Development of coagulant synthesis byproducts from cengar clay as adsorbent in post-coagulation peat water treatment

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Abstract. Cengar clay was used as a precursor for liquid coagulant and adsorbent. It was calcined at 700°C for 1 hour followed by extracting with 0.2 moles H_2SO_4 at 80 and 100°C for 2 hours respectively. The main products are liquid coagulant of $LC_{1(80-2)}$ and $LC_{1(100-2)}$ which applied to coagulate the peat water. The liquid coagulants were characterized for pH and cation contents. And then after coagulation, peat water were adsorbed by using each extraction byproducts of liquid coagulant include $LCA_{1(80-2)}$ and $LCA_{1(100-2)}$ having adsorbent-peat water ratio 0.5:100 and 1:100 (w/v). Minerals characteristic of adsorbents were characterized using X-ray diffraction method. The several peat water parameters were analyzed for pH, color, turbidity, and organic substances. The results achieved that liquid coagulants were containing bivalent cation (Ca and Mg) far more than trivalent cation (Al and Fe) and pH 7-8. On the other hand, the adsorbent has found of kaolinite, montmorillonite, muscovite and calcite minerals. The liquid coagulant has not been able to improve the overall parameters analyzed. However, the $LC_{1(80-2)}$ coagulant achieved only removal efficiency of color 12.47%, turbidity 17.59% and organic substances 2.55% respectively. Meanwhile, the most effective adsorbent for post-coagulation peat water was achieved by $LCA_{1(80-2)}$ on 1:100 ratio that increases the water pH becomes neutral, removal efficiency of color 96.57%, turbidity 98.03% and organic substances 81.55%, respectively. Therefore, the adsorbent performance is much better than the coagulant in peat water treatment. As a conclusion, the adsorption step can cope up with the bad condition of post-coagulation of peat water.

1 Introduction

Surface and groundwater, and industrial or household wastewater contain many different types of metallic, inorganic, and organic compounds that are hazardous to a human being,

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animals, and plants. By 2050, global population is expected to reach up to 9.3 billion and the world may be under great freshwater scarcity [1]. Therefore, the removal of toxic organic pollutants from water is inevitably essential in this present scenario.

In the recent past, various types of clay have been increasingly used in several remediation and pollution control processes. This usage is being inexpensive and abundant in Indonesia, especially in Riau Province. Natural mineral clays possessed specific surface chemical properties, e.g., cation exchange capacity, and adsorptive affinity for some organic and inorganic compounds, which have led to an investigation on the potential use of clays as an adsorbent for treating heavy metal, and inorganic pollutants, or as coagulant agents [2, 3].

In this report, it has been investigated the application of clay from Riau Province. Clay originated from Cengar of Kuantan Singingi has been reported as coagulant due to its contained Al and Fe 14.37% and 1.01%, respectively [4]. The previous experiment [5] has been revealed that calcinated Cengar clay at 700°C for 3 hours and extracted by H_2SO_4 0.2 moles at 100°C for 2 hours appeared to repair some of peat water parameters. It was met Permenkes No.416/Menkes/PER/IX/1990, such as several parameters of odorless, having pH 8.02, turbidity 4 NTU, Total Dissolved Solid (TDS) 278 mg/L, and Total Suspended Solid (TSS) 7 mg/L. On the other hand, the advanced process is still needed to repair its parameters of color and organic substances.

Liquid coagulant was produced after extraction process of clay as precursor using H_2SO_4, and there was residual solid as minor product found from this experiment. The residual solid would become waste if it disposed to the environment. Even though this residue is thought still have an adsorption ability, so it can be used as an adsorbent post-coagulation peat water. Adsorption process will remove the soluble and insoluble organic pollutants. The removal capacity ranging from 80 to 99% was reported [6]. The residual solid adsorbent is expected to remediate color and organic substances of post-coagulation peat water. There were many studies revealed elsewhere using clay as a coagulant [7-11] or an adsorbent [12, 13], but herein, it was reported the economic strategy for peat water treatment with combine both of coagulation-adsorption process.

2 Materials and methods

The materials used were as follow; natural clay (originated from Kuantan riverside, Cengar Village, Kuantan Singingi District, Riau Province), peat water (collected from Rimbo Panjang, near of Pekanbaru), 98% H_2SO_4 (E-Merck), $KMnO_4$ (E-Merck), $H_2C_2O_4.2H_2O$ (E-Merck), Whatman filter paper No. 42, aluminum foil, buffer solution pH 4, 7 and 9.

Natural clay washed with aquadest, dried, and then crushed to have powder have a desired particle size range of $100 \leq x \leq 200$ mesh. The clay powder is dried 105°C in an oven by gravimetry method. Furthermore, the clay was calcined in a furnace Nebertherm L31R at 700°C for 1 hour. And then a 30 g of the calcined clay was extracted using 360 mL H_2SO_4 0.2 moles. And then heating over an hot plate stirrer REXIM RSH-1DR L120 having a stirring speed of 700 rpm at 80°C ($LC_{1(80-2)}$) and 100°C ($LC_{1(100-2)}$) for 2 hours. The mixture was allowed for ± 24 hours. Liquid coagulant was withdrawn using pipette from the top inch of the supernatant. Liquid coagulants are measured of acidity by pH meter pen pH-009(I), and the content of Al^{3+}, Fe^{3+}, Na^{+}, K^{+}, Ca^{2+}, and Mg^{2+} cations using ICP-EOS Perkin Elmer type Optima 8000. The solid precipitate (LCA) was filtered using Whatman No. 42. LCA is given a symbol according to the extraction temperature in the sulfuric acid, ie $LCA_{1(80-2)}$ for 80°C and $LCA_{1(100-2)}$) at 100°C. LCA was dried in the oven at the temperature of 105°C for ±24 hours and allowed to dry in a desicator for ± 6 hours. LCA is ready used as andsorbent for peat water after coagulation. The chemical composition of natural clay and adsorbent is determined by X-Ray Diffraction (XRD) Pan Analytical type Empyrean.

2.1 Coagulation-floculation process of peat water

Liquid coagulant ($LC_{1(80-2)}$, $LC_{1(100-2)}$) and peat water sample were contacted with ratio 1:10 (v/v) in a beaker glass. The beaker was agitated by magnetic stirrer at various mixing time with speed (160 rpm) for 2 minutes and slow mixing (40 rpm) for 10 minutes. After agitation stop, the suspension was allowed to settle undisturbed for 6 hours. A sample was withdrawn using a pipette from the top inch of supernatant to detect the change of pH, color, odor, TSS, TDS, and organic substance. The result of the analysis was compared to PERMENKES No.146/MEN/KES/PER/IX/1990 “about the Water Quality Requirements.”

2.2 Adsorption of peat water post-coagulation process

Minor product extraction of natural clay ($LCA_{1(80-2)}$, $LCA_{1(100-2)}$) and peat water after coagulation were mixed with a variable ratio of 0.5:100 and 1:100 (w/v). It was stirred evenly for 1 minute and allowed to stand for 24 hours. The supernatant was analyzed having same analysis parameters of the coagulation-flocculation process.

3 Results and discussion

3.1 Characterization of liquid coagulant

The various temperature effect of natural clay extraction was investigated. Cation concentration of liquid coagulant is represented in Table 1.

Table 1. Cation concentration (mg/L) and pH of liquid coagulant.

Cation	$LC_{1(80-2)}$	$LC_{1(100-2)}$
Al^{3+}	1.22	1.25
Fe^{3+}	0.24	0.22
Na^{+}	5.10	7.91
K^{+}	16.10	21.59
Ca^{2+}	558.06	539.41
Mg^{2+}	79.82	53.11
pH	8.0	7.4

$LC_{1(80-2)}$: Liquid Coagulant; calcination (t=1 hour) and extraction (T = 80ºC, t = 2 hours), $LC_{1(100-2)}$: Liquid Coagulant; calcination (t=1 hour) and extraction (T = 100ºC, t = 2 hours)

Based on Table 1, mono and divalent cation were extracted more than trivalent by H_2SO_4 in both coagulants. Alkaline and alkaline earth metal are elements which have standard reduction potential more positive than trivalent cation (Al and Fe), means mono and divalent cation will be more reactive than trivalent. Therefore both coagulants have provided a slightly alkaline, namely pH 7.4 for $LC_{1(100-2)}$ and 8 for $LC_{1(80-2)}$. The first coagulant has slightly less alkaline because the solvent is more evaporated at a higher temperature (100°C). The results that are not much different were also found in liquid coagulants of $LC3_{(80\text{-}2)}$ and $LC3_{(100\text{-}2)}$ [14].

3.2 Liquid coagulant performance for peat water

The first step to improve the quality of peat water was through a coagulation process using liquid coagulant extracted from natural clay in sulfuric acid. The cations of clay, such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+} have been extracted by sulfuric acid to form sulfate salts, and the salts can be ionized in water to mono, bi, and trivalent cations. All of these cations can act as coagulants, but the trivalent ($Al3^+$ and $Fe3^+$) cations have the highest affinity in the coagulation process, following the rules of Schulze and Hardy. The trivalent cations have the lowest critical coagulation concentration among other cations, monovalent and bivalent, making them the most efficient in destabilizing colloidal particles [15, 16]. Coagulation occurs in acidic conditions, due to the density of cation in the coagulant is quite high that the charge neutralization and complex reaction between coagulant species and colloidal particles was dominated by the coagulation mechanism [17].

In this regard, poor coagulation process has occurred. It probably because of Al and Fe in the liquid coagulant (pH 7-8) does not redissolve, because in accordance [18] that at pH 4.5-8 both of these cations are as a precipitated hydroxide of aluminum and ferric. Another reason that Al and Fe at pH > 6 form a negatively charged complex, $Al(OH)_{4-}$ and $Fe(OH)_{4-}$ [19]. The both were affected the coagulation process.

Table 2. Characteristic of peat water before and after coagulation treatment.

Parameters	**Pre-treatment**	**Coagulation treatment**		**Permenkes No. 416/Menkes/PER/IV /1990**
		$LC_{1(80\text{-}2)}$	**$LC_{1(100\text{-}2)}$**	
Color, TCU	6170	5400	5780	50
Odor	Odorless	Odorless	Odorless	Odorless
pH	4.9	4.9	4.6	6.5-9
Turbidity, NTU	108	89	93.7	25
TDS, mg/L	432	387	366	no data
TSS, mg/L	176	65.5	69	1500
Organic substances, mg/L	355.07	346.02	334.04	10

Peat water which coagulated by two kinds of coagulant experienced insignificant improvement (represent in Table 2). As a result, it was found that based on the color, pH, turbidity, TSS, and organic substance is not feasible to be used as a source of clean water. According to Fig. 1, the highest removal efficiency for color, turbidity, and TSS was achieved by $LC_{1(80\text{-}2)}$. It probably because of bivalent cations concentration are higher than the other coagulant (Table 1). Bivalent cations have the role as a coagulant, even though its effectivity is lower than the trivalent cations. On the other hand, pH value of 8 is the best condition to precipitate of Fe and Al.

The comparison of the result with previous research [5, 14] is represented in Table 3. This is purposed to know the effectivity of liquid coagulant. $K_{100\text{-}2}$ achieves the highest removal efficiency percentage. It was probably happened due to the cation Al, and Fe concentration of each coagulant is different significantly.

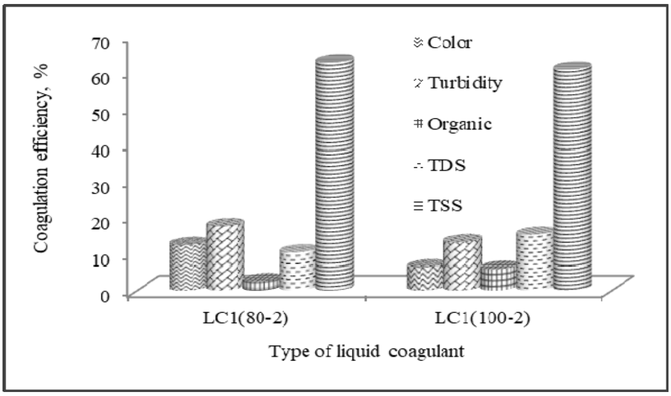


Fig. 1. Efficiency of coagulation process of peat water by two liquid coagulants.

The cation of Al and Fe concentration in $K_{(100-2)}$ are 6.923 mg/L and 4.235 mg/L, compared to this research $LC_{1(80-2)}$ contained 1.22 mg/L of Al and 0.24 mg/L of Fe, while there are 0.59 mg/L of Al and 0.08 mg/L of Fe in the $LC_{3(80-2)}$ of liquid coagulants, respectively. Based on Schulze Hardy rule, the power destabilization colloidal particles is influenced by the greater valency of the opposite charge ion of colloidal particle surface (counter ion). The greater valency of cation, the CCC will be smaller [15, 16]. Hence the colloidal particles will be coagulated effectively. However, in this research, mono and bivalent cations concentration of $LC1_{(80-2)}$ is higher than trivalent cations. So, the performance of $LC_{1(80-2)}$ was occurred ineffective on peat water treatment.

Table 3. Comparison of liquid coagulant performance.

Parameters	**Coagulation efficiency, %**		
	$LC_{1(80-2)}$	**$K_{(100-2)}$ [5]**	**$LC_{3(80-2)}$ [14]**
Color	12.50	56.90	13.6
Turbidity	17.59	84.61	13.5
TDS	10.41	85.74	-
TSS	62.78	96.80	-
Organic substance	2.55	82.51	6.5

The main factor that caused differences between Al and Fe cations which extracted in liquid coagulant is the clay as a precursor on synthesized liquid coagulant. The clay is a local natural resource which has heterogenous mineral distribution. It might cause differences amount of extracted cation concentration, although the condition was the same.

3.3 Adsorbent performance of peat water post-coagulation

According to Fig. 2, the decreasing efficiency of colloidal particles is influenced by the byproduct adsorbent of liquid coagulant (LCA), it was found of about 96% color, 98%

turbidity, 82% organic substance respectively, and pH 7.5. It probably because clay activated by H_2SO_4 has high cation exchange capacity. Proton H^+ at the surface of LCA has a role as an active adsorption site.

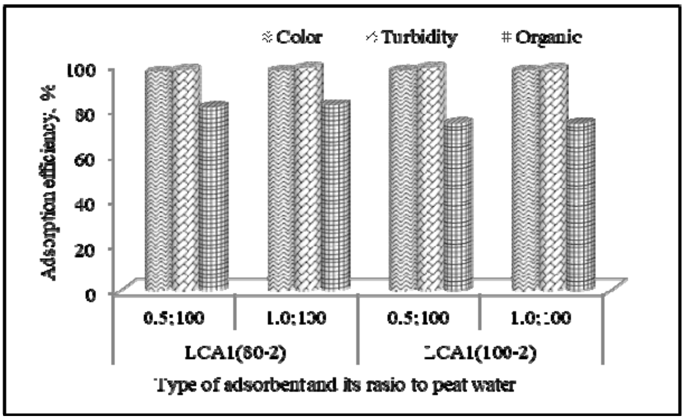
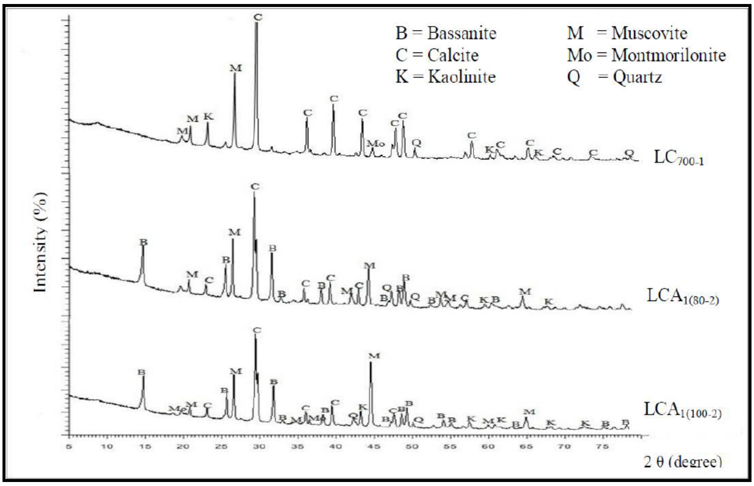


Fig. 2. Adsorbent performance after coagulation process.

The appearance of the color of peat water has been proved caused by anionic molecules including humic and fulvic acid. The molecules are hydrophilic colloidal that produce of dissociation of carboxyl and phenolic functional groups [20]. This negative charge has been neutralized by cation at the surface of the clay. The dosage effect of adsorbent on adsorption of peat water after coagulation was shown in Fig. 2. From the figure, it was observed that the percentage removal of colloidal substance slightly increased on increasing the adsorbent dose from 0.5 to 1 g. This is due to the excessive availability of exchangeable sites or the occurrence of interfacial interaction between adsorbent and adsorbate [6].

3.4 Characterization of calcined and extracted clay



Note: LC_{700-1} = Calcined Cengar Clay at temperature 700ºC for 1 hour, $LCA_{1(80-2)}$ = Byproduct adsorbent of liquid coagulant; calcination (t = 1 hour) and extraction (T = 80ºC, t = 2 hours), $LCA_{1(100-2)}$ = Byproduct adsorbent of liquid coagulant; calcination (t = 1 hour) and extraction (T = 100ºC, t = 2 hours).

Fig. 3. XRD profiles of oriented samples of LC_{700-1}, $LCA_{1(80-2)}$, and $LCA_{1(100-2)}$.

The residue of liquid coagulant is applied as an adsorbent for peat water after the coagulation process. The adsorbent was characterized by X-Ray Diffraction to determine the mineral composition. The XRD pattern is given in Fig. 3 which showed that the clay was mainly composed of montmorillonite, muscovite, kaolinite, quartz, and calcite respectively. Even though, there was another mineral (bassanite $CaSO_4.2H_2O$) was found in LCA. It was probably due to an effect of clay activated by H_2SO_4 which is involved of sulfate ion (SO_42-) and led to the surface interlayer of clay that contains calcium, and then can produce bassanite.

Calcined clay at temperature 600-700°C has been found to change to gamma alumina phase perfectly [21]. Gamma alumina is a phase which can dissolve in acidic and alkaline condition, and as a result, Al in calcined clay will be extracted easily [22]. As a fact to this experiment, Al and Fe extracted in coagulant was obtained poor. Fig. 2 showed that the clay as a precursor of liquid coagulant composed of mineral non-clay (calcite) dominantly. So, liquid coagulant contained amount of Al and Fe cations has lower than other cations.

3.5 Coagulation-adsorption performance on peat water treatment

In Table 4, the best coagulation-adsorption performance was achieved in the pair of $LC_{1(80-2)}$-$LCA_{1(80-2)}$ with 1:100 (w/v) ratio of adsorbent: peat water. According to Fig. 3, that montmorillonite mineral was contained in $LCA_{1(80-2)}$ by 18.66° and 37.30°.

Table 4. Coagulation-adsorption performance on peat water treatment.

Parameters	**Coagulation-adsorption treatment**			
	$LC_{1(80-2)}$ - $LCA_{1(80-2)}$		**$LC_{1(100-2)}$ - $LCA_{1(100-2)}$**	
	0.5:100 (w/v)@	**1:100 (w/v)@**	**0.5:100 (w/v)@**	**1:100 (w/v)@**
Color, TCU	209	185	186	188
Odor	Odorless*	Odorless *	Odorless *	Odorless *
pH	7.5*	7.5*	7.7*	7.6*
Turbidity, NTU	2.52*	1.75*	1.78*	2.33*
Organic Substance, mgL^{-1}	67.62	63.83	88.48	89.11

@: ratio of adsorben (LCA) : peat water, *: fulfilled Permenkes No.416/ Menkes/PER/IV/1990.

There are many types of clay, but montmorillonite clays are to have highest sorptive capacity in comparison to the other. Montmorillonite is recognized as an excellent adsorbent owing to the existence of active sites such as the surface and ion-exchange sites [23]. So, the decreasing parameter efficiency of color and turbidity by $LCA_{1(80-2)}$ is higher than another. The table was also shown that three water parameters of odor, pH, and turbidity had met Permenkes No.416/Menkes/PER/IV/1990 after being absorbed by the four adsorbents on both the adsorbent-peat water (w/v) ratio.

4 Conclusions

Synthesized liquid coagulant proved that have pH about 7.4-8 and cation concentration Al 1.22-1.25 mg/L, Fe 0.22-0.24 mg/L respectively. The liquid coagulant was ineffective to improve peat water quality. The adsorbent of $LCA_{1(80-2)}$ of a byproduct of liquid coagulant on 1:100 (w/v) ratio was improved the parameters of peat water, by removing as much as the color 96.57%, turbidity 98.03%, organic substances 81.55% and pH 7.5 respectively. So does combine of $LC_{1(80\text{-}2)}$ and $LCA_{1(80\text{-}2)}$ being the most effective pair of liquid coagulant-adsorbent on reduces the measured parameters. The adsorbent performance is much better than the liquid coagulant in the peat water treatment.

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