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Influence of Mangosteen Pericarp (MP) in Coagulation Treatment and Membrane Fouling

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The available conventional water treatment processes has not readily met the drinking water quality. The chemical used in treatment process will produce by-product that might affect the treated water quality. In light of this research was carried out to investigate the effectiveness of Mangosteen Pericarp (MP) powder as a new coagulant aid in coagulation and ultrafiltration hybrid process. This was done by using doses of 0.05 g/L, 0.10 g/L, 0.15 g/L, 0.20 g/L, 0.25 g/L, and 0.30 g/L of the MP powder together with aluminum sulphate (Alum) as coagulant. The turbidity, UV_{254} and pH were determined for all the samples. MP is highly potential in improving the turbidity removal efficiency during coagulation process. It was found that most significant improvement of the turbidity removal efficiency was recorded near to neutral pH which is pH 6 and pH 8 with 0.3 g MP to harvest 97.9 % and 98.6 % removal efficiency. The optimum has recorded at 0.2 g Mp with pH 10 to obtain 99.5 % turbidity removal efficiency. In the presence of Humic Acid (HA), pH was the major factor in enhancing the turbidity and UV_{254} removal where at pH 10 with 0.2 g MP can capture up to 99.6 % of turbidity and 97.6 % of UV_{254}. The favourable micro micro-intercoiled texture of MP enable to entrap the impurities in the coagulation process in order to sustain the membrane flux by reducing the membrane fouling.

1. Introduction

Good water quality is an essential need for all living organisms. Water shortage problem becomes serious due to the population has been increasing year-by-year. From a total of 1,055 river monitoring stations in Malaysia, it has been reported that half of it had polluted (Amneera et al., 2013).

The occurrence of natural organic matter (NOM) as well as HA arise in water resource directly affected the quality of drinking water lead to disinfection byproduct (DBPs) by disinfectant (Xu et al., 2016). With the present of suspended solid in water bodies acting as a shield to protect the microorganisms and viruses against disinfection (Perkins et al., 2016). In order to meet the requirements of stringent water standard regulations, advance technology ultra-membrane filtration has been widely used to meet sustainable development. The HA, suspended solid and colloidal particulate matters are known as a major membrane foulants and obstacles for the membrane technology (Zhao et al., 2015). In most cases, foulants adsorbed in the membrane bloack the pores. It is then followed by the cake formation on membrane surface (Zhang and Ding, 2015). Pretreatment upon the test water prior membrane filtration must be investigated. Some studies found that coagulation was effective in reducing membrane fouling by combination of the UF with coagulation (Xu et al., 2015). Even though such coagulation can enhance membrane flux permeability, a large amount of chemical have to be applied to ensure coagulation efficiency (Ahmad et al., 2006).

An approach to reducing chemical dosage must be investigated and desirable to develop membrane with higher water flux and sustainable pretreatment. The use of natural plant based aider which is environmental friendly may be an interesting alternative. Further investigation on coagulation and membrane technology by applying the green concept has been conducted in this study.

Mangosteen has been selected in this research because large number of Mangosteen Pericarp (MP) are generated every years (Chen et al., 2011). On the other hand, carcinogenic risk related to traditional coagulants can be reduced since MP have toxic free (Pedraza-Chaverri et al., 2008) and anti-cancer properties (Wang et al., 2012). The safety of drinking water can be guaranteed. It is well known that the treated water quality, cost

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of water treatment and life span of the system directly reflect its practicability. This paper reports on the potential of MP as a natural coagulant aid for turbidity removal and HA in the water. The use of MP in coagulation system is then correlated to membrane performance.

2. Materials and Method

2.1 Pericarp of Mangosteen Preparation

MP collected from Sungai Lembing, Kuantan wet market were pre-treated by washing it in DI water. It isthen boiled in water bath until the supernatant produced is colourless for complete removal of the Mangosteen dye color (Gloria et al., 2012). The supernatant was removed and the sedimentary MP was collected. It was then dried in oven at 40 ˚C. Finally, it was grounded by using electric grinder machine with siever in size between 90 µm – 125 µm (Patale and Pandya, 2012). The powder from Mangosteen was kept in tight container. It is now ready to use.

2.2 Water Samples

2 sets of synthetic water were prepared in kaolin test water and HA-kaolin test water. This is due to turbid and HA present ubiquitous in natural water (Xu et al., 2011). Kaolin stock solution was prepared by adding 10 g of kaolin (Sigma-Aldrich, CSA no: 1332-58-7) in 1 L deionised water (DI) with stirring at 20 rpm for 1 h and then kept in room temperature for at least 24 h to allow complete hydration of the kaolin (Dong et al., 2015). The HA stock solution was prepared by adding 1 g of HA (Sigma-Aldrich, CSA no: 1415-93-6) together with 0.4 g NaOH (Merck Millipore, CSA no: 1310-73-2) in 1 L DI water under continuous stirring for 30 min (Dong et al., 2015). The kaolin test water was prepared by adding kaolin stock solution in 1 L DI water with adjusted turbidity in 125 ± 25 NTU. Whereas, HA-kaolin test water was prepared by adding 10 mL of HA stock solution in to the kaolin test water with adjusted UV_{254} in 0.3 ± 0.025. The pH solutions were controlled in 4, 6, 8 and 10. The DI water was used for dilution of stock solutions as well as for any reagent preparation during the experiment.

2.3 Coagulation Process

The alum was used ($Alk(SO_4)_2 \cdot 12H_2O$) which purchased from Sigma-Aldrich, USA. Stock solution of alum was prepared with a concentration of 10 g/L and kept in 4 °C (Harfouchi et al., 2016). 10 mL of alum stock solution and desired amount of MP was added in the coagulation test with rapid mixing at 125 rpm for 1 min followed by slow mixing speed at 40 rpm for 30 min flocculation and then 30 min quiescent settling. The same procedure was repeated for sample with different pH condition. The pH was adjusted by adding 1.0 M NaOH and 1.0 M HCl solutions. Samples were collected after 30 min from 2 cm depth surface water to measure the targeted characteristics such as turbidity and UV-spectrophotometer at 254 nm.

2.4 Ultrafiltration (UF) Process

The ultrafiltration experiments were conducted by using a dead-end stirred cell ultrafiltration unit lab-scale (Amicon, Model 8200) with a maximum volume capacity of 300 mL. After jar test coagulation, the effluent was decanted from the beaker to the dead-end ultrafiltration membrane unit (Am Inc, China) with cut-off molecular weight of 50 kDa. The effective membrane area was 14.6 cm². Undergoing ultrafiltration, stirring velocity was kept constant in low speed to prevent floc aggregates from settling (Feng et al., 2015). At the preliminary filtration stage, the membrane was underwent compaction with DI water at 50 kPa in order to ensure solution are fully occupied in the membrane pores (Zularisam et al., 2007). Constant nitrogen gas was used at 150 ± 5 KPa in the time frame 30 min. Permeate was weighted by electronic balance connected to a computer which recorded the permeate mass on the balance every 10 s. The filtration of any model solution was carried out with the same pressure and time frame. The water flux was measured.

2.5 Membrane Fouling

The flux reduction of the water flux was indicated the membrane irreversible fouling. It is calculated by comparing the DI water flux before and after filtration as Eq(1).

$$\mathrm{FR_{DWF}} = (\mathrm{DWF_b} - \mathrm{DWF_a})/\mathrm{DWF_b} \times 100\ \% \tag{1}$$

Where FR_{DWF} is the flux reduction of DI water flux, %; DWF_b is the DI water flux before filtration, L/(m^2h) and DWF_a is the DI water flux after filtration, L/(m^2h).
The relative flux investigated in this studied showed the stabilised flux of the model solution, as shown by Eq(2).

$$RF = DF/DWF_b \tag{2}$$

Where RF is the relative flux and DF is model solution flux.

2.6 Effect of MP and pH in Coagulate Efficiency

Coagulants are widely used in water treatment process. In this paper, MP was selected as natural aid in the treatment. Without MP, the turbidity removal efficiency for the kaolin test water has showed lowest removal efficiency as shown in Figure 1. The additional of MP in coagulation process, the turbidity has been recorded increased its removal efficiency and reaching stable step at 0.1 g of MP was added. Where the most significant improvement of the turbidity removal efficiency is near to neutral pH which is pH 6 and pH 8 with 0.3 g MP in 97.9 % and 98.6 % removal efficiency respectively. The compounds presence in the MP with a long-linear side chain (Tatsuzawa et al., 2013) could increase the neutralisation and promoted removal efficiency. The higher the pH in the kaolin test water, the higher turbidity removal efficiency. The pH affected the surfaces charge of the coagulation process and also stabilisation of the suspension where higher removal efficiency was observed at higher pH values. Similar trend also reported by Awad and Eldemerdash (2014). Higher pH in solution increases the density and toughness of the floc formed, enable the colloids to coalesce and aggregated to promote a better result in turbidity removal efficiency by homogeneous nucleation precipitation.

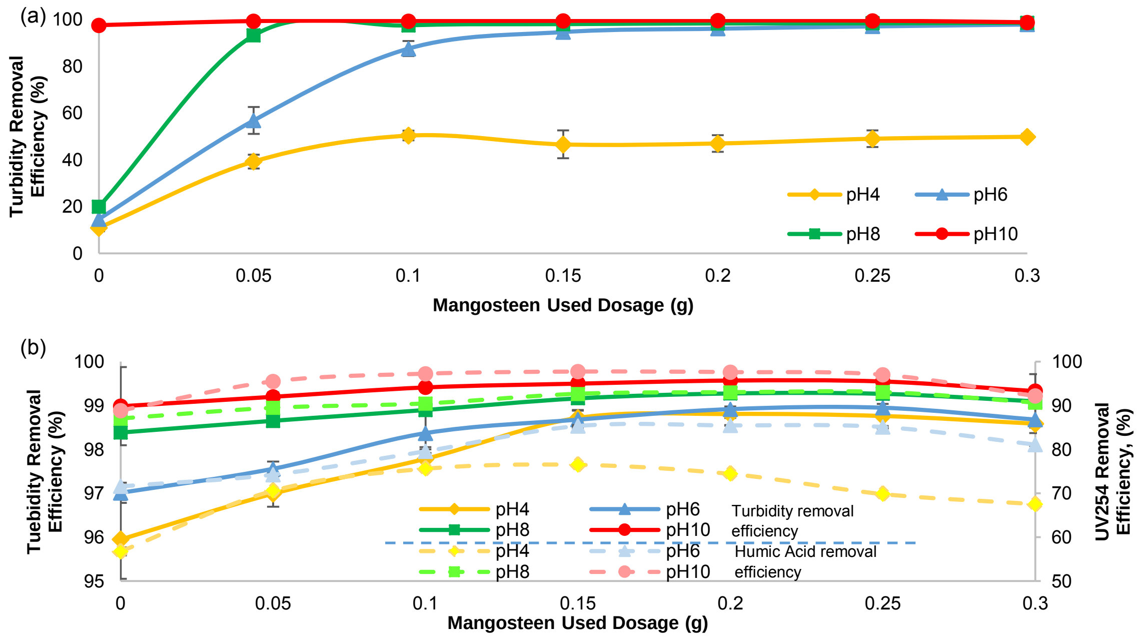

Figure 1: (a) Kaolin test water in respect to various pH values. (b) HA-Kaolin Test water in respect to various pH values. The solid line indicates to turbidity removal efficiency and the dashed line indicates to UV254 removal efficiency.

Similar treads for the HA-kaolin test water, the turbidity and UV_{254} removal efficiency increases with increase the MP dosage and pH value. It was supported by Hsiung et al. (2016) that the present of humic acid in solution offers a stronger adsorption force to agglomerate. Humic at pH > 5 formed adsorption on the surface of $Al(OH)_3$ to form flocs more denser and leading to a maximum removal of humic substance as reveal by Duan et al. (2002).

2.7 Influence of Kaolin and HA-kaolin in Membrane Ultrafiltration

Figure 2(a) and 2(b) show the kaolin test water at pH 4 have the lowest relative flux in the absent of MP and higher relative flux at higher MP dose. When HA present in the feed water, it could increase hydrophilicity of the membrane to attract more water molecules to penetrate through the membrane (Mänttäri et al., 2000) and as a result, relative flux of membrane increases as shown in Figure 2(c) and 2(d). Similar trend also reported by Chen et al. (2015). The relative flux in HA-kaolin feed solution at pH 10 ultrafiltration is more stable and narrowing the range relative flux in 0.001 - 0.028. Where, at pH 4 shows unstable flux with widen relative flux range in 0.021 - 0.055.

2.8 Membrane Surface Functional Group Analysis

From the FTIR spectrum analysis, the active groups are boost to bind and react to form flocs from it can thus be identified. In the spectrum there shows significant adsorption bands at 2,111 cm^{-1}, 1,600 cm^{-1}, 1,434 cm^{-1}, and 1,018 cm^{-1}. These bands are quite similar to others natural coagulant aid used in the coagulation process (Ali et al., 2015). Peak at 2,111 cm^{-1} shows the presence of C=N stretching of thiocyanate (SCN). The bands region between 1,800 cm^{-1} and 1,500 cm^{-1} are number of overlapping bands between 1,650 cm^{-1} and 1,556 cm^{-1}. These set can be assigned to C=O bond stretching, the carbonyl group is present in the fatty acid and protein structures. It was supported from the previous researcher found that the spectrum at between 1,600 cm^{-1} and 1,400 cm^{-1} can increases the adsorption of the flocs to aggregate (Zhang et al., 2012).

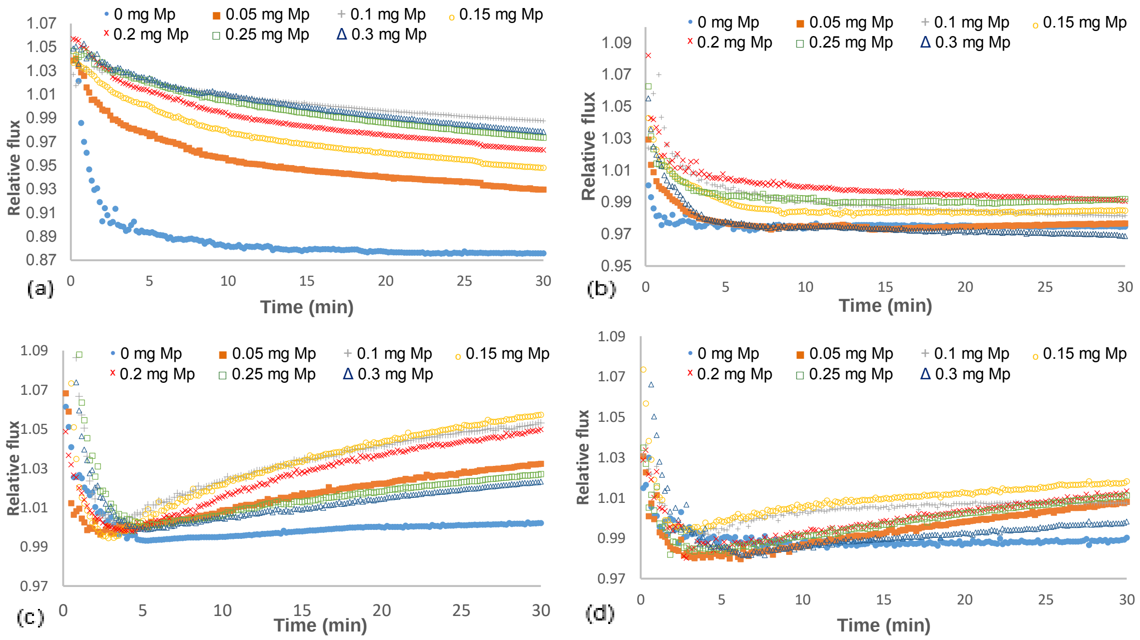

Figure 2 : Relative flux for (a) Kaolin test water in pH 4; (b) Kaolin test water in pH 10; (c) HA-Kaolin test water in pH 4; (d) HA-Kaolin test water in pH 10

2.9 FE-SEM Images of Microstructure MP and Membrane Cross section

Figure 3(a) present the MP having rough with cracks surface morphology facilitates the process of adsorption due to the interstices and the long chain protein component (Araújo et al., 2010) of the MP. In addition, inside the cracking exhibits a strong intercoiled texture characteristic as shown in Figure 3(b) increase the impurities entrapped in its structure for removal away from the solution. In lower pH values higher the ionic strength (Jia et al., 2016) to compress the particles double layer in decreasing the its thickness (Liu et al., 2014) and results the residues particle in feed solution easier penetrated through the membrane as compared to higher pH as shown in Figure 2(c) and(d). Consequently, the permeate solution in lower pH had slightly higher turbidity compared to higher pH. This can be proved by the FESEM results as shows in Figure 3(c) and Figure 3(d). The used membrane in pH 4 has very less pore blocked, whereas in pH 10 used membrane has observed the pore was blocked and affected the permeate flux slowdown even though the HA acting to attract the water molecules penetrates through the membrane.

3. Conclusions

The removal efficiency of turbidity and UV254 by using MP as coagulant aid in the coagulation process. Further treatment by membrane process showed its tremendous potential as a plant-based coagulant aid in the water treatment process. Most significant turbidity removal efficiency by added mangosteen pericarp were observed at pH 6 and pH 8 with 0.3 g Mp to get 97.9 % and 98.6 % turbidity removal efficiency respectively. The optimum is 0.2 g Mp at pH 10 with 99.5 % turbidity removal efficiency. When present the humic acid in the solution, optimum has been recorded at pH 10 with 0.2 g Mp to captured 99.6 % of turbidity and 97.6 % of UV254. Although the mangosteen pericarp could enhance the coagulation performance, but the major factor contributed in humic removal was believed to be affected by pH. MP has favorable micro-intercoiled texture that entrapped the impurities in water . Thus it enhances the relative flux by reducing the membrane foulants. Compared to alum, MP do not need pH adjustment to improve the coagulation turbidity removal effectiveness without being hazardous. For future study, it is recommended that the MP can be used for real wastewater or river water.

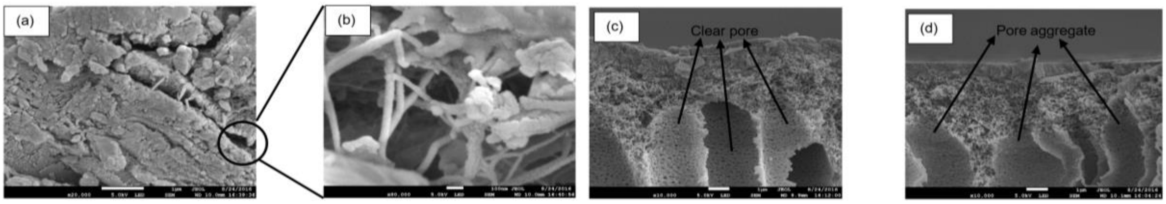

Figure 3: FE-SEM micrographs of (a) Mp magnification 20,000, (b) Mp magnification 80,000, (c) pH 4 used membrane cross section with magnification 10,000 and (d) pH 10 used membrane cross section with magnification 10,000

Acknowledgments

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