Full Length Research Paper

Evaluation on the application of immobilized konkoli (*Maesopsis eminii*) immobilized leaves for the removal of Pb^{2+}, Cd^{2+} and Zn^{2+} in aqueous solution

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Calcium alginate immobilized konkoli leaves (KIL) was studied as a bio-sorbent for the sorption of Pb^{2+}, Cd^{2+} and Zn^{2+} in aqueous solution. The sorption capacities for Pb^{2+}, Cd^{2+} and Zn^{2+} were found to be 98.52, 90.1 and 81.34% respectively. The sorption behavior with respect to contact time, initial pH, ionic strength and initial metal ion concentration were investigated in order to determine the optimum sorption conditions. The result showed that the metal ion uptake by KIL decreases with increasing ionic strength while increase in initial metal ion concentration led to an increase in metal ion uptake. Maximum sorption was found to occur at pH 6 for Pb^{2+} and pH 5 for both Cd^{2+} and Zn^{2+}. The sorption capacity of KIL is encouraging and therefore may be used in the bio-remediation of wastewaters.

Key words: Konkoli leaves, immobilization, sodium alginate, sorption, metal ions.

INTRODUCTION

Fresh water quality and availability remain one of the most critical environmental and sustainability issues of the twenty first century (Adebo and Adetonyinbo, 2009). Water will continue to be a major issue with definite and profound importance on our live and that of the planet earth. The availability of safe and reliable source of water is an essential pre-requisite for sustainable development.

However, with the ever increasing scientific and industrial developments, man is continually exposed to some health hazards from heavy metal through water intake among other sources. 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. The concentration of these metals needs to be reduced to meet the ever changing legislative standards. Wuyep et al. (2007) reported that the metals of most immediate concern are cadmium, cobalt, lead, nickel, mercury and zinc. The presence of such metals (>5 mgcm^{-3}) (Wuyep et al., 2007) in aquatic environment,

causes severe damage to aquatic life, killing microorganisms during biological water purification process. Moreover, these metals have exacting consequences on human such as brain damage, reproductive failures, nervous system failures, tumor formation etc (Wuyep et al., 2007).

Conventional processes for removal of metals from industrial waste include chemical precipitation, oxidation-reduction, filtration, electrochemical technique and other sophisticated separation procedure using membranes. These processes are expensive and time consuming and have inherent limitations (Akporhonor and Egwaikhide, 2007; Adebo and Adetonyinbo, 2009; Osemeahon et al., 2007). The need for economical and effective method of removing heavy metals from waste water has resulted in the search for unconventional materials that may be useful in reducing the levels of accumulation of heavy metals in the environment. Biological methods such as bio-sorption or bio-accumulation strategies for the removal of metal ions may provide an attractive alternative to existing technologies (Akporhonor and Egwaikhide, 2007).

Konkoli tree is one of the trees that grow wild in the south, east and middle belt of Nigeria. The seed gum is widely used as a thickener in soup and other traditionally

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baked products, primarily because of high viscosity, binding and swelling propensity (Barminas and Eremosele, 2002; Osemeahon et al., 2007).

In our earlier experiments (Osemeahon et al., 2007, 2008, 2011), we reported the potential use of konkoli seed gum for various industrial products. However, konkoli seed is produce relatively in small quantity and only once a year for both man and animals to compete for. Whereas konkoli leaves are abundantly produced and are available all year round. To the best of our knowledge, no report is presently available on the industrial application of konkoli leaves which are presently wasting away in the wild. In this experiment, we set out to evaluate the application of immobilized konkoli leaves as a bio-sorbent for the removal of lead, cadmium and zinc metal ion from aqueous solution.

MATERIALS AND METHODS

Sodium alginate, calcium chloride, sodium chloride, sodium hydroxide, hydrochloric acid, cadmium chloride, zinc chloride, lead chloride, were product from the British Drug House (BDH), while konkoli leaves were purchased from Taraba State of Nigeria. All the materials were used as supplied.

Preparation of konkoli leaves

The konkoli (*Maesopsis eminii*) leaves were sun-dried, pounded in a mortar into powder and sieved through 100 μm sieve screen to produce a fine powder. The sieved material was packed in a polythene bag for further use. 4.0 g of the leave was mixed with 100 cm^3 of distilled water to obtained 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 et al., 2002). 0.12 M of calcium chloride was prepared according to a standard procedure described by (Wuyep et al., 2007).

Immobilization of the konkoli leaves

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 konkoli leave. 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 chosen for this study were Pb^{2+}, Zn^{2+} and Cd^{2+}. A concentration of 200 ppm of each of the metal ion was prepared. From aforementioned concentration, 50 cm of solution of the metal ion was taken into the conical flask; 0.2 g of dried KIL was added and then shaken vigorously for 2 h by using flask shaker (Stuart

Scientific, SF1). The solution was then filtered and the residual metal ion concentration determined using Atomic Absorption Spectrophotometer (AAS) (210 VGP Buck Scientific) (Osemeahon et al., 2007).

KIL sorbent sorption capacity

For this equilibrium studies, 0.2 g of the sorbent was shaken with 50 cm^3 of Pb^{2+} ion solution at room temperature for 24 h. The synthetic waste water sample was filtered and analyzed for residual metal ion concentration using AAS (Charamathy et al., 2001). This process was repeated for all the metal ions studied.

Effect of pH on sorption capacity

The sorption characteristics of the KIL at different pH values (1.0 to 6.0) were investigated at 30°C. 1.0 M hydrochloric acid and 1.0 M sodium hydroxide was used to adjust the solution pH as the case may be. The residual metal ion was measured as stated previously (Charamathy et al., 2001).

Effect of the ionic strength on sorption capacity

Useful information regarding the effect of the ionic strength was obtained by measuring the sorption of KIL in various concentrations of NaCl solution (0.1 to 2.0; % w/w). 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 (Wuyep et al., 2007).

Effects of the contact time on sorption capacity

To determine the kinetics of the sorption for the various metal ions, several set of samples consisting of 0.2 g of the dried sorbent and 50 cm^3 of the metal ion solution for each of the ions was prepared. As the samples were undergoing agitation (with the flask shaker), they were removed one after the other at a predetermined time interval ranging from 0.5 to 24 h for analysis. The solution was filtered and analyzed for residual metal ion. This was done for all metal ions at 30°C (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 samples consisting of 50 cm^3 each of different metal ion concentrations ranging from 5 to 100 ppm, but each containing 0.2 g of the dried KIL was prepared and shaken until an equilibrium was achieved at 30°C. The synthetic waste water was filtered and analyzed for residual ion concentration (Osemeahon et al., 2007).

RESULTS AND DISCUSSION

KIL sorption capacity

The equilibrium sorption for Pb^{2+}, Zn^{2+} and Cd^{2+} of KIL are shown in Figure 1. It was observed that KIL can take up a significant quantity of Pb^{2+}, and relatively, the lowest amount is from Zn^{2+}. The values of 98.52, 91.7 and 81.34% for Pb^{2+}, Cd^{2+} and Zn^{2+} respectively were found.
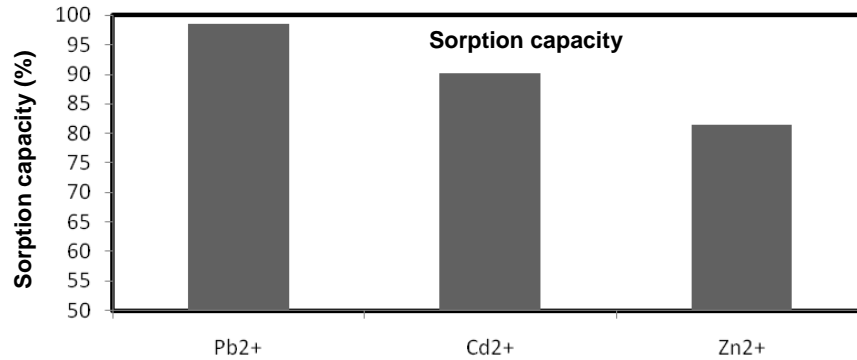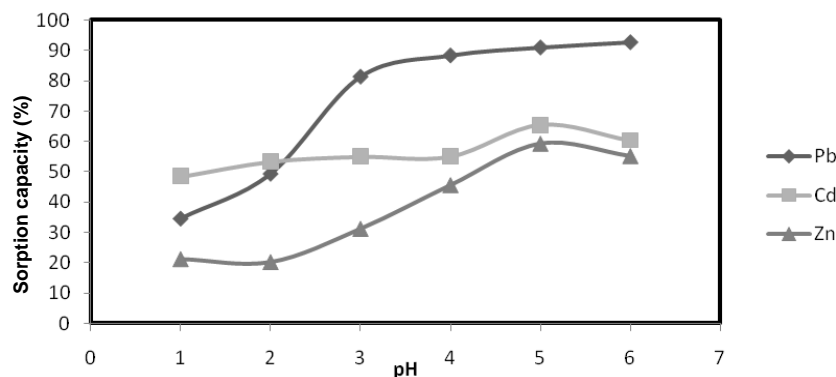
Figure 1. Sorption capacity for Pb^{2+}, Cd^{2+} and Zn^{2+} by KIL.

Figure 2. Effect of pH on sorption of Pb^{2+}, Cd^{2+} and Zn^{2+} by KIL.

The report from the present study are comparable with those reported for konkoli seed gum and other similar studies (Osemeahon et al., 2007; Lee and Lin, 2000; Charamathy et al., 2001). Although, the sorption capacity recorded for lead in this work (98.52%) is relatively lower than that of konkoli seed gum (99.8%) reported by Osemeahon et al. (2007), by a very small margin. The differences observed in the sorption capacities for the different metal ions can be explained in terms of the differences in hydration free energy, the ability of metal to form covalent bond with ligand, the metal polymeric cations within the membrane structure and the nature of the surface sites available (Cooper et al., 2002).

Effect of pH

pH plays an important role in the sorption of the metal ions by different sorbents. Figure 2 depicts the effect of pH on removal of metal ions. It was seen at low pH values that the sorption is low, but as the pH of the solution increases, the metal ions uptake increases, however, at different level depending on the metal. The trend of result obtained was similar to the ones reported by other workers (Souag and Buayada, 2009; Osemeahon et al., 2007; Wuyep et al., 2007; Chen and

Wu, 2000).

The optimal pH of sorption for the different metal ions is 6 for Pb^{2+} and 5 for Cd^{2+} and Zn^{2+}. The pH of the sorption media is related to the metal sorption - mechanism of the surfaces from the water and reflected the nature of the physiochemical interaction of the ions in solution and nature of the sorption sites (Osemeahon et al., 2007). Therefore, it can be suggested that the differences in the pH optima for different metal ions could probably be due to the differences solution chemistry of the metal ions (Mcox et al., 2002).

The pH influences the equilibrium of metal ion uptake in aqueous solution. The counter reaction of the competing hydrogen ion as well as the chemistry of the active binding sites of the sorbent is responsible for the depression in sorption capacity. Increasing the pH leads to precipitation of insoluble hydroxide or hydrated oxide, thereby lowering the metal ion availability for sorption. On the other hand, a decrease in pH results in the increase in the hydrogen ion concentration and hence possible competition for binding sites (Yen-Peng and Sung, 2000).

Effect of time on sorption

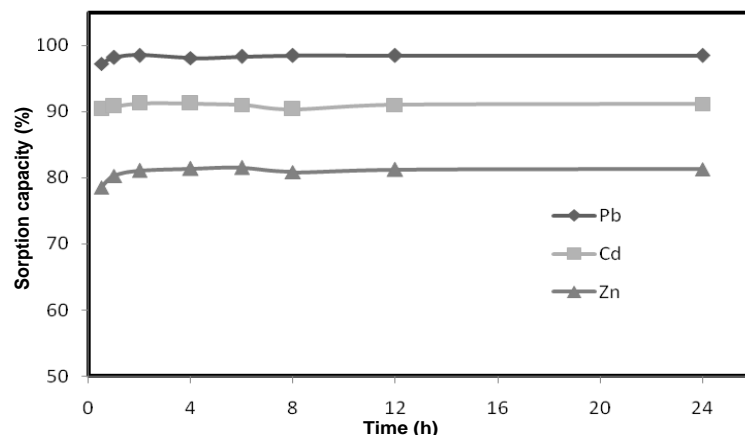The effect of contact time on sorption capacity is shown

Figure 3. Effect of contact time on sorption of Pb^{2+}, Cd^{2+} and Zn^{2+} by KIL.
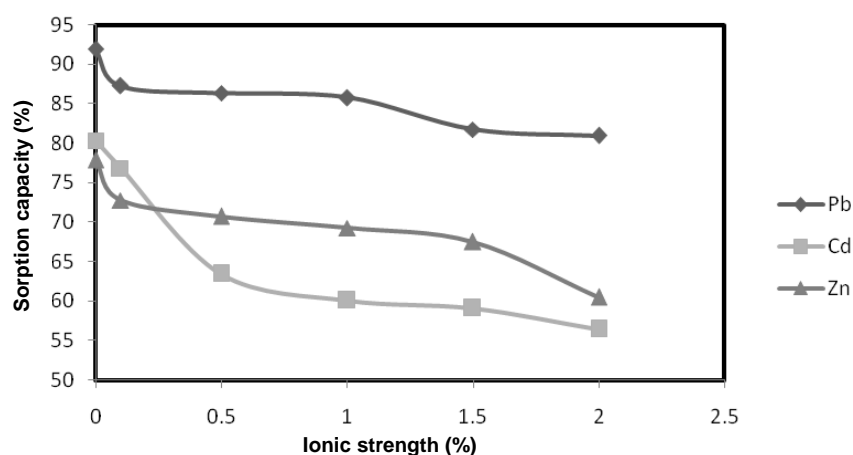

Figure 4. Effect of ionic strength on sorption of Pb^{2+}, Cd^{2+} and Zn^{2+} by KIL.

in Figure 3. Saturation was reached after 2 h of contact time for all the metal ions, but high sorption rate were observed during the first 30 min. Equilibrium time of 30 min was recorded for Pb^{2+} and 2 h for the rest of the metal ions.

The rapid sorption of metal ions is attributed to highly porous structure of the sorbent which provide readily access and large surface area for the sorption of the metal ions to the binding site (Aiabuk et al., 2007). This result demonstrates that the sorbent (KIL) can compete favorably with other industrial sorbents in terms of kinetics.

Effect of ionic strength on sorption

Industrial waste and natural water often contains dissolved salt which competes with heavy metal ions for binding sites on the sorbent carbon chain (Osemeahon et al., 2008; Cox et al., 2000), hence, there is need to

investigate the level of influence of this factor on the sorption capacity of KIL.

The effect of the ionic concentration on the removal of the heavy metal ions from the waste water by KIL is represented in Figure 4. It was observed that the sorbent showed a decrease in sorption capacity with increase in initial ion concentration for all the metal ions studied.

The decrease in sorption capacity with increasing ionic strength is primarily attributed to the difference in the ionic osmotic pressure between the sorbent and the external solution (Lee and Lin, 2000; Osemeahon et al., 2008). The difference in osmotic pressure between the sorbent and the external solution decreases as the ionic strength of external solution increases. Therefore, the sorption of metal ion decreases when the ionic strength of external solution increases (Lee and Lin, 2000). From this experiment, the coexistence of metal ions in same solution caused the interference with the performance of KIL sorbent. Therefore a pretreatment of the effluent will remove the interfering ion and this appears to improve
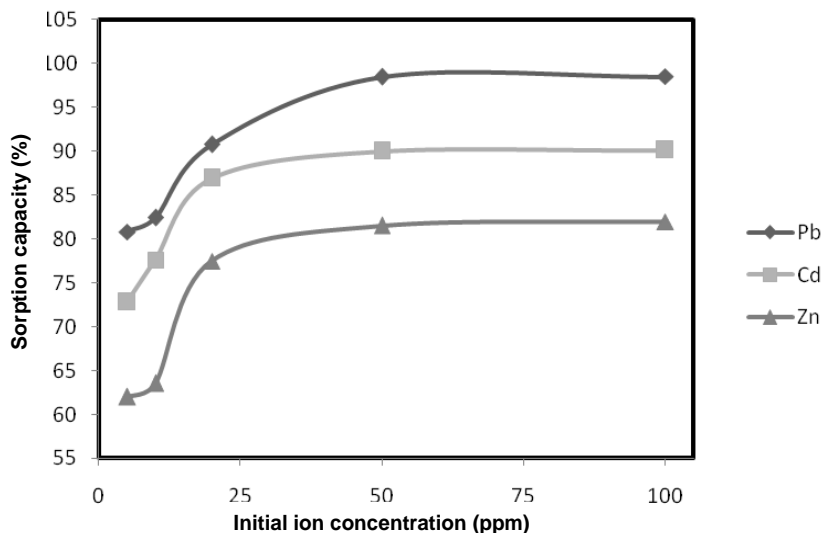
Figure 5. Effect of initial ion concentration on Pb^{2+}, Cd^{2+} and Zn^{2+} by KIL.

the efficiency of the sorbent (Osemeahon et al., 2008).

Effect of initial ion concentration

The result of metal ions sorption by the KIL as a function of initial metal ion concentration is shown in Figure 5. It was observed that the sorption efficiency of the metal ions by the sorbent increases with initial ion concentration but leveled up at certain point of the initial ion concentration. This behavior can be explained in term of increase in flux of the metal ion. The flux of the metal ion varies directly with the metal ion concentration, and hence, there should be an increase in flux with increase in initial concentration as reported by Iulia et al. (2007). The constant regime observed for all metal ions is explained as the point of saturation.

One of the problems of using conventional methods for the removal of the metal ions from the aqueous systems is effectiveness of the sorbent when the metal ion is present at a very low concentration (Asiagwu et al., 2009). The behavior of KIL even at low concentration of 5 ppm (removal of 80.8, 72.8 and 62% for Pb^{2+}, Cd^{2+} and Zn^{2+} respectively) shows that KIL sorbent can even be used at low metal ion concentration. This may reduce the present problem associated with most sorbents performance at low metal ion concentration.

Conclusion

KIL were immobilized and the sorption behavior in aqueous solution was studied. Sorption capacities of 98.52, 90.1 and 81.34% for Pb^{2+}, Cd^{2+} and Zn^{2+} respectively were obtained. It was observed that the uptake of metal ion by KIL decreases as the ionic strength of the external solution increases. While on the other hand, an increase in the initial metal ion concentration gave rise to increase metal ion uptake. The study revealed that KIL has potential for bioremediation of wastewater.

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