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A Novel Hybrid Approach of Activated Carbon and Ultrasound Cavitation for the Intensification of Palm Oil Mill Effluent (POME) Polishing

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33 **Abstract**

34 This investigation focuses on activated carbon (AC) adsorption and ultrasound (US)
35 cavitation for polishing the palm oil mill effluent (POME). Both AC adsorption and US
36 cavitation were investigated individually, in series and operating them in a combined way.
37 The efficiency of above processes has been evaluated in terms of removal of chemical
38 oxygen demand (COD) and total suspended solids (TSS). For the individual operation, the
39 optimisation studies were carried out by using the following conditions: AC dosage (50-200
40 g/L); contact time (2, 4, 6 h); US power amplitude (50% and 80%) and US cavitation time
41 (30-180 min). The optimisation studies utilising US power amplitude (50%) and cavitation
42 time (15 min) followed by AC adsorption using minimum AC dosage (50 g/L) and contact
43 time (30 min) resulted in ~100% COD and 83.33 % TSS removals which meets the discharge
44 limits set by the Department of Environment (DoE), Malaysia. The hybrid operation was also
45 studied by simultaneously employing AC adsorption and US cavitation and it was observed
46 that an adsorption dosage of 50 g /L resulted into achieving 73.08 % COD and 98.33 % TSS
47 removals within 15 min of US irradiation. With the possibility of continuous and feasible
48 sonochemical reactors, this hybrid approach of US cavitation followed by AC adsorption
49 could be an alternative processing technique for POME polishing.

50 **Keywords:** Palm oil mill effluent, POME, activated carbon, ultrasound, cavitation, polishing,
51 treatment, intensification

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56 1. Introduction

57 The Malaysian palm oil industry is the world's most organised national agricultural sector
58 (Oswal et al., 2002; Yacob et al., 2006). The wastewater produced during palm oil processing
59 is termed as palm oil mill effluent (POME) which is acidic, non-toxic and viscous in nature
60 (Wu et al., 2009; Ahmad et al., 2005). POME is considered to be one of the most dominant
61 sources of environmental pollution in Malaysia because of the large volume produced by the
62 palm oil mills along with a high concentration of chemical oxygen demand (COD) (65000
63 mg/L) and biochemical oxygen demand (BOD) (25000 mg/L) (Lam and Lee, 2011). The
64 Department of Environment (DoE), Malaysia has set standards for the discharge limits of
65 POME in order to prevent the environmental pollution. Table 1 shows the Environmental
66 Quality Act (EQA) 1974 for POME discharge (Wu et al., 2010). It was estimated that in year
67 2014, the total crude palm oil production was 19.66 million tonnes (MPOB, 2014) with
68 approximately 44 millionm³ of POME was generated from Malaysian palm oil mills. If the
69 POME is discharged without any further treatment, the BOD generated will be equivalent to
70 the waste generated by 75 million people which is 2.5 times the current population in
71 Malaysia (Ahmad and Chan, 2009).

72 Treating POME with anaerobic digestion followed by aerobic post treatment using the
73 ponding system is very popular among the palm oil mills, mainly because of the lower
74 equipment cost and simpler operational control to achieve the discharge limits (Poh and
75 Chong, 2009; Chaiprapat and Laklam, 2011; Zinatizadeh et al., 2007) set by the DoE,
76 Malaysia. However, there are few disadvantages to using this biological treatment, for
77 example, longer hydraulic retention time (HRT), huge investment in land for ponds and
78 digesters, and problems associated with methane gas collection which is identified to be one
79 of the most important reasons for the greenhouse effect in the environment (Bhatia et al.,

80 2007). Even after aerobic ponding, many mills are unable to achieve the discharge limits set
81 by the DoE, Malaysia (Ahmad et al., 2009; Bhatia et al., 2007).

82 Recently, due to the huge volume of treated POME discharged into the rivers along with the
83 increased uptake of water from the upper streams for the milling activities, it is predicted that
84 the rivers are no longer capable to sustain the continuous increase in the pollutants load (Wu
85 et al., 2010). The DoE, Malaysia has taken stern action by revising the discharge limit for
86 BOD from 100 mg/L to 20 mg/L (MPOA, 2010). Even though the revised discharge limit
87 has been enforced particularly in East Malaysia, the revised BOD limit has yet to be
88 implemented successfully throughout Malaysia (MPOA, 2010). Many palm oil mills have
89 adopted POME polishing technologies which include chemical treatment, biological
90 treatment with attached growth system and membrane bioreactor to add on to the current
91 treatments and thereby meeting the revised limits (Wu et al., 2010; Idris et al., 2010). The
92 above technologies often unsustainable and even fail after several months of plant trials
93 industrially. Chemical treatment is unsuitable due to the higher chemical cost, besides it fails
94 to meet the BOD limits set by the DoE, Malaysia (MPOA, 2010). Biological treatment fails
95 to further digest the remaining BOD whilst giving minimal colour reduction (Wu et al.,
96 2010). Membrane bioreactor is economically not viable due to fouling problems and low
97 BOD and colour reduction although the treated effluent quality does meet the TSS discharge
98 limits (Bhatia et al., 2007; Ahmad et al., 2009).

99 To date, research investigations on POME polishing is very limited and the lack of lab-scale
100 studies could be the major reason for the failure of industrial plant trials. On the other hand,
101 existing biological treatment such as aerobic ponding system fails to further bring down the
102 BOD to the revised discharge limits due to the limitation in the design of operation system
103 based on ponding technology as well as due to the characteristics of treated effluent itself
104 which contains the components that are difficult to be digested biologically. Only two lab-

105 scale POME polishing studies have been reported so far. The investigation using
106 ultrafiltration (UF) membrane system (Idris et al., 2010) achieved 92.8% COD and 99.3%
107 colour removals. Whereas, POME polishing using Fenton oxidation achieved 75.2% COD
108 and 92.4% colour removals and the Solar-Fenton oxidation resulted into 82.4% COD and
109 95.1% colour removals (Aris et al., 2008). Although the above treatment methods delivered
110 promising results, the cost and operation of these methods are neither cheap nor easy to
111 commercialise industrially. The disadvantages of the above proposed treatment methods and
112 the limitation in the biological treatment necessitate to find out an alternative method for the
113 efficient polishing of POME.

114 In the present investigation, polishing of biologically digested POME using AC adsorption
115 and US cavitation have been examined and a comparison in the process efficiency of these
116 two techniques has been presented. Both AC adsorption and US cavitation have been
117 investigated individually and in a hybrid mode for the removal of COD and TSS. The
118 investigation with individual operation was aimed to establish the baseline performance for
119 comparison while the hybrid operation forms the novelty of this investigation.

120 Adsorption is a physical separation process in which the adsorbed material is not chemically
121 altered (Soto et al., 2011; Rafatullah et al., 2010). During adsorption, the components to be
122 removed accumulate at the interface between the AC (adsorbent) and the wastewater (liquid
123 phase). The adsorbing capacity of AC is always associated with very high surface area per
124 unit volume (Demir et al., 2008; Chiang et al., 2012). In this process, the material being
125 adsorbed (e.g., pollutant) is removed from one phase (e.g., wastewater) and transferred to
126 another phase (e.g., AC) (Joseph et al., 2012). AC is one of the most popular adsorbents and
127 hence used extensively for wastewater treatment (McCafferty et al., 2000; Miyake et al.,
128 2003).

129 Cavitation is defined as the formation, growth and subsequent collapse of bubbles over a
130 small time period resulting in the generation of large magnitudes of energy over a specific
131 location (Gogate, 2002; Mahamuni and Adewuyi, 2010; Gallipoli and Braguglia, 2012). The
132 four types of cavitation are acoustic, hydrodynamic, optic and particle. Among these four
133 types, only acoustic and hydrodynamic cavitation has gained much popularity among
134 researchers and industries owing to their energy efficiency and ease of commercialisation
135 (Gogate, 2002; Mahamuni and Adewuyi, 2010). Acoustic or ultrasonic cavitation is defined
136 as the application of sound waves in the range of 16 to 100 kHz thereby creating pressure
137 variations to generate the required cavitational intensity (Jyoti and Pandit, 2000).
138 Hydrodynamic cavitation is defined as the velocity variations that are being created by the
139 operating pressure differences induced by using a specific geometry which acts as a
140 cavitation generator (Sivakumar and Pandit, 2002; Chakinala et al., 2008). According to
141 modelling studies using Rayleigh–Plesset equation, during the collapse of these bubbles
142 (Sivakumar and Pandit, 2002), higher temperatures and pressures (5000k and 1000 atm)
143 occur in the liquid phase (Sivakumar and Pandit, 2002).

144 Employment of US cavitation technology for the wastewater treatment is not fully explored
145 as yet. There are reports of using US cavitation technology for the degradation of a wide
146 variety of contaminants. Sivakumar et al. investigated the degradation of p-nitrophenol by
147 employing a dual frequency flow cell of frequencies 25 and 40 kHz with 120 W as the power
148 input (Sivakumar et al., 2002). It was reported that the effect of coupled frequencies was
149 much higher than the individual frequency operation and the rate constants were inversely
150 proportional to the operating temperature. Dichloromethane and O-dichlorobenzene were
151 degraded by using a double frequency system of 16 and 20 kHz in the power range of 200-
152 500 W/plate (Thoma et al., 1997). Degradation studies were also undertaken for p-
153 nitrophenol and carbon tetrachloride (CCl₄) by using an ultrasonic probe of 20 kHz with 135

154 W power input. It was reported that the presence of CCl_4 was beneficial as it increased the
155 rate of degradation of p-nitrophenol (Hua and Hoffman, 1996). Coupling sonication via an
156 ultrasonic bath of 40 kHz frequency and 150 W of power input followed by wet oxidation on
157 the refractory waste containing organic acids and sodium sulfate (Na_2SO_4) was carried out. It
158 was observed that such a coupling of ultrasound and wet oxidation improved the rate of
159 degradation as compared to sonication or wet oxidation alone (Ingale and Mahajani, 1995).

160 By looking at the potential behind US cavitation, it is definitely a possible option and could
161 be further explored for the degradation of POME. Thus, the present investigation examines
162 the effectiveness of ultrasonic cavitation for POME polishing where it degrades the organic
163 components of POME that are difficult to be digested biologically. With ultrasonic cavitation
164 the degradation or oxidation of organic components occurs through pyrolysis and free radical
165 attack (Gogate, 2002). Volatile, non-polar and hydrophobic components are easily degraded
166 by pyrolysis as they easily enter into the cavitation bubbles in the vapour form and exposed to
167 the collapsing conditions of bubbles. Besides pyrolysis, hydroxyl radicals or H_2O_2 generated
168 in the bubbles attack the components and induce oxidation.

169 Previous research investigations have shown that a higher colour (80-93%), COD (75-85%)
170 and TSS (91-97%) removal efficiencies were possible using AC adsorption in various types
171 of effluents including textile, pulp and paper industries (Satyawali and Balakrishnan, 2007;
172 Ahmad and Hameed, 2009; Ayoub et al., 2011). A comparative study was carried out for
173 residual oil and TSS removal in POME utilising chitosan, bentonite and activated carbon
174 (Ahmad et al., 2005). It was reported that chitosan was observed to achieve better TSS
175 (99.8%); oil and grease removal (99%) when compared to activated carbon and bentonite.
176 Another comparative study was carried by Osuidea et al., 2006 for the tertiary treatment of
177 POME utilising modified sawdust with propenoic acid and activated carbon which was
178 previously clarified using iron (III) chloride and lime resulting in a clear effluent with broader

179 reuse applicability. Therefore, AC adsorption and US cavitation technologies seem to be
180 viable and have potential to explore them for polishing the POME. AC adsorption is expected
181 to be able to adsorb traces of difficult to digest organic components instantaneously for a
182 reduction in COD and TSS while US cavitation is expected to demonstrate a similar
183 performance by degrading or oxidising these organic components.

184 Besides their individual applications, the hybrid process of AC adsorption and US cavitation
185 is aimed at reducing the operation time and improving the finally treated effluent quality
186 either by degradation of difficult to be adsorbed pollutants by US cavitation or by the
187 adsorption of difficult to be degraded pollutants onto AC. Preliminary studies with individual
188 operation of AC adsorption and US cavitation focusing on the optimisation of treatment
189 efficiencies were conducted. Following this, the effectiveness of AC adsorption and US
190 cavitation in series and in a combined operation was then explored.

191 **2. Materials and methods**

192 **2.1 Chemicals and reagents**

193 Biologically digested POME samples were collected from the last pond before discharge
194 from a palm oil mill in Dengkil, Malaysia. The samples were at room temperature (25.5 ± 3
195 $^{\circ}\text{C}$) and the characteristics of the sample differ based on the processing facilities of palm oil,
196 climate, season and environmental conditions. The COD and TSS were in the range of 4700
197 ± 550 mg/L and 1800 ± 282 mg/L respectively. The samples were preserved at less than 4°C
198 to avoid biodegradation and were allowed to thaw to room temperature before use. The term
199 “biologically digested POME” would be addressed as “POME” in the subsequent sections for
200 the sake of simplicity. AC (40 grade) was supplied by GlobeChem (Malaysia) Sdn. Bhd.
201 Distilled water was used for diluting 37 % hydrochloric acid (Merck, Germany) and sodium

202 hydroxide pellets (R&M chemicals, NJ, USA) into a 5 M solution for pH adjustment of the
203 effluent.

204 **2.2 Methods**

205 **2.2.1 Optimisation of AC adsorption**

206 The experiments were carried out in a digital orbital shaker (Heidolph unimax 1010,
207 Germany), enabling eight conical flasks to be mixed at a time. Each flask was filled with 100
208 ml of POME with AC at different dosages between 50-200 g/L and the flasks were rapidly
209 shaken at the speed of 100 rpm for various mixing times (2-6 h). At the end, the samples were
210 centrifuged (Eppendorf 5430, Hamberg, Germany) at 3000 rpm for 15 min and the
211 supernatant (polished POME) was collected for COD and TSS analysis.

212 **2.2.2 Optimisation of US cavitation**

213 A bench-top industrial ultrasonic processor (Model UIP 1000hd, 20 kHz, 1000 W, Hielscher,
214 Teltow, Germany) was employed for this study. It consists of an electrical generator, an IP65
215 grade transducer and a cylindrical titanium sonotrode (horn) (Fig. 1). 200 ml of POME taken
216 in a reactor was subjected to ultrasound and was cooled using an external cooling jacket,
217 where the temperature was maintained at 20 °C. The mechanical vibrations at the sonotrode
218 could be varied by adjusting the power amplitude from 50 to 100%. The maximum power
219 output of 1000 W could be delivered by using the maximum power amplitude of 100%. The
220 conditions employed for the optimisation were: US power amplitude (50% and 80%) and US
221 cavitation time (30-180 min).

222 **2.2.3 US cavitation followed by AC adsorption**

223 Using the previous optimisation studies, US irradiation was carried out at 50% power
224 amplitude for 90 min where samples were taken at an interval of 15 min for COD and TSS

225 analysis. After treatment with ultrasound, the samples were then subjected to AC adsorption
226 using 200 g/L dosage for up to a contact time of 6 h. This AC adsorption was carried out in a
227 digital orbital shaker using 100 rpm. At the end of this process, the samples were centrifuged
228 (Eppendorf 5430, Hamberg, Germany) at 3000 rpm for 15 min with the supernatant (polished
229 POME) was collected for COD and TSS analysis. Studies were also conducted by reducing
230 the US cavitation time to 15 min from 90 min followed by utilising AC adsorption with the
231 reduced dosage of 50 g/L and with a contact time of 2 h.

232 **2.2.4 Coupled operation of AC adsorption and US cavitation**

233 Coupled operation was conducted by applying US into a reactor containing POME with AC,
234 by employing an amplitude of 50% with varying AC dosage (50-200 g/L POME) and also the
235 cavitation time (5-90 min). At the end of the process, the samples were centrifuged
236 (Eppendorf 5430, Hamberg, Germany) at 3000 rpm for 15 min with the supernatant (polished
237 POME) was collected for COD and TSS analysis.

238 **2.3 COD and TSS analysis**

239 The COD measurements were carried out using COD vials (HR 20-1500 mg/L, supplied by
240 Arachem (M) Sdn. Bhd.) according to American Public Health Association (APHA) Standard
241 method 8000 using a spectrophotometer (HACH model DR 2800, USA). TSS measurements
242 were also carried out by following the APHA Standard method 8006 using a
243 spectrophotometer (HACH model DR 2800, USA) by using 10 ml of sample in a specially
244 designed quartz cell.

245 **3. Results and discussion**

246 **3.1 Optimisation of POME polishing by using AC adsorption: Effect of AC dosage and** 247 **contact time**

248 The effects of AC dosage and contact time were investigated for POME polishing by using
249 the dosage in the range of 50-200 g/L, an operation time of 2, 4 and 6 h, a mixing speed of
250 100 rpm and at a pH 8.4 (actual pH of POME). [Fig. 2\(a\)](#) shows that an increase in the AC
251 dosage and contact time increased the removal efficiency of TSS. On the other hand, the
252 extent of TSS removal shows a larger increment when the contact time increased at lower
253 adsorbent dosage. It becomes evident that the contact time plays a crucial role in TSS
254 removal especially when the AC dosage was low as the insoluble particles of TSS required
255 longer contact time to be adsorbed on the available active sites as compared to the soluble
256 components contributed to COD. For the COD removal ([Fig. 2\(b\)](#)), an AC dosage of 200 g/L
257 with a contact time of 2 h was found to be most efficient operating parameters in attaining
258 ~100% removal efficiency. For an AC dosage of 50 g/L, $97.8 \pm 0.03\%$, $98.9 \pm 0.22\%$ and
259 $\sim 100 \pm 0.07\%$ COD removals were obtained at 2, 4 and 6 h respectively.

260 Maximum COD removal (~100%) was observed for AC dosages of 150 g/L and 200 g/L
261 irrespective of the contact time. The components present in POME were removed to a
262 maximum extent either by using an increased adsorbent dosage or by increasing the contact
263 time by using a lower AC dosage via AC adsorption. These findings are in support of the
264 observations reported earlier by several authors ([Mohanty et al., 2008](#); [Mohammed and](#)
265 [Chong, 2014](#); [Shavandi et al., 2012](#)). The increased adsorbent dosage indirectly refers to the
266 increased surface area, which means an increased availability of adsorption sites to adsorb the
267 organic compounds during the treatment. The adsorption mechanism of AC for the removal
268 of organic compounds was purely physical and chemically unaltered. The three major
269 mechanisms associated with the adsorption are physisorption, chemisorption and ion-
270 exchange ([Ahmaruzzaman, 2008](#)). In treating the POME, physisorption could be considered
271 as the driving mechanism which is mainly due to the Van der Waals force of attraction
272 between the organic molecule and the adsorbent. Due to this, the intermolecular adsorption

273 takes place between the positively charged adsorbent (AC) and the negatively charged
274 adsorbate (components of POME) on the available surface energy sites (Malik, 2004).
275 Normally the exchange of electrons does not happen during the physiosorption. Similarly, the
276 same phenomenon of physiosorption could be the reason for the increased contact time with
277 improved removal efficiency. By increasing the contact time, the intermolecular interactions
278 between the adsorbate and adsorbent due to the Van der Waals force of attraction has
279 indirectly improved, resulting in higher removal efficiency. Thus, maximum removal for
280 COD (~100%) and TSS (~100%) was obtained at the contact time of 6 h and with the AC
281 dosage of 200 g/L.

282 **3.2 Optimisation studies of POME polishing by the individual operation of US** 283 **cavitation: Effect of US amplitude and cavitation time**

284 Experiments were conducted using the cavitation time of 30-180 min and US power
285 amplitudes of 50% and 80%. Samples were collected and analysed for COD and TSS at 30
286 min intervals. It was observed that for TSS reduction, 50% amplitude resulted into the TSS
287 reduction of 95 ± 1.96 % after 90 min of US irradiation and the removal remained constant
288 until the end of operation (180 min) (Fig. 3(a)). When the study was conducted using 80%
289 amplitude, there was no increase in the TSS reduction after 30 min of operation; with the
290 maximum TSS reduction of 82.77 ± 4.71 % was observed after 60 min of cavitation time.

291 For COD, (Fig. 3(b)), 80% reduction was observed in the first 30 min of operation and then a
292 fluctuation in the COD reduction was observed till 180 min of ultrasonic irradiation for both
293 amplitudes. These observations are in good agreement with Sangave and Pandit (2004), who
294 have investigated the effect of ultrasound pretreatment on the biological degradation of
295 distillery wastewater and Sivakumar et al. (2014), who investigated the role of H₂O₂ in the
296 fluctuating patterns of COD during the treatment of POME using pilot-scale triple frequency

297 ultrasound cavitation reactor. Normally for the degradation of organic compounds utilising
298 ultrasound cavitation, selection of proper power amplitude is highly crucial.

299 The ultrasound passage in the liquid induces sonochemical reactions as well as hydrodynamic
300 mechanical shear forces. Generally sonochemical reactions are effective at higher frequencies
301 i.e. 200-1000 kHz whereas the hydrodynamic mechanical shear forces are dominating at
302 lower frequencies less than 100 KHz ([Sangave and Pandit; 2004](#)). In the present study, these
303 hydrodynamic mechanical shear forces are responsible for the transformation of the
304 molecules structurally rather than the complete degradation of the effluent wastewater
305 ([Sangave and Pandit; 2004](#)). The sonochemical reactions could be explained by 4 different
306 types of mechanisms namely hot spot, electrical, plasma discharge and supercritical
307 ([Adewuyi, 2001](#)). Normally when US is irradiated into the effluent, formation of many
308 microbubbles occurs in the first stage followed by the violent collapse of these bubbles
309 producing localised hot spots of super critical conditions involving high temperature and
310 pressure. Owing to this, the dissociation of water molecules to generate hydroxyl radicals
311 occurs. Normally the degradation is possible in three different regions of the bubble. The first
312 region would be the inner region of bubble having higher pressure and temperature; the
313 second region would be the interface between the bubble and the bulk liquid and the final
314 region would be the bulk solution. Normally pyrolysis and free radical attack are responsible
315 for the first two regions whereas the hydroxyl radical attack is the predominant reaction that
316 occurs at the bulk liquid ([Gogate, 2002](#)). The degradation of organic compounds normally
317 depends upon the concentration of the energy dissipated during the violent collapse of the
318 generated bubble cavities ([Sivakumar et al., 2014](#)). This means that larger the bubble size
319 higher the degradation rate of organic compounds.

320 However this may not be true for all the cases due to the limitations with the formation of
321 bubble cloud. The bubble cloud formation arises when the number of bubble cavities per unit

322 volume of liquid is higher and there might be a possibility of larger bubble formation which
323 disturbs the sound waves transmitted between the vessel walls and the transducer tip. Due to
324 this interference, only very less concentration of cavitation energy dissipates into the system
325 to induce the degradation of POME. Thus the resultant energy dissipated by using 80%
326 power amplitude predicted to be lower than by using 50%.

327 It was also observed that the degradation rates were higher in the initial periods (within 30
328 min) and this observation matches with the findings of [Desai et al. \(2008\)](#). During the free
329 radical attack, the abundant free radicals generated couple with each other forming hydrogen
330 peroxide which could be considered as less reactive compared to the free radicals and hence
331 intense sonochemical degradation could not be achieved ([Gogate, 2008](#)). This negative effect
332 of formation of hydrogen peroxide contributes to a greater extent after 30 min of operation
333 for the POME degradation. These studies support that 50% amplitude and 90 min cavitation
334 time are the suitable parameters for POME polishing which could remove $79.46 \pm 1.68\%$ of
335 COD and $95.83 \pm 1.96\%$ of TSS.

336 **3.3 Hybrid process of AC adsorption and US cavitation**

337 To increase the polishing efficiency of POME combining US cavitation and AC adsorption,
338 “in series” and “combined operations” were explored. Based on their results of individual
339 operations as presented in the previous sections, AC adsorption achieved removal efficiencies
340 of ~100% COD and TSS as compared to US cavitation which removed $79.46 \pm 1.68\%$ of
341 COD and $95.83 \pm 1.96\%$ of TSS. This observation of US cavitation indicates the degradation
342 of complex organic matter into simpler forms which can be further adsorbed by AC whilst
343 enhancing the overall performance either with improved treatment efficiency or shorter
344 operation time. Therefore, US cavitation followed by AC adsorption and then employing
345 them in combined operation is significant in the investigation. In addition, the wider

346 industrial use of AC adsorption further supports the justification for such arrangement. In the
347 coupled operation, simultaneous degradation of pollutants by US cavitation and adsorption of
348 the resultant components onto AC is expected to lead to further enhancement in the treatment
349 efficiency.

350 **3.3.1 US cavitation followed by AC adsorption**

351 Two approaches have been followed: the first approach focuses on further enhancing the
352 treatment efficiency by applying the parameters obtained from the previous optimisation
353 studies by using AC adsorption and US cavitation. Whereas, in the second approach the
354 treatment time for both US cavitation and AC adsorption was reduced without jeopardising
355 the treatment efficiency.

356 [Fig. 4](#) shows the treatment efficiency of US cavitation followed by AC adsorption at the
357 optimum operating conditions (US power amplitude (50%), cavitation time (90 min), AC
358 dosage (200 g/L) and AC contact time (6h)) obtained from the previous optimisation studies.

359 When this pretreated POME using US cavitation was further treated with AC adsorption,
360 there was a further improvement in overall treatment efficiency with complete removal of
361 COD and TSS. This improvement is mainly due to the effect of two different physical
362 treatments employing longer operation time at high AC dosage. It was further studied with
363 minimum AC dosage (50 g/L), AC contact time (2 h), US power amplitude (50%) and
364 cavitation time (15 min) and the results obtained have been shown in [Fig. 5](#).

365 The major reason for this study was to increase the removal efficiency of COD, TSS and by
366 shortening the total operation time of 90 min of US cavitation and 6 h of AC adsorption along
367 with minimizing the AC dosage. When the total operation time is shortened with minimum
368 AC dosage, it would be much more energy efficient and also commercially adaptable. After

369 the initial 15 min of US cavitation, the removal for COD and TSS were $83.61 \pm 2.40\%$ and
370 $84.92 \pm 1.96\%$ respectively as shown in Fig. 5. This improvement in the removal was mainly
371 due to the abundant availability of hydroxyl free radicals in the initial periods (within 15
372 min). After US cavitation it was then further treated with AC adsorption for 30 min and the
373 removal efficiency was improved (100 % COD removal). However, for TSS removals, no
374 improvement could be observed (Fig. 5(a)). This could be due to lower AC dosage (50 g/L)
375 and shorter AC contact time (2 h). If improved removals of TSS were desired, the AC dosage
376 and its contact time should also be increased. Thus, it could be concluded from this study that
377 15 min of US cavitation time with 50% amplitude followed by 30 min of AC adsorption at a
378 dosage of 50 g/L is sufficient to achieve the legislative requirements stated by DoE, Malaysia
379 by obtaining a maximum removal of COD ($\sim 100\%$) and TSS removal of $\sim 83\%$. When the
380 COD concentration was not detected from the final treated effluent, the BOD concentration
381 can be regarded as not detected without the need for further analysis. The shorter operation
382 time (15 min US cavitation + 30 min AC adsorption) with lower US power amplitude (50%)
383 and AC dosage (50 g/L) used are the keys to ensure that novel hybrid process of US
384 cavitation followed by AC adsorption is suitable for POME polishing. However, more
385 research should be focused on the scale-up of this combination by improving the degradation
386 efficiency both efficiently and economically before using this for POME polishing on an
387 industrial scale.

388 **3.3.2 AC adsorption integrated with US cavitation**

389 Investigations were made by varying the AC dosage, 50-200 g/L for 90 min of US cavitation
390 at 50% amplitude. It could be observed from Fig. 6 (a) that for all the AC dosages from 50-
391 200 g/L there is an increase in the COD removal efficiency within the first 15 min of US
392 cavitation. Maximum COD removals of $73.08 \pm 4.06\%$ for 50 g/L, $76.27 \pm 0.75\%$ for 100 g/L
393 and $78.82 \pm 4.36\%$ for 150 g/L were observed after 15 min of US operation.

394 The maximum COD reduction (~100% removal) was achieved at the dosage of 200 g/L after
395 15 minutes of US cavitation. The reason could be due to the free radical generation and their
396 direct attack on the complex organic molecules which were simultaneously adsorbed on the
397 active energy sites of the AC. However, for the TSS reduction (Fig. 6(b)), it was observed
398 that lower dosage i.e. 50 g/L shows a reduction of 98.33 ± 0.78 %.

399 For 100 g/L, it was observed that as the cavitation time increased the TSS removal efficiency
400 decreased. This could be due to the breakdown of the granular AC by the energy released
401 during the cavitation which in turn probably resulting into higher concentration of suspended
402 solids (Gogate, 2002). Another possible reason could be due to the formation of hydrogen
403 peroxide as well as due to degassing effects (Sivakumar and Pandit, 2001). This was mainly
404 because of the abundant OH radicals generated throughout the course of reaction thereby
405 allowing the recombination of such radicals into hydrogen peroxide and decreasing the
406 degradation rate of POME. Overall, it could be concluded that 50 g/L achieved a COD (73.08
407 ± 4.06 %) and TSS (98.33 ± 0.78 %) removal within 15 min of US cavitation.

408 **3.4 Performance comparison between AC adsorption and US cavitation**

409 Table 2 shows the performance comparison between individual, series (US cavitation
410 followed by AC adsorption) and coupled operations of AC adsorption and US cavitation.

411 It is clear that AC adsorption shows predominant removal efficiency for COD and TSS when
412 it was operated individually, compared to US cavitation. However, the major drawback for
413 this AC adsorption is the requirement of longer contact time (6 h) and higher dosage (200
414 g/L). On the other hand, US cavitation achieved good removals of COD (79.46 ± 1.68 %) and
415 TSS (95.83 ± 1.96 %) within a shorter operation time of 90 min. When US cavitation and AC
416 adsorption were applied in series, the total operation time was further reduced to 45 min (15

417 min US cavitation and 30 min AC adsorption) with good results for TSS ($83.61 \pm 2.40\%$) and
418 COD ($\sim 100\%$) removals.

419 In the case of AC adsorption coupled with US cavitation, the operation time was further
420 reduced to 15 min with AC dosage of only 50 g/L, obtaining $73.08 \pm 4.06\%$ COD and 98.33
421 $\pm 0.78\%$ TSS removals. It could be concluded that due to the lengthy operation time and the
422 amount of AC involved, even though AC adsorption in separate operation shows very good
423 removal performance on POME, it will not be a promising treatment alternative for
424 commercialization. On the other hand, series operation using US cavitation followed by AC
425 adsorption with a shortened operation time (45 min) and lower AC dosage (50 g/L) achieves
426 the discharge limits set by the DoE. Thus the present work highlights the use of US cavitation
427 with AC adsorption as a suitable alternative for POME polishing treatment in terms of the
428 destruction of complex organic pollutants.

429 **4. Conclusions**

430 The optimisation studies were conducted for POME polishing employing individual
431 application of AC adsorption and US cavitation, applying them in series and then in a
432 combined mode. For AC adsorption, it was observed that increasing the AC dosage (200 g/L)
433 and contact time (6 h) has resulted into complete COD ($\sim 100\%$) and TSS ($\sim 100\%$) removals
434 for POME polishing. The major drawback for this AC adsorption is the requirement of longer
435 contact time (6 h) and higher dosage (200 g/L). However, for US cavitation, 50% amplitude
436 and 90 min cavitation time were selected as the suitable operating condition which achieved
437 the maximum removal of $79.46 \pm 1.68\%$ for COD and $95.83 \pm 1.96\%$ for TSS respectively.
438 The investigation was further continued by utilising US cavitation (15 min) followed by AC
439 adsorption (2 h contact time with the dosage of 50 g/L), which showed good COD ($\sim 100\%$)
440 and TSS ($\sim 83\%$) removals. Hybrid process of AC adsorption and US cavitation had resulted

441 in the maximum COD ($73.08 \pm 4.06\%$) and TSS ($98.33 \pm 0.78\%$) removals for 50 g/L dosage
442 and 15 min US irradiation time. The obtained results clearly demonstrate the potential of
443 operating US cavitation (15 min) followed by AC adsorption (30 min) which could be used
444 as a polishing step after the anaerobic-aerobic treatment of POME in the industries. In this
445 case, the total treatment time was shortened to 45 min and achieved the discharge limits set
446 by the Department of Environment (DoE), Malaysia for COD and TSS removal. With the
447 possibility of continuous and feasible ultrasonic cavitational reactors, this hybrid approach of
448 US cavitation followed by AC adsorption in series could be an alternative green processing
449 technique for polishing the POME.

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- 597

1 **Figure Captions**

2 Figure 1. Experimental setup of POME treatment using ultrasound horn system

3 Figure 2. Effect of dosage of activated carbon on (a) TSS removal (%) and (b) COD removal
4 (%) at different contact time

5 Figure 3. Effect of ultrasound cavitation time and amplitude on (a) TSS removal (%) and (b)
6 COD removal (%)

7 Figure 4. Effect of ultrasound cavitation (90 min) followed by activated carbon adsorption (6
8 h contact time and 200 g/L dosage) on (a) TSS removal (%) and (b) COD removal (%)

9 Figure 5. Effect of ultrasound cavitation (15 min) followed by activated carbon adsorption (2
10 h contact time and 50 g/L dosage) on (a) TSS removal (%) and (b) COD removal (%)

11 Figure 6. Effect of activated carbon adsorption coupled with ultrasound cavitation on (a) TSS
12 removal (%) and (b) COD removal (%)

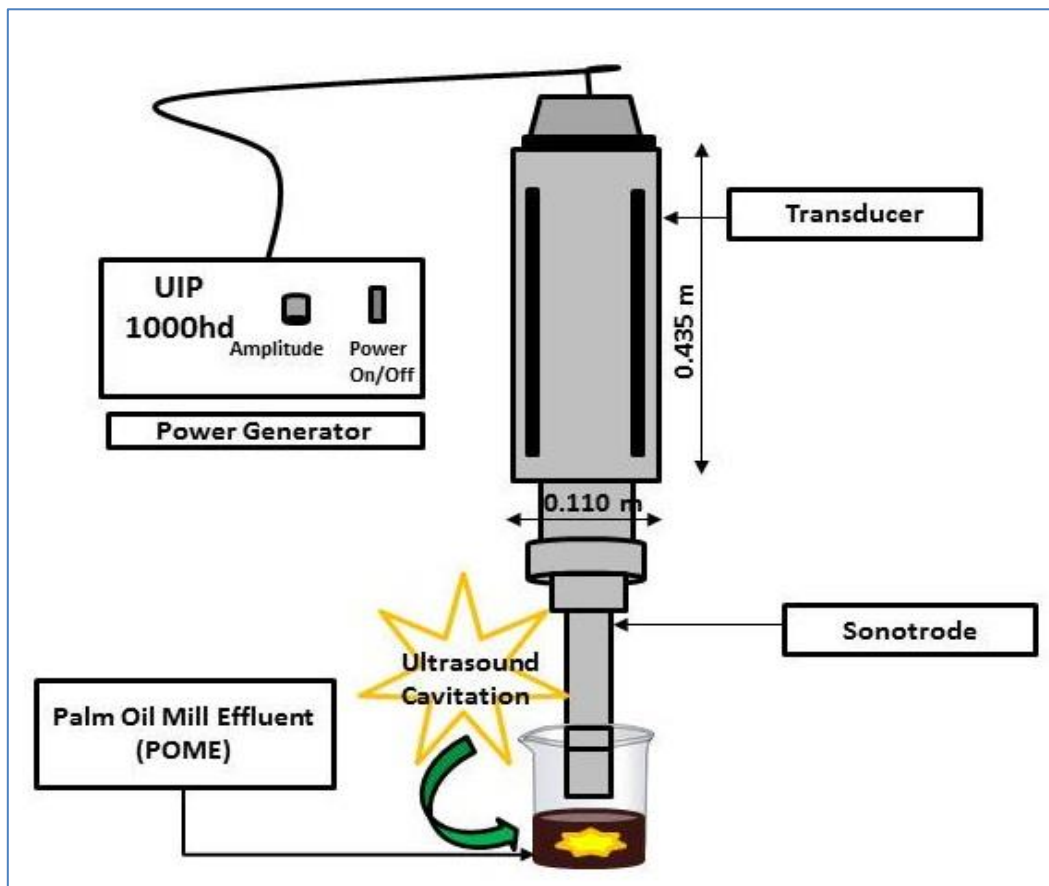
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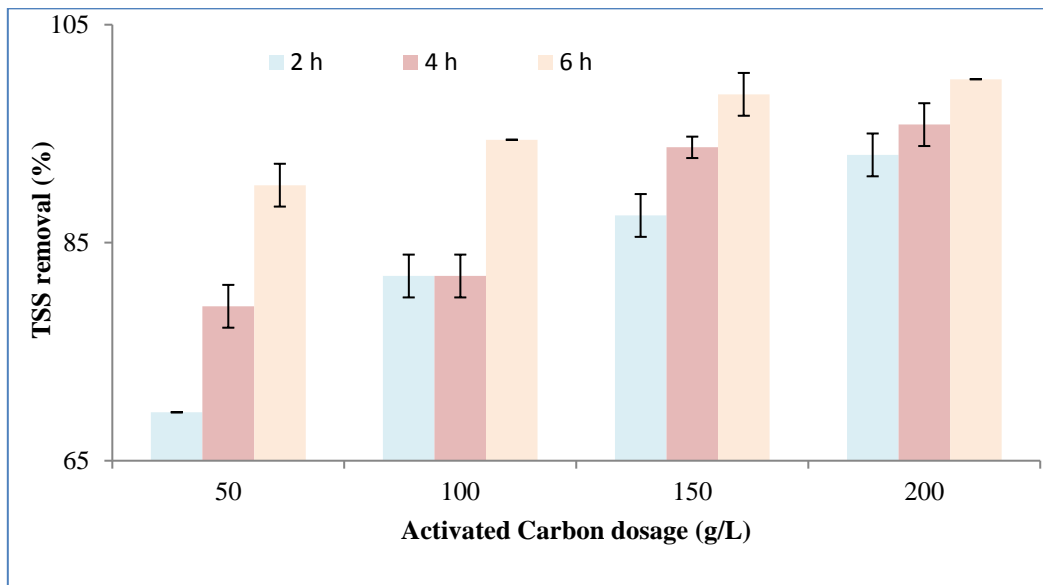
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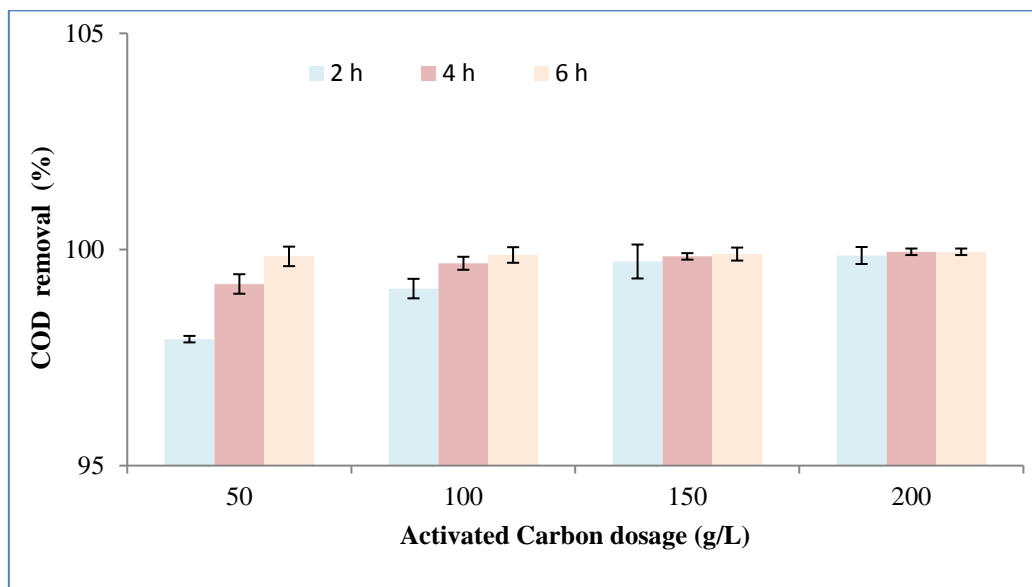
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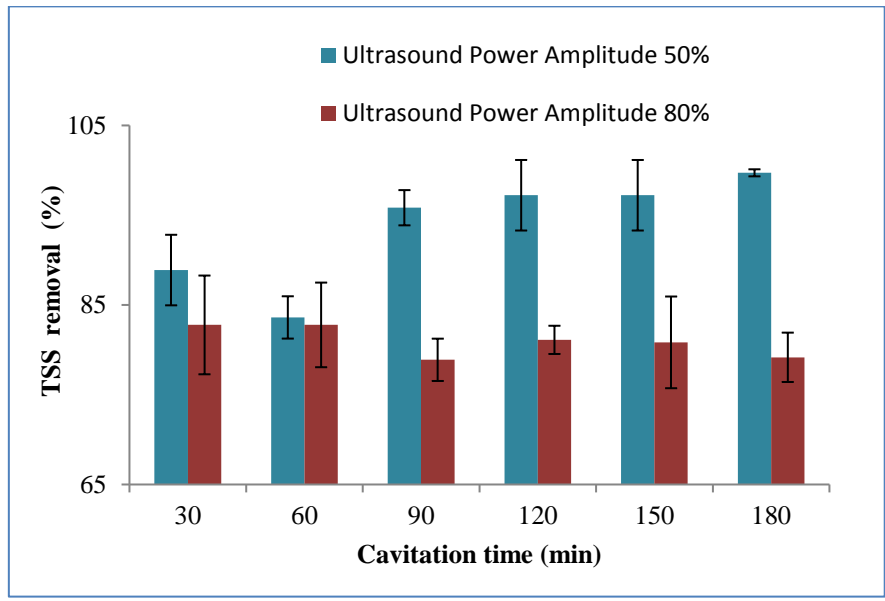
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Fig. 2.

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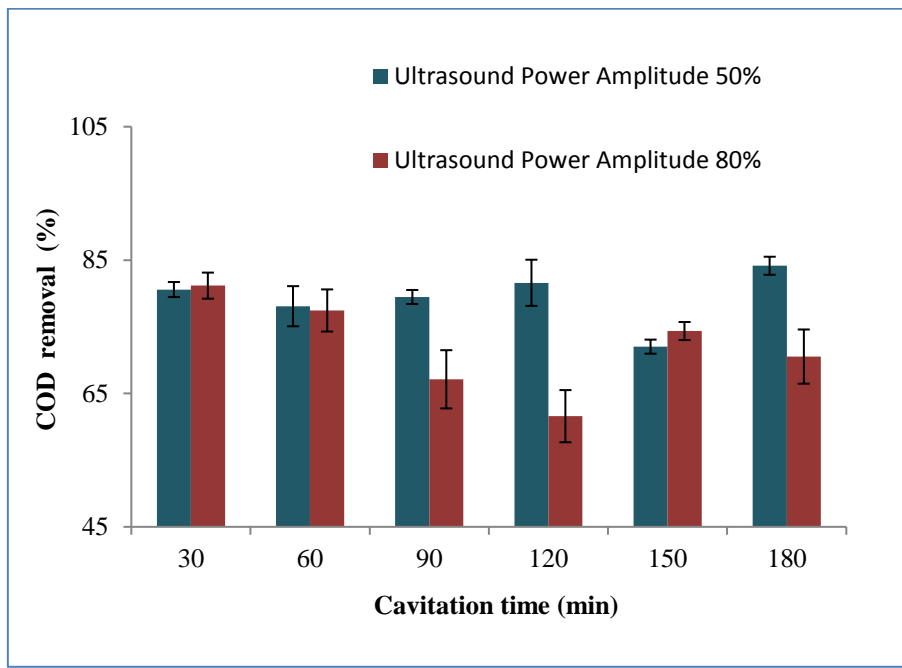


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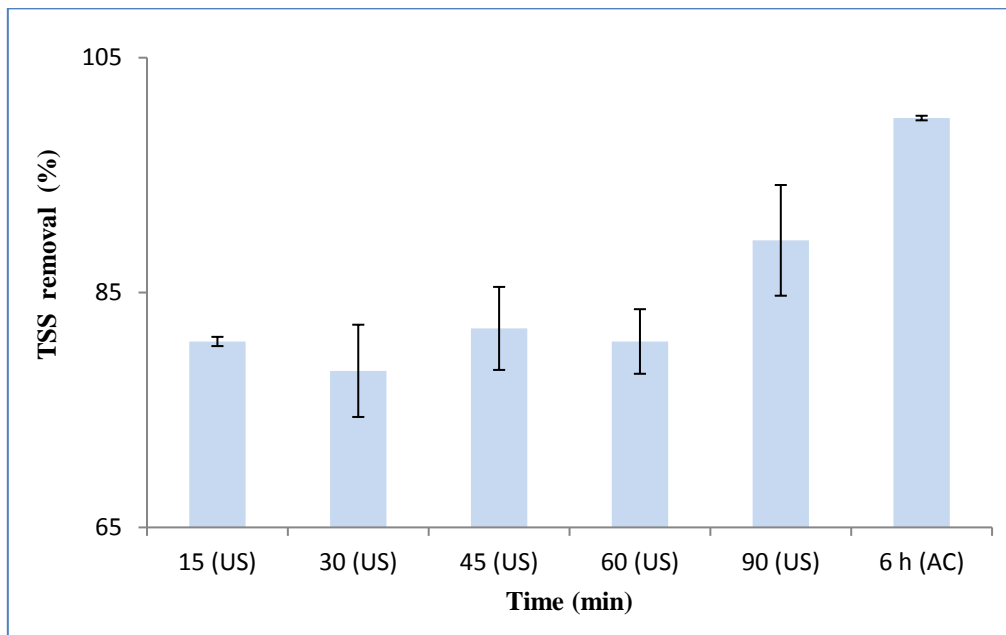
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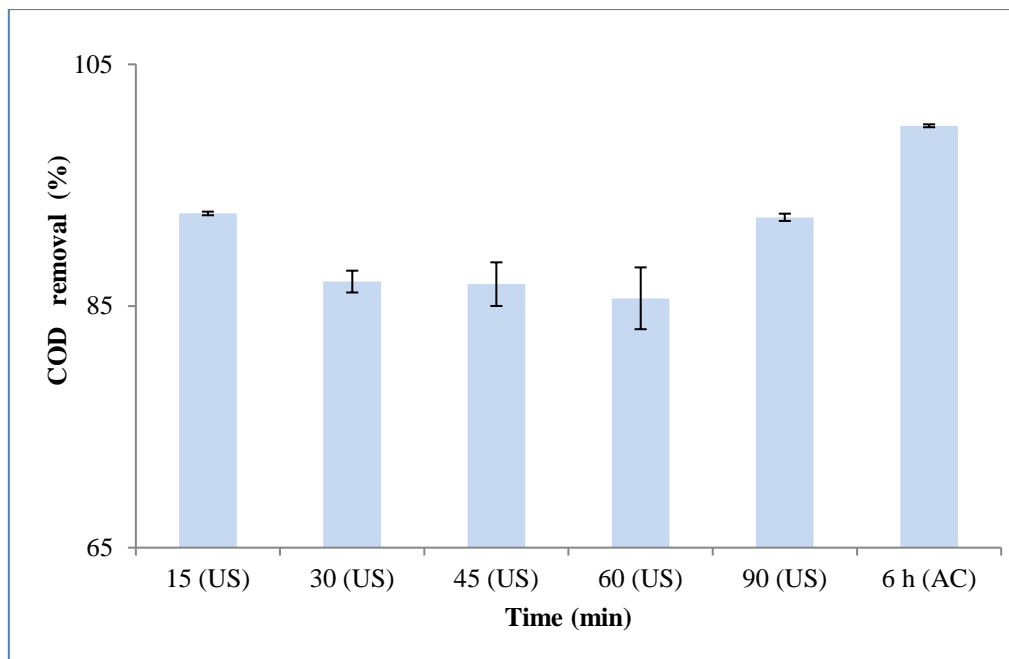
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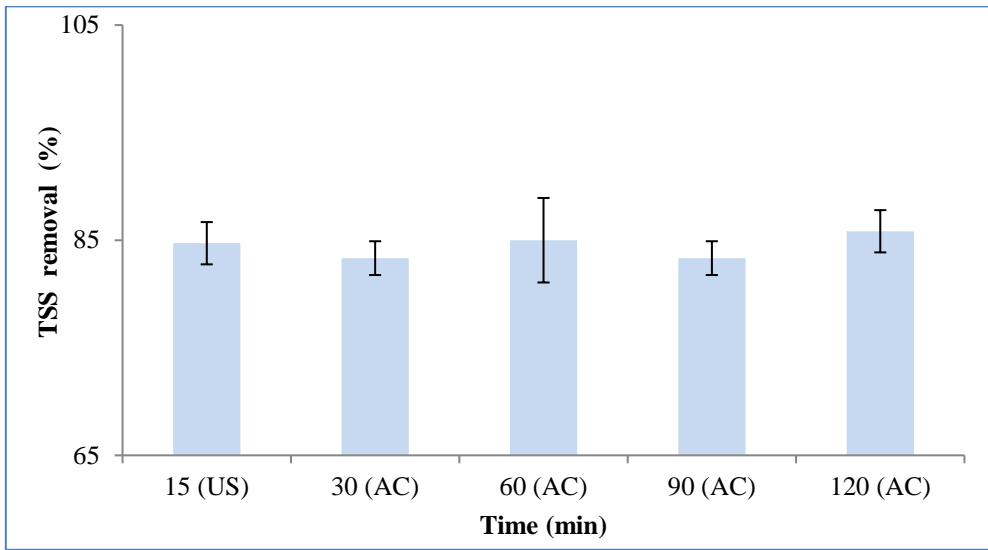
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Fig. 4.

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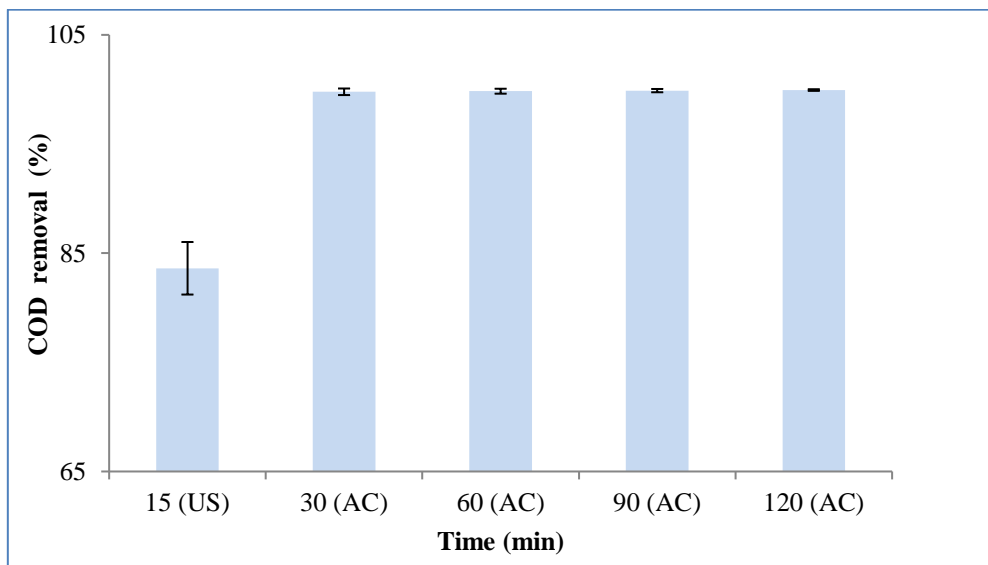


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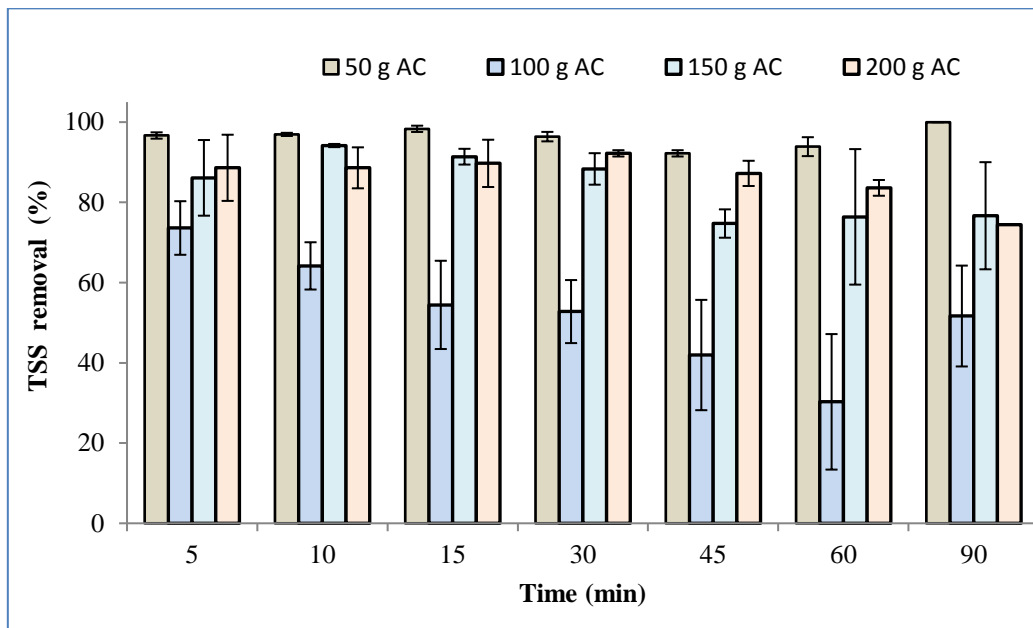
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Fig. 5.

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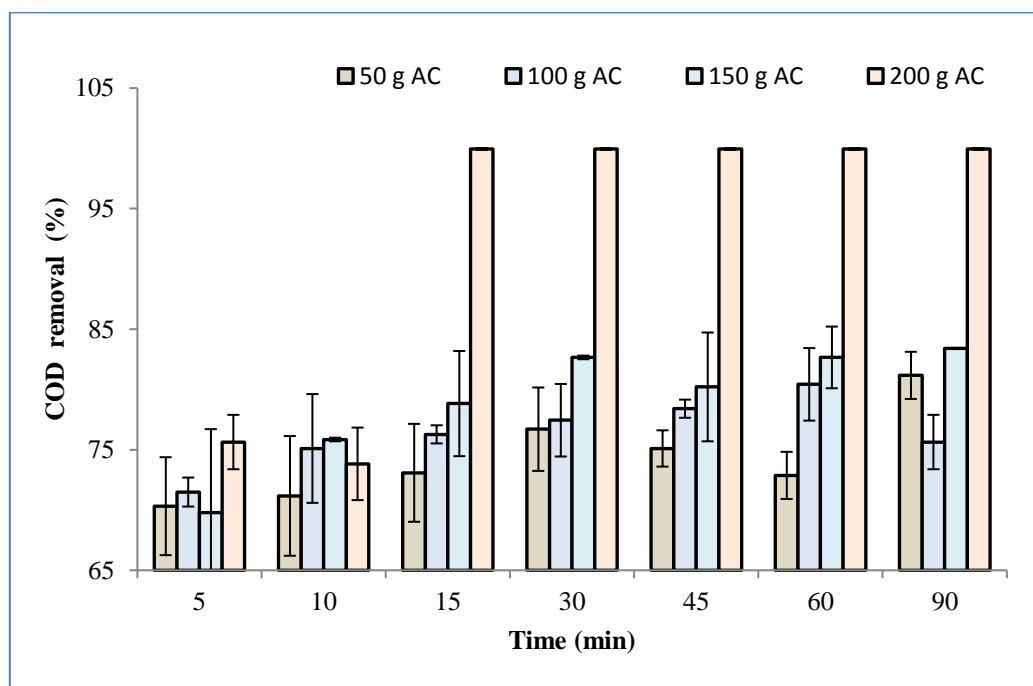
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(a)



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(b)

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Fig. 6.