

PREPARATION AND CHARACTERIZATION OF ALGINATE BEADS BY DROP WEIGHT

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(Received: January 2014 / Revised: June 2014 / Accepted: June 2014)

ABSTRACT

The preparation and characterization of macro alginate beads are always associated with appropriate techniques involving precise measurement of shape, size, volume and density of the products. Depending on the type of application, encapsulation of macro alginate beads can be accomplished by various techniques including chemical, ionotropic, physical and mechanical methods. This work describes a method for preparing macro alginate beads through drop weight. The macro beads (2.85–3.85 mm) were prepared via different concentrations of alginate (0.5, 1.0, 1.5 and 2.0 g/L), dripping tip size (0.04–0.14 cm) and immersion into a predetermined concentration of calcium chloride (CaCl₂) bath. A custom made dripping vessel fabricated from acrylic plastic, connected to an adjustable dripping clamp was used to simulate the dripping process of the molten alginate at different tip sizes. It was observed that at different dripping tips, the correction factor for the alginate slurry was found in the range of 0.73–0.83. Meanwhile, the lost factor, K_{LF} was observed at 0.93–2.3 and the shrinkage factors were limited to 2.00% from the overall distributed data. It was concluded that liquid properties had no effect on the liquid lost factor. The bead size prediction for different concentrations of alginate solution was compared to the experimental data. Subsequently, it was concluded that increasing the tip size caused the bead size to deviate almost 20% when compared to the experimental and predicted values, respectively.

Keywords: Alginate; Bead; Calcium; Encapsulation; Harkin-Brown

1. INTRODUCTION

Investigations on the liquid properties in terms of cohesiveness, surface structure and surface tension have long been studied since the early 1900's (Harkins & Brown, 1919). These studies have contributed significantly towards the determination of surface tension in a liquid at different density and with the capillary held at a constant. Generally, surface and interfacial tension in liquid is one of the important aspects in chemical processes and applications. Surface tension is defined as the cohesive force between the liquid molecules (Chan et al., 2009) that enables the force to act like a piece of sheet film at the outer surface of the liquid molecule. In terms of industrial application, surface tension gives an important character to the quality of edible oil, lubricant oil, ink jet deposition, food, grade gel and pesticide substances during product manufacturing.

The applications of alginate in an encapsulation technique are a great interest nowadays because of hydrocolloid properties, its easy-to-form properties, and the possession of a high resistance against physical and chemical modifications.

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Permalink/DOI: <http://dx.doi.org/10.14716/ijtech.v5i2.182>

It is worth mentioning that encapsulation is known as a process of confining active compounds within the matrix of a membrane (Chan et al., 2010). The techniques of encapsulation can vary in different ways including physical, chemical and mechanical methods, depending on the kind of liquid being used and the choice of applications. Encapsulation compounds can vary from living cells to microbial cells or enzymes, hormones, drugs, oils and flavors (Chan et al., 2009). Apart from that, encapsulation compounds have been extended to include organic and inorganic materials, such as recycled activated-alumina (Kim et al., 2013), nanoporous SBA 15 (Cheraghali et al., 2013), 3-aminopropyl-triethoxysilane (APTEOS) (Chen et al., 2013), magnetic sodium alginate gel beads ($\text{Fe}_3\text{O}_4@SA\text{-Zr}$) (Li et al., 2013a), graphene oxide (Li et al., 2013b), peat (Vecino et al., 2013), Aluminium-Cerium (Swain et al., 2013) and many more. Undeniably, as far as the authors are concerned, the application of alginate in encapsulation is one of the materials of choice due to its wide range of applications in pharmaceutical, biomedical, water treatment, foods and textile industries. Generally, alginate is derived from a brown seed algae and consists of a linear unbranched polysaccharide, a naturally occurring copolymer between α -D-mannuronic acid residues (M-block) and its epimer, R-L-guluronic acid, and its residues (G-block) (Zhao et al., 2007). It is widely known that sodium alginate is highly soluble in water. Therefore, the inclusion of di-valent ions, such as Ca^{2+} , which act as a gelling agent, is capable of forming droplets or forming a membrane of alginate beads in the gelling bath. However, the cross-linking strength of Ca^{2+} is dependent on the type of alginate and CaCl_2 being used, respectively (Dohnal & Štěpánek, 2010).

Previous works on techniques for generating alginate beads have been studied by various researchers (Daemi & Barikani, 2012; Pu & Chen, 2001; Seifert & Phillips, 1997; Klokk & Melvik, 2002). Conventional techniques to produce round type alginate macro beads can be accomplished by using the dripping technique. In this technique, the molten alginate solution is injected through a capillary at a determined volumetric rate and allowed to fall under gravity. This method has been regarded as the simplest and easiest approach in the field of macro bead preparation. However, formation of the beads with a desired size and in a spherical shape often needs trial and adjustment, not only of the liquid properties, but as well as the experimental set-up that is often tedious and time consuming. In addition to that, high quality alginate beads require an in-depth understanding of materials properties including density, surface tension, viscosity, swelling and solubility in cross-linking solutions. However, there are very limited data or reported work on the physical properties of alginate beads for the purpose of using adsorbent materials during the adsorption process. This work aims to identify the possibility of determining the macro alginate bead properties before and after detachment from the dripping vessel and to propose a model to predict the shape and size of the macro alginate bead. The sizes of the beads produced were quantified based on the principle of Tate's Law. Finally, the overall bead size prediction was validated from the experimental data and the model developed based accordingly on the Harkin-Brown correction factor.

2. METHODOLOGY

2.1. Materials

The alginate ($\text{C}_6\text{H}_7\text{O}_6\text{Na}$) powder used in this work was obtained locally and supplied by R&M Chemicals (Malaysia) with a low molecular weight that was preferred because it is widely used in many encapsulation processes (Chan et al., 2009). The characterization of the alginate was provided by the manufacturer and is listed in Table 1. Figure 1 shows the typical molecular structure of alginate.

Table 1 Alginate characterization

Specification	Content
Assay	91-106%
Moisture	Max 15%
Matter insoluble in water	Max 1%
Loss of ignition, loI at 1100 °c	Max 25%
Molecular weight	85000
Viscosity; max at 2 g/L(used spindle no. 4), mPas	65

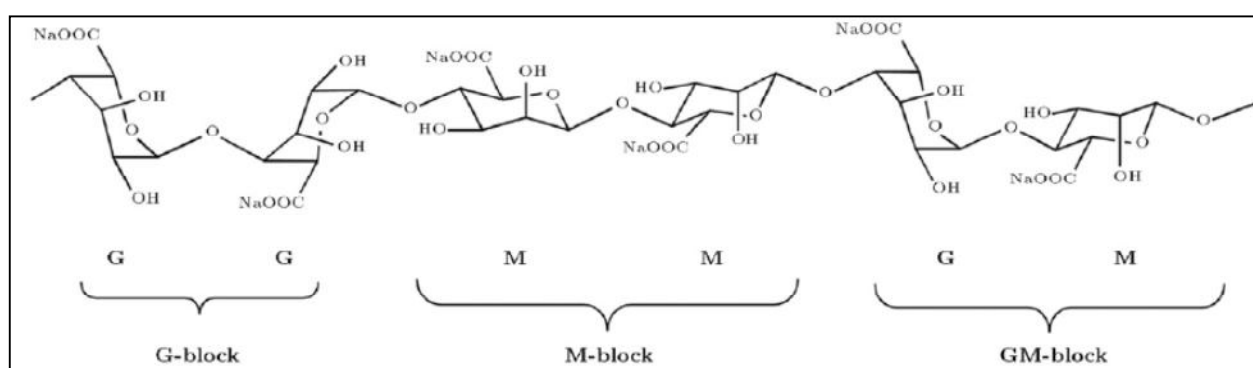


Figure 1 Typical chemical structure of alginate (Daemi et al., 2012)

2.2. Alginate solution measurement

The viscosity of the alginate solutions was measured by using a laboratory viscometer model DV II+Pro (Brookfield, USA). The spindle used during the measurement was based on the manufacturer's recommendation of SC4-27. During the measurement, the alginate solutions were mixed at 80°C in 15-minute intervals and the spindle speed was maintained at 20 rpm throughout the process. The density of the alginate solutions was determined by using a 25 ml densimeter (Blaubrand, Germany) and was compared with the density of water as the reference value. The surface tension of the alginate solutions was determined based on the drop weight method. Generally, as the size of the droplet increases following the size of the dripping tip, the weight of the droplets also increased. By applying Tate's Law, the downward force due to gravity that is pulling the droplets becomes greater than the surface tension force. However, the residual alginate solution may remain, surrounding the circumference of the dripping tip and as a result become an upward force. Therefore, the force exerted during the detachment of the alginate solution can be written as:

$$\text{Upward force} = 2\pi r\gamma \quad (1)$$

$$\text{Downward force} = mg \quad (2)$$

Equating (1) and (2) gives:

$$\gamma = \frac{mg}{2\pi r} \quad (3)$$

Where r is the radius of dripping tip, γ is the surface tension of the droplet, m is the mass of falling droplet and g is the gravitational acceleration. During the detachment of the alginate solution falling into the gelling solution, a significant amount of liquid may remain attached in the dripping tip. Hence, a correction needs to be applied to allow for the surface tension as is shown in the following equation:

$$\gamma = \frac{mg}{2\pi r(r/V^{1/3})} \quad (4)$$

where V is the drop volume.

Generally, the correction factor refers to an overall size correction factor that is used to correct Tate's Law in order to predict the size of the alginate beads by considering the liquid lost factor and the shrinkage factor.

2.3. Experimental set up

A laboratory-based experimental set up for the detachment of the alginate solution is shown in Figure 2. An acrylic vessel, complete with an adjustable clamp for each different tip size, was fabricated in order to study the variation of the shape and the size of the alginate droplets during detachment. Different concentrations of alginate solution (0.5, 1, 1.5, and 2 g/L), respectively, were prepared with known optimized preparation conditions prior to the present work. In addition, a gelling bath (CaCl_2 solution) with a known concentration was kept constant during the experimental activity in order to minimize the effects of uncontrolled factors. Different tip sizes (ranging from 0.4–1.4 mm) were purchased from Sigma Aldrich (Malaysia). A silicone tube (size 17) was connected to a peristaltic pump model by MasterFlex (Cole Parmer, USA) and a constant flow rate of 30 ml/min was applied to ensure a uniform supply in the vessel during the detachment process. For every change of the dripping tip, the alginate solution was first left flowing out from the vessel to ensure a complete homogenous solution and a void-free environment in the vessel. By following a rule of thumb, the withdrawn alginate solutions were fixed at 25% of the initial volume prepared. To minimize the effects of temperature changes, the entire experimental work was done in an ambient temperature of 25°C.

2.4. Shape and size analysis

To gather data about the alginate solution before and after the formation of droplets, freeze image analysis was employed to measure the size and shape of the alginate. Therefore, a standstill digital camera (Canon, Japan) complete with stroboscope with a capability of 1400 frames/second was used to assist in the image capture during the detachment process. Furthermore, the overall size and shape of the droplets were quantified by an image analyzer. Prior to the image analysis, multiple images were first captured and then checked for uniformity of the beads produced and compliance with the desired objectives.

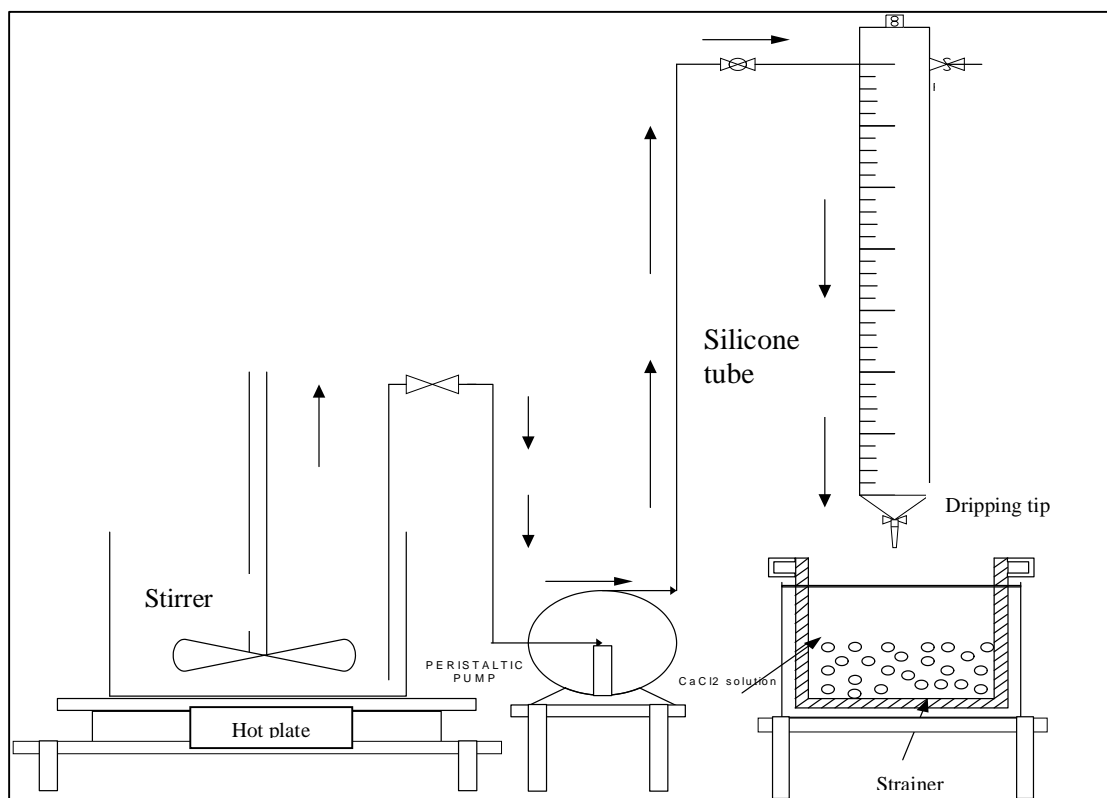


Figure 2 Experimental set up

3. RESULTS AND DISCUSSION

3.1. Properties of the alginate solutions

Prior to the drop weight analysis, the alginate solutions were tested for their density, viscosity and surface tension. To obtain these measurements, specific methods for analysis were strictly followed and compared to standard liquid properties available elsewhere. A complete range of alginate solution properties at different concentrations is shown in Table 2. Generally, it can be seen that as alginate concentration increased, the value of density increased uniformly. At a low concentration of alginate concentration (0.5g/L), the density was comparable to the density of water (1000 kg/m^3). Also, as the concentration of alginate increased from 0.5 to 2.0 g/L, the viscosity also increased. In this work it was observed that the values of viscosity were inbetween the range of 47 to 65 mPas which were ideal for encapsulation process. This is because higher viscosity ratings in alginate solutions will only impede the encapsulation of alginate in the gelling bath. This finding is in agreement with the work done by Seifert and Phillips (1997). More importantly, the viscosity of the alginate solutions in this work indicates that for every additional unit of 0.5g in 1 L of water, an increasing level of dynamic resistance was exerted in the various solutions. Hence, the higher friction rate of alginate molecules in water with different velocities led to an increase in shear resistance and simultaneously increased the viscosity in the solutions. To confirm this finding, the shear stress of the alginate solutions at different concentrations was measured by using a rheostress meter (Haake, Germany). Steady increases in the viscosity changed the rheology nature of the alginate solution and this finding was clearly observed at a shear rate of 45/s (data not shown). It shows that an increasing viscosity of alginate solutions was reducing shear stress and was in agreement with the work by Oliveira et al. (2010).

Surface tension determines the tendency of a liquid surface to resist external force. In this case, the surface tension of the alginate solution was decreased from 69 to 44 mN/m as the

concentration increased from 0.5 to 2 g/L. These findings are in agreement with other reported work elsewhere (Al-Hajry et al., 1999; Babak et al., 2000). The main reason behind these findings can be attributed to the alginates' properties. Low concentrations of alginates were correlated with the tight binding of bivalent metal cations. Therefore, cooperative binding of different molecules of the alginate polymer and water increased surface activity. Meanwhile, increasing concentration of alginate molecules in water dispersed their G-block chains and rendered their surface activity. However, it is worth mentioning that these assumptions are only applicable in this experimental work, whereas some variations may exist depending on the source of the alginates, the presence of impurities and the method used to measure surface tension of the solutions which has been discussed by Chan et al. (2009). In fact, it has also been summarized by Lencina et al. (2013) which indicated that the hydrocolloidal properties of alginates were largely dependent on the ability to hydrate them in forming viscous solutions through dispersions or the gelling process.

Table 2 Properties of alginate solutions under different concentrations

Concentration (g/L)	Density, ρ (kg/m ³)	Viscosity, ν (mPas)	Surface tension, γ (mN/m)
0.5	998	47	69.14
1.0	1006	59	59.65
1.5	1008	61	53.31
2.0	10091	65	43.45

3.2. Drop weight analysis

The shape and size analysis was assessed based on the model developed by Chan et al. (2009). By modifying Tate's Law, the size of the alginate solution before and after detachment from the dripping tip was estimated by considering the liquid lost factor, (K_{LF}) and the shrinkage factor (K_{SF}). Finally, the overall correction factor (K) can be described as:

$$d_p = K_{SF}K_{LF} \left(\frac{0.06d_T\gamma}{\rho g} \right)^{\frac{1}{3}} \quad (5)$$

$$= K \left(\frac{0.06d_T\gamma}{\rho g} \right)^{\frac{1}{3}} \quad (6)$$

Where d_p is the diameter of the macro bead alginate (mm), d_T is the outer diameter of tip (mm), ρ is the density of alginate solutions, g is the gravitational force and γ is the surface tension of the alginate solutions. Meanwhile, the liquid lost factor and shrinkage lost factor were determined by first finding the fraction of an ideal drop volume and then this was compared to the real volume of the alginate during detachment (V_{real}/V_{ideal}). V_{real} can be found from the weight of the drop and the density of the liquid (Harkins & Brown, 1919). On the contrary, the ideal drop volume is defined as the volume detached from a capillary and this can be predicted by Tate's Law. The curve for determining these fractions as a function of the dimensionless tip radius is, $r/V_{real}^{1/3}$ where r is the tip radius. When $r/V_{real}^{1/3}$ has been determined, the fraction of the ideal drop volume can be easily obtained from the curve. Therefore, K_{LF} can be written as:

$$K_{LF} = \left[\frac{V_{real}}{V_{ideal}} \right]^{\frac{1}{3}} \quad (7)$$

For the shrinkage factor, the shrinkage ratio was determined by the assistance of image analysis before and after the gelation process of the alginate solution during detachment. The diameters of alginate drops were measured and the shrinkage factor can be written as:

$$K_{SF} = \frac{d_p}{d_d} \quad (8)$$

Where d_p and d_d are the diameters of alginate before and after gelation. Figure 3 shows the Harkin-Brown correction factors against a dimensionless tip radius for different concentrations and tip radii.

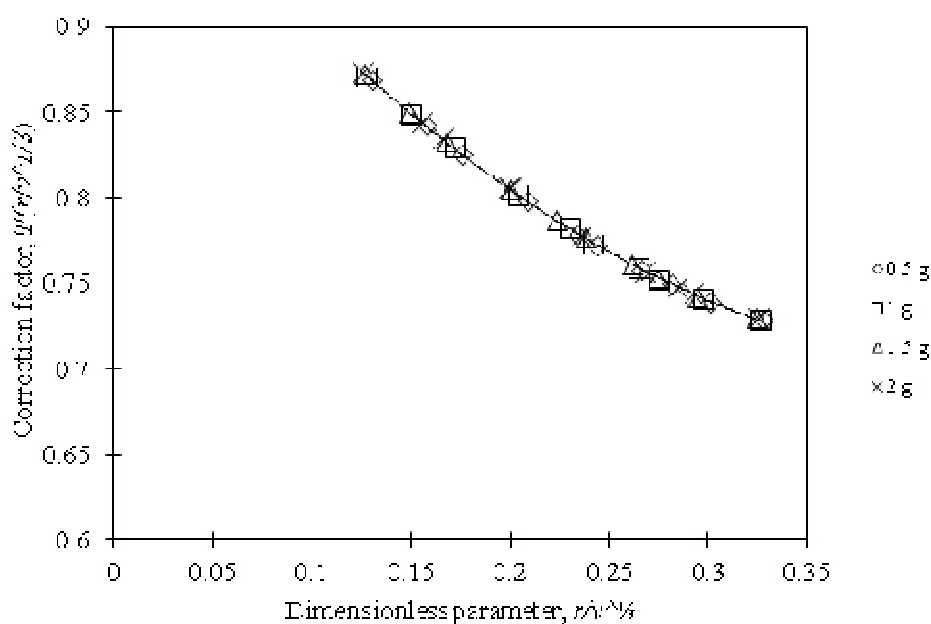


Figure 3 Harkin-Brown correction factors

It can be seen that the correction factors varied from 0.73–0.83 and corresponded to a range from 0.13–0.3 of dimensionless parameters. The plotted curve best fit into a polynomial equation and was in agreement with the works by various authors (Lando & Oakley, 1967; Wilkinson & Kidwell, 1971; Skelland & Slaymaker, 1990; Pu & Chen, 2001). It should be noted that the correction factors were calculated based on the assumption that the drop size residues govern the same contact angle with the tip as that of the drops related to the maximum volume that could be supported by the tip itself. The values of $r/V^{1/3}$ were found to expand beyond the recommended boundary (0.65–0.95) because the tip sizes used were less than 0.30 cm ((Harkins & Brown, 1919; Wilkinson & Kidwell, 1971). In addition, owing to different surface tensions exerted in the alginate solutions, the deviations of $r/V^{1/3}$ were as expected and this finding conformed to the findings of the other works concerning the tip size and these findings were later expanded to $r/V^{1/3}$ from 0.31–1.225 and $\Psi(r/V^{1/3})^3$ from 0.535–0.721, $r/V^{1/3}$ from 0.0638–4.45 and $\Psi(r/V^{1/3})^3$ from 0.19–0.94, respectively (Vacek & Nekovář, 1973; Campbell, 1970; Wilkinson & Kidwell, 1971).

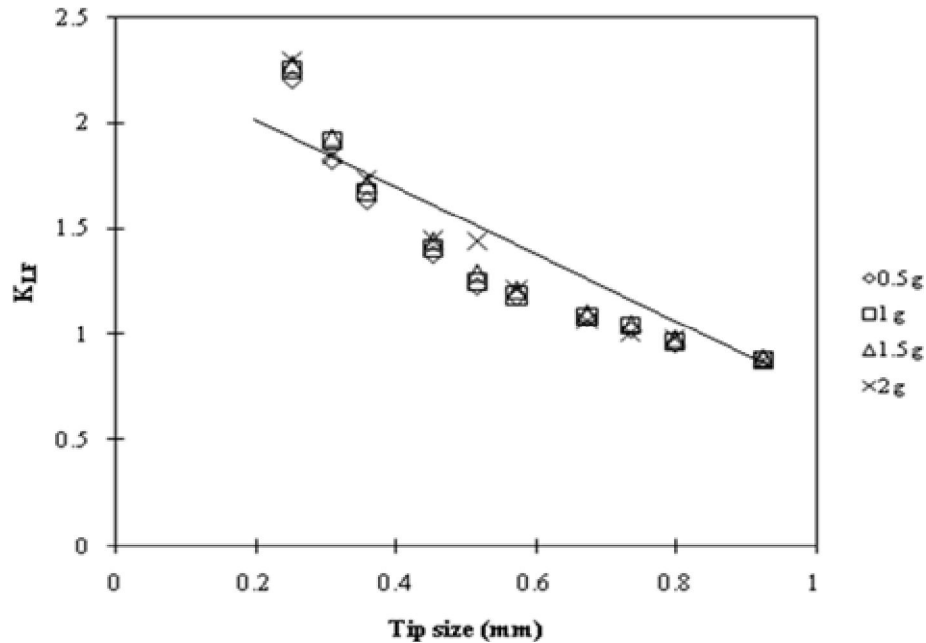


Figure 4 Liquid lost factors against tip sizes

Figure 4 shows the liquid lost factors at the different tip sizes. It was observed that the liquid lost factor was independent from the liquid properties, but highly dependent on the tipping size. As the tipping size increased, the liquid lost factor reduced from 2.3 to 0.8 which corresponds to the alginate concentrations. The plotted curves shows that the relationship between liquid lost factor and tip size was a better fit in the linear form ($R^2=0.893$). Therefore, the relationship between liquid lost factor and tip size can be written as:

$$K_{LF} = 2.471 - 1.926d_T \quad (9)$$

Next, the shrinkage factor was determined by calculating the shrinkage of the alginate drops before and after gelation. As can be seen from Figure 5, the shrinkage ratio was found mostly to be distributed from 0.2 to 1.5% at levels of different concentration of alginate solutions. It can be inferred that the shrinkage ratio had no effect on the tip size as confirmed in the result by Chan et al., (2009). As the alginate concentration increased from 0.5 to 2 g/L, the shrinkage ratio was maintained between 0.2 to 1.5% regardless of the tip size. Therefore, it can be assumed that the shrinkage ratio may be influenced by the M/G ratio of alginate powder. The calculated K_{SF} for alginate solutions in this work was found at 0.98, considering 2% of the average shrinkage ratio. Considering the low concentration of alginate solutions, the shrinkage of the beads after the gelling process was attributed to the hydrogel network during cross-linking. This phenomenon causes high water loss and eventually reduces the volume of the beads significantly (Chrastil, 1991; Velings & Mestdagh, 1995). Alternatively, lower concentrations of alginate in the gelling solutions also might be the reason for the high shrinkage ratio whereby the beads would easily be deformed whenever the surface tension of the gelling bath was accordingly exceptionally higher than the alginate solutions. Previous studies have demonstrated that, lower degrees of shrinkage were largely influenced by the M/G ratio as they affect the gelation mechanism (Simpson et al., 2003; Simpson et al., 2004; Klöck et al., 1997). However, depending on the purpose and application, the degree of shrinkage can vary from 10 to 50%. Since this work only focuses on the low molecular weight of the alginate, this consideration could not be verified. Further work needs to be done accordingly by comparing different M/G ratios in order to investigate the effects of shrinkage ratio.

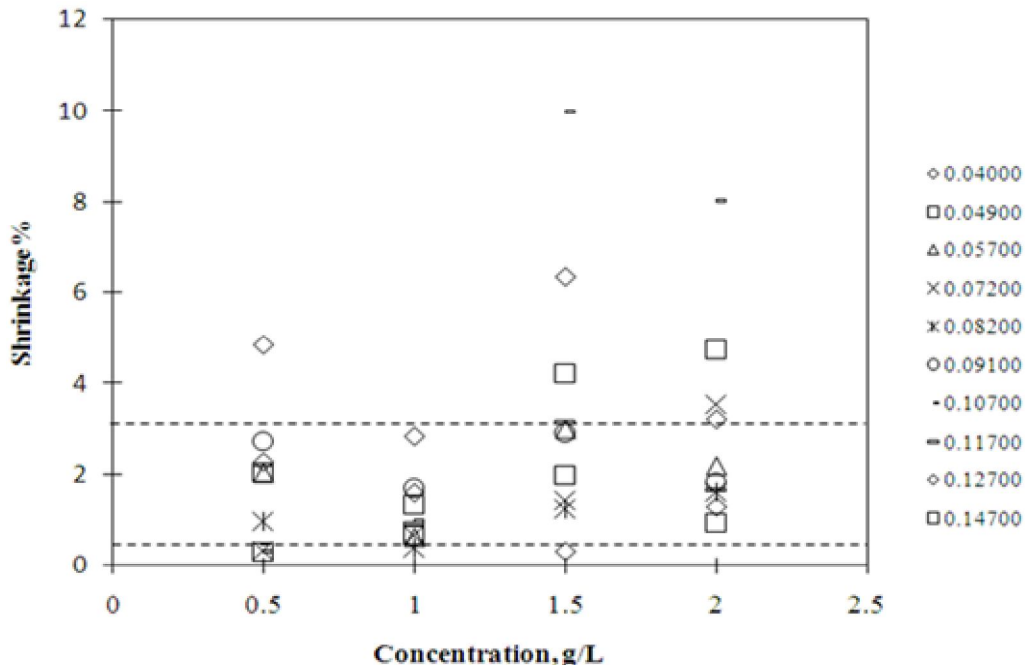


Figure 5 Shrinkage ratios against alginate concentrations

Finally, the overall size prediction model taking into account the liquid lost factor and the shrinkage factor can be written as:

$$d_p = 0.98(2.471 - 1.926d_T) \left(\frac{0.06d_T\gamma}{\rho g} \right)^{\frac{1}{3}} \tag{10}$$

and verified with experimental data to determine the accuracy and the model applicability. The plot between the experimental and prediction data is shown in Figure 6. The plotted data between the predicted and the experimental were compared to the tip size. It can be seen that by increasing the tip size, this action would increase the size of the bead for the case of the prediction model, whereas the experimental bead size would remain in the range of 2.65 to 3.85 mm, respectively. Wide variation of the prediction bead size was attributed mainly due to the values of shrinkage and liquid lost factors during image analysis, before and after gelling. However, the prediction model was found to be approximately closer to the experimental value when the tip size was in the range of 0.044 to 0.124 cm, indicating good justification of the shrinkage constant. Therefore, it can be deduced that the applicability of the model is valid for the tip size range between 0.044–0.124 cm, whereby the low molecular weight of the alginate powder has to be used whenever reproducible experimental work is needed. In addition, when dripping tip is increased, the model is insufficient to estimate the appropriate bead size correctly, due to the liquid loss and shrinkage conditions. Swelling and gelling conditions also might be the reasons for the deviations of the calculated bead size during detachment.

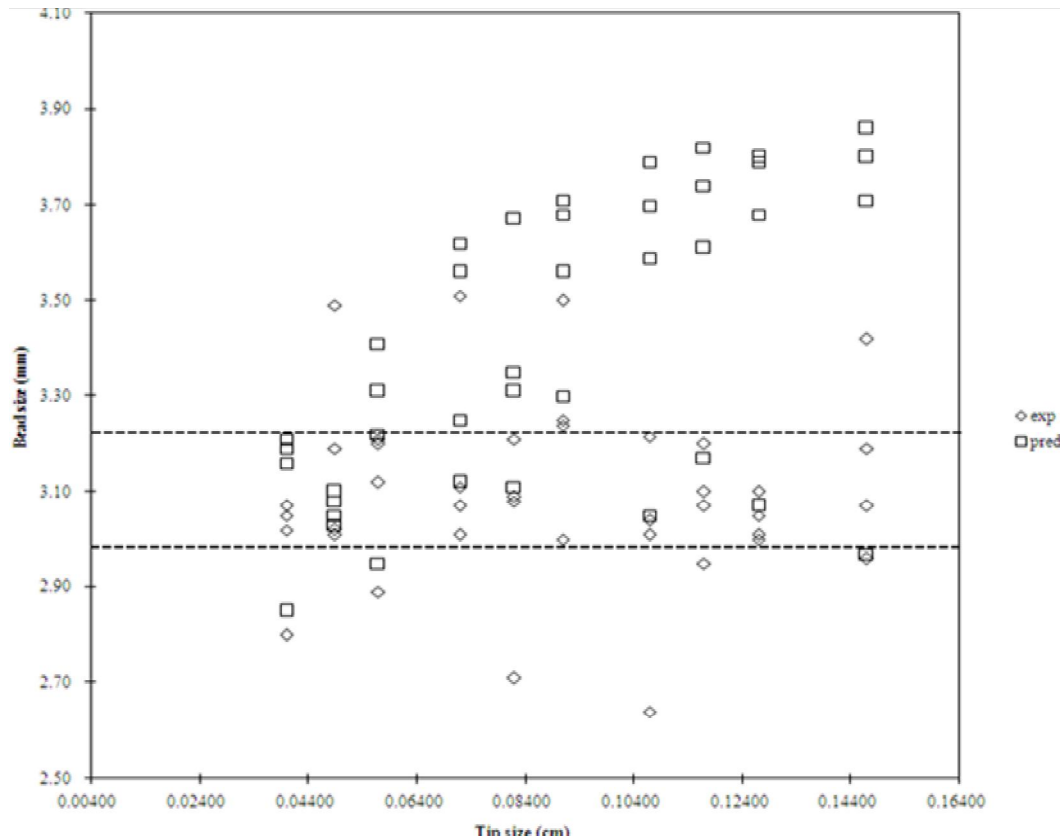


Figure 6 Beads size variation against tip size.

4. CONCLUSION

This study concerns the applicability of Tate's Law for a bead size prediction model. By utilizing a low molecular weight alginate, it was observed that the viscosity values were in the range of 47–65 mPas, and the surface tension exerted in the solutions were in the ranges of 43.45 to 69.14 mN/m. When tested for drop weight analysis, the alginate solutions followed a polynomial trend as recommended by the Harkin-Brown correction factors which lies in the ranges of 0.73 to 0.83. Meanwhile, from the experimental and prediction bead size, it was assumed that increasing tip size gradually, reduced the overall predicted size of the beads because of shrinkage and liquid lost factors, respectively. Accordingly, it can be concluded that the developed model is adequate for the prediction of bead size in the range of 2.9 to 3.25 mm. The prediction model developed for the shape and size of macro alginate beads produced through the drop weight method in this work could be employed for process optimization as well as evaluating process limitations in the field of macro encapsulation.

5. ACKNOWLEDGEMENT

The authors would like to acknowledge financial support received from Universiti Sains Malaysia through PRGS (8047071) and MyBrain under Ministry of Higher Education for the scholarship awarded.

6. REFERENCES

- Al-Hajry, H.A., Al-Maskry, S.A., Al-Kharousi, L.M., El-Mardi, O., Shayya, W.H., Goosen, MFA., 1999. Electrostatic Encapsulation and Growth of Plant Cell Cultures in Alginate. *Biotechnology Progress*, Volume 15, pp. 768–774
- Babak, V.G., Skotnikova, E.A., Lukina, I.G., Pelletier, S., Hubert, P., Dellacherie, E., 2000. Hydrophobically Associating Alginate Derivatives: Surface Tension Properties of Their

- Mixed Aqueous Solutions with Oppositely Charged Surfactants. *Journal of Colloid and Interface Science*, Volume 225, pp. 505–510
- Campbell, J., 1970. Surface Tension Measurement by the Drop Weight Technique. *Journal of Physics D: Applied Physics*, Volume 3, pp. 1499
- Chan, E.-S., Lee, B.-B., Ravindra, P., Poncelet, D., 2009. Prediction Models for Shape and Size of Ca-alginate Macrobeads Produced through Extrusion–dripping Method. *Journal of Colloid and Interface Science*, Volume 338, pp. 63–72
- Chan, E.S., Yim, Z.H., Phan, S.H., Mansa, R.F., Ravindra, P., 2010. Encapsulation of Herbal Aqueous Extract through Absorption with Ca-alginate Hydrogel Beads. *Food and Bioproducts Processing*, Volume 88, pp. 195–201
- Chen, J.H., Xing, H.T., Guo, H.X., Li, G.P., Weng, W., Hu, S.R., 2013. Preparation, Characterization and Adsorption Properties of a Novel 3-aminopropyltriethoxysilane Functionalized Sodium Alginate Porous Membrane Adsorbent for Cr(III) Ions. *Journal of Hazardous Materials*, Volume 248–249, pp. 285–294
- Cheraghali, R., Tavakoli, H., Sepehrian, H., 2013. Preparation, Characterization and Lead Sorption Performance of Alginate-SBA-15 Composite as a Novel Adsorbent. *Scientia Iranica*, Volume 20, pp. 1028–1034
- Chrastil, J., 1991. Gelation of Calcium Alginate. Influence of Rice Starch or Rice Flour on the Gelation Kinetics and on the Final Gel Structure. *Journal of Agricultural and Food Chemistry*, Volume 39, pp. 874–876
- Daemi, H., Barikani, M., 2012. Synthesis and Characterization of Calcium Alginate Nanoparticles, Sodium Homopolymannuronate Salt and its Calcium Nanoparticles. *Scientia Iranica*, Volume 19, pp. 2023–2028
- Dohnal, J., Štěpánek, F., 2010. Inkjet Fabrication and Characterization of Calcium Alginate Microcapsules. *Powder Technology*, Volume 200, pp. 254–259
- Harkins, W.D., Brown, F., 1919. The Determination of Surface Tension (Free Surface Energy), and the Weight of Falling Drops: The Surface Tension of Water and Benzene by the Capillary Height Method. *Journal of the American Chemical Society*, Volume 41, pp. 499–524
- Kim, K.H., Keller, A.A., Yang, J.K., 2013. Removal of Heavy Metals from Aqueous Solution using a Novel Composite of Recycled Materials. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Volume 425, pp. 6–14
- Klöck, G., Pfeffermann, A., Ryser, C., Gröhn, P., Kuttler, B., Hahn, H.J., Zimmermann, U., 1997. Biocompatibility of Mannuronic Acid-rich Alginates. *Biomaterials*, Volume 18, pp. 707–713
- Klokk, T.I., Melvik, J.E., 2002. Controlling the Size of Alginate Gel Beads by Use of a High Electrostatic Potential. *J. Microencapsul*, Volume 19, pp. 415–24
- Lando, J.L., Oakley, H.T., 1967. Tabulated Correction Factors for the Drop-weight-volume Determination of Surface and Interracial Tensions. *Journal of Colloid and Interface Science*, Volume 25, pp. 526–530
- Lencina, M.M.S., Andreucetti, N., Gómez, C., Villar, M., 2013. *Recent Studies on Alginates Based Blends, Composites, and Nanocomposites*. in Thomas, S., Visakh, P. M. and Mathew, A. P. (eds.) *Advances in Natural Polymers*. Springer Berlin Heidelberg
- Li, X., Qi, Y., Li, Y., Zhang, Y., He, X., Wang, Y., 2013a. Novel Magnetic Beads based on Sodium Alginate Gel Crosslinked by Zirconium(IV) and their Effective Removal for Pb²⁺ in Aqueous Solutions by using a Batch and Continuous Systems. *Bioresource Technology*, Volume 142, pp. 611–619

- Li, Y., Du, Q., Liu, T., Sun, J., Wang, Y., Wu, S., Wang, Z., Xia, Y., Xia, L., 2013b. Methylene Blue Adsorption on Graphene Oxide/Calcium Alginate Composites. *Carbohydrate Polymers*, Volume 95, pp. 501–507
- Oliveira, S., Almeida, I., Costa, P., Barrias, C., Ferreira, M.R., Bahia, M.F., Barbosa, M., 2010. Characterization of Polymeric Solutions as Injectable Vehicles for Hydroxyapatite Microspheres. *AAPS PharmSciTech*, Volume 11, pp. 852–858
- Pu, B., Chen, D., 2001. A Study of the Measurement of Surface and Interfacial Tension by the Maximum Liquid Drop Volume Method: II. Viscosity Effect on the Tension Measurement. *Journal of Colloid and Interface Science*, Volume 235, pp. 273–277
- Seifert, D.B., Phillips, J.A., 1997. Production of Small, Monodispersed Alginate Beads for Cell Immobilization. *Biotechnology Progress*, Volume 13, pp. 562–568
- Simpson, N.E., Grant, S.C., Blackband, S.J., Constantinidis, I., 2003. NMR Properties of Alginate Microbeads. *Biomaterials*, Volume 24, pp. 4941–4948
- Simpson, N.E., Stabler, C.L., Simpson, C.P., Sambanis, A., Constantinidis, I., 2004. The Role of the CaCl₂-guluronic Acid Interaction on Alginate Encapsulated BetaTC₃ Cells. *Biomaterials*, Volume 25, pp. 2603–2610
- Skelland, A.H.P., Slaymaker, E.A., 1990. Effects of Surface-active Agents on Drop Size in Liquid-liquid Systems. *Industrial and Engineering Chemistry Research*, Volume 29, pp. 494–499
- Swain, S.K., Patnaik, T., Dey, R.K., 2013. Efficient Removal of Fluoride using New Composite Material of Biopolymer Alginate Entrapped Mixed Metal Oxide Nanomaterials. *Desalination and Water Treatment*, Volume 51, pp. 4368–4378
- Vacek, V., Nekovář, P., 1973. A Note on Residual Drop and Single Drop Formation. *Applied Scientific Research*, Volume 28, pp. 134–144
- Vecino, X., Devesa-Rey, R., Cruz, J.M., Moldes, A.B., 2013. Entrapped Peat in Alginate Beads as Green Adsorbent for the Elimination of Dye Compounds from Vinasses. *Water, Air, and Soil Pollution*, Volume 224, pp. 1–9
- Velings, N.M., Mestdagh, M.M., 1995. Physico-chemical Properties of Alginate Gel Beads. *Polymer Gels and Networks*, Volume 3, pp. 311–330
- Wilkinson, M.C., Kidwell, R.L., 1971. A Mathematical Description of the Harkins and Brown Correction Curve for the Determination of Surface and Interfacial Tensions. *Journal of Colloid and Interface Science*, Volume 35, pp. 114–119
- Zhao, Y., Carvajal, M.T., Won, Y.Y., Harris, M.T., 2007. Preparation of Calcium Alginate Microgel Beads in an Electrodispersion Reactor using an Internal Source of Calcium Carbonate Nanoparticles. *Langmuir*, Volume 23, pp. 12489–12496