### Effect of Some Physical Properties on the Swelling Behaviour of Biomass Membranes

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#### ABSTRACT

The membranes of Detarium microcarpum seeds (DMS) and Alfzelia africana seeds (AAS) were developed. The water uptake capacities for DMS and AAS were found to be 500% and 390% respectively. The percentage of water uptake by Detarium microcarpum membrane and Alfzelia africana membrane, both increased with increased in the concentration of DMS and AAS as well as pH. The effect of contact time on water uptake showed that the water uptake increases gradually from 30 minutes to 2 hours and rapidly from 2 hours to 4 hours which mark the saturation point of the bio-sorbent. The water uptake of both membranes decreased with increase in ionic strength and temperature. This study revealed that Alfzelia africana and Detarium microcarpum membranes have high water uptake capacities, therefore, the study presents both DMS and AAS plant seeds as potential bio-sorbents for industrial use.

Keywords: Alfzelia africana seeds, Detarium microcarpum seeds, membrane, water uptake capacities

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#### **INTRODUCTION**

Water pollution is a worldwide problem and its control has become increasingly important in recent years. Aqueous heavy metal pollution represents an economical environmental problem due to their toxic effects and accumulation throughout the food chain.<sup>[1]</sup> Heavy metal contaminants exist in aqueous wastewaters of many industries, such as metal plating facilities, mining operations and tanneries. The contamination of water with substances which have adverse effect on human beings, animals and plant is called water pollution.<sup>[2]</sup>

Removal of heavy metal ions from effluents can be achieved by various methods such as: chemical precipitation, ion exchange, electrochemical treatment, reverse osmosis, solvent extraction, lime coagulation, adsorption on activated carbon, etc.<sup>[3]</sup>

These existing technologies for wastewater treatment have major problems, costs involved in the construction of waste water treatment plants are un-economical, it consumes lot of space, and commercially they are unattractive and have disposal problems.<sup>[4]</sup>

The technologies are divided into three types namely biological, chemical and physical.<sup>[5]</sup> The technologies like electro floatation, electro kinetic coagulation, coagulation combined with floatation and filtration, conventional oxidation methods by oxidizing agents irradiation and electrochemical processes are the technologies which fall under chemical methods. These chemical technologies are having many

disposal problems. Ions exchange and membrane technologies are very costly.<sup>[4,5]</sup>

The search for new technologies involving the removal of toxic metals ions from waste waters has directed attention to biosorption based on metal binding capacities of various biological materials. Biosorption can be defined as the ability of biological materials to accumulate heavy metals ions from wastewater through or physicometabolically mediated chemical pathways of uptake.<sup>[3]</sup> Its major advantages over conventional treatment methods include low cost, high efficiency of metal removal from solution, minimized chemical and/or biological sludge, less or nutrient requirement, no additional regeneration of bio-sorption and recovery.<sup>[1,3]</sup> possibility of metal Therefore, removal of toxic heavy metals ions to an environmentally safe level in a cost effective and environment friendly manner assumes great importance. Alfzelia Detarium mircocarpum and africana are used as thickeners in soup and other traditional products in Nigeria because of their binding properties, viscosity and swelling propensity which are some of the characteristics of a good sorbent<sup>[6]</sup>

Assessment of the phytochemical contents of the seeds of Alfzelia africana and Detarium microcarpum seeds contained Alkaloids (59.62%), (61.78%), flavoniods (9.75%), (41.89%) tannins (62.22%),(80.74%) and saponins (0.88%),(0.61%).<sup>[6]</sup> Flavonoids are a group of polyphenolic compounds that are found in fruits and vegetables, these metabolites possess some functional groups and their presence in the seeds indicates that they could have potential to bind metal ions from aqueous solution.<sup>[7]</sup> This study was set out to prepare membranes of *Detarium* microcarpum and Alfzelia africana seeds with an objective of studying their swelling behaviours so as to ascertain its industrial potential as bio-sorbents.

#### MATERIALS AND METHODS Materials

Sodium alginate, methanol, glutaraldehyde, hydrochloric acid, sodium hydroxide and sodium chloride were purchased from British Drug House (BDH). The mature dry seeds of *Alfzelia african and Detarium microcarpum* seeds were bought at Ovoko market, Nsukka Local Government Area, Enugu State, Nigeria. All chemical used in this work were of analytical grades and were used as supplied.

#### **Preparation of Biomass**

The seeds were sorted to remove debris and were stored in Polyethylene bags to avoid contamination. The traditional method of processing was used in treating both types of seeds. The seeds after storing were dried, roasted, soaked in warm water and the shells of the thickeners were removed manually and the seeds were dried in an oven at 60°C for 48 hours. They were then milled with blender and the pulverized samples were stored in paper bags for further analysis.<sup>[8]</sup>

The powdered seeds were filtered through 100  $\mu$ m sieve screen to obtain fine powder, which was packaged in a polyethylene bag and stored at room temperature (25°C). Sodium alginate was prepared by weighing 8.00 g and was made up to 100 cm<sup>3</sup> mark with distilled water in a volumetric flask and left overnight for complete dissolution to give 8% w/w.

#### **Membranes Preparation**

Detarium microcarpum seeds solution of (20 ml) and sodium alginate of (80 ml) with 0.1ml of glutaraldehyde (25%) in water were mixed. This mixture was stirred for 2 hrs at  $25^{\circ}$ C and was poured uniformly on a plastic tray. The membrane was allowed to dry at room temperature  $(25^{\circ}$ C) for 72 hours. The cast membrane was cross-linked by immersing in a 1% HCl solution taken in an equimolar mixture of methanol and water for 24 hrs.

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It was washed thoroughly in water and allowed to dry.<sup>[9]</sup> These processes were repeated for *Alfzelia africana* Membrane.

#### **Determination of Water Uptake**

The modified "Tea bag" method reported by Osemeahon *et al.*<sup>[8]</sup> was employed in this study. This involved the insertion of 2g of clean dried membrane samples into a transparent polyethylene bag, the assembly was weighed before adding 100ml of distilled water, after which it was sealed and kept undisturbed for 24hrs at room temperature to attain equilibrium. At the end of the equilibrium period, the excess solution was carefully sucked out using microsyringe, the polyethylene bag with the wet sample was weighed again. The percentage water uptake was determined using the following equation.

Water uptake (%) =  $[(Wx - Wy/Wy] \times 100/1]$ 

where Wx and Wy represent weight of dry and wet membrane samples, respectively.

#### Determination of the Effect of Time on Water Uptake

A mass of 2 g of *Detarium microcarpum* membrane was inserted in a polyethylene bag and weighed, 100ml of distilled water was then added. The modified tea bag method as reported earlier was used. At the end of the equilibrium period, the excess water was sucked out using a microsyringe, the polyethylene bag with the wet sample was weighed again. The percentage of water uptake was determined at different time interval, ranging from 30minutes to 24hours. This process was repeated for Alfzelia africana membrane.

#### Determination of the pH on Water Uptake

The water uptake behaviour of *Detarium microcarpum* membrane at different pH values (pH 2–12) was investigated at 30°C for 24 hours using the modified tea bag method. Standard solution of 2.0 M HCI and 1.0 M NaOH were used to adjust the solutions to the required pH values. At the end of the equilibrium period, the excess solution was sucked out using a microsyringe, the polyethylene bag with the wet sample was reweighed. The percentage water uptake was determined at different pH with the range stated above to ascertain the influence of hydrogen ion concentration. This process was repeated for *Alfzelia Africana* membrane.

#### Determination of the Effect of Ionic Strength on Water Uptake

A mass of 2 g of the dried membrane of *Alfzelia africana* seeds was inserted into a polyethylene bag and weighed. 100ml of sodium chloride solution of various concentrations (0.1–1.0 M) was added. At the end of the equilibrium period of 24 hours at 30°C, the excess solution was sucked out using a micro-string, the polyethylene bag with the wet sample was weighed again. The percentage of water uptake was determined using the formulae reported earlier.<sup>[9]</sup> The process was repeated for the membrane of *Detarium microcarpum* Seeds.

#### Determination of the Effect of Temperature on Water Uptake

A mass of 2 g of Alfzelia africana membrane was inserted into а polyethylene bag and weighed. 100 ml of distilled water was added, sealed and allowed to stay for 24 hours. The assembly was kept at a constant temperature using a regulated water bath. At the end of the equilibrium period, the excess water was sucked out using a micro-string; the polyethylene bag with the wet sample was weighed again. The percentage of water uptake was determined. The procedure was repeated for various temperatures ranging from 30°C to 80°C, in each case the average of three determinations was taken.<sup>[9]</sup> The process was repeated for the

membrane of *Detarium microcarpum* Seed.

#### **RESULTS AND DISCUSSIONS** Water Uptake Capacities of DMS and AAS Membranes

Figure 1 presents the water uptake capacities of DMS and AAS, at room temperature for a period of 24 hours respectively. The result showed that DMS has the highest water uptake capacity of 500% followed by AAS with 390%. The Water uptake capacity of the biomass can be attributed to the amount of cellulose content, the porosity of the fibres.<sup>[10]</sup> The degree of crystallinity of the polymer membrane can also affect the water uptake capacity. The more crystalline the polymer network is, the less water it will absorb due to less void spaces. The surface chemistry of the fibres could also be an influential factor to the biomass water uptake capacity.<sup>[11]</sup> The difference between the water uptake capacities of DMS and AAS observed can be explained in terms of differences in hydrophilicity, which is also reflected in the different water uptake capacities measured. The differences in porosity and cellulose content, natural fibres with higher cellulose content had

higher swelling properties than that of less cellulose content.<sup>[12]</sup> This phenomenon can also be explained by the difference in the surface chemistry of the fibres since both bio-sorbents were developed from two different plant seeds.

#### Effect of DM and AA Concentration on Water Uptake Capacity

Figure 2 presents the effect of DM and AA concentration on water uptake capacity. The study revealed that the water uptake of DMS and AAS increases as the concentration of DM and AA increases. The result showed that water uptake increases from 120% to 350% and from 105% to 320% for DMS and AAS respectively. This result is in agreement with various reports.<sup>[8,13]</sup> This may be due to the increase in the available binding sites in the biomass. This also may be due to the increase in the presence of polar oxygen containing groups which makes the biomass hydrophilic. This increase in hydrophilicity is due to the increase in the concentration of DM and AA seeds in the membrane. This also shows that the percentage of water uptake by DMS and AAS is a function of the concentration of seeds in the membrane.

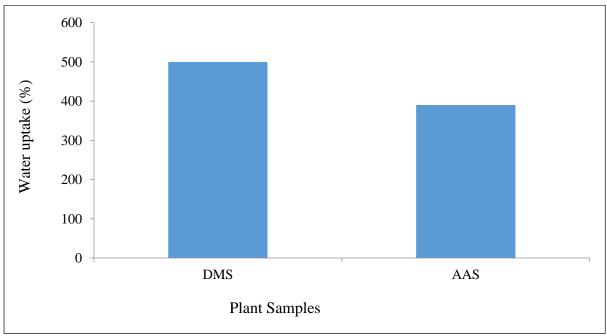


Fig. 1. Water uptake capacities of DMS and AAS.

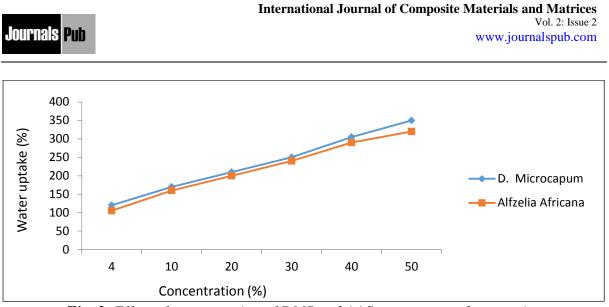


Fig. 2. Effect of concentration of DMS and AAS on water uptake capacity.

## Effect of pH of *DMS* & *AAS* on Water Uptake

Figure 3 presents the effect of pH on water uptake. At the pH range of 2.0-7.0, the percentage of water uptake changed from 260% to 320% and from 220% to 340% for DMS and AAS, respectively. These showed incremental differences of 60.01% 120.0% for DMS and for AAS. respectively. However, from pH 7.0 to 12.0, the percentage of water uptake jumped from 320% to 600% for DMS and from 340% to 520% for AAS. Both membranes showed very sharp differences in their increment of water uptake ranges of 280% and 180% for DMS and AAS respectively. This showed that, the amount of water uptake absorbed by DMS and AAS, between the pH values of 7.0 to 12.0 are three times and two times as the water

uptake between pH values of 2.0 to 7.0 for DMS and AAS respectively. On the whole, the percentage of water uptake increases with increasing pH values which showed that alkaline pH favours higher water uptake by DMS and AAS biomass. This is due to the presence of the -OH group in solution with increasing pH value.<sup>[14]</sup> The variation in water uptake by the biomass of DMS and AAS at different pH could be due to the differences in the sensitivity of cell wall molecules of the plant cells to pH or/and the formation of more hydroxides with increase in pH.<sup>[15]</sup> The difference in the surface chemistry of the different membranes (cations and anions) could also be the reason for the variation in water uptake by DMS and AAS.<sup>[11]</sup>

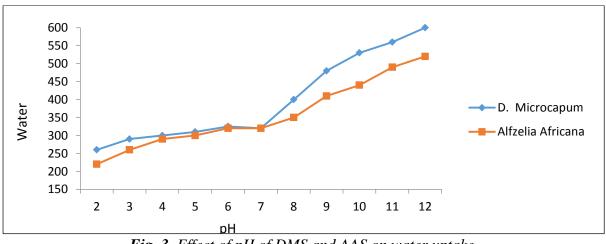


Fig. 3. Effect of pH of DMS and AAS on water uptake.

# Effect of Contact Time on DMS and AAS Water Uptake

Figure 4 presents the effect of contact time on water uptake by DMS and AAS. It was observed that the rate of water uptake increases gradually from 30 min. to 3 hours and rapidly up to 4 hours which marked the saturation point of the membrane. The water uptake then reduced from 4 hours gradually until equilibrium was reached. Perhaps, the rapid water uptake of the DMS and AAS could be due to the density of their polymer networks. The hydrophilic nature and porosity of the polymers may also be a factor.<sup>[16]</sup> This can also be explained based on diffusion phenomenon.<sup>[17]</sup> The behaviour may also be explained based on the crystallinity of the polymer membranes. Crystallinity affects the rate of diffusion of water molecules into the membrane, high

crystallinity means less void space between polymer molecules and hence a reduction in diffusion rate of the water molecules into the polymer membranes.<sup>[16]</sup>

# Effect of Ionic Strength on DMS and AAS Water Uptake

Figure 5 presents the effect of ionic strength on water uptake. It is evident that the water uptake decreased with increasing concentration of NaCl. This result is attributed to the decrease in the expansion of the polymer networks, which could be as a result of the repulsive forces of the counter ions on the polymeric chain shielded by the ionic charge. Therefore, the difference of the osmotic pressure between the external solution and the polymer network decreases with increases in the ionic strength of the saline concentration.<sup>[18]</sup>

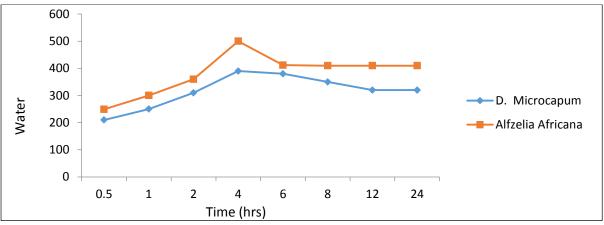


Fig. 4. Effect of contact time on DMS and AAS water uptake.

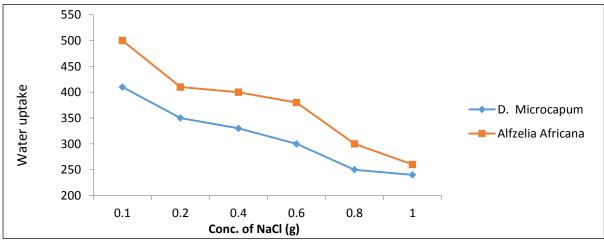


Fig. 5. Effect of ionic strength on DMS and AAS water uptake.

# Effect of Temperature on DMS and AAS Water Uptake

Figure 6 presents the effect of temperature on water uptake by DMS and AAS. The result showed that water uptake decreases from 30 to 70°C by both DMS and AAS. DMS and AAS decreases from 400% to 240% and from 450% to 280%, respectively. The trend of this result can be as a result of the contraction of the pores of the membranes with increase in temperature.<sup>[19]</sup> This contraction of the pore sizes and some binding sites limit the access of water molecules into the membranes which translate to decrease in water uptake. This can also be due to the low weight of the polymer molecules and weak polymer networks of the membrane which can dissolve with increasing temperature.<sup>[20]</sup>

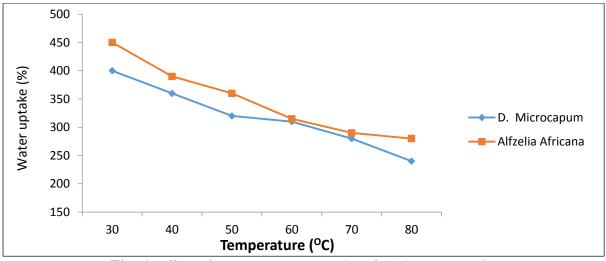


Fig. 6. Effect of temperature on DMS and AAS water uptake.

#### CONCLUSION

In this work, the membranes of D. microcarpum and A. africana seeds were successfully developed. The DMS and AAS showed a reasonable percentage of water uptakes. The water uptake capacities were found to be 500% and 390% for DMS and AAS respectively. It was observed that the water uptake of both DMS AAS decreases and as the temperature and the ionic strength of the external solution increases. But on the contrary, the percentage of water uptake of both DMS and AAS increases as the pH of the solution and concentration of the biomass increases.

However, the time for maximum water uptake by DMS and AAS was obtained at 4hrs. This work revealed that DMS and AAS (membranes) can be developed and can equally be used for the remediation of wastewater. Therefore, this work presents DMS and AAS as potential sorbent for industrial use.

#### REFERENCES

- [1] Volesky B., Holan Z.R. Biosorption of heavy metals, *Biotechnol Prog.* 1995; 11: 235–50p.
- [2] Kajal S.O., Khan F., Pandey P.K., et al. A review on heavy metals uptake by plants through biosorption, DOI: 10. 7763/IPEDR Vol. 75: 78–83p.
- [3] Volesky B. Biosorbents for metal recovery, *Trends Biotechnol*. 1987; 5: 96–101p.
- [4] Saifuddin N., Raziah A.Z. Remoal of heavy metals from industrial effluent using saccharomyces cerevisiae (baker's yeast) immobilised in chitosan/lignosulphonate matrix, J Appl Sci Res. 2007; 3(12): 2091–9p.

- [5] Veglio F., Beolchini F., Gasbarro A. Biosorption of toxic metals: an equilibrium study using free cells of *Arthrobacter* sp., *Process Biochem*. 1997; 32: 99–105p.
- [6] Igwenyi I.O., Azoro B.N. Proximate and plytochemical compositions of four indigenous seeds used as soup thickeners, *Environ Sci J Toxicol Food Technol.* 2014; 6: 45–9p.
- [7] Chamarthy S., Wseo C., Marshell W.E. Adsorption of selected toxic metals by modified peanut shells, *J Chem Technol Biotechnol*. 2001; 76: 593–7p.
- [8] Osemeahon S.A., BArminas J.T., Aliyu B.A., et al. Evaluation on the application of immobilized konkoli leaves for the removal of Pb, Cd, and Zn in aqueous solution, *Afr J Pure Micro Biol.* 2007; 70(11) :435–43p.
- [9] Baminas J.T., Ajayi J.O., Osemeahon S.A. Development of Sodium alginate and *Konkoli* gum-grafted-Polycrylamide blend membrane Science Forum, *J Pure Appl Sci.* 2005; 8: 70–9p.
- [10] Charkravaty A.C. Swelling behaviour and comparative porosity of some vegetable textile fibers at different moisture regains, *Textile Res J.* 2011; 41(4): 318–21p.
- [11] Baltazar A., Bismack A. Wetting behaviour moisture uptake and electro kinetic properties of lignocellulosic fibres, *Cellulose J.* 2007; 14(2): 115–27p.
- [12] Clesceri L.S., Greenberg A.E., Eaton A.D. Standard Methods for the Examination of Water and Wastewater. 20th Edn. American Public Health Association, Washington; 1998, 3-65-3-68p.
- [13] Lokeshwari N., Joshi K. biosorption of heavy metal (Chromium) using biomass global, *J Environ Res.* 2009; 3(1): 29–35p.

- [14] Godjevargova T., Simeonova A., Dimov A. Absorption of lead and copper on modified polysaccharide bead, J Chem Technol Biotechnol. 2001; 79: 283–8p.
- [15] Chandra Sekhar K., Kamalaa C.T., Chary N.S., et al. Removal of lead from aqueous solutions using an immobilized biomaterial derived from a plant biomass, *J Hazard Mater*.
- [16] Mustafa C., Ilyas K., Halil D., et al. Effect of water adsorption on the wear behaviour of sol-gel processed exposy/silica hybrids, *Sci Res Essays*. 2012; 7(7): 805–12p.
- [17] Khazaei J. Water adsorption characteristics of three wood varieties, *Cercetari Agronomice in Moklova.* 2008; XLI2(134): 5–16p.
- [18] Murali Y., Mohan Y., Kurt E. Polyamphylytic Hydrogels: Poly (N-Isopropylacrylamide) Based Stimuli Responsive Networks With Poly (Ethyleneimine). Laboratory of Applied Macromolecular Chemistry, Department of Material Science and Engineering, Gwangju Institute of Science and Technology (GIST), 2006, 500–712p.
- [19] Gong R., Ding Y., Liu H., et al. Lead biosorption and desorption by intact and pretreated *Spirulina maxima biomass, Chemosphere.* 2005; 58(1): 125–30p.
- [20] Horike S., Matsuzawa S., Yanaura K. Preparation of cross linked gels with maleate-denatured poly (Viny alcohol) and its application to drug release, *J Appl Polym Sci.* 2002; 85: 139–52p.