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THE POTENTIAL USE OF TITANIUM TETRACLORIDE ($TiCl_4$) AS AN ALTERNATIVE FOR COAGULANT IN TEXTILE WASTEWATER TREATMENT

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ABSTRACT

The effluents from textiles industries, wastewater, contain different types of dyes, which are difficult to be biodegraded because of its high molecular weight and complex structures. One of the processes to treat this problem is by salt coagulation using Fe and Al. However, this method still requires futher processing in order to produce recyclable sludge. The purpose of this research is to study the possibility of $TiCl_4$ to be used as an alternative coagulant in wastewater treatment so that the coagulated sludge can be recycled and produce TiO_2. 20% of $TiCl_4$ solution was tested on the wastewater sample. The experiments in the study were varied in the use of $TiCl_4$ dosage, the pH of the process and the characteristics of the floc formed. The floc characteristics then were analyzed with SEM EDX, to determine the mechanisms involved in the process, the testing of the zeta potential was conducted. The efficiency of the process was then measured by measuring the TSS. The effectiveness of the process was compared with the results of experiments using $Al_2(SO_4)_3$ as a coagulant.This study indicates that Ti based coagulants are effective and promising coagulants for the textile wastewater treatment. $TiCl_4$ is able to reduce the TSS in wastewater up to 71.31%, while a decrease in TSS using $Al_2(SO_4)_3$ as a coagulant only amounted to 27.87 %. In addition, the flocculated sludge resulted can be recycled and reproduced as functional TiO_2 photocatalyst which has a significant advantage over the conventional coagulants.

Keywords: Coagulant; Reprocess; Sludge; $TiCl_4$; TiO_2

1. INTRODUCTION

Textile industry is one of the biggest users of water and complex chemicals in various processes. The unused materials from the processes are discharged as wastewater that is high in colour, Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), pH, temperature, turbidity and toxic chemicals. The direct discharge of this wastewater into the water bodies such as lakes, river, etc may pollute the water and affect the ecosystem. The effluents from textiles industries, wastewater, contain different types of dyes which which are difficult to be biodegradedbecause of its high molecular weight and complex structures (Gao et al,2007). These effluents produce high concentration of inorganic salts, acid and bases in biological reactors leading to the increase of the treatment cost (Babu, et al, 2007). Moreover, the conventional textile industries generate residuals of chemicals that evaporate into the air that we breathe or are absorbed through our skin. Some of the chemicals are heavy metals present in either the free form in effluents or absorbed in the suspended solid and arecarcinogenic (Bayramoglu and Arica, 2007). Researchers has observed that the coagulation/flocculation is one of the most common technologies applied in the textile

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industry. Regardless of the generation of considerable amount of sludge, it is still used in developed and in developing countries. Since the mechanism of coagulant applied to decolourise wastewater is still not absolutely clear, colour removal by coagulation is found in some cases very effective, in some other cases, however, has failed completely (Verma, 2011). Coagulation of dye –containing wastewater- has been used for many years as the main treatment or pretreatment due to its low capital cost (Golob, et al,2005). The most commonly used salt coagulants are Fe and Al, which still require further treatment. The most commonly used coagulants are alum sulfate, poly aluminum chloride, $FeSO_4$ and $FeCl_3$ (Zhao, et al 2014). However, the main drawback of the conventional coagulant relies on the large quantity of the sludge produced after the treatment. In fact, the treatment of sludge after the coagulation/flocculation is considered to be one of the most costly and enviromentally problematic challenges of all water treatment processes. To circumvent the issue of sludge disposal, a novel titanium based coagulant has been proposed by Shon et al (Checkli, et al 2014). The possibility of using titanium compounds as a coagulant in water treatment was first investigated by Upton and Buswell in 1937 (Zhao, et al, 2011). They found that titanium sulfate ($Ti(SO_4)_2$) was better in removing fluoride due to the quadrivalent cation than the trivalent alumunium or iron ion. They also noted that ilminite extract gave much better coagulation in the colored water than alumunium or ferric sulfates. Recent report showed that the removal of organic matter of different molecular sizes by Ti salt flocculation was similar to that of the most widely used Fe and Al- salt flocculation. The significant advantage of using titanium tetrachloride ($TiCl_4$) as a coagulant is that its flocculated sludge can be recovered to produce a valuable by product namely titanium dioxide (TiO_2) by thermal treatment, which is not possible with the conventional coagulants (Lee, et al, 2009). TiO_2 is the most widely used metal oxide, which applications include photocatalysis, cosmetics, paints, electronic paper and solar cell (Hoffman, et al, 1995). The toxicity of the supernatant after $TiCl_4$ coagulations is very low and the residual Ti salt concentration in the treated water meets The World Health Organization's (WHO) guidelines (0,5-15 μg/L) for drinking water standards (Zhao, 2014). Therefore, $TiCl_4$ is expected to be a promising alternative coagulant to the commonly used conventional coagulant.

2. METHODOLOGY/ EXPERIMENTAL

2.1 Water Source and Coagulant

$TiCl_4$ solution (20%, density = 1,150g / mL) was obtained from Merck and used directly without specific treatment. The solution is then referred to as a stock solution. The stock solution of $Al_2(SO_4)_3$ was prepared at 2 g/L. The deionized water was used for all the reagent preparations.

The artificial wastewater used was made from 100 ppm reactive dyes solution stirred for 1 hour, while for the water source was taken from Citarum River as it is contaminated by the textile wastewater. The water was collected in spring season,and the water temperature was at 25-30^{0}C.

2.2 Jar Test

The coagulation test was conducted using the jar tester at different initial pH values. The test solution pH was controlled by adding the NaOH or HCl solution. The determination of the optimal dosage was conducted after measuring the initial pH. Then, a two-stage mixing process, including the rapid (1 min stage at 100 rpm) and slow mixing (10 min stage at 20 rpm), followed by a settling stage for 30 minutes.

2.3. Analysis

The performance of the coagulant was evaluated by measuring the colour, TSS and zeta Potential. The measurement of colour absorbance was conducted using Spectrophotometer Shimadzu, TSS gravimetric method was performed according to the SNI 06-6989.3-2004, and Zeta Potensial by electrophoretic methode. This experiment was carried out at the Chemical Analysis Laboratory of Polytechnic STTT Bandung. The zeta potential measurement was carried out at the Pharmacy Department of ITB, while SEM EDX analysis was done at BSCA ITB. The zeta potential of solution and SEM EDX evaluations were carried out at the optimal dossage.

3. RESULTS AND DISCUSSIONS

3.1 Effect of Initial pH and Zeta Potential

The performance of initial pH for each coagulant, the performance of coagulant by measuring colour absorbance, and the suitable pH was selected if the colour absorbance getting lower after the processing using the coagulant are shown in Table 1.

Table 1 Effect of Initial pH at Coagulation Process Using $TiCl_4$ and $Al_2(SO_4)_3$

pH	Colour Intencity Measured at Wavelength 380 nm		
	Initial Colour Intencity	Coagulant	
		$TiCl_4$	$Al_2(SO_4)_3$
Acid	1,245	0,017	0,996
Neutral		1,293	0,004
Base		1,340	1,002

From the data above, it can be observed that the use of $TiCl_4$ coagulant was optimum at acidic pH condition, while the use of $Al_2 (SO_4)_3$ coagulant was optimum at neutral condition. Acidic condition on coagulant $TiCl_4$ is obtained by dissolving it into a dye solution (without the addition of acid). The hydrolysis of metal ions occurs immediately after the contact with water and the neutralization capabilities of coagulant is associated with the positive charge of the hydrolyzed species. The charge neutralization capability of $TiCl_{4,}$ compared with $Al_2(SO_4)_{3,}$ shows that the hydrolysis of the less positive events is supportive for to the efficient coagulation. Dyes organic matter is removed mainly by the complexation of dyes organic matter with soluble metal species into the insoluble precipitates at pH<6, while the adsorption onto precipitated metal hidroxides predominated the dyes organic matter removal process at pH>6 (Gregor, etc, 1997). Thus, in this study, the dyes organic matter was likely to be removed by charge neutralization between the negatively charged organic matter and the postively charged metal hydrolyzates at pH<6. In addition, at pH>6, the adsorption and sweep flocculation were assumed to play a dominant role during the coagulation process. As noted by Zhang, the flocs formed by sweep flocculation were larger than those by the charge neutralization and hence, need further aggregation. (Ray, etc, 1987). This may be the reason for the large floc size rate at high pH values for $TiCl_4$. For $Al_2(SO_4)_{3,}$ the largest flocs formed at pH 6 could be attributted to the combined coagulation mechanism. The charge neutralization (Al Species reacted with dyes organic matter and neutralized negative charges), adsorption, and sweep flocculation substanstially reduced the negative charges on dyes organic matter, promoting their adsorption on Al species and further aggregation). At pH>6, the hydrolyzates of $Al_2(SO_4)_3$ were more likely transformed to $Al(OH)_3$ dan $Al(OH)^-_4$. The suspension system was therefore difficult to be destabilized, resulting in the decrease in both floc size.

The zeta potential is a parameter of electrical charge between the colloidal particles. The higher the zeta potential value, the more it will prevent the occurrence of flocculation (colloidal merging events from small to large). The mechanism depends on the stability of colloidal dispersions zeta potential. The zeta potential repel shows the levels between the similar charged particles adjacent to each other. The colloids with the high value of the zeta potential are electrically stable, while the colloids with low potential value tend to coagulate / flocculate.

The waste is processed in the form of dye to be reacted with various types of coagulants and measured its zeta potential, the results can be seen in Table 2.

Table 2 Zeta Potential Measurement

Material	Potential zeta (mV)
Dyestuff	0,34
$TiCl_4$	-0,11
$Al_2(SO_4)_3$	0,16

Table 2 shows that at the optimum pH for each coagulant, the waste is composed of positively charged metal. The significant difference in charge between the waste and natural coagulant will determine the mechanism of coagulation. The initial pH variations also affect the results of coagulation/flocculation process. The initial pH influences the value of the zeta potential solutions related to the ability of the hydrolysis of the coagulants. The important mechanism for particle removal depends on the pH. In general, particle removal at acidic pH was dominated by the complexation with dissolved metals into unstable precipitaates. However, the coagulant mechanism varies with the type of coagulant and conditions. For $TiCl_4$, at alkaline pH, the negative charge of the dye will probably be neutralized by the positive charge of the hydrolized coagulants to produce flocks with a positive charge due to an excess of positive charge hydrolization on the surface of the flocks. At alkaline pH, a fast bulk hydrolysis occurred, generating the type of coagulant with a positive charge, resulting in a precipitation of $Ti(OH)_4$. Thus, $TiCl_4$ was not able to achieve perfect neutralization.

3.2 Analysis of TSS

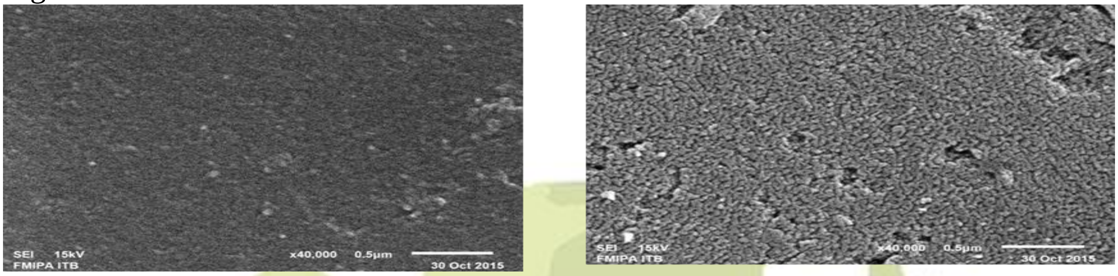
Parameters measurement included the TSS (Total Suspended Solid) value of the waste. The testing was conducted usingvarious concentrations of two kinds of coagulant ($TiCl_4$ and $Al_2(SO_4)_3$) applied on the textile artificial wastewater. The use of Al_2 $(SO_4)_3$ coagulant was less efficient than the use of $TiCl_4$ coagulant. It can be seen in table 3 that the coagulation process using $TiCl_4$ reached efficiency of TSS 34,15%, while using Al_2 $(SO_4)_3$ coagulant only reached 19,51%. This TSS performance was carried out at the optimum dossage, which is 100 ppm for $TiCl_4$ and 400 ppm for $Al_2(SO_4)_3$ coagulants.The data of TSS measurement can be seen in Table 3.

Table 3TSS of Artificial Waste Water after Coagulation Process

Parameter	Coagulant	Dossage(ppm)	Efficiency (%)
TSS	$TiCl_4$	100	34,15
	$Al_2(SO_4)_3$	400	19,51

3.3 Morphology of the Flocs

The morphology of the flocs was analyzed using SEM EDX analysis of the flocs after coagulation/flocculation process using both coagulants at the optimum dosage. The flocs morphology is analyzed by SEM, while the containing ions were analyzed by EDX. The morphology of flocs formed after the cogulation/flocculation can be seen in Figure 1 below.



$TiCl_4$ 100 ppm $Al_2(SO_4)_3$ 400 ppm

Figure 1 Morphological Flocs Formed after Coagulation/Flocculation Process

Fig. 1 shows that the use of $TiCl_4$ as a coagulant produces sludge that is more solid than the $Al_2(SO_4)_3$ coagulant. The strength of this stability can be beneficial for the separation of sludge. In addition, EDX test was also conducted to determine the composition of the formed coagulant and flocs. The EDX test data can be seen in Table 4 below:

Table 4 Analysis of EDX $TiCl_4$ and $Al_2(SO_4)_3$

Coagulant	Concentration (%)							
	C	O	Na	Al	Si	S	Cl	Ti
$TiCl_4$	20,66	33,54	1,00	-	1,49	5,29	2,74	26,56

It can be seen from the table above that in the treatment using $TiCl_4$ as the coagulant, the mud still contains Ti in it, so there is a possibility to recycle the sludge to be used for producing TiO_2 compound using a particular treatment.

4.4 Analysis Parameters for the Real TextileWastewater

The analysis was carried out for the original waste taken from the Citarum River. The wastewater coagulation processing was performed by using each coagulant at its optimum concentration. The results of the analysis are presented in Table 5 below:

Table 5 TSS Measurements of Real Waste Water

Parameter	Coagulant	Dossage (ppm)	Efficiency (%)
TSS	$TiCl_4$	100	**71,31**
	$Al_2(SO_4)_3$	400	27,87

From the table above,it can be seen that the $TiCl_4$ was effective as a coagulant used to decrease the parameter of TSS. Thus, the $TiCl_4$ is more efficient than $Al_2(SO_4)_3$.

4. CONCLUSION

Based on the experimental results, the conclusionis as follows:

$TiCl_4$ was a promising coagulant in textile wastewater treatment in which 100 ppm of TSS can be reduced up to 71,31 %. Compared with the $Al_2(SO_4)_3$, $TiCl_4$ shows a better performance in removing TSS both for artifical and real wastewater. Morphologically, the flocs formed by $TiCl_4$ causes the sludge to be more solid than that of the $Al_2(SO_4)_3$. It means that it can be removed easily.The compound $TiCl_4$ has a potential to overcome the limitations of the use of the conventional coagulants. The sludge from the $TiCl_4$ as a coagulant can be processed further to produce TiO_2

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