COAGULATION-FLOCCULATION MECHANISM OF *HYLOCEREUS UNDATUS* FOLIAGE IN WASTEWATER TREATMENT

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***Abstract*—The floc particles formed during perikinetic and orthokinetic flocculation from molecular point of view was investigated and the effect of pH on zeta potential during coagulation flocculation process of wastewater using *hylocereus undatus* foliage was determined. Dragon fruit foliage is known to carry the characteristics of a natural coagulant. However, no previous study is carried out to unlock the fundamental theory behind the coagulation – flocculation mechanism in the application of *hylocereus undatus* foliage as a plant-based coagulant. Hence, this study was conducted without the addition of any synthetic coagulants and zeta potential was used as parameter in observing magnitude charges between particles. Jar test experiments were done using pharmaceutical wastewater and *hylocereus undatus* foliage as coagulant with different range of pH and analytical analysis was performed. Through FTIR spectroscopy, it was found that the functional groups of aliphatic primary amines, secondary amines and carboxylic acids, which are among protein-specific groups, were accountable for good coagulation activity. The zeta potential of dragon fruit foliage was found to be +0.433 mV indicating it to be a cationic coagulant. The mechanism of coagulation process is suggested to be charge neutralization and absorption since the zeta potential of wastewater was initially -7.72 mV but decreases to -2.65 mV at optimum pH 3. Moreover, as the pH increases the zeta potential becomes more negative due to the dominant adsorption of OH^- in alkaline pH conditions.**

***Keywords*— Dragon fruit foliage, Hylocereus undatus foliage, Natural coagulant, Plant based coagulant, Wastewater treatment**

I. Introduction

Coagulation and flocculation methods are widely adopted for wastewater treatments since they are proven to effectively remove existing colloidal particles in wastewater [1]. Common coagulants are inorganic or synthetic polymers that remove dissolved chemical species and its turbidity in wastewater besides promoting accumulation of suspended particles prior to sedimentation [2]–[4]. Most industries apply chemical-based substances like aluminium sulphate (alum) due to its high efficiency in water treatment, easily attainable, easy to handle and cost lower than other chemical-based coagulants [5]–[7].

However, many disadvantages associated with the use of chemical-based coagulants in wastewater treatment were found through previous research. Among the disadvantages are namely; large chemical sludge formation in scheduled waste, inefficiency in low temperature conditions and changes in pH of treated water [8]. Hence, to counter the previously listed disadvantages, natural coagulants are proposed as alternatives for chemical-based ones. Further studies have been done for natural coagulants extracted either from plants such as *Moringa oleifera* seeds and dragon fruit foliage, from animals like *chitosan* derived from shrimp shells or microorganisms [2].

In addition, dragon fruits are one of the natural coagulants that are commonly known in replacing the use of chemical-based coagulants. There are two types of dragon fruits, namely *hylocereus polyrhizus* and *hylocereus undatus*, that were studied as possible effective plant-based coagulant in treating wastewater. [1] Thus, many research conducted and still ongoing studies are done to focus more on the recent application of parts of dragon fruits, such as its peels, foliage and pulps, as a natural coagulant in wastewater treatment process.

Dragon fruits are originally a native plant from Mexico, Central America and South America and are also known as strawberry pears or pitayas and now are cultivated beyond local markets in few Southeast Asian countries like Malaysia, Vietnam, Philippines and Taiwan. The wide amount of dragon fruits production in dragon farms consequently produces a large amount of dragon fruit foliage. It is also found suitable as an alternative for chemical-based coagulant due to its low procurement cost, biodegradability, abundance and easy availability [1], [8].

Limited research conducted has investigated on the application of dragon fruit foliage as a natural coagulant in the process of treating wastewater. Studies on determining the optimum conditions of *hylocereus undatus* foliage such pH value, dosage, sedimentation time and drying temperature had also been done before [2], [3], [6]. However, no previous study is carried out to unlock the fundamental theory behind the coagulation – flocculation mechanism when it comes to the application of *hylocereus undatus* foliage as a plant-based coagulant.

Therefore, one of the objectives of this study is to investigate the floc particles formed during perikinetic and orthokinetic flocculation from molecular point of view using Fourier-transform infrared (FTIR) spectroscopy. Next, is to determine the effect of pH on zeta potential during the coagulation – flocculation process using *hylocereus undatus* foliage with Malvern Zeta sizer Nano-ZS.

II. METHODOLOGY

A. Preparation of hylocereus undatus *foliage as natural coagulant*

Hylocereus Undatus foliage was collected from a dragon fruit farm in Sungai Pelek, Sepang, Selangor. The thorns from the foliage were removed before being washed and later oven-dried at 50˚C for 4 days. The dried foliage was sieved and milled into powder form with particle size of 0.25mm.

B. *Collection of wastewater sample*

A sample of waste water, discharged prior to the industrial effluent treatment system, was taken from a pharmaceutical industry in Selangor.

C. *Jar test experiment*

This experiment was conducted to observe the coagulation and flocculation process of wastewater treatment using jar floc test unit. The initial pH, COD and turbidity of wastewater were determined using the standard method. To determine the optimum dosage concentration of foliage, six beakers were filled with 250 mL of wastewater sample each with adjusted pH of 7 and different dosage of dried foliage of 0.075 to 0.2g was added in each beaker, for 300 to 800 mg/L. The rapid mixing was executed at 120 rpm for 1 minute and slow mixing at 60 rpm for 20 minutes, before the paddles were withdrawn and the beakers were left for 1 hour for sedimentation process. The supernatant of the sediment was taken to determine their COD and turbidity. Then a new set of jar test was done by adjusting the pH of wastewater with range of 3 to 9, with the same amount of dried foliage added as coagulant. After the stirring and sedimentation process, the final COD and turbidity levels were checked.

D. *Determination of chemical oxygen demand (COD)*

The water sample was diluted with the ratio of 1:10 with distilled water. Then, 2mL of sample was pipetted into the high range COD digestion reagent vial. A blank sample was also prepared with 2 mL of deionized water, and the outer vial was rinsed with deionized water and cleaned with a paper towel. The vials were then heated on a COD reactor at 150˚C for 2 hours. After the heating process the vials was then let cool for approximately 30 minutes and the reactor was turned off. Once the vials were cooled down to room temperature, the spectrophotometer (Model DR 2800: HACH, Loveland, USA) was switched on. The program for COD HD was selected and then the COD readings were taken in mg/L. The COD readings were taken three times and the average triplicate samples was calculated for record purposes.

E. *Determination of turbidity*

The turbidity meter (Model 2100Q; HACH, Loveland, USA) was switched on prior the experiment. The blank sample was prepared using 10 mL distilled water poured into the vial. Other samples were diluted with distilled water with ratio of 1:10 into the vials. The outside of the vials was cleaned and placed into the turbidity meter before the ‘read’ button was pressed to get the reading in mg/L. The turbidity readings were taken three times and the average triplicate samples was calculated for record purposes.

F. *Analytical analysis*

The floc formed from the sedimentation was taken and the organic compounds were analyzed with FTIR spectroscopy (Model Spectrum One: PerkinElmer, Waltham, USA). Next, zeta sizer (Model Zeta sizer Nano-ZS: Malvern, Worcestershire, UK) was used in measuring the zeta potential of the supernatants from the jar test experiment and the dragon fruit coagulant and its effect on pH during the coagulation – flocculation process.

III. RESULTS AND DISCUSSION

A. *Characterization of waste water sample*

Table 1 shows the characteristics of pharmaceutical effluent before the pretreatment of coagulation – flocculation. In comparison to the regulatory standard discharge limit for both Standards A and B set by the Department of Environment (DOE), it is obvious that treatment of effluent is required before it is deemed safe to be discharged to the environment. Plus, the COD concentration of the influent appears to be around 20 times higher than the standard discharge limit.

Table 1: Values of selected parameters of raw pharmaceutical effluent

Parameters	Raw effluent	Regulatory standard discharge limit	
		Standard A	Standard B
pH	5.38	6.0 – 9.0	5.5 – 9.0
COD (mg/L)	2323	50	100
Turbidity (NTU)	897	-	-

B. *Determination of optimum dosage concentration of* hylocereus undatus *foliage*

Figure 1 and Figure 2 show the graphs for the determination of optimum dosage concentration required as a coagulant, in terms of the percentage removals for turbidity and COD levels. It was found that the optimum dosage of *hylocereus undatus* foliage was 700 mg/L in which the turbidity and COD removals were 81.7% and 68.6%, respectively. The turbidity and COD removals were observed to be declining when the coagulant dosage was added above the optimal dosage (700 mg/L). Saturation of polymer bridge sites due to overdosing can be a factor of the re-stabilization of the destabilized particles. This is due to the insufficient number of particles in creating more particles bridges among the colloidal particles. [9]

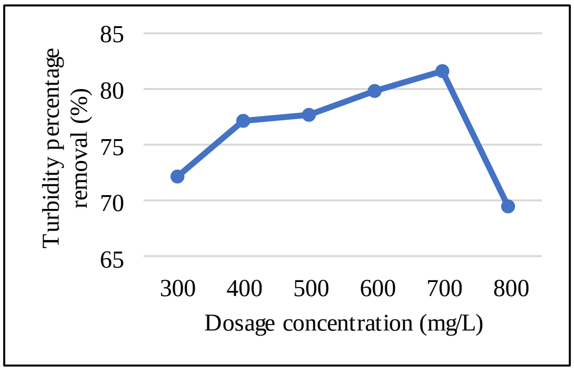

Figure 1: Percentage removal for turbidity against different dosage concentration

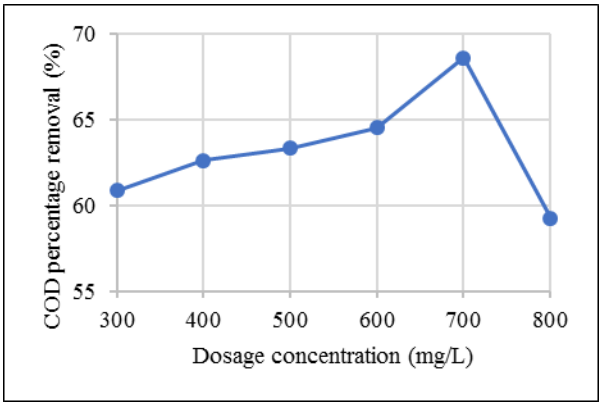

Figure 2: Percentage removal for COD level against different dosage concentration

C. *Coagulation – Flocculation mechanism from molecular point of view*

FTIR Analysis

Figure 3 shows an FTIR spectrum for *hylocereus undatus* foliage as a natural coagulant. Meanwhile, the peaks and its functional groups are listed in Table 2. The peak at 3324.58 cm^{-1} indicates the presence of medium aliphatic primary amines and medium secondary amines. This is due to the range of aliphatic primary amines are within 3400 to 3300 cm^{-1} and 3350 to 3310 cm^{-1} for secondary amino. A study done by Abidin, Madehi & Yunus (2017) revealed that aliphatic amines groups are responsible for activity of good coagulation process [10], [11]. In addition, both peaks 1602.82 at 1029.02 cm^{-1} also signify the presence of medium C-N stretching for amine groups. Meanwhile, the peak at 1411.52 cm^{-1} denotes the presence of a carbonyl compound, which is a medium O-H stretching carboxylic acid. According to Abdel-aziz, Hamed, Mouafi & Abdelwahed (2011), the groups that are effective for coagulation – flocculation process are amino (amines and amides), carboxyl and hydroxyl groups [10], [12]. Therefore, these functional groups are among the common protein-specific groups that are responsible in the turbidity removal in water through coagulation process.

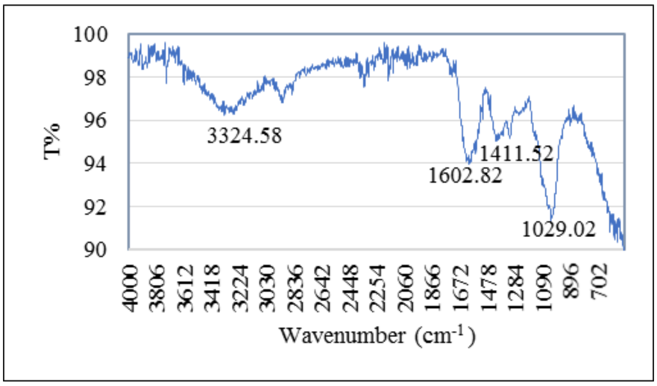

Figure 3: FTIR analysis of *hylocereus undatus* foliage

Table 2: The peaks and its functional groups

Peaks (cm^{-1})	Functional groups
3324.58	Aliphatic primary amines, secondary amines
1602.82	Amines
1411.52	Carbonyl compounds (carboxylic acid)
1029.02	Amines

D. *Effect of pH on the zeta potential*

Figure 4 and 5 show the data for the percentage removals of turbidity and COD levels after coagulation – flocculation process done at different pH. It was observed that the optimal pH for this experiment was 3 since the percentage of turbidity and COD removals was and 80.6% and 69.1%, respectively. The experiment was not done with lower range of pH since pH below than 3 would be difficult to adjust as an increase of [H^+] ions could not be dissociated easily. Plus, coagulation activity works effectively at lower pH since coagulation of suspended matter works better under acidic conditions. Coagulants are less attracted to anionic compounds at higher pH due to its lesser tendency to form positive charges [8], [10].

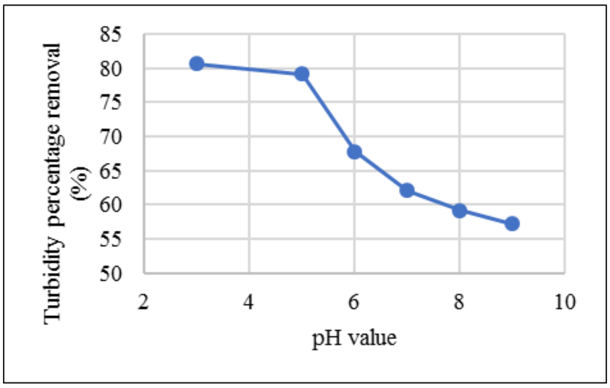

Figure 4: Percentage removal for turbidity against pH value

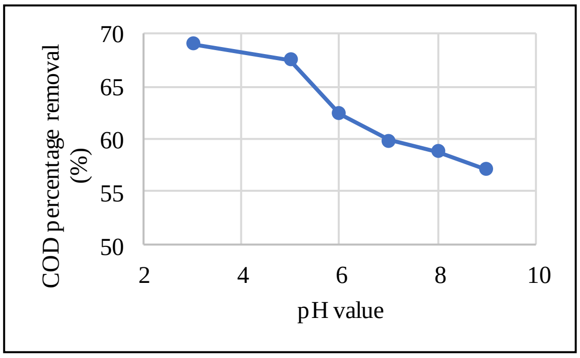

Figure 5: Percentage removal for COD level against pH value

Figure 6 shows the zeta potential of the *hylocereus undatus* foliage as coagulant, wastewater sample and its supernatants at different pH namely, 3, 5, 6, 7, 8 and 9. It was found that the zeta potential of the foliage was +0.433 mV while the initial wastewater was -7.72 mV. Taking the zeta potential of the supernatant after jar test done at different pH, pH 3 was found to be the optimum pH with -2.65 mV. This could be due to the more protonation of amino groups at acidic pH value. Moreover, this suggested that the coagulation – flocculation mechanism involves charge neutralization and absorption.

The positive zeta potential of dragon fruit foliage indicates that it contains cationic functional groups, classifying it as a cationic coagulant. The amines in the dragon fruit foliage could have undergone ionization that produced carboxylate and H^+ ions attracted colloidal particles that eventually destabilized and caused formations of floc [13]. However, the zeta potential becomes more negative as the pH increased. This could be largely contributed by the deprotonation of carboxylic acids groups carrying negative charges, whilst most of the amine groups have been deprotonated, hence explaining the lack of positive charges. Plus, in a more alkaline pH conditions, the adsorption of OH^- ions are more dominant [14].

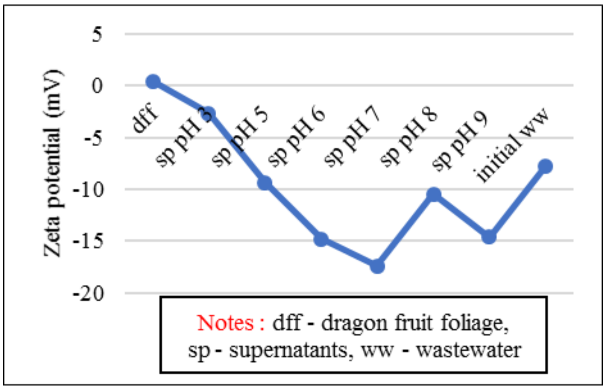

Figure 6: The zeta potential of *hylocereus undatus* foliage, wastewater sample and its supernatants

IV. Conclusion

The optimum dosage concentration of *hylocereus undatus* foliage required in treating pharmaceutical wastewater is 700 mg/L with the COD and turbidity removal of 68.6% and 81.7%, respectively. Moreover, through the FTIR spectroscopy it was found that the presence of functional groups of aliphatic primary amines, secondary amines and carboxylic acids. These are among protein-specific groups that are accountable for good coagulation activity. The zeta potential of dragon fruit foliage was +0.433 mV and the zeta potential of wastewater pre-jar test experiment was -7.72 mV. The optimum pH was 3 since the zeta potential of the supernatant was found to be -2.65 mV, suggesting that charge neutralization and absorption to be the mechanism for coagulation process. The positive zeta potential value of dragon fruit foliage indicated that it is a cationic polyelectrolyte. Moreover, as the pH increases the zeta potential becomes more negative due to the dominant adsorption of OH^- in alkaline pH conditions.

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