1

2

3

4

5

6

Process Intensification of Anaerobically digested Palm Oil Mill Effluent (AAD-POME) Treatment Using Combined Chitosan Coagulation, Hydrogen Peroxide (H$_2$O$_2$) 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.

16

17

18

19

20

21

22

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

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

25

26

1

27   **Graphical Abstract**
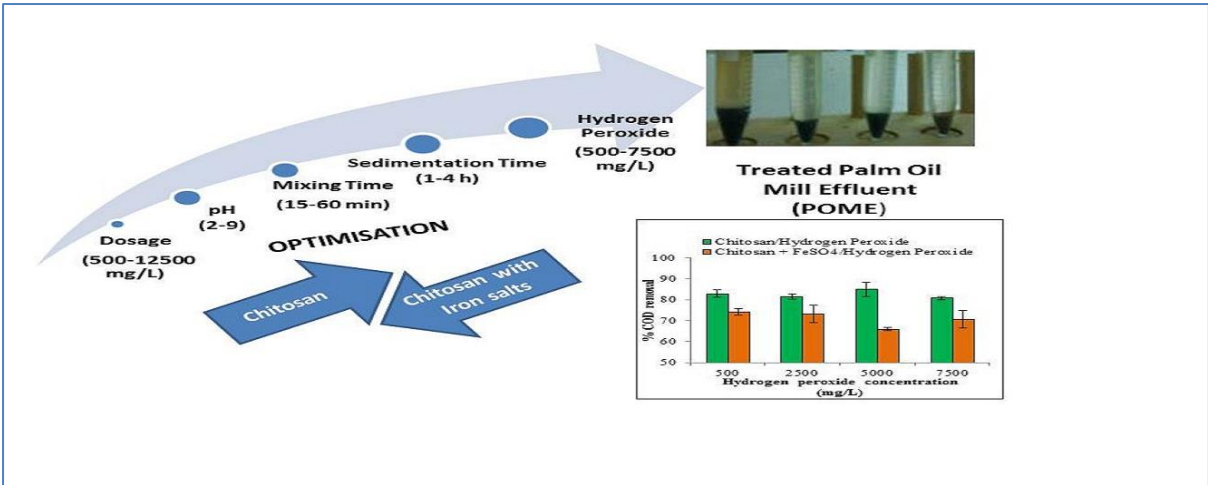
30   **Highlights**

31   • An eco-friendly green processing method for Anaerobically digested POME treatment has been
32   investigated.
33   • Combined chitosan coagulation with AOPs was utilised.
34   • Higher COD ($82.82\pm1.71\%$) removal for chitosan/H_2O_2 compared to chitosan-Fenton oxidation was
35   observed.
36   • Chitosan-Fenton oxidation was found to be favourable for higher TSS removal but not for COD
37   removal.
38   • Comparison of performance with other technologies has been reported with economic analysis.

40   **Research significance**

41   Industrial wastewater treatment exploiting advanced oxidation processes (AOPs) involves generation of

42   hydroxyl radicals (OH·) to degrade the organic components and is a well-documented approach. In the present

43   study, natural biomaterial Chitosan as a coagulant combined with various AOP's have been investigated for the

44   anaerobically digested palm oil mill effluent (AAD-POME) treatment. Research investigations to-date on the

45   post-treatment of POME is very limited and the lacking of lab-scale study could be the major reason for the

46   failing industrial plant trials. Hence the current study explores the possibility and reports in detail on an

47   alternative eco-friendly green processing technique for POME treatment. The objectives of present investigation

48   focuses on the post-treatment of AAD-POME primarily by coagulation using (a) chitosan (b) chitosan with

49   FeSO$_4$ (c) chitosan with H_2O_2 and (d) chitosan with Fenton oxidation. The results conclude that chitosan with

50   H_2O_2 proved to be the most promising alternative for POME treatment compared to chitosan with Fenton

51   oxidation.

53 **Abstract**

54 The present study investigates the removal efficiency of chemical oxygen demand (COD) and total suspended

55 solids (TSS) of anaerobically digested palm oil mill effluent (AAD-POME) in batch studies through the

56 following 4 strategies: coagulation by chitosan, addition of ferrous sulphate ($FeSO_4$), chitosan with hydrogen

57 peroxide (H_2O_2) and chitosan with Fenton oxidation. The parameters tested were: chitosan dosage (500-12500

58 mg/L), $FeSO_4$ dosage (500-12500 mg/L), mixing time (15-60 min), sedimentation time (1-4 h), initial pH (2-9)

59 and H_2O_2 (500–7500 mg/L). Coagulation only by using chitosan (2500 mg/L) achieved the maximum COD and

60 TSS removal of 70.22±0.23% and 85.59±0.13% respectively. An increase in the TSS removal (98.7±0.06 %)

61 but with a reduction in the COD removal (62.61±2.41%) was observed when $FeSO_4$ (2500 mg/L) was added

62 along with chitosan (2500 mg/L). Alternatively, an improvement in the COD (82.82±1.71%) and TSS

63 (89.92±0.48 %) removal efficiencies was observed when chitosan was coupled with H_2O_2 (500 mg/L). Finally

64 chitosan (2500mg/L) integrated with Fenton oxidation ($FeSO_4$ of 2500 mg/L and H_2O_2 of 500 mg/L) resulted in

65 100% TSS and 73.08±4.11% COD removals. Overall chitosan with H_2O_2 proved to be the most promising

66 alternative for POME treatment compared to chitosan with Fenton oxidation.

67 *Keywords:* Palm oil mill effluent, POME, Treatment, Chitosan, Hydrogen peroxide, Coagulation, Chemical

68 oxygen demand, Total suspended solids.

69

70

71

72

73

74

75

76

77

78

79

80

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 anaerobbic 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·) 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).

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

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

159 is capable of removing COD and color from the POME and thus a viable treatment option. However the

160 effectiveness of chitosan coupled with Fenton oxidation has never been explored for POME.

161 Thus, the objectives of present investigation focus on the post-treatment of AAD-POME primarily by

162 coagulation using (a) chitosan (b) chitosan with $FeSO_4$ (c) chitosan with H_2O_2 and (d) chitosan with Fenton

163 oxidation. Besides, the investigation also looked into evaluating and optimising the suitable process conditions

164 such as dosage, mixing time, sedimentation time and pH for the effective treatment of AAD-POME.

165 **2 Experimental**

166 **2.1 Materials**

167 Anaerobically digested POME (AAD-POME) was collected from Ulu Kanchong Oil Palm Mill, Rantau,

168 Malaysia. The collected POME samples were at a temperature of 27.5±2.5 °C and the characteristics of samples

169 differed based upon the processing of palm oil, climate and operating conditions during the sampling period.

170 The COD and TSS of the samples were 15290±855 mg/L and 14950±2400 mg/L respectively. Chitosan, a white

171 fine powder with a molecular weight of 350 kDa with 95% deactylation was obtained from Chitin-Chitosan

172 Research Centre of Universiti Kebangsaan Malaysia. $FeSO_4$ was purchased from R&M chemicals, (NJ, USA).

173 Distilled water was used for diluting 37 % fuming H_2O_2 (Merck, Germany) and sodium hydroxide pellets (R&M

174 chemicals, NJ, USA) to prepare 5M solution for pH adjustment.

175 **2.2 Methods**

176 The experiments were carried out in a conventional jar-tester (Loviband water testing, model ET720, Germany)

177 which accommodates six glass reactors at a time and all the reactors were simultaneously mixed at the same

178 speed using the stainless steel paddles. Each reactor was filled with 200 ml of POME and the coagulant was

179 added into POME and mixed rapidly for various periods (15-60 min) with different doses of chitosan and

180 ferrous sulphate (500-12500 mg/L). The effect of sedimentation time (1-4 h) and the effect of pH (2-9) were

181 also investigated. The role of hydrogen peroxide (500–7500 mg/L) in the treatment was also considered. At the

182 end of the treatment, the samples were taken from the clarified supernatant layer to determine the COD, TSS

183 and Zeta potential (ζ).

184 **2.3 Analysis**

185 The COD test was carried out using COD vials (HR 20-1500 mg/L) following the American Public Health

186 Association (APHA) standard method 8000 using a spectrophotometer (HACH model DRB 2000). TSS was

187   measured by following the APHA standard method 8006 using a spectrophotometer (HACH model DR 2800)

188   by filling 10 ml of sample in a specially designed glass bottle. Zeta potential was calculated using Zetasizer

189   (Malvern 2000, UK) and pH was tested using a pH meter (Martini Instruments, NC, USA).

190   **3 Results and discussion**

191   **3.1 Effect of dosage**

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

193   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

194   removals were observed. A further increase in the dose to 2500 mg/L improved the COD removal to 70.22 ±

195   0.23 %, whereas the removal of TSS remained the same (85.59 ± 0.13 %). A decrease in the COD (66.57 ±

196   7.13%) was observed when the dosage was finally increased to 12500 mg/L which may be probably due to

197   overdosing of chitosan. Similar observations were noticed by Zhu et al. **2011** during the coagulation process by

198   employing polymeric aluminium ferric sulphate (PAFS). It has been observed that when the dosage was

199   increased more than the optimum, restabilisation of colloidal particles of POME occurs, decreasing the COD

200   and TSS removal efficiencies. From the results it is evident that optimising the chitosan dose is important for the

201   increased removal of COD and TSS.

202   The obtained results could be explained by three different mechanisms i.e. charge neutralisation, patch

203   flocculation and micro-bridging. Charge neutralisation of the colloidal particles is normally achieved by the

204   addition of coagulant aids of opposite charges (Zhu et al. **2011**; Assaad et al. **2007**). The organic molecules in

205   POME are normally negatively charged and the coagulant aids are positively charged in nature. Thus, when

206   these coagulant aids are introduced to the effluent, attraction of oppositely charged ions occurs owing to Van der

207   Waals forces resulting in neutralisation of charges and hence the formation of larger agglomerates (Wu et al.

208   **2008**; Crini and Badot **2008**; Gérente et al. **2007**). The bridging of colloidal particles is achieved by the addition

209   of polyelectrolytes and is very similar to the charge neutralisation by the coagulant aids. The colloidal particles

210   are attracted to the long polymer chains of these polyelectrolytes forming a bridge resulting in the agglomeration

211   and coagulation (Varma et al. **2004**; No and Mayers **2000**). POME contains various types of colloidal

212   particulates including organic components and is negatively charged. Chitosan is a linear polyelectrolyte and has

213   a positive charge at acidic conditions and thus attracts the negatively charged colloidal particles of POME and

214   destabilizes them resulting in agglomeration (Ravi Kumar **2000**). Besides, amine functional groups of chitosan

215   help to adsorb components of POME into larger agglomerates thereby achieving the maximum COD removal at

216   lower dosages of chitosan (Ravi Kumar **2000**). The obtained results using chitosan could be compared with the

217   previous results for olive oil wastewater where it was observed that increasing the chitosan dosage achieved the

218   maximum TSS removal (Rizzo et al. **2008**). Based on this study, the optimised chitosan dosage of 2500 mg/L

219   was used for further investigation to treat POME using $FeSO_4$.

220   The effect of dosage of $FeSO_4$ was studied in the range of 500-12500 mg/L. Maximum COD removal of 62.61 ±

221   2.41 % (**Fig. 2 (a)**) and TSS removal of 98.7 ± 0.06 % (**Fig. 2 (b)**) were achieved for 2500 mg/L of $FeSO_4$.

222   Further it was observed that with the addition of $FeSO_4$ to chitosan, TSS removal increased from 85.59 ± 0.13 %

223   (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

224   COD removal was decreased from 70.22% (2500 mg/L of chitosan alone) to 62.61 ± 2.41 % (2500 mg/L of

225   chitosan with 2500 mg/L of $FeSO_4$). Similar observations were earlier reported by Ginos et al. **2006** while using

226     $FeSO_4$ coupled with poly-electrolytes where a maximum TSS removal of 95-98% with the lower COD removal

227   of 22-28% was noticed for olive mill wastewater treatment. This observation clearly indicates that addition of

228     $FeSO_4$ is favourable for TSS removal but not for COD removal. The obtained results could be further supported

229   by analysing the zeta potential. **Fig. 3** shows the zeta potential measurements using different doses of chitosan

230   and chitosan with $FeSO_4$.

231   Zeta potential (ζ) is defined as the electrical potential difference between the colloidal particles and the solution

232   and it is an indirect way of measuring the charge of colloidal particles. Isoelectric point is defined as the

233   condition where the colloidal particles have enough counter ions so that they can be electrically neutral and zeta

234   potential is zero. The highest degree of agglomeration is achieved at this isoelectric point (Ariffin et al. **2012**). It

235   was observed that increasing the chitosan dosage increased the ζ value nearing the isoelectric point (mV=0).

236   Similar observations were earlier reported by Ariffin et al. for the paper and pulp mill wastewaters using a

237   hybrid flocculant system of PolyDADMAC and polyacrylamide (Ariffin et al. **2012**). The observed ζ values

238   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 $FeSO_4$

239   which were very close to the isoelectric point. Thus, a consistency in the results was observed in this range of

240   dosage with COD and TSS removal. Hence at the end of this study, 2500 mg/L of chitosan and 2500 mg/L of

241     $FeSO_4$ were selected for further investigation.

242   **3.2 Effect of mixing time**

243   The effect of mixing time (15-60 min) was studied for the optimised chitosan and chitosan with $FeSO_4$ dosages

244   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.

303 The highest degree of agglomeration is achieved at the isoelectric point. The surface charges increase when the

304 pH increased from 2 to 5 for both the coagulants whereas there was a decrease in the surface charge at neutral

305 pH 7. The surface charge of POME gets decreased due to the charge neutralisation mechanism at neutral pH

306 indirectly improving the coagulation efficiency and hence the COD and TSS removals. At an alkaline pH, an

307 increase in the surface charge decreases the coagulation efficiency. This trend was very similar to the

308 observations as reported by Zhu et al. 2011. At the end of this study, pH 7 was chosen to be the optimum pH

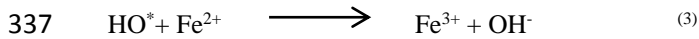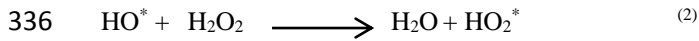309 which is also the pH after the aerobic digestion of POME and which resulted in the COD and TSS removals.

310 **3.5 Effect of hydrogen peroxide**

311 The effect of hydrogen peroxide (500-7500 mg/L) on the COD and TSS removals was investigated and the

312 results have been shown in **Fig. 10**, whereas **Fig. 11** shows the surface charge measurements.

313 For chitosan, it was observed that at the lowest H_2O_2 concentration (500 mg/L), COD and TSS removal

314 efficiencies were 82.82 ±1.71 % (**Fig. 10(a)**) and 89.92 ±0.48 % (**Fig. 10(b)**) respectively along with a zeta

315 potential of 0.175 mV (**Fig. 11**). The reason for introducing H_2O_2 was to increase the generation of hydroxyl

316 radicals (OH·) thereby improving oxidation and hence the removal of chemical components of POME. H_2O_2 is

317 widely used in the advanced oxidation processes (AOPs) for wastewater treatment. When this AOP is coupled

318 with chemical coagulation, an increase in the removal of chemical components of POME could be expected. It

319 was evident from the observation that the COD removal efficiency was increased from 66.59 ± 7.13 % (for 2500

320 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

321 removal efficiency was improved from 85.15 ± 0.47 % (for 2500 mg/L chitosan without H_2O_2) to 89.92 ± 0.48

322 (for 2500 mg/L chitosan with 500 mg/L H_2O_2). When the concentration of H_2O_2 was further increased to 5000

323 mg/L, a maximum removal of 91.80 ± 1.30% in the TSS and 84.95 ± 3.32% in the COD was achieved. Hence

324 an external addition of H_2O_2 improves the removal of chemical components of POME by oxidation due to the

325 abundant availability of OH· radicals. This confirms that the radical attack is the main pathway for the POME

326 degradation which significantly increases the performance of chitosan coagulation. Whereas, when the

327 concentration of H_2O_2 was further increased to 7500 mg/L there was a reduction in the removal efficiency of

328 both the COD as well as TSS. This observation could be explained due to the over abundant generation of

329 hydroxyl radicals, which in turn results in the formation of hydrogen peroxide and finally reduces the oxidation

330 as hydrogen peroxide is relatively a weak oxidising agent as compared to OH· radicals (Harish Prashanth and

331 Tharanathan 2007; Chu et al. 2012). a possibility of oxidation of FeSO$_4$ by H$_2$O$_2$ into Fe$_2$(SO$_4$)$_3$ at pH 7 as well

332 as oxidation of chitosan by H$_2$O$_2$ must

333 Thus an optimum concentration of H$_2$O$_2$ (500 mg/L) is found to be suitable for POME treatment. Apart from

334 this, the effect of Fenton oxidation was also investigated using ferrous sulphate. The mechanism involved in the

335 Fenton oxidation has been shown in the following equations (2-10) (Sychev and Isak 1995):

336 $$HO^* + H_2O_2 \longrightarrow H_2O + HO_2^* \qquad (2)$$

337 $$HO^* + Fe^{2+} \longrightarrow Fe^{3+} + OH^- \qquad (3)$$

338 $$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + H^* + HO_2^* \qquad (4)$$

339 $$HO^* + HO^* \longrightarrow H_2O_2 \qquad (5)$$

340 $$H_2O^* + H_2O_2 \longrightarrow O_2 + H_2O + HO^* \qquad (6)$$

341 $$Fe^{3+} + HO_2^* \longrightarrow Fe^{2+} + O_2 + H^+ \qquad (7)$$
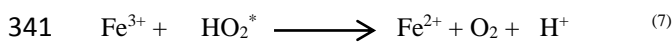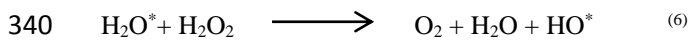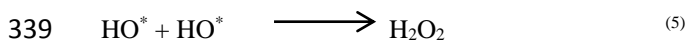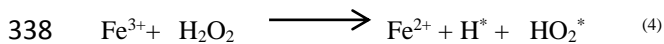
342 In the presence of organic substrate (XH), the primary product of the oxidation would be the organic radical, X•,

343 which possesses mainly reducing properties and may be consumed through the reactions with H$_2$O$_2$ and Fe^{3+}.

344 $$HO^* + XH \longrightarrow H_2O + X^* \qquad (8)$$

345 $$X^* + H_2O_2 \longrightarrow XOH + HO^* \qquad (9)$$

346 $$X^* + Fe^{3+} \longrightarrow Fe^{2+} + H^+ + Product \qquad (10)$$

347   It was also observed that chitosan with Fenton oxidation reduced the COD removal from 82.82 ± 1.71 % (for

348 2500 mg/L chitosan with 500 mg/L H$_2$O$_2$) to 73.08 ± 4.11% (for 2500 mg/L chitosan with 2500 mg/L FeSO$_4$

349 and 500 mg/L H$_2$O$_2$). Thus, chitosan with Fenton oxidation does not show any favourable result for the COD

350 removal and it could be concluded that the chitosan with H$_2$O$_2$ proves to be producing better results for POME

351 as compared to chitosan with Fenton oxidation.

352 **3.6 Economic analysis and performance comparison with other technologies**

353 The chitosan coagulation coupled with H$_2$O$_2$ as a POME treatment method has been compared to other reported

354 work to evaluate its performances and has been shown in Table 2.

355

356

357

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 1m³ of POME under optimum conditions is MYR/m³ 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).

374   **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**

375

376

377   **4 Conclusions**

378   The effectiveness of chitosan, $FeSO_4$, combined chitosan with H_2O_2 and combined chitosan with Fenton

379   oxidation were evaluated for the AAD-POME. From the results it could be concluded that chitosan has been

380   identified as an effective coagulant for maximum COD removal. Also, $FeSO_4$ addition to chitosan is favourable

381   for TSS removal but not for COD removal. The TSS removal was improved from 66.59 % (2500 mg/L of

382   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

383   was improved from 85.15 % (2500 mg/L chitosan without any H_2O_2) to 89.92 % (2500 mg/L chitosan with

384   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

385   mixing time; 1 h of sedimentation time; and a pH of 7. It could be concluded that chitosan coagulation coupled

386   with H_2O_2 proves to be a better alternative for the post-treatment of anaerobically digested POME due to its

387   improved performance, safe handling and availability.

388   **Acknowledgements**

392

References

394   1. Abood A, Bao J, Abudi Z, Zheng D, Gao C (2013) Pretreatment of nonbiodegradable landfill leachate

395   by air stripping coupled with agitation as ammonia stripping and coagulation–flocculation processes

396   Clean Technol Environ Policy 15**:** 1069-1076

397   2. Aboulhassan MA, Souabi S, Yaacoubi A, Baudu M (2006) Improvement of paint effluents coagulation

398   using natural and synthetic coagulants aids. J Hazard Mater 138: 40–45

399   3. Ahmad AL, Chong MF, Bhatia S (2009) A comparative study on the membrane based palm oil mill

400   effluent (POME) treatment plant. J Hazard Mater 171: 166-174

401   4. Ahmad AL, Sumathi S, Hameed BH (2006) Coagulation of residue oil and suspended solid in palm oil

402   mill effluent by chitosan, alum and PAC. Chem Eng J 118: 99-105

403   5. Al-Shorgani N, Kalil M, Ali E, Hamid A, Yusoff, W (2012) The use of pretreated palm oil mill

404   effluent for acetone–butanol–ethanol fermentation by Clostridium saccharoperbutylacetonicum N1-4.

405   Clean Technol Environ Policy 14**:** 879-887

406   6. Andreozzi R, Caprio V, Insola A, Marotta R (1999) Advanced Oxidation Processes (AOP) for water

407   purification and recovery. Catalysis Today 53: 51-59

408   7. Ariffin A, Razali MAA, Ahmad Z (2012) PolyDADMAC and polyacrylamide as a hybrid flocculation

409   system in the treatment of pulp and paper mills waste water. Chem Eng J 179: 107-111

410   8. Assaad E, Azzouz A, Nistor D, Ursu AV, Sajin T, Miron DN (2007) Metal removal through synergic

411   coagulation–flocculation using an optimised chitosan-montmorillonite system. Appl Clay Sci 37: 258–

412   274

413   9. Bhatia S, Othman Z, Ahmad AL (2007) Coagulation and flocculation process for POME treatment

414   using Moringa oleifera seeds extract: Optimization studies. Chem Eng J 133: 205-212

415   10. Bhatia S, Othman Z, Ahmad AL (2007) Pretreatment of palm oil mill effluent (POME) using Moringa

416   oleifera seeds as natural coagulant. J Hazard Mater 145: 120–126

417   11. Bolto B, Gregory J (2007) Organic polyelectrolytes in water treatment. Water Res 41: 2301-2324

418   12. Bratskaya SY, Avramenko VA, Schwarz S, Philippova I (2006) Enhanced flocculation of oil-in-water
419   emulsions by hydrophobically modified chitosan derivatives. Colloids Surf A 275: 168–176

420   13. Cailean D, Teodosiu C, Friedl A (2014) Integrated Sono-Fenton ultrafiltration process for 4-
421   chlorophenol removal from aqueous effluents: assessment of operational parameters (Part 1). Clean
422   Technol Environ Policy 16: 1145-1160

423   14. Chaiprapat S, Laklam T (2011) Enhancing digestion efficiency of POME in anaerobic sequencing
424   batch reactor with ozonation pretreatment and cycle time reduction. Bioresource Technol 102: 4061-
425   4068

426   15. Chan YJ, Chong MF, Law CL (2010) Biological treatment of anaerobically digested palm oil mill
427   effluent (POME) using a Lab-Scale Sequencing Batch Reactor (SBR). J Environ Manage 91: 1738-
428   1746

429   16. Chen Y, Liu C, Nie J, Wu S, Wang D (2014) Removal of COD and decolorizing from landfill leachate
430   by Fenton's reagent advanced oxidation. Clean Technol Environ Policy 16: 189-193

431   17. Cheng WP, Chi FH, Yu RF, Lee YC (2005) Using chitosan as a coagulant in recovery of organic
432   matters from the mash and lauter wastewater of brewery. J Polym Environ 13: 383–388

433   18. Chi FH, Cheng WP (2006) Use of chitosan as coagulant to treat wastewater from milk processing
434   plant. J Polym Environ 14: 411–417

435   19. Chong MF (2007) Simulation and design of membrane based palm oil mill effluent (POME) treatment
436   plant from pilot plant studies .PhD. Thesis. Universiti Sains Malaysia

437   20. Chu L, Wang J, Dong J, Liu H, Sun X (2012) Treatment of coking wastewater by an advanced Fenton
438   oxidation process using iron powder and hydrogen peroxide. Chemosphere 86: 409-414

439   21. Chu L, Wang J, Dong J, Liu H, Sun X (2012) Treatment of coking wastewater by an advanced Fenton
440   oxidation process using iron powder and hydrogen peroxide. Chemosphere 86: 409-414

441   22. Chungsiriporn J, Prasertsan S, Bunyakan C (2006) Minimization of water consumption and process
442   optimization of palm oil mills. Clean Technol Environ Policy 8: 151-158

443   23. Crini G, Badot PM (2008) Application of chitosan, a natural aminopolysaccharide, for dye removal
444   from aqueous solutions by adsorption processes using batch studies: a review of recent literature. Prog
445   Polym Sci 33: 399–447

446   24. Divakaran R, Pillai VNS (2001) Flocculation of kaolinite suspensions in water by chitosan. Water Res
447   35: 3904–3908

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

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

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

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

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

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

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

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

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

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

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

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

472   37. Kestioğlu K, Yonar T, Azbar N (2005) Feasibility of physico-chemical treatment and Advanced
473   Oxidation Processes (AOPs) as a means of pretreatment of olive mill effluent (OME). Process Biochem
474   40: 2409-2416

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

477   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

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

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

511   56. Wu TY, Mohammad AW, Jahim JM, Anuar N (2009) A holistic approach to managing palm oil mill
512   effluent (POME): Biotechnological advances in the sustainable reuse of POME. Biotechnol Adv 27:
513   40-52

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

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

518   59. Zinatizadeh AAL, Mohamed AR, Mashitah MD, Abdullah AZ, Isa MH (2007) Optimization of pre-
519   treated palm oil mill effluent digestion in an up-flow anaerobic sludge fixed film bioreactor: A
520   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) with$FeSO4$ (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)

23

24

25

26

27

28

Fig. 1

29

30

31

32

33

34

35

36

37

38

39
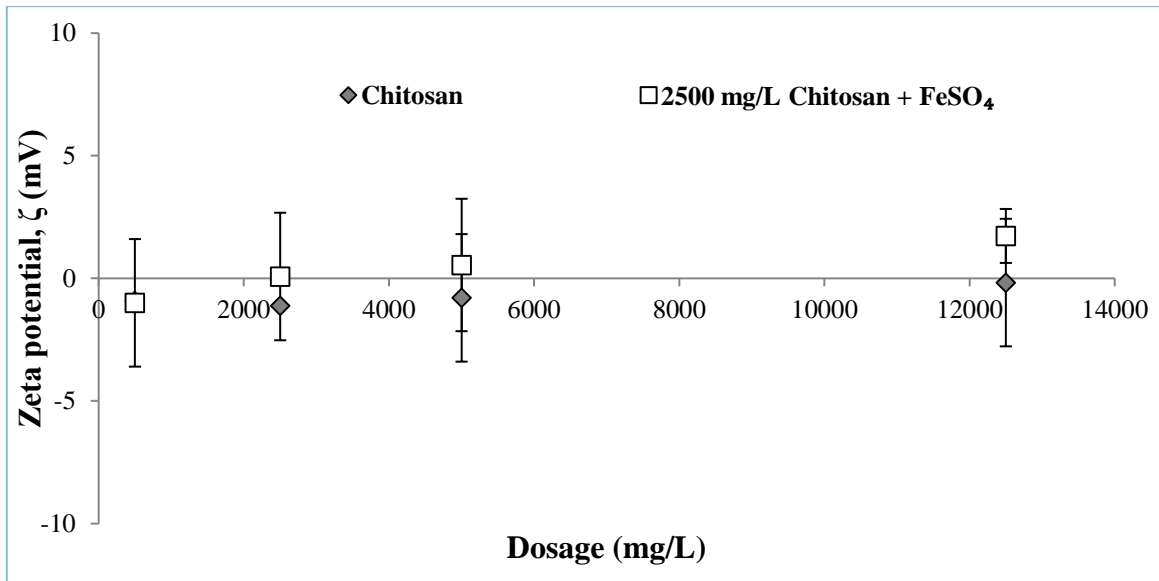
40
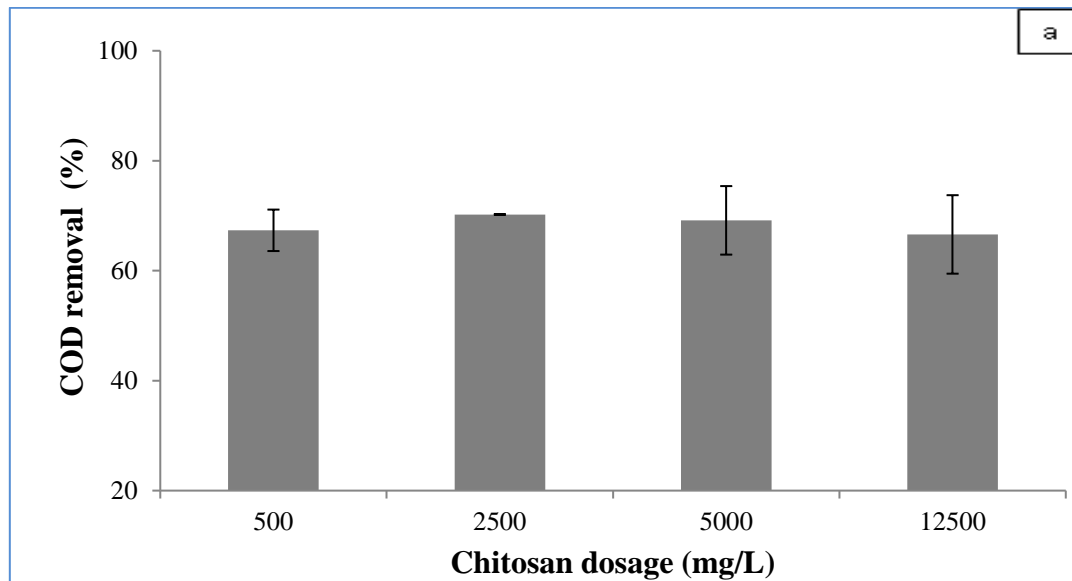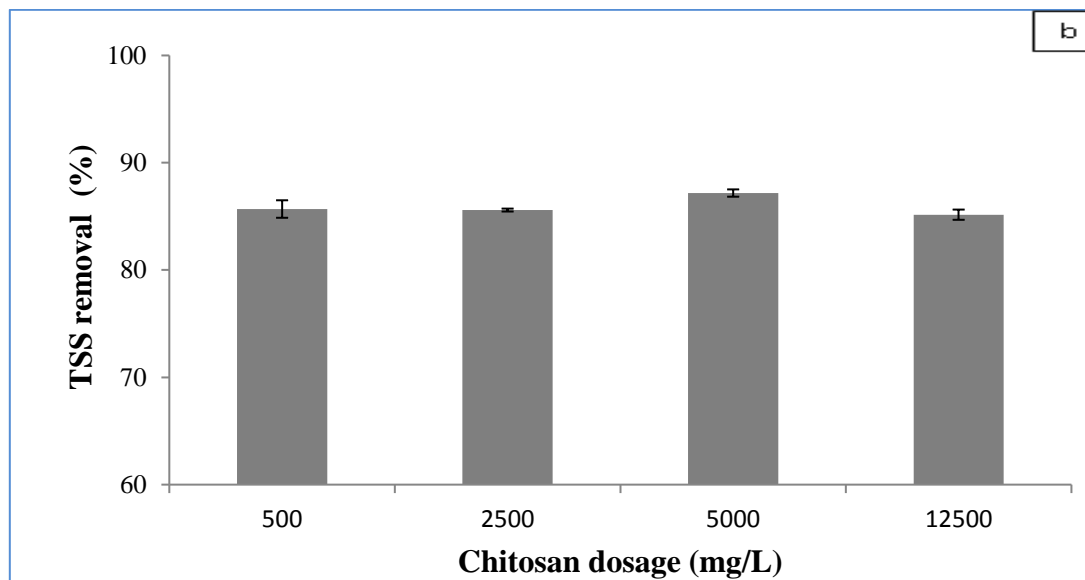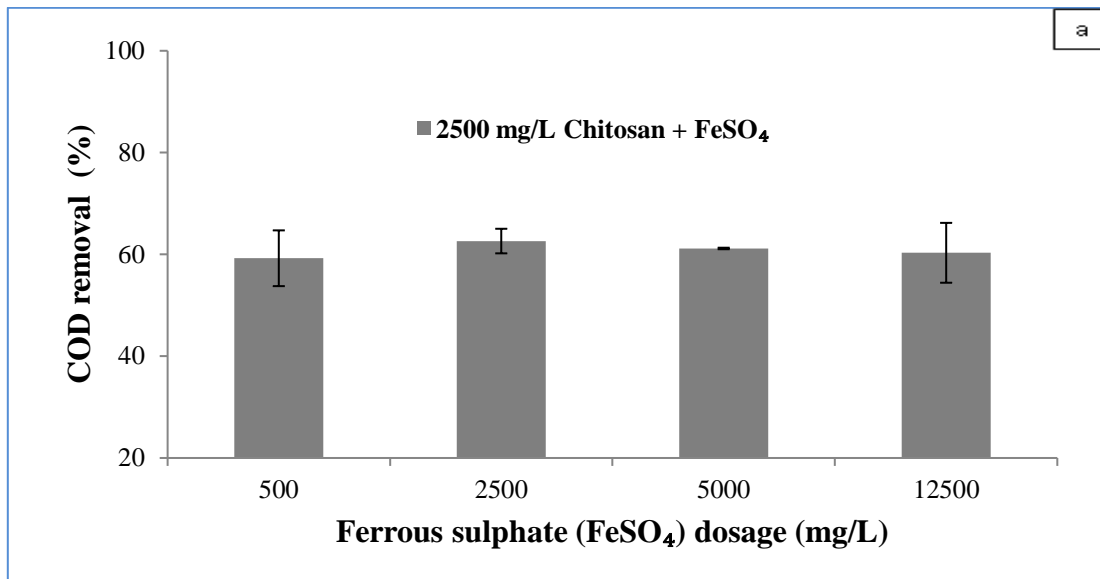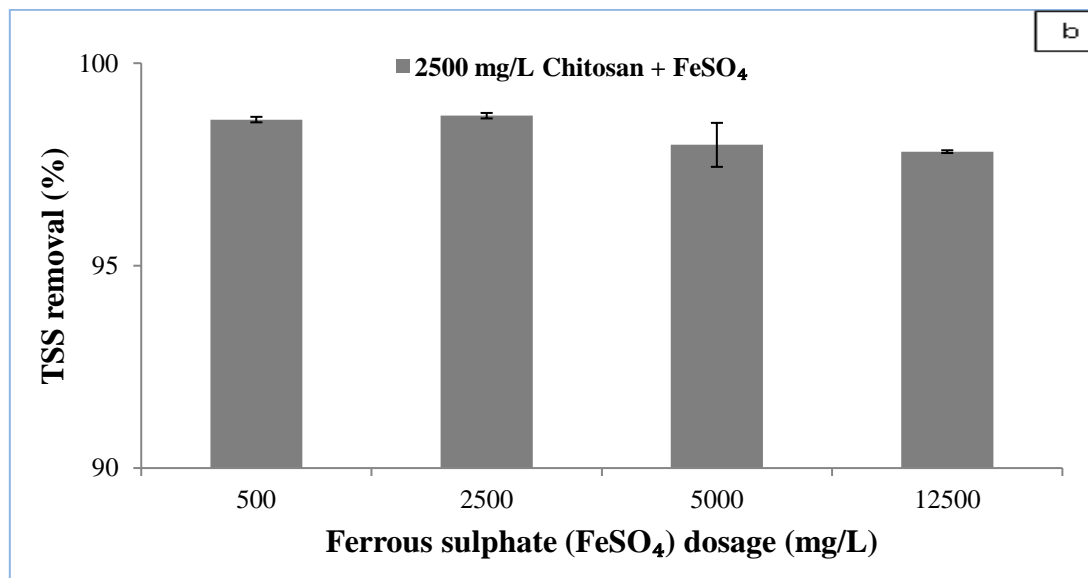
Fig.2

42

43

44

45

46

47

48

49

50

51

52

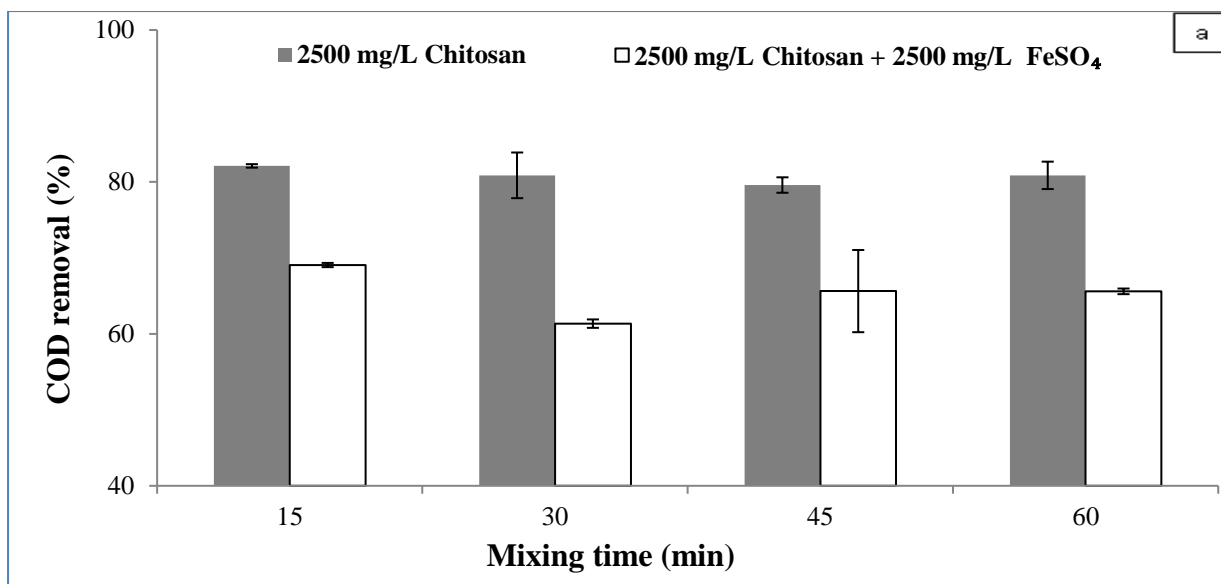53   **Fig.3**

54

55

56

57

58

59
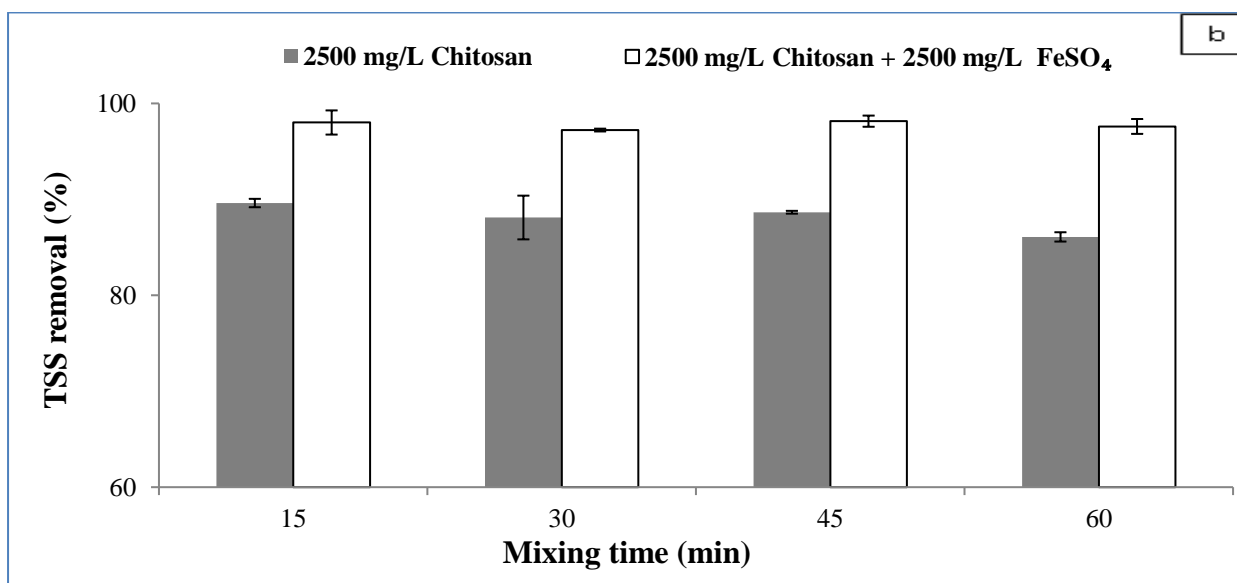
60

61

62

63
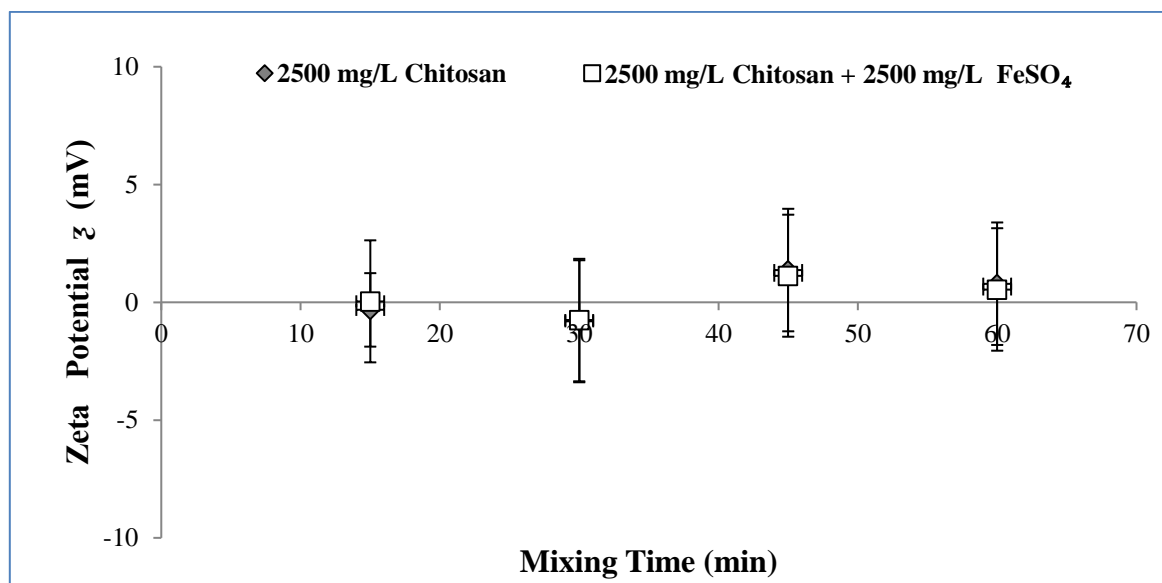
64

65

66

67

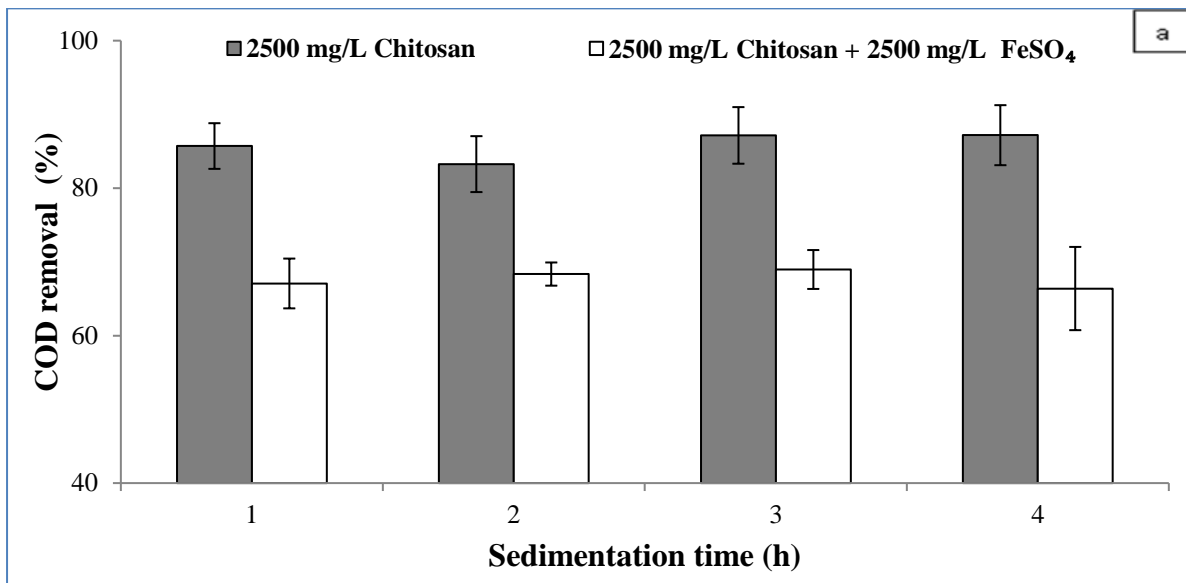68   **Fig. 4**

69

70

71

72

73

74

75

Fig.5

77

78

79

80

81

82

83

84

85

86

87

88

89

90

91   **Fig. 6**

92

93

94

95

96

97

98

99

100

101

102   **Fig.7**
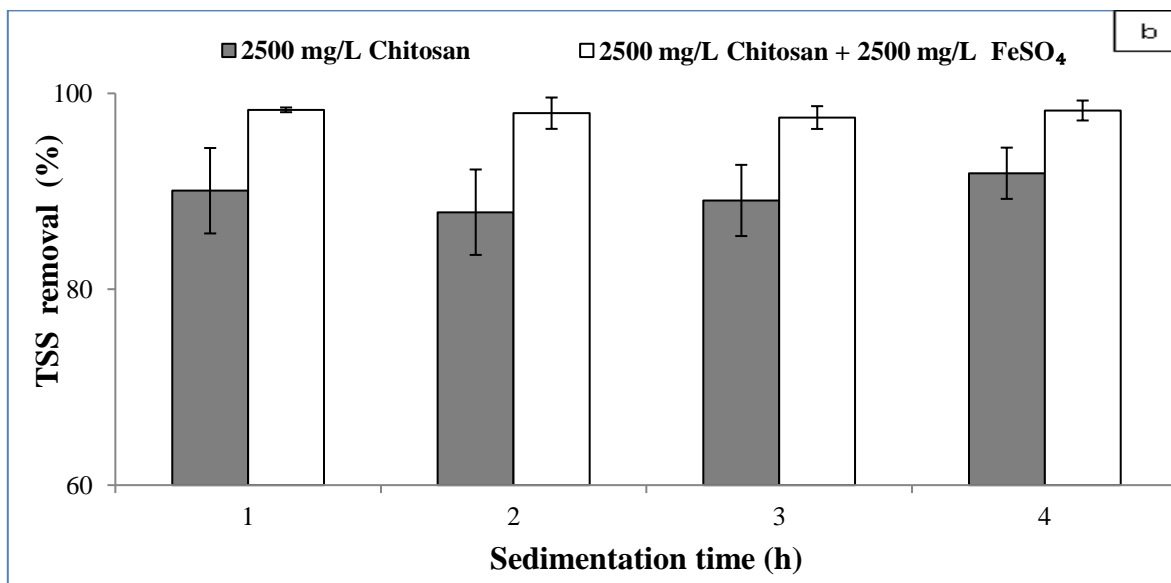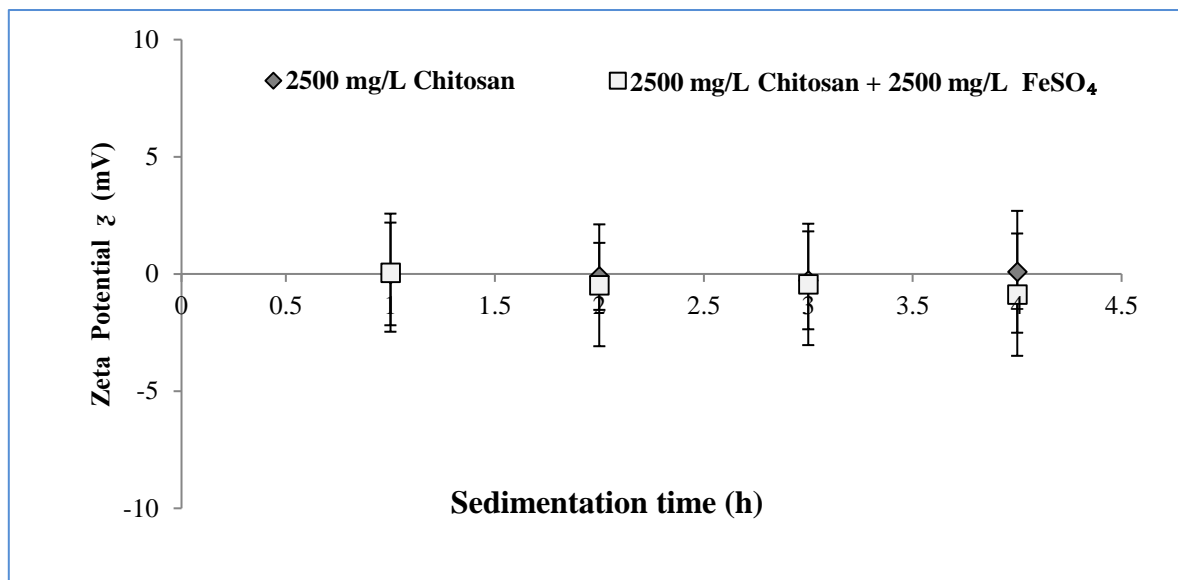
103

104

105

106

107

108

109

110

111

112

113

114

Fig. 8

115
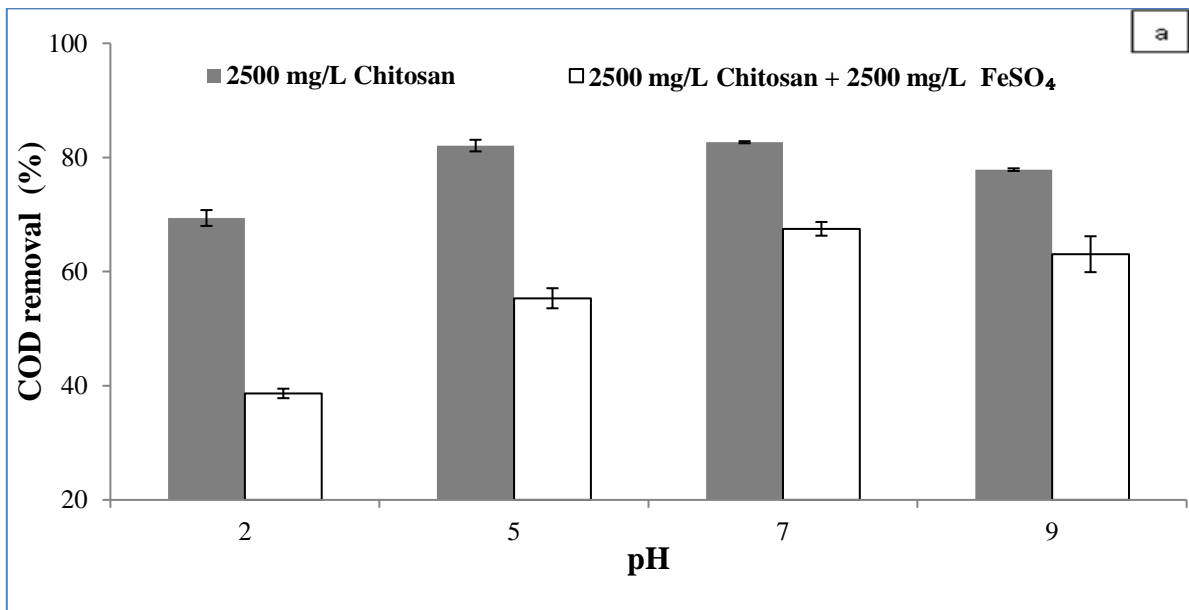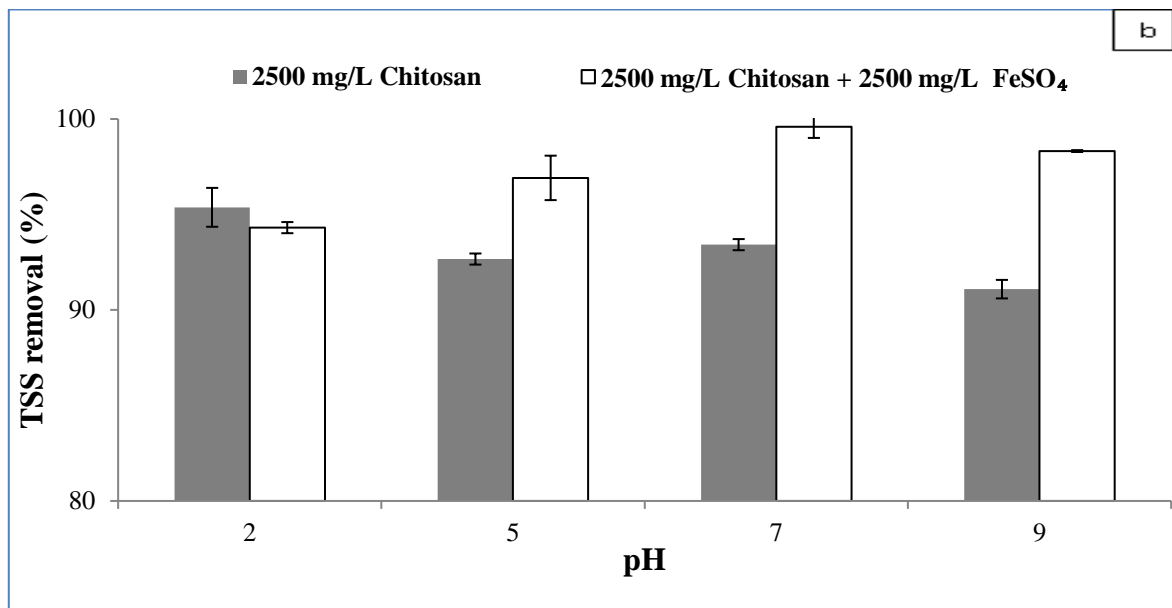
116

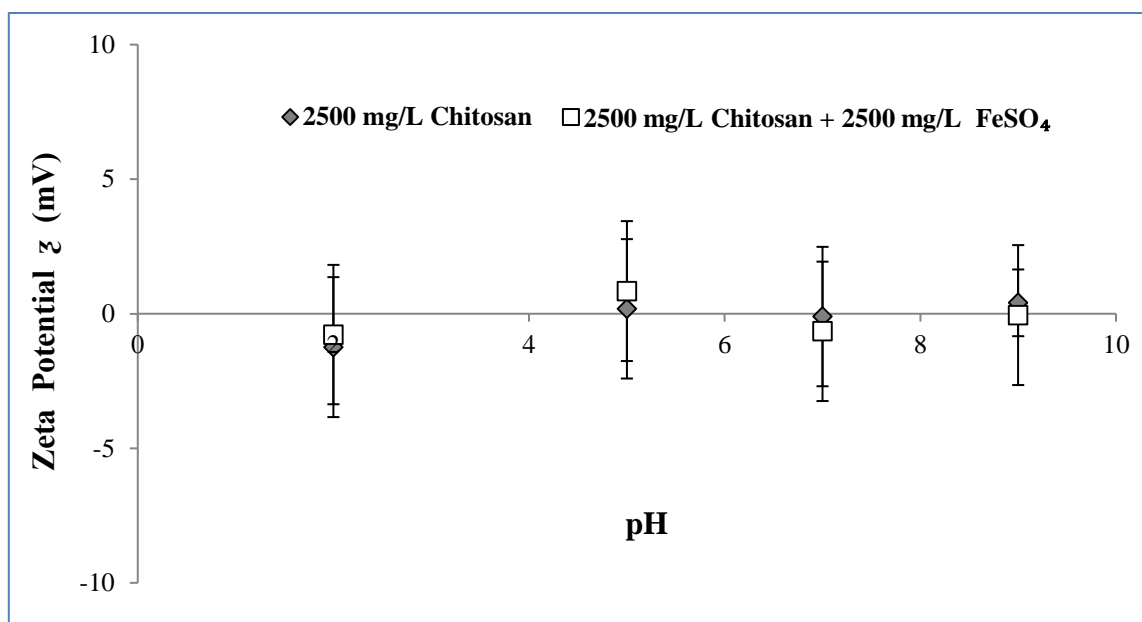117

118

119

120

121

Fig. 9

122

123

124

125

126

127

128
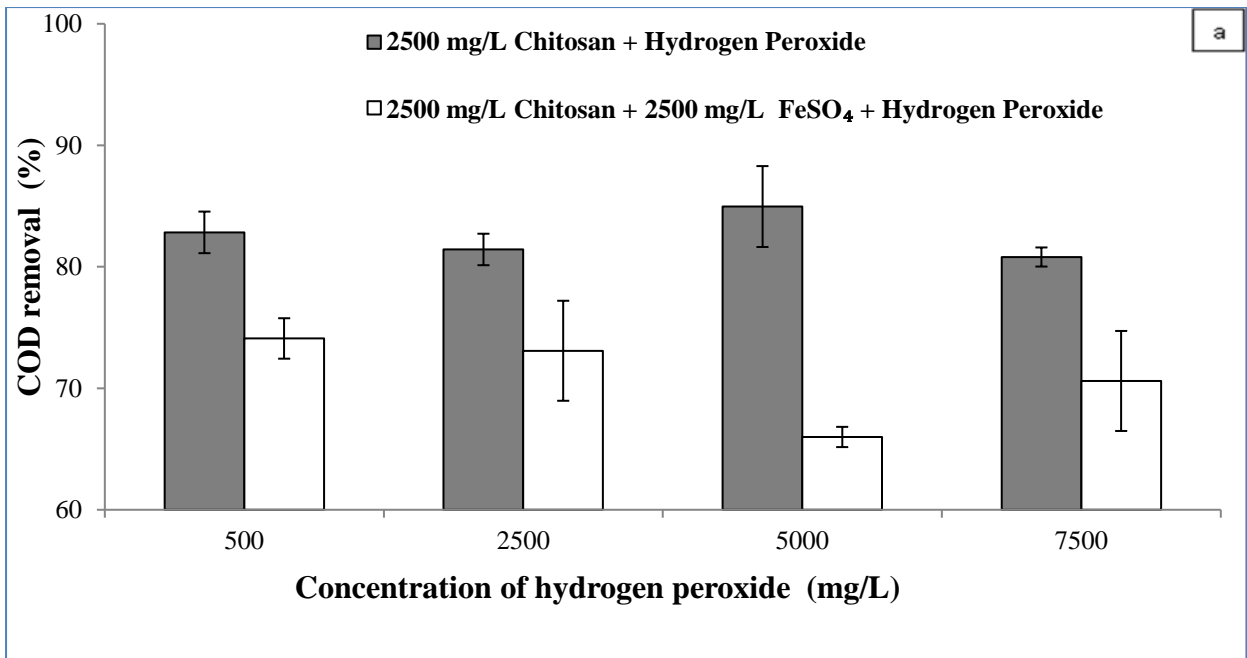
129

130

131

132

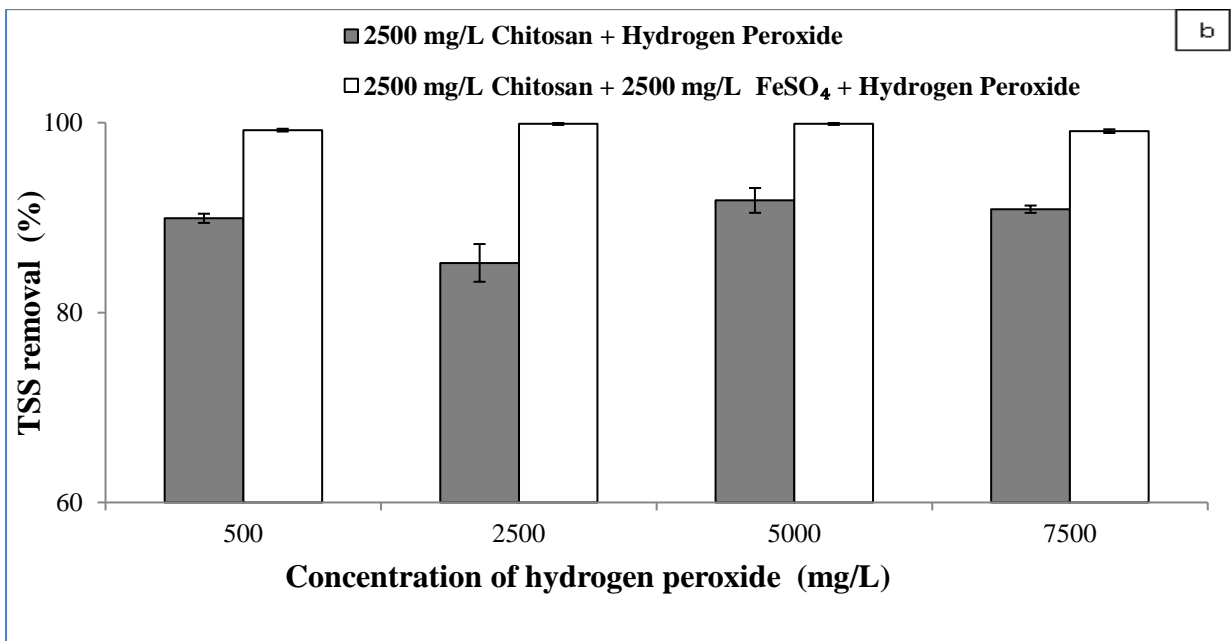
133

134   **Fig.10**
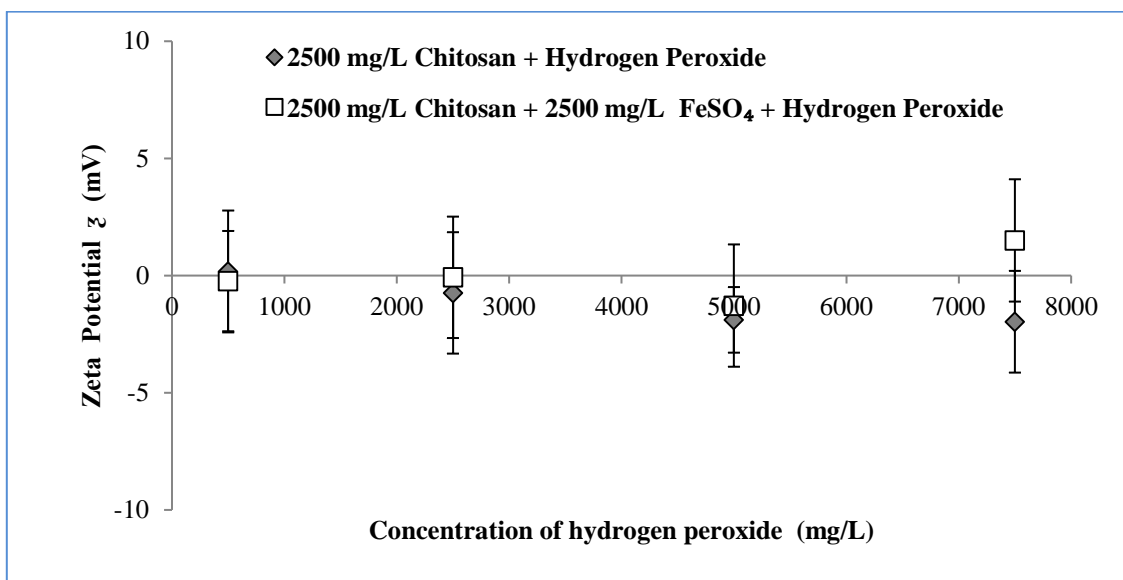
135

136

137

138

139

140

141

142

143   **Fig.11**

144

145

146

147

1 **List of tables**

2 **Table 1**

3 POME discharge standards set by Department of Environment (DoE), Malaysia under the
4 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

5 a: All parameters are in mg/L except pH

6 **Table 2**

7 Performance comparison between activated carbon (AC) adsorption and ultrasound (US)

8 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

9 *ND: Not detected