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**EmAIT**

Journal homepage: http://publisher.uthm.edu.my/ojs/index.php/emait

Emerging Advances in Integrated Technology

e-ISSN : 2773-5540

# Decolourisation of Sewage using Commercial Tannin-Based Coagulant

**Azreen Ibrahim[1], Junidah Lamaming[1], Lorita Nakolas[1], Vielyn Jinus[1], Abu Zahrim Yaser[1*]**

[1]Chemical Engineering Programme, Faculty of Engineering,
University Malaysia Sabah, 88400 Kota Kinabalu, Sabah, MALAYSIA

*Corresponding Author

DOI: https://doi.org/10.30880/emait.2021.02.02.001
Received 30 July 2021; Accepted 18 October 2021; Available online 15 November 2021

**Abstract:** In this work, the effectiveness of removing colour and total suspended solid (TSS) from complex organic particulate artificial sewage (COPAS) via the coagulation process was studied. Organo-floc (OF), a tannin-based coagulant derived from the plant was used as a coagulant. OF was applied in a jar test experiment at the various dosages at 57 rpm for 5 min, and 30 min sedimentation time to find out the optimum dosage for colour and TSS removal. Zeta potential, pH and conductivity were also analysed. Experiment with tannin dosage of 125 ppm resulted in the highest colour and TSS removal of 94% and 79%, respectively. Organo-floc showed promising results in decolourisation and TSS removal from artificial sewage.

**Keywords:** coagulation, decolourisation, natural coagulant, sewage, tannin

## 1. Introduction

Sewage exists as a by-product of industrial activities such as textile and dye industry effluent, agricultural effluent, and other industries, as well as from human products. In fact, sewage production is unavoidable, however it can be treated in a proper way to be released into the rivers or the ponds. The treating method can be varied, as long as the result of the treated sewage meets the standards of the Department of Environment (DOE), Malaysia [1]. This is important to ensure that there are no related pollutants that could harm the aquatic organisms, the river, the environment, and humans since humans and aquatic organisms depend on water for living.

As an alternative to inorganic chemicals in the coagulation/flocculation process, tannin-based coagulants can be used to play the same role as chemical coagulants in sewage wastewater treatment. Tannin can be found in various parts of plants like the wood, seeds, stems, and roots [2]. Tannins are phenolic compounds with molecular weights ranging from 500 to 3000 g/mol that are water soluble. Tannins are polyphenolic secondary metabolites found in higher plants that can take the form of galloyl esters or polymeric and oligomeric proanthocyanidins with varying inter-flavanyl coupling and substitution patterns [3][5].

Tannin can be used in various applications in the pharmaceutical industry, food industry, wood industry, animal husbandry, nanotechnology, leather industry, and other industrial applications [6] and one of the applications is as a coagulant to clean the wastewater. Tannin performance for sewage treatment has been studied by many researcher and in our previous work [7], we examined the colour removal efficiency of landfill leachate and found that around 81.8% of colour was reduced when using tannin. Al-Gheethi [8] succeeded in performing TSS removal and discovered that 92% of TSS removal was achieved when using tannin coagulant to treat sewage. The study also reported that turbidity, surfactant, and total coliform were deduced with the results of 83.6%, 80% and 89.6% respectively. Recently, Lorena Lugo [9] has experimented with municipal sewage treatment using tannin-based coagulant and

*Corresponding author: zahrim@ums.edu.my

achieved to 86% TSS and 88% COD removal. Rajesh Singh [10] studied how tannin-based coagulant performed on domestic wastewater and discovered that it was able to achieve a deduction in COD, turbidity, and BOD of up to 69%, 95% and 60% accordingly. Another researcher [11], recently attempted to find out the efficiency of tannin coagulant on domestic sewage and found that the turbidity removal achieved up to 84% and the TSS up to 90%.

Releasing untreated sewage could have a negative impact on health and aquatic life due to the lack of light radiation from reaching submerged vegetation. Thus, slowing down photosynthesis as well as decreasing the dissolved oxygen released results in suffocating fish life as they do not have sufficient oxygen. Besides, TSS and colour sewage may cause membrane fouling if not reduced [12]. The TSS size may be the same as the membrane pore or even greater, which causes pore blockage, causing a cake layer to form due to accumulated solid particles on the membrane area. So, in order to minimize the membrane fouling, coagulation-flocculation is applied at the pre-treatment. Generally, common coagulants such as alum, ferric chloride, poly aluminium chloride (PAC), and aluminium chloride are used in sewage treatment. However, these coagulants have their disadvantages where they could cause harmful effects on human health [13]. For example, aluminium salts together with synthetic organic polymers are the factors that have a negative impact on human health, such as Alzheimer [12][13]. Other than that, it produced a high amount of sludge [13]. For example, inorganic coagulants such as PAC can cause an increase in sludge volume and metal concentrations in sludge [13].

In this study, by using the idea of Prieto et al. [14] which used COPAS, manipulated it to get the same characteristics as the real sewage as an alternative sewage. Then tannin-based coagulant can be further investigated. Cat food has been selected in this study as it can be modified to represent it as the wastewater itself and has a lower cost to apply in this research.

The objective of this study is to analyse the performance of tannin-based coagulant towards artificial sewage in terms of TSS, pH, colour, conductivity, and zeta potential analysis. This study also determined the optimum dosage of tannin-based coagulant in sewage treatment on the maximum removal of TSS and colour. This research will allow researchers to used artificial sewage based as a new possible alternative to be use in the future related to sewage. The results from this study could be useful as a reference for any future studies related to tannin coagulant used to treat sewage as an alternative to inorganic coagulant. Artificial sewage has the potential to reduce time consumption and the desired concentration of sewage can be chosen instead of retrieving the real sewage.

## 2. Methodology

### 2.1 Artificial Sewage Preparation

"Cutiez Cat" by Perfect Companion Group (PCG) was used as the raw material for cat-food based sewage which was prepared by using standard raw sewage (300 mg/L) as a guide on how much mass of dried cat food needed to be added. Since the cat-food is in solid condition, it needs to be powdered so that it will easily dissolve with the water. Around 150 mg of powdered cat food was added. The calculation uses the formula for concentration (1):

$$Concentration = \frac{mass\ of\ powdered\ cat\ food(g)}{Volume\ of\ water(L)} \tag{1}$$

### 2.2 Jar Test

In this experiment, the coagulant used was tannin, which is organo-floc (OF). The coagulant dosage that will be used is in the range of 50 mg/L to 200 mg/L that will be added to 500 mL of artificial sewage solution. The jar test was conducted with a mixing operation condition of 57 rpm for 5 min and settling time for 10 min. After settling time occurs, the supernatant is taken for 20 mL using a syringe at the clear upper of the solution (2 cm from the liquid surface) for TSS, colour, pH, zeta potential, and conductivity measurement. The results will be taken three times to get the average of the measurements.

### 2.3 Analytical Methods

Total suspended solids were determined by using filter apparatus assembled with suction. The filter was dried in an oven at 105 $^{o}$C and was cooled in the desiccator before being placed in the apparatus to filter the sample of COPAS. The filter was then weighed after cooling. After filtering was done, the filter was removed and dried in the oven at 105 $^{o}$C for one hour, then cooled. After that, the filter was weighed. The weight of the initial filter and final filter was used to measure the value of total suspended solids of the sample using equation (2):

$$Total\ suspended\ solids = \frac{(A-B)\ x\ 1000}{Sample\ volume,\ ml} \tag{2}$$

where A is the initial weight of the filter and B is the final weight of the filter.

Colour was analysed at a 455 nm wavelength using a UV/vis-spectrophotometer (Perkin Elmer Lambda 365) in the unit of Platinum-cobalt (PtCo). However, in this case, the apparent colour is sampled without filtering or centrifuging used in this analysis. The removal percentage of colour was calculated using the values of initial colour concentration and final colour concentration using equation (3):

$$Colour\ removal = \frac{(C_o - C_f)}{C_o} \times 100 \tag{3}$$

where $C_o$ is the initial colour concentration and $C_f$ is the final colour concentration.

The pH and conductivity were measured using a pH meter (HI 9611-5, Hanna). The Zeta potential was obtained by using a zetasizer machine (Malvern Zetasizer Nano Series model ZS). Standard deviation was used in this study to determine the differences between the parameters of artificial sewage quality before and after coagulation by interpreting the data obtained using excel.

## 3. Result and Discussion

The effectiveness of the organo-floc on artificial sewage was investigated. The supernatant of each sample was analysed in terms of total suspended solids, colour, pH, conductivity, and zeta potential.

### 3.1 Artificial Sewage Concentration Determination

In this study, artificial sewage will be used to examine the performance of tannin-based coagulant rather than real sewage. The TSS of artificial sewage has been compared with typical sewage characteristics. The experiment with TSS was conducted in triplicate to obtain the average results for TSS. In this determination of total suspended solids in the artificial sewage, there are different concentrations of artificial sewage used as shown in **Table 2** and **Fig. 1**. The TSS of artificial sewage that should be gained is 300 mg/L, since the regular concentration of TSS in Malaysia is in that value [15]. Thus, the concentration of artificial sewage that might have 300 mg/L of total suspended solids is around 0 to 1 g/L (**Table 2**). However, this value does not show the specific value of 300 mg/L of TSS in artificial sewage. Therefore, by referring to this result, a smaller scope of the artificial sewage concentration was done, which is in the range of 0 to 5 g/L (**Fig. 1**) to find a more accurate artificial sewage concentration of approximately 300 mg/L. **Fig. 1**, showing that at 0.68 g/L of artificial sewage concentration might have 300 mg/L of total suspended solids. Therefore, the concentration of artificial sewage (0.68 g/L) is then used for further analysis, such as colour, pH, conductivity, and zeta potential.

**Table 1 - Artificial sewage characteristics data**

| Parameters | Unit | Value |
|---|---|---|
| **Total suspended solids** | mg/L | 193 |
| **Colour** | PtCo | 1929 |
| **pH** | - | 7.2 |
| **Conductivity** | µs/cm | 169 |
| **Zeta Potential** | mV | -24 |

**Table 2 - Total suspended solids value of various concentrations of artificial sewage**

| Artificial Sewage (g/L) | TSS (mg/L) |
|---|---|
| **0** | 0 |
| **1** | 143 |
| **10** | 3764 |

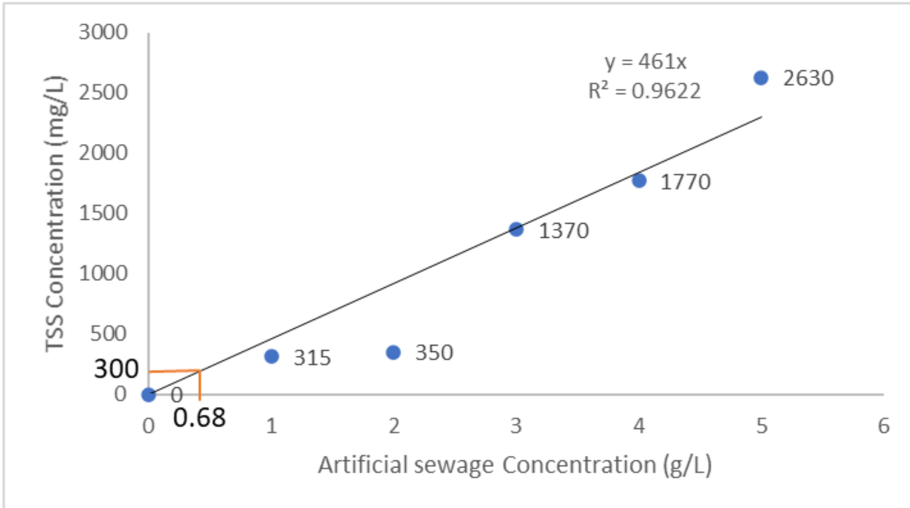


**Fig. 1 - Total suspended solids concentration, TSS (mg/L) against Artificial Sewage**

## 3.2 Coagulant Dosage Required for Treatment of Artificial Sewage

The total suspended solids at 0.68 g/L of artificial sewage were 193 mg/L. The total suspended solids (TSS) in the supernatant water decreases with increasing coagulant dose, but the total suspended solids value increases rapidly after the optimal dose is reached. If the amount of coagulant added is too high, agglomeration will decrease. This is likely due to repulsive charges between colloids contained in artificial sewage. The positive charge of the coagulant adsorbed by the colloidal particles which have a negative charge in the artificial sewage sample led to an attraction with each other, but as more coagulant was added, the positive charge in the sample increased, which caused the charges to stabilize again and begin to repel each other. Generally, colloids and suspended particles in wastewater have a negative charge on the surface, which causes an electrostatic repulsion with each other and consequently prevents their sedimentation and removal [16]. As shown in **Table 1**, the particles contained in the artificial sewage had a negative charge, and the zeta potential was -24 mV. The addition of cationic substances, such as tannin-based coagulants, makes the particles unstable [17]. The long chains of tannin-based coagulant polymers contain positively charged amino groups [18], and characterize coagulants as cationic coagulants. Organo-floc (OF) is a cationic coagulant that can destabilize anionic colloids by being positively charged [7], [19], [20] by the presence of phenolic groups [18]. This shows that the zeta potential value increases with increasing coagulant dose. This means that the number of positive charges in artificial sewage is increasing and shows that OF has a positive charge. Likewise, as observed by Hameed et al. [21], the zeta potential value increases with increasing coagulant dose in the neutralizing charge mechanism. Therefore, the higher the positive charge of the artificial sewage, the more the particles will start to repel each other, and the agglomeration will decrease, resulting in a higher TSS value after optimal dosage of OF. The optimal dose of organic flocs (OF) obtained was 125 mg/L, resulting in 79% removal of TSS and 94% removal of colour.

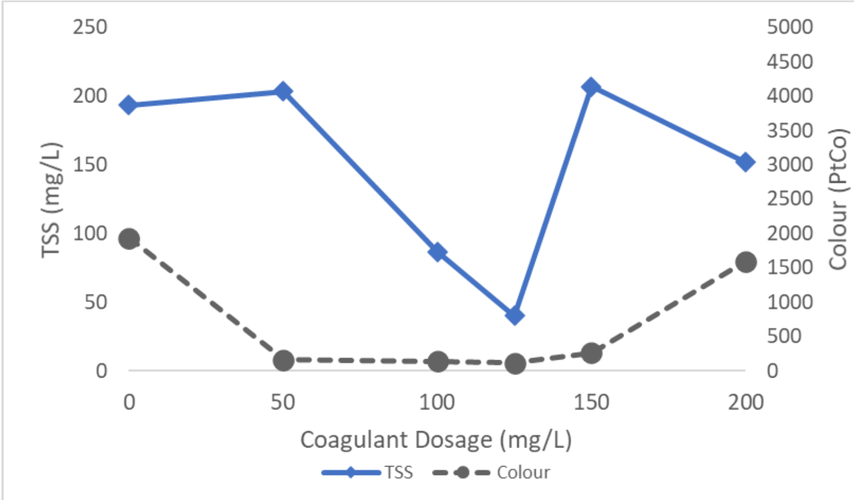


**Fig. 2 - TSS and the colour of various dosages of coagulant**

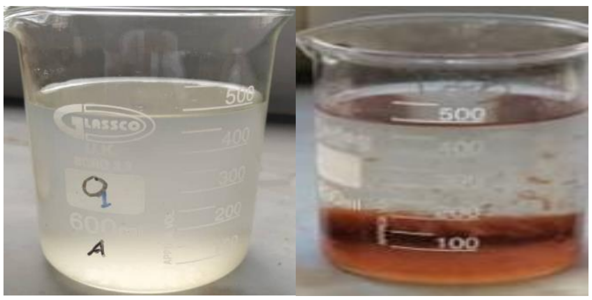

**Fig. 3 - Artificial sewage before and after coagulation at 125 mg/L of coagulant dosage**

At 125 mg/L dosage of coagulant, the colour of the artificial sewage as shown in **Fig. 3** becomes clearer and it can be seen that the OF colour was sediment on the bottom of the beaker. As the coagulant dosage increased, the colour concentration of the artificial sewage decreased, but after reaching the optimum coagulant (125 mg/L) dosage, it indicates that the colour density is starting to rise. **Fig. 2** shows the colour results when the coagulant was administered. De Oliveira et al. [22] emphasized that increasing the concentration of plant coagulants in water increases polymerization and makes the colour browner, with higher tannin doses contributing to higher colour values. This explains why the colour value increases after optimal coagulant is reached. Decolourisation with modified tannin coagulant generally increases flocs through coagulation-like mechanisms such as adsorption to improve precipitation and improve colour removal efficiency [11] [15].

Sanchez Martin et al. [3] highlight that a tannin-based coagulant (92 mg / L) was used for sewage treatment, and the BOD5 and COD removal rates were the highest at 60% and 40%, respectively. In other studies, Hameed et al. [21] achieved 43% of total suspended solids removal and 90% of turbidity removal using tannin-based coagulant at 35 mg/L dosages. The best decolourisation of sewage which is 73% and 90% turbidity removal, was achieved by Grehs et al. [23] with tannin dosages of 50 to 80 mg/L.

**Table 3 - Result comparison of this study with the previous study**

| | **Sewage** [3] | **Sewage**[23] | **Sewage**[26] | **Artificial sewage (This study)** |
|---|---|---|---|---|
| **Optimum Dosage (mg/L)** | 92 | 35 | 50 - 80 | 125 |
| **Colour removal (%)** | - | - | 73 | 94 |
| **TSS removal (%)** | - | 43 | | 79 |

| | | | | |
|---|---|---|---|---|
| **COD removal (%)** | 40 | - | | - |
| **Turbidity removal (%)** | - | 90 | 89 | - |
| **$BOD_5$ removal (%)** | 60 | - | - | - |

In the study, the pH value became slightly more acidic as the coagulant dose increased (**Fig. 4**). This indicates that the addition of the coagulant did not change the pH of the artificial sewage. Arismendi et al. [16] pointed out that the method of adding hydrochloric acid by chemical denaturation of tannin does not affect the final pH of treated wastewater due to the secondary metabolites that the produced hydronium ions react and absorb. It supports the previous statement that the pH of the sample is not affected by the coagulant. The pH without the addition of coagulant was 7.2 but decreased to 6.5 at the 200 mg/L coagulant dose. Changing the pH has the potential to accelerate the removal of colour from the cause of the process [20]. The colour value decreased at pH 7.2-6.8. This shows that colour removal is effective in this range of pH. Lower than pH 6.8, colour and TSS removal is not efficient. However, the decreasing trend in pH values in **Fig. 4** is likely due to proton dissociation from the tannin protonated tertiary nitrogen. In highly acidic conditions, quaternary nitrogen is introduced into the tannin polyphenol structure by reaction with an amines and aldehydes [18]. Even in this state, Ibrahim and Yaser [7] also state that a bridging mechanism is likely to occur. In contrast to pH, the conductivity of artificial sewage tends to increase with increasing dose of coagulant (**Fig. 4**). This could be an unreacted tannin coagulant in artificial sewage. After treatment with the cationic coagulant tannin, the zeta potential value was found to decrease as the amount of tannin dosage increased. (**Fig. 5**) suggests that charge stabilization occurred in the artificial aqueous solution. This means that a neutralizing charge mechanism has occurred.

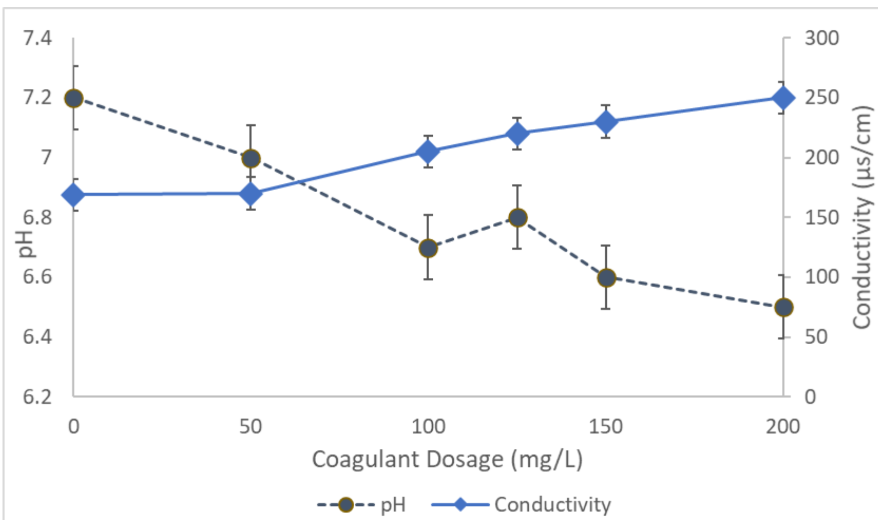


**Fig. 4 - pH and conductivity result for different dosages of coagulant**

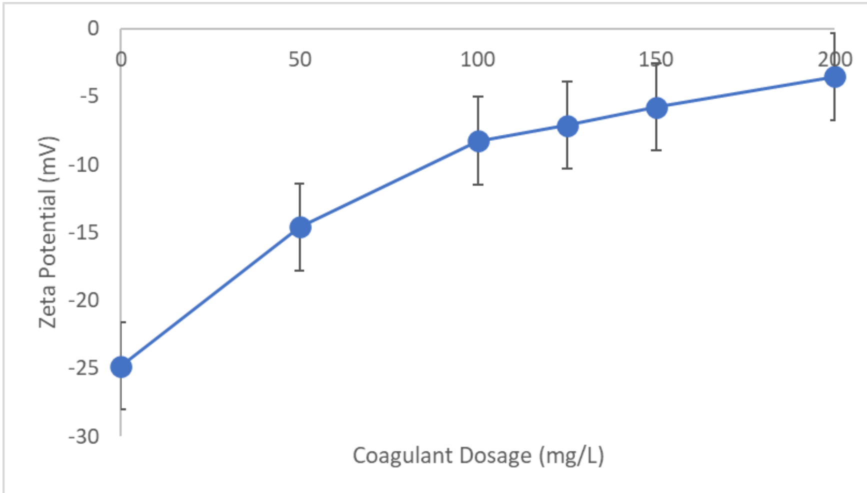


**Fig. 5 - Zeta potential of COPAS for different dosages of coagulant**

## Conclusion

A tannin-based coagulant as an alternative sewage made from cat-food was successfully made and analysed. The optimum dosage of tannin used for coagulation process of sewage concentration of 0.68 g/L is 125 mg/L since the colour removal is more efficient (90%) at this dosage. Apart from that, TSS removal also shows the highest (94%) by using this tannin dosage. pH value, conductivity, and zeta potential are in the range of 6.5-7.2, 160-250 µS/cm, and -25 to -1 mV respectively. Overall, this study proved that tannin coagulant can treat sewage as an alternative to inorganic coagulant and artificial sewage can be implemented to reduce time consumption and choose the desired concentration sewage instead of retrieving real sewage which has a varied concentration. However, the implementation of artificial sewage can still be improved with further studies.

## Acknowledgement

The authors would like to thanks Universiti Malaysia Sabah for funding this research under the grant SPB0001-2020 and postdoctoral awarded to Dr. Junidah Lamaming.

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