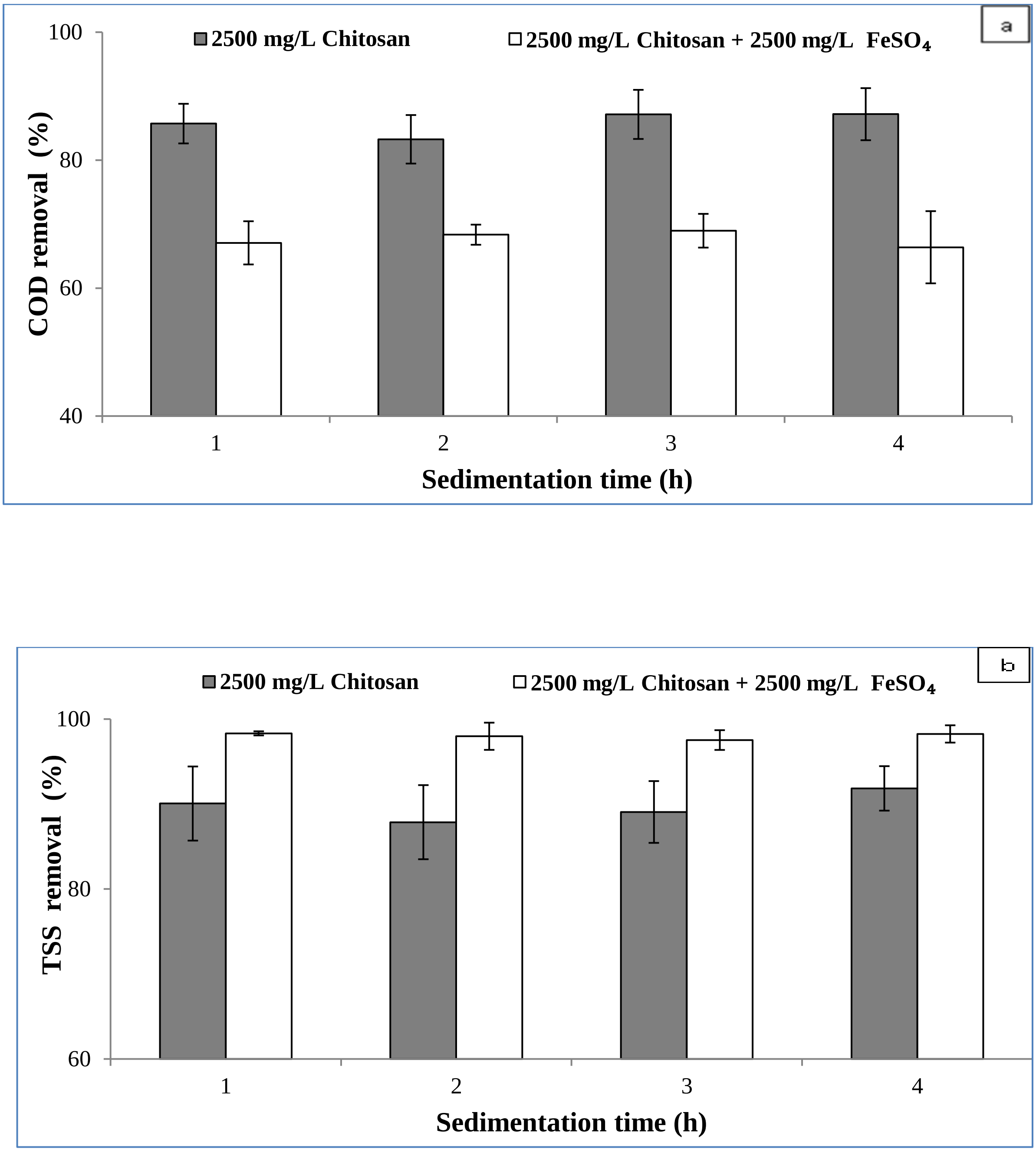

a
■ 2500 mg/L Chitosan
□ 2500 mg/L Chitosan + 2500 mg/L FeSO4
COD removal (%)
100
80
60
40
1
2
3
4
Sedimentation time (h)
b
■ 2500 mg/L Chitosan
□ 2500 mg/L Chitosan + 2500 mg/L FeSO4
TSS removal (%)
100
80
60
1
2
3
4
Sedimentation time (h)

Fig. 6

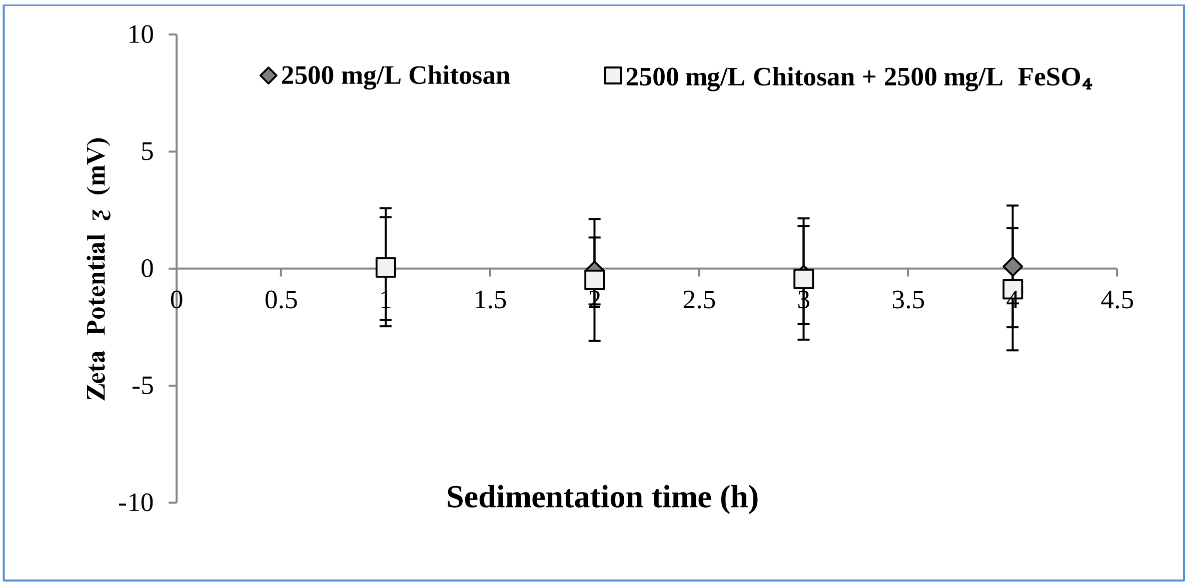

◆2500 mg/L Chitosan
□2500 mg/L Chitosan + 2500 mg/L $FeSO_4$
Zeta Potential ƺ (mV)
10
5
0
-5
-10
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
Sedimentation time (h)

Fig.7

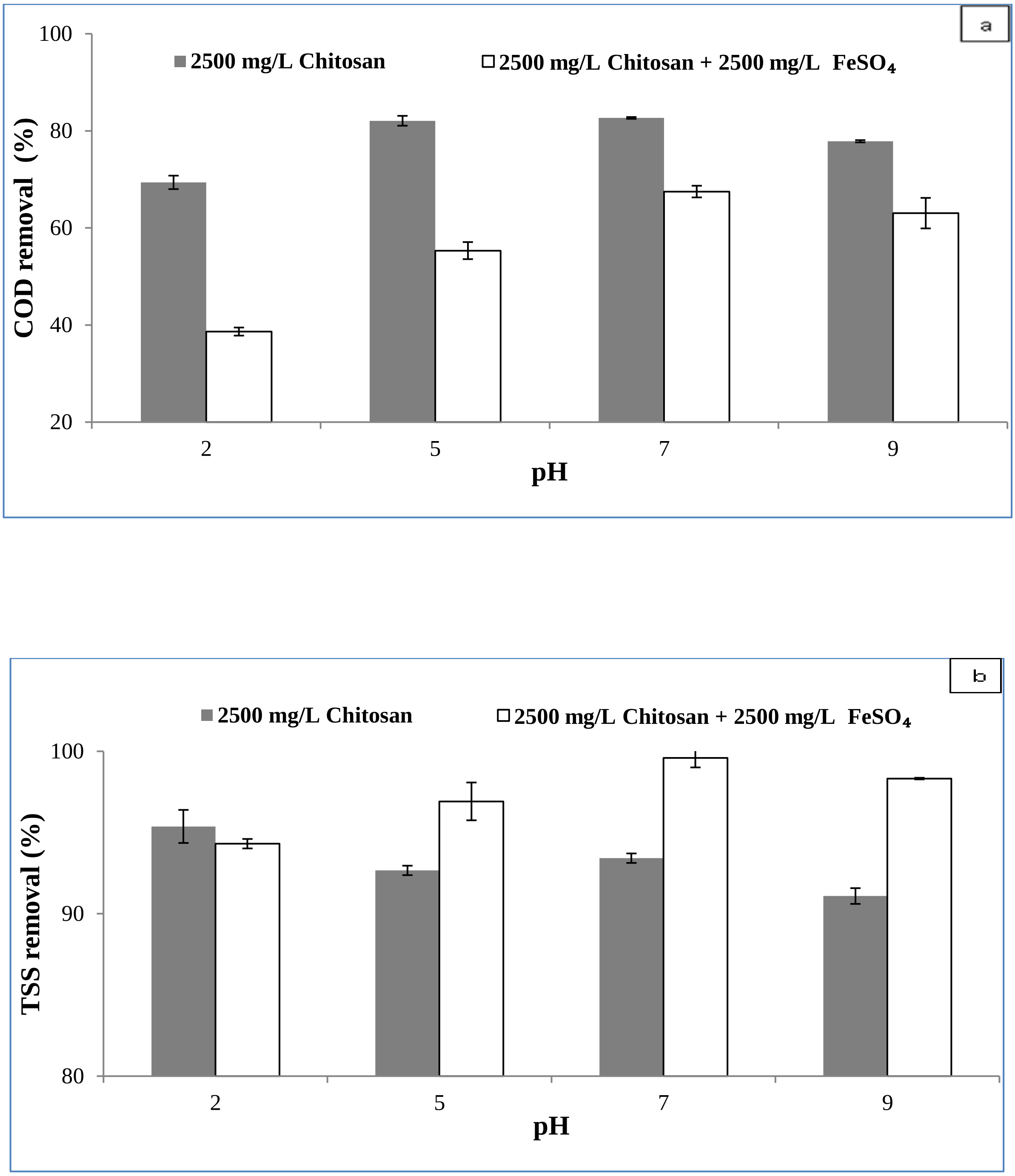

a
2500 mg/L Chitosan
2500 mg/L Chitosan + 2500 mg/L FeSO$_4$
COD removal (%)
100
80
60
40
20
2
5
7
9
pH
b
2500 mg/L Chitosan
2500 mg/L Chitosan + 2500 mg/L FeSO$_4$
TSS removal (%)
100
90
80
2
5
7
9
pH

Fig. 8

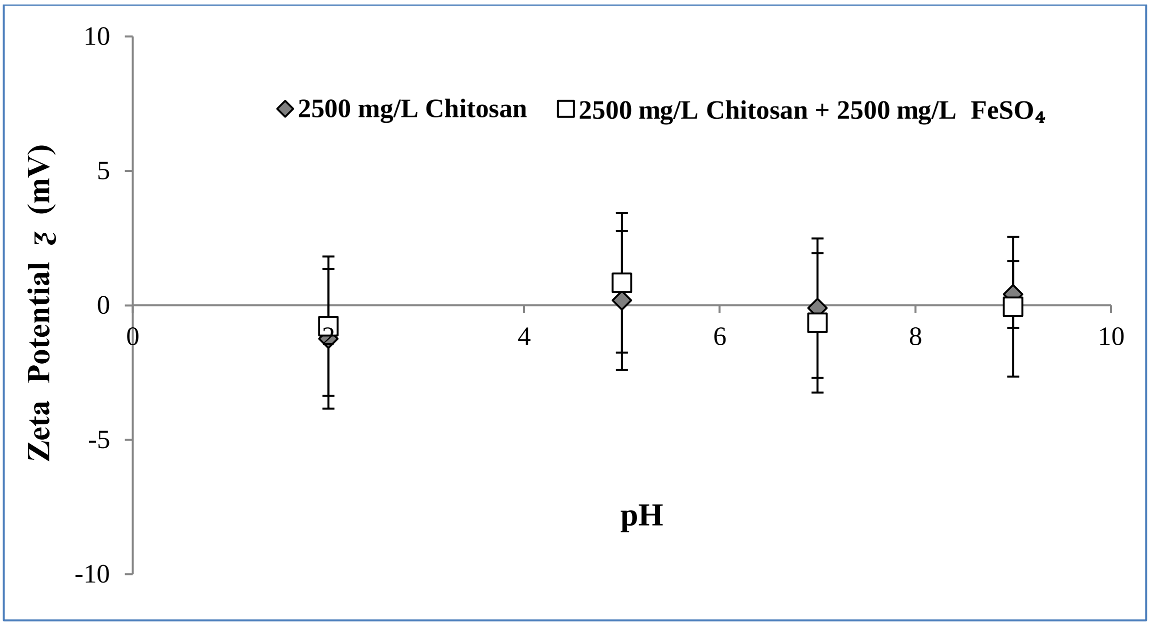

10
5
0
-5
-10
Zeta Potential ƺ (mV)
◆2500 mg/L Chitosan
☐2500 mg/L Chitosan + 2500 mg/L FeSO4
0
2
4
6
8
10
pH

Fig. 9

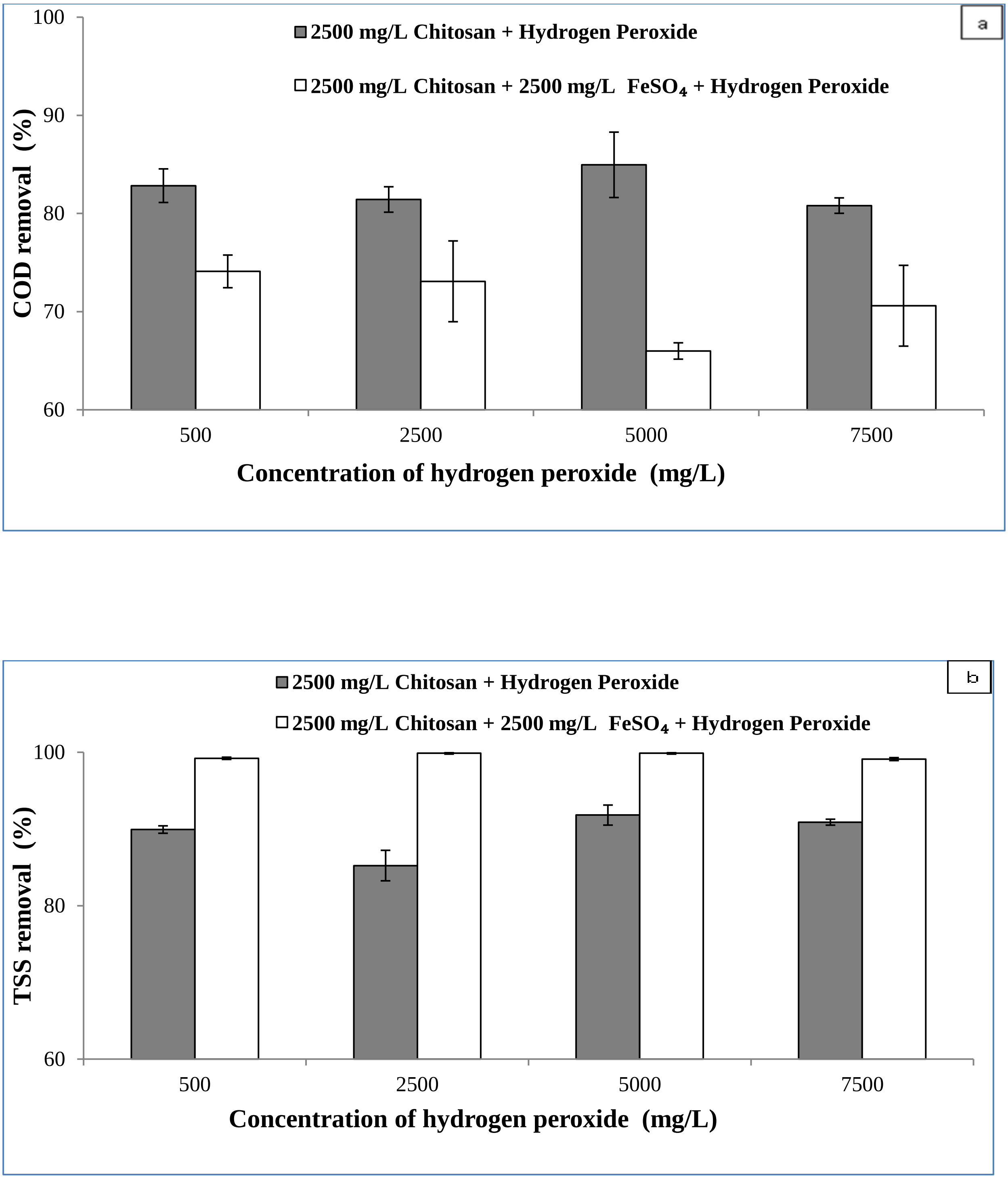

a
2500 mg/L Chitosan + Hydrogen Peroxide
2500 mg/L Chitosan + 2500 mg/L FeSO$_4$ + Hydrogen Peroxide
COD removal (%)
100
90
80
70
60
500
2500
5000
7500
Concentration of hydrogen peroxide (mg/L)
b
2500 mg/L Chitosan + Hydrogen Peroxide
2500 mg/L Chitosan + 2500 mg/L FeSO$_4$ + Hydrogen Peroxide
TSS removal (%)
100
80
60
500
2500
5000
7500
Concentration of hydrogen peroxide (mg/L)

Fig.10

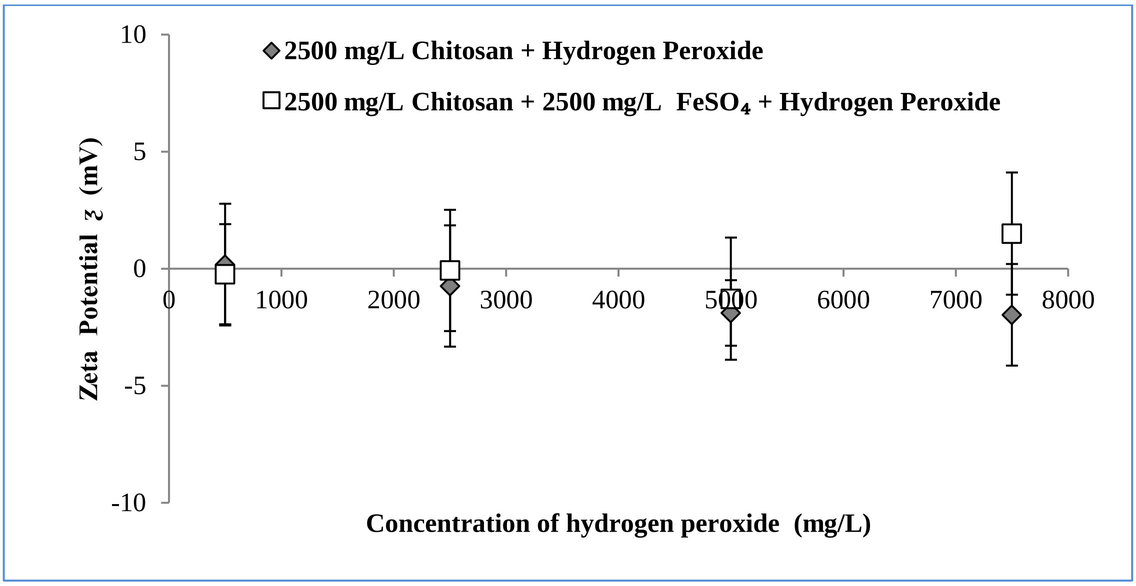

10
5
0
-5
-10
Zeta Potential ζ (mV)
0
1000
2000
3000
4000
5000
6000
7000
8000
Concentration of hydrogen peroxide (mg/L)
◆2500 mg/L Chitosan + Hydrogen Peroxide
□2500 mg/L Chitosan + 2500 mg/L FeSO₄ + Hydrogen Peroxide

Fig.11

List of tables

Table 1

POME discharge standards set by Department of Environment (DoE), Malaysia under the Environmental Quality Act 1974

Parameters[a]	Discharge limits
Biochemical oxygen demand	100
Chemical oxygen demand	Not legislated
Total suspended solids	400
Total nitrogen	200
Oil & grease	50
pH	5 - 9

a: All parameters are in mg/L except pH

Table 2

Performance comparison between activated carbon (AC) adsorption and ultrasound (US) cavitation on COD (mg/L) and TSS (mg/L)) removals from POME

Operating conditions	COD (mg/L)	BOD (mg/L)	TSS (mg/L)
Biologically digested POME	4700±550	1355± 434	1800±282
AC adsorption (6 h, 200 g AC/L)	ND*	ND*	ND*
US cavitation (50% amplitude, 90 min cavitation time)	965± 49.49	260±60.10	75±35.35
US cavitation followed by AC adsorption (50% amplitude & 15 min cavitation time, 50g AC/L & 30 min AC contact time)	ND*	ND*	310±56.56
US cavitation (50% amplitude, 15 min cavitation time) coupled with AC adsorption (50 g AC/L)	1265±190.91	360±106.06	30±14.14

*ND: Not detected