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Study on the Swelling Behaviour of Immobilized Stereospermum Kunthianum Plant Materials (Stem-Bark , Leaves, Root And Seed)

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Abstract- This paper studies the swelling behaviour of Stereospermum kunthianum plant parts (stem-bark, leaves, root, and seed) at various parameters (kinetics, temperature, pH and ionic strength).The plant parts were prepared by entrapping bio-sorbent with in a polymeric matrix of calcium alginate to produce immobilized bio-sorbents. Result shows that, in water, percentage water uptake increase with increase in time. The water absorbency for the immobilized plant samples in various salt solutions decrease with increasing ionic strength and temperature. The percentage water uptake for the plant parts were 363.6%, 330.6%, 263.6% and 240% for stem-bark, leaves, roots and seed respectively. The plant stem-bark and leaves has the highest percentage water uptake. These observations indicate that these plant samples have potentials in metal ions sorption from aqueous solution because in bioremediation process, the higher the water uptake by the sorbent, the higher metal ions it can remove from the aqueous medium.

Index Terms- Stereospermum-kunthianum, Immobilization, Water-uptake, Swelling.

I. Introduction

Bioremediation is one of the remediation processes in the treatment of wastewater using low-cost biomass in the sorption of metals from aqueous medium. In this aspect, the ability of the sorbent to remove the metal ions is greatly influenced by the swelling behaviour of the sorbent. The higher the water uptake by the sorbent, the higher metal ions it can remove from the aqueous medium (Espert et al., 2002). This therefore necessitates the study of the swelling behaviour of *Stereospermum kunthianum* plant samples (stem-bark, leaves, root, and seed) before its application as sorbent. Due to environmental awareness and government policies, many industries are looking for new materials which are environmentally friendly (Ramedive et al, 2012). With enhancement of environmental protection consciousness of people , natural fibers have shown great promises in a variety of applications that were previously dominated by synthetic fibers. This is due to their biocompatibility, possible biodegradation, non-toxicity and abundance(Xue et al, 2012).

The world wide availability of natural fibers and other abundantly accessible plant-waste is a motivator towards achieving sustainable technology in this aspect of science. History shows that humans collected raw materials from the wild to use as ropes or textiles and later, societies developed and learned how to cultivate such crops (Akil, 2011). The incorporation of fibers and fillers into composites affords a means of extending and improving the properties of the composites that meets the requirements of most engineering applications. Consequently these improvement are associated with economic advantages such as low production costs and resin consumption (Aziz et al., 2004).

In view of the above, Natural lignocellulose fibers have been receiving considerable attention as substitutes for synthetic ones. This is because the natural fibers among other benefits exhibit many advantageous properties such as low density, low cost, high stiffness, bio-degradability, reduced energy consumption, high degree of flexibility during processing and it is a renewable source (Ramedive,2013). Some of the potential applications of natural fibers are in metal ion adsorption, textiles, packaging, paper manufacturing industries etc. Therefore, an understanding of the hygroscopic properties of natural fibers is very important to improve the long time performance of composites reinforced with these fibers and also its sorption capability (Saikia., 2010).

Stereospermum kunthianum belongs to the family *Bignoniaceae*. It is a deciduous shrub or tree 3-15 m high. The plant is found in dry areas of deciduous forest, rocky outcrops, termite mounds and margins of evergreen forests (Choudhury et al, 2011). The plant is used in treating water by communities where the plant is commonly found (Fori, 2013). Traditionally, the plant samples have medicinal values. Leaf infusion is used for treating wounds. Stem-bark decoction is used to cure bronchitis and pneumonia (Hanwa et al,2009). Roots are used in treating venereal diseases and respiratory ailments. The pods are chewed with salt for coughs and are used in treatment of ulcers.(Falodun et al. 2012)

Stereospermum Kunthianum plant has come to interest due to its importance in innovative application in water treatment/purification and its medicinal values by communities where it is commonly found.

The objective of these work is to compare the water up-take of *Stereospermum kunthianum* plant materials (stem-bark, leaves, root and seed) under different parameters.(kinetics, pH, Ionic concentration and temperature to find out which part of the plant has highest water uptake ability so that attention will be given to it, to be converted into an industrial product to enhance its full potentials in water treatment/purification. The plant is been used by communities for water treatment in its natural form and creates problems of debris on the water and fouling (smelling) of water if it stays for more than 24 hours. Hence attention will be given to the plant part that has the highest water uptake ability for bioremediation process.

II. MATERIALS AND METHODS

Materials

Sodium- alginate, Calcium- Chloride, Sodium- Chloride, Hydrochloric- acid, Sodium- hydroxide. These chemicals were of analytical grade and were used as supplied. *Stereospermum Kunthianum* plant samples used (stem, leaves, root and seed) was obtained from Creek in Waka-Biu, Borno state, Nigeria.

Methods

Preparation of samples

The stem bark, root, and leave samples were freed from sand particles and dead dried tissues by carefully scraping with spatula and were chopped to pieces, air dried for two weeks, and the pods were collected and left to stand for a week for complete drying. The pods were broken with hand to expose the winged and coated seeds. The seeds were left to stand for 24 hours followed by removal of seed coat using local mortar and pestle. The broken seed coat and wings were blown off with the aid of gravitational forceand wind. The bear seeds obtained were milled into powder using pestle and mortar. The pulverized samples were stored in polyethylene bags for further analysis.

Dissolution of plant samples

The dissolution of the *Stereospermum kunthianum plant sample* was done by weighing 4.00g of the stem bark powder and dissolved in 100cm^3 of water and label mixture A, then the mixture poured into a separating funnel and allowed to stand for 12 hours for separation into various fraction. The process was repeated for root, leaves and seeds respectively.

Preparation of Sodium Alginate and Calcium Chloride to Immobilized Sample

Sodium alginate was prepared by weighing 4.00g and making it up to 100cm^3 mark with distilled water in a volumetric flask and left overnight for complete dissolution to give 4% w/w. 0.12M calcium chloride was prepared by weighing 26.28g into 1L volumetric flask and make up to the mark with distilled water (Wuyep et al,2007)

Synthesis of Immobilized Samples of *Stereospermum kunthianum*

25cm^3 viscous layers of dissolved *Stereospermum kunthianum* stem- bark sample was mixed with 25cm^3 of 4% stock solution of sodium alginate and stirred vigorously for even mixing in 250cm^3 beakers. The mixture was then transferred into another beaker containing 30cm^3 of 0.12M calcium chloride solution. The reaction was allowed retention time of 1hour for complete precipitation. The precipitated blend solid of the stem-bark sample was filtered and dried at room temperature (30^{0}C) for 24hours. The dried solid were stored in polyethylene bag for further use, Wuyep (2007). The same procedure was repeated for the leaves, root and seed samples.

Determination of water uptake by the *Stereospermum kunthianum* Immobilized Samples.

The modified "Tea bag" method reported by Osemeahon et al, (2003) was employed in this study. This involves the insertion of 2g of clean dried immobilized sample of stem bark into a transparent polyethylene bag, the assembly was weigh before adding 100ml of distilled water and was hermitically sealed and kept undisturbed for 24hours at 30^{0}C to attain equilibrium. At the end of the equilibrium period, the excess solution was carefully sucked out using micro syringe, the polyethylene bag with the wet sample was reweighed. The percentage water uptake was determined using the following equation.

Water uptake (%) =(Wx – Wy /Wx × 100/1

Where Wx and Wy represent weight of the dry and wet immobilized blend samples respectively (Barminas et al., 2005).

Determination of the Effect of Time on Water Uptake by *Stereospermum Kunthianum*

The effect of contact time on water uptake by *Stereospermum kunthianum* immobilized samples was determined at room temperature. 2 g of the immobilized stem was inserted in a polyethylene bag and weighed before adding 100ml of distilled water, using the modified tea bag method as reported earlier (Osemeahon, 2003). At the end of the equilibrium period, the excess water was sucked out using a micro syringe ,the polyethylene bag with the wet sample was reweighed, The percentage water uptake was determined at different time interval ranging from 60 minutes to 24hours. The process was repeated for the immobilized root, leaves and seed samples respectively.

Determination of the Effect of pH on Water Uptake by *Stereospermum Kunthianum*

The water uptake behaviour of *Stereospermum Kunthianum* immobilized stem at different pH values (pH 2 - 12) was investigated at 30^{0}C for 4hours using the modified tea bag method. A standard of 1.0 M HCl and 1.0 M NaOH was used to adjust the solutions to the required pH as the case may be. At the end of the equilibrium period, the excess solution was sucked out using a micro syringe; the polyethylene bag with the wet sample was reweighed. The percentage water uptake was determined at different pH within the range stated above. The process was repeated for the immobilized root, leaves and seed samples respectively.

Determination of the Effect of Ionic Strength on Water Uptake by *Stereospermum Kunthianum*

2.0 g of the clean and dried *Stereospermum kunthianum* immobilized stem-bark was inserted into a polyethylene bag and weigh before adding 100 ml of sodium chloride solution of various concentrations (0.1 M – 1.0 M w/w) using the modified tea bag method. At the end of the equilibrium period of 4 hours at 30^{0}C, the excess solution was sucked out using a micro stringe; the polyethylene bag with the wet sample was reweighed. The percentage water uptake was calculated using the formula reported earlier (Barminas et al., 2005). The process was repeated for the *Stereospermum kunthianum* immobilized root, leaves and seed samples respectively.

Determination of the Effect of Temperature on Water Uptake by *Stereospermum Kunthianum*

The effect of temperature on water uptake by *Stereospermum kunthianum* was determined. 2.0 g of the immobilized stem-bark was inserted in a polyethylene bag and weigh before adding 100ml of distilled water, the polyethylene bag was sealed and allowed to stay for 4hours. 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 were reweighed. The percentage water uptake was determined as reported earlier. The procedure was repeated for various temperatures ranging from 30^o to 80^oC. The process was also repeated for the immobilized root, leaves and seed samples respectively.

III. RESULTS AND DISCUSIONS

Sorption capacities of Different *Stereospermum Kunthianum* Samples

Figure 1 presents the sorption capacities of different *Stereospermum Kunthianum* plant samples at room temperature for the sorption period of 24 hours. The result shows that stem have the highest water-uptake ability, followed by leaves, root and seed respectively.

Plant natural fibers are made up of cellulose, hemicelluloses and lignin. The cellulose is held by amorphous hemicelluloses and fibers are cemented together in the plant by lignin. Lignocelluloses cell walls of plants contain hydroxyl and other oxygen containing groups that attract water through hydrogen bonding. The hemicelluloses are mainly responsible for water absorption. In view of the above, the stem-bark has the highest amount of hemicelluloses followed by leaves, root and seed respectively since it has the highest percentage absorption capacity.

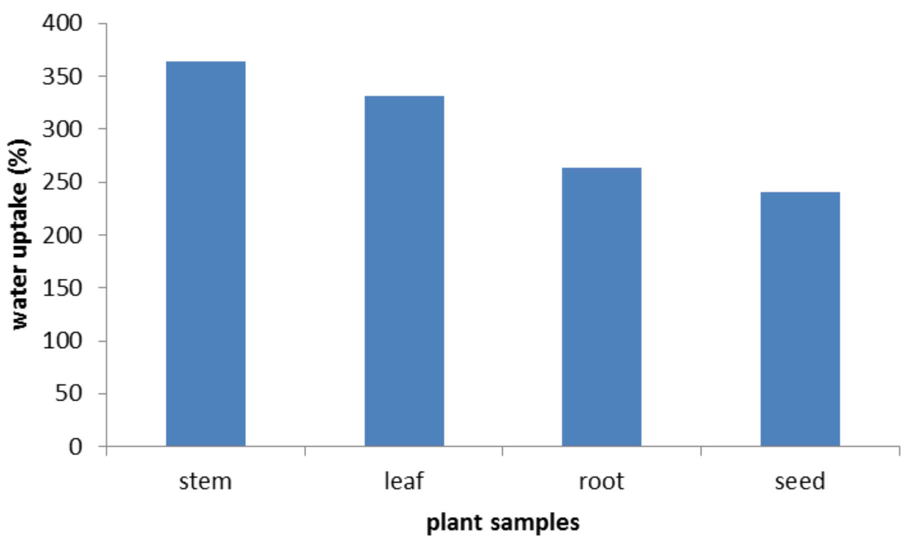

Figure 1: Absorption capacities of plant samples at 30^OC

Effect of Time on Water uptake by *Stereospermum Kunthianum* Samples

Result on contact time on percent water uptake at 30^oc is shown on Figure 2. It can be seen that the rate of uptake of water by immobilized plant samples increases steadily up to 7 hours then began to fall slightly. The swelling kinetics for sorbent is significantly influenced by the swelling capacity and apparent density of the polymer.(Lee and Lin.,2000). Previous studies by (Osemeahon et al., 2003, Toti et al., 2002), supports the increase in the rate of water uptake with in the first few hours of this experiment. The swelling ratio increases with increase in time because the structure of the polymers affects the swelling of the samples depending on the composition of polymeric matrix. The water sorption is caused among other factors by the hydrophilic nature of the plant samples.

The swelling of plant samples in water is attributed to the interaction between the hydrophilic cellulose molecules of the plant samples fibers in water molecules .Cellulose which is the main constituents of plant fibers contain three hydroxyl (-OH) groups, these hydroxyl groups form hydrogen bonds between the cellulose molecules and exposing these bonds to water which causes them to be broken (Jayamol et al., 2001). The hydroxyl groups then form new hydrogen bonds with water molecules which cause swelling. When the plant samples are immersed in water, the hydrophilic fibers swell, and the high cellulose content in the plant fibers contributes to more water penetrating into the interface through the voids induced by swelling of fibers with time (Njoku and Obikwelu, 2008).

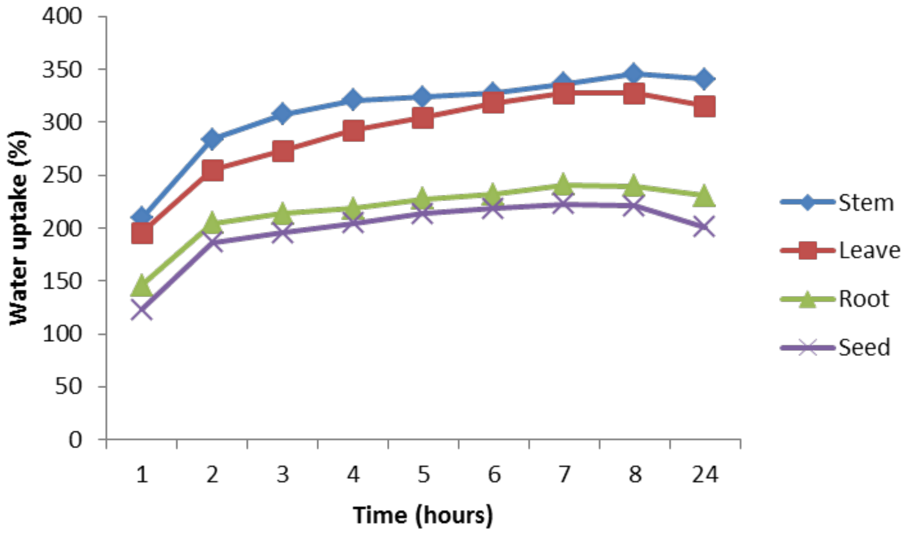

Figure 2: Effect of contact time on equilibrium mass % of uptake of water at 30^{O}C

Effect of Temperature on Water Uptake by *Stereospermum Kunthianum* Plant Samples

Figure 3 is the effect of temperature on water uptake by *Stereospermum kunthianum* plant samples. The result showed that, water uptake decrease with increase in temperature. Decrease in water uptake by polymeric sorbents with increase in temperature was also reported by Osemeahon et al., 2003, Toti et al., 2002. Increase in temperature during water absorbency give more compacted form of membrane resulting in reduction of cross linking density of the membrane which causes the pore to be narrower and the suction sites be hidden or in accessible to the water molecules. (Barminas and Osemeahon, 2005). When the temperature is increased, the moisture saturation time is greatly shortened; weight gain is higher for samples at lower temperature than higher temperature (Dhakal et al., 2006). This is attributed to the fact that the water sorption as the temperature increases is governed respectively by the wetting of fibres and the capillary sorption process because of the heat involved. This is due to the hydrophilic property of cellulosic fibres as more water molecules penetrate into the micro cracks present in these fibres, making the fibres swell faster and eventually leading to failure of water uptake at higher temperature (Sombastsompop et al., 2004).

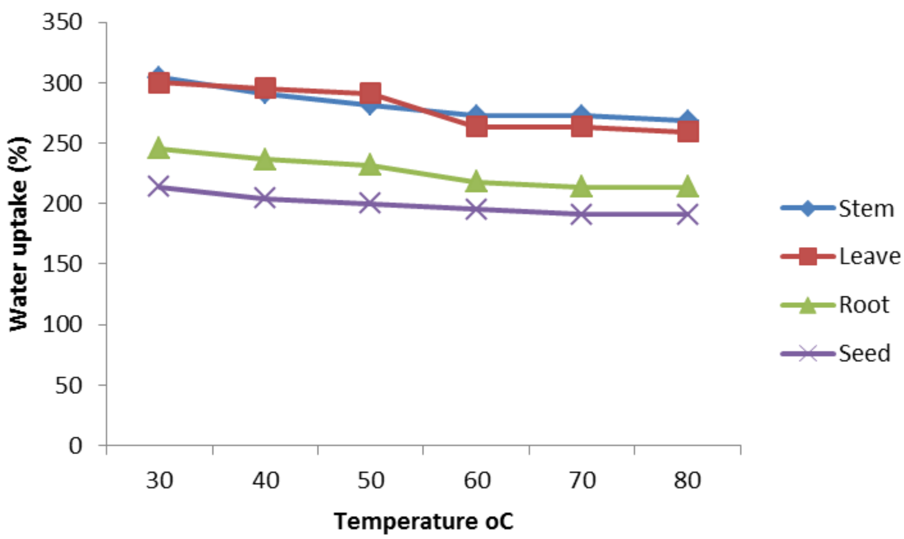

Figure 3: Effect of temperature on equilibrium mass % uptake of water at 30^{o}c

Effect of pH on water uptake by *Stereospermum kunthianum* plant Samples

The effect of pH on *Stereospermum Kunthianum* plant samples on water uptake is presented on Figure 4. It can be observed that the plant samples absorbed less water in acidic solution than the alkaline solution. This is due to the change in the surface topography of the plant fibers as a result of replacement of hydroxyl group by hydrophobic esters in which chemical modification takes place as the acid substitute the cell wall hydroxyl groups making the surface more hydrophobic. (Sampathkuma et al., 2012). In all the figures of the plant samples, it was observed that water up-take increases with change of the pH of the swelling medium from pH 2 to pH 6 and remain static at pH 7. As the pH of the medium increases from pH 8 to pH 12, there is significant increase of water absorption by all the plant samples. This is due to the fact that, at lower pH values the –$CONH_2$ groups do not ionize and keep the network at its collapse state. At high pH values it get partially ionizes and the charged –COOH groups repel each other leading to increase in swelling of the polymer .

Similar observation was reported by Nkafamiya , Barminas and Osemeahon (2011), that hydrogels are pH sensitive. Also, it was reported that the swelling of microgels, prepared with grafting of poly onto guar gum, increases when the pH of the medium changes from acid to alkaline because of the saponification of the –CONH2 to the –COOH group (Soppimath et al.,2001).

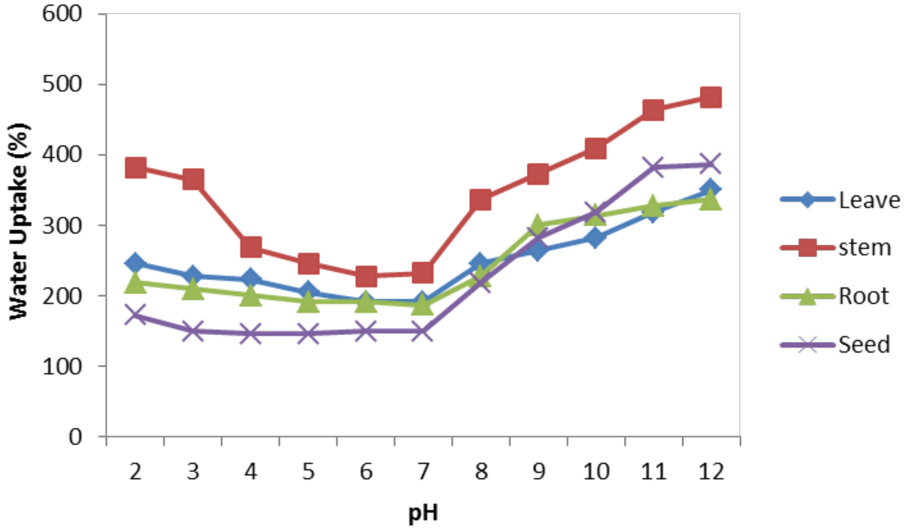

Figure 4: Effect of pH on equilibrium mass % of uptake of water at 30^o

Effect of Ionic Strength on Water uptake by *Stereospermum kunthianum* plant Samples

Figure 5 is the percentage water uptake by *Stereospermum kunthianum* plant samples at various Ionic concentrations from 0.1 M to 1.0 M. The result shown on this figure indicate that the water absorbency for the immobilised plant samples in various salt solutions decrease with increasing ionic strength of salt solution. This result is attributed to the decrease in the expansion of the polymer network which was caused by repulsive forces of the counter ions on the polymeric chain shielded by the ionic charge .Therefore, the difference of the osmotic pressure between the polymer network and the external solution increased with increased in the ionic strength of the saline concentration. This is possible due to the difference in the ionic osmotic pressure between the plant samples and the external solution (Lee and Lin, 2000).

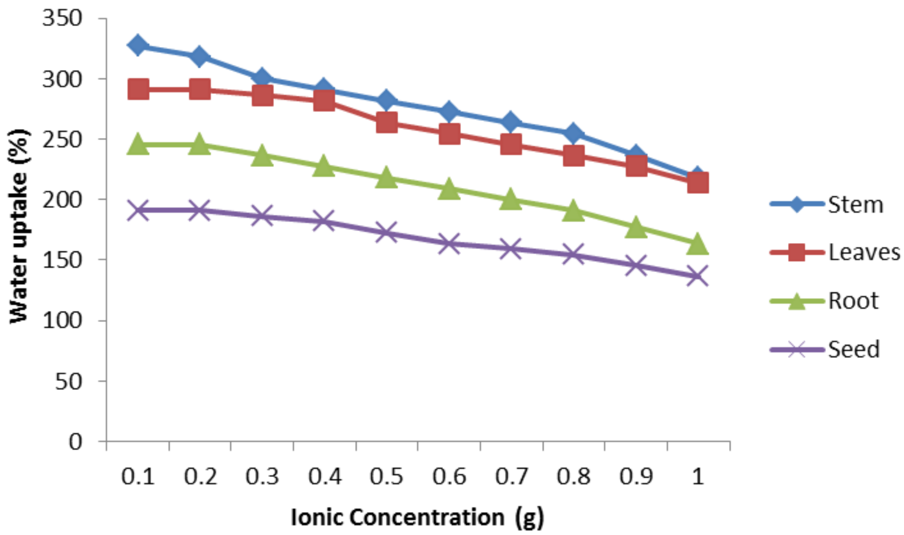

Figure 5: Effect of ionic strength on equilibrium mass % of uptake of water at 30^{o}C

IV. Conclusion

The effect of water uptake by *Stereospermum kunthianum* plant samples has been studied at room temperature under various conditions of concentration, temperature, kinetics, ionic strength, and pH. Immobilization of *Stereospermum kunthianum* plant samples (stem-bark, Leaves, Root and Seed) was achieved by encaging them within stable polymeric matrix of calcium alginate. The results obtained from the water uptake were satisfactory. There was an increase in water uptake by the bio sorbents as contact time, pH of the medium and the concentration of *Stereospermum kunthianum* plant samples increases. While a decrease in water uptake was recorded as the temperature and ionic strength increases. Therefore, since *Stereospermum kunthianum* stem bark has high water uptake ability, it may be a good biomas in the sorption of heavy metals in aqueous solution.

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