

1 **A comprehensive study on floc characterization and coagulant performance of natural**  
2 ***Cassia obtusifolia* seed gum in treatment of raw pulp and paper mill effluent**

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## 13 ABSTRACT

14 The pulp and paper industry generates 30-180 m<sup>3</sup> of wastewater per ton of manufactured pulp  
15 and 20-70 m<sup>3</sup> of wastewater per ton of manufactured paper and paperboard. Coagulation process  
16 is widely applied as a pre-treatment or primary treatment to remove suspended solids from  
17 industrial effluent including pulp and paper mill effluent (PPME). Nevertheless, the use of  
18 inorganic coagulants, such as alum, poses deleterious environmental impacts and risks to living  
19 organisms include low biodegradability, increase of metal content in discharged effluent,  
20 generation of toxic sludge. In view of this, the present study investigated the potential use of  
21 natural *Cassia obtusifolia* seed gum in treatment of raw and undiluted PPME through  
22 coagulation process. Recommended conditions (pH 5, 0.75 g/L dosage, 10 rpm and 10 min slow-  
23 mixing, and 1 min settling time) allowed *C. obtusifolia* gum removed high total suspended solids  
24 and chemical oxygen demand up to 86.9 and 36.2%, respectively. Findings from the present  
25 study showed that the coagulation efficiency using *C. obtusifolia* gum was comparable to alum.  
26 Also, *C. obtusifolia* gum, alum, and their flocs were shown to have distinctive features when  
27 characterized. The difference in peak occurrence from Fourier-transform infrared spectroscopy  
28 analysis indicated that the mechanism of floc formation using *C. obtusifolia* gum and alum  
29 differed. Besides that, dissimilar thermal decomposition stages were observed for *C. obtusifolia*  
30 gum and alum through thermogravimetric analysis. Scanning electron microscope images  
31 showed that flocs formed using *C. obtusifolia* gum was highly fibrous-like and aggregate,  
32 whereas irregularly-shaped and aggregate for alum. In conclusion, *C. obtusifolia* gum could be  
33 served as a promising alternative to alum as a natural coagulant in treatment of PPME.

34 **Keywords:** Alum; Plant-based coagulant; Primary treatment; Coagulation; Wastewater treatment

35

## 36 **1. Introduction**

37           The pulp and paper industry is a very water-intensive industry. 30-180 m<sup>3</sup> of wastewater  
38 is discharged per ton of pulp manufactured whereas 20-70 m<sup>3</sup> of wastewater is discharged per  
39 ton of paper and paperboard manufactured (Rintala and Puhakka, 1994). The toxic substances  
40 present in pulp and paper mill effluent (PPME) include various types of chlorinated compounds  
41 and pollutants such as extractives, waxes, sterols, suspended solids, fatty acids, diterpene  
42 alcohols, tannins, lignin and its derivatives (Wong et al., 2010; Oller et al., 2011; Dhir et al.,  
43 2012). In short, the contaminants in PPME are a source of major environmental concern due to  
44 its toxicity, carcinogenic risk, and accumulation in soil and water environments (Pérez et al.,  
45 2001; Wu et al., 2013a).

46           Generally, pulp and paper mill industry in Malaysia and most developing countries  
47 employs screening, coagulation-flocculation and/or primary clarification as primary treatment  
48 (Keow, 2005; Yuan et al., 2007). Coagulation is widely used in the removal of turbidity, total  
49 suspended solids, and metals from the effluent. Without undergoing appropriate separation, the  
50 solids and/or toxic substances from the raw wastewater may hinder subsequent biological  
51 treatments, resulting in lower treatment efficiency (Renault et al., 2009; Sarawasthi and  
52 Saseetharan, 2012).

53           Coagulation of PPME was studied previously using inorganic coagulants such as alum,  
54 iron-based salts, polyaluminium chloride (PAC), polyacrylamides (PAMs), and  
55 polydiallyldimethylammonium chloride (polyDADMAC) (Renault et al., 2009; Wang et al.,  
56 2011). Although the coagulation efficiency of using these inorganic coagulants is well-proven,  
57 they pose detrimental effects on human health, produce large volume of sludge and are

58 ineffective in low-temperature water (Yin, 2010). Moreover, aluminium-based coagulants have  
59 been proven to be associated with Alzheimer's disease in human beings (Yin, 2010).

60 Based on the aforementioned disadvantages, the use of natural coagulant and its  
61 derivative in coagulation process has received wide interest recently (Graham, 2008). Generally,  
62 natural coagulants pose minimal health risk to living organisms, are highly biodegradable as  
63 compared to inorganic coagulants, and are cost effective (Sanghi et al., 2006; Yin, 2010). Plant-  
64 based coagulants such as mustard seed extract (Bodlund et al., 2014), rice starch (Teh et al.,  
65 2014), guar gum (Mukherjee et al., 2013), banana stem juice (Alwi et al., 2013), *Moringa*  
66 *oleifera* (Muthuraman and Sasikak, 2014) and others were found to be effective in water and  
67 wastewater treatment. To the best of our knowledge, the use of natural and unmodified *Cassia*  
68 *obtusifolia* seed gum as a plant-based natural coagulant in the treatment of raw and undiluted  
69 PPME has yet to be investigated.

70 *Cassia obtusifolia* L. is a plant of the Leguminosae family (subfamily Caesalpinoideae)  
71 (Tripathi et al., 2011). It grows up to 2 m in height and bears 20-cm pods, which contain  
72 cylindrical seeds (Shreeji Impex, 2010; Vadivel et al., 2011). *C. obtusifolia* seed has a structure  
73 of 1,4- $\beta$ -D-mannopuranose units with 1,6 linked  $\alpha$ -D-galactopyranose units, mannose to  
74 galactose ratio of 5:1, and molecular weight of 100000-300000 g/mol (Hallagan et al., 1997). It  
75 is grown extensively in China, India and Korea (Vadivel et al., 2011). According to the  
76 Department of Agriculture, Fisheries and Forestry, Queensland, Australia (2014), the amount of  
77 *C. obtusifolia* seeds that harvested from seed reserves is estimated at 2000 seeds/m<sup>2</sup> of soil.

78 The objective of the present study was to investigate the potential use of *C. obtusifolia*  
79 seed gum as a natural coagulant in treatment of raw and undiluted PPME. The suitability of  
80 using other natural coagulants and alum during the treatment of raw and undiluted PPME was

81 also investigated and compared with *C. obtusifolia* gum. In addition, the effects of various  
82 operating conditions, such as initial pH, coagulant dosage, settling time, slow-mixing velocity,  
83 and slow-mixing time, on total suspended solids (TSS) and chemical oxygen demand (COD)  
84 removals using *C. obtusifolia* gum were studied. Coagulant and flocs characteristics were also  
85 analysed using scanning electron microscope (SEM), Fourier-transform infrared spectroscopy  
86 (FTIR), and thermogravimetric analysis (TGA).

## 87 **2. Materials and Methods**

### 88 **2.1. Preparation of *C. obtusifolia* seed gum coagulant**

89 *C. obtusifolia* seeds (Fig. 1) were procured from a local medicine store and ground into  
90 finer granules using Pulverisette 14 Variable Speed Rotor Mill. The ground seeds were kept in a  
91 tight-closed glass bottle. Fresh *C. obtusifolia* gum stock solution of 25 g/L was prepared daily.  
92 Alum (aluminium sulfate octadecahydrate) was purchased from Sigma-Aldrich with A.C.S grade  
93 and used as a control without further purification.

94

### 95 **2.2. Characterization of *C. obtusifolia* seed gum coagulant and its flocs**

96 The zeta potential of PPME samples was measured using a zeta potential analyser (Malvern  
97 Zetasizer Nano-ZS). In addition, the infrared spectra of *C. obtusifolia* gum, alum, and flocs were  
98 recorded using a FTIR spectrometer (Thermo Scientific Nicolet iS10) from 400 to 4000  $\text{cm}^{-1}$ .  
99 TGA of the coagulants and flocs were determined using a thermal analyzer (TA Instrument TGA  
100 Q50) under nitrogen atmosphere with a heating rate of 10  $^{\circ}\text{C}/\text{min}$  to 800  $^{\circ}\text{C}$ . The flocs  
101 morphology was analyzed using a SEM (Hitachi S3400N-II model).

102

### 103 **2.3. Preparation of raw and undiluted PPME**

104 Raw PPME was collected from a local board and paper mill in Kajang, Selangor, with an  
105 estimated effluent generation of 25000 m<sup>3</sup>/day. The average pH, TSS, and COD characteristics  
106 were 7.15, 841 mg/L, and 1453 mg/L, respectively. The collected wastewater was immediately  
107 stored at 4 °C to reduce possible biodegradation. The raw PPME was used in jar-test experiments  
108 without introducing any dilution.

109

### 110 **2.4. Jar-test experiment**

111 The initial pH of the raw and undiluted PPME was adjusted (pH 3-8) using 1 mol/L HCl or  
112 NaOH solution. *C. obtusifolia* gum (dosage from 0-2.0 g/L) was added into the PPME during  
113 flash-mixing stage at 150 rpm for 5 minutes. The effluent was then subjected to slow-mixing  
114 (slow mixing velocity and time were 0-50 rpm and 0-25 min, respectively) and allowed to settle  
115 for 0-5 min. The supernatant of the sample was taken 2 cm below the surface level for  
116 determining the final TSS and COD of the treated PPME.

117

### 118 **2.5. Analytical methods**

119 HACH DR 2700 <sup>TM</sup> was used for measuring TSS and COD of the samples. The TSS and  
120 COD were analysed using Photometric Method and Reactor Digestion Method, respectively.  
121 Each experimental run was repeated in three replicates (n=3). The coagulation efficiency of each  
122 experimental run was represented by TSS and COD removals as shown in Eq. (1) and (2):

123 
$$\text{TSS removal, \%} = \frac{\text{TSS}_i - \text{TSS}_f}{\text{TSS}_i} \times 100\% \quad (1)$$

124 
$$\text{COD removal, \%} = \frac{\text{COD}_i - \text{COD}_f}{\text{COD}_i} \times 100\% \quad (2)$$

125 where  $\text{TSS}_i$  and  $\text{TSS}_f$  are initial and final TSS values (mg/L) whereas  $\text{COD}_i$  and  $\text{COD}_f$  are  
126 initial and final COD values (mg/L), respectively.

127

### 128 **3. Results and discussion**

#### 129 **3.1. Potential use of natural coagulants in reducing TSS from raw and undiluted PPME**

130 The suitability of using various unmodified plant-based natural coagulants, namely *C.*  
131 *obtusifolia* gum, guar gum, tannic acid, xanthan gum and acacia were evaluated in treatment of  
132 raw and undiluted PPME (Fig. 2). It was apparent that only *C. obtusifolia* gum exhibited positive  
133 coagulant activity up to 87.7% of TSS removal as compared to the settling without coagulant  
134 (57.0% of TSS removal). However, a reduction in coagulation performance was observed with  
135 the use of guar gum, tannic acid, xanthan gum or acacia (Fig. 2). Since these coagulants did not  
136 contribute in the coagulation process of raw PPME, these coagulants remained suspended in the  
137 solution, as seen in Fig. 3, resulting in a decrease of coagulation performance. In brief, *C.*  
138 *obtusifolia* gum was effective in treating raw PPME and was utilized throughout the course of  
139 this study as a potential natural coagulant.

140

### 141 3.2. *Effect of initial pH*

142 Charge on hydrolysis pollutant and precipitation of metal hydroxides are determined by the  
143 initial pH of the solution (Sanghi et al., 2006). Therefore, pH is an important condition  
144 investigated during the coagulation treatment of PPME.

145 TSS and COD removals were investigated for PPME with initial pH values ranged from 3-  
146 8. Fig. 4 shows the effect of initial pH on the TSS and COD removals of raw PPME. Based on  
147 the results, *C. obtusifolia* gum exhibited higher coagulation activity (with maximum TSS and  
148 COD removals of 89.9% and 33.9%, respectively) under acidic conditions from pH 3-5. Since  
149 the unmodified *C. obtusifolia* gum is a non-ionic polymer, the proposed coagulation mechanism  
150 involved could be adsorption with interparticle bridging. Therefore, the charge of *C. obtusifolia*  
151 gum in the solution did not play a critical role for this mechanism. The possibility that *C.*  
152 *obtusifolia* gum performed better under acidic range (pH 3-6) was attributed to the slightly  
153 hydrolysed organic pollutants that promoted better adsorption onto *C. obtusifolia* gum.

154 On the other hand, alum performed better around neutral conditions (with maximum TSS  
155 and COD removals of 93.5% and 34.5%, respectively). Alum resulted in lower TSS and COD  
156 removals below pH 5. Under acidic environment, alum dissociates to form  $Al^{3+}$ , which is not  
157 conducive for the adsorption of colloid, adhesion, bridging and cross-linking, thus, reducing the  
158 coagulation efficiency (Zheng et al., 2011). In contrast, polymeric species of alum under alkaline  
159 conditions promotes adsorption of colloids onto its surface (Zheng et al., 2011). Therefore, an  
160 increase in TSS and COD removals from raw PPME were observed above pH 6.

161 Fig. 4 also shows that the recommended pH for coagulation process was specific to  
162 different coagulants. Using One-way ANOVA analysis, the recommended initial pH of PPME



163 for *C. obtusifolia* gum was pH 5 whereas for alum, it was at pH 7. Subsequent effects were  
164 studied under the recommended initial pH for both *C. obtusifolia* gum (pH 5) and alum (pH 7).

165

### 166 **3.3. Effect of coagulant dosage**

167 Study on the effect of coagulant dosage not only serves for economic evaluation purpose  
168 but also to prevent excessive use of coagulant in treated PPME and other industrial wastewaters  
169 (Šćiban et al., 2009). An increase in removal efficiencies followed by a plateau-type profile was  
170 attained with an increase of dosage either using *C. obtusifolia* gum or alum (Fig. 5). An increase  
171 of *C. obtusifolia* gum from 0 to 0.75 g/L showed substantial improvement of TSS (57.3-85.3%)  
172 and COD (1.0-35.3%) removals. Similar trend was also observed for the addition of alum from 0  
173 to 0.20 g/L (47.6-88.8% TSS and 0.9-29.4% COD removals). Alum is usually high in charge  
174 density when it is dissolved in the suspension (Ahmad et al., 2006). As a result, lower dosage of  
175 alum (73% lower than *C. obtusifolia* gum) was recommended to destabilize the colloidal system  
176 (Ahmad et al., 2006).

177 Sweep flocculation is less sensitive towards the change in coagulant dosage (Yukselen  
178 and Gregory, 2004). Based on the current findings using either alum or *C. obtusifolia* gum in  
179 PPME treatment (Fig. 5), an increase in coagulant dosage further enhanced the coagulation  
180 efficiency of the system. Thus, sweep flocculation was ruled out as a possible coagulation  
181 mechanism for both *C. obtusifolia* gum and alum. Similar trend was also observed by Miller et  
182 al. (2008). Their results further supported the current study that the coagulation mechanism of *C.*  
183 *obtusifolia* was adsorption with interparticle bridging.

184 After performing One-way ANOVA analysis, the recommended dosages of *C. obtusifolia*  
185 gum and alum were 0.75 g/L (85.2% TSS and 35.3% COD removals) and 0.20 g/L (88.8% TSS  
186 and 29.4% COD removals), respectively. In view of this, following investigations on the effects  
187 of other operating conditions were based on these recommended dosage values.

188 Raw PPME used in the present study had negative zeta potential values at -11.5 mV (Fig.  
189 6). At the recommended conditions of *C. obtusifolia* gum, the zeta potential remained negative (-  
190 11.5 to -8.5 mV) and relatively constant despite the increases in *C. obtusifolia* gum dosages,  
191 suggesting that the coagulation mechanism of *C. obtusifolia* gum was unlikely to be charge  
192 neutralization (Miller et al., 2008). In comparison, an increase in alum dosage from 0 to 2 g/L led  
193 to a significant increase of zeta potential values (-11.5 to -2.4 mV). The present results showed  
194 that the coagulation mechanism using alum was based on adsorption and charge neutralization  
195 (Albuquerque et al., 2013).

196

### 197 **3.4. Effect of settling time**

198 Settling time was studied as it influences the overall cost and coagulation efficiency of  
199 the treatment process (Ahmad et al., 2008). Fig. 7 indicates that coagulation process without  
200 introducing settling yielded lower TSS removal (72.6 and 64.9% for *C. obtusifolia* gum and  
201 alum, respectively). On the other hand, the allowance of settling time from 10 s to 1 min resulted  
202 in slight improvement of TSS (8.2 and 8.3 % increase for *C. obtusifolia* gum and alum,  
203 respectively) and COD removals (5.9 and 5.1% increase for *C. obtusifolia* gum and alum,  
204 respectively). The present results were concurrent with Merzouk et al. (2011) who reported that  
205 the settling time was less significant as compared to the other studied effects, such as initial pH,

206 coagulant dosage, slow-mixing velocity and slow-mixing time. Removal efficiencies of TSS and  
207 COD after 1 min showed no further substantial improvement in coagulation activity through one-  
208 way ANOVA analysis. Consequently, investigation of subsequent parameters hereafter was  
209 based on the settling time of 1 min for both *C. obtusifolia* gum and alum. Settling time achieved  
210 in this study is comparably low with the coagulation system employed by Ahmad et al. (2008)  
211 who used alum and polyacrylamide as a coagulant and flocculant, respectively in PPME  
212 treatment to achieve a settling time of 12s.

213

### 214 ***3.5. Effect of slow-mixing velocity***

215 Two mixing regimes occur in coagulation process, namely rapid-mixing and slow-mixing  
216 (Zhang et al., 2013). Rapid-mixing is required to induce uniform distribution of coagulation into  
217 suspension (Yukselen and Gregory, 2004). Lin et al. (2013) reported that the effect of rapid  
218 mixing on high turbidity wastewater is insignificant. Apart from maintaining particles in  
219 suspension, slow-mixing promotes flocs formation, complexation (for alum coagulant) and  
220 adsorption of organics onto the coagulants for precipitation and settling of insoluble solids  
221 (Kumar et al., 2011; Zhang et al., 2013).

222 For this purpose, study on the effect of slow-mixing velocity was conducted from 0-50  
223 rpm at the recommended pH, dosage, and settling time for *C. obtusifolia* gum and alum. In the  
224 absence of slow-mixing (0 rpm), both TSS and COD removals were low for either *C. obtusifolia*  
225 gum or alum (Fig. 8). Therefore, slow-mixing step in coagulation process was crucial in  
226 promoting flocs growth (Özacar and Şengi, 2002). The recommended slow-mixing velocity for  
227 both *C. obtusifolia* gum and alum was 10 rpm with TSS and COD removals of 83.0 and 36.4%

228 for *C. obtusifolia* gum whereas 90.4 and 36.5% for alum, respectively. A drop in TSS removal of  
229 both *C. obtusifolia* gum and alum was observed at higher mixing velocities (>30 rpm and > 40  
230 rpm, respectively) due to flocs breakage (Merzouk et al., 2011). Flocs breakage occurred from  
231 surface erosion of flocs by turbulent drag or bulgy deformation and flocs splitting (Özacar and  
232 Şengil, 2002; Xiao et al., 2010; Zhang et al., 2013). In the present study, the suggested slow-  
233 mixing velocity was 10 rpm for both *C. obtusifolia* gum and alum.

234

### 235 **3.6. Effect of slow-mixing time**

236 In addition to the study on the effect of slow-mixing velocity, Zhang et al. (2013)  
237 reported that the slow-mixing duration also contributed to achieving optimal coagulation  
238 performance. Therefore, the effect of slow-mixing time was also investigated in the present  
239 study.

240 Fig. 9 shows that both *C. obtusifolia* gum and alum exhibited an increase in TSS (52.2-  
241 86.9% for *C. obtusifolia* gum and 62.2-91.6% for alum) and COD removals (2.2-36.2% for *C.*  
242 *obtusifolia* gum and 7.2-33.7% for alum) when the slow-mixing duration were raised from 0-10  
243 min. No further significant removals in TSS and COD were observed beyond 10 min of slow-  
244 mixing. The slight drop in TSS removal for *C. obtusifolia* gum from 10 to 15 min was due to the  
245 re-dispersion and re-stabilization of flocs, which was in agreement with the results obtained by  
246 Özacar and Şengil (2002). Thus, the optimal slow-mixing time for both *C. obtusifolia* gum  
247 (86.9% TSS and 36.2% COD removals) and alum (91.6% TSS and 33.7% COD removals) was  
248 10 min. The untreated and treated raw PPME using *C. obtusifolia* gum is shown in Fig. 3.

### 249 3.7. FTIR analysis

250 Both *C. obtusifolia* gum and alum were analyzed using FTIR to determine the presence  
251 of active functional groups in both coagulants. *C. obtusifolia* gum (Fig. 10) had a broad and  
252 strong band at  $3277\text{ cm}^{-1}$  due to O-H stretching whereas the presence of C-H linkages was  
253 indicated at  $2923\text{ cm}^{-1}$  (Singh et al., 2007; Singh et al., 2010). Peaks of -CH- group was observed  
254 at  $2853\text{ cm}^{-1}$  whereas peak at  $1744\text{ cm}^{-1}$  represented the stretching of C=O ester group (Singh et  
255 al., 2007; Singh et al., 2010). Additional peaks at  $1634$  and  $1239\text{ cm}^{-1}$  represented the presence  
256 of carbonyl C=O stretching vibrations in primary and tertiary amides, respectively (Fatombi et  
257 al., 2013). N-H groups in amides formed intermolecular hydrogen bonds between the coagulants  
258 and suspended solids to aid the coagulation process (Fatombi et al., 2013). The weak bands at  
259  $1417$  and  $1378\text{ cm}^{-1}$  were due to bending vibrations of  $\text{CH}_3$  and the scissor vibration of  $\text{CH}_2$ ,  
260 most likely indicating the presence of COOH groups (Ni et al., 2012). Carboxyl groups provided  
261 adsorption sites for the suspended solids during coagulation process (Yin, 2010). Small peaks at  
262  $1147$  and  $1027\text{ cm}^{-1}$  arised from C-O stretching of ester (Singh et al., 2007; Singh et al., 2010).

263 On the other hand, alum (Fig. 10), which is dodecahydrates, had a broad peak at  $2958\text{ cm}^{-1}$ ,  
264 due to the existence of OH groups in alum (Rong et al., 2013). At  $1652\text{ cm}^{-1}$ , OH stretching  
265 resulted from the hydroxyl group within alum and also the Al-O bond vibrations (Ni et al.,  
266 2012). Additional peaks at  $1058\text{ cm}^{-1}$  was due to  $\text{SO}_4^{2-}$  stretching whereas peak at  $923\text{ cm}^{-1}$  was  
267 assigned to the possible HOO matrix (Singh et al., 2012; Frost et al., 2013). The presence of OH  
268 and HOO groups were due to the formation of hydrogen bonds between alum and suspended  
269 solids during coagulation process (Baranović, 2014).

270 The bands at the region  $1738\text{-}2113\text{ cm}^{-1}$  of PPME suspended solids (Fig. 11) disappeared  
271 in the flocs when *C. obtusifolia* gum was used. These alterations indicated interaction between *C.*

272 *obtusifolia* gum and suspended solids, which resulted in formation of composite species (Ni et  
273 al., 2012). On the other hand, an occurrence of additional peaks from 2050-2284  $\text{cm}^{-1}$  (Fig. 11) as  
274 compared to alum in the flocs was attributed to new interactions between alum and suspended  
275 solids after binding (Singh et al., 2007).

276

### 277 **3.8. TGA**

278 The thermal decompositions of *C. obtusifolia* seed gum, alum, PPME suspended solids,  
279 and flocs formed using *C. obtusifolia* and alum are presented in Fig. 12. TGA was used to  
280 investigate the thermal decomposition of carbonaceous materials and the thermal stabilities of  
281 each sample with the elevation of temperature (Lee et al., 2012). According to Fig. 12a, up to  
282 13% and 35% weight loss of moisture and volatile compounds were lost at temperature below  
283 200 °C for *C. obtusifolia* seed gum and alum, respectively (Lee et al., 2012). As the temperature  
284 elevated from 200-600 °C, significant amount of weight loss (49-58%) were observed for all  
285 samples (Figs. 13a and 13c) due to gradual decomposition of the samples.

286 The decomposition stages for each sample were distinguished from the differential  
287 thermal gravimetric (DTG) curves (Figs. 12b and 12d). From Fig. 12b, two significant mass  
288 change regions were observed for *C. obtusifolia* seed gum whereas three for alum. In contrast to  
289 Fig.13b, Fig, 9d shows three significant and similar mass change regions for all samples. At  
290 lower temperature, intra and intermolecular moisture was evaporated with an increase of  
291 temperature (Lee et al., 2012). The sudden loss of mass observed in alum after 100°C could be  
292 due to the loss of absorbed species such as water (Fig. 12a). Thus, DTG peaks of alum were  
293 more prominent than *C. obtusifolia* at lower temperature after 100°C (Fig. 12b and 12d) which

294 indicated alum has more hygroscopic components in it as compared to *C. obtusifolia* (Lee et al.,  
295 2012). The organic components of *C. obtusifolia*, alum, and PPME suspended solids started to  
296 degrade around 200 °C. Temperatures beyond 300°C indicated significant weight loss due to  
297 severe decomposition of all samples. Lee et al. (2012) stated that most of the components in all  
298 samples were decomposed at high temperature. In the present study, this occurred at  
299 temperatures above 600°C (Fig. 12d). the weightlessness at high temperatures is due to the total  
300 decomposition of sample (Lee et al., 2012). Similarly, this was observed at temperatures beyond  
301 650 °C of *C. obtusifolia* seed gum whereas DTG curve of alum indicates a peak at 800 °C (Fig.  
302 12b).

303

### 304 **3.9. Morphology of flocs**

305 Flocs formed after coagulation treatment process are usually separated from the treated  
306 effluent via sedimentation, flotation, filtration, or/and thickening techniques. Therefore, the  
307 evaluation of flocs physical characteristics is important to determine their removal efficiency  
308 (Syzgula et al., 2009). Scanning electron microscopy (SEM) images showed that the flocs  
309 formation by using *C. obtusifolia* gum was highly fibrous-like and aggregate (Fig. 13a), whereas  
310 irregularly-shaped and aggregate flocs were observed for alum (Fig. 13b). The aggregate  
311 structure of flocs resulted in fast settling time of 1 min for both *C. obtusifolia* gum and alum  
312 (Fig. 7).

## 313 **4. Conclusion**

314 In many countries, waste management systems are undergoing changes due to the threat  
315 of global climate change and other environmental issues (Nouri et al., 2012), resulting somewhat

316 a larger number of cases in water resource management have been studied from the sustainability  
317 perspective (Wu et al., 2013b). The present study pursued a new alternative coagulant, namely *C.*  
318 *obtusifolia* seed gum that is biodegradable and natural to environment and living organisms. The  
319 use of unmodified *C. obtusifolia* gum in treatment of raw and undiluted PPME showed positive  
320 and comparable results against commercially used alum. Under recommended conditions (pH 5,  
321 0.75 g/L dosage, 10 rpm and 10 min slow-mixing, and 1 min settling time), *C. obtusifolia* gum  
322 yielded significant TSS and COD removals of 86.9 and 36.2%, respectively. The present study  
323 proved that *C. obtusifolia* gum was a promising and effective natural coagulant in substituting  
324 harmful inorganic coagulants such as alum in coagulation process of industrial effluent.

### 325 **Acknowledgements**

326 The authors would like to thank Monash University Malaysia for providing W.  
327 Subramonian with a PhD scholarship.

### 328 **References**

- 329 Ahmad, A.L., Sumathi, S., Hameed, B.H., 2006. Coagulation of residue oil and suspended solid  
330 in palm oil mill effluent by chitosan, alum and PAC. Chem. Eng. J. 118, 99-105.
- 331 Ahmad, A.L., Wong, S.S., Teng, T.T., Zuhairi, A., 2008. Improvement of alum and PACl  
332 coagulation by polyacrylamides (PAMs) for the treatment of pulp and paper mill  
333 wastewater. Chem. Eng. J. 137, 510-517.
- 334 Albuquerque, L.F., Salgueiro, A.A., Melo, J.L.d.S., Chiavone-Filho, O., 2013. Coagulation of  
335 Indigo Blue present in dyeing wastewater using a residual bittern. Sep. Purif. Technol.  
336 104, 246-249.



- 337 Alwi, H., Idris, J., Musa, M., Ku Hamid, K.H., 2013. A preliminary study of banana stem juice  
338 as a plant-based coagulant for treatment of spent coolant wastewater. J. Chem. art.  
339 no. 165057.
- 340 Baranović, G., 2014. Intramolecular resonance-assisted hydrogen bonds: A theoretical description  
341 by means of atomic charges and charge fluxes. Spectrochim. Acta A 117, 465-472.
- 342 Bodlund, I, Pavankumar, A.R., Chelliah, R., Kasi, S., Sankaran, K., Rajarao, G.K., 2014.  
343 Coagulant proteins identified in Mustard: A potential water treatment agent. Int. J.  
344 Environ. Sci. Technol. 11, 873-880.
- 345 Department of Agriculture, Fisheries and Forestry, Biosecurity Queensland, 2014. Sicklepods.  
346 [http://www.daff.qld.gov.au/\\_data/assets/pdf\\_file/0013/51052/IPA-Sicklepod-PP18.pdf](http://www.daff.qld.gov.au/_data/assets/pdf_file/0013/51052/IPA-Sicklepod-PP18.pdf)  
347 (accessed 20.05.14.).
- 348 Dhir, A., Prakash, N.T., Sud, D., 2012. Coupling of solar-assisted advanced oxidative and  
349 biological treatment for degradation of agro-residue-based soda bleaching effluent.  
350 Environ. Sci. Pollut. Res. 19, 3906-3913.
- 351 Fatombi, J.K., Lartiges, B., Aminou, T., Barres, O., Caillet, C., 2013. A natural coagulant protein  
352 copra (*Cocos nucifera*): Isolation, characterization, and potential for water purification.  
353 Sep. Purif. Technol. 116, 35-40.
- 354 Frost, R.L., Xi, Y., Scholz, R., López, A., Granja, A., 2013. Infrared and Raman spectroscopic  
355 characterization of the sulphate mineral credite  $\text{-Ca}_3\text{Al}_2\text{SO}_4(\text{F},\text{OH})_2\text{H}_2\text{O}$  – and in  
356 comparison with the alums. Spectrochim. Acta A 109, 201-205.

- 357 Graham, N., Gang, F., Fowler, G., Watts, M., 2008. Characterisation and coagulation  
358 performance of a tannin-based cationic polymer: A preliminary assessment. *Colloid.*  
359 *Surface A* 327, 9-16.
- 360 Hallagan, J.B., Du, B.N., Pariza, M.W., Putnam, J.M., Brozelleca, J.F., 1997. Assessment of  
361 cassia gum, *Food Chem. Toxicol.* 35, 625-632.
- 362 Keow, D.C., 2005. Wastewater treatment for the recycled pulp and paper mill industry. *Jurutera,*  
363 29-30.
- 364 Kumar, P., Teng, T.T., Chand, S., Wasewar, K.L., 2011. Treatment of paper and pulp mill  
365 effluent by coagulation. *Int. J. Civil Environ. Eng.* 3, 222-227.
- 366 Lee, K.E., Morad, N., Teng, T.T.T., Poh, B.T., 2012. Development, characterization and the  
367 application of hybrid materials in coagulation/flocculation of wastewater: A review.  
368 *Chem. Eng. J.* 203, 370-386.
- 369 Lin, J.-L., Pan, J.R., Huang, C., 2013. Enhanced particle destabilization and aggregation by  
370 flash-mixing coagulation for drinking water treatment. *Sep. Purif. Technol.* 115, 145-151.
- 371 Merzouk, B., Gourich, B., Madani, K., Vial, Ch., Sekki, A., 2011. Removal of a disperse red dye  
372 from synthetic wastewater by chemical coagulation and continuous electrocoagulation. A  
373 comparative study. *Desalination* 272, 246-253.
- 374 Miller, S.M., Fugate, E.J., Craver, V.O., Simth, J.A., Zimmerman, J.B., 2008. Toward  
375 understand the efficacy and mechanism of *Opuntia* spp. As a natural coagulant for  
376 potential application in water treatment. *Environ. Sci. Technol.* 42, 4274-4279.

- 377 Mukherjee, S., Pariatamby, A., Sahu, J.N., Sen Gupta, B., 2013. Clarification of rubber mill  
378 wastewater by a plant based biopolymer - Comparison with common inorganic  
379 coagulants. *J. Chem. Technol. Biotechnol.* 88, 1864-1873.
- 380 Muthuraman, G., Sasikala, S., 2014. Removal of turbidity from drinking water using natural  
381 coagulants. *J. Ind. Eng. Chem.* 20, 1727-1731.
- 382 Ni, F., Peng, X., He, J., Zhao, J., Luan, Z., 2012. Preparation and characterization of composite  
383 biofloculants in comparison with dual-coagulants for the treatment of kaolin suspension.  
384 *Chem. Eng. J.* 213, 195-202.
- 385 Nouri, J., Nouri, N., Moeni, M., 2012. Development of industrial waste disposal scenarios using  
386 life-cycle assessment approach. *Int. J. Environ. Sci. Technol.* 9, 417-424.
- 387 Oller, I., Malato, S., Sánchez-Pérez, J.A., 2011. Combination of advanced oxidation processes  
388 and biological treatment for wastewater decontamination – a review. *Sci. Total Environ.*  
389 409, 4141-4166.
- 390 Özacar, M., Şengil, A., 2002. The use of tannins from Turkish acorns (*Valonia*) in water  
391 treatment as a coagulant and coagulant aid. *Turkish J. Eng. Env. Sci.* 26, 255-263.
- 392 Pérez, M., Torrades, F., Peral, J., Lizama, C., Bravo, C., Casas, S., Freer, J., Mansilla, H.D.,  
393 2001. Multivariate approach to photocatalytic degradation of a cellulose bleaching  
394 effluent. *Appl. Catal. B* 33, 89-96.
- 395 Renault, F., Sancey, B., Badot, P.-M., Crini, G., 2009. Chitosan for coagulation/flocculation  
396 processes- An eco-friendly approach. *Eur. Polym. J.* 45, 1337-1348.

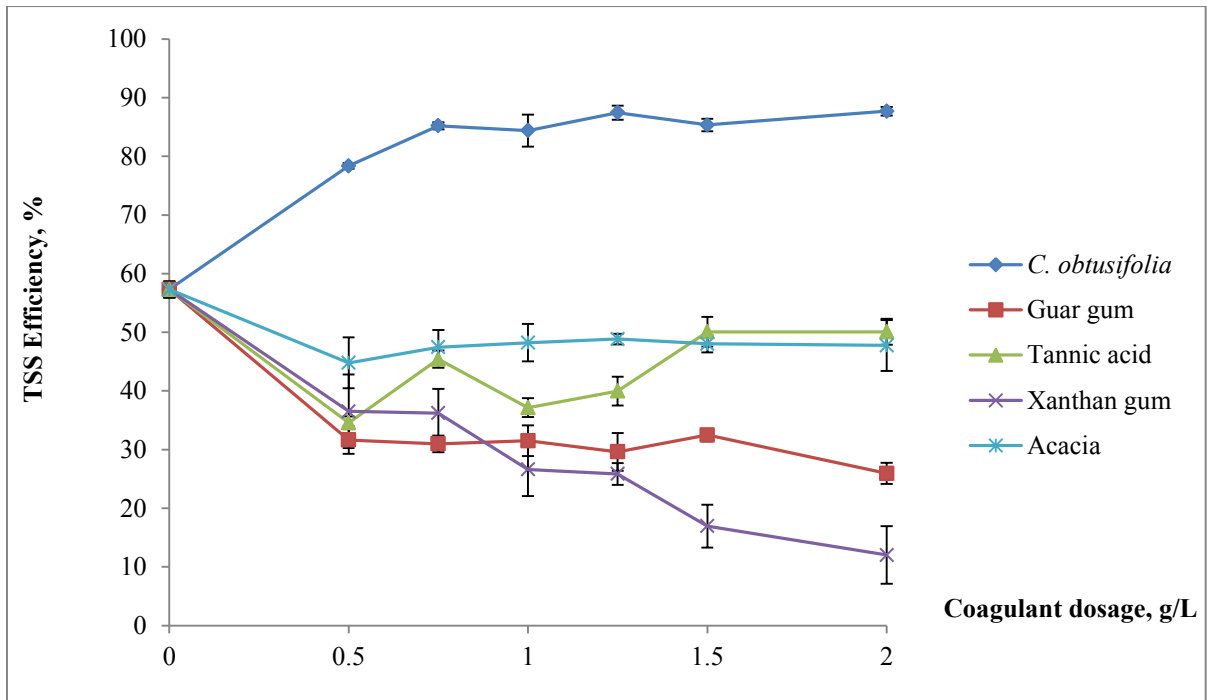
- 397 Rintala, J.A., Puhakka, J.A., 1994. Anaerobic treatment in pulp and paper mill waste  
398 management: A review. *Bioresource Technol.* 47, 1-18.
- 399 Rong, H., Gao, B., Dong, M., Zhao, Y., Sun, S., Wang, Y., Yue, Q., Li, Q., 2013.  
400 Characterization of size, strength and structure of aluminium-polymer dual-coagulant  
401 flocs under different pH and hydraulic conditions, *J. Hazard. Mater.* 109, 201-205.
- 402 Sanghi, R., Bhattacharya, B., Singh, V., 2006. Use of *Cassia javahikai* seed gum and gum-g-  
403 polyacrylamide as coagulant aid for the decolourization of textile dye solutions.  
404 *Bioresource Technol.* 97, 1259-1264.
- 405 Sarawasthi, R., Saseetharan, M.K., 2012. Simultaneous optimization of multiple performance  
406 characteristics in coagulation-flocculation process for Indian paper industry wastewater.  
407 *Water Sci. Technol.* 66, 1231-1238.
- 408 Šćiban, M., Klačnja, M., Antov, M., Škrbić, B., 2009. Removal of water turbidity by natural  
409 coagulants obtained from chestnut and acorn. *Bioresource Technol.* 100, 6639-6643.
- 410 Shreeji Impex, 2010. Cassia Tora seeds. <http://www.shreejinilank.com/cassia-tora-seeds.htm>  
411 (accessed 01.04.14.).
- 412 Singh, P.K., Kumar, P., Seth, T., Rhee, H.-W., Bhattacharya, B., 2012. Preparation,  
413 characterization and application of nano CdS doped with alum composite. *J. Phys. Chem.*  
414 *Solids* 73, 1159-1163.
- 415 Singh, V., Singh, S.K., Maurya, A., 2010. Microwave induced poly(acrylic acid) modification of  
416 *Cassia javanica* seed gum for efficient Hg(II) removal from solution. *Chem. Eng. J.* 160,  
417 129-137.

- 418 Singh, V., Tiwari, S., Sharma, A.K., Sanghi, R., 2007. Removal of lead from aqueous solutions  
419 using *Cassia grandis* seed gum-graft-poly(methylmethacrylate). J. Colloid Interf. Sci.  
420 316, 224-232.
- 421 Syzgula, A., Guibal, E., Palacin, M.A., Ruiz, M., Sastre, A.M., 2009. Removal of an anionic dye  
422 (Acid Blue 92) by coagulation-flocculation using chitosan. J. Environ. Manage. 90, 2979-  
423 2986.
- 424 Teh, C.Y., Wu, T.Y., Juan, J.C., 2014. Optimization of agro-industrial wastewater treatment  
425 using unmodified rice starch as a natural coagulant. Ind. Crop. Prod. 26, 17-26.
- 426 Tripathi, V.R., Kumar, S., Garg, S.K., 2011. A study on trypsin, *Asoergillus flavus* and *Bacillus*  
427 sp. protease inhibitory activity in *Cassia tora* (L.) syn *Senna tora* (L.) Roxb, seed extract.  
428 BMC Compliment. Altern. Med. 11.
- 429 Vadivel, W., Kunyanga, C.N., Biesalski, H.K., 2011. Antioxidant potential and type II diabetes-  
430 related enzyme inhibition of *Cassia Obtusifolia* L.: Effect of indigenous processing  
431 methods. Food Bioprocess Technol. 5, 2687-2696.
- 432 Wang, J.-P., Chen, Y.-Z., Wang, Y., Yuan, S.-J., Yu, H.-Q., 2011. Optimization of the  
433 coagulation-flocculation process for pulp mill wastewater treatment using a combination  
434 of uniform design and response surface methodology. Water Res. 45, 5633-5640.
- 435 Wong, S.S., Najafpour, G.D., Teng, T.T., Zuhairi, A., Zinatizadeh, A., 2010. Treatment of pulp  
436 and paper mill wastewater with cationic and anionic polyelectrolytes. Iran. J. Energ.  
437 Environ. 1, 106-115.

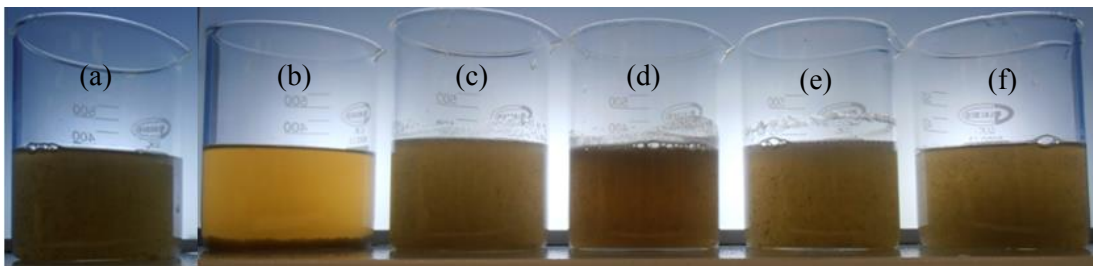
- 438 Wu, T.Y., Guo, N., Teh, C.Y., Hay, J.X.W., 2013a. Introduction, in: Wu, T.Y., Guo, N., Teh,  
439 C.Y., Hay, J.X.W., *Advances in Ultrasound Technology for Environmental Remediation*.  
440 Springer, Netherlands, pp. 1-4.
- 441 Wu, T.Y., Mohammad, A.W., Lim, S.L., Lim, P.N., Hay, J.X.W., 2013b. Recent advances in the  
442 reuse of wastewaters for promoting sustainable development, in: Sharma, S.K., Sanghi,  
443 R. (Eds.), *Wastewater Reuse and Management*. Springer, Netherlands, pp. 47-103.
- 444 Xiao, F., Yi, P., Pan, X.-R., Zhang, B.-J., Lee, C., 2010. Comparative study of the effects of  
445 experimental variables on growth rates of aluminium and iron hydroxide flocs during  
446 coagulation and their structural characteristics. *Desalination* 250, 902-907.
- 447 Yin, C.-Y., 2010. Emerging usage of plant-based coagulants for water and wastewater treatment.  
448 *Process Biochem.* 45, 1437-1444.
- 449 Yuan, R., Guan, R., Liu, P., Zheng, J., 2007. Photocatalytic treatment of wastewater from paper  
450 mill by TiO<sub>2</sub> loaded on activated carbon fibers. *Colloid. Surface A* 293, 80-86.
- 451 Yukselen, M.A., Gregory, J., 2004. The effect of rapid mixing on the break-up and re-formation  
452 of flocs. *J. Chem. Technol. Biotechnol.* 79, 782-788.
- 453 Zhang, Z., Liu, D., Hu, D., Li, D., Ren, X., Cheng, Y., Luan, Z., 2013. Effects of slow-mixing on  
454 the coagulation performance of polyaluminium chloride (PACl). *Chin. J. Chem. Eng.* 21,  
455 318-323.
- 456 Zheng, H., Zhu, G., Jiang, S., Tshukudu, T., Xiang, X., Zhang, P., He, Q., 2011. Investigations of  
457 coagulation-flocculation process by performance optimization, model prediction and  
458 fractal structure of flocs. *Desalination* 269, 148-156.



**Fig. 1.** *C. obtusifolia* seeds.



**Fig. 2.** Coagulation efficiency using different potential natural coagulants in treatment of raw PPME. (pH = 5; rapid-mixing velocity = 150 rpm; rapid-mixing time = 5 min; slow-mixing velocity = 10 rpm; slow-mixing time = 15 min; settling time = 60 min; n=3)



**Fig. 1.** Initial investigation of (a) raw PPME treatment using (b) *C. obtusifolia*, (c) guar gum, (d) tannic acid, (e) xanthan gum, and (f) acacia

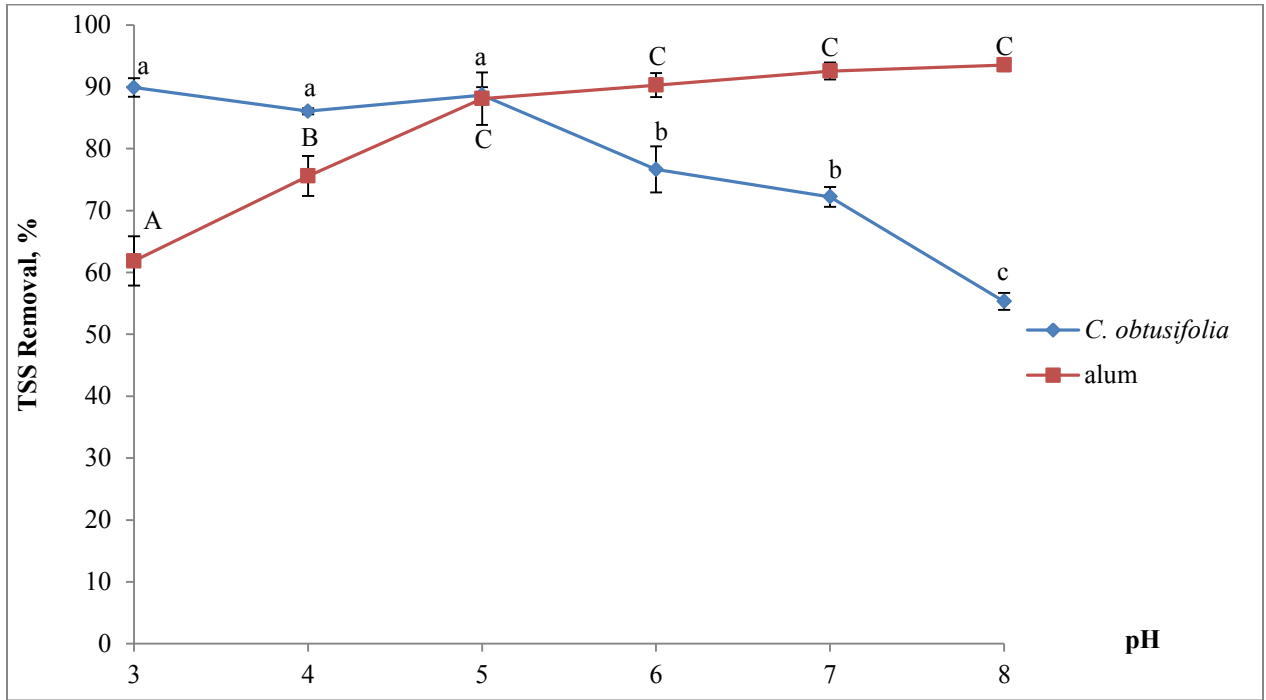


Fig. 4 (a)

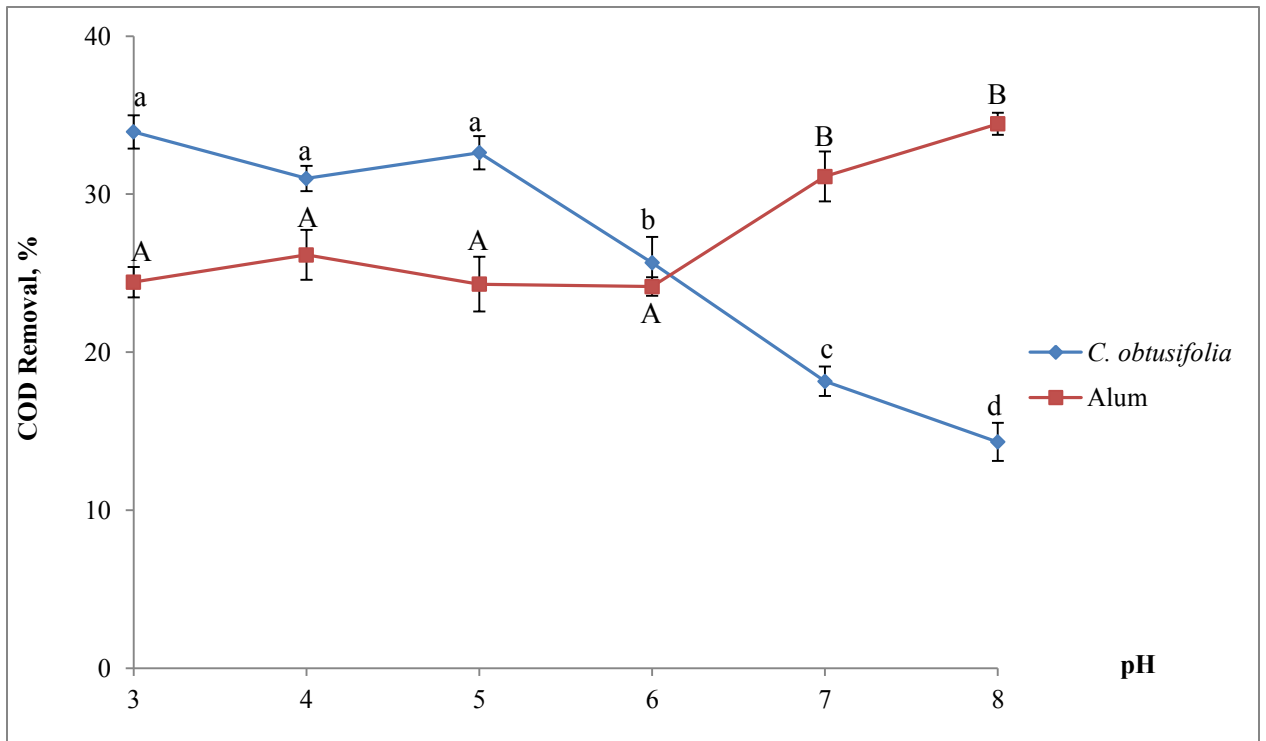
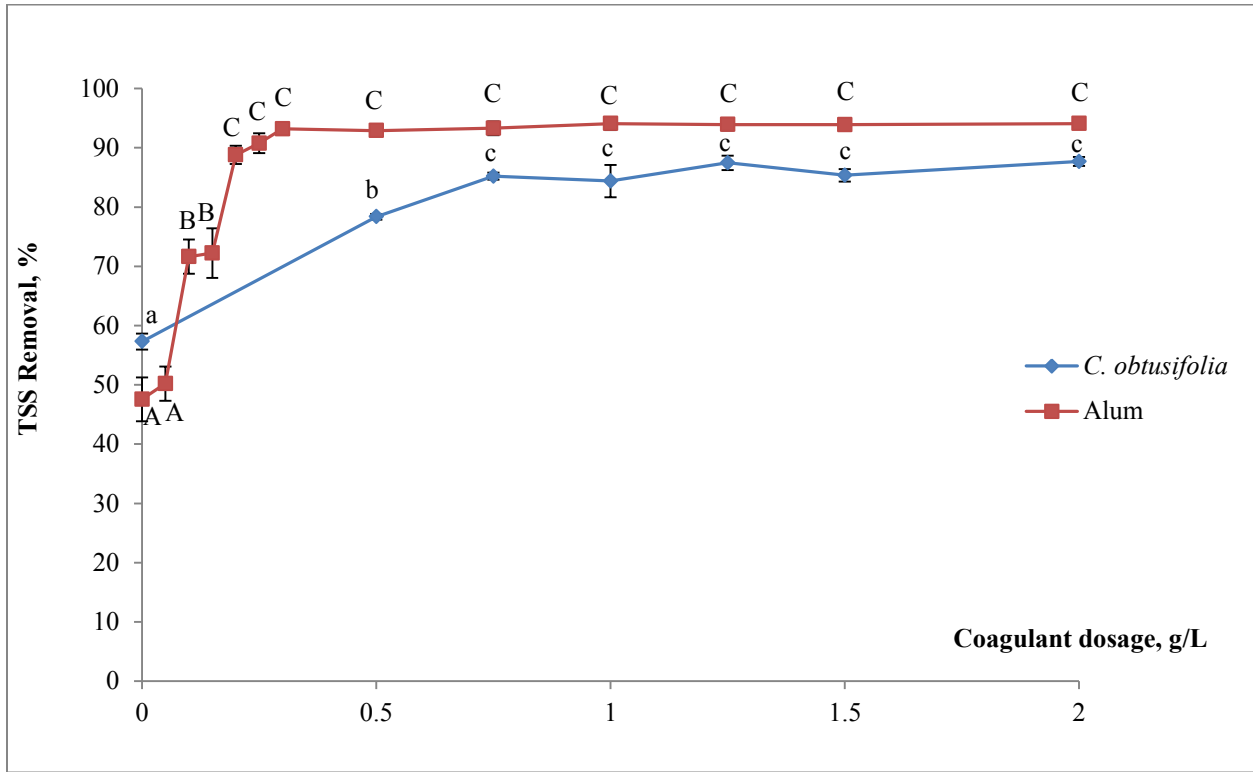


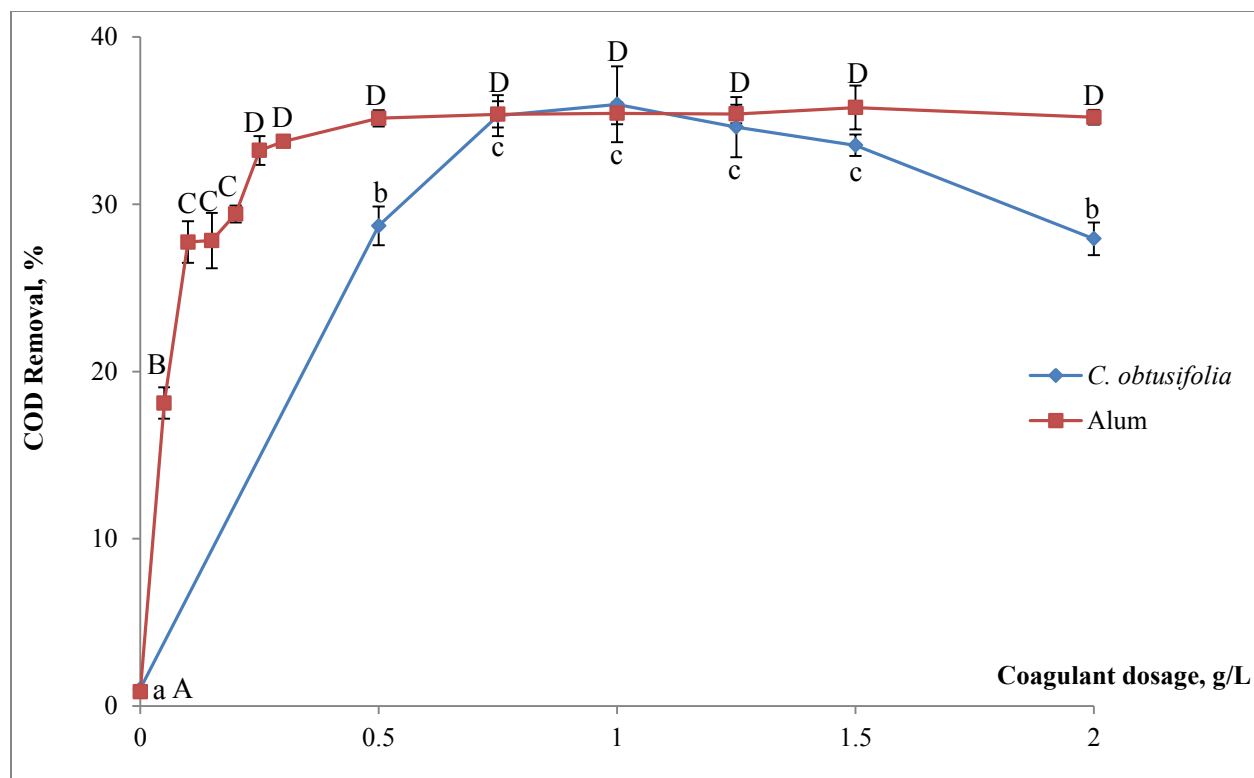
Fig. 4 (b)



**Fig. 4.** Effect of pH on (a) %TSS removal; (b) % COD removal. (*C. obtusifolia* = 1.5 g/L; Alum = 1.0 g/L; rapid-mixing velocity = 150 rpm; rapid-mixing time = 5 min; slow-mixing velocity = 10 rpm; slow-mixing time = 15 min; settling time = 60 min; n=3)

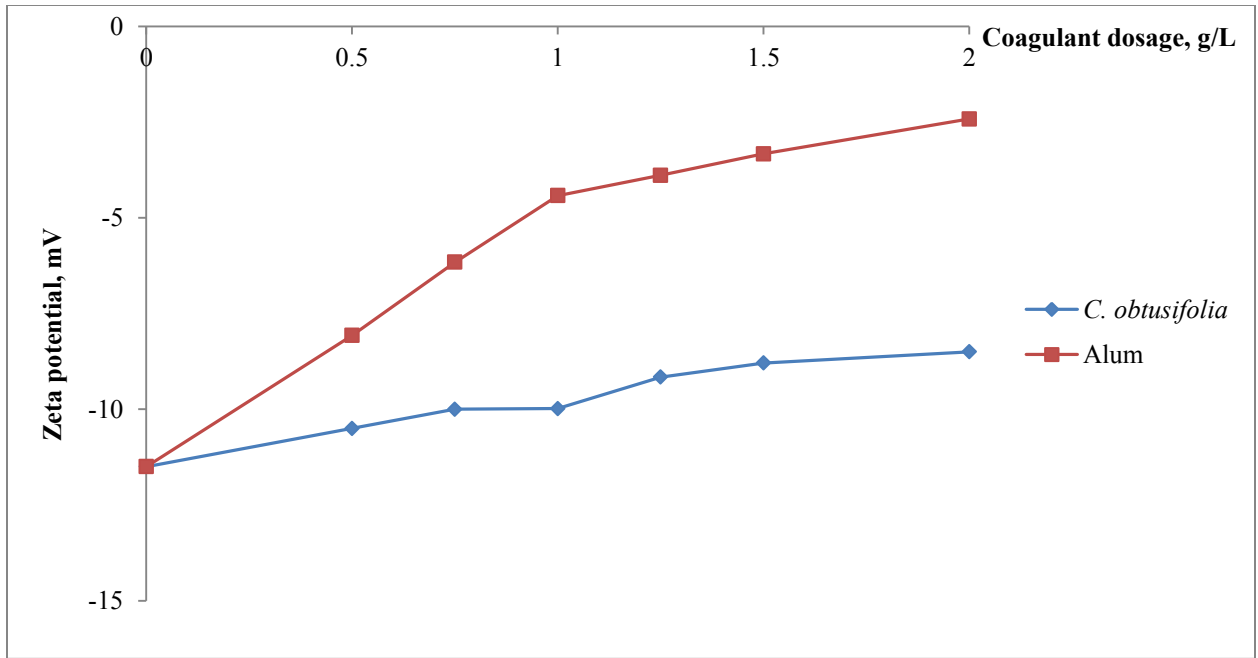


**Fig. 5 (a)**



**Fig. 5 (b)**

**Fig. 5.** Effect of *C. obtusifolia* and alum dosage on (a) %TSS removal; (b) % COD removal. (pH = 5 for *C. obtusifolia* experiments; pH = 7 for alum experiments; rapid-mixing velocity = 150 rpm; rapid-mixing time = 5 min; slow-mixing velocity = 10 rpm; slow-mixing time = 15 min; settling time = 60 min; n=3)



**Fig. 6.** Zeta potential of pre-treated raw PPME using *C. obtusifolia* and alum at different coagulant dosage under recommended treatment conditions

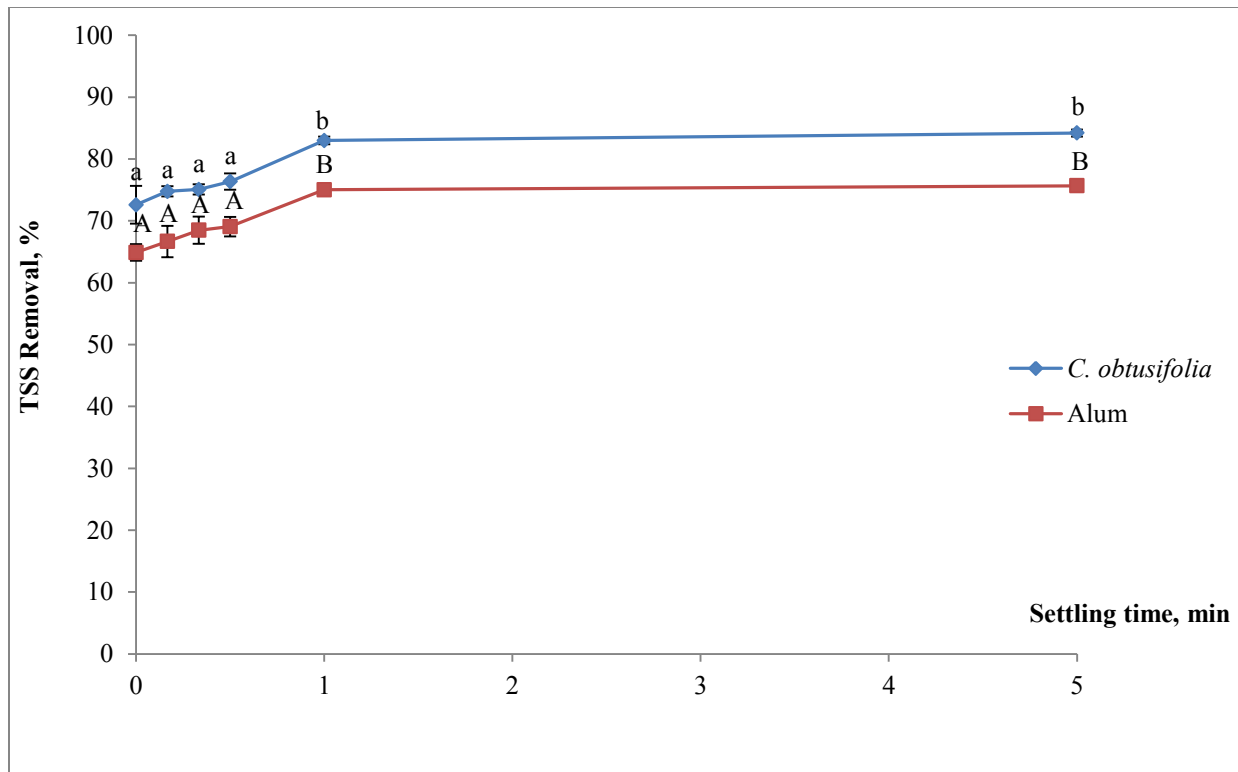


Fig. 7 (a)

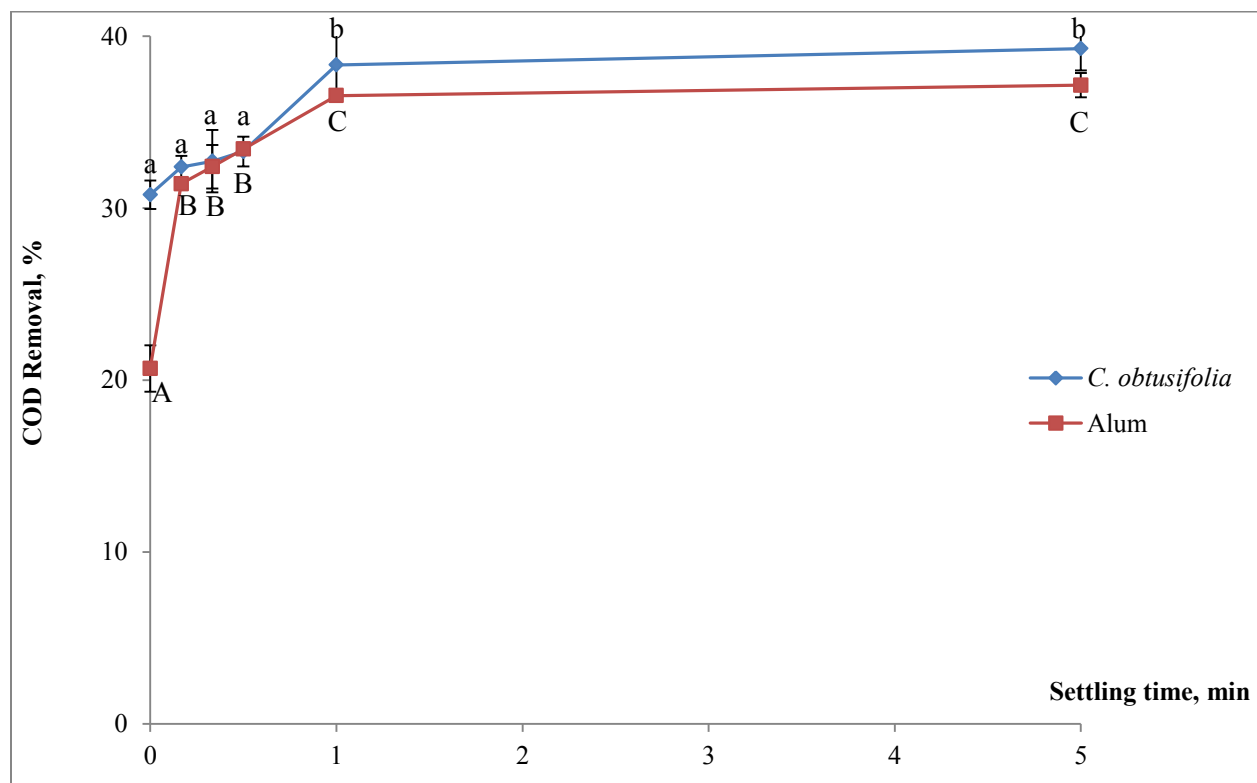
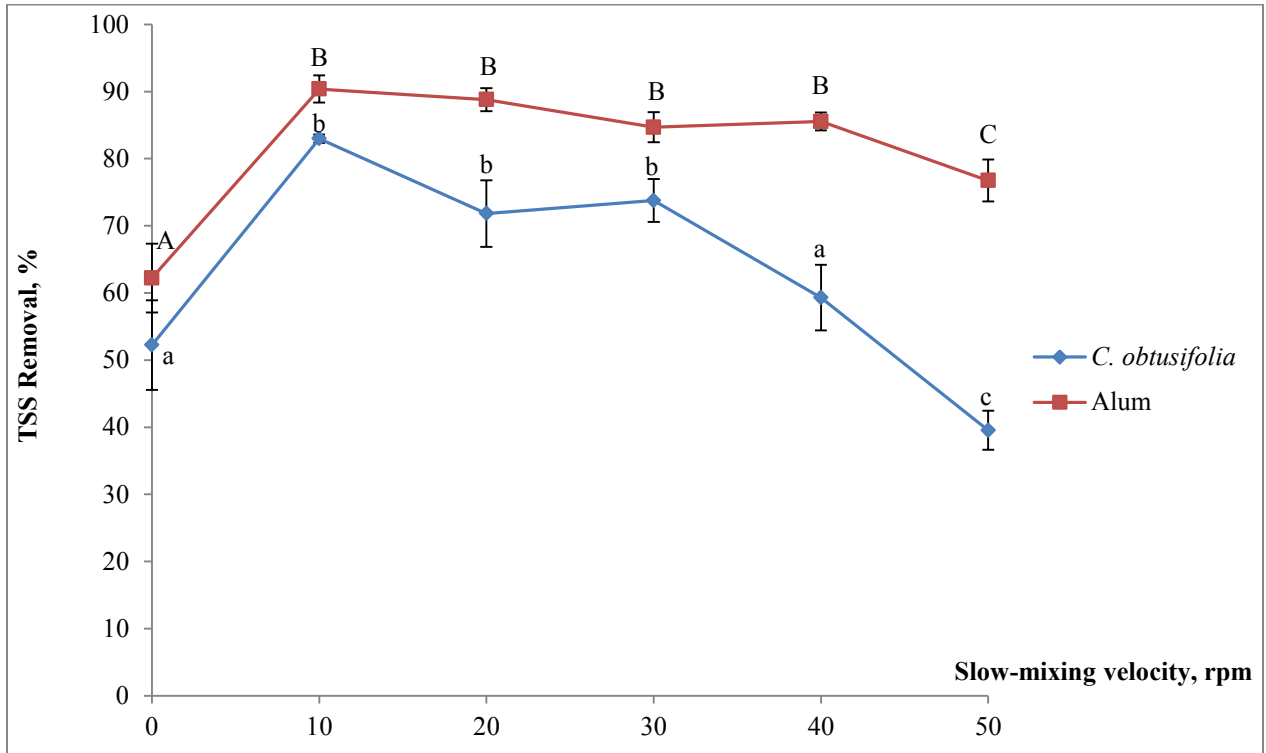
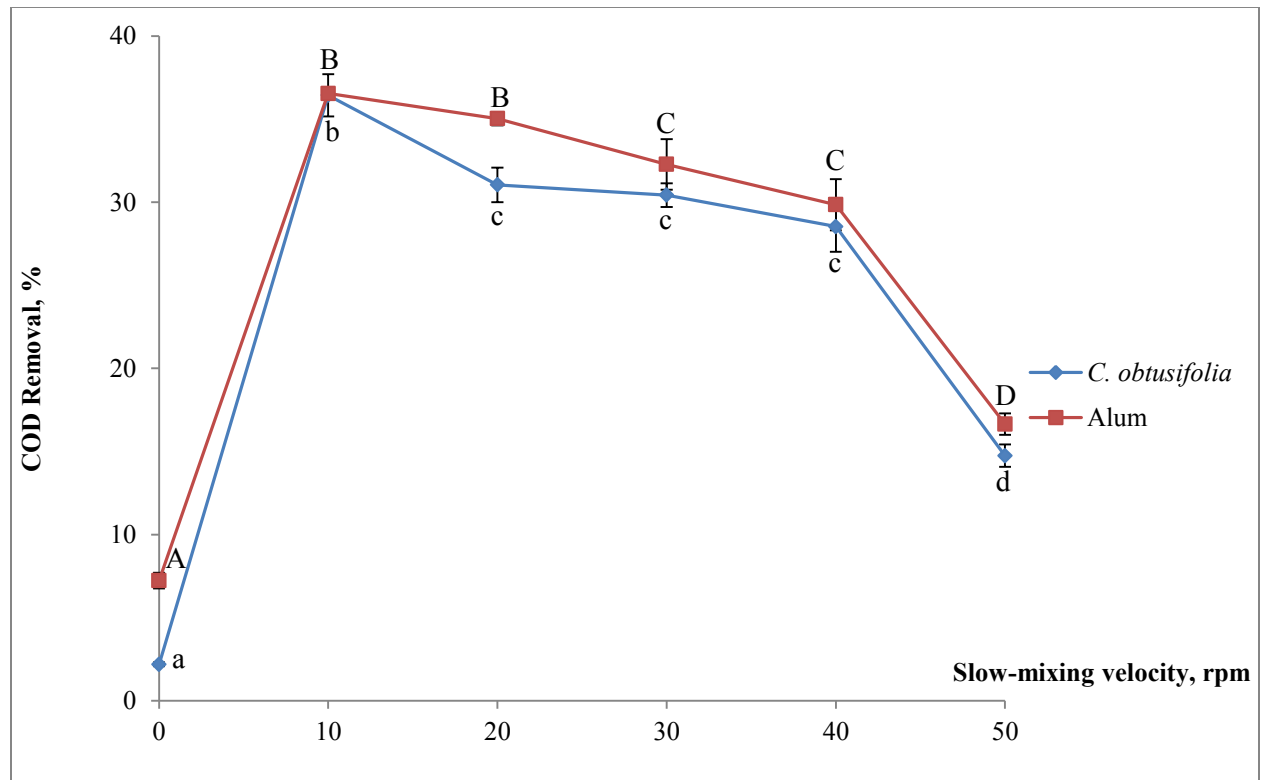


Fig. 7 (b)

**Fig. 7.** Effect of settling time on (a) %TSS removal; (b) % COD removal. (pH = 5 and dosage = 0.75 g/L for *C. obtusifolia* experiments; pH = 7 and dosage = 0.20 g/L for alum experiments; rapid-mixing velocity = 150 rpm; rapid- mixing time = 5 min; slow-mixing velocity = 10 rpm; slow-mixing time = 15 min; n=3)



**Fig. 8 (a)**



**Fig. 8 (b)**

**Fig. 8.** Effect of slow-mixing velocity on (a) %TSS removal; (b) % COD removal. (pH = 5 and dosage = 0.75 g/L for *C. obtusifolia* experiments; pH = 7 and dosage = 0.20 g/L for alum experiments; rapid-mixing velocity = 150 rpm; rapid- mixing time = 5 min; slow-mixing time = 15 min; settling time = 1 min; n=3)

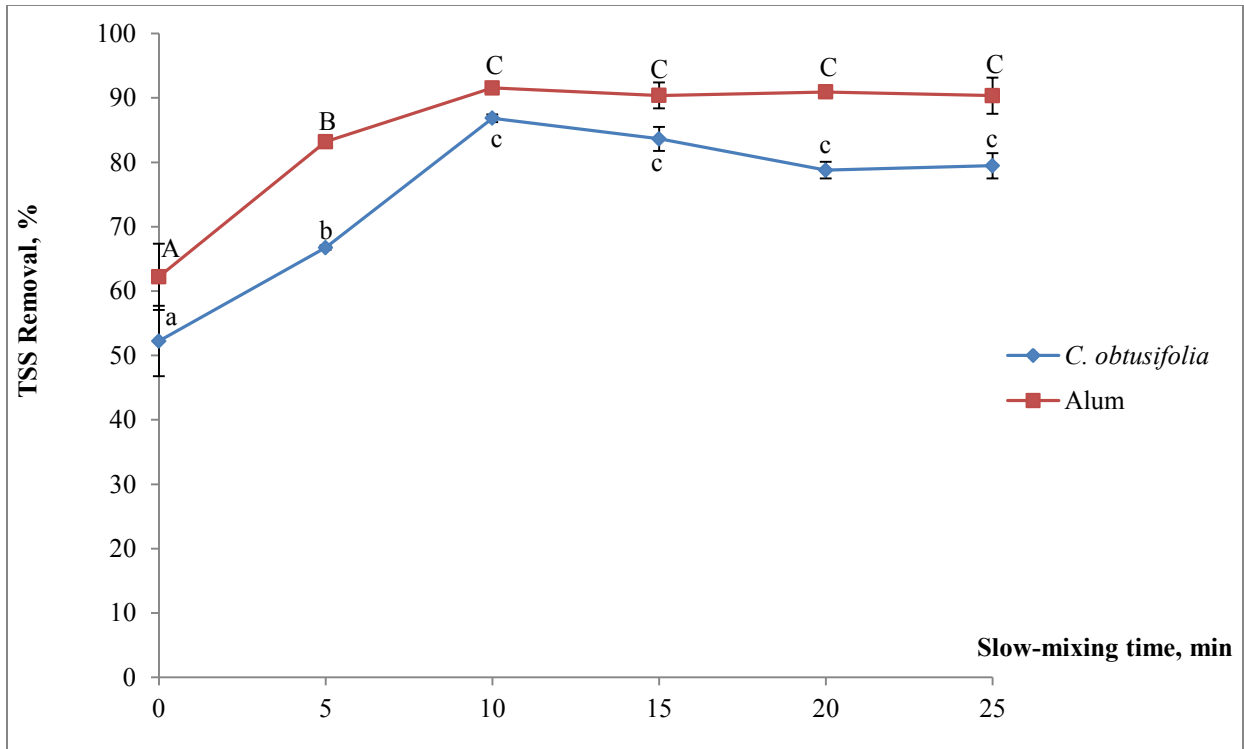


Fig. 9 (a)

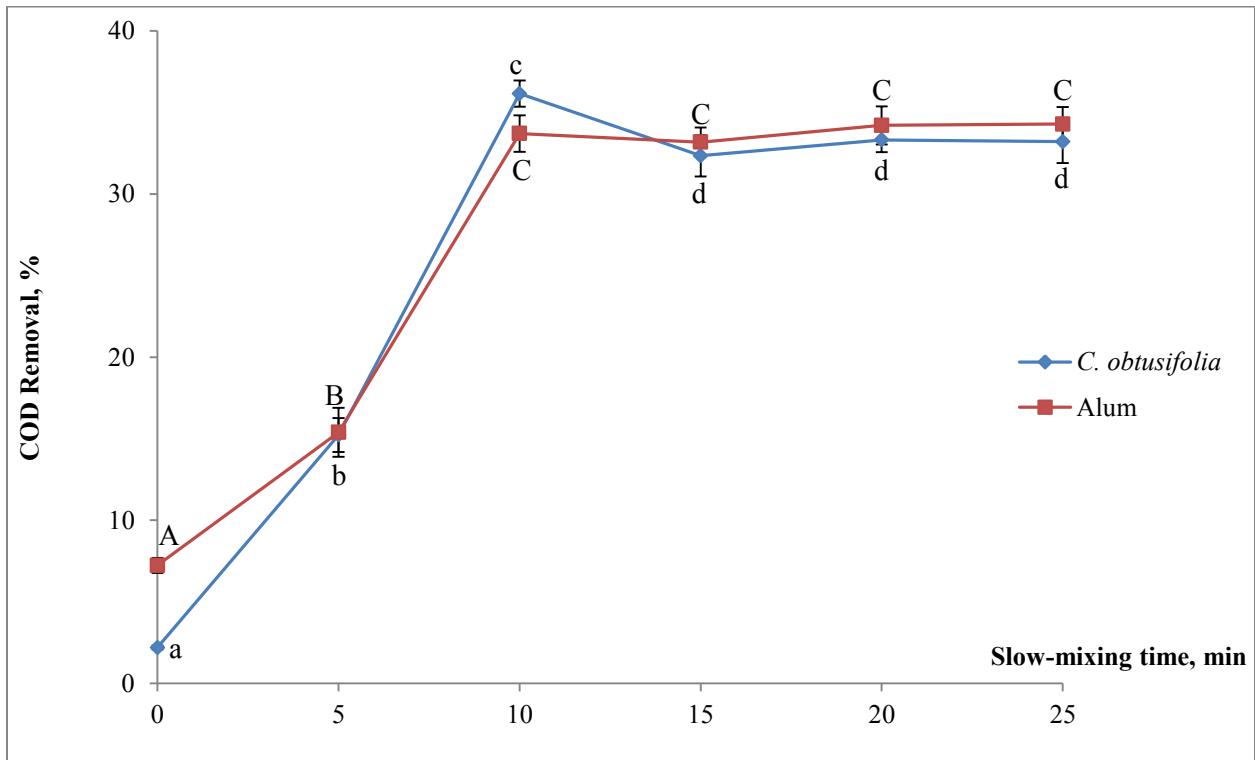


Fig. 9 (b)

**Fig. 9.** Effect of slow-mixing time on (a) %TSS removal; (b) % COD removal. (pH = 5 and dosage = 0.75 g/L for *C. obtusifolia* experiments; pH = 7 and dosage = 0.20 g/L for alum experiments; rapid-mixing

velocity = 150 rpm; rapid- mixing time = 5 min; slow-mixing velocity = 10 rpm; settling time = 1 min; n=3)

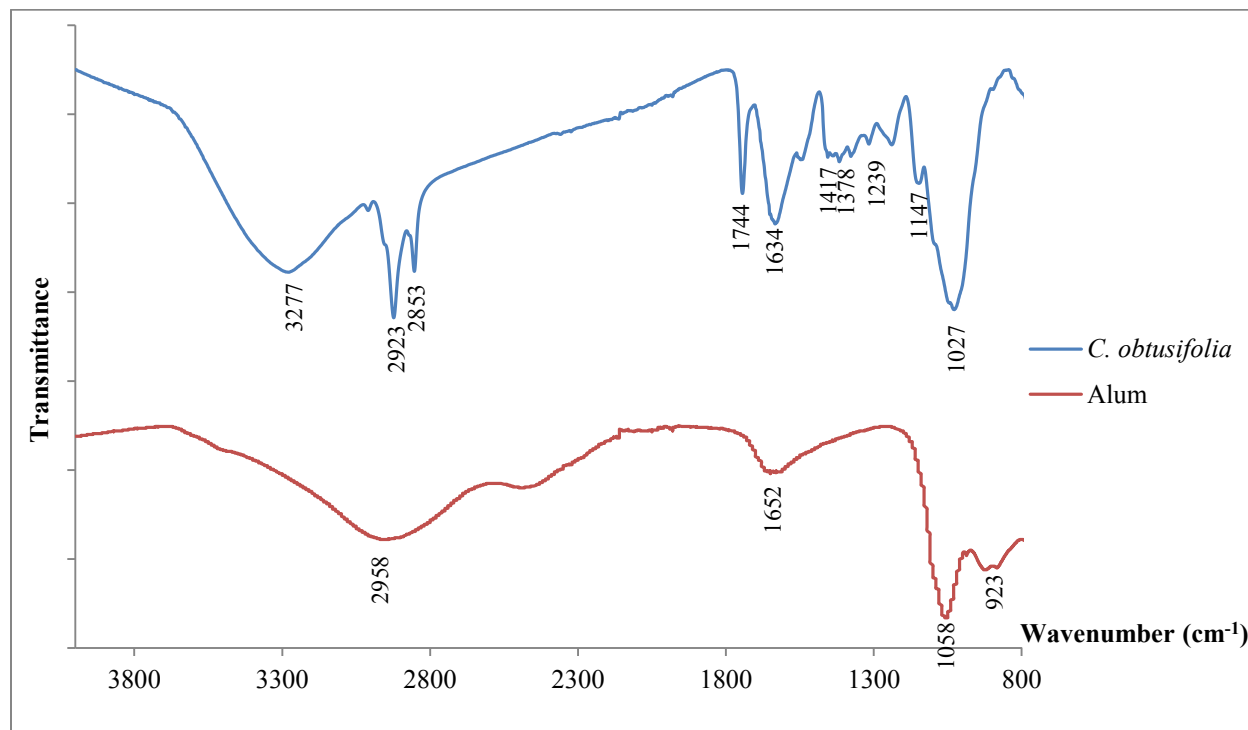
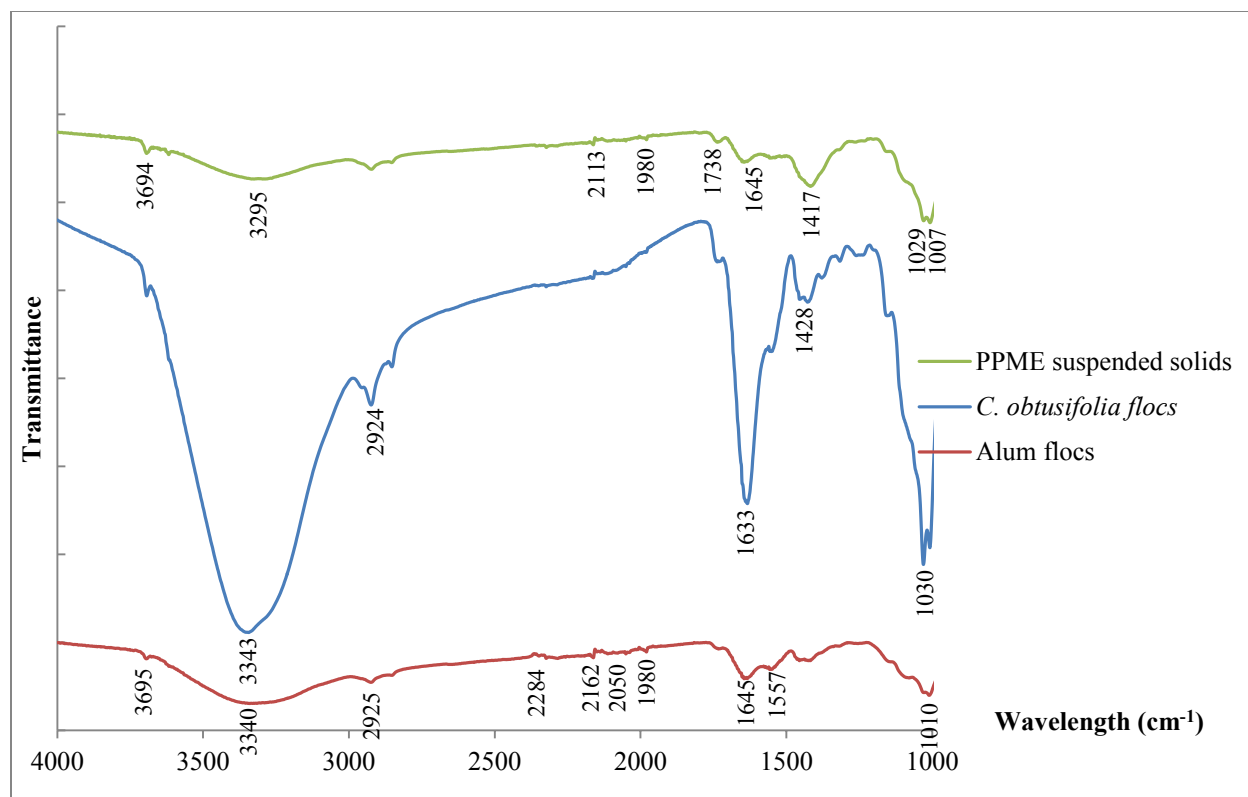


Fig. 10. IR spectra of *C. obtusifolia* seed gum and alum





**Fig. 11.** IR spectra of PPME suspended solids, *C. obtusifolia* flocs, and alum flocs

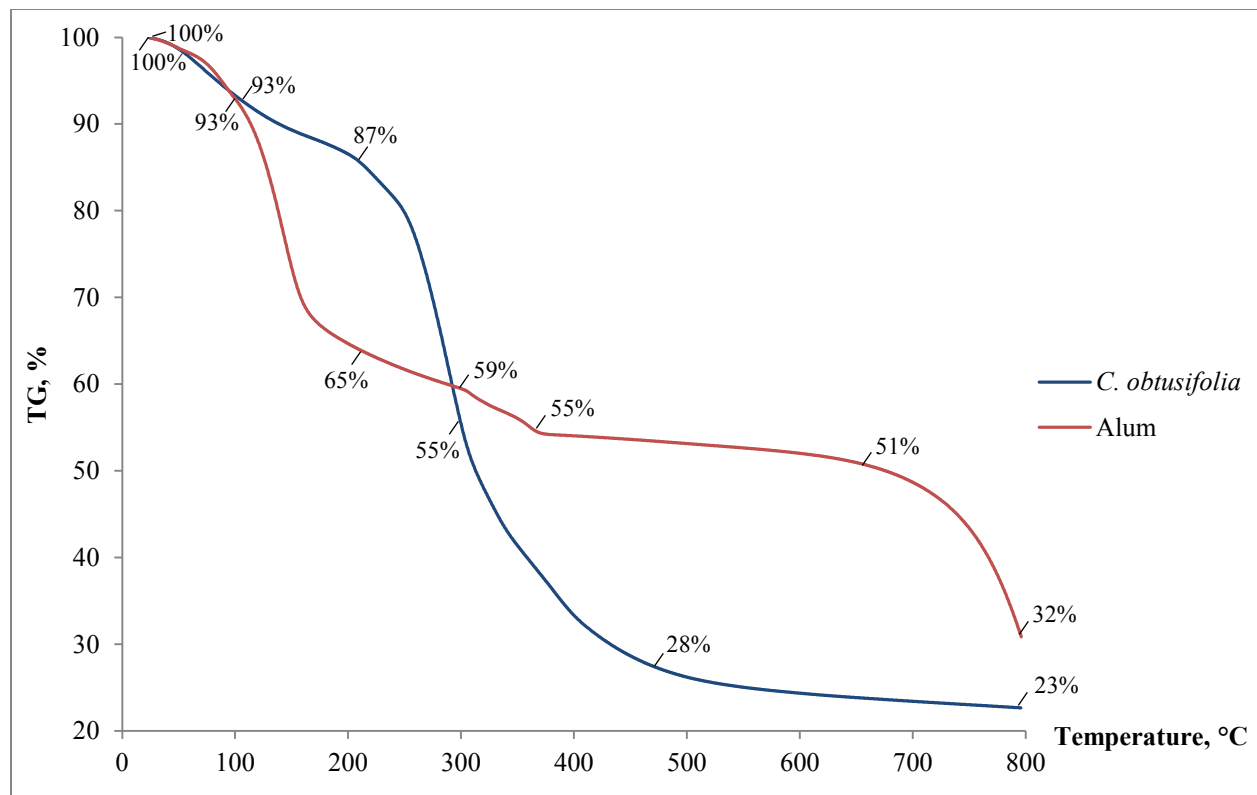


Fig. 12 (a)

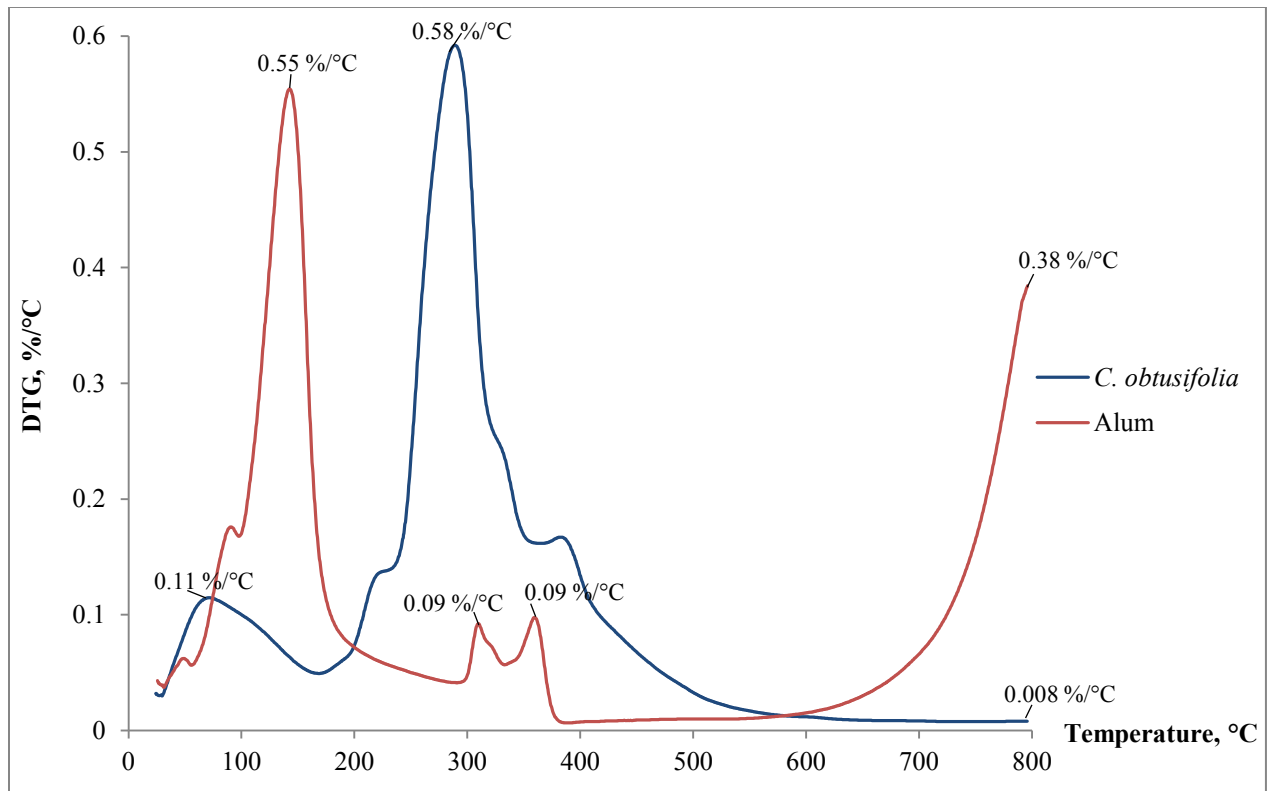


Fig. 12 (b)

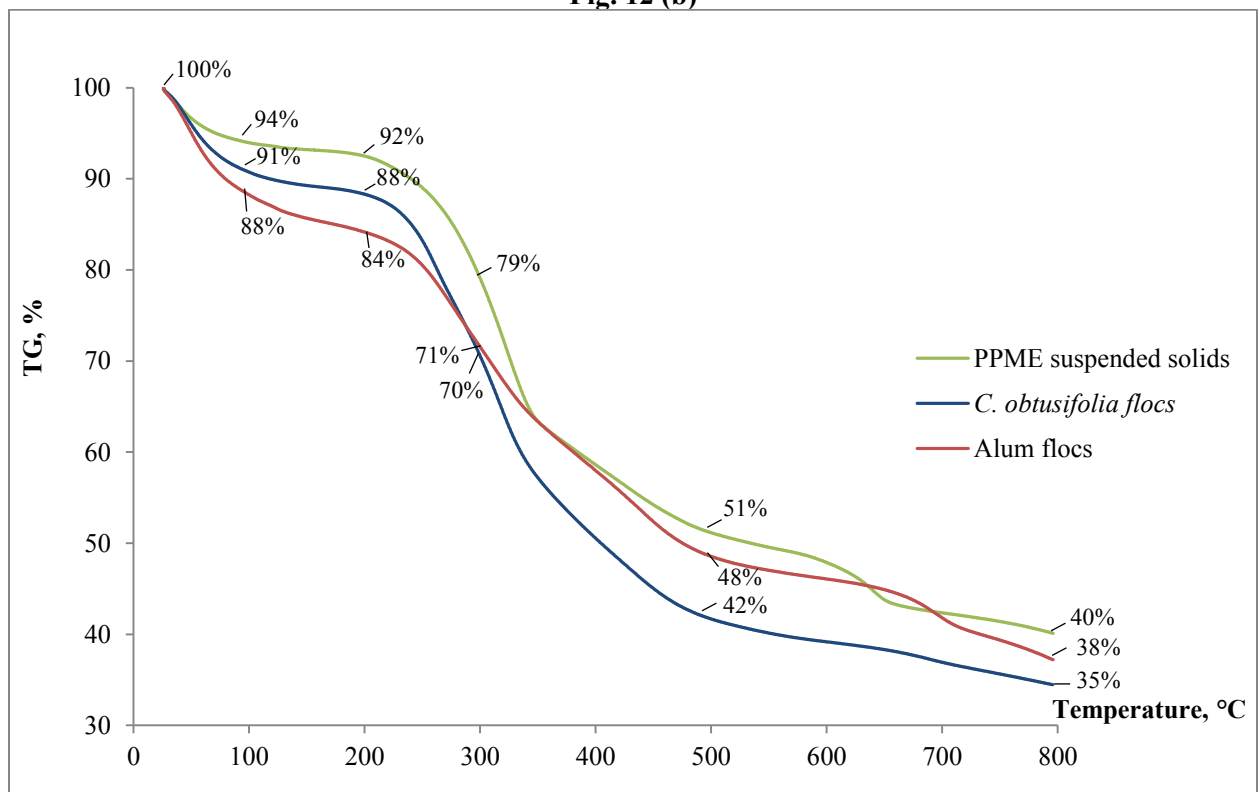
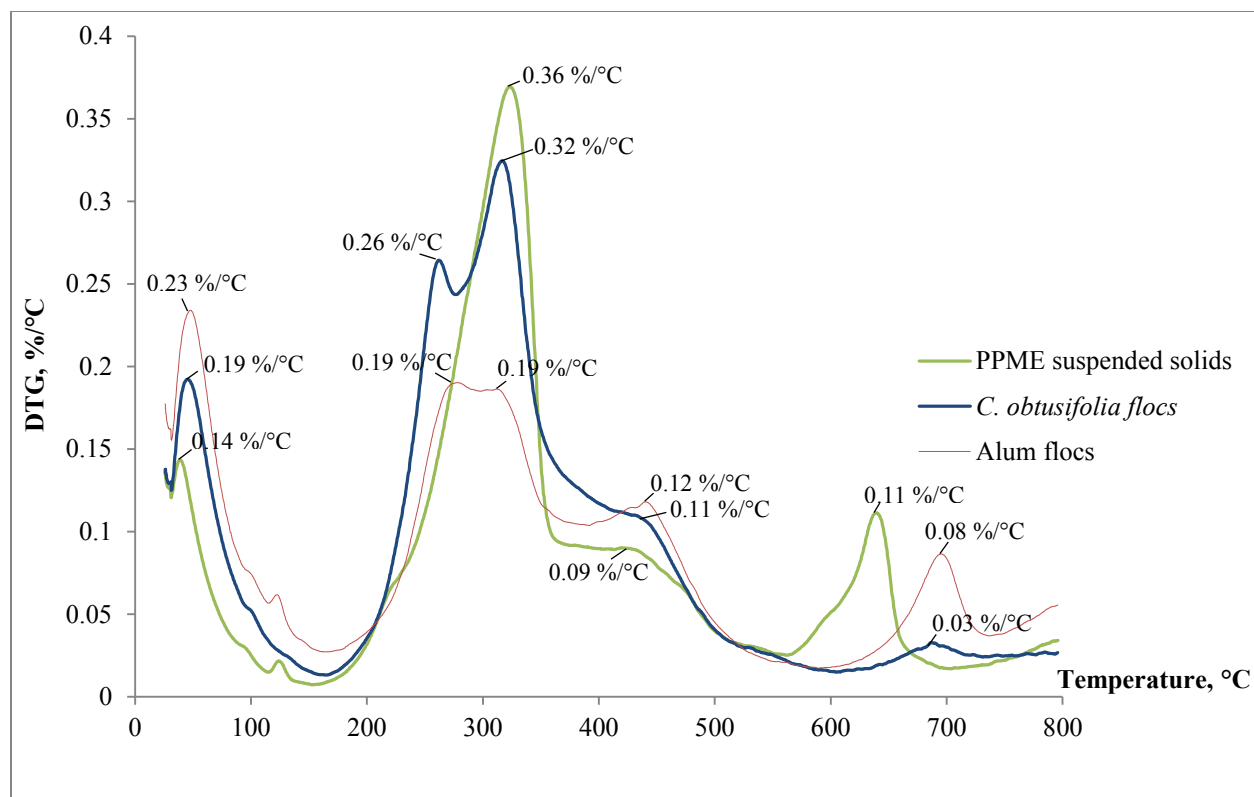
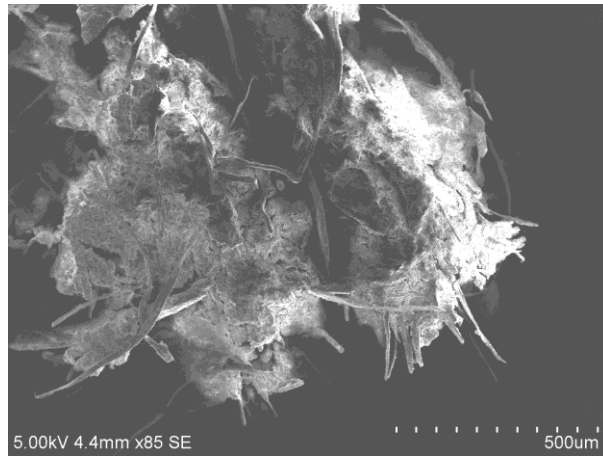


Fig. 12 (c)

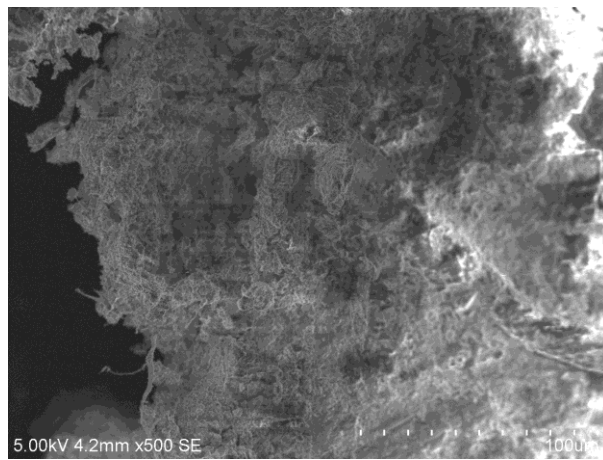


**Fig. 12 (d)**

**Fig. 12.** (a) TG plot of *C. obtusifolia* seed gum and alum; (b) DTG plot of *C. obtusifolia* seed gum and alum; (c) TG plot of PPME suspended solids, *C. obtusifolia* flocs, and alum flocs; (d) DTG plot of PPME suspended solids, *C. obtusifolia* flocs, and alum flocs



**Fig. 13 (a)**



**Fig. 13 (b)**

**Fig. 13.** SEM images (a) *C. obtusifolia* flocs; (b) alum flocs