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The potential of tropical fruit peels as ion exchangers for water hardness removal

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Abstract. The presence of high amount of mineral compounds such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) in water attributed to occurrence of water hardness. Hard water causes lime scale in the kettle when boiling, and forms reddish brown stains on the clothes after washing. This study was carried out to investigate peels of durian, jackfruit and passion fruit as a potential cation exchanger for water hardness removal determining by EDTA titration. A synthetic hard water of 714.05 mg CaCO_3/L was prepared to evaluate the removal efficiency of cation exchangers prepared from raw and sodium hydroxide-citric acid (NaOH-CA) modified fruit peels for 30 min, 60 min, and 90 min contact times. Results showed that raw peel of durian had the highest ($p \leq 0.05$) efficiency (24%) for water hardness removal followed by jackfruit (21.87%) and passion fruit (6.5%). This was because the total cellulose content in durian peel powder and fibre was higher as compared to jackfruit peel and passion fruit peel. Hydroxyl group in the cellulose was the main group responsible in ion exchange with Ca^{2+} and Mg^{2+} for water hardness removal. For NaOH-CA modified peels, jackfruit demonstrated the highest ($p \leq 0.05$) water hardness removal efficiency (62.05%) as compared to passion fruit (29.63%) and durian (10.42%) for 90 min contact time. This phenomenon can be explained by citric acid anhydride produced from esterification. Citric acid anhydride produced was combined with hydroxyl groups of cellulose and hemicellulose and formed the ester linkage and increased the number of carboxylate groups on the ion exchange surface. Result showed that water retention capacity is directly proportional to water hardness removal efficiency for modified fruit peels ($R^2 = 0.8181$). This evidence that water retention capacity of lignocellulosic material is a good indicator of cross-linking which has a direct effect on ion exchange capability. Both raw durian peel and NaOH-CA modified jackfruit peel showed great ability in water hardness removal, hence the cost of chemicals involved in modification has to be considered for a good recommendation as great potential lignocellulosic material to be used for water hardness removal.

Keywords: Tropical fruit peel, Water hardness, EDTA titration, Water retention capacity



1. Introduction

The occurrence of hard water is the dissolution of mineral compounds such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) from limestone when the rainwater passes through underground before it reaches reservoirs. Hard water causes lime scale in the kettle when boiling and forms reddish brown stains on the clothes after washing. Long term exposure of bathtub and sink to hard water might lead to formation of scum as well.

Water softening is a method involves removal of Ca^{2+} and Mg^{2+} which aims to reduce the effects of hard water. Many studies have been attempted the use of citric acid modified lignocellulosic materials derived from agro wastes for removal of heavy metal ions from aqueous solution. These lignocellulosic materials were sugar beet pulp [1], lemon [2], Moringa oleifera leaves [3], lawny grass [4], barleystraw [5], soybeanstraw [6], and bagasse [7]. Recently, pine cone has been used specifically as ion exchanger for calcium and magnesium ions removal [8]. Karnitz et al. [9] also discovered the removal of Ca^{2+} and Mg^{2+} using mercerized cellulose and sugarcane bagasse embedded with EDTA dianhydride. In addition, sugarcane bagasse modified using tartaric and citric acids in microwave assisted solvent-free synthesis has been tried to eliminate calcium ions from aqueous solutions [10].

Therefore, this study was carried out to investigate tropical fruit peels, which are dispose of as wastes, as potential lignocellulosic material for ion exchanger for hard water removal. Tropical fruits with high percent of peels of durian, jackfruit (55-65%) and passion fruit (45-52%) [11] were selected in this study. Fruit peels were undergone treatments of sodium hydroxide (NaOH) saponification and citric acid (CA) esterification. Raw and NaOH-CA treated fruit peels were subjected to synthetic hard water at contact times of 30, 60, and 90 min to evaluate and compare for their water hardness removal efficiency.

2. Materials and methods

2.1 Fruit peels collection and preparation

Three types of tropical fruit peels, i.e., jackfruit, passion fruit and durian, were used to investigate water hardness removal efficiency. These fruit peels were selected because of their high percentage of skin portion in whole fruit [11]. Jackfruit and passion fruit were obtained from a fruit stall located at Port Dickson (Negeri Sembilan, Malaysia). Durian peels were collected from a durian stall located at Cheras (Malaysia). Fruit peels were removed from pulps using a knife and cut into pieces using a scissor. After washing with distilled water, the peels were placed under the fan for 2 hours to remove the excess water. The peels was weighed before subjecting to oven (AX 30 Serial, Carbolite, United States) for drying at 80 °C until constant weight was obtained. Once the constant weight of each fruit peel achieved, the peels were blended into smaller size form using a blender (MX-900M, Panasonic, Malaysia). The blended fruit peel was put into a plastic bag before keeping in a freezer (NR-A8013FTG, Panasonic, Malaysia) until the experiment.

2.2 Modification of Fruit Peels

Modification of fruit peels was carried out into two stages according to Altundoğan et al [8]. Firstly, fruit peel was saponification with sodium hydroxide (NaOH) solution and subsequently, esterification with citric acid (CA). Fifty grams of fruit peel was weighed then mixed with 1L of 0.1M NaOH solution in a 2-L conical flask. The mixture was stirred at 200 rpm for one hour. Base-washed fruit peel was poured onto perforated ladle and further rinsed with distilled water repeatedly. Then, the fruit peel was soaked in distilled water with the ratio of 20 ml of water to 1g of modified products and stirred at 200 rpm for two hours. The sample was rinsed again with distilled water to ensure all NaOH was being removed. Then, sample was dried in an oven at 80 °C till constant weight obtained. After the base-washed (saponified) fruit peel sample was dried, it was mixed with a 0.6M CA in a ratio of 1.0 g fruit peel: 7.0 mL CA for 2 hours. The NaOH-CA treated fruit peel was dried for 24 hours at 80 °C in an oven. The dried NaOH-CA treated fruit peel was further heated at 120 °C for 90 min on a magnetic hot plate. Distilled water was added to modified products in a ratio of 20 ml of water to 1 g of modified fruit peel. In order to remove unreacted acid, sample was stirred at 200 rpm for 2 hours. Modified fruit peel sample was dried under the fan for 2 hours and then heated in an oven at 80 °C until constant weight achieved.

The efficiency of water hardness removal was carried out by subjecting 1 g of raw or NaOH-CA treated fruit peels into 40 mL of synthetic hard water in a 100-mL beaker. Mixture in the beaker was placed and stirred on a magnetic stirrer. After contact time of 30 min, mixture was filtered to obtain the treated water for water hardness analysis. Experiment was conducted in duplicate for each contact times of 30, 60 and 90 min.

2.3 Water retention capacity analysis

Sodium nitrate powder (NaNO_3) of 4.25g was mixed with 300 mL distilled water in a beaker to prepare 0.1 M NaNO_3 solution. A glass rod was used to stir the mixture in order to homogenize it. The mixture was transferred into 500 mL of volumetric flask and distilled water was added till the mark. Volumetric flask was inverted by 180° repeatedly to homogenize the solution. The weights of four empty centrifuge tubes were measured. Fruit peel sample of 0.5g was transferred into the centrifuge tube and the weight was measured. NaNO_3 solution was added to centrifuge tube till 10 mL. Then, the mixture was kept in freezer (NR-A8013FTG, Panasonic, Malaysia) for 16 hours at 4°C . After 16 hours thawing, the mixture was centrifuged for 2 hours at 3600 rpm by a centrifuge (Sigma 2-6E, Sigma Laborzentrifugen, United Kingdom). Supernatant was removed carefully and weight of centrifuge tube containing fruit peels was measured. The experiment was carried out in duplicate for each fruit peel sample.

2.4 Synthetic hard water preparation and different water sources collection

In order to prepare synthetic hard water, 2.51g of calcium carbonate (CaCO_3) powder was measured and dissolved into 2000 ml distilled water. The mixture was placed on a magnetic stirrer and 37% hydrochloric acid (HCL) solution was added drop by drop to ensure CaCO_3 powder dissolved completely. Magnesium chloride (MgCl_2) solution was prepared by dissolving 3.33g of magnesium chloride powder into 2000 ml distilled water. Then, both CaCO_3 solution and MgCl_2 solution were mixed and homogenized. The hardness of this synthetic hard water was determined using EDTA titration method and the total hardness of 714.05 mgCaCO_3/L was recorded. The synthetic hard water prepared was used to evaluate the efficiency of raw and modified fruit peels on water hardness removal.

Waters from four different sources were collected to evaluate their hardness. Distilled water and tap water were collected in UCSI University's laboratory. Spritzer mineral water was bought from a nearby local market. Well water was harvested from an agriculture farm located in Negeri Sembilan (Malaysia) and stream water was obtained from a forest reserve area. All the waters from different sources were transferred and stored in the laboratory till determination of hardness using EDTA titration method. Distilled water was used as a control to compare with other water samples because it did not contain any hardness ions such as calcium and magnesium ions. This was proved when EBT indicator was added into distilled water, the solution turned blue instead of wine red. After titrating with 0.01M EDTA solution, the solution was still remained blue colour. This was because there were no calcium and magnesium ions in distilled water to react with EBT indicator to form an unstable complex which was wine red in colour. If there were any hardness ions such as Ca^{2+} and Mg^{2+} ions react with EBT indicator, wine red colour mixture will be formed.

2.5 Water hardness determination using EDTA titration

For determining the total hardness of water sample, 20 mL of water sample was accurately measured using a calibrated pipette and transferred into a 250-mL conical flask. Two millilitres of ammonia buffer solution was added to water sample to obtain the pH between 9 and 10. A pinch of Erichrome Black T (EBT) indicator was added to the mixture until it turned to wine red colour. The burette was filled with 0.01 M EDTA titrant and adjusted the level to zero mark after fixing at the burette stand. The water sample was titrated with EDTA titrant until water sample colour turned from red to blue and the amount of titrant used was recorded. The titration was performed in triplicate for each sample water.

2.6 Statistical Analysis

Data obtained were analysed using Microsoft® Excel's Data Analysis software. Single factor ANOVA was selected to generate confidence intervals for the differences between the means at $p \leq 0.05$. Values were expressed as mean \pm standard deviation ($n=6$).

3. Results and discussion

3.1 Water Hardness of Different Water Sources

Results showed that mineral water contained the highest ($p < 0.05$) amount of total water hardness, followed by tap water, well water and stream water (Fig. 1). The total hardness content for mineral water, tap water, well water and stream water were 90.09 mgCaCO₃/L, 29.36 mgCaCO₃/L, 6.01 mgCaCO₃/L and 4.67 mgCaCO₃/L respectively. Total water hardness of tap water found in this study was higher as compared to previous finding done by Park et al [12]. They reported 24.8 mgCaCO₃/L of tap water in Gwanju Institute of Science and Technology, South Korea. Hardness of water is varied at different geographical locations, even though in the same country. Ver ísimo et al [13] reported that the hardness of tap waters were varied greatly at different locations in Portugal. Tap water found in countryside Gouveia and North of Vila Praia de Âncora were considered soft at 9.4 mgCaCO₃/L and 15 mgCaCO₃/L [13]. Although Leiria and Tomer are located at the center of Portugal, the hardness of tap water was differed significantly which was 59 mgCaCO₃/L and 225 mgCaCO₃/L, respectively.

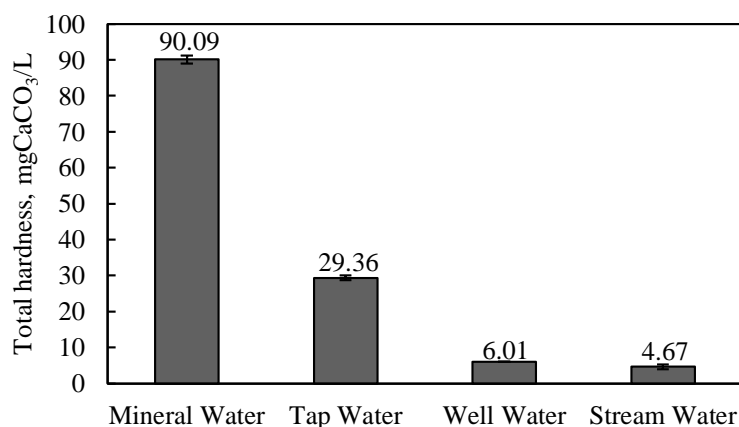


Fig. 1 Hardness of waters from different sources

3.2 Effect of raw and NaOH-CA modified fruit peels on total water hardness removal

Results indicated that durian and jackfruit peels have significantly higher ($p < 0.05$) efficiency in removal of water hardness as compared to passion fruit peel, irrespective of contact time (Fig. 2). Among the raw fruit peels (Fig. 2a), durian peel showed the highest removal efficiency (17%) as compared to jackfruit (15.33%) and passion fruit (0.84%), at 30 min contact time. Although the water hardness removal efficiency increases as contact time increases, the increment was not significant, irrespective of fruit peels. The different efficiency of fruit peels on water hardness removal can be explained from the vary components that made up the fruit peels. Fruit peel is structured with three layers of plant cell walls, which are middle lamella, primary cell wall, secondary cell wall and tertiary cell wall. Primary cell wall consists mainly cellulose, hemicellulose, pectin and proteins. Secondary cell wall has the same components with primary cell wall but it is thick and inelastic due to the presence of lignin and more cellulose [14]. Cellulose is responsible for ion exchange mechanism between cellulose and both calcium and magnesium ions. Hydroxyl group in the cellulose was the main group which involved in the ion exchange with Ca²⁺ and Mg²⁺ for water hardness removal. Total cellulose content in durian peel powder and fibre was higher as compared to jackfruit peel and passion fruit peel, therefore, led to higher water hardness removal.

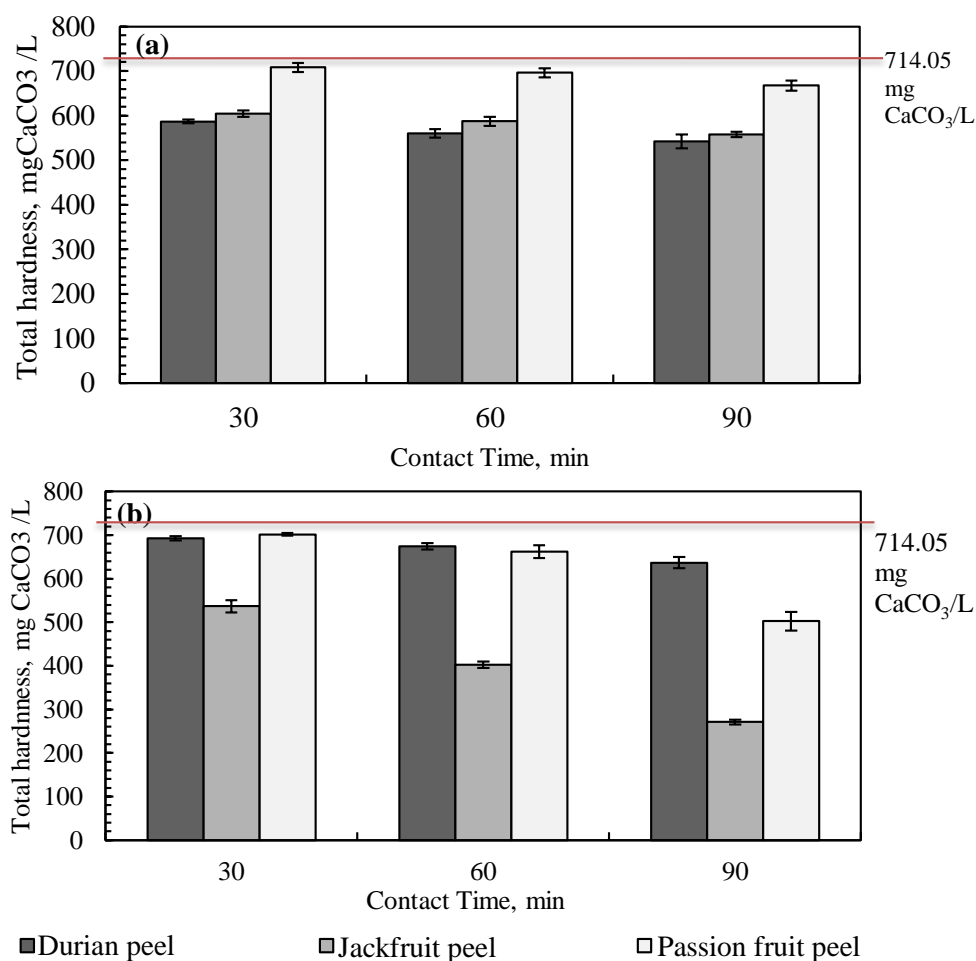


Fig. 2 Total water hardness using (a) raw, and (b) modified fruit peels at contact times of 30, 60, and 90 min

Results showed that raw jackfruit peel had the higher hardness removal efficiency compared to passion fruit peel (Fig. 2a). There was no research have done on the determination of jackfruit peels in terms of cellulose, hemicellulose, lignin and pectin. There was only a research showed that the outer peel of jackfruit which is in calcium and pectin, constitutes about 59% of the ripe fruit [15]. Lignin content for jackfruit might be higher than passion since it is harder due to content more woody tissue. Lignin is a natural amorphous cross-linked resin that has an aromatic three-dimensional polymer structure containing a number of functional groups such as phenolic, hydroxyl, carboxyl, benzyl alcohol, methoxyl, and aldehyde groups, making it potentially useful as an adsorbent material for removal of heavy metals from water [16]. Hydroxyl and carboxyl group in lignin can be used for ion exchange with calcium and magnesium ions for water hardness removal. This can be explained why jackfruit peels had higher water hardness removal ability than passion fruit peels.

Modified jackfruit peel and modified passion fruit peels in this study have better ability of water hardness removal can be explained by the esterification with citric acid. When the base fruit peels were further heating with 0.6 M citric acid (CA), citric acid anhydride produced was combined with hydroxyl groups of cellulose and hemicellulose and formed the ester linkage and increased the number of carboxylate groups on the ion exchange surface. The increase of carboxylate groups allowed more capacity of fruit peels to bind with the positively charged metal ions, thus more Ca²⁺ and Mg²⁺ can be removed and leads to more water hardness removal modified fruit peels. However, the ability of raw fruit peels to remove water hardness was lower than modified fruit peels can be explained by existing

of lignin. Without disruption of structure of lignin by modification, lignin is a constituent of cell wall and it provides support, rigidity and stiffness to the fruit peels. It is hydrophobic to water thus it inhibits the adsorption of water by the fruit peels.

Modified fruit peels supposed would have better ability of hardness removal compared to raw fruit peels. However, raw durian peels showed a better ability on hardness removal by giving the lower total hardness of treated water compared with the results of water treated by modified durian peels (Fig. 2a). This was most probably during the NaOH-CA modification process, a lot of durian peel residues were washed away when rinsing with distilled water which led to lesser amount of cellulose and resulted less efficiency of hardness removal.

3.3 Effect of water retention capacities of fruit peels on water hardness removal

The effect of water retention capacities of raw and modified fruit peels on water hardness removal efficiency is illustrated in Fig. 3. Among the fruit peels, jackfruit has been discovered having the lowest ($p \leq 0.05$), while durian showed the highest ($p \leq 0.05$) water retention capacity, for both raw and modified. Water retention capacities for modified peels of durian and jackfruit were higher compared to the raw. However, modified passion fruit peel has lower water retention capacity in comparison to the raw. There was no obvious trend between water retention capacity and water hardness removal for the raw fruit peels (Fig. 3a). However, modified fruit peels demonstrated an obvious relationship ($R^2 = 0.8181$) between water retention capacity and water hardness removal efficiency (Fig. 3b). Results indicated that the lower the water retention capacity, the higher the water hardness removal efficiency. Modified jackfruit peel, which has the lowest water retention capacity of 3.1 g/g, gave the highest water hardness removal of 62.06%, followed by passion fruit peel (4.31 g/g) of 29.63% and durian peel (8.07 g/g) of 10.84%. Water retention capacity of lignocellulosic material is a good indicator of cross-linking which has direct effect on ion exchange capability [17]. Results of this study were in agreement with a previous study done by Gupta et al. [17]. They reported that the lower water retention capacity might lead to higher cross-linking effect for ion exchange. Modified fruit peels have higher cross-linking of ester bond. They observed that lower water retention capacity facilitated a better ion exchange between lignocellulosic material and hardness ions which resulted higher water hardness removal efficiency. Durian peel fibre contains higher lignin percentage compare to durian peel powder. Carboxylate and hydroxyl groups in the durian peel powder are responsible for the forming of ester linkage [17]. After the modification of durian peel, most of the durian peel powder was lost. This might lead to the decrease of water hardness removal efficiency of modified durian fruit peel in comparison to the raw.

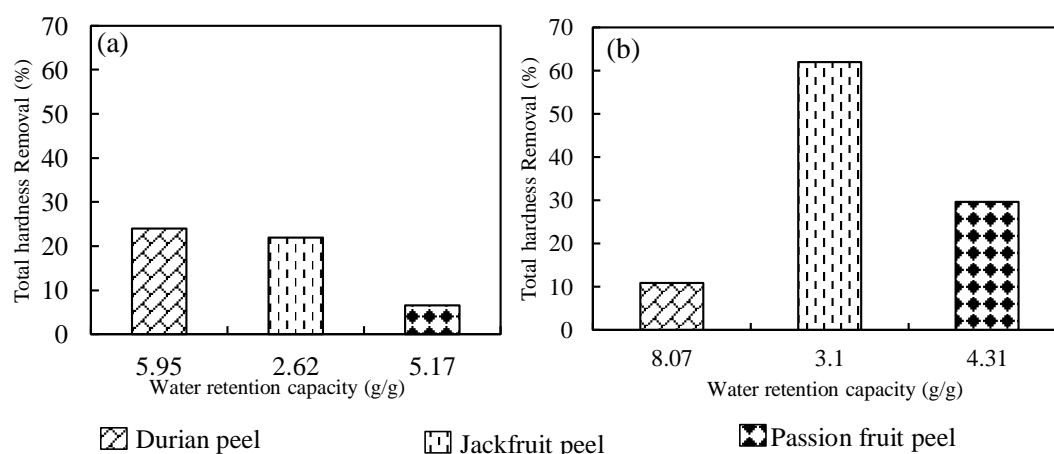


Fig. 3 Effect of water retention capacity on total hardness removal for (a) raw, and (b) modified fruit peels

Result showed that raw passion fruit peel has higher ($p \leq 0.05$) water retention capacity as compared to the modified. This result is in agreement with previous study done by Altundoğan et al. [8]. They

reported that raw pine cone had a higher water retention capacity compared with the NaOH-CA modified pine cone. Water retention capacity of the fruit peels has been proven affected by fruit peel components such as cellulose, hemicellulose, lignin and pectin.

4. Conclusion

Among the raw fruit peels, this study revealed that durian peel had the highest water hardness removal efficiency as compared to peels of jackfruit and passion fruit. As such, raw durian peel showed great potential which could be used as lignocellulosic material for water hardness removal. However, NaOH-CA modified jackfruit peel demonstrated 38% higher in water hardness removal efficiency in comparison to the raw durian peel. This phenomenon can be explained from citric acid anhydride produced by the esterification of fruit peels with citric acid. When the base fruit peels were further heating with 0.6 M citric acid (CA), citric acid anhydride produced was combined with hydroxyl groups of cellulose and hemicellulose and formed the ester linkage and increased the number of carboxylate groups on the ion exchange surface. The increase of carboxylate groups allowed more capacity of fruit peels to bind with the positively charged metal ions, thus more Ca^{2+} and Mg^{2+} can be removed and leads to more water hardness removal modified fruit peels. Since both raw durian peel and NaOH-CA modified jackfruit peel gave great ability in water hardness removal, economic factor, which the cost of chemicals involved in modification, has to be taken into account for a good recommendation. Although no obvious trend was observed between water retention capacity and water hardness removal efficiency for the raw fruit peels, there was an obvious relationship for modified fruit peels. Water retention capacity of lignocellulosic material is a good indicator of cross-linking which has direct effect on ion exchange capability.

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