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

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ABSTRACT

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

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

1. Introduction

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

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

Coagulation of PPME was studied previously using inorganic coagulants such as alum, iron-based salts, polyaluminium chloride (PAC), polyacrylamides (PAMs), and polydiallydimethylammonium chloride (polyDADMAC) (Renault et al., 2009; Wang et al., 2011). Although the coagulation efficiency of using these inorganic coagulants is well-proven, they pose detrimental effects on human health, produce large volume of sludge and are ineffective in low-temperature water (Yin, 2010). Moreover, aluminium-based coagulants have been proven to be associated with Alzheimer's disease in human beings (Yin, 2010).

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

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

The objective of the present study was to investigate the potential use of *C. obtusifolia* seed gum as a natural coagulant in treatment of raw and undiluted PPME. The suitability of using other natural coagulants and alum during the treatment of raw and undiluted PPME was also investigated and compared with *C. obtusifolia* gum. In addition, the effects of various operating conditions, such as initial pH, coagulant dosage, settling time, slow-mixing velocity, and slow-mixing time, on total suspended solids (TSS) and chemical oxygen demand (COD) removals using *C. obtusifolia* gum were studied. Coagulant and flocs characteristics were also analysed using scanning electron microscope (SEM), Fourier-transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA).

2. Materials and Methods

2.1. Preparation of C. obtusifolia seed gum coagulant

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

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

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

2.3. *Preparation of raw and undiluted PPME*

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

2.4. *Jar-test experiment*

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

2.5. *Analytical methods*

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

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

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

where TSS_i and TSS_f are initial and final TSS values (mg/L) whereas COD_i and COD_f are initial and final COD values (mg/L), respectively.

3. Results and discussion

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

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

3.2. Effect of initial pH

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

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

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

Fig. 4 also shows that the recommended pH for coagulation process was specific to different coagulants. Using One-way ANOVA analysis, the recommended initial pH of PPME for *C. obtusifolia* gum was pH 5 whereas for alum, it was at pH 7. Subsequent effects were studied under the recommended initial pH for both *C. obtusifolia* gum (pH 5) and alum (pH 7).

3.3. Effect of coagulant dosage

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

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

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

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

3.4. Effect of settling time

Settling time was studied as it influences the overall cost and coagulation efficiency of the treatment process (Ahmad et al., 2008). Fig. 7 indicates that coagulation process without introducing settling yielded lower TSS removal (72.6 and 64.9% for *C. obtusifolia* gum and alum, respectively). On the other hand, the allowance of settling time from 10 s to 1 min resulted in slight improvement of TSS (8.2 and 8.3 % increase for *C. obtusifolia* gum and alum, respectively) and COD removals (5.9 and 5.1% increase for *C. obtusifolia* gum and alum, respectively). The present results were concurrent with Merzouk et al. (2011) who reported that the settling time was less significant as compared to the other studied effects, such as initial pH, coagulant dosage, slow-mixing velocity and slow-mixing time. Removal efficiencies of TSS and COD after 1 min showed no further substantial improvement in coagulation activity through one-way ANOVA analysis. Consequently, investigation of subsequent parameters hereafter was based on the settling time of 1 min for both *C. obtusifolia* gum and alum. Settling time achieved in this study is comparably low with the coagulation system employed by Ahmad et al. (2008) who used alum and polyacrylamide as a coagulant and flocculant, respectively in PPME treatment to achieve a settling time of 12s.

3.5. Effect of slow-mixing velocity

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

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

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

3.6. Effect of slow-mixing time

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

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

3.7. FTIR analysis

Both *C. obtusifolia* gum and alum were analyzed using FTIR to determine the presence of active functional groups in both coagulants. *C. obtusifolia* gum (Fig. 10) had a broad and strong band at 3277 cm^{-1} due to O-H stretching whereas the presence of C-H linkages was indicated at 2923 cm^{-1} (Singh et al., 2007; Singh et al., 2010). Peaks of -CH- group was observed at 2853 cm^{-1} whereas peak at 1744 cm^{-1} represented the stretching of C=O ester group (Singh et al., 2007; Singh et al., 2010). Additional peaks at 1634 and 1239 cm^{-1} represented the presence of carbonyl C=O stretching vibrations in primary and tertiary amides, respectively (Fatombi et al., 2013). N-H groups in amides formed intermolecular hydrogen bonds between the coagulants and suspended solids to aid the coagulation process (Fatombi et al., 2013). The weak bands at 1417 and 1378 cm^{-1} were due to bending vibrations of CH_3 and the scissor vibration of CH_2, most likely indicating the presence of COOH groups (Ni et al., 2012). Carboxyl groups provided adsorption sites for the suspended solids during coagulation process (Yin, 2010). Small peaks at 1147 and 1027 cm^{-1} arised from C-O stretching of ester (Singh et al., 2007; Singh et al., 2010).

On the other hand, alum (Fig. 10), which is dodecahydrates, had a broad peak at 2958 cm^{-1}, due to the existence of OH groups in alum (Rong et al., 2013). At 1652 cm^{-1}, OH stretching resulted from the hydroxyl group within alum and also the Al-O bond vibrations (Ni et al., 2012). Additional peaks at 1058 cm^{-1} was due to SO_4^{2-} stretching whereas peak at 923 cm^{-1} was assigned to the possible HOO matrix (Singh et al., 2012; Frost et al., 2013). The presence of OH and HOO groups were due to the formation of hydrogen bonds between alum and suspended solids during coagulation process (Baranović, 2014).

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

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

3.8. TGA

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

The decomposition stages for each sample were distinguished from the differential thermal gravimetric (DTG) curves (Figs. 12b and 12d). From Fig. 12b, two significant mass change regions were observed for *C. obtusifolia* seed gum whereas three for alum. In contrast to Fig.13b, Fig, 9d shows three significant and similar mass change regions for all samples. At lower temperature, intra and intermolecular moisture was evaporated with an increase of temperature (Lee et al., 2012). The sudden loss of mass observed in alum after 100°C could be due to the loss of absorbed species such as water (Fig. 12a). Thus, DTG peaks of alum were more prominent than *C. obtusifolia* at lower temperature after 100°C (Fig. 12b and 12d) which indicated alum has more hygroscopic components in it as compared to *C. obtusifolia* (Lee et al., 2012). The organic components of *C. obtusifolia*, alum, and PPME suspended solids started to degrade around 200 °C. Temperatures beyond 300°C indicated significant weight loss due to severe decomposition of all samples. Lee et al. (2012) stated that most of the components in all samples were decomposed at high temperature. In the present study, this occurred at temperatures above 600°C (Fig. 12d). the weightlessness at high temperatures is due to the total decomposition of sample (Lee et al., 2012). Similarly, this was observed at temperatures beyond 650 °C of *C. obtusifolia* seed gum whereas DTG curve of alum indicates a peak at 800 °C (Fig. 12b).

3.9. Morphology of flocs

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

4. Conclusion

In many countries, waste management systems are undergoing changes due to the threat of global climate change and other environmental issues (Nouri et al., 2012), resulting somewhat a larger number of cases in water resource management have been studied from the sustainability perspective (Wu et al., 2013b). The present study pursued a new alternative coagulant, namely *C. obtusifolia* seed gum that is biodegradable and natural to environment and living organisms. The use of unmodified *C. obtusifolia* gum in treatment of raw and undiluted PPME showed positive and comparable results against commercially used alum. Under recommended conditions (pH 5, 0.75 g/L dosage, 10 rpm and 10 min slow-mixing, and 1 min settling time), *C. obtusifolia* gum yielded significant TSS and COD removals of 86.9 and 36.2%, respectively. The present study proved that *C. obtusifolia* gum was a promising and effective natural coagulant in substituting harmful inorganic coagulants such as alum in coagulation process of industrial effluent.

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Fig. 1. *C. obtusifolia* seeds.

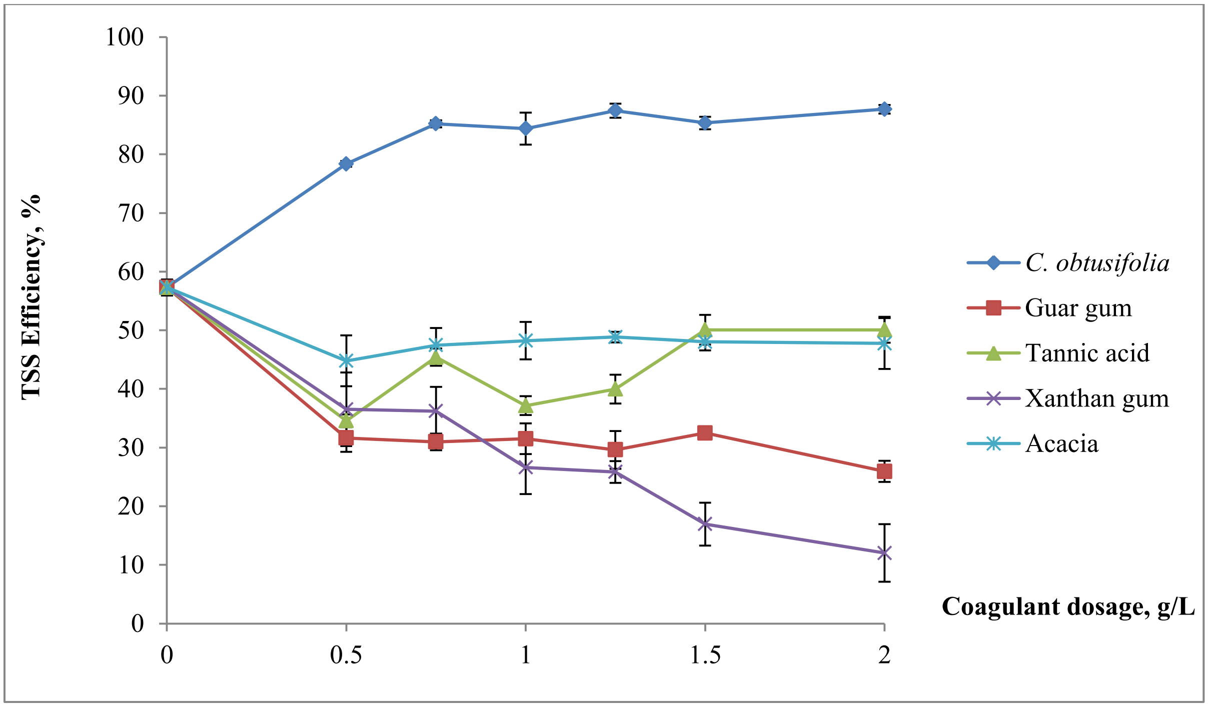


Fig. 2. Coagulation efficiency using different potential natural coagulants in treatment of raw PPME. (pH = 5; rapid-mixing velocity = 150 rpm; rapid-mixing time = 5 min; slow-mixing velocity = 10 rpm; slow-mixing time = 15 min; settling time = 60 min; n=3)

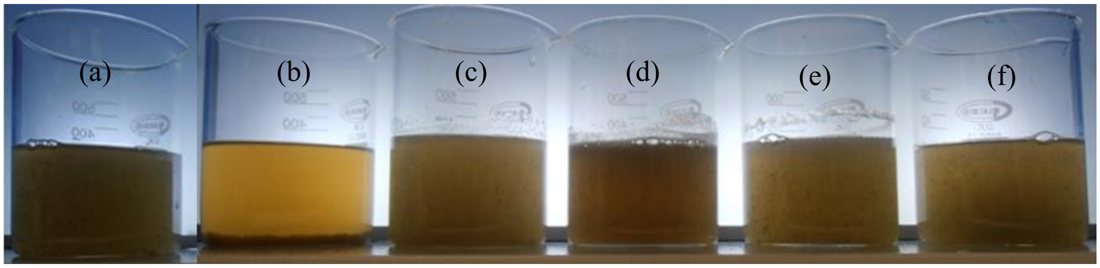
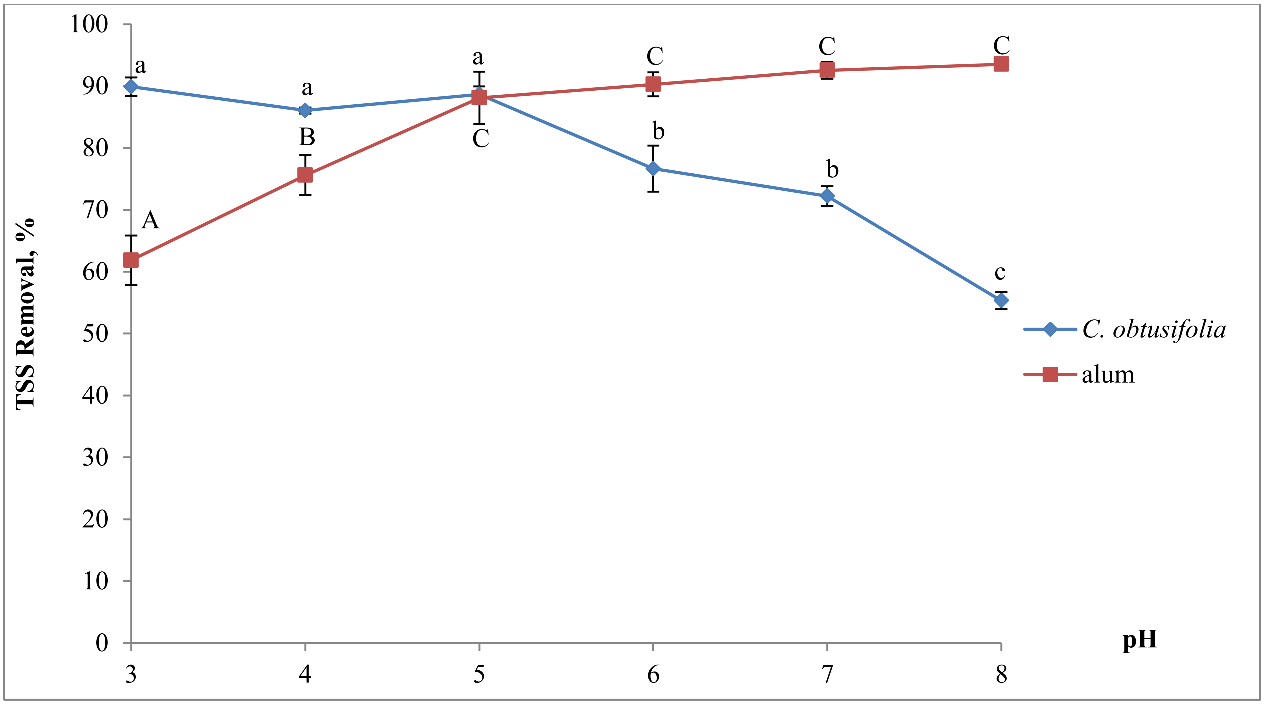
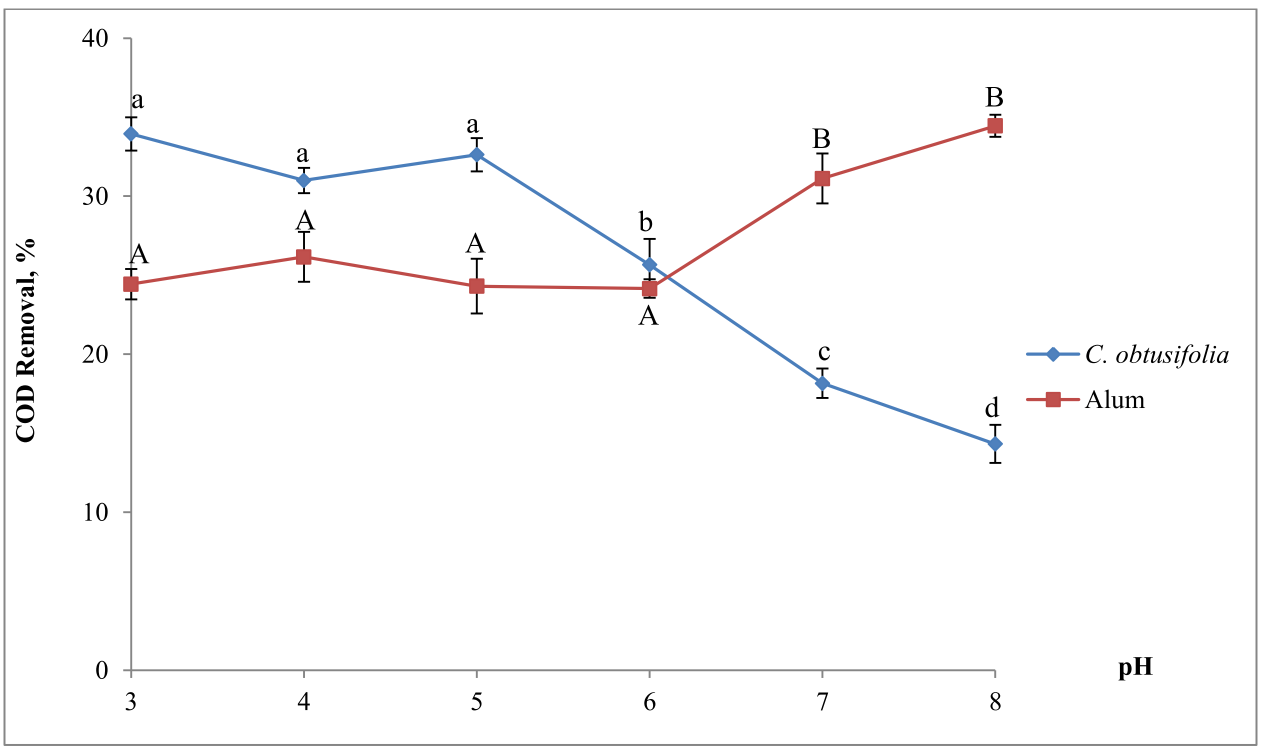


Fig. 1. Initial investigation of (a) raw PPME treatment using (b) *C. obtusifolia*, (c) guar gum, (d) tannic acid, (e) xanthan gum, and (f) acacia



TSS Removal, %
100
90
80
70
60
50
40
30
20
10
0
3
4
5
6
7
8
pH
a
a
a
b
b
c
A
B
C
C
C
C
C. obtusifolia
alum

Fig. 4 (a)



COD Removal, %
40
30
20
10
0
3
4
5
6
7
8
pH
a
a
a
b
c
d
A
A
A
A
B
B
C. obtusifolia
Alum

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)

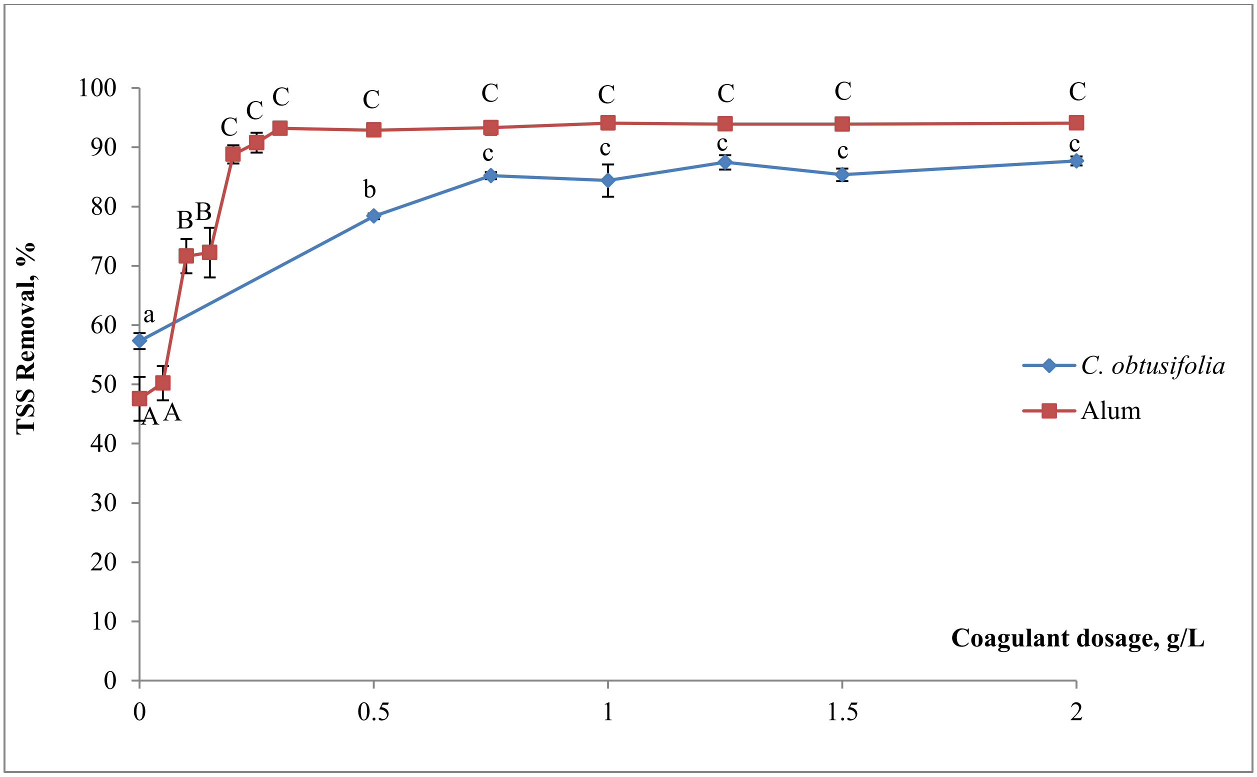


Fig. 5 (a)

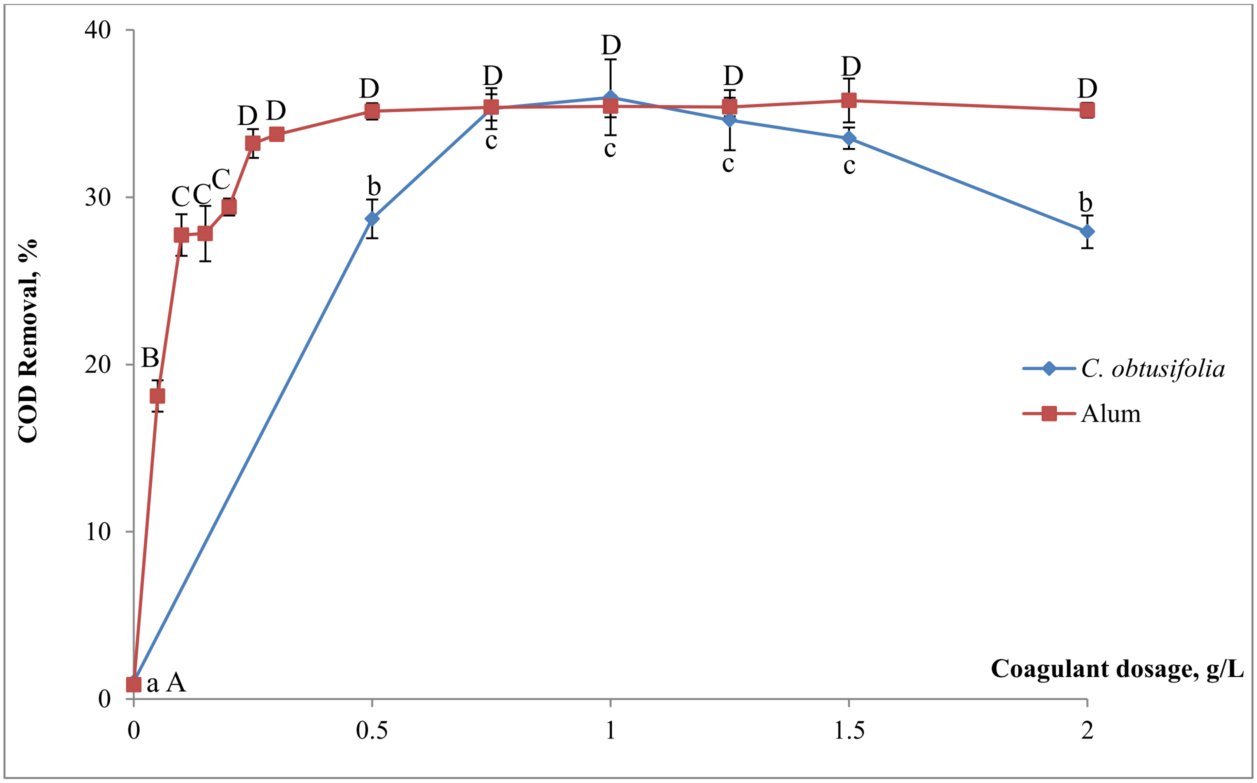


Fig. 5 (b)

Fig. 5. Effect of *C. obtusifolia* and alum dosage on (a) %TSS removal; (b) % COD removal. (pH = 5 for *C. obtuisfolia* 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)

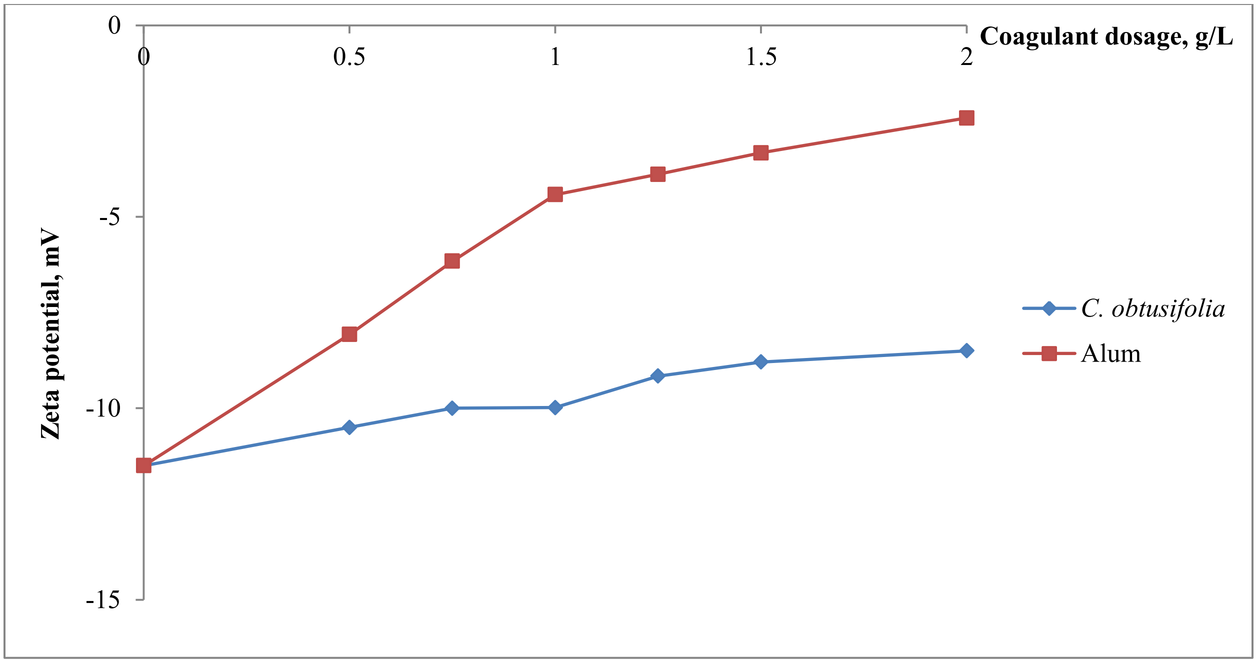
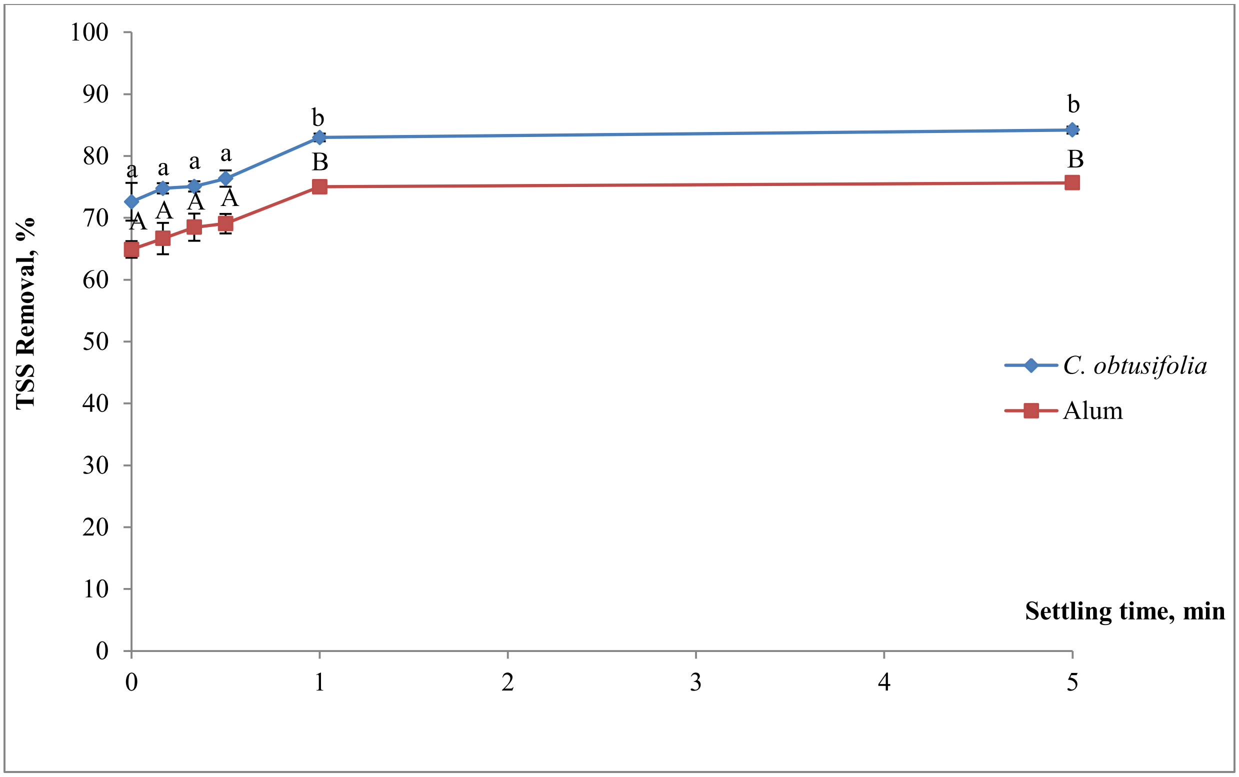
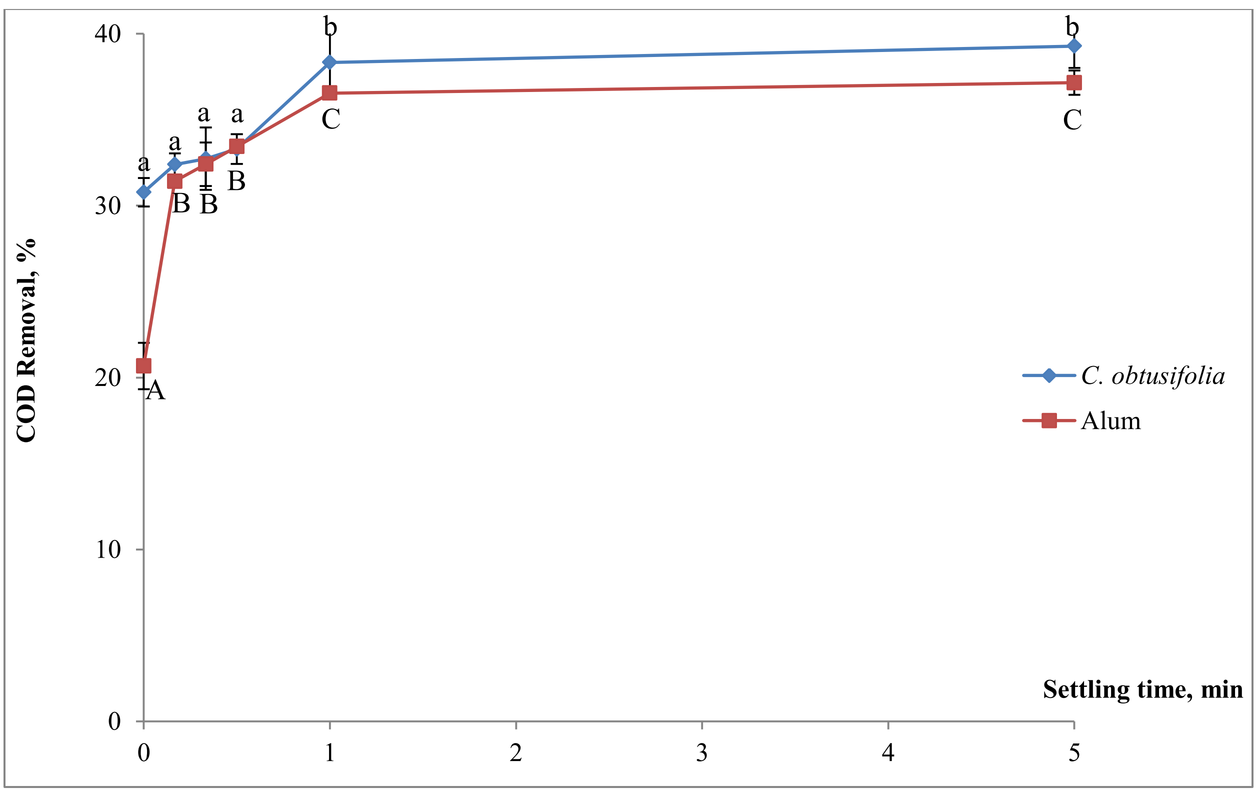


Fig. 6. Zeta potential of pre-treated raw PPME using *C. obtusifolia* and alum at different coagulant dosage under recommended treatment conditions



TSS Removal, %
100
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
Settling time, min
C. obtusifolia
Alum
a
A
b
B

Fig. 7 (a)



COD Removal, %
40
30
20
10
0
0
1
2
3
4
5
Settling time, min
C. obtusifolia
Alum
a
A
B
b
C

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)

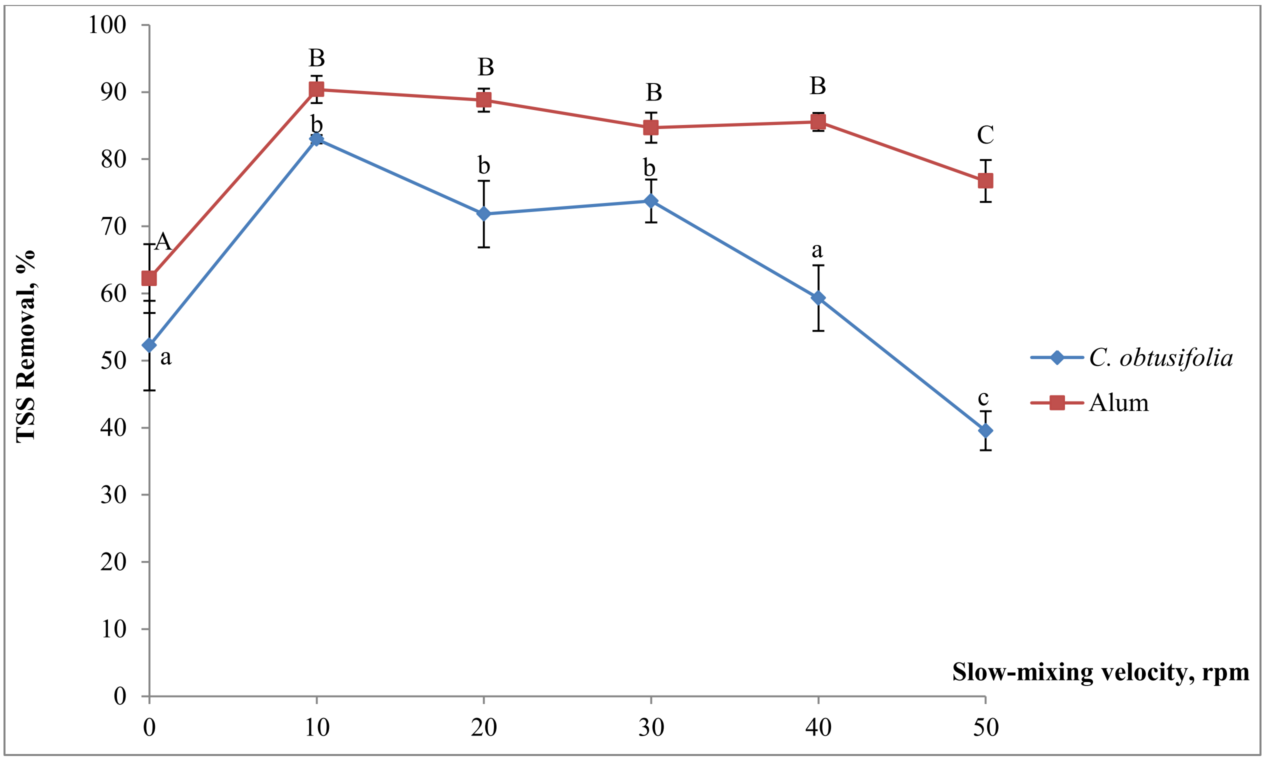


Fig. 8 (a)

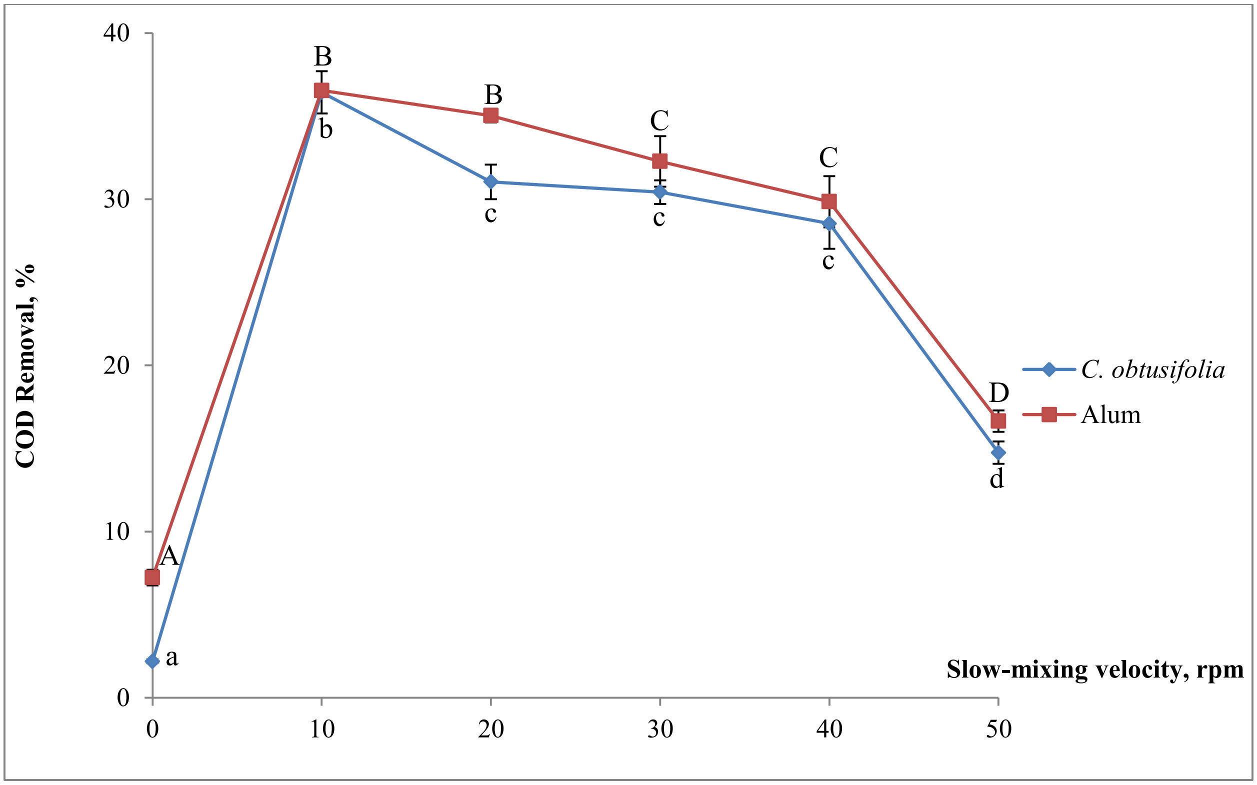


Fig. 8 (b)

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)

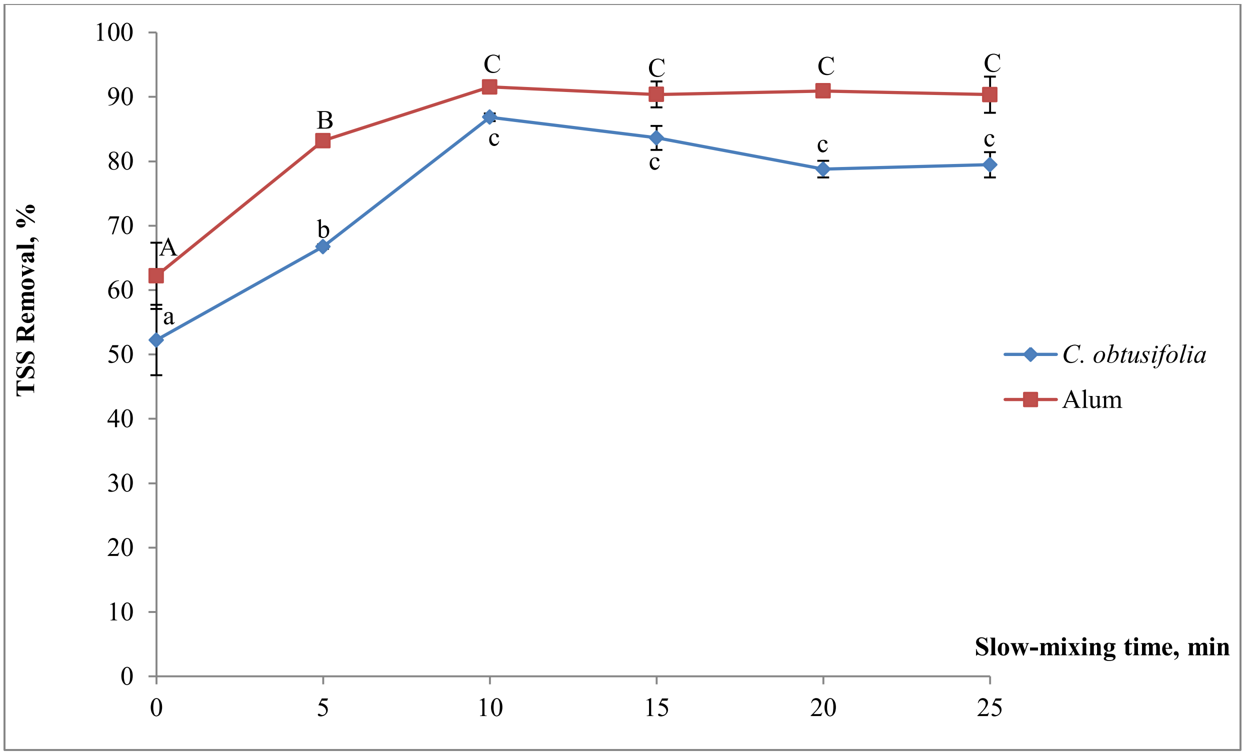


Fig. 9 (a)

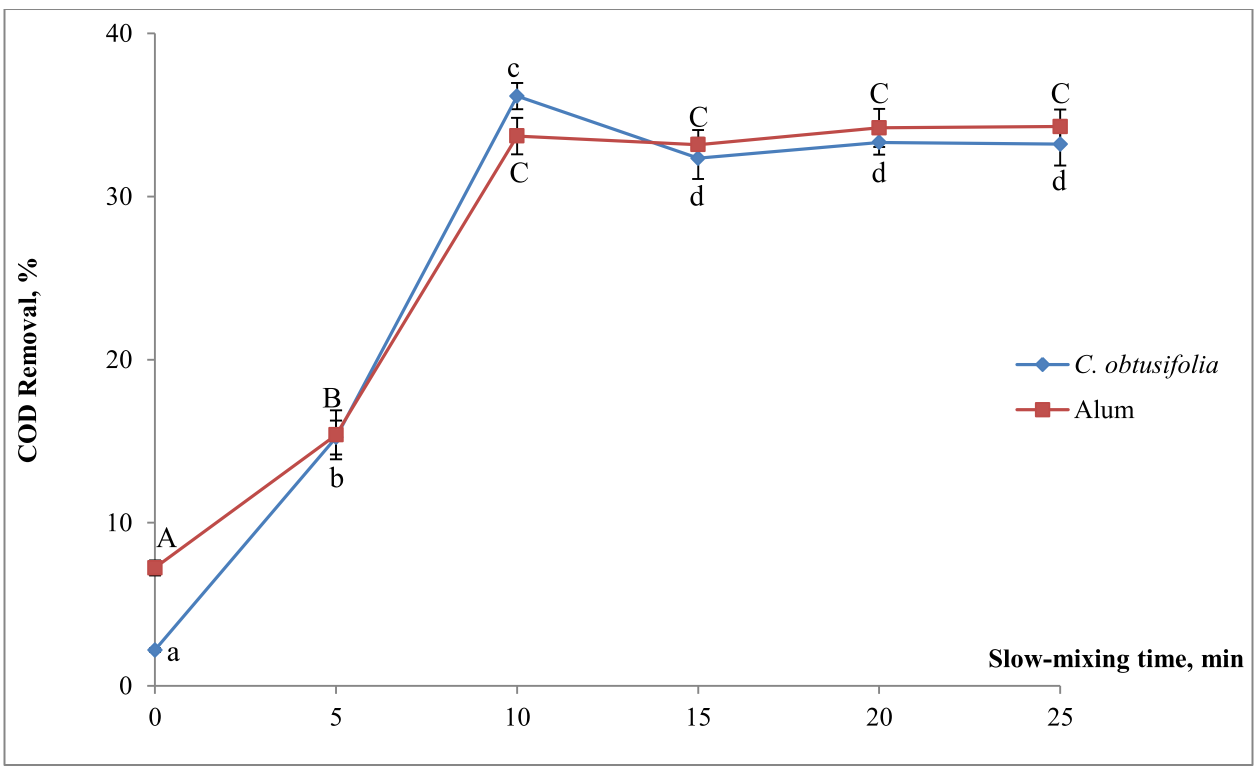


Fig. 9 (b)

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)

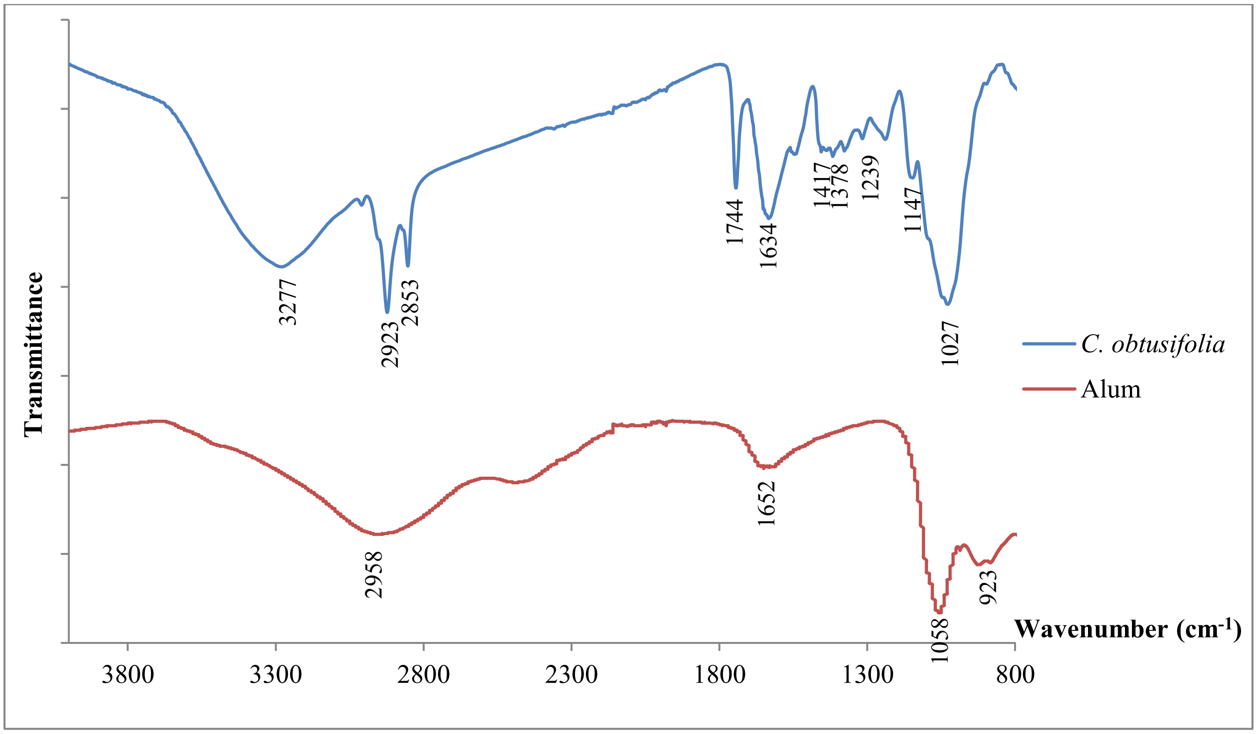


Fig. 10. IR spectra of *C. obtusifolia* seed gum and alum

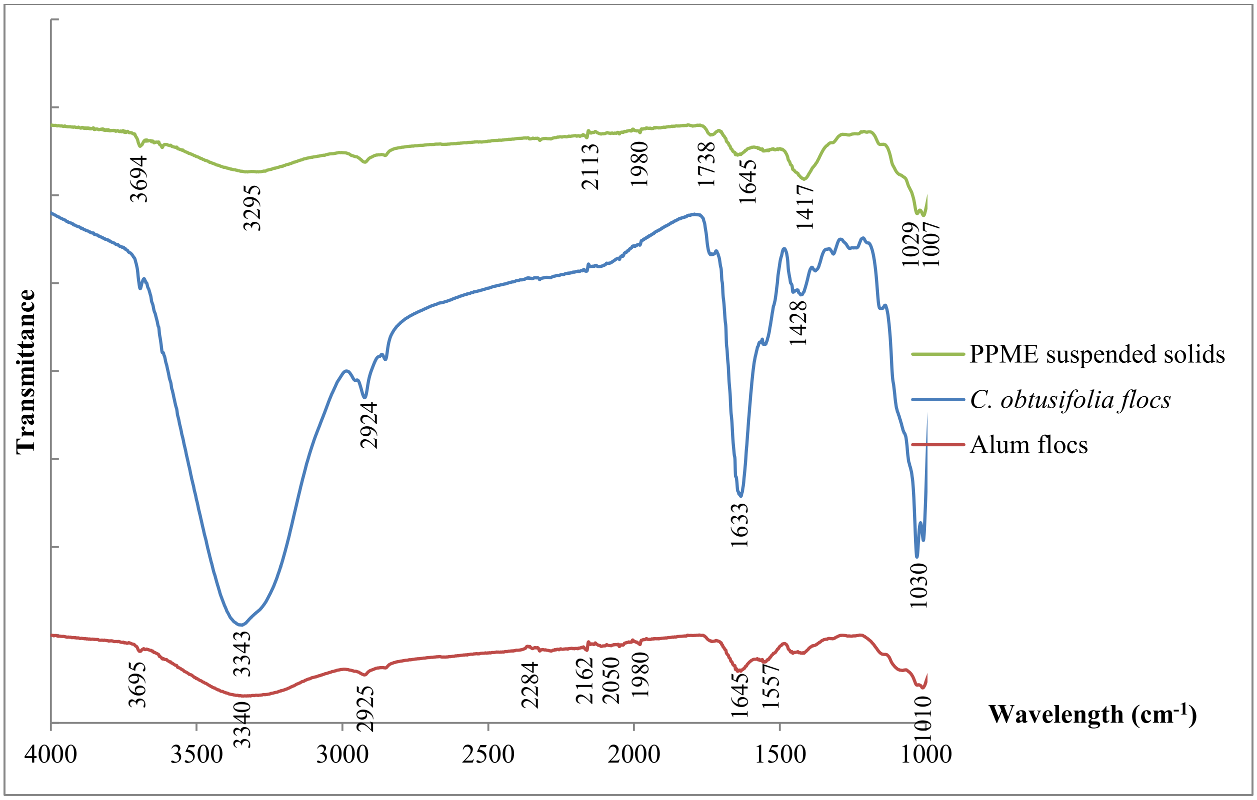


Fig. 11. IR spectra of PPME suspended solids, *C. obtusifolia* flocs, and alum flocs

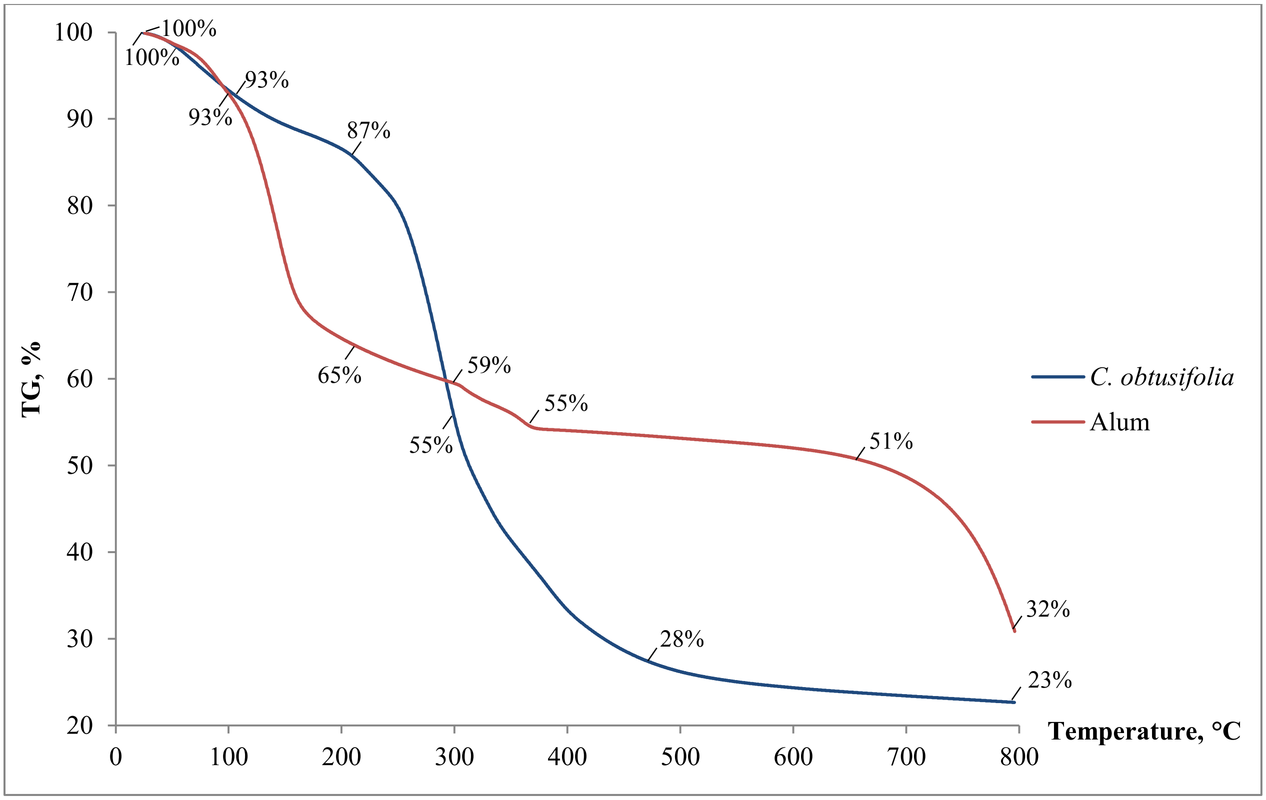

TG, %
100
90
80
70
60
50
40
30
20
0
100
200
300
400
500
600
700
800
Temperature, °C
C. obtusifolia
Alum
100%
100%
93%
93%
87%
65%
59%
55%
55%
51%
28%
32%
23%

Fig. 12 (a)

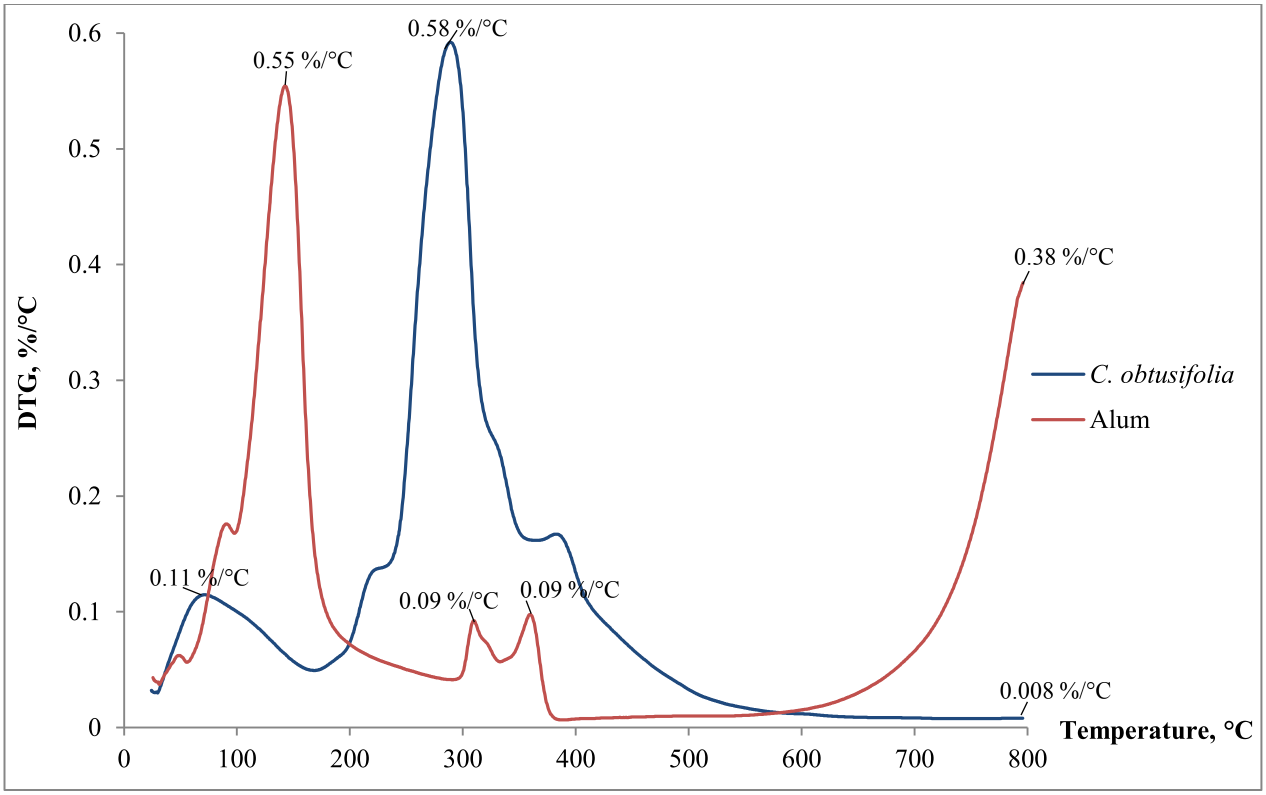


Fig. 12 (b)

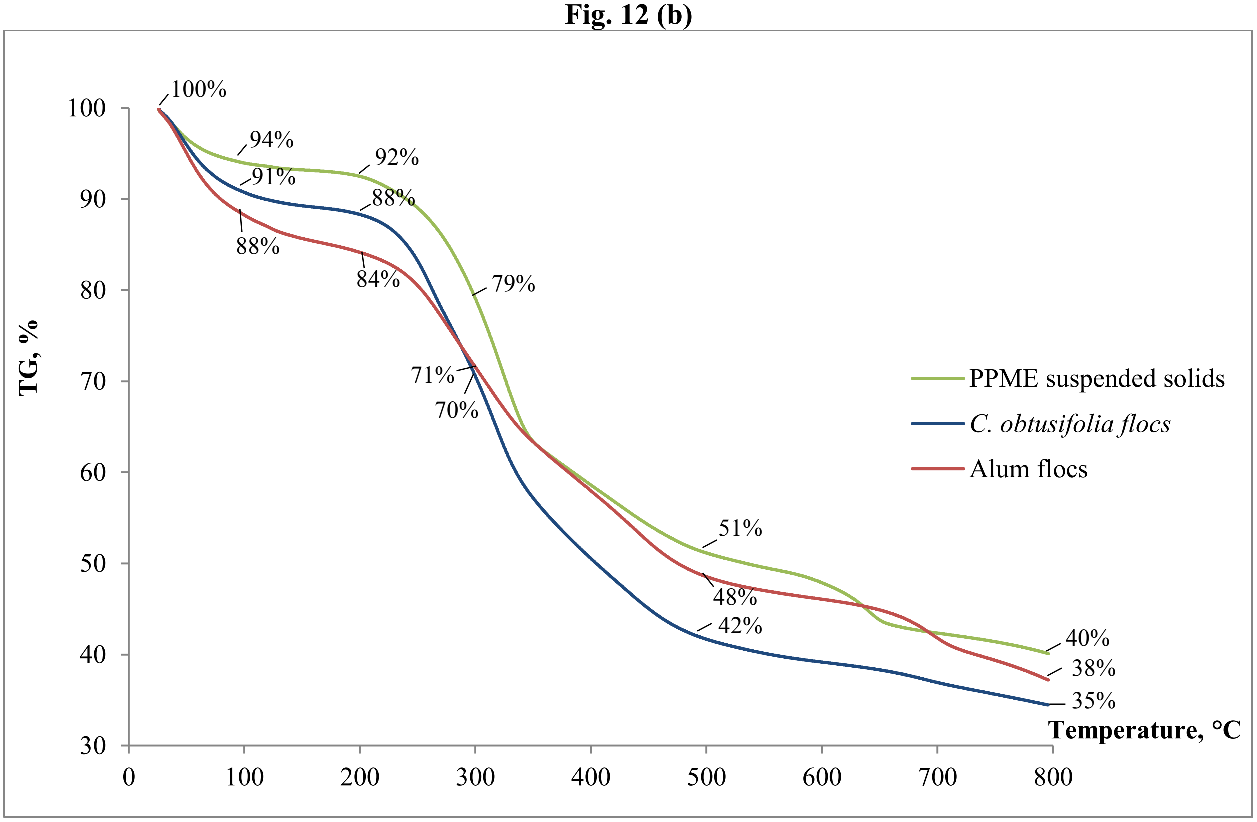


Fig. 12 (c)

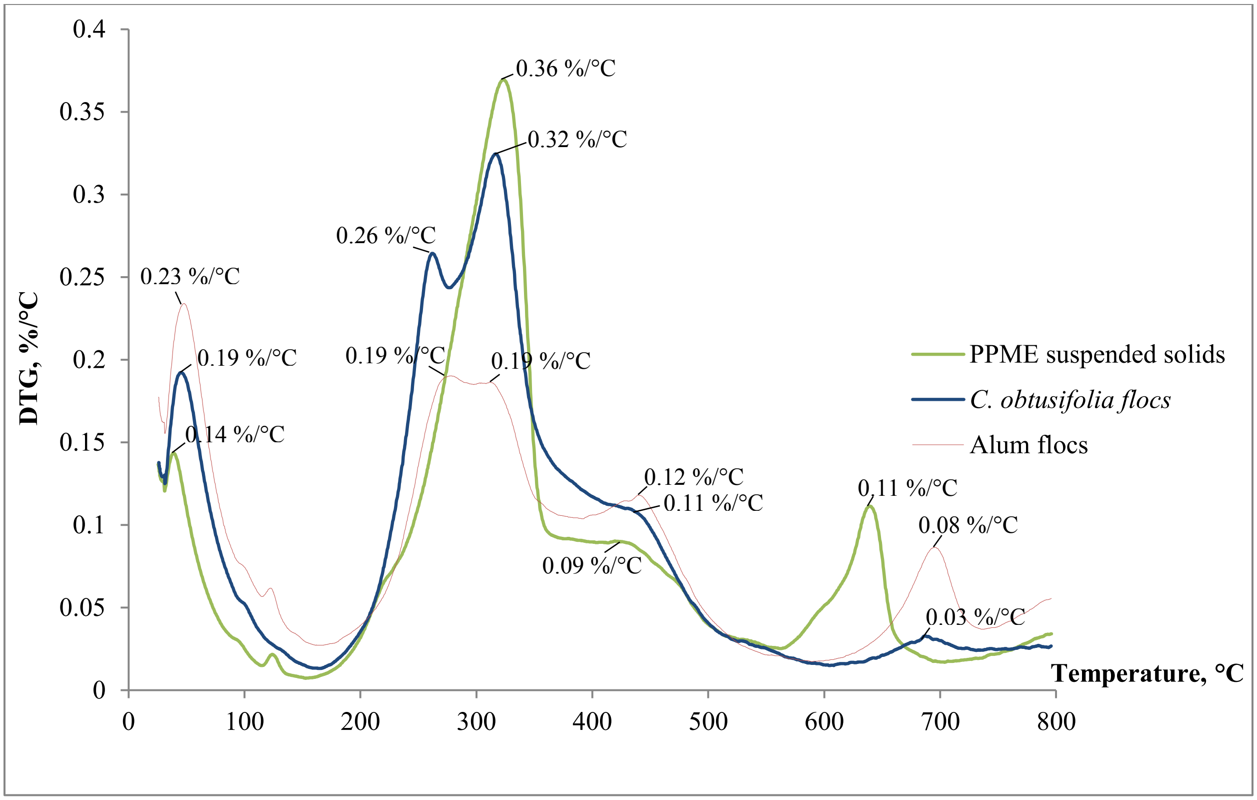


Fig. 12 (d)

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

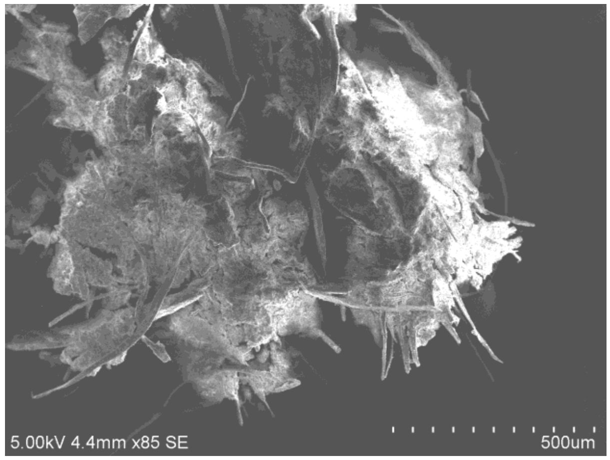


Fig. 13 (a)

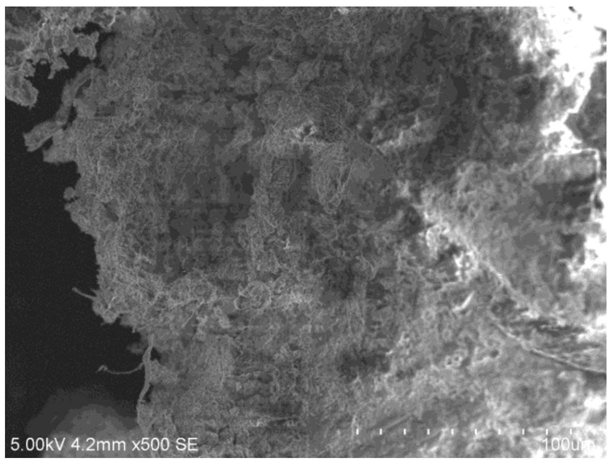


Fig. 13 (b)

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