The 2nd International Conference on Chemistry and Material Science (IC2MS) IOP Publishing
IOP Conf. Series: Materials Science and Engineering 833 (2020) 012042 doi:10.1088/1757-899X/833/1/012042

Particle Size Effect on the Water Vapour – Activated Tamarind Seeds (Tamarindus indica L.) Toward the Adsorbent Physical Properties

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Abstract. The increasing problem of dyestuff liquid waste in the textile industry occurs due to the low adsorption of textiles toward dyes. Therefore, various efforts have been made to enhance the fabric's absorption. One method that has been done is by adding biomass-derived dye-binding additives which act as an adsorbent. One of potential biomasses is tamarind seeds. The purpose of this study is to determine the effect of particle size of tamarind seeds, which is physically activated, on the adsorbent character. The variation of adsorbent particle size applied were -80 + 100 mesh (177-149 μm), -100 + 120 mesh (149-125 μm), -120 + 150 mesh (125-99.3 μm) and less than 150 mesh (<99.3 μm). Tamarind seed was activated using water vapour at high pressure prior to the application. The adsorbent characters were studied based on particle size distribution, powder porosity, average relative molecular mass, and hydrophilicity. In addition, tamarind seed chemical structure was analysed using Fourier Transform Infra-Red (FTIR) spectrophotometry, while adsorbent potency was studied in the form of an adsorbent thin film. The results showed that based on the analysis of particle size distribution, adsorbents with the best activation results was obtained by particle size of 125-149 μm. The highest porosity was achieved by particle that smaller than 99.3 μm and the highest average relative molecular mass, based on the Mark–Houwink approach, was obtained by particle size of 125-149 μm. The highest hydrophilicity, which was determined based on the contact angle, was obtained by particle sizes of 99.3-125 μm.

1. Introduction
Waste dyes in the textile industry are one of the main sources of wastewater pollution. 5-10% of the dyestuffs used in the textile dyeing process are unutilized as waste. This is due to the low adsorption of dye substances in the textile substrate. One of efforts made to increase the fabric's absorption on dyes is to use an adsorbent as a dye-binding additive that can be obtained from biomass [1,2].

Tamarind seeds are one of the biomasses which is lately have been widely developed as an adsorbent. Some application of tamarind seeds are as adsorbsents, among others, in metal adsorption, reduce turbidity on the surface of the water and adsorb methylene blue from the dye waste [3–6].

The tamarind seeds consist of 20-30% seed bark, commonly called testa and 70-75% kernel or endosperm [7,8]. Kernel of tamarind seeds contains a lot of carbohydrates, in the form of polysaccharides ranging from 65-72% [9]. The structure of carbohydrates in tamarind seeds has a hydroxyl group as the main functional group and acts as a reaction point for the formation of
polymers[10]. The presence of hydroxyl groups in the carbohydrate structure of tamarind seeds gives a role in the interaction with hydroxyl groups in fabric fibers through the formation of hydrogen bonds. The adsorbent character greatly influences the efficiency of the adsorption process. The adsorbent character can be modified through activation, both physically and chemically. Physical activation using water vapor at high pressure can increase the specific surface area of tamarind seed kernel powder by 18.42% and increase its porosity. The purpose of this study is to determine the influence of the particle size of the adsorbent powder from the tamarind seed kernel on the physical properties. The adsorbent characteristics were studied based on the distribution of particle size, porosity, average molecular mass based on viscosity and hydrophilicity. As support, chemical structure analysis was carried out by FTIR spectrophotometry.

2. Experimental

2.1. Apparatus and materials
The materials used in this research are tamarind seeds (Tamarindus indica L.) obtained from PT. Bintang Jaya, Surabaya, East Java, Indonesia.

The instruments used in this research were particle size analyzer (PSA-Cilas Particle Size Analyzer 1090 D), contact angle analysis using goniometer (contact angle measurement system) and identification of functional groups using FTIR spectrophotometer (Shimadzu FTIR 8400S).

2.2. Tamarind seeds preparation and activation
The tamarind seed kernels were crushed using a grinder so that they are in the form of powder. The powders were sieved using filters of various size, i.e. 80 mesh (177 µm), 100 mesh (149 µm), 120 mesh (125 µm) and 150 mesh (99.3 µm) to obtain variations in the size of tamarind seed kernel powders. A total of 20 g of powdered kernel tamarind seeds of various sizes were then placed in containers made of filter paper and their masses were measured. Furthermore, the container which has been filled with acid seed kernel was placed above the filter, so it does not touch the water at the bottom of the autoclave. After closing the autoclave, it was then heated at a fixed temperature. When the water vapor starts to come out, the vapor outlet was closed, and the heating was continued for 30 minutes. After completion (no more steam comes out), the autoclave lid was opened. The resulting activation powder was then removed and placed in a desiccator. After 2 to 3 hours, the powder and the container were weighed. This activation method was carried out for powders of all different sizes.

2.3. Characterization of adsorbent
The activated adsorbent powders were characterized for particle size distribution, adsorbent porosity, average relative molecular mass, hydrophilicity, and functional group analysis. Particle size distribution was analysed using particle size analyser (PSA). The porosity of the adsorbent powders is estimated from the ratio of bulk density to dimensional density. The average relative molecular mass of the adsorbent is determined using the Ostwald viscometer. Hydrophilicity was determined based on the contact angle of the liquid on the surface of the solids observed using a goniometer device connected to the camera. The solid used comes from a thin film formed from an acid seed gel. Goniometer results in the form of images that were further processed using contact angle measurement software. Furthermore, the identification of functional groups was done by Fourier Transform Infra Red (FTIR) spectrophotometry method at 400-4.000 cm⁻¹.

3. Results and Discussion

3.1. Particle size distribution
The particle size of the activated tamarind seed kernel powders was analyzed using a particle size analyzer (PSA), and the results of the analysis, as a particle volume distribution curve, are presented in
Figure 1. Distribution patterns for curves a and b shows non-symmetric distributions, whereas curves c and d tend to form symmetric distributions. The results of the curve interpretation are listed in Table 1.

![Graphs](image1.png)

Figure 1. Particle size distribution graph (a = 177-149 µm; b = 149-125 µm; c = 125-99.3 µm; d = < 99.3 µm).

| Particle size (µm) | Diameter percentage |
|--------------------|---------------------|
|                    | 10 (%)  | 50 (%)  | 90 (%)  |
| 177-149            | 47.02 µm | 249.1 µm | 430.65 µm |
| 149-125            | 37.46 µm | 120.99 µm | 249.23 µm |
| 125-99.3           | 23.97 µm | 57.81 µm | 129.05 µm |
| < 99.3             | 28.57 µm | 57.35 µm | 119.2 µm |

Table 1. Percentage distribution of particle size.

An important parameter of particle size is the 50% distribution, which gives information about the mean value of the particle size. Activation causes an increase in particle size in the size of 149-177 µm tamarind seeds kernel powder. This is likely due to the phenomenon of particle agglomeration. The smaller the particle size, the symptoms of agglomeration tend to decrease. The two smallest particle sizes which are smaller than 99.3 µm and 99.3-125 µm have low resolution. Therefore, the two-particle sizes are still not well separated. The best activation results are for sizes 125-149 µm because they provide median, mean and mode values that are almost the same as the particle size before activation.
3.2. Porosity
The porosity in this experiment is approached from the value of bulk density. Density is determined by picnometry in solvents with different polarities so that the powder does not dissolve. Figure 2 shows the results of the measurement of the bulk density.

![Figure 2](image)

**Figure 2.** Density of adsorbent powder each particle size (A = 177-149 µm; B = 149-125 µm; C = 125-99.3 µm, D = <99.3 µm).

Bulk density, in this research, is determined based on the average density of powders for a certain volume in a specific medium. The medium used is toluene. Bulk density includes the density of solids also accommodates the presence of empty space in the form of pores. Therefore, bulk density can be used as a reference to estimate porosity. In Figure 2, the particle size of 125-149 µm has the highest density so it has the lowest porosity. In Figure 1(b), the particle size distribution appears to widen, so that the low porosity is not caused by particle size. Most of the natural polymers such as polysaccharide have relatively inflexible chains. Therefore, the size is no longer the dominant factor, because the polymers chain is no longer in the form of a flexible random coil. The transition in configuration, namely chain entanglement has occurred. Therefore, the polymer will be denser, empty space is reduced and the density is higher [11].

3.3. Average relative molecular mass
In Figure 3, the highest intrinsic viscosity was achieved for particles with a size of 125-149 µm.

![Figure 3](image)

**Figure 3.** Gel viscosity of each particle size of the adsorbent powder (A = 249.1-120.99 µm; B = 120.99-57.81 µm; C = 57.81-57.35 µm D = <57.35 µm).
Polysaccharides with high hydroxyl groups in the water medium absorb water and form a gel. High density causes higher friction between polymer molecules so that the flow rate was also slower. This causes the disperse system to become more viscous and provides the highest intrinsic viscosity. Although the polysaccharide molecule shape is not the only influential factor but based on the Mark–Houwink approach, the particle size has the highest average molecular mass. Tamarind polysaccharide has been known not to form a gel, except in appropriate conditions. One of the conditions is by removing galactose residues from tamarind xyloglucan. Therefore, activation using water vapor at high pressure and temperature is likely to be able to remove galactose residues from the polysaccharides of tamarind kernel seeds [12].

3.4. Hydrophilicity

The hydrophilicity of a surface shows the ability of polar fluids, such as water, to spread on the surface of a solid. This ability is expressed as the spreading coefficient. If the coefficient is small, the liquid will form droplets at a certain angle. On this basis, hydrophilicity is determined based on the analysis of the contact angle. The observation results of contact angles for various particle sizes are shown in Figure 4.

Figure 4 is a form of water droplets when dropped on the surface of a thin film of tamarind kernel powder. The droplet shape is then processed using contact angle measurement software to obtain the contact angle value in Table 2.

![Figure 4](image-url)

**Figure 4.** Liquid droplets on thin films that have been processed using contact angle measurement software (A = 249.1-120.99 µm; B = 120.99-57.81 µm; C = 57.81-57.35 µm D = <57.35 µm).

Overall, all thin films are hydrophilic because they have a contact angle that smaller than 90°. For larger particles, such as 125-149 µm and 149-177 µm, they both have the same hydrophilicity. The most
hydrophilic thin film was produced from particle sizes of 99.3-125 μm. Whereas if the particle size is smaller than 99.3 μm, thin films tend to have higher hydrophobicity.

| Particle size (μm) | Contact angle left angel | Contact angle right angel |
|-------------------|--------------------------|---------------------------|
| 249.1-120.99      | 64.2561                  | 63.41442                  |
| 120.99-57.81      | 64.2152                  | 64.1928                   |
| 57.81-57.35       | 50.9454                  | 51.90771                  |
| <57.35            | 82.4322                  | 79.42909                  |

The spreading coefficient of water on the thin film surface is a balance between cohesion force and adhesion force. The cohesion force is originated from the attraction between water molecules while the adhesion force is due to attraction of water with the thin film surface. Thin films are hydrophilic and have a high affinity for water because acid kernels are polysaccharides that have polar functional groups, namely hydroxyl. However, the rate of spread is determined by the surface tension of the water and the surface tension of the thin film and the interface tension of both. The higher the difference in surface tension of thin films compared to water, the affinity for water increases. The surface tension of the film is affected by the film structure and surface morphology. It is suspected that this factor resulting in particle size of 99.3-125 μm being more hydrophilic. Whereas when the size is smaller than 99.3 μm, the adhesion force decreases due to lower molecular mass. Thus, the forming films have lower surface tension. As a result, the affinity for water is reduced [13].

3.5. Functional groups analysis
Figure 5 is the spectrum of the adsorbents using the FTIR spectrophotometer. The patterns on the three spectrums are identical. Complete spectrum interpretation is presented in Table 3. The main difference occurs in the stretching vibrations for hydroxyl groups in the region of 3300-3400 cm⁻¹.

![Figure 5](image)

**Figure 5.** Functional groups analysis using FTIR spectrophotometer on tamarind seed powder and film.

The three spectra exhibit the character of a wide hydroxyl functional group, indicating a hydrogen-bond hydroxyl group. This is also supported by the bending vibration of hydroxyl functional group. Hydrogen bonds occur both inter and intramolecularly. The intensity of the hydroxyl group uptake for powder is lower than that of the film. The difference in intensity indicates the effect of activation which
causes an increase in the number of hydroxyl groups. It is assumed that the diffusion of water vapor into the cavity will reduce the hydrogen bonds, hence hydroxyl groups are relatively free.

| Functional groups | Wavenumber (cm⁻¹) | Kernel powder without activation | Kernel powder activated | Film |
|-------------------|-------------------|---------------------------------|-------------------------|------|
| O-H stretching    | 3405              | 3380                            | 3283                    |      |
| C=O stretching    | 1744              | 1744                            | 1744                    |      |
| C=C stretching    | 1648              | 1646                            | 1642                    |      |
| O-H bending       | 1387              | 1395                            | 1374                    |      |
| C-O-C             | 1044              | 1048                            | 1044                    |      |

4. Conclusion

Based on particle size analysis, the adsorbent powder with the best activation results is in the adsorbent powder particle size 125-149 µm. The highest porosity was obtained from adsorbent made of particle size smaller than 99.3 µm and the largest density was shown by the adsorbent made of particle size of 125-149 µm. The highest hydrophilicity was produced on thin films from adsorbents prepared from particle size of 99.3-125 µm.

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