Evaluation Of Sorption Behavior Of Immobilized Karkashi Leaves (Sesamum Indicum) On Pb^{2+}, Cu^{2+} And Zn^{2+} In Aqueous Solution

S. A. Osemeahon, M. A. Hamma'Adama, A. M. Kolo, I. J. Opara

ABSTRACT: The sorption capacity of Immobilized karkashi leaves (IKAL) for the removal of metal ions (Pb^{2+}, Cu^{2+} and Zn^{2+}) were studied using batch experiments. The residual metal ion concentrations were investigated using atomic absorption spectrophotometer (AAS). The influence of factors such as contact time, initial concentration, ionic strength, pH and temperature were investigated. The metal ion sorption capacity by IKAL decreases with increasing ionic strength but increases with increasing pH values and initial metal ion concentration. The sorption rate for the metal ions (Pb^{2+}, and Cu^{2+}) was rapid and reached equilibrium within first 30 minutes while equilibrium was established within 1hr for Zn^{2+}. The maximum sorption capacity for Pb^{2+}, Cu^{2+} and Zn^{2+} were found to be 80.75%, 40.60% and 39.55% respectively. From this study the sorption capacity of IKAL sorbent showed that the abundantly wasted Karkashi leaves could be turned into an environmentally friendly and cost effective sorbent for the removal of heavy metal ions from wastewater.

Keywords: Immobilization, karkashi leaves, heavy metal ions, sorption capacity.

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Introduction

Heavy metals are generally recognized to be a threat towards humans and ecosystems because of their high-potential toxicity (Rameshet al., 2013). They are usually stable and non-biodegradable within the ecosystem. As a result, they tend to bioaccumulate in living tissues thereby causing some serious health concerns (Lukman et al., 2013). Human exposure to heavy metals has risen dramatically as a result of an exponential increase of their use in several industrial, agricultural, domestic and technological applications(Paul et al.,2012).Heavy metals are the main cause of water pollution as these are not biodegradable and accumulate in food chain (Seema and Savita, 2014).Due to the discharge of large amounts of metal-contaminated wastewater, industries bearing heavy metals, such as Cd, Cr, Cu, Ni, As, Pb, and Zn, are the most hazardous among the chemical-intensive industries. Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders (Barakat, 2011). Therefore it is necessary to treat metal contaminated wastewater prior to its discharge to the environment. Wastewater regulations were established to minimize human and environmental exposure to hazardous chemicals**.**

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Removal of heavy metals from industrial wastewaters can be accomplished through various treatment options, including such unit operations as chemical precipitation, coagulation, complexation, activated carbon adsorption, ion exchange, solvent extraction, foam flotation, electro-deposition, cementation, and membrane operations. **(**Gunatilake, 2015). Generally, these processes are efficient in removing the bulk of metals from solution at high or moderate concentrations. However, the shortcomings of most of these methods are the high operational and maintenance costs, generation of toxic sludge and complicated procedure involved in the treatment. (Ferda and Selen, 2011).Also chemical processes make metal recovery difficult and increase the pollution load on the environment. These constraints have caused the search for alternative methods that would be efficient for metal sequestering. Such a possibility offers a method that uses sorbents of biological origin for removal of heavy metals from aqueous solution based on metal binding capacities of various biological materials of little or no cost (Jimohet al., 2011). Karkashi plant is a flowering plant in the genus sesamum. It is an annual plant growing 50 to 100 cm (1.6 to 3.3ft) tall. The flower may vary in colour with some being white, blue or purple. The fruit naturally splits opens to release the seeds by splitting along the septa from top to bottom or by means two apical pores, depending on the varietals cultivars. The useful parts in the Sesame plant are the leaves and seeds. It is used primarily as soup thickeners and other traditional foods products in Nigeria mainly because of their high viscosity, binding and swelling propensity. At present, only a small fraction of this plant is utilized and the rest left to waste away in the wide. The aim of this research therefore is to immobilize karkashi leaves for the sorption of metal ions (Zn^{2+}, Cu^{2+}, Pb^{2+},) in aqueous solution for possible application in wastewater remediation.

MATERIAL AND METHODS

Calcium Chloride ($CaCl_2$), sodium Alginate (Na-Alg), Sodium Chloride, sodium hydroxide, hydrochloric acid, copper chloride, zinc chloride, lead chloride, were products from the British Drug House (BDH). The karkashi leaves

was obtained from Mayor-Ranewo ward, Taraba State, Nigeria.

Preparation of Sodium Alginate and Calcium Chloride

Sodium alginate was prepared by dissolving 4.0 g in 100 cm^3 of distilled water in a volumetric flask. This was left overnight for complete dissolution to give 4% w/w. 0.12 M $CaCl_2$ was prepared with distilled water in a 250 cm^3 volumetric (Osameahon, 2011).

Preparation of Karkashi Leaves

The karkashi leaves were dried at room temperature 30^0C. It was then pounded in a mortar into powder and sieved through 100µm sieve screen to produce a fine powder. The sieved material was packed in a polythene bag for further use. 4.0 g of the leaves powder was dissolved in 100 ml of water.

Procedure for immobilization of Karkashi Leaves

The standard procedure reported by (Osamehon et al 2011) was employed. 25 mL of viscous layer of dissolved karkashi was mixed with 25 ml of 4% stock solution of sodium alginate and stirred vigorously in a 250 ml beaker to obtain a homogeneous mixture. The mixture was subsequently poured into another beaker containing 30 ml of 0.12 M calcium chloride solution. The reaction was allowed retention time of 1 hour for complete precipitation of immobilized Karkashi leaves. The precipitated solid was filtered and allowed to dry at room temperature (30^0C). The dried solid mass was stored in a polythene bag for further use.

Determination of Metal ions in Solution

A concentration of 200 ppm of each of the metal ion under study (Pb^{2+}, Cu^{2+} and Zn^{2+}) was prepared with distilled water as reported by (Barminas et al, 2005). From the stock 50 ml of solution of metal ion was taken into a conical flask; 0.2 g of dried immobilized karkashi was added and then shaken vigorously for 2 hours using flask shaker (Model: Stuart Scientific, SFI). The solution was then filtered and the residual metal ion concentration determined using atomic absorption spectrophotometer (Model VGP-210).

Sorption Capacity of Immobilized Karkashi

0.2 g of the immobilized karkashi (Sorbent) was shaken with 50 ml of 200 ppm of metal ion solution at room temperature (30^0C) for 24 hours as similarly reported by (Charmarthy et al, 2001). The synthetic wastewater sample was filtered and analyzed for residual metal ion concentration using AAS model VGP-210.

Effect of pH On Sorption Capacity

The effect of pH on the sorption capacity of immobilized karkashi leaves was investigated at room temperature (30^0C) (Chamarthy et al, 2001). The pH was varied from 1 to 6. 2.0 M HCl and 0.1 M NaOH was used to adjust the pH of the metal ion solutions to the desired value. The concentration of each metal ions removed was determined using AAS.

Effect of Ionic Strength on Sorption Capacity

Effect of ionic strength was investigated by measuring sorption capacity of the immobilized Karkashi leaves in various concentrations of NaCl solutions. Different concentrations (0.00-0.34 M) of NaCl were added to adjust the ionic strength of the metal ion solutions and the equilibrium concentration of the residual metal ion determined.

Effect of Temperature on Sorption Capacity

The effect of temperature on the absorption capacity of the immobilized solid was investigated. 0.2 g of the dried immobilized was shaken with 50 ml of the metal ion solution at 30^0 C. The synthetic wastewater was filtered and analyzed for residual metal ion concentration. This process was repeated at different temperature ranging from 30 to 90^0 C.

Effect of Sorption Kinetics (Time)

The effect of the contact time on the adsorption of Zn^{2+}, Cu^{2+}, and Pb^{2+} was also investigated. Eight different sets of sample consisting of 0.2 g of the dried immobilized Karkashi leaves and 50 ml of the metal ion solution were prepared. The solutions were agitated at a fixed stirring speed (with flask shaker), for varying time periods ranging from 3 minutes to 24 hours. Each sample was removed after a particular time. The solution were filtered and analyzed for residual metal ion using AAS.

Effect of Initial Metal ion Concentration on Sorption Capacity

Effect of initial metal ion concentration on sorption capacity was carried out at 30^0C with different samples consisting of 50 mL each of metal ion concentration ranging from 5-100ppm and 0.2 g of dried immobilized karkashi were prepared and shaken until equilibrium is reached. The synthetic wastewater was analyzed for residual metal ion concentration.

RESULTS AND DISCUSSION

Sorbent Sorption Capacity

The sorption capacity for the different metal ions using karkashi leaves sorbent is shown in figure1. It is observed that the sorbent has different affinity for each metal ion (Pb^{2+}, Cu^{2+} and Zn^{2+}). The sorbent sorption capacity obtained for the metal ions were 80.75%, 40.60% and 39.55% respectively. The differences observed in the sorption capacities for different metal ions can be explained in terms of;

- Differences in hydration free energy; metals have different solvation tendencies in the sorbent.
- The ability of metal to form covalent bond with ligand (immobilized karkashi leaves).
- The metal polymeric cations within the matrix structure expand the inter atomic electrostatic interaction in the polymer matrix for sorption.
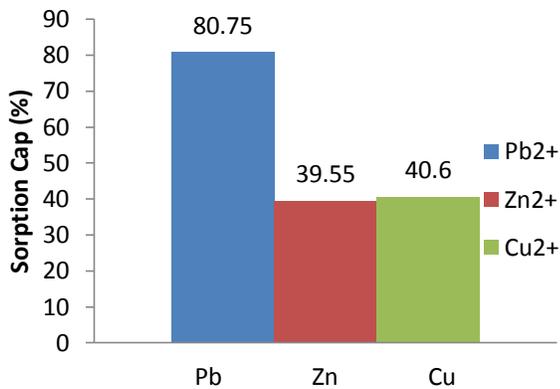- The nature of the surface sites available (Muhammad, 2014).

Figure 1: Sorption Capacity of metal ions

Effect of pH on Sorption Capacity

The pH is an important controlling parameter in the heavy metal adsorption process and thus the role of hydrogen ion .In the biosorption phenomenon, the pH value affects two aspects: metal ion solubility and biosorbent total charge, since protons can be adsorbed or released. The effect of pH on sorption capacity of the metal ions on sodium alginate/immobilized Karkashi leaves (Na-Alg/IKAL) at pH (1-6) is shown in figure 2. The result of the pH study shows that maximum sorption occurred at pH 3 for the metal ions. This can be attributed to the fact that at higher pH values, the lower number of H^+ and greater number of ligands with negatives charges results in greater metal ion biosorption. Deprotonation of these functional groups occurs on increasing pH and these behave as negatively charged moieties which start attracting the positively charged metal ions. At pH 1-2, low adsorption was observed, which is as a result of high concentration and high mobility of H^+ ions, the hydrogen ions are preferentially adsorbed rather than the metal ions. On the other hand as the pH is lowered, the overall surface charges will become positive, which will inhibit the approach of positively charged metal cations **(**Nour,2014). Further increase in pH lead to, a drastic decrease in adsorption percentage which could be as a result of Weakening of electrostatic force of attraction between the oppositely charged sorbet and sorbent that ultimately leads to the reduction in sorption capacity.

Effect of Temperature on Sorption Capacity

Figure 3 represents the effect of temperature on sorption capacity for the metal ions Pb^{2+}, Cu^{2+} and Zn^{2+} by IKAL. The result shows an initial increase in sorption with increase in temperature at 30-40^{0}C.The optimum temperature for the sorption of the metals is at 40^{0}C. The increase of adsorption with temperature could be due to changes in Pore size of the adsorbent, causing intra-particle diffusion within the pore expansion within the active surface site when the temperature increases. It also could be explained that the movement of the metal ion to the adsorbent increases with an increase in temperature is sorption is chemisorptions **(**Noppadol, 2014) However, the magnitude of such increase continues to decline as temperatures are increased from 40 to 90ºC. This is as a result of the following;

- With increasing temperature, the attractive forces between IKAL surface and metal ions are weakened and the sorption decreases.

- At high temperature, the thickness of the boundary layer decreases, due to the increased tendency of the metal ion to escape from the IKAL surface to the solution phase, which results in a decrease in adsorption as temperature increases.
- The decrease in adsorption with increasing temperature, suggest weak adsorption interaction between IKAL surface and the metal ion, which supports physisorption.(Michael and Ayebaemi, 2005)
- The decrease in adsorption with increasing temperature could be a result of an increase in the average kinetic energy of the metal ions. This leads to insufficient attractive forces between the metal ions and the adsorbent, to hold the metal ions at the active site.
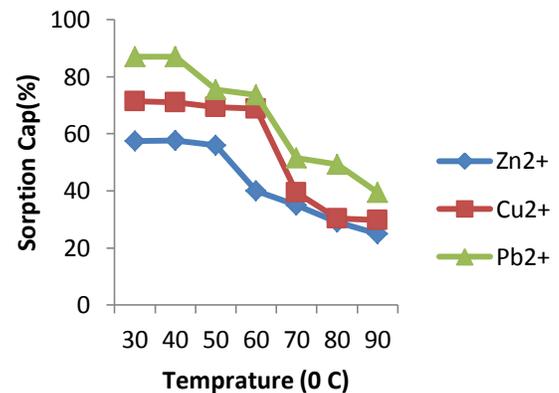

Figure 3: Effect of temperature on sorption capacity

Effect of Time on Sorption Capacity

Figure 4 shows the percentage removal of the various metal ions by IKAL sorbent. From the result of the sorption experiment, $Pb^{2+}$and Cu^{2+} ions reached optimum sorption at 30 minutes with sorption capacity of 86.85 and 81 .85 respectively while Zn reached maximum sorption within 1hr with sorption capacity of 75%.This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system. Therefore, the contact time of 30 minutes is sufficient time for bonding between metal ions (Pb^{2+} and Cu^{2+}) and sorbent **(**Vikal et al**,** 2015**).** The plot revealed that the rate of percent metal ions removal is higher at the beginning. This was probably due to larger surface area of the IKAL being available at beginning for the adsorption of metal ions (Jaber,2013) After the contact time of 30 minutes, for Cu^{2+} and Pb^{2+} and 1 h for Zn^{2+} as the time increased further, the amount adsorbed reduces as equilibrium was reached, and the adsorption sites became saturated to maximum uptake capacity.
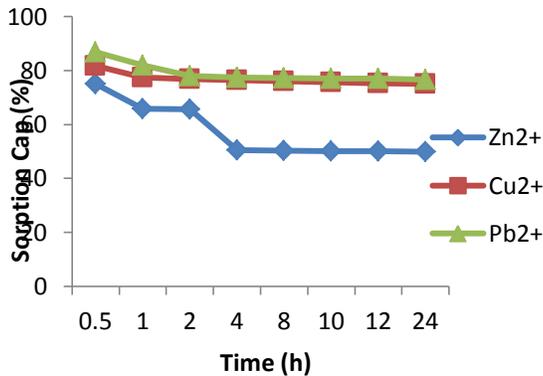
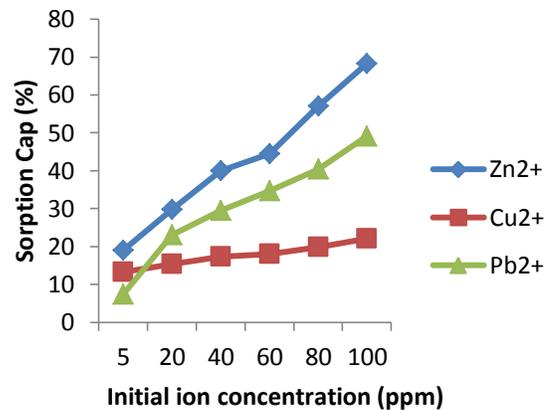**Figure 4:** *Effect of kinetics (time) on sorption capacity.*

Effect of Ionic Strength on Sorption Capacity

The effect of ionic strength is shown in figure 6. The plot indicates that sorption capacity of metal ions decreases with increasing ionic strength of the salt solution. Often metal ions (Ca^{2+}, Na^{2+}, and Mg^{2+}) are found in natural and industrial water. These metals compete with the metals ions under study. The decrease in metal ions sorption with increasing concentration of exchange cations could be due to both a decrease in the activity of metal ions as a result of an increase in ionic strength and the ionic competition for the exchange sites (Wonae, 2001).Also theoretically, when the electrostatic forces between the adsorbent surface and adsorbate ions were attractive an increase in ionic strength will decrease the adsorption capacity (Yahya, 2007).
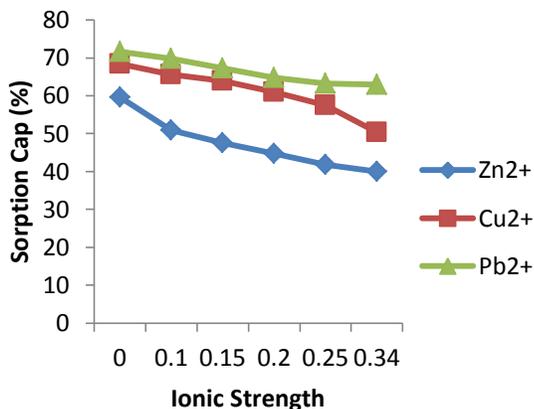

Figure 5: *Effect of ionic strength on sorption capacity.*

Effect of Initial Metal ion on Sorption Capacity

The variation in the amount of metal ion on to the Karkashi leaves with increasing initial metal ion concentration is illustrated in Figures 5. The result showed that the sorption capacity increased with increase in metal ion concentration for all metals under study due to the increase in number of binding sites. This observation could also be explained in terms of progressive increase in the columbic interaction between the cationic species in water and the sorbent sites. Moreover, more adsorption sites were being covered as the metal ions concentration increases. Besides, higher initial concentrations lead to an increase in the flux of the metal ions towards the active sites (Jimoh et al., 2011).

Figure 6: *Effect of initial metal ion concentration on sorption capacity.*

CONCLUSION

The present study shows that low cost karkashi leaves was immobilized and successfully used for the sorption of metal ions (Pb^{2+}, Cu^{2+}, and Zn^{2+}) in aqueous solution. The maximum sorption capacity of IKAL for metal ions is 80.75, 40.60 and 39.55% respectively. Metal uptake by IKAL decreases with increase in ionic strength but increases with increase in initial metal ion concentration. This study on sorption behavior of IKAL has demonstrated that it can be used for wastewater remediation.

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