# EFFECT OF DOUBLE SCREW EXTRUDER PROCESS CONDITIONS ON THE INTRINSIC ALGINATE VISCOSITY OF *Sargassum cristaefolium*

*)Doni Ferdiansyah, *)Sugiono, **)Abdul Qadir Jailani
*)Lecture of Fisheries Science, Universitas Islam Madura
**)Lecture of Aquaculture, Universitas Tidar
E-mail: doni.ferdiansyah.df@gmail.com

**Abstract**

The purpose of this study was to determine the conditions of the extrusion process which gave a maximum value of intrinsic viscosity response. The 2k factorial design was used to determine the effect of temperature, screw speed and pH on intrinsic viscosity and determine the accuracy of the first-order polynomial model. The temperature treatment, screw speed and pH of alginate extraction extrusion process have a significant influence on intrinsic viscosity. The maximum intrinsic alginate viscosity value of 416.16 ml/g occured under conditions of extrusion process temperature of 60ºC, screw speed 75 rpm and pH 10. Quadratic first-order polynomial model, planning of research center temperature 60ºC, screw speed of 75 rpm and pH 10 were appropriate.

***Keywords: Alginate, double screw extruder process, intrinsic viscosity, Sargassum cristaefolium***

## Introduction

Alginates were polysaccharides found in the matrix of brown algae cell walls ranging from 8-40%, composed of linear polymers β-(1-4) -D-mannuronate (M) and α-L-guluronate (G) (Boisseson *et al.*, 2004; Draget and Taylor, 2011). Alginates were widely used in the food and non-food industries as additives to stabilize the emulsion, thickener and gel forming systems (Torres *et al.*, 2007; Hernandez-Carmona, 2013). Alginate needs for the domestic industry were currently estimated at more than 2000 tons per year all of which were met from imported products (Laksmono *et al.*, 2013). Indonesia has a large potential of alginophyte resources, but cannot be optimally utilized given the development of domestic alginate extraction methods can not produce alginate with high rheological quality.

The main stage in the alginate extraction protocol was alkali extraction, classically this extraction was carried out by a batch process in an alkaline salt solvent, this extraction method requires a lot of reactants and water volume, a long extraction time (1-5 h), and relatively low intrinsic viscosity (Torres *et al.*, 2007; Fertah *et al.*. 2014). The potential of reactive extrusion as an alternative technology for alginate extraction has been carried out by Vauchel *et al.* (2007). This extrusion reactivation process was more effective than a batch process with several advantages, namely a short extraction time (10 minutes), the volume of water and reactants was reduced by 50%, the rheological properties of alginate were higher than the batch process. Kartika *et al.* (2010) stated that the condition of the double screw extruder process, screw speed, temperature and solvent affect the yield and quality of the product, as well as the optimal process conditions (temperature, screw speed, solvent pH) alginate extraction with double screw extruder still not known yet.

Extrusion process conditions (temperature, screw speed and pH) affected the movement of algae in the extruder thread, specific mechanical energy and alginate quality (Hernandez-Carmona *et al.*, 1999; Torres *et al.*, 2007; Kartika *et al.*, 2010; Baron *et al.*, 2010 ; Fertah *et al.*, 2014). It was therefore important to understand the effect of extrusion process conditions on alginate quality. The purpose of this study was to determine the conditions of the extrusion process which gives a maximum value of intrinsic viscosity response.

## Material and Method

This research was conducted at the Technopark Laboratory of the Bogor Agricultural University, in March-August 2017.

*Sargassum cristaefolium* was obtained from the poteran island of Sumenep Madura, KOH, formaldehyde, distilled water, hydrochloric acid (HCl) 37%, ethanol 99.8%, $Na_2CO_3$. All chemicals have a degree of technical purity obtained from CV. Makmur Sejati, CV. Krida Tama Persada.

**Double screw extruder**

Alginate extraction experiments were carried out with a Berto Industry BEX-DS-2256 double screw extruder. Barrel diameter and L / D ratio were 20 cm and 4:1. Capacity of 7 kg/h, die diameter of 8 mm, screw speed 0-180 rpm, auger speed (feed rate) 0-35 rpm. Three thermal induction heating modules, the barrel temperature was cooled with an air compressor and monitored from the control panel. The schematic of the Berto Industry BEX-DS-2256 modular barrel and double screw extruder screw profile can be seen in Figure 1.

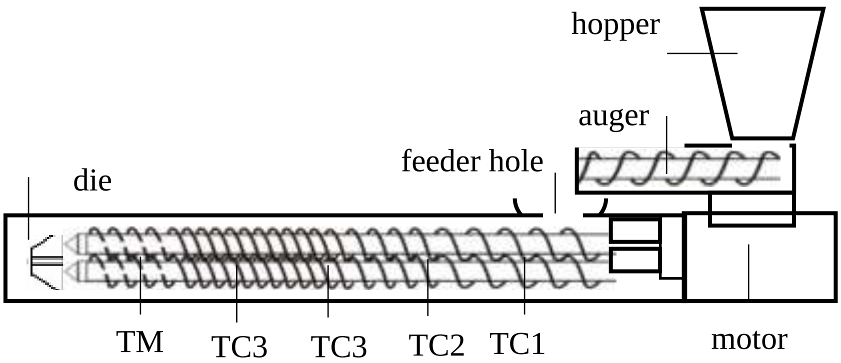



**Figure 1.** Schematic of the modular barrel and thread profile of the Berto Industry BEX-DS-2256 double screw extruder. TC = simple transfer groove (TC1 = 300 mm, TC2 = 220 mm, TC3 = 140 mm, TC4 = 120 mm), TM = stirring groove (80 mm), Total thread length = 800 mm

**Experimental Design**

The alginate extraction experimental design of the extrusion process used a factorial design with 3 variables, namely temperature (x1), screw speed (x2), and pH (x3). Each variable consists of 2 levels coded -1 and +1 was expanded with 3 central replications coded 0 (Gazpersz, 1992), the experimental design was presented in Table 1 below.

**Table 1.** Factorial Design of $2^3$ with Center Point Expansion

| No | Actual Variable and Code | | | | | | Response |
|---|---|---|---|---|---|---|---|
| | Temperature (°C) | $x_1$ | Screw speed (rpm) | $x_2$ | pH | $x_3$ | Viskositas intrinsik (ml/g) |
| 1 | 40 | -1 | 50 | -1 | 8 | -1 | 212.89 |
| 5 | 40 | -1 | 50 | -1 | +12 | +1 | 210.30 |
| 7 | 40 | -1 | 100 | +1 | 8 | -1 | 255.52 |
| 3 | 40 | -1 | 100 | +1 | 12 | +1 | 249.00 |
| 2 | 80 | +1 | 50 | -1 | 8 | -1 | 243.79 |
| 4 | 80 | +1 | 50 | +1 | 12 | +1 | 145.20 |
| 6 | 80 | +1 | 100 | -1 | 8 | -1 | 287.22 |
| 8 | 80 | +1 | 100 | +1 | 12 | +1 | 193.50 |
| 9 | 60 | 0 | 75 | 0 | 10 | 0 | 411.20 |
| 10 | 60 | 0 | 75 | 0 | 10 | 0 | 401.45 |
| 11 | 60 | 0 | 75 | 0 | 10 | 0 | 416.16 |

Based on experimental data, a regression analysis and the suitability of the first order polynomial equation model were performed:

$$Y=\beta_0+\beta_1x_1+\beta_2x_2+\beta_1x_3 \quad \text{..........} (1)$$

Where Y was the response variable, β0 was the intercept coefficient; βi, βii, βij were the linear regression coefficients, and x123, the code of the three independent variables were temperature, screw speed and pH.

**Research Implementation**

**Sample Preparation**

Brown algae were washed with fresh water until clean, soaked in 0.1% KOH for 1 h and washed to remove alkaline residues (Subaryono and Apriani, 2010). Brown algae were dried in the sun, milled and filtered 60 mesh. Brown algae soaked in 0.1% formaldehyde solution 1 night, washed throughly and dried with a cabinet dryer temperature of 45°C for 6 h (Wedlock and Fasihuddin, 1990; Hernandez-Carmona *et al.* 1999).

*Pre-extraction*

Brown algae dissolved in 0.03 M HCl pH 3 for 60 minutes solvent ratio 1:20 (w / v) is stirred constantly with a 500 rpm homogenizer, then washed with distilled water to neutral pH and drained with pressure (Hernandez-Carmona *et al.* 1999).

*Alginate Extraction with Double Screw Extruder*

Pre-extracted chocolate algae was added with a solution of $Na_2CO_3$ pH 8-12 gradually in a solvent ratio of 1: 3 (w/v), stirred until homogeneous and included in the extruder hopper. The alginate was extracted with a double screw extruder Berto Industry BEX-DS-2256 under conditions of speed operation thread 50-100 rpm, temperature 40-80°C, auger speed (feed rate) 30 rpm and die diameter 8 mm. Brown algae enter the double screw extruder and move between two rotating threads then come out as an extrudate homogeneous brown algae solution. The extruder was taken and dissolved in $Na_2CO_3$ ratio 1:10 (w/v), the alginate filtrate was centrifuged at 5000 rpm, 10 minutes, the supernatant was taken. The alginate filtrate was added with a 96% ethanol ratio of 1: 2 (v / v) left for 1 night and filtered. Alginate is washed twice with 70% ethanol and 96% filtered and pressed, the alginate is dried in an oven at 45°C for 24 h and milled 60 mesh.

*Intrinsic Viscosity*

Measurement of the viscosity of the alginate sample was carried out with a capillary viscometer Ubbelohde (Canon, USA) with a capillary diameter of 0.56 mm at 25°C. Alginate solution was prepared by dissolving 30 mg of alginate in 10 ml distilled water for 5 h at room temperature (25°C), then a series of alginate concentrations of 0.05-0.3 g/dL was made. Solution flow time t, measured relative to the solvent flow time, t0. Intrinsic viscosity was determined by extrapolation from ɳsp/c to zero concentration (Chee *et al.,* 2011).

Relative viscosity,

$$\eta = \frac{t}{t_0} \qquad \text{............ (2)}$$

Specific Viscosity,

$$\eta_{sp} = \eta - 1 \qquad \text{........ (3)}$$

Reduced Viscosity,

$$\frac{\eta_{sp}}{c} = \frac{\eta - 1}{c} \qquad \text{........ (4)}$$

Intrinsic Viscosity,

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} \qquad \text{........ (5)}$$

*Specific mechanical energy*

Spesifik Mechanical Energy (SME) werre calculated based on the following equation:

$$\mathrm{SME} = \frac{\mathrm{P}}{\mathrm{Qs}} \quad \text{with } \mathrm{P} = \frac{\mathrm{V \times I \times \cos}\, Q \times \mathrm{Ss}}{\mathrm{Ss}max} \qquad (6)$$

Where P was the motor power (W), I was the electric current (57.64 A), Qs was the feed material speed (kg/h), cosQ was the power factor of the electric motor (0.95), Ss was the screw rotation speed when operating (50-100 rpm), V was the electric voltage (380 volts) and Ssmax was the maximum speed of the scew rotation (180 rpm). This was a specification of the Berto Industry BEX-DS-2256 extruder (serial number: BC-0405-054-08-004).

*Data Analysis*

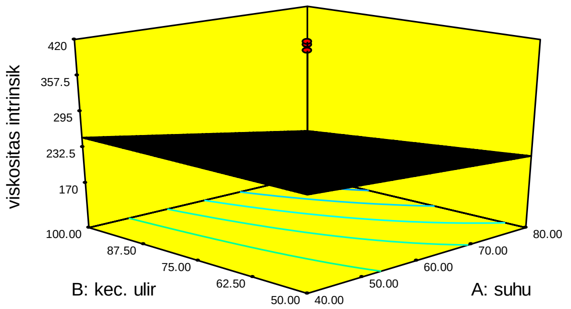
Data analysis and the accuracy of the polynomial equation model were carried out with the expert design program version 7 for analysis of the intrinsic viscosity range.

**Results and Discussions**

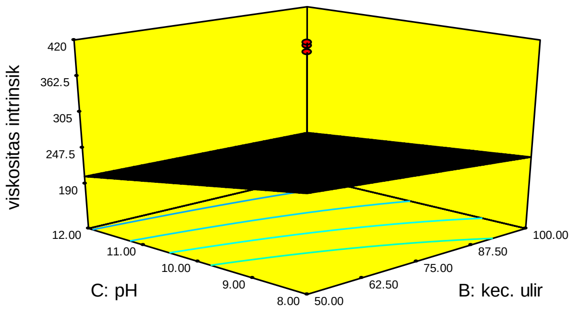
*Intrinsic Viscosity*

The study of the effect of the extraction conditions on the extrusion process has a significant effect on the viscosity of the intestinal alginate viscosity (Figure 2). Intrinsic viscosity increases at 60°C, 75 rpm and pH 10, then decreases at 80°C, screw speed 100 rpm, pH 12 (Table 1). This was related to the increase in the extractability of large molecular weight alginates at 60°C, screw speed 75 rpm and pH 10. While at a temperature of 80°C, screw speed 100 rpm and pH 12 alginate viscosity decreases due to degradation of the alginate polymer chain. These was in accordance with that reported by Torres *et al.* (2007) that the specific viscosity of alginate from brown algae increases at 60°C then decreases at 80°C.

a.




b.




c

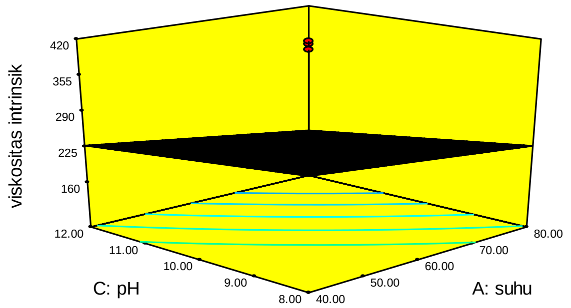



**Figure 2.** Surface response to the effect of the extrusion process on intrinsic viscosity, variations in screw speed and temperature (a); variations in pH and screw speed (b); variations in pH and temperature (°C).

Sellimi *et al.* (2015) stated that alginate viscosity was very sensitive to heating, viscosity decreases with increasing heating temperature. Decreased alginate viscosity at high temperatures due to the degradation of the alginate polymer chain (Fertah *et al.,* 2014). Alginate viscosity was stable at pH 10, at pH 12 the alginate degraded due to the β-elimination reaction, whereas at low pH hydrolysis was catalyzed by the proton (Smidsrod *et al.* 1969; Haug *et a1.* 1963; 1967). The condition of the extrusion process with a screw speed of 75 rpm increases the extractability of large molecular weight alginates, whereas at a screw speed of 100 rpm the integrated alginate polymer chain. Kartika *et al.* (2010) stated that increasing screw speed causes the specific effects of mechanical energy to become stronger as a result of the alginate polymer chain being degraded (Figure 3).

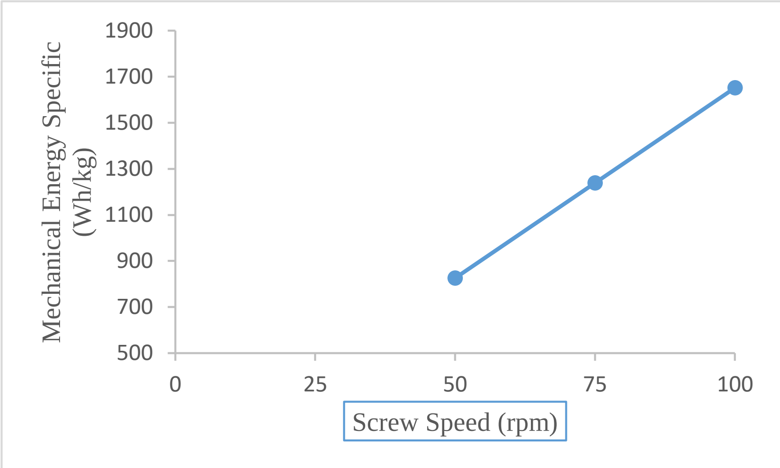



**Figure 3.** Effect of screw speed on mechanical energy specific

**Model Accuracy Analysis**

The prediction of the polynomial model of the first-order experimental calculation results of the intrinsic viscosity response was as follows:

$$y= 225.04-25.27x_1-8.59x_2-24.81x_3-11.14x_1.x_2-4.76x_1.x_3+6.06x_2.x_3-11.34x_1.x_2.x_3 \quad \text{…..... (8)}$$

Variance analysis results found that the model was significant at the level of confidence ($\alpha$ = 0.05), this showed that the temperature treatment, screw speed and pH of alginate extraction the extrusion process significantly influences the intrinsic viscosity response. Effect of single factors and temperature interactions, screw speed and pH of alginate extraction the extrusion process has a negative effect on intrinsic viscosity.

**Table 2.** Analysis of various first order polynomial regression models

| Diversity sources | Quadratic amount | Estimated coefficient | db | Quadratic Center | F value | Prob>F |
|---|---|---|---|---|---|---|
| Model | 13120.39 | | 7 | 1874.34 | 33.47 | 0.0293* |
| A-temperature | 5108.58 | -25.27 | 1 | 5108.58 | 91.21 | 0.0108 |
| B-screw speed | 589.96 | -8.59 | 1 | 589.96 | 10.53 | 0.0833 |
| C-pH | 4926.27 | -24.81 | 1 | 4926.27 | 87.96 | 0.0112 |
| AB | 992.35 | -11.14 | 1 | 992.35 | 17.72 | 0.0521 |
| AC | 180.88 | -4.76 | 1 | 180.88 | 3.23 | 0.2142 |
| BC | 294.03 | +6.06 | 1 | 294.03 | 5.25 | 0.1490 |
| ABC | 1028.31 | -11.34 | 1 | 1028.31 | 18.36 | 0.0504 |
| Arch | 74320.63 | 184.56 | 1 | 74320.63 | 1326.96 | 0.0008* |
| Pure error | 112.02 | | 2 | 56.01 | | |
| JK Total | 87553.04 | | 10 | | | |
| $R^2$ | 0.9915 | | | | | |
| Adj-$R^2$ | 0.9619 | | | | | |
| C.V | 2.56 | | | | | |

Curvature test was significant at the level of confidence $\alpha$ = 0.05. This showed that the first order experimental polynomial model was quadratic (Gazpersz, 1992; Montgomery 2005). Sugiono *et al.* (2014) reported that if the curvature test was significant, it meant that the polynomial model was quadratic. The midpoint of the planning was appropriate, the optimal response was around 60°C, the screw speed was 75 rpm and the pH was 10 (Figure 4).

Evaluation of the accuracy of the quadratic model of intrinsic viscosity response based on the model significance parameters (p <0.05), correlation coefficient ($R2\geq0.8$) and coefficient of variance (C.V $\leq$ 10%). Based on these parameters the first-order polynomial equation in response to intrinsic viscosity of alginate meets these criteria and appropriate (Table 2). The research can be continued with second-order experimental process optimization.

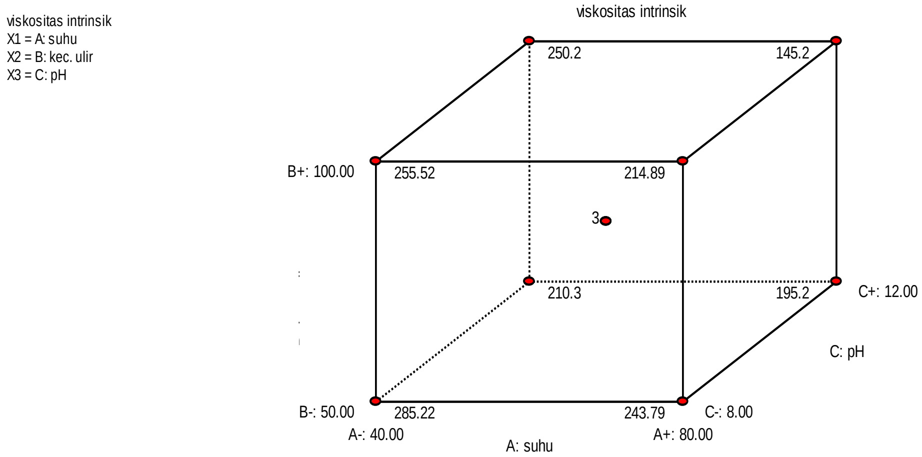



**Figure 4.** Effect of temperature, screw speed and pH on intrinsic viscosity

## Conclusions

Based on the results of the study it can be concluded:

1. The temperature treatment, screw speed and pH of alginate extraction extrusion process have a significant influence on intrinsic viscosity.
2. The maximum intrinsic viscosity value of 416.16 ml/g occured at a temperature of 60ºC, screw speed 75 rpm and pH 10 were appopriate. With a quaratic first order olynomial model, planning research center temperature 60ºC, screw speed 75 rpm and pH 10 were appopriate.

## Acknowledgement

The author would like to thank DRPM DIKTI for funding this research through the 2016 Doctoral Dissertation Research Grant, UIM and all those who have assisted in this research.

## References

Baron, R., P. Vauchel, R. Kaas, A. Arhaliass and J. Legrand. 2010. Dynamical modeling of a reactive extrusion process: focus on residence time distribution in a fully intermeshing co-rotating twin-screw extruder and application to an alginate extraction process. Chem. Eng. Sci. 65: 3313-3321

Boisseson, M.R.D., Leonard M., Favre E., Hubert P., Marcha l P. and Dellacherie E., 2004. Physical alginate hydrogels based on hydrophobic or dual hydrophobic/ionic interactions: Bead formation, structure, and stability. J.of Coll. and Interface Sci. 273: 131–139

Chee, Swee-Yong, P. K. Wong and C. L. Wong. 2011. Extraction and characterisation of alginate from brown seaweeds (Fucales, Phaeophyceae) collected from Port Dickson, Peninsular Malaysia. J. Appl. Phycol. 23:191–196

Draget, I. Kurt and C. Taylor. 2011.Chemical, physical and biological properties of alginates and their biomedical implications.Food Hydrocoll. 25(2): 251–56.

Fertah M., A. Belfkira, E. M. Dahmane, M. Taurirte,A. Brouillette and M. Taurirte. 2014. Extraction and characterization of sodium alginate from Moroccan *Laminaria digitata* brown seaweed. Arabian J. of Chem. 5(3):1878-1888

Gaspersz, 1992. Metode perancangan percobaan. Armico. Bandung. P.202-271

Haug, A., B. Larsen and O. Smidsrod.1963. The degradation of alginates at different pH values. Acta. Chem. Scand. 17(5): 1466-1468

Haug, A., B. Larsen and O. Smidsrod. 1967. Alkaline degradation of alginate. Acta. Chem. Scand. 21: 2859-2870

Hernandez-Carmona G., D.J. McHugh,D.L.Arvizu-Higuera and Rodriguez-Montesinos. 1999. Pilot plant scale extraction of alginate from *Macrocystis pyrifera*. 1. Effect of pre-extraction treatments on yield and quality of alginate. J.Appl. Phycol. 10: 507-513.

Hernandez-Carmona. 2013. Conventional and alternative technologies for the extraction of algal polysaccharides. Woodhead publishing limited. Mexico. 472-514.

Kartika, I. A., P. Y. Pontalier andL. Rigal. 2006. Extraction of oleic sunflower oil by twin-screw extruder: screw configuration and operating conditions effects. In.Proc. 16th International Sunflower Conference. Processing, Technology and New Uses. Fargo. ND USA. P 811-816.

Kartika, I. A., P. Y. Pontalier and L. Rigal.2010. Twin-screw extruder for oil processing of sunflower seeds : Thermo-mechanical pressing and solvent extraction in a single step.Ind. Crops Prod. 32(3): 297–304.

Montgomery D. C. 2005. Response surface methods and designs. New York. USA: John Willy and Sons. Inc.

Sellimi, S., I. Younes, H.B. Ayed, H. Maalej, V.Montero, M.Rinaudo, M.Dahia, T.Mechichi, M. Hajji and M. Nasri. 2015. Structural, physicochemical and antioxidant properties of sodium alginate isolated from a Tunisian brown sea weed. Int. J. Biol. Macromol.72: 358–1367

Smidsrod, O., A. Haug andB. Larsen. 1963. Degradation of alginate in the presence of reducing compounds. Acta. Chem. Scand. 17(10): 2628-2637

Smidsrod, O., B. Larsen, T. Painterand A. Haug. 1969. The role of intramolecular autocatalysis in the acid hydrolysis of polysaccharides containing 1.4-linked hexuronic acid. Acta. Chern. Scand. 23: 1573-1580

Subaryono, S.N.K. Apriani. 2010. Pengaruh dekantasi filtrat pada proses ekstraksi alginat dari *Sargassum* sp. terhadap mutu produk yang dihasilkan. JPB. Kelautandan Perikanan. 5 (2): 165-175

Sugiono, S.B. Widjanarko and L. A. Soehono. 2014. Extraction optimization by response surface methodology and characterization of fucoidanfrom brown seaweed*Sargassum polycystum*. Int. J. ChemTech Res. 6(1): 195-205.

Torres, M.R., A.P.A.Saosa, E.A.T.S.Filho, D.F.Melo, J.P.A.Feitosa, R.C.M.D. Paula and M.G.S.Lima. 2007. Extraction and physochemical characterization of *Sargassum vulgare* alginate from Brazil. Carbohydr. Res. 342:2067-2074.

Vauchel, P., R., Kaas, A. Arhaliass, R. Baron and J. Legrand. 2008. A new process for extracting alginates from *Laminaria digitata*: reactive extrusion. Food and Bioprocess Technol. 1(3): 297-300.

Wedlock D.J. and Fasihuddin B.A., 1990. Effect of formaldehyde pre-treatment on the intrinsic viscosity of alginate from various brown seaweeds. *Food Hydrocoll.* 4(1): 41-47