Bioremediation of Wastewater with Immobilized Dargaza (*Grewia Mollis*): Effect of Some Physical Properties

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Abstract: *The sorption capacity of immobilized Grewia mollis (IGM) for the removal of metal ions (Pb^{2+}, Zn^{2+} and Cu^{2+}) was investigated using Atomic Absorption Spectrophotometer (AAS). The sorption capacity was performed by batch experiments as a function of experimental parameters like effect of pH, contact time, ionic strength, initial metal ion concentration and temperature on sorption of metal ions from aqueous solution. The metal ion sorption capacity of immobilized Grewia mollis increases with increase in metal ions concentration and pH values but decreases with increase in ionic strength. The sorption rate was rapid and reached equilibrium within 30 minutes for Pb^{2+} and Zn^{2+} and 1hr for Cu^{2+}. The maximum sorption capacity for Pb^{2+}, Zn^{2+}, and Cu^{2+} was found to be 86.55, 54.95, and 58.83 respectively. The results from these studies show that Grewia mollis will be useful for removal of toxic metal ions from waste water and it can also be turned into an environmentally friendly and cost effective sorbent for wastewater.*
Keywords: *Immobilized Grewia mollis (GM), sodium alginate, metal ions, sorption.*

I. Introduction

The removal of toxic heavy metal ions from aqueous waste streams is currently one of the most important environmental issues being investigated(Oyedeji and Osinfade, 2010). Heavy metals are presently in the soil, natural water and air, in various forms and may become contaminant in food and drinking water. Some of them are constituent of pesticide, paints, fertilizers etc.

Heavy metals cannot be degraded or destroyed (Mona *et al.*, 2014*)* thus; they are dangerous because they tend to bioaccumulate. These compounds accumulate in living things any time they are taken up and stored faster than they are broken down. Exposure to heavy metals, even at trace level, is a risk to human beings. Rapid industrialization and urbanization has resulted in accumulation of heavy metals in the environment due to their waste disposal without any treatment (Khalil, 2012). Whenever toxic heavy metals are exposed to the natural eco-system, accumulation of metal ions in human bodies will occur through either direct intake or food chains (Omar *et al.*, 2011).

Physico-chemical methods such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery filtration, ion exchange and membrane technologies have been widely used to remove heavy metal ions from industrial waste water. These processes may be ineffective or expensive, especially when the heavy metal ions are in solutions containing in the order of 1 – 100 mg dissolved heavy metal ions. Other methods such as biosorption/ bioaccumulation for the removal of heavy metal ions may provide an attractive alternative to physico-chemical methods. As such, it is necessary to search for alternative sorbents, which are low-cost, often naturally occurring biodegradable products that have good adsorbent properties and low value to the inhabitants (Enemose*et al.,* 2013). Biosorption is emerging as a sustainable effective technology. Biosorption of heavy metals from aqueous solutions is a relatively new process that is proven very promising in the removal of contaminants from aqueous effluents. Adsorbent materials derived from low cost Agricultural wastes and plant materials can be used for the effective removal and recovery of heavy metal ions from waste water stream (Peter Papoh*et al.,* 2011).

Grewia mollis (Dargaza) is a shrub or small tree up to 20 ft. tall, of malvaceae family widely distributed within the northern and middle belt of Nigeria. Various part of the plant is used in food and medicine. In Nigeria, the stem bark powder or mucilage is used as a thickener in local cakes made from beans or corn flour commonly called "Kosai" and punkasau in Hausa (Nigeria), respectively. The dried stem bark is ground and the powder mixed with beans or corn flour thereby enhancing the texture of the food products. In addition, the mucilaginous property of the bark is used traditionally by the Yoruba people of Nigeria at Child birth.

Grewia mollis flower and young shoots are sometimes used as a soup or sauce vegetable. The infusion of the bark obtained by cold or hot maceration in water is used in beaten mud floors or mixed with the mud or

the walls of huts to give a smooth surface. Studies on*Grewia mollis* indicated the presence of tannins, saponins, flavonoids, glycosides, phenols, steroids and the absence of alkaloids. The presence of these chemical substances may enable IGM to take up water from aqueous solution and hence a potential candidate for sorption of metal ions from aqueous medium. This study therefore set out to evaluate the potential of IGM as a sorbent for the removal of metal ions from aqueous solution.

II. Materials And Methods

Sodium alginate, calcium chloride, sodium chloride, sodium hydroxide, hydrochloric acid, copper chloride, zinc chloride, lead chloride, were product from the British Drug House (BDH), while dried stem bark of *Grewia mollis* was collected at Karim-Lamido Local Government of Taraba State, Nigeria. All the materials were used as supplied.

Preparation of *Grewia mollis* (GM)

The hard outer part of the stem bark was removed by peeling manually and the inner soft tissue cut into pieces and dried to constant weight in an oven at 50^0C. The dried sample was pulverized using mortar and pestle, and sieved to obtain a fine powder. The sieved material was kept in a brown glass container for further use. 4.0 g of the stem bark was dissolved in 100 cm^3 of distilled water to obtain solution A.

Preparation of sodium alginate and calcium chloride

Sodium alginate was made by weighing 4.00 g and making it up to 100 cm^3 mark with distilled water in a volumetric flask and left overnight for complete dissolution to give solution B (Toti *etal.,* 2002). 0.12 M of calcium chloride was prepared according to a standard procedure described by (Wuyep *et al*., 2007).

Immobilization of the *Grewia mollis*

25 cm^3 of solution A and 25 cm^3 of solution B were mixed and stirred vigorously in 250 cm^3 beaker, to obtain a homogenous mixture. The mixture was subsequently poured into another beaker containing of 0.12 M calcium chloride solution. A retention time of 1 h was allowed for the reaction to obtain complete precipitation of the immobilized *Grewia mollis*. The precipitated blend solid was removed and allowed to dry at room temperature (30°C). The dried solid mass was stored in a polythene bag for further use (Wuyep et al., 2007).

Determination of metal ion in solutions

The metal ion determination in solution was studied using the method reported by (Osemeahon et al 2007). The metal ions of interest include Pb^{2+}, Zn^{2+} and Cu^{2+} 200. Concentration of each of the metal ion (ppm) was prepared. From aforementioned concentration, 50 cm of solution of the metal ion was taken into the conical flask; 0.2 g of dried *Grewia mollis* was added and then shaken vigorously for 2 h using flask shaker (Stuart Scientific, SF1). The solution was filtered and the residual metal ion concentration determined using Atomic Absorption Spectrophotometer (AAS) (210 VGP Buck Scientific).

Grewia mollis sorbent sorption capacity

Standard method was employed for the equilibrium studies of sorption capacity of the sorbent. 0.2 g of the sorbent was shaken with 50 cm^3 of Pb^{2+} ion solution at room temperature for 2 h. The synthetic waste water sample was filtered and analyzed for residual metal ion concentration using AAS. This process was repeated for all the metal ions studied(Charamathy *et al*., 2001)

Effect of pH on sorption capacity

The sorption capacity of *Grewia mollis* at 30^0C was investigated at different pH values (1.0 to 6.0). 2.0 M hydrochloric acid and 2.0 M sodium hydroxide was used to adjust the solution pH as the need arises. The residual metal ion was measured as previously stated (Charamathy *et al*., 2001).

Effect of the ionic strength on sorption capacity

To ascertain the effect of ionic strength on sorption in different concentrations of NaCl solution 0.1 to 2.0; % w/w was used. 0.2 g of the sample was added to 50 cm^3 of the prepared NaCl solution and the equilibrium concentration of the residual metal ion determined.

Effect of Temperature on Sorption Capacity

The effect of temperature on the sorption capacity of the immobilized solid was investigated. 0.2 g of the dried immobilized *Grewia mollis* was shaken with 50 cm^3 of the metal ion solution at 30^0 C. The synthetic waste water was filtered and analyzed for residual metal ion concentration. This process was repeated at different temperature ranging from 30 to 90^0 C.

Effects of the contact time on sorption capacity

The kinetics of the sorption for the various metal ions was studied as a function of initial metal ion concentration at 30^0C. 0.2 g of the immobilized *Grewia mollis* and 50 cm^3 of the metal ion solution for each of the ions were prepared. Each mixture was shaken constantly in a shaker over time interval ranging from 0.5 to 24 h. At the end of each contact time, the mixture was removed, filtered and its concentration was determined using AAS. The solution was filtered and analyzed for residual metal ion (Osemeahon *et al*., 2007).

Effect of the initial metal ion concentration on sorption capacity

The effect of the initial metal ion concentration on the sorption capacity of different metal ion was determined at 30^0C. 0.2 g of the dried sorbent was prepared and shaken until equilibrium was achieved with samples consisting of 50 cm^3 each of different metal ion concentrations ranging from 5 to 100 ppm. The synthetic wastewater was filtered and analyzed for residual ion concentration (Osemeahon*et al*., 2007).

III.   Results And Discussion

Immobilization of *Grewismollis* stems Bark

The purpose of immobilization is to cage the sample, increase the mechanical strength, density, porosity and open more pores. *Grewiamollis* was immobilized by caging it within the matrix of sodium alginate which contains hydroxide (--OH) groups. The cross-linking of the OH groups in SA with calcium ion forms a network through bridge (Xiao et al., 2002). This insoluble network immobilizes soluble stem bark dargaza gum, and the insoluble biomass to obtain the immobilized *Grewismollis*stem bark (IGM).

Sorbent Sorption Capacity

The sorbent sorption capacity for the metal ions (Pb^{2+}, Zn^{2+}, Cu^{2+})is shown in Figure 1. The result shows that *Grewiamollis* has sorption capacity for the three heavy metal ions. The uptake of the metal ion is higher in Pb^{2+} and relatively lower in Zn^{2+} and Cu^{2+}. The sorption capacity for the metal ion is 86.55, 54.95, and 58.83 respectively. The difference in sorption capacity of the metals is attributed to differences in metal affinity to the sorbent to form ligand. It is also as a result of differences in solubility (hydration energy) of the metal ions in the sorbent (Khalil et al., 2012). The differences in electronegativity metal may also affect the sorption behavior of certain ions. Metals of higher electronegativity can adsorb more easily (Enemose et al., 2013).
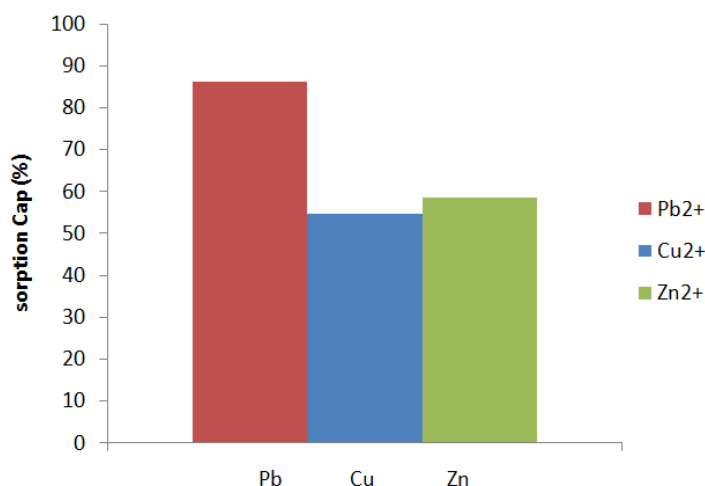

Figure 1: Sorption capacity of metal ions

Effect of Concentration of *Grewiamollis* Bark on Sorption Capacity

Figure 2. Shows that the uptake by sorbent increases with increase in the concentration of the *Grewiamollis* this is an expected result because as the sorbent concentration increases, the number of sorbent particles surrounding the metal ions or ratio of sorbent binding sites to metal ions increases, therefore, these sites attach more ions to their surfaces. Increase in sorption with sorbent concentration can be attributed to increased adsorbent surface area and sorption sites. (Kailas, 2010)**.** Also due to the availability of more binding sites for complexation of metal ions (Prabakaran and Arivoli, 2012).
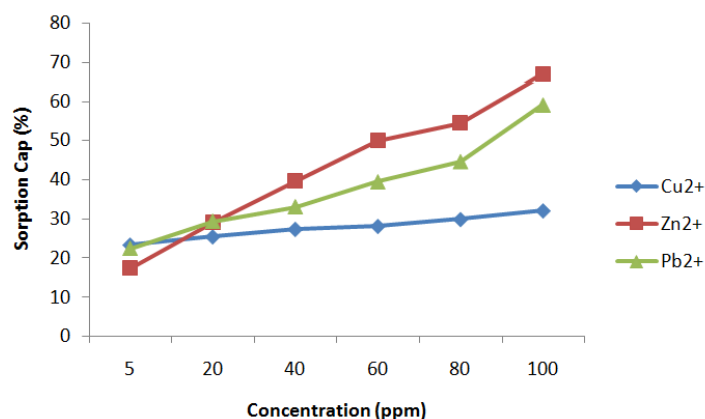
Figure 2: Effect of concentration of *Grewiamollis* bark on sorption capacity.

Effect of pH on Sorption Capacity

The effect of pH is presented in Fig. 3. The pH of solution of metal ion sorption on the immobilized *Grewiamollis* was studied at 30^0C and varying the pH of metal solution from 1.0 to 6.0. From the graph , the result shows that Cu^{2+} and Zn^{2+} has maximum sorption capacity at pH 3 while Pb^{2+} has its maximum sorption capacity at pH 4. This can be justified on the basis that at lower pH values(1-2), the H^+ ions compete with the metal cation for the adsorption sites in the system, which in turn leads to partial releasing the later (Abdel-Ghani, *et al.,* 2007).

At low pH (below 3), there was excessive protonation of the active sites on IGM surface and this often refuses the formation of links between metal ions and the active site. At moderate pH values (3 to 6), linked $H^+$is released from the active sites and adsorbed amount of metal ions is generally found to increase. Moreover, at higher pH values (above 6), precipitation is dominant and both ion exchange and aqueous metal hydroxide formation may become significant mechanisms in the metal removal process. In practice, metal precipitation is generally not a stabilized form of heavy metal as the precipitation can sometimes be very small in size, and upon the neutralization of the effluent from the wastewater treatment plant, the solubility of the metals increases resulting in a recontamination of the waste outlet stream (Jaber,2013).
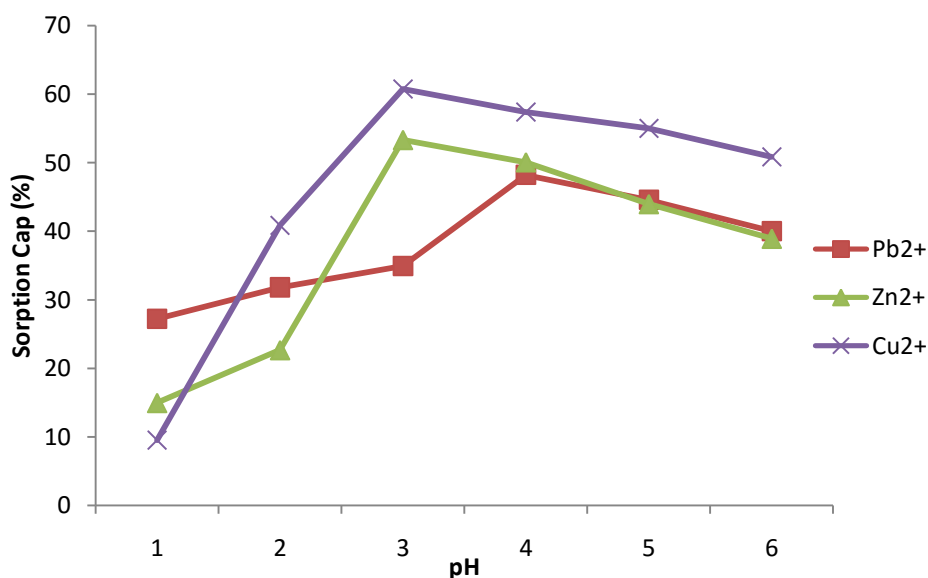

Figure 3: Effect of pH on sorption capacity

Effect of Time on Sorption Capacity

The effect of contact time on the sorption of metal ion is shown in figure 4. The sorption of Pb2+ and Zn2+ was rapid , optimum sorption was obtained after 30 minutes while Cu2+ reached equilibrium after 1 h . The removal of metal ion was rapid in the initial stage of contact and gradually decreased with time until equilibrium was reached. The initial rapid uptake was due to diffusion of metal ions onto the surface of sorbent. This may be attributed to the highly porous structure of sorbents and the particle size, which provide large surface area for the sorption of metals on the binding sites. The sorption process was faster, it could be because

of the largest amount of metal ions attached to the sorbent within 30 minutes. The constant stage probably due to the less availability of active sites thus, the sorption becomes less efficient in constant stage. The non-uniform pattern of sorption observed could be attributed to non-uniform surface area or binding of the biomass (Aishatu and Barminas, 2015)
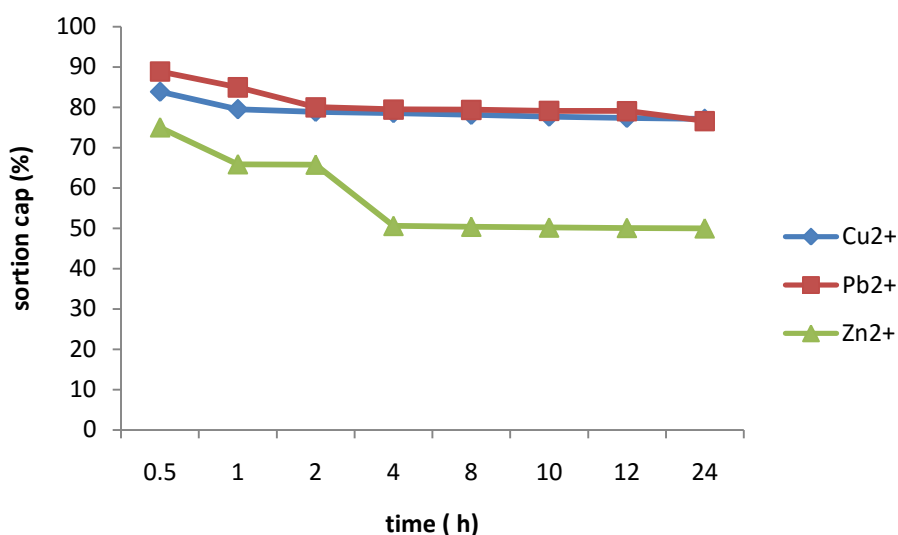

Figure 4: Effect of time on sorption capacity

Effect of Temperature on Sorption Capacity

Results of metal ion sorption experiments carried out at different temperatures ranging from $30\text{-}90^0$C are shown in figure 5. Temperature is a crucial parameter in adsorption reactions.It can be seen that the sorption capacity decreases with anincrease in temperature for all metal ions studied. From the graph, the maximum sorption capacities for Pb^{2+},Zn^{2+} and Cu^{2+} at 30^0C are 85.2, 53.35 and 50.35. The decrease in sorption capacity with increase in temperature may be attributed to:

i.   Sportive processes are exothermic; therefore, an increase in temperature should reduce sorption.
ii. The change in solubility of the solute as a result of the temperature change.
iii. Reduction in size of sorbent with temperature which leads to formation of less porous sorbent with less bonding sites and thus lowers the distribution ratio(Kd) values at high temperature. (Alessandro, 2001)
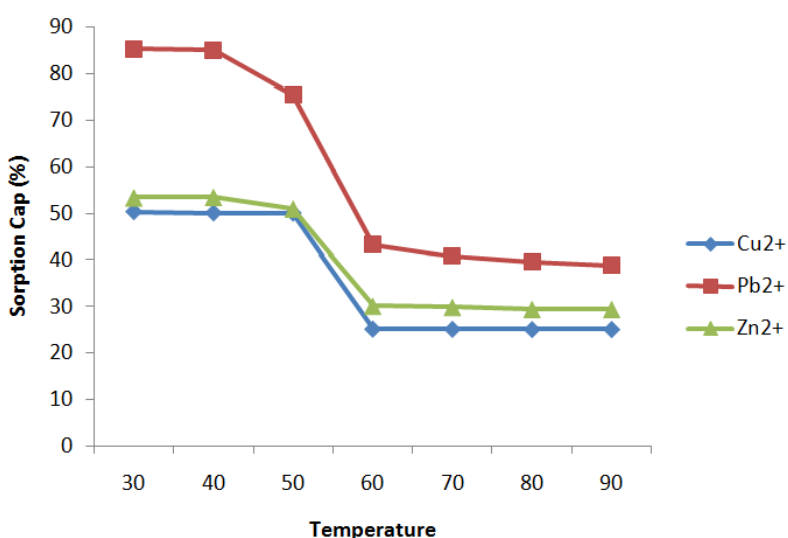

Figure 5: Effect of temperature on sorption capacity

Effect of Ionic Strength on Sorption of metal ions

Dissolved salt are usually found in natural water and industrial waste which competes with metal ions for sorption sites on the sorbent. This decreases activity of metal ions in solution due to increase in non-ideality of solution with ionic strength. This non-ideality is due to increasing electrostatic interaction and resulting

formation of ion pairs. Since metal ion sorption is governed by its activity in solution, decreased activity in solution means decreased adsorption on sorbent. Effect of ionic strength on sorption is shown in figure 6. The decrease in metallic ion sorption with the increase in the ionic strength is generally attributed to: (i) the increase in competition for sorption sites among the cation index and the metallic ions.

(ii) Changes in the free ion activity. (iii) The type of surface, surface charge effect and alterations in the electrostatic potential on the adsorption plane and; (iv) the type of metal (Marico 2011). Thus, pretreatment of is often recommended for the removal of interfering ions to improve sorption efficiency (Kuyucak*et al.,* 2008).
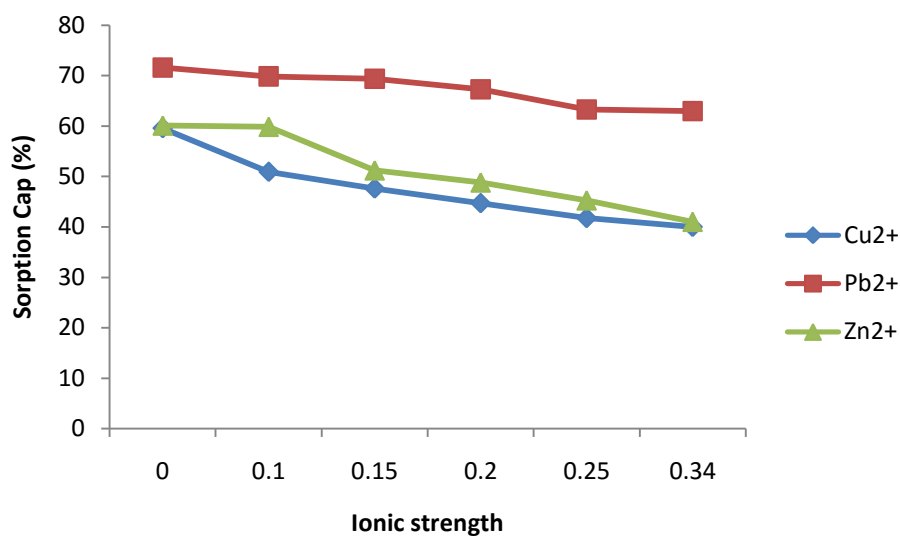

Figure 6: Effect of ionic strength on sorption capacity

Effect of Initial metal ion Concentration on Sorption Capacity

       In Figure 7, shows the sorption capacities of the sorbent as a function of the initial ion concentration. The initial concentration provides an important driving force to overcome all mass transfer resistance of metal between the aqueous and solid phases (Kailas, 2010)

       Sorption and removal of heavy metals by (IGM) largely depend on the initial concentration of metals in the solution. In this study, metal sorption generally increases with increase in metal concentration in the solution.The rapid increases in the uptake of all the metal ions can be attributed to the interaction between the metal ions and the active sites of the adsorbent. This is because the higher the concentration of metal ions, the higher the amount of Pb, Cu and Zn present in the solution, thus the more adsorption of the metal ions occur on the adsorption site of the absorbent (Aishatu and Barminas,2015).
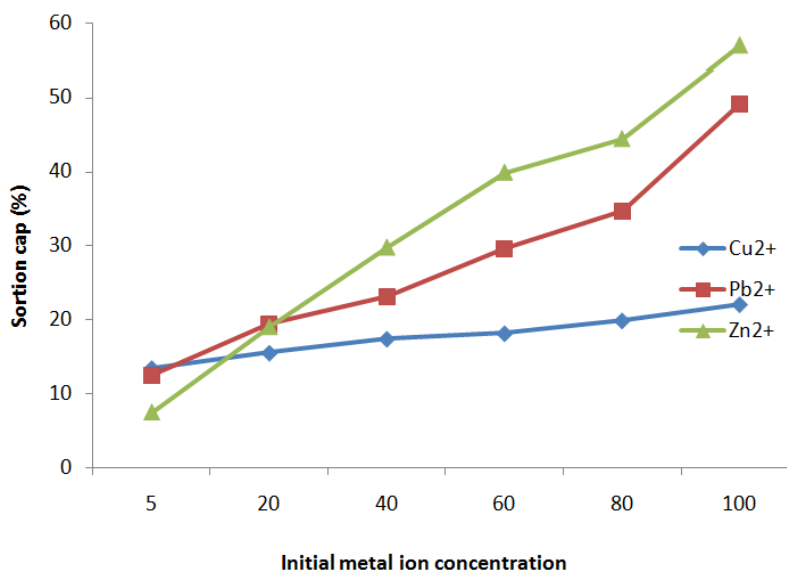

Figure 7: Effect of initial metal ion concentration

IV. Conclusion

Grewiamollis stem bark was immobilized and the sorption behavior in aqueous solution was studied. Sorption capacities of 86.55%, 54.95% and 58.85% for Pb^{2+}, Cu^{2+} and Zn^{2+} respectively were obtained. It was observed that the uptake of metal ion by IGM decreases as the ionic strength of the external solution increases. While on the other hand, an increase in the initial metal ion concentration resulted to increase metal ion uptake. The study is an indication that IGM can be used for bioremediation of wastewater.

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