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Surface Morphological Characteristics on Unmodified Cucurbita as a Biosorbent Potential for Chloride and Sulphate

Sabariah Musa[1], Nur Huda Mohamad[1]
[1]*(Department of Water and Environmental Engineering, Faculty of Civil and Environmental Engineering, Universiti Tun Hussein Onn Malaysia, Malaysia)*

Abstract: Groundwater is a second thought for a safe water supply to fulfil the needs of living creatures on the earth surface. In Universiti Tun Hussein Onn Malaysia (UTHM), groundwater can be extracted from pumped well at Research Centre for Soft Soil Malaysia (RECESS) area, but the quality was not promising as drinking water supply. The purposes of this study were to characterize the surface morphology of unmodified Cucurbita as biosorbent for each part from peel, flesh and seed and determine the effectiveness of Cucurbita components by using biosorbent amount optimization. From the Scanning Electron Microscope (SEM) result, some porous surface texture was spotted and it was believed to assist in entrapping and adsorbing the contaminants exists in groundwater. The biosorption method involved cucurbita components namely peel, flesh and seed as sorbent while the groundwater acted as solvent that contains chloride and sulphate ions as sorbate. Three parameters were assessed namely chloride, sulphate and pH on series of biosorbent amount which affects biosorption performance. The percentage of biosorbent for optimization that was analyzed in this study was 0.05%, 0.1%, 0.15% and 0.2%. The Ionize Chromatography (IC) result showed that peel was proven to be the most effective component in removing chloride and sulphate in groundwater by 16.8% and 12.8% respectively. Meanwhile, the data obtained showed that increases in adsorbent amount helped in reducing the pH value of groundwater. Hence, as referred to the Drinking Water Standard published by Malaysia Ministry of Health, concluded that pH and sulphate exist within permissible limit which are 6.5-9.0 and 250 mg/L while chloride ceased to present within 250 mg/L boundary. As a conclusion, cucurbita can be classified as a potential biosorbent for groundwater treatment but some improvements must be implemented to bring a significant impact for the benefit of mankind through a safe drinking water supply and cost effective treatment.

Keywords: Cucurbita, pumpkin, groundwater, biosorption process

I. INTRODUCTION

Malaysia is one of the blessed countries in the world and one of the fortunes received by Malaysia is a high rainfall amount. This favorable condition, however, has made people take for granted the continuous supply of water and pay less attention on its wise management. In Selangor for example, clean water supply has been a very familiar issue heard and this is likely to be contributed by the population boom and pollution that takes place. Projections show that by 2025, more than 3.1 billion people will be living in water stress areas as population growth causes more countries and regions to become water scarce [1].

As surface water depleted, people opted for fast yielded alternatives and groundwater is found to be one. Groundwater, or subsurface water, is a term used to denote all the water found below ground surface. Groundwater is generally considered as the best source for potable water as it is believed to be well protected from contamination. Nevertheless, the intention of exploiting groundwater as direct drinking water is not easily permissible unless it follows the guidelines. This is due to the principal dissolved constituents in groundwater such as calcium, magnesium, sodium, bicarbonate, sulfate and chloride which present in the form of electrically charged ions.

Groundwater is a hidden treasure for people around the world. Groundwater originates from precipitation running on the surface of the earth. A portion of it will flow into the soil and enter the river, while the other part will infiltrate through the soil and kept in. The accumulation of the infiltrated water will increase with time and eventually, groundwater storage exists. The crucial role of groundwater as natural resources can be simply identified by the sole dependency on groundwater for water supply of several countries in the world such as Denmark and Saudi Arabia. As a source of water supply, groundwater is more favourable compared to surface water due to its higher quality, better protected from potential pollution, less subjected to seasonal and perennial fluctuations, and much more uniformly spread over large area. At certain places, groundwater might even exist without surface water availability [3].

Chloride and sulfate which belongs to non-metals group are believed possess the ability to impair human health. According to the U.S. Council of Environmental Quality, cancer risk is higher by 93% among people who drink chlorinated water compared to those who do not. Meanwhile, the previous case studies have suggested that drinking water containing high concentrations of sulfate is related with the occurrence of diarrhea in people [1].

Groundwater can become contaminated from natural sources or various types of human activities. The study area, Research Centre for Soft Soil Malaysia (RECESS), UTHM has a clay property in which it consists of chlorides, manganese, sulphates and nitrates [2]. These elements contribute to the groundwater contamination. Therefore, the groundwater treatment is now perceived as a priority in continuation of increasing water supply demand.

Pumped well at RECESS is a good platform to carry out groundwater treatment process since it is used daily. The location of RECESS itself has brought a doubt, where it is a flat area and situated around 20 km from the sea, thus, making it prone to natural contamination such as saltwater intrusion [2]. Groundwater samples were collected from RECESS, UTHM contains a few contaminants such as chlorides, manganese, sulphates and nitrates. Therefore, a further treatment is required to remove the existing contaminants for the sake of cleaner and safer water supply to the community.

In this study, an environmental friendly method was proposed in which biosorbent is utilized as chloride and sulfate remover in groundwater by biosorption process. The biosorbent that was used originates from agro-waste in which to be specific, fruit peel, flesh and seed under cucurbita species. Apart from being economic as this study reuses easily attainable material, utilization of agro-waste also assists in managing serious disposal problem worldwide.

Previously, various methods for water purification have been introduced to this study field. Among those, there are several remarkable solutions identified such as reverse osmosis, ion exchange, and adsorption [4]). Sorption involves transfer of ions from water to the soil, as for instance, from solution phase to the solid phase. Sorption actually describes a group of processes, which includes adsorption and precipitation reactions [5]. Adsorption technology has been found successful in removing different types of inorganic anions such as fluoride, nitrate and bromide from water by using various materials as adsorbents. Future study should jot down an important fact in which, the selection of appropriate material for the removal of specific types of anions will affect the accomplishment to achieve optimum removal rates.

Cucurbita (pumpkin) as shown in Fig.1 was selected as a biosorbent potential in groundwater treatment due to several factors. The inherent functional groups such as hydroxyls, carboxylates, amines, amides and others play a remarkable role in determining the adsorption capacities of different adsorbents. Apart from that, lignin, hemicelluloses and cellulose have been spotted as major storage media for organic pollutant; therefore, increased amounts of these in an agricultural waste material can contribute to higher adsorption rate [6]. Pumpkin was sorted out as a potential biosorbent because it owns carboxylic group, cellulose, hemicellulose and lignin.

(a) (b) (c) (d)

Fig 1. (a) Whole of *Cucurbia* or pumpkin was used in this study, (b) peel, (c) flesh, (d) seed

The study on the efficiency of contaminants removal by selected biosorbent is essential to prepare for the industrial application of biosorption, as it gives the information about the equilibrium of the process which is mandatory in order to design the biosorption system. Since biosorption is determined by equilibrium, it is largely influence by several factors such as pH, temperature, biosorbent amount and contact time.

In this study, the process of biosorption was influenced by the concentration of biomass in the solution. High dosage of biosorbent was suggested leads to interference between the binding sites. Decrease of biomass concentration in the suspension in groundwater sample enhances the adsorption performance, thus increases contaminants uptake per gram of biosorbent, as long as the biosorbent is not saturated [7].

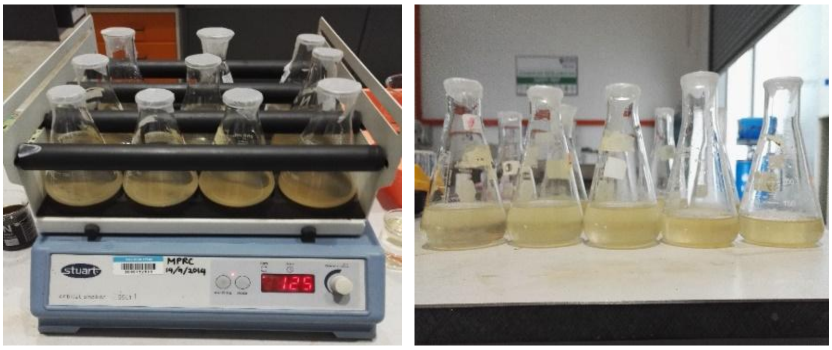
II. MATERIALS AND METHODS

RECESS is an area where the groundwater samples were collected. Water samples were collected for several times, each done during sunny day to ensure a reliable average result. The biosorbent which is cucurbita was obtained from local fruit stall in Parit Raja, Batu Pahat, Johor.

The collected cucurbita components namely peel, flesh and seed was washed with tap water before rinse it with distilled water. The biosorbent was sun-dried and stored in room temperature. 100 g of cucurbita peel was pre-treated with 2L of 10% nitric acid for 24 hours then washed with distilled water and finally soaked in 2L of distilled water for another 24 hours in order to remove surface impurities and residue of nitric acid on the peel. Meanwhile, for flesh and seed, there were no such needs since they are protected inside by the peel. Subsequently, the rind, flesh and seed were oven-dried at 60°C for a few days to reach a fully dry state. 60°C was recommended as a drying temperature to preserve the fiber structure of cucurbita components from damaging.

Before the peel, flesh and seed can be utilized, all the components were finely grinded or blended to increase the total surface area for higher adsorption capacities. There were different methods of crushing since grinder was only applicable to seed component hence, a dry blender was used for peel and flesh. Later, the grinded or blended cucurbita components were sieved through < 300 µm sieve to ensure it turned into powder form. Next, the pulverized cucurbita was tested for characterization of surface morphology by utilizing Scanning Electron Microscope (SEM).

The optimization process was conducted by making the biosorbent amount as the variable. The amount of biosorbent was varied at 0.05 g, 0.1 g, 0.15 g and 0.2 g from 100 ml groundwater sample. Batch study was carried out in this stage. The flasks were placed on an orbital shaker and agitated at 125 rpm in room temperature for 60 minutes as shown in Fig. 2. Subsequently, the suspension was filtered through 0.45 µm glass micro fiber filter paper.



(a) (b)

Fig 2. (a)The groundwater sample was placed on orbital shaker and (b) optimization process in the laboratory

Then, the groundwater parameters namely pH, chloride and sulphate were identified through laboratory testing held based on analysis using Ionize-Chromatography (IC) and pH meter. Lastly, the removal percentage of chloride and sulphate were calculated by using Eq. 1 in order to determine the effectiveness of each cucurbita components;

$$\text{Removal (\%)} = \frac{Initial\ \ cont.-Final\ \ cont.}{Initial\ \ cont.} \text{x } 100\% \qquad \text{(Eq. 1)}$$

III. RESULT AND DISCUSSIONS

The groundwater that was collected from RECESS was characterized in order to analyze the contaminants present. Meanwhile, the cucurbita was characterized before the biosorption process by utilizing Scanning Electron Microscope. Lastly, the biosorbent amount was optimized through batch study.

Characterization of Groundwater from RECESS

According to Table 1, pH and sulphate showed a permissible value for drinking water standard according to the Ministry of Health Malaysia which is pH 6.5-9.0 and 250 mg/L respectively. However, the number displayed by chloride in groundwater was considered very high after comparing with the standard, 250 mg/L. In conjunction with the obtained record, groundwater treatment for chloride is a must since 600 mg/L was already categorized as salty for consumers [8]. Therefore, high dilution is needed approximately 100 to 1000 times in order to be able reading the chloride content in groundwater.

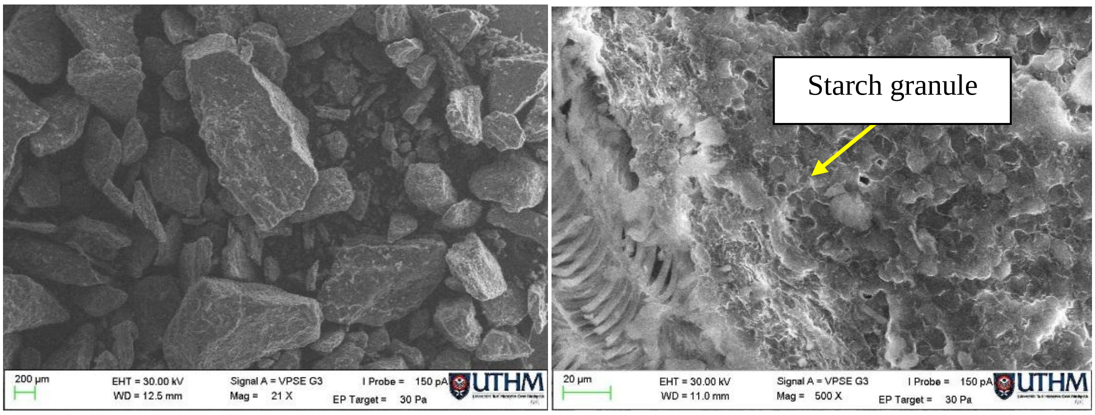
Table 1. Concentration of parameters involved

Sample	pH	Chloride (ppm)	Sulphate (ppm)
1	7.82	2397.52	92.82
2	8.02	2398.34	99.25
3	7.42	2465.33	95.50
Average	7.75	2420.40	95.86

Characterization of Cucurbita by using Scanning Electron Microscope

Scanning Electron Microscope (SEM) was used before the biosorption process in order to determine the surface morphology of the cucurbita components namely peel, flesh and seed. Fig. 3 to Fig. 5, cucurbita components displays different surface morphology such as porous and crystalline. The porous surface texture is believed to assist in entrapping and adsorbing the contaminants exists in groundwater [9]. Apart from apparent structure, it is also crucial to identify the chemical elements which aid in adsorption performance. In general, the process of biosorption can be described as an ion exchange with groups present on the surface of the cell wall that may include carboxyl, sulfonate, phosphoryl, amido, amino, and imidazole [10].

From Fig. 3 (a), a well-graded particle of peel component which consists of various sizes can be seen and this contributes in providing more opportunities for entrapping contaminants. There are also some cracks present in Fig. 3 (b), results in a system of a porous network [11]. These pores will contribute to the performance of biosorption by providing binding sites for the contaminants to fill in. Apart from that, there is a cluster of bounded starch granules with large amount that can be observed and this existence can be further linked to its ability of being a biosorbent [6].



(a) (b)

Fig 3. Result of SEM for peel (a) 21x magnification (b) 500x magnification

From the surface morphology of flesh observed in Fig. 4 (a), the particles can be classified under uniformly-graded as the sizes are not much different to another. Meanwhile from Fig. 4 (b), some pores and a small amount, segregated starch granules appeared.

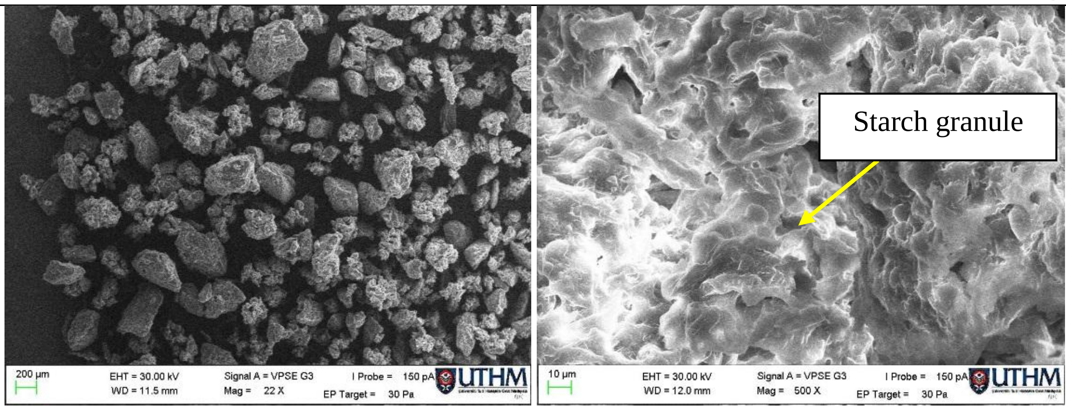


Fig 4. Result of SEM for flesh (a) 22x magnification (b) 500x magnification

As shown in Fig. 5 (a), the powder was made up of gap-graded fine particles which do not have regular, fixed shape and size. Aside that, based on Fig. 5 (b), there is a small amount of starch granules exist on the crystalline surface.

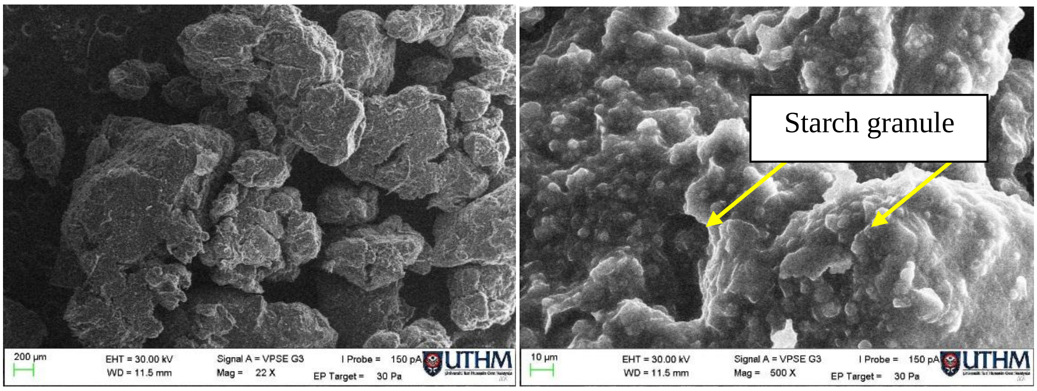


Fig 5. Result of SEM for seed (a) 22x magnification (b) 500x magnification

Effect of Biosorbent Amount in Biosorption

As stated in the previous studies [12], there are several factors affecting the biosorption process and biosorbent amount is among the determinants. The effect of biosorbent amount in biosorption was verified in terms of removal percentage and uptake capacity. Fig 6 and 7 show the graphs of chloride and sulphate removal against biosorbent amount for each cucurbita components namely peel, flesh and seed.

(a) Chloride

Fig 6 shows three lines representing the percentage of removal for chloride according to the biosorbent components. For peel, the removal percentage showed a significant performance from 5.30% at 0.05g to 16.83% at 0.1g but the value flopped to 4.7% at 0.15g and displayed nil at 0.20g. Meanwhile for flesh, the removal percentage recorded a positive response from 0.62% at 0.05g to 4.82% at 0.1g. The peak of performance is located between 0.1g to 0.15g from 4.82% to 9.87% but it fluctuates at 0.2g with reading 9.21%. Aside peel and flesh, seed also appears good in interval of 0.05g and 0.1g from 3.05% to 7.83%. However, at 0.15g, the value dropped to 3.77% and at 0.2g, no removal percentage was spotted. The low removal at 0.5g can be dissected over the possibility of low adsorption site availability on the biosorbent.

On the other hand, the graph is back to descending motion from 0.15 for all components. This can be further elaborated on the possibility of biosorbent abundance that overlap on adsorption sites thus causing a reduced total surface area. The highest removal percentage of chloride in the groundwater was 16.83% and 7.83% which occur at 0.1g for both peel and seed whilst for flesh, the optimum biosorbent amount is 0.15g by 9.87%. As off this data elaboration, peel was proven to be the most effective in removing chloride in groundwater since it shows the highest removal efficiency compared to other components due to the presence of starch granule cluster.

(b) Sulphate

Fig. 7 shows the performance of biosorbent components assessed in respect to the percentage of sulfate removal. For peel, the removal percentage showed a remarkable performance from nil at 0.05g to 12.76% at 0.1g but the value dropped to 3.03% at 0.15g and displayed nil once again at 0.20g. Meanwhile for flesh, the removal percentage recorded a positive response from no removal record at 0.05g to 0.69% at 0.1g. The peak of performance is located between 0.1g to 0.15g from 0.69% to 4.41% and it continued to rise with reading 7.18% at 0.2g. Aside peel and flesh, seed also appears good in interval of 0.05g and 0.1g from 0% to 7.56%. However, at 0.15g, the value fell to 3.47% and at 0.2g, no removal percentage was spotted. The low removal at 0.5g can be dissected over the possibility of low adsorption site availability on the biosorbent.

Thus, the result is back to descending motion from 0.15g for peel and seed. This can be further elaborated on the possibility of biosorbent abundance that overlap on adsorption sites thus causing a reduced total surface area. Even so, for flesh, the acquired data from 0.15g exhibits increment. The highest removal percentage of sulphate in the groundwater was 12.76% and 7.56% respectively which occur at 0.1g for both peel and seed whilst for flesh, the optimum biosorbent amount is 0.2g by 7.18%. As off this data elaboration, peel was proven to be the most effective in removing sulphate in groundwater because it performed better than flesh and seed due to the presence of starch granule cluster.

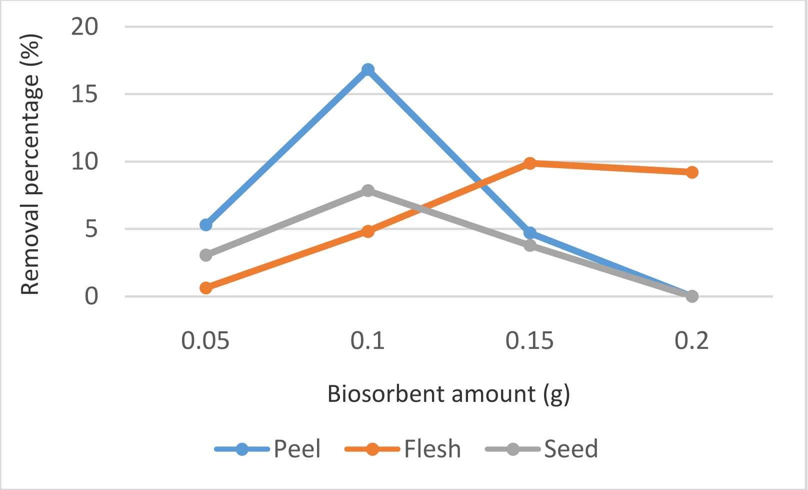


Fig 6. Removal percentage of chloride against biosorbent amount

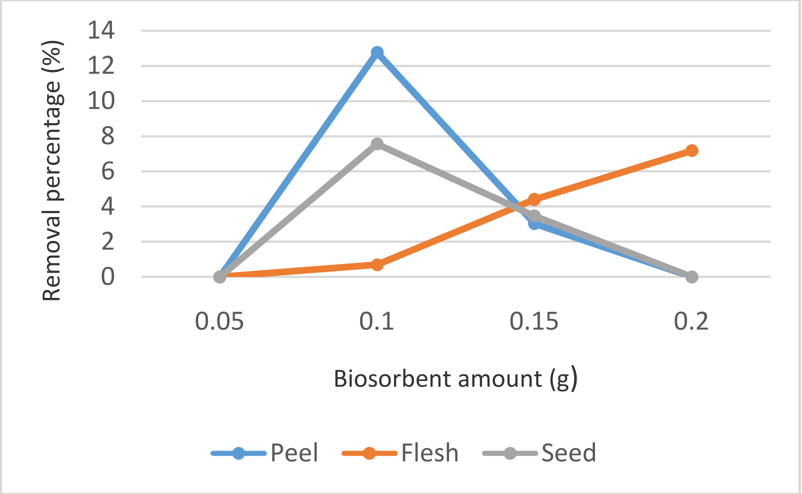


Fig 7. Removal percentage of sulphate against biosorbent amount

Effect of Biosorbent Amount in Biosorption

After treating groundwater with pulverized cucurbita, pH meter was used in order to verify the impact of biosorbent amount towards pH value according to the samples taken. For the first sample, the pH value of raw groundwater before treatment is 7.82, second sample is 8.02 and the third sample is 7.42. After treatment with pulverized cucurbita, the values are as shown in Fig. 8, Fig. 9 and Fig. 10 respectively.

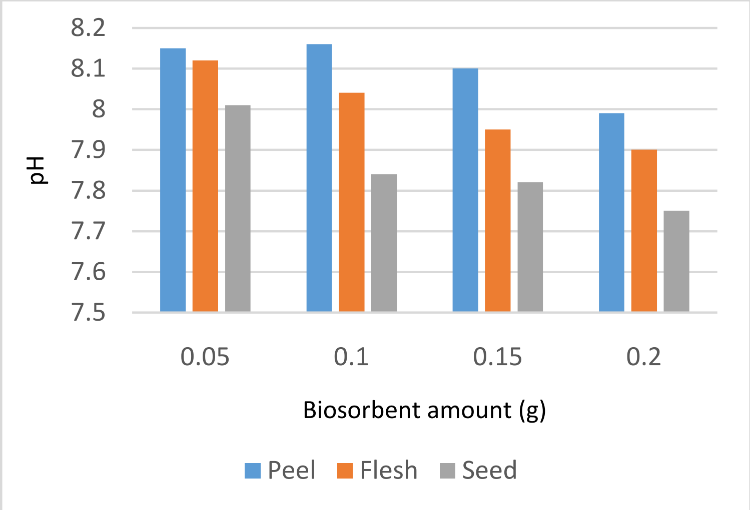


Fig 8. Value of pH and biosorbent amount for Sample 1

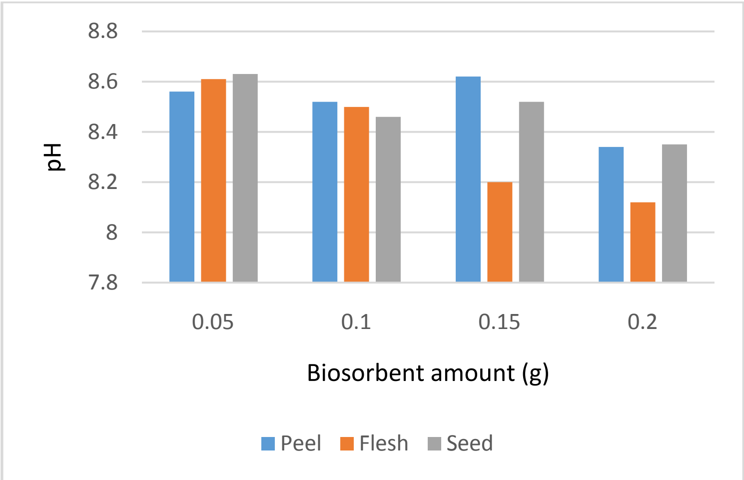


Fig 9. Value of pH and biosorbent amount for Sample 2

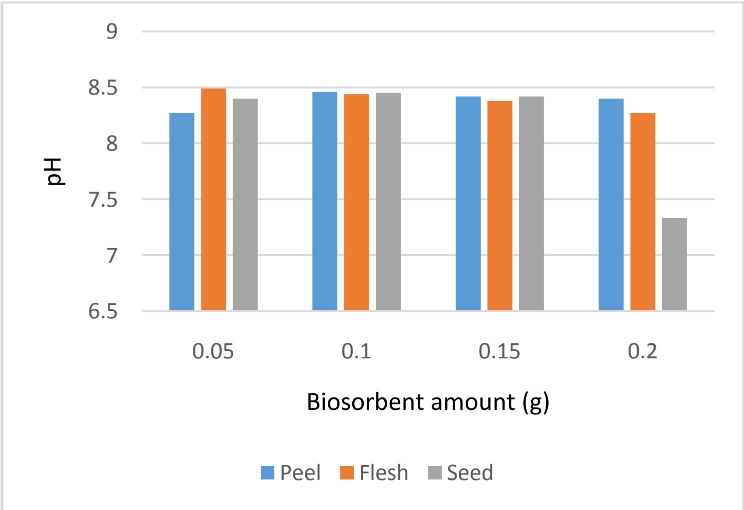


Fig 10. Value of pH and biosorbent amount for Sample 3

Based on Fig. 8 to 10, the initial pH of groundwater before treatment for all samples were already good with record of 7.82, 8.02 and 7.42 respectively. However, from the trend of data shows that the pH value increases compared to the initial reading of groundwater but it slowly fluctuates as the biosorbent amount added. This occurrence can be further explained by the existing carboxylic acid in pumpkin which contributes in increasing acidity result after the biosorbent amount was added.

IV. CONCLUSION

The conclusion in this study was pointed out based on the analysis of groundwater treatment by utilizing cucurbita as a potential biosorbent. Principal aspect included SEM which yields the peel as the best component for adsorption process due to the porous network and presence of starch granule cluster from its surface morphology.

The parameter that was optimized in this study is biosorbent amount in cucurbita. The optimum biosorbent amount for chloride removal using peel and seed was 0.1g while for flesh was 0.15g. Meanwhile, for sulphate removal, the optimum biosorbent amount for peel and seed remained the same with 0.1 g but flesh changed to 0.2g. The best removal percentage was owned by peel with its highest record of 16.83% and 12.76% for chloride and sulphate respectively. In overall, 0.1 g was chosen as the best optimum biosorbent amount.

As a conclusion, the cucurbita components namely peel, flesh and seed was proven as a potential unmodified biosorbent in groundwater treatment especially for chloride and sulphate. In spite of that, raw or unmodified biosorbent is still left behind due to the presence of contaminants in itself and some capabilities that are not brought to its full capacity such as more porous surfaces by using activated carbon modification.

V. Acknowledgements

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