Treatment of Paint Wastewater by Using Tacca Leontopetaloides Starch as a Natural Coagulant and Calcium Oxide as a Coagulant Aid.

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***Abstract*- The research works involve the study of effectiveness of *Tacca Leontopetaloides* starch as a natural coagulant and Calcium Oxide and as its coagulant aid for the treatment of paint wastewater. Three main parameters were studied; chemical oxygen demand (COD), turbidity and heavy metals removal of effluent. Coagulation treatment using jar test were performed with a flocculation system where the effects of paint wastewater pH as well as *Tacca Leontopetaloides* starch dosage on coagulation effectiveness were probed. The highest record of COD and turbidity removal percentage were 95% and 60% respectively, observed for effluent at optimum pH 7 using 90 mL dosage. The metals concentration after treatment also showed significant removal which complied with Standard B of Environmental Quality (Industrial Effluent) Regulations 2009 stipulated by the Department of Environment (DOE), Malaysia. It could be conclude that *Tacca Leontopetaloides* starch showed great potential as a natural coagulant for water treatment purposes and could be applied in the pre-treatment stage of Malaysian paint wastewater prior to secondary treatment.**

***Keywords* – Paint wastewater, Wastewater treatment, Coagulation-flocculation, Tacca Leontopetaloides, Calcium oxide, Turbidity removal**

I. INTRODUCTION

Water is the most ample compounds found in nature, covering approximately three-fourths of the surface of the earth. However, there are several factors that have limit the amount of water available for human use as the ocean and other saline water bodies which cover 97% of total water supply are not suitable for most purposes. The remaining 3% including little over 2% is the glaciers and ice caps, along with the atmospheric and soil moisture is inaccessible. Therefore, humans only left with the remaining 0.62% found in fresh water lakes, rivers, and groundwater supplies to be used to support human needs [1]. During this era, the growth of populations and industrial activities has been uncontrollable, especially those which overuse of water in their production. In 2005, the World Water Development Report (WWDR) has published global estimates [2] that the water reserves in the world could decline by up to 40% by 2030 under the current business-as-usual (BAU) scenario [3].

The usage of water in the production especially chemical production is widely known. However, some of the productions are overused the water usage causing a concern to the scientific community as it is one of the environmental issues. The effluent from industrial may contain toxic compound which can endanger the aquatic life when it is discharge directly to the water bodies. In India and many developing countries these water treatment sludge discharged directly into downstream side of the river or disposed into nearby stream which ultimately meet the downstream river. This has causes negative impact on the quality and aquatic life [4].

Therefore, to counter the environmental issues that have arose from the industrial activities, attention has focused on research into wastewater treatment methods since this method will not only decreases the disposal into water bodies but also can cut the production cost if the wastewater can be reused back. For this research, the raw paint wastewater is being studied as the paint manufacturing industry consume large amount of water in their production thus produce large amount of wastewater per day. From the article by Salihoglu et al [6], the management of hazardous wastes of automobile manufacturer in Turkey has the highest share of the costs, which paint sludges cover 57.6% of the distribution of the cost.

The paint wastewater discharged from its manufacturing plant is considered source of environmental contamination due its high coloration, turbidity, strong odor, and contain high loads of organic and toxic chemical substances such as surfactants, bactericides, oils, solvents, and preservative agents [7]. It also have high biological oxygen demand (BOD) and chemical oxygen demand (COD) which is very dangerous to the environment, specifically aquatic life if the effluent is discharged directly to the water bodies. In addition, since these effluents have high coloration, it can block the sunlight pathway passed through into the water bodies, thus prevent photosynthesis of aquatic plants to occur. The heavy metals presences in the paint wastewater are also a major concern as they are toxic and can be carcinogenic. Hence, a proper treatment is really necessary to prevent any harm to the environment.

Several papers have reported the use of different methods for the treatment of paint wastewater, which include some methods such as coagulation/

electrochemical method [13; 5], adsorption [14], and acclimatized microbial consortia [11]. In the Silva et al. study, the paint wastewater is treated for disposal or reuse application. The water-based wastewater is treated with aluminium sulfate coupled with electrochemical methods to degrade residual hazardous organic substances. In this case, the use of electrode materials that exhibit a high overpotential for the oxygen evolution reaction (OER), such as SnO2, PbO2, DSA and boron-doped diamond (BDD), enable effluents that contain organic compounds to be transformed into biodegradable substances, which eventually be mineralized to CO_2 and H_2O. However, the sludge produced from the coagulation process must be properly managed and kept in good practice [13].

Method that can be used to treat the paint wastewater and often referred as either unit operations or unit processes. Unit operations usually involve removing of contaminant by physical forces while unit processes involve biological and/or chemical reactions [1]. For biological treatment, it requires large area, high maintenance, long retention time, and pond treatment can gives odor problems.

Although alum is widely used in the wastewater treatment, it has some defect; such as relatively high costs, harmful effects on human health, produced large volume of sludge after the treatment process and also affect the pH of the treated water. Hence, green technology is introduced which operation involved energy efficiency, recycling, safety and health concerns, renewable resources, and more to counteract the undesirable chemical sludge from wastewater treatment [12]. Natural coagulants are extracted from natural plants or animals. The plant based polymeric coagulants are considered as a green option as it met the requirements of green technology as enumerated above. It also biodegradable mostly has natural pH and can significantly reduce the cost of water treatment [15; 16]. There are various types of plants that can be used as natural coagulant such as Opuntia species, Aloe Vera, Moringa Oleifera, Ocimum Basilicum, malva nut seeds, some aquatic plants, cabbage and others [12].

Therefore, coagulation is the best methods to treat the industrial wastewater as it is easy operation, relatively simple design and low energy consumption [8, 12] and for this research, *Tacca Leontopetaloides* starch is used a natural coagulant. The coagulation process is crucial in the treatment strategy and primarily aimed at destabilizing the colloidal particles, causing turbidity in the raw water [9]. The destabilizes colloidal particles will clustered into larger aggregates which will settled in the sedimentation process or further removed in the subsequent filtration process [10].

In this research, the raw paint wastewater was characterized. Jar Test experiments was carried out for the coagulation test by adding the *Tacca Leontopetaloides* starch at varied pH of raw paint wastewater. The purpose of this research is to improve the coagulation-flocculation process applied to the paint wastewater by using *Tacca Leontopetaloides* starch as coagulant and Calcium Oxide (CaO) powder as coagulant aid.

II. METHODOLOGY

A. *Raw Paint Wastewater Characteristics*

Paint wastewater samples were collected from the discharges of a paint factory in Klang, Selangor, Malaysia. The samples were collected from the waste pit which source from the cleaning process and machine-processing operation. It mainly characterized by its dark grey or blackish in colour and also contained high concentrations of organic matter including paints, additives, surfactant and others. The wastewater samples were also high in chemical oxygen demand (COD) and biological oxygen demand (BOD), generated effluent was discharged into municipal sewer. To conserve its characteristics, the samples were store at 5ºC, the characteristics were as shown in the Table 1.

B. *Coagulant and Flocculant Used*

In this study, the following stocks solution of coagulant and flocculant were prepared; (1) *Tacca Leontopetaloides* starch and (2) Calcium Oxide powder.

To prepare the *Tacca Leontopetaloides* starch, the *Tacca Leontopetaloides* powder (10 g) were mixed with 500 mL of distilled water and heated at 150 ºC, 500 rpm for 2 hours. The starch solution was then let to cool to the room temperature. The fresh *Tacca Leontopetaloides* starch (Figure 1) was stored in a refrigerator at 7 ºC to ensure its freshness. To avoid any fermentation, the coagulation experiments using this *Tacca Leontopetaloides* starch as a natural coagulant were carried out on the same day.

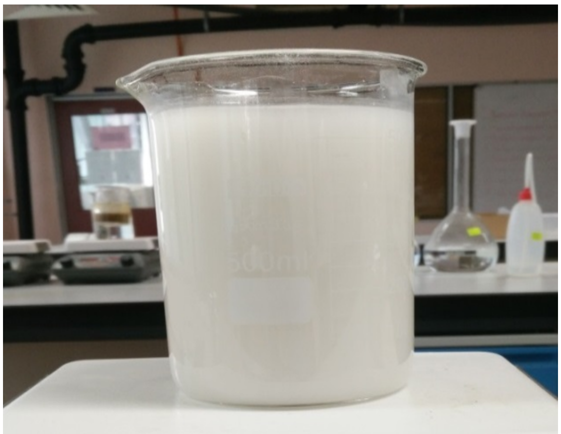

Fig. 1: Tacca Leontopetaloides Starch

C. *Coagulation Flocculation Jar Test Experiments*

Coagulation-flocculation tests using jar test were performed in the laboratory with a bioblock flocculation that include six-paddle rotor (24.5 mm x 63.5 mm) for 600 mL high-shape beakers, and all the tests were conducted at room temperature. A rotation speed of 120 rpm was applied for 1 minute, followed by slow mixing for 20 minute at 50 rpm to keep the flocs particles uniformly suspended. The settling of flocs particles were then observed and recorded. At the end of the assay, the resulting flocs were left to stand for 1 hour to ensure sedimentation.

The test consist of two different experiments; (1) Using *Tacca Leontopetaloides* starch with CaO powder as coagulant and coagulant-aid respectively at pH range 5 to 10, and (2) Using *Tacca Leontopetaloides* starch with CaO powder as coagulant and coagulant-aid respectively at pH 7 with dosage of natural coagulant range 15 to 90 mL into the raw paint wastewater. Later, the supernatant was collected to determine the COD, turbidity, and heavy metal contents were determined using the standard method.

D. *Performance Evaluation*

To evaluate the efficiency of coagulant and flocculants on paint industry wastewater treatment, the following parameters were considered: turbidity, chemical oxygen demand, colour, the amount the sludge formed and the presence of the heavy metals. Turbidity test was measured using portable turbidimeter (Model HACH 2100P). The principle of the turbidity measurement based on a comparison of the intensity of light scattered by the sample [17]. The sample cell was placed into the turbidimeter and the turbidity value shown in NTU unit. The total turbidity percentage removal was calculated as follows:

$$turbidity\ percentage\ removal \approx \frac{A-B}{A} \times 100\%$$

where A is turbidity of raw paint wastewater (NTU) and B is turbidity after treatment (NTU).

The pH meter brand Mettler Toledo was used in this study to measure the pH value of the sample. The COD test was measured using COD Reactor (Model HI 839800) and UV Spectrophotometer HACH model. Chemical oxygen demand (COD) refers to the amount of oxygen required to oxidize the organic compounds in a water sample to carbon dioxide and water. COD percentage removal was calculated as follows:

$$COD\ percentage\ removal \approx \frac{A-B}{A} \times 100\%$$

where A is COD of raw paint wastewater (mg/L), and B is COD after treatment (mg/L).

The heavy metals presence in the raw wastewater and treated wastewater were determined by using Inductively Coupled Plasma (ICP-OES) model Thermo Scientific iCap 6000 Series Alpha Analytical prepared in the laboratory. The value of concentration of the metals was then compared to the environmental quality standards required by the Department of Environment in Malaysia.

III. RESULT AND DISCUSSION

The paint wastewater were characterized by including substantial organic matter, heavy metals, and high suspended solid. Since the paint wastewater contained high concentrations of chemical oxygen demand (COD), biological oxygen demand (BOD) and suspended solids (SSs), the wastewater does not meet the environmental quality standards required by the Department of Environment in Malaysia. In order to meet this requirement, a proper wastewater treatment method is necessary. BOD/COD index indicates that a biological treatment would be difficult, and so the physicochemical process is required. The coagulation flocculation process using *Tacca Leontopetaloides* starch as a natural coagulant in combination with coagulation aids was used in the treatment of the effluent for this research. Treatment efficiency was evaluated in term of pollutant removals (turbidity, heavy metals, COD, and colour) as well as in terms of sludge production.

A. *Characterization of Raw Paint Wastewater*

Table 1 shows the characteristics of raw paint wastewater before the coagulation flocculation treatment. The values were much higher compared to previous results [6; 9; 20]. The differences were due to the machinery sources processing the wastewater, and this was indicated by the raw paint wastewater containing high loads of organic and toxic chemical substances such as surfactants, bactericides, oils, solvents, and preservatives agents [7]. It is apparent that treatment of wastewater is required before it can be discharged into the environment since the COD concentration alone is more than 125 times higher than the Standard B discharge limit.

Table 1: Characteristics of raw paint wastewaters

Parameter	Raw paint wastewater
Temperature (ºC)	22.9
pH	4.28
Chemical Oxygen Demand (mg/L)	25105.49
Turbidity (NTU)	26.83
Color	Grey

B. *Effect of pH on Tacca Leontopetaloides Starch*

The pH solution is an important factor in the coagulation process [18]. The use of coagulant at its optimum pH displays maximum pollutant removal. Therefore, controlled pH of the raw paint wastewater determines the effectiveness of *Tacca Leontopetaloides* starch in the coagulation flocculation process, where it determines the maximum turbidity, COD and heavy metals removal. To optimise the pH of the coagulation flocculation process, a known volume and concentration of prepared *Tacca Leontopetaloides* starch and Calcium Oxide (CaO) powder were added to a jar containing 6 of paint wastewater at different pH values adjusted with concentrated H_2SO_4 and NaOH solution. The effect of coagulation pH (pH of wastewater during coagulation flocculation process) on turbidity and COD removal percentage from jar tests for coagulation of paint wastewater using 70 mL of 10% *Tacca Leontopetaloides* starch and 10 g of CaO was shown in the Figure 2.

From the graph, the highest recorded turbidity removal percentage was observed for effluent pH 7 at 79.91% and the lowest efficiency was at pH 10 (3.09%). This result indicated that at pH 7, the maximum amount of coagulant is converted to solid phase flocs particles. At pH lower or higher of this pH of minimum solubility, the charges produce by taccalondides as a natural polymer from the *Tacca Leontopetaloides* starch for bridging and entrapping the microfloc to form larger floc were very low; thus, the adsorption on the surfaces of precipitated floc particles was very minimal.

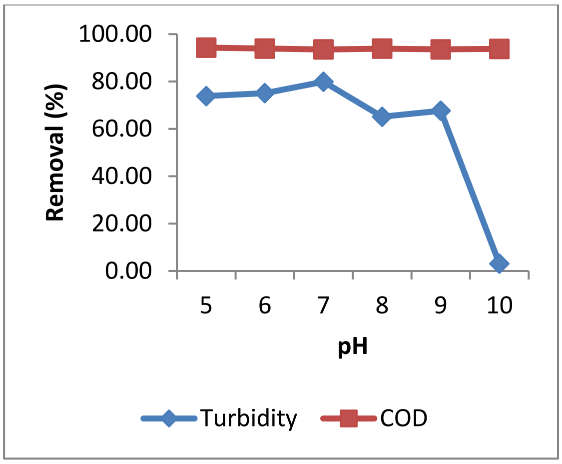

Fig. 2: Effect of raw paint wastewater pH on *Tacca Leontopetaloides* starch coagulant effectiveness.

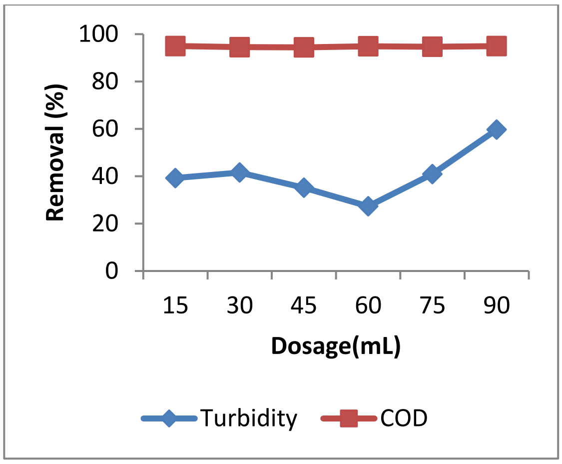

Fig. 3: Effect of *Tacca Leontopetaloides* starch coagulant dosage on coagulation flocculation effectiveness.

This was due to the when it was in higher pH, the chemical functional groups associated with organic were ionized and results in increasing of negative charge. Nevertheless, at lower pH there was no ionization of any functional groups and organic removal was achieved mainly due to the adsorption. The mechanism of pollution removal, therefore, was different under the different pH condition [19].

The COD removal percentages were also observed. The highest COD percentage removal was at pH 5 (94.30%), and at pH 5, 6, 7, 8, 9 and 10 the percentage of COD removal were almost the same value which was higher than 90%. These mean that the *Tacca Leontopetaloides* starch as natural coagulant and CaO powder as flocculant can effectively remove high percentage of COD form the paint wastewater using coagulation flocculation process.

C. *Effect of Dosage of Tacca Leontopetaloides Starch*

To determine the optimum dosage (in mL) of *Tacca Leontopetaloides* starch to be used in the natural coagulation treatment, different volumes of a stock solution of coagulant were added to the raw paint wastewater along with the 10 g of Calcium Oxide (CaO) as a coagulant aid. Optimum pH 7 of raw paint wastewater was kept constant to determine the effectiveness of coagulation flocculation process. This pH value was selected based on the findings in this study reported above. For *Tacca Leontopetaloides* starch, the dosages range from 15 to 90 mL, and the volume of raw paint wastewater used was 300 mL.

The results of the parameters of turbidity and chemical oxygen demand (COD) removals were shown in Figure 3. It is clearly showed that for the quantitative removal of 60% of turbidity and 95% of COD, under experimental conditions of the coagulant flocculation test, a minimum dosage of 90 mL of *Tacca Leontopetaloides* starch and 10 g of CaO were required. The coagulant dosage should be proportional to the quantity of colloids present. A further increase in coagulant dose will only cause destabilization of the particles as the charge reversal on the colloids occurs [19].

D. *Metals Removal*

The paint wastewaters are considered as source of environmental contamination due to its high coloration, turbidity, strong odor, and contain high loads of organic and toxic chemical substances. Excessive amounts of any metal may cause health hazards, only those metals that are harmful in relatively small amounts are commonly labelled toxic; other metals are group as nontoxic group.

In this research, some of the metal elements presences in the wastewater were shown in Table 2 and compliance with the Environmental Quality (Industrial Effluent) Regulations 2009 stipulated by the Department of Environment (DOE), Malaysia. The pH value of treated paint wastewater complied with the pH range (5.5 – 9.0) stipulated by the DOE, Malaysia. The metals also complied with the Standard B except the Arsenic and Cadmium concentration; this was because the Arsenic concentration cannot be determined by using ICP-OES while concentration of Cadmium (0.54 mg/L) was much higher than the standard which at 0.02 mg/L. Furthermore, value for COD concentration (1266 mg/L) after the treatment was still higher than standards A and B. Although *Tacca Leontopetaloides* starch is applicable as a natural coagulant in the pretreatment process of wastewater, and further treatment is needed before it can be discharged into the environment. Nevertheless, *Tacca Leontopetaloides* starch showed high potential as a natural coagulant for wastewater treatment purposes.

Table 2: Compliance of treated paint wastewater using *Tacca Leontopetaloides* starch with Malaysian standard effluent discharge limit.

Parameter	**Treated Paint Wastewater (mg/L)**	**Acceptable Condition for Discharge**	
		Standard A	**Standard B**
Temperature (°C)	23.28	40	40
pH value	7.0	6.0 –9.0	5.5 – 9.0
COD	1266	80	200
Arsenic	-114.92	0.05	0.10

Chromium	0.55	0.20	1.00
Copper	0.60	0.20	1.00
Cadmium	0.54	0.01	0.02
Iron	0.56	1.00	5.00
Magnesium	1.19	-	-
Manganese	0.44	0.20	1.00
Zinc	0.94	2.00	2.00
Silver	0.76	0.10	1.00
Barium	1.28	1.00	2.00
Beryllium	0.56	-	-
Cobalt	0.61	-	-
Nickel	0.60	0.20	1.00
Strontium	8.52	-	-
Vanadium	0.48	-	-

IV. CONCLUSION

Tacca Leontopetaloides was very much effective as a plant-based natural coagulant for the treatment of paint wastewater. It proved that at pH 7 with 90 mL dosage *Tacca Leontopetaloides* starch and 10 g Calcium Oxide (CaO) powder have capability to reduce 60% of turbidity and 95% of chemical oxygen demand (COD). The coagulation flocculation treatment in this research also showed tremendous metals removal from the raw paint wastewater. *Tacca Leontopetaloides* starch contains taccalondides as a natural polymer for bridging and entrapping the microfloc to form larger floc. Although the final discharge did not comply with the standard effluent discharge limits A and B stipulated by the Department of Environment (DOE) Malaysia, with COD concentration is still 6 times higher and Cadmium presence in the treated paint wastewater is exceeding the standard, it is suggested that *Tacca Leontopetaloides* starch can be a good candidate to reduce the physicochemical parameters from the paint wastewater. *Tacca Leontopetaloides* may offer an alternative to traditional coagulants in wastewater treatment as it unique properties along with the availability make *Tacca Leontopetaloides* an exciting and promising agent for the pollution removal from wastewater.

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