Preparation and Characterization of Biosorbents Beads (Bagasse-Calcium Alginate and *Jatropha curcas*- Calcium Alginate Beads)

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Abstract - This work concerns with the preparation, characterization and application of vegetable stalks alginate biosorbent beads (Bagasse-calcium alginate and *Jatropha curcas* calcium alginate) which were prepared by the association of bagasse waste powder or *Jatropha curcas* powder and calcium alginate via sodium alginate. Calcium alginate beads are formed when sodium alginate salt is added dropwise to a fixing solution of calcium chloride. The utilized materials in this work were sugarcane bagasse and *Jatropha curcas* stalks waste. In the preparation of three types of beads (calcium alginate beads, bagasse-calcium alginate beads and *Jatropha curcas*-calcium alginate beads) by using the optimum conditions were found to as 2% w/v of vegetable stalk powder, 6% sodium alginate and 10% calcium chloride. The physicochemical properties of three types of prepared beads such as the size of beads, moisture content, swelling percent, and pH were determined. The prepared biosorbent beads were qualitatively and quantitatively characterized by FT-IR,TGDTA, XRD, and SEM analyses.

Keywords : agricultural waste, bagasse calcium alginate beads, *Jatropha curcas*-calcium alginate beads, biosorbent

1. INTRODUCTION

Bagasse is the fibrous residue remaining after sugar cane stalks are crushed to extract their juice and is currently used as a renewable resource in the manufacture of pulp and paper products and building materials. A typical chemical analysis of bagasse might be on a washed and dry bagasse.

Cellulose	45% - 55%
Hemicellulose	20% - 25%
Lignin	18% - 24%
Ash	1% - 4%
Waxes	< 1%

The main chemical constituents of bagasse are cellulose, hemicellulose and lignin. Hemicellulose and cellulose are present in the form of hollow cellulose in bagasse which contributes to about 70% of the total chemical constituents present in bagasse. Another chemical constituent present in bagasse is lignin. Lignin act as a binder for the cellulose fibers and also behaves as an energy storage system (Monteiro *et al.*, 1998). *Jatropha curcas* L. commonly known as physic nut, belonging to the family Euphorbiaceae, is a multipurpose plant valued not only for its medicinal properties and resistant to various stress but also for its use as an oil seed crop (Heller, 1996; Staubmann, 1999; Openshaw, 2000).

Alginic acid is a heteropolymer comprising polyuronic groups. It is derived from common commercial algae extracted commonly from brown seaweeds. It has the ability to bind multivalent cations being the basis of their gelling properties, leading to the formation of covalent bonds yielding insoluble gel(Martinsen *et al*.,1989).

Calcium alginate beads are formed when sodium alginate salt is added dropwise to a fixing solution of calcium chloride. Calcium alginate beads has been one of the most extensively investigated biopolymers for binding multivalent cations. So, it has been used for the removal of heavy metals from dilute aqueous solutions (Apel and Torma, 1993).

Jatropha curcas has not been fully studied for its metabolic profile. The main stem of the plant should be cut once the tree in 1 m tall. This will lead to increase branching of the tree. The more branches a plant has, the higher the production of fruits and therefore more seeds. Every year, branches grow near the base and these should be removed and replanted elsewhere. It is very important to cut the tree in time and keep it in proper shape (Sukarin *et al*.1987). These removing or cutting branches are agricultural waste which were prepared dry *Jatropha curcas* powder and they can be used as low cost heavy metal adsorbent in this paper.

2. EXPERIMENTAL

Bagasse waste were obtained from Sugarcane plant from Ein Mae Township, Ayeyarwaddy Division and *Jatropha curcas* stalk waste were kindly supplied by Myanmar Five Star Line, Part of Terminal, Thaketa Township, Yangon. The waste were rinsed three times with distilled water, dried, cut and grounded to obtain a fine powder. The fine powder was

sieved to get the particle size range of 105-125 μm. These bagasse powder and *Jatropha curcas* stalk powder were stored in separately in tightly sealed bottle and they were ready to use.

2.1 Preparation of Biosorbent Composite Beads from Vegetable Stalks Powder

Various concentration of sodium alginate solution (2%, 4%, 6%, 8% w/v) were prepared,corresponding to constant amount 2 g of Biomass (bagasse or *Jatropha curcas*) and the prepared solution was stirred at constant rate (~150 rpm) at 60ºC for 6 hours. Using a syringe, the mixture was injected in droplets into 10% w/v of calcium chloride to form beads. The biocomposite beads were allowed to stay in calcium chloride solution with slow stirring for another 6 hours until it become harden. The beads were allowed to harden in this solution for 24 hours. After this time, hard spherical beads were dried at room temperature and collected in an air container.

2.2 Determination of Physicochemical Properties of Prepared Biosorbent Composite Beads

Determination of Swelling Properties

Prepared three types of biosorbent composite beads weighing individually 0.5 g was placed in 100 mL of water at room temperature. It took 24 hours long enough to reach the equilibrium swelling of the composite beads in vacuum desiccator for about 3 hours. Based on these two values, the water swelling percent were calculated by following equation.

$$\text{Swelling Percent}\,(\%) = \frac{W_s - W_d}{W_d} \text{ x } 100$$

Where, W_s = combined weight of sample and water absorb at a given time
(Weight of sample in grams swollen in water)
W_d = weight of sample in grams in dry state

Determination of Moisture Properties

Moisture content was analyzed by AOAC method (Pearson, 1976). Sample 1 g was placed in an oven at 110ºC for 2 hr. Then the sample was accurately weighed and cooled at normal temperature. The moisture content was calculated by using the following equation.

$$\text{Moisture content}\,(\%) = \frac{(A - B)}{A} \text{ x } 100$$

Where, A = weight of sample in grams
B = weight of sample in grams after cooling

Determination of pH

The sample 0.5 g was placed in a 100 mL of pyrex beaker and 50 mL of distilled water was added into it. Then the contents were boiled for 3 min and the water insoluble precipitate was filtered. The filtrate was cooled at room temperature and the pH of the sample was determined by using a pH meter.

Determination of Solubility Behaviour of Biosorbent Beads

About 1 g of biosorbent beads from each type was added into 50 mL of the different types of solutions and was stirred for a period of 24 hours. The weights of the beads were determined after the test in each solution. The differences in weight before and after tests give information on the stability of beads in the solution.

2.3 Characterization of Prepared Biosorbent Composite Beads (Calcium Alginate, Bagasse-Calcium Alginate and *Jatropha curcas*-Calcium Alginate Beads)

The prepared biosorbent composite beads were characterized by FT-IR, UV, Thermal, ED-XRF and XRD Analysis.

3. RESULTS AND DISCUSSION

Figure 1 shows that the calcium alginate beads, bagasse, calcium alginate beads and *Jatropha curcas* calcium alginate beads. In the preparation of the beads, sodium alginate concentration was very important, if the concentration of sodium alginate was very low, no formation of beads and if the concentration of sodium alginate was very high, the solution was very viscous and difficult to pass through the syringe.

Figure 1. (a) Calcium Alginate Beads (b) Bagasse-Calcium Alginate Beads (c) *Jatropha curcas*- Calcium Alginate Beads

Table 1. Preparation of Calcium Alginate, Bagasse-Calcium Alginate and *Jatropha curcas*-Calcium Alginate Beads

No	Weight of Biomass/g	% w/v of Sodium Alginate	Remark
1	2	2	No formation of beads
2	2	4	Slightly aggregated
3	2	6	Spherical beads
4	2	8	Viscous to make beads

3.1 Physicochemical Properties of Three Types of Biosorbent Beads

Swelling Property

The swelling characteristics of three type of biosorbent beads were determined by the swelling the beads in water at room temperature. The degree of swelling (swelling percent) of calcium alginate, bagasse-calcium alginate and *Jatropha curcas*-calcium alginate beads in deionized water was tabulated in Table 2. The equilibrium degree of swelling, after one, of immersion time for calcium alginate beads was 9.28%; bagasse- calcium alginate beads was 30.99% and *Jatropha curcas*- calcium alginate beads was 22.24%.

The prepared bagasse- calcium alginate beads is more hydrophilic than other beads, which showed much a decreased in degree of swelling. These results showed that calcium alginate and *Jatropha curcas* calcium alginate beads are more compact than bagasse calcium alginate beads.

Solubility Behaviour

Solubility tests for three types of biosorbent beads were carried out using some organic and inorganic solvents at room temperature. The results of the dissolution tests are present in Table 2. It can be found that three types of biosorbent beads are significantly increased the chemical stability in acid and basic media.

Determination of Moisture Content

Moisture content of prepared biosorbent beads were analyzed by AOAC method (Pearson, 1976). Prepared beads 1 g was placed in an accurately weighed crucible and heated in an oven at 100ºC for 2 hr to remove the water. Then, the sample was cooled until normal temperature and then weighed again. Heating and cooling were repeated until a constant mass was obtained.

Table 2. Physicochemical Properties of CA, BCA and JCA Beads

CA = Calcium Alginate Beads

BCA = Bagasse-Calcium Alginate Beads

JCA = *Jatropha curcas*- Calcium Alginate Beads

Sample	Moisture (%)	Swelling Percent (%)	Solubility									pH
			H_2O	Ether	HCl	NaOH	$NaHCO_3$	H_2SO_4	H_3PO_4	Acetone	Acetic Acid	

CA	2.92	9.28	-	-	decolorized	±	±	decolorized	±	-	-	5.9
BCA	2.78	30.99	-	-	decolorized	±	±	decolorized	±	-	-	6.2
JCA	2.76	22.24	-	-	decolorized	±	±	decolorized	±	-	-	6.0

(+) soluble

(-) insoluble

(±) slightly soluble

3.2 Characterization of Prepared Biosorbent Composite Beads

Calcium Alginate, Bagasse-Calcium Alginate(BCA) and *Jatropha curcas*- Calcium Alginate(JCA) Beads

FT-IR Analysis

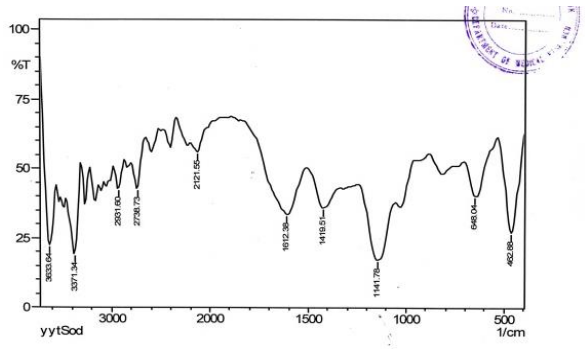


Fig.2. FT-IR spectrum of sodium alginate

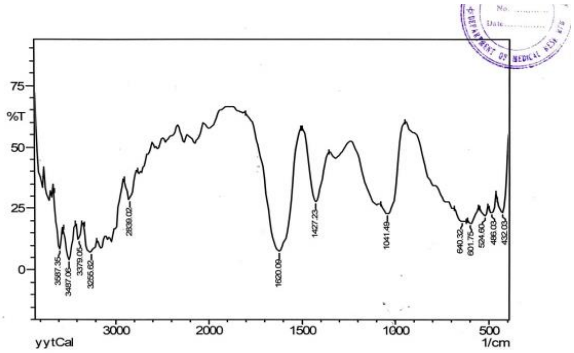


Fig. 3. FT-IR spectrum of calcium alginate bead

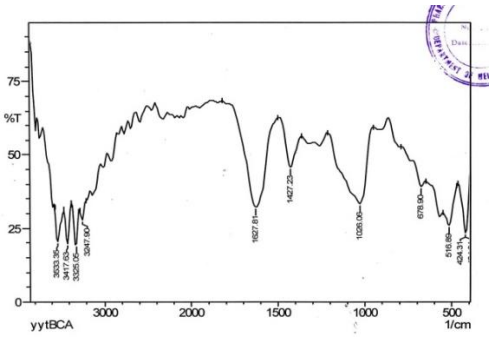


Fig. 4. FT-IR spectrum of bagasse calcium alginate beads

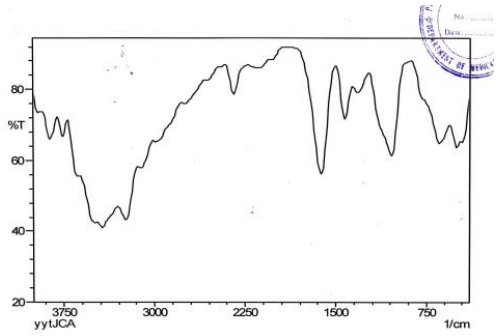


Fig. 5. FT-IR spectrum of *Jatropha curcas*- calcium alginate beads

Table 3 FT-IR Spectrum Assignment for Sodium Alginate, Calcium Alginate and Prepared Biosorbent Beads

No	**Frequency of Different Samples (cm^{-1})**				**Literature* frequency (cm^{-1})**	**Band Assignments**
	Sodium alginate	**Calcium alginate**	**BCA**	**JCA**		

1	3633	3487	3533	3244	3200, 3600	$\nu_{(O-H)}$ stretching
2	2738	2839	-	-	2800-3000	$\nu_{(C-H)}$ aliphatic, ν_{CH_2, CH_3}
3	1612	1620	1627	1620	1600-1950	$\nu_{asy\ (C=O)}$ carbonyl
4	1420	1427	1427	1420	1400-1470	$\nu_{sym\ (C=O)}$ carbonyl
5	1142	1041	1026	1040	1000-1200	$\nu_{(C-O)}$ alcohol, Na^+ is replaced by Ca^{2+}
6	462	486-524	424	720	450-1000	δ_{C-H}, δ_{C-C}, δ_{C-O} (aromatic)

*(Silverstein, 1981)

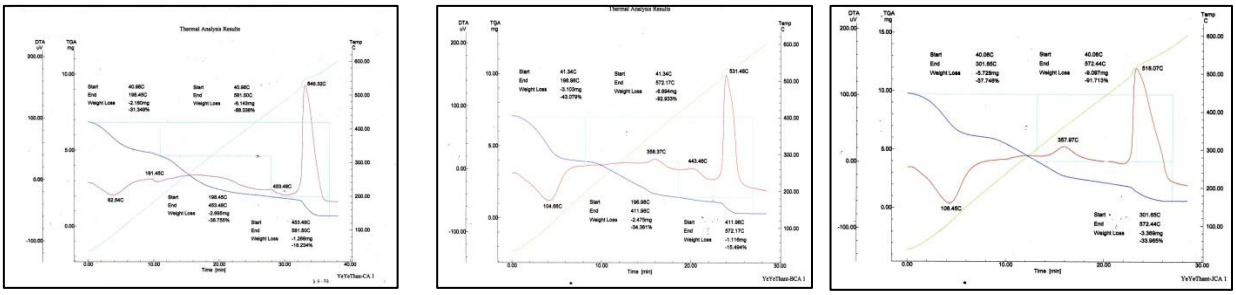
Thermal Analysis for Prepared Biosorbent Beads

On the basis of TG-DTA profiles, Figures 3.4 a, b and c present the break in temperature corresponding to dehydration, depolymerization, decomposition and phase change temperature of calcium alginate, bagasse-calcium alginate beads and *Jatropha curcas* - calcium alginate.

Figure 3. (a), calcium alginate beads shows the sharp endothermic peak at 82.54ºC and weight loss of 23.23% due to loss of bound water, sorbed water and depleting of functional group. The sharp exothermic peak at 181.45ºC with weight loss 26.83% which is due to decomposition of alginate fragments. Other sharp exothermic peaks at 453.48ºC with weight loss 23.68% which is due to decomposition of the branch chain of alginate and Another sharp exothermic peak at 546.32ºC with weight loss 14.99% is due to depolymerization of alginate.

Figure 3. (b) shows the bagasse-calcium alginate beads shows the sharp endothermic peak at 104.66ºC and weight loss of 43.079% due to loss of bound water, sorbed water and depleting of functional group. The sharp exothermic peak at 358.37ºC with weight loss 34.36% which is due to decomposition of alginate fragments and other sharp exothermic peaks at 531.48º with weight loss 15.49% which is due to depolymerization of alginate.

Similarly Figure 3. (c) shows the thermal decomposition of *Jatropha curcas*-calcium alginate beads and the reasons are the same mentioned in Table 3.



(a) **(b)** **(c)**

Figure6. Thermogram of (a) CA bead, (b) BCA bead and (c) JCA bead

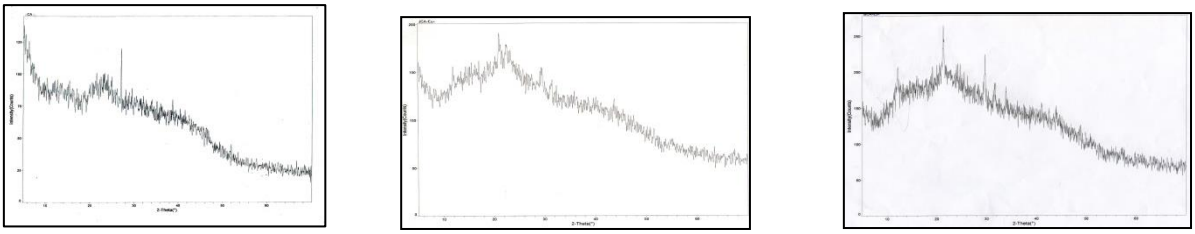
Table 4. Thermal Analysis Data for Prepared Biosorbent Beads

Type of sample	Temp. range (ºC)	Break temp. (ºC)	Weight loss (%)	Remark
CA	40.98-139	82.54	23.23	Loss of bound water, sorbed water and depletion of functional group
	139-258	181.45	26.83	Decomposition of some of the fraction of polymer chain

	258-511	453.48	23.68	Decomposition of alginate fragments
	511-561	546.32	14.99	Depolymerization of alginate
BCA	41.34-196.9	104.6	43.079	Loss of bound water, sorbed water and depletion of functional group
	196.9-411.9	356.37	34.361	Decomposition of alginate fragments
	411.9-572.1	531.48	15.494	Depolymerization of alginate
JCA	40.06-136	106.45	32.10	Loss of bound water, sorbed water and depletion of functional group
	136-360	357.9	38.46	Decomposition of alginate fragments

XRD Analysis

Figures 3.6 (a), (b) and (c) show that XRD spectra of vegetable stalk alginate biosorbent beads. According to the diffractogram of prepared biosorbent composite beads can be identified to be more of the amorphous type at room temperature.



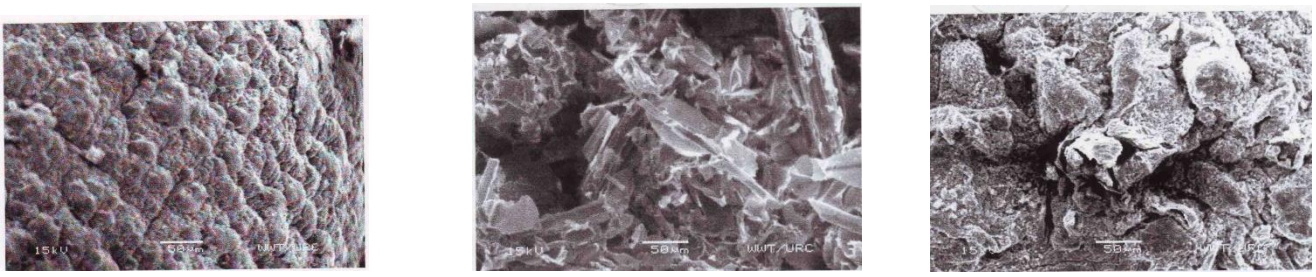
(a) (b) (c)

Figure 7. XRD diffractogram of (a) CA beads (b) BCA beads (c) JCA beads

SEM Analysis

Figures8.(a),(b) and (c) show the surface morphology of prepared calcium alginate beads, bagasse-calcium alginate beads and *Jatropha curcas* calcium alginate beads.

SEM images of Bagasse-Calcium Alginate Beads (Figure 8. b) and *Jatropha curcas*- Calcium Alginate Beads (Figure 8.c) revealed a cluster form of aggregate with cavitated pores. It can be also found as the beads have threaded matrix and porous nature. Therefore, these beads may be responsible for the enhanced specific adsorption properties and may be used as adsorbent for the removal of heavy metals, dyes and organic pollutants in wastewater.



(a) (b) (c)

Figure 8. SEM photographs of (a) Calcium alginate beads (b) Bagasse-calcium alginate beads (c) *Jatropha curcas*-calcium alginate beads

CONCLUSION

The result of the investigation have shown that effective and biosorbent can be prepared by blending 6 % w/v of sodium alginate and 10% w/v of calcium chloride to form calcium alginate beads and 6% w/v of sodium alginate, 2% w/v of vegetable stalk powder and 10% w/v of calcium chloride to form vegetable stalk alginate biosorbent beads. From the investigation of physicochemical properties of three types of beads, the moisture content of calcium alginate, bagasse-calcium alginate and *Jatropha curcas*-calcium alginate beads were found to be 2.92%, 2.78% and 2.76% respectively. The solubility of three types of beads were commonly insoluble in acid and base solutions. The swelling properties of calcium alginate beads, bagasse- calcium alginate beads and *Jatropha curcas*- calcium alginate beads were 9.28%, 30.99% and 22.24% respectively. The higher the degree of swelling for water molecules, the hydrophilic nature of bagasse-calcium alginate beads were greater than calcium alginate and *Jatropha curcas*-calcium alginate beads.

ACKNOWLEDGMENT

I would like to thank everyone for helping with this research work.

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