

Removal of Lead Ions and Turbidity from Waste Water by Adsorbent Materials Derived from Cactus Leaves

Moses M. Mbugua Margaret M. Nga'ng'a Benson Wachira Harun M. Mbuvi*
Department of Chemistry, Kenyatta University, P.O. Box 43844-00100, Nairobi, Kenya

Abstract

The current work explores simple ways of developing cheap adsorbents materials from Cactus, a plant easily found in dry and semi-arid regions for use in water purification. The adsorption capacity and efficacy of its biomass, charcoal, ash and ash residue in removal of lead ions and turbidity from contaminated water is reported. The biomass was obtained by drying and grinding dry leaves to powder. Ash was obtained by heating the dry leaves in a furnace while the residue was obtained by dissolving and removing the soluble fraction. The charcoal was prepared by heating dry cactus leaves in a furnace in limited air. Batch experiments were carried out to determine the effect of initial concentration, PH, contact time, temperature and adsorbent dose on percentage removal of Pb^{2+} and turbidity. The data for Pb^{2+} adsorption on ash residue was found to best fit in the Langmuir isotherm model while biomass, charcoal and ash data best fitted in the Freundlich model. Adsorption capacities for lead ions on ash residue, ash, charcoal and biomass were 1000.0000, 173.6201, 13.3352 and 3.1696mg/g respectively. The findings showed that the adsorbents are effective in removal of turbidity and lead (II) ions from contaminated water.

Keywords: "lead", "Adsorption", "isotherms", "cactus", "green adsorbents"

Introduction

Water scarcity remains a major concern worldwide and more so in developing countries like Kenya where it is projected that per capita available water will likely drop to 359m³/year by 2020 as a result of population growth^[1]. Further, the rapid and continuous expansion and increase of urban centers has resulted to increased pollution of the water sources. Consequently, provision of safe water to the people is an urgent development priority.

Sources of safe drinking water, especially in developing and underdeveloped countries are facing serious threat from contamination emanating from industrial, agricultural and natural activities. Contamination of the water resources by heavy metals is increasingly a matter of great concern to developing African countries^[2]. Indeed, recent studies in Kenya have reported substantial levels of mobile and bioavailable heavy metal in soil and water at proximities of open-air mechanical workshops^[3,4]. There are several ways that dissolved heavy metals can be removed from water that include ion exchange, reverse osmosis, precipitation, ultrafiltration, electrodialysis and adsorption^[5]. Most of them require high energy and advanced operations that are out of reach to many low income earners found in arid and semiarid rural areas which suffer from acute water shortages.

Opuntia. vulgaris commonly called cactus, nopal (Mexico), or prickly pear grows readily in Mexico, Texas and other arid and semi-arid regions^[6]. In Kenya it grows naturally in Nakuru, Lower Eastern and in most arid and semi-arid regions of the Country. There is little information in literature regarding evaluation of *Opuntia spp.* as a water clarifier; however, its mucilage has been used to kill bacteria, remove heavy metals as a low cost adsorbent and turbidity removal from wastewater^[7].

Provision of clean and safe drinking water to low income earners requires continuous exploration into

[1] Dessu, S. B.; Melesse A. M.; Bhat M. G.; McClain M. E. Assessment of water resources availability and demand in the Mara River Basin. *Catena*, 2014, 115, 104-114

[2] Kpan, J.; Opoku, B.; Gloria, A. Heavy Metal Pollution in Soil and Water in Some Selected Towns in Dunkwa-on-Off in District in the Central Region of Ghana as a Result of Small Scale Gold Mining. *Journal of Agricultural Chemistry and Environment*. 2014, 3, 40-47.

[3] Chengo K.; Murungi J.; Mbuvi H.M. Speciation of Zinc and Copper in Open-Air Automobile Mechanic Workshop Soils in Ngara Area-Nairobi Kenya. *Resources and Environment*, 2013, 3, 145-154.

[4] Chengo K.; Murungi J.; Mbuvi H.M. Speciation of Chromium and Nickel in Open-Air Automobile Mechanic Workshop Soils in Ngara Area-Nairobi Kenya. *World Environment*, 2013, 3, 143-154.

[5] Burton, F.; Tchobanoglous, G. wastewater engineering treatment, disposal and reuse (Metcalf and Eddy, Inc.), 1991, McGraw-Hill, New York.

[6] Barbera, G.; Inglese, A.; Pimenta-Barrios, E. Agro-ecology, cultivation and uses of cactus pear. Food and Agricultural Organization of the United Nations: Rome, 1995, p219.

[7] Miller, M.S., Fugate, J.E., Oyanedel, V., Smith, J.A., and Zimmerman, J.B. Efficacy and Mechanism of *Opuntia spp.* As a Natural Coagulant for potential Application in Water Treatment. *Environmental Science and Technology*, 2008, 42, 4274-4279.

ways to develop relatively simple and cheap water filtration materials using locally available resources that can be used to remediate water at household level. In an attempt to develop cheap adsorbents accessible to people living in remote and very dry regions, the present work aimed at developing adsorbents using cactus leaves as the raw material. Indeed findings herein suggest that cactus derivatives are adsorbent materials for heavy metal removal from contaminated water. This work was done between the months of January 2013 to February 2014 at Kenyatta University, Chemistry department, research laboratory.

MATERIALS AND METHODS

Chemicals

Stock solutions of lead with a concentration of 1000 mg/L were prepared by dissolving 1.60 g lead nitrate 99+ % ACS (SIGMA ALDRICH) in 1000 mL distilled water in volumetric flask. The solution was then diluted to obtain standard solutions

Sampling and sample treatment

The plant samples were collected from Nakuru County and the species identified by taxonomist. They were washed with distilled water in order to remove dirt, cut into small pieces and dried in an oven at 60°C for 48 hours.

Preparation of natural coagulant cactus biomass, ash, ash residue and charcoal

Dry *Opuntia vulgaris* was prepared by cutting fresh *Opuntia spp.* into strips of 1 cm width and dried in an oven at 60° C for 48 hours and ground to powder to prepare biomass. Ash was obtained by heating the dry plant material in a furnace at 600 °C with excess air for 24 hours. Ash residue was prepared by dissolving the ash in distilled water to remove the soluble alkali, filtered, washed with distilled water and dried in an oven at 100°C. Ash was obtained by heating (dry cactus) in excess oxygen at 600 °C. Charcoal was prepared by heating the dry cactus in a furnace at temperature of 350° C for 24 hours in limited air^[1].

Instrumentation

Lead concentrations in the various solutions were determined using atomic absorption spectrophotometer model AAS 4141, ECIL, India at wave length 283.3nm in flame mode using air-acetylene flame. The pH meter, model PHEP, Hanna instrument, Italy, was used in this study between pH ranges 2-12 at a temperature of 22.7°C. Turbidimeter, model 2100P (HACH) was used to determine the turbidity of water. The concentration of the Pb²⁺ was assayed in triplicates by use of an AAS with air-acetylene flame. The accuracy of the instrument was checked by triplication of samples. A series of standards were prepared for instrumental calibration by serial dilution of a working solution (100 mg/L) they were prepared from analytical grade stock solution (1000 mg/L) from Alpha chemika and s.d. fine- chem ltd. A standard and blank sample was run after every seven samples to check instrumental drift. Calibration curve method was used to quantify the heavy metal concentration.

Batch experiments

A temperature-controlled water-bath shaker (DKZ-1 NO.1007827) was used for the batch adsorption experiments. The experiments were performed at the same shaking speed. For each experimental run, 50mL aqueous solution of known concentrations of Pb²⁺ ion were put in 120mL plastic bottles that contained known masses of cactus biomass, ash, ash residue and charcoal. These bottles were agitated at a constant shaking rate of 150 rpm and temperature of 25°C, centrifuged and filtered. The concentration of Pb²⁺ ions in the filtrates obtained were measured using flame atomic adsorption spectrometry. Amount of Pb²⁺ ions adsorbed per unit mass of adsorbed and the percentage of Pb²⁺ ions removed were calculated using the equations 1 and 2 respectively

$$q_e = \frac{(C_o - C_e)}{m} V \dots\dots\dots \text{Equation 1}$$

$$R = 100 \frac{C_o - C_e}{C_o} \dots\dots\dots \text{Equation 2}$$

Where,

q_e = Amount of Pb²⁺ ions adsorbed per unit mass of adsorbed at equilibrium

C_o = Initial concentration of sorbate

C_e = Concentration of sorbate at equilibrium

[1]Toles, C.A., Marshall, W.E., John, M. M.Granular activated carbons from nutshells for the uptake of metals and organic compounds. *Carbon, Elsevier*, 1997, 35, 1407-1414.

m = mass of sorbate (atomic mass)

V = volume of solution

Effect of the various parameters on the percentage of Pb^{2+} ions adsorbed

The effects of various parameters (adsorbent dose, contact time, initial concentrations, pH and temperature) on the percentage of Pb^{2+} ions adsorbed were investigated by varying the parameter of interest while keeping all the others constant. The effect of initial concentration was investigated by varying initial concentration from 2 to 2000 mg/L at same conditions of: 0.1g of adsorbents, temperature of 25 °C, agitation speed of speed of 150 rpm, pH 6.0, and contact time of 2hrs. The effect of the adsorbent dosage was investigated by varying the doses from 0.1 to 2.5 g/50mL at same conditions of: 10mg/L Pb^{2+} ion solutions, pH 6.0, agitation speed of speed of 150 rpm, temperature of 25°C and contact time of 2hrs. The effect of contact time was investigated by varying contact time from 1 to 1440min at same conditions of: 0.1g of adsorbents, 10mg/L Pb^{2+} ion solutions, temperature of 25°C, agitation speed of speed of 150 rpm, pH 6.0. The effect of pH was investigated by varying pH from 2 to 12 at same conditions of: 0.1g of adsorbents, 10mg/L Pb^{2+} ion solutions, temperature of 25°C, agitation speed of speed of 150 rpm, contact time 2hrs.

Turbidity

Turbid water was obtained from *Chania River* found in Kiambu County, Kenya. The effect of doses was investigated by agitating 50 mL of turbid water with 0.1, 0.5, 1.0, 1.5, 2.0 and 2.5 g of adsorbents for 2 hrs. The solution was then filtered using whatman No. 1 filter paper and turbidity of the filtrate determined using a turbidimeter. All these studies were conducted at 25°C, pH 6.5, 93 NTU and shaking speed 150 rpm.

RESULTS AND DISCUSSIONS

Chemical composition of cactus ash

Table 1: Elemental analysis of cactus ash

Element/compound	Cl	K ₂ O	CaO	MnO	Fe ₂ O ₃	CdO	PbO
Ash % composition	4.8	40.7	48.4	1.5	0.3	4.2	0.2

Elemental analysis of cactus ash was carried out using X-ray Florescence (XRF) and the results are presented in table 1. As shown in table 1, the major components of the ash were CaO and K₂O at 48.4 and 40.7 % respectively. Other components were Cl, CdO, MnO, Fe₂O₃ and PbO at 4.8, 4.2, 1.5, 0.3 and 0.2 % respectively. This indicates that the ash is basic based on the high percentage of K₂O. In order to rule out removal of metal cations through precipitation as oxides in basic conditions, the ash residue was also investigated.

Effect of adsorbent dose

Figure 1 shows how the percentage removal of Pb^{2+} ions varied as adsorbent doses were increased from 0.1 to 2.5 g. The percentage removal of Pb^{2+} ions by cactus biomass increased from 89.38% to 99.51% and remained constant above the dosage of 1.5g, percentage removal by cactus ash and its residueremained fairly constant at 99.7% for all doses while removal by charcoal was 97.20% at 0.1g and 97.88% at 0.5g but reduced to 91.34 % at 2.5g. This decrease can be attributed to the concentration gradient between the sorbent and the sorbate; an increase in charcoal concentration causes a decrease in the amount of metal sorbed onto a unit weight of the charcoal. However metal adsorption efficiency was increased with increase in adsorbent dose.

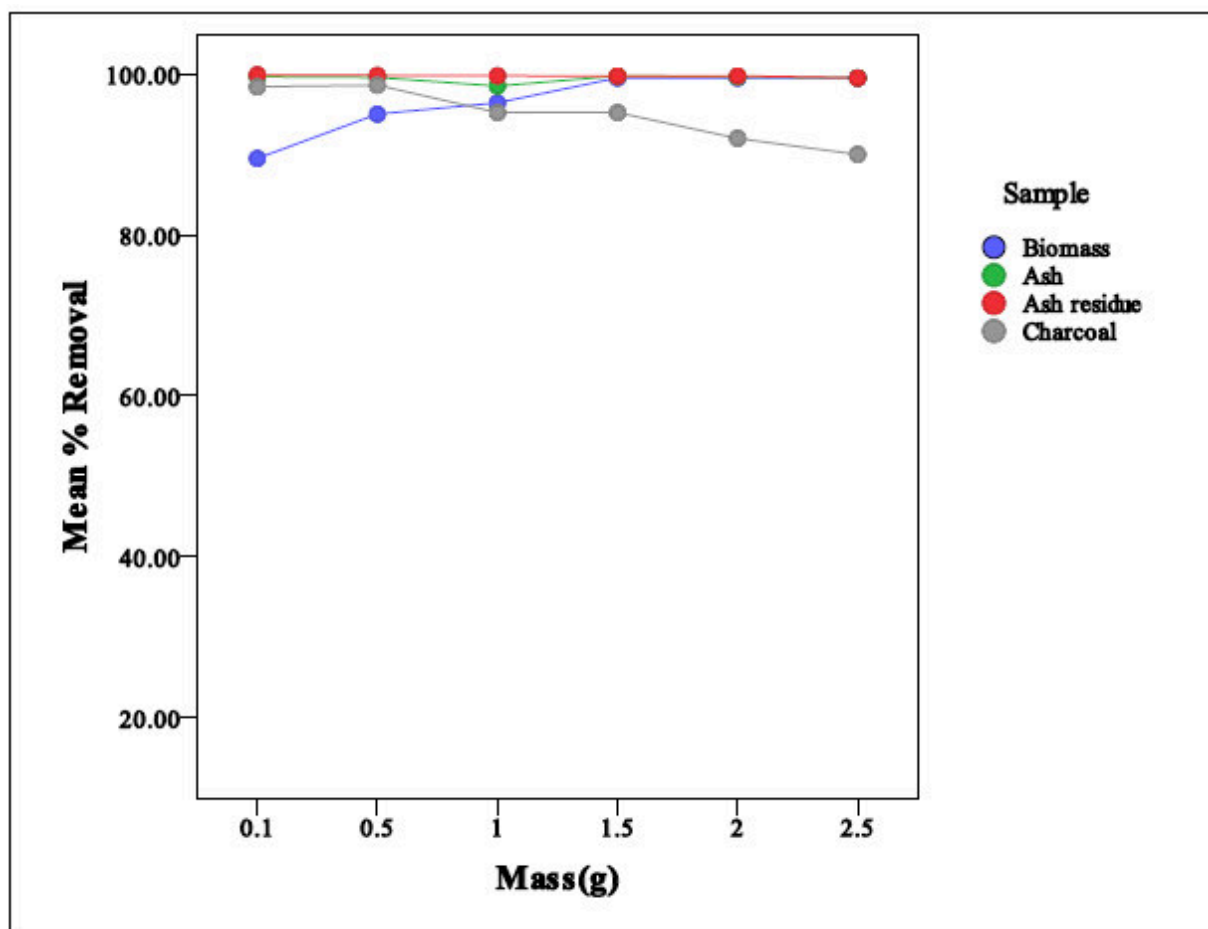


Fig.1: Effect of adsorbent dosage on percentage removal of Pb^{2+} ions at (Temperature = 25 °C, time = 2hrs, concentration = 10 mg/L, shaking speed = 150 rpm, pH=6.0)

This revealed that the adsorption sites remain unsaturated during the adsorption reaction whereas the number of active sites and available surface area for adsorption increased by increasing the adsorbent dose. Similar trends, was observed for lead and cadmium removal using *Chlorella Vulgaris* as biosorbent^[1].

4.2 Effect of pH

Figure 2 shows variations in percentage removal of lead (II) at various pH conditions. At pH 2 all the sorbents gave low percentage removal values of 1.797, 0, 46.49 and 0 % for biomass, ash, ash residue and charcoal respectively. These values increased to 75, 98.5, 99.9 and 84.2 at pH5 and 82.5, 98.5, 99.8 and 91.6% at pH 9.

[¹]Gaber E., YahiaAandAbdulrahim A. Cadmium and Lead.Biosorption by *Chlorella Vulgaris*. Sixteenth International Water Technology Conference, IWTC, 2012, Istanbul, Turkey,

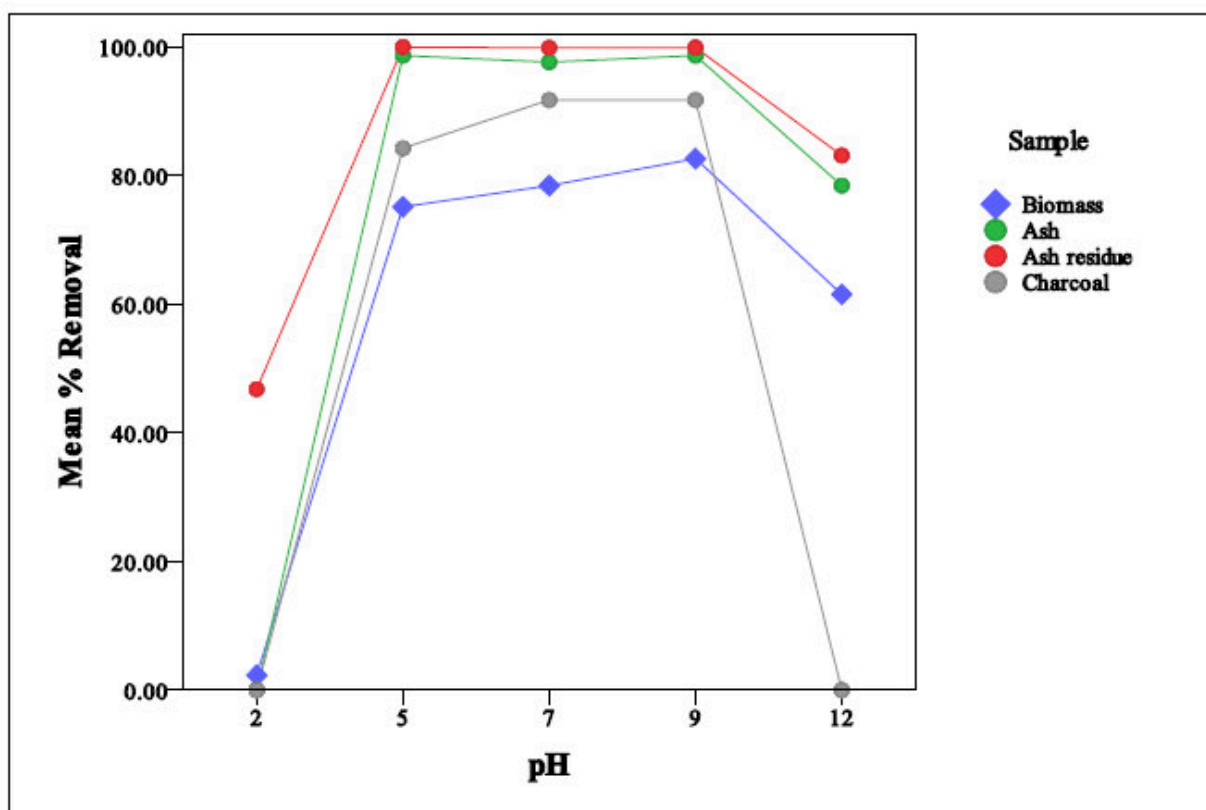


Fig.2. Effect of pH on percentage removal of Pb^{2+} ions at ($T=25^{\circ}C$, dose= 0.1g, concentration= 10mg/L, time= 2hrs, shaking speed=150rpm)

Under basic conditions at pH 12, the values reduced to 61.3, 78.3, 83 and 0% respectively. At low pH, values decreased because protons compete with metal ions for sorption sites on the adsorbent surface^[1] hence adsorption of the metals is low. However, with the increase of pH, adsorption increases. The enhanced adsorption with increasing pH from 2 to 9 indicates that adsorbent's surface become more negatively charged at higher pH values, the precipitation is dominant or both ion exchange and aqueous metal hydroxide formation may also become significant mechanisms in the metal removal process^[2]. Also, the pH dependence of the metal biosorption observed in this study could be qualified to more pronounced electrostatic attraction taking place between the biosorbents and the metal ions at higher pH^[3,4]. Maximum percentage removal of lead (II) by cactus biomass, charcoal, ash and ash residue were found to be 82.52, 91.67, 98.53 and 99.86 respectively at pH range of 5-9.

4.3 Effect of Contact Time

The effect of contact time on the amount of lead (II) ions adsorbed was investigated at initial concentration of 10mg/g of the metal ions. The extent of removal of metal ions by cactus biomass, ash, ash residue and charcoal with respect to time is shown in Fig.3. The optimal removal efficiency for biomass, charcoal, ash and ash residue was reached within 60, 90, 30 and 30minutes respectively. The percentage removal at 15 minutes were 72.7, 87.1, 98.1 and 98.2% and increased to optimum values of 81.2, 96.57, 99.5 and 99.5% for biomass, charcoal, ash and ash residue respectively. The adsorption of the metals remained almost constant above optimum time and the difference between the adsorptive uptake at 1 and 2hrs for all the adsorbents was less than 1% of that at 24 hrs. Hence, a steady-state approximation was assumed and a quasi-equilibrium situation was considered at $time = 2$ hrs. Contact time is one of the most effective factors in batch adsorption process. Adsorption rate initially increased rapidly, however, after some time the rate becomes almost constant. This is because all the available

[1] Kumar P.S, Ramakrishnam K, Kiropha S.D and Sivanesan S. Thermodynamic and Kinetics Studies of Cadmium Adsorption from Aqueous Solution onto Rice husk. *Brazilian journal of chemicals engineering*, **2010**, 27, 347-355

[2] Ajaelu, C.J., Iboronke, O.L., Adedeji, V and Olafisoye, O. Equilibrium and Kinetic studies of biosorption of heavy metal (Cadmium) on *Cassia Siamea* Bark. *American-Eurasian Journal of Scientific Research*, **2011**, 6, 123-130

[3] Jafari N and Senbari Z. Removal of Pb (II) ions from Aqueous solutions by *Cladophora rivularis* (Linnaeus) Hoek. *The scientific world journal*, **2012**, 10, 1-6

[4] Ajamal, M., Rao, R.A., Anwar, S., Ahmad, J and Alunad, R. Adsorption studies on rice husk. Removal and recovery of Cd (II) from wastewater. *Bioresource Technology*, **2003**, 86, 147-149

active centers on the adsorbent have been occupied and there are no further sites and hence no further adsorption is possible^[1].

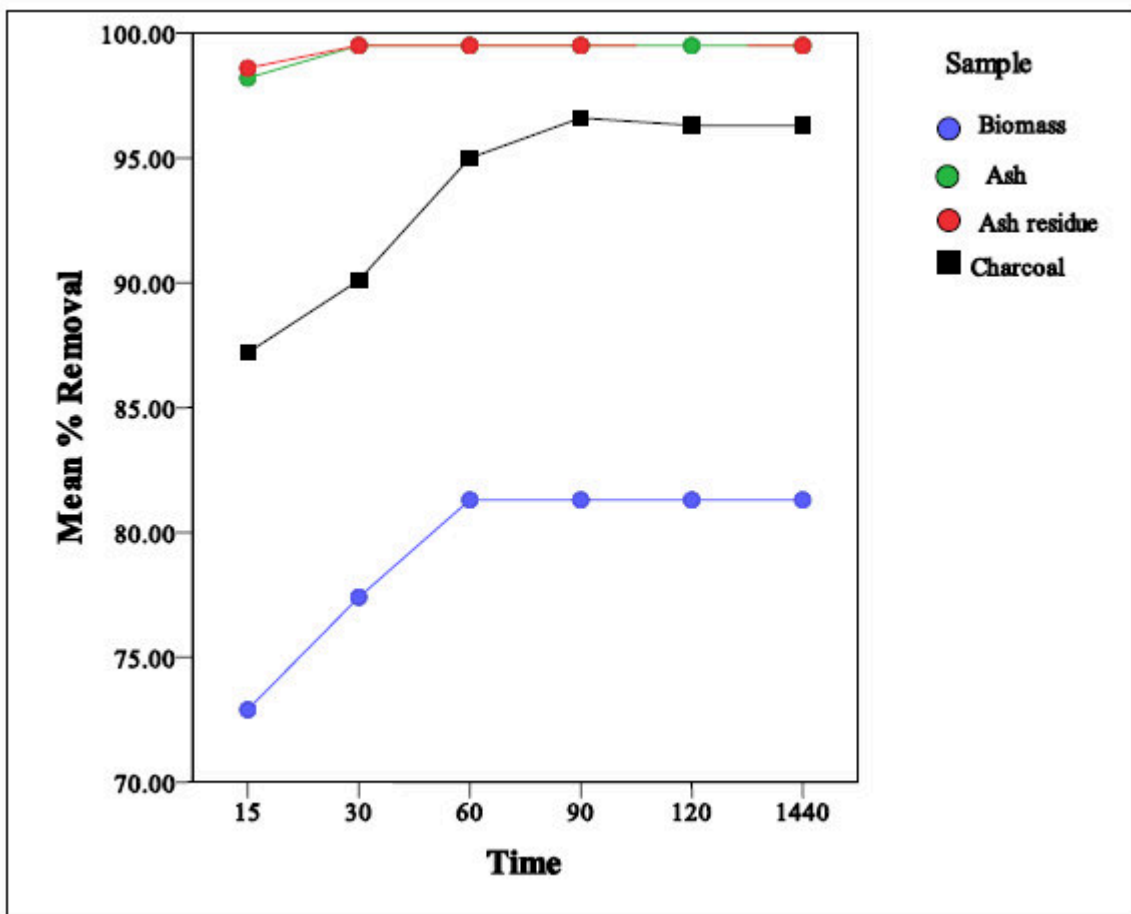


Fig.3. Effect of contact time on percentage removal of Pb^{2+} ions at ($T=25^{\circ}C$, dose=0.1g, concentration=10mg/L, pH=6.0, shaking speed=150 rpm)

4.4 Effect of temperature

The effect of temperature on percentage removal of Pb^{2+} ions by cactus biomass, ash, ash residue and charcoal is presented in figure 4. Experiments were performed at temperatures of $25^{\circ}C$, $35^{\circ}C$, $45^{\circ}C$, $55^{\circ}C$ and $65^{\circ}C$ using different initial concentrations of 10 mg/L at pH 6 of the solutions. As shown, the equilibrium uptake of the metals by different adsorbents was affected by temperature. The percentage removal decreased for biomass and ash from 89.7 to 76.9 and 97.2 to 83.8 % respectively. This is mainly due to the decreased surface activity, suggesting that adsorption between lead and cactus biomass is an exothermic process. Percentage removal by charcoal and ash residue increased from 98.2 to 98.5 and 99.6 to 99.8 % respectively.

^[1]Sarioglu and Atay, U.A. Removal of Methylene Blue by using Biosolid. *Journal of Global Nest*, 2006, 8(2):113-120

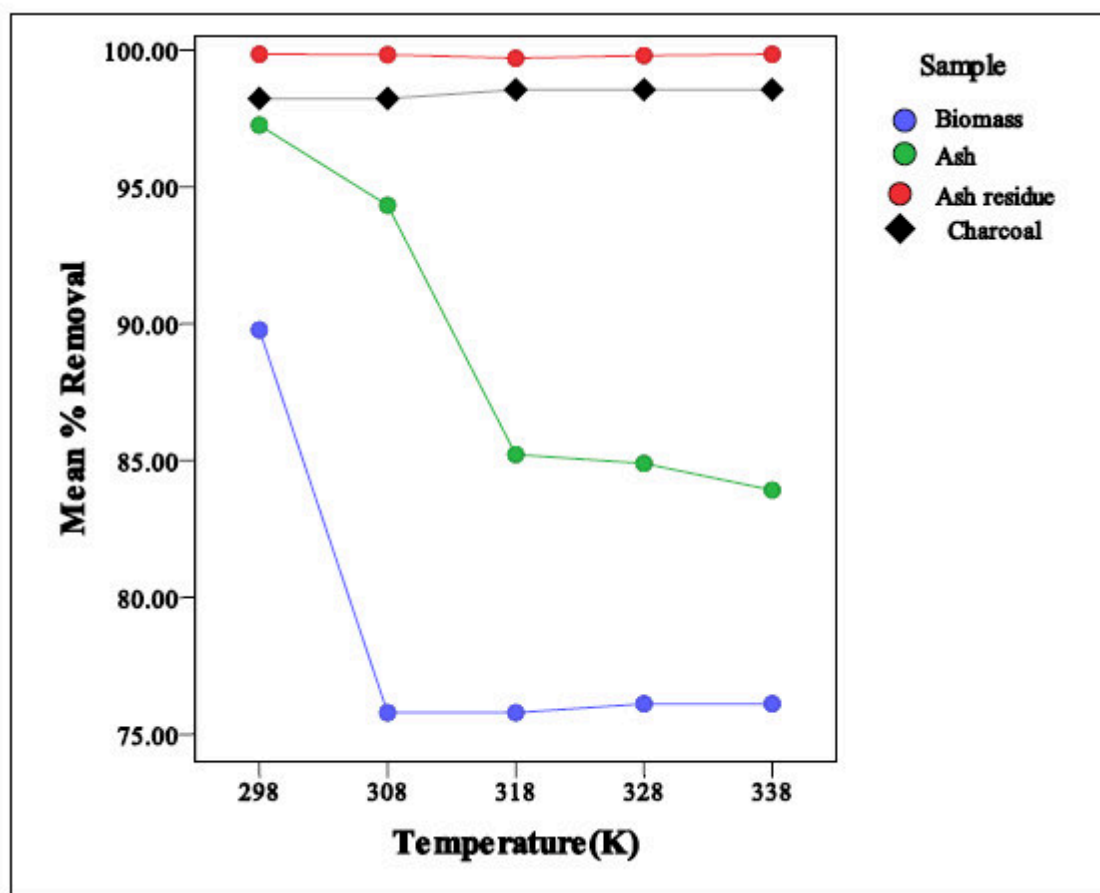


Fig.4. Effect of temperature on percentage removal of Pb^{2+} ions at (Concentration=10mg/L, dose= 0.1g, time=2hrs, pH=6.0 shaking speed=150rpm)

The increase in adsorption with the rise of temperature may be due to increase in swelling of the adsorbent allowing more active sites to become available for lead. This suggest that adsorption between lead (II) and cactus biomass and its processed product is an exothermic reaction. Similar results were reported for cadmium removal using rice husk as biosorbent^[1]. The optimum temperature for lead (II) adsorption on cactus biomass, ash, ash residue and charcoal was found to be 25°C within the temperature range studied as in fig.4

[¹]Kumar P.S, Ramakrishnam K, Kiropha S.D and Sivanesan S. Thermodynamic and Kinetics Studies of Cadmium Adsorption from Aqueous Solution onto Rice husk. *Brazilian journal of chemicals engineering*, 2010, 27, 347-355

4.5 Effect of initial metal ion concentration

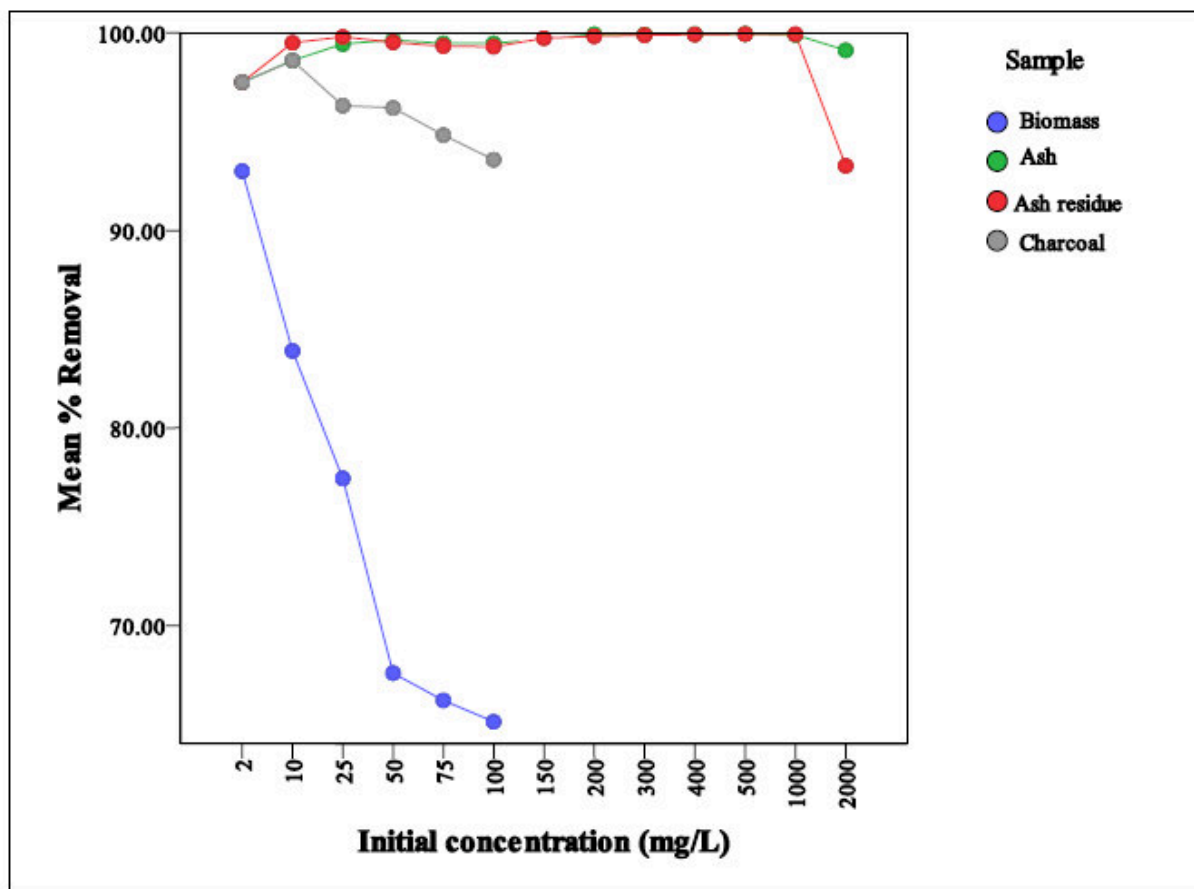


Fig.5. Effect of initial metal ion concentration on removal of Pb^{2+} ions at (T=298k, dose=0.1g, time=2 hrs, pH=6.0 shaking speed=150rpm)

The effect on percentage removal by cactus biomass and its processed products as a function of initial metal concentrations of Pb^{2+} ions was studied at different concentrations in batch experiment. As shown in Figure 5 the percentage removal by charcoal, ash and ash residue increased as the initial metal ion concentration was increased to optimum values of 98.53, 99.9 and 99.9 at initial concentrations of 10, 1000 and 1000mg/L respectively. The percentage removal by biomass reduced from 93.9% at 2mg/L to 64.9% at 100mg/L. Initial metal ion concentration in solution influences metal uptake. The removal capacity of the metal ion is decreased with the increase in the metal ion concentration as a result of saturation of the binding sites, although the amount of the metal ions adsorbed increases with the increase in the initial metal ion concentration^[1]. This is due to increased initial ion concentration thus providing a larger driving force to overcome all mass transfer resistance between the solid phase and the aqueous phase, hence resulting in higher metal ion adsorption.

4.6 Turbidity

Figure 6 shows the effect of dosage of cactus biomass and its processed products on turbid water obtained from *Chania* river in Kenya. Its initial turbidity value was found to be 93NTU. Four different biosorbents of cactus were investigated to remove suspended solids (turbidity). Cactus biomass, ash, ash residue and charcoal formed large flocks with impurities in the sample which facilitated settling and as a result, a clear supernatant was produced. The percentage removals on treatment with varying doses of between 0.1 to 2.5g were found to vary as shown in figure 6. 0.1g of biomass recorded the best removal of 78.1%. This value reduced to 70.6, 40.9, 36.9, 31.90, and -1.43% at the doses of 0.5, 1, 1.5, 2 and 2.5 respectively. Similarly charcoal recorded its best percentage removal of 82.8 at a dose of 0.1g. Its removal then reduced to 62.7, 35.5, 20.1, 5.0 and -27.2% at the doses of 0.5, 1, 1.5, 2 and 2.5 respectively. However, minimal increments in percentage removal were observed for Ash and its residue at 95.3, 97.5, 98.9, 98.9, 98.9 and 98.6 for doses of at the doses of 0.1, 0.5, 1, 1.5, 2 and

^[1]Katircioglu, H., Aslim, B., Turker, A.R., Atici, T., Beyatli, Y. Removal of Cadmium(II) ion from aqueous system by dry biomass immobilized like and heat inactivated. *Oscillatoria Sp.* H1 isolated from freshwater(Mogan lake). *Bioresource Technology*, 2008,99, 4185-4191

2.5g of ash respectively. Similarly percentage removal by ash residue increased marginally to optimum value of 98.9% for doses above 1g. Cactus ash and ash residue decreased turbidity of the water from 93NTU to 1NTU. The highest removal efficiency reached was 98.92% by ash and ash residue which is comparatively similar to the highest removal efficiency obtained for surface Water and Landfill Leachate using *C.Opuntia* as a biosorbent^[1].

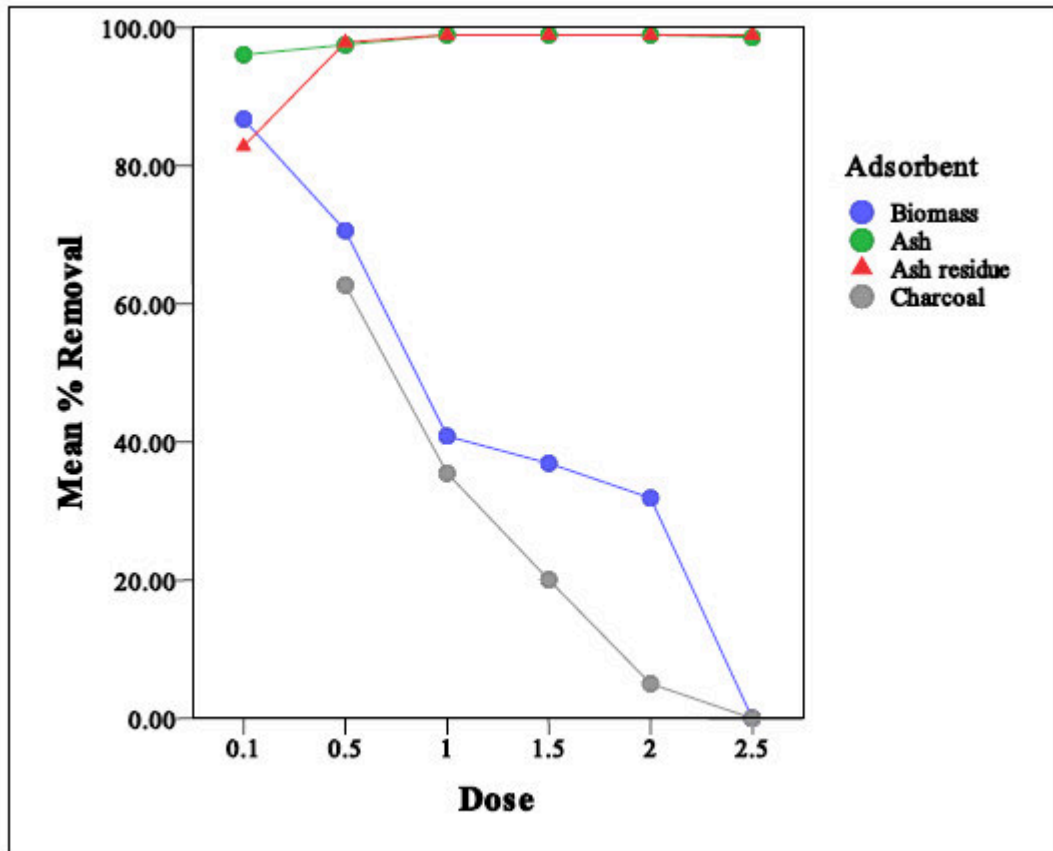


Fig.6. Effect of dosage of cactus biomass, ash, ash residue and charcoal on turbidity of Chania River water at time= 2hrs, temperature=25°C, pH=6.5, shaking speed=150rpm, turbidity=93NTU

Adsorption isotherm models

Table 2: Langmuir and Freundlich isotherm constants for lead adsorption

Adsorbent	LANGMUIR			FREUNDLICH		
	$q_{max}(mg/g)$	b	R^2	K_f	R^2	$1/n$
Biomass	40.2422	0.0716	0.8410	3.1696	0.9980	0.6340
Ash	3278.6885	0.0266	0.0110	173.6201	0.5330	0.9910
Ash residue	1000.0000	0.1056	0.8870	111.1732	0.5410	0.6990
Charcoal	67.3401	0.3159	0.9020	13.3352	0.9630	0.7450

The data obtained from sorption studies were fitted to Langmuir and Freundlich isotherm models. Thermodynamic constants of the two models are presented in Table 2. As shown, sorption data from biomass, ash

[1] Yin C. Y., Suhaimi A. T., Lim Y. P., MohdSafirumNizan I., SitiNorAsiah A. and Ahmad Mahyuddin M. M. Turbidity Removal from Surface Water and Landfill Leachate Using Cactus *Opuntia*. *The Institution of Engineers*, 2007, 68, 61-64.

and charcoal best fitted the Freundlich model on the basis of coefficient factor R^2 of 0.998, 0.533 and 0.963 respectively and $1/n$ values of 0.634, 0.991 and 0.745 respectively. Values of $1/n$ less than 1 show favorable nature of physical adsorption of metal ion onto the adsorbents^[1]. The results indicate that the uptake of lead (II) occurs on a heterogeneous surface by multilayer biosorption. In the study the k_f for cactus biomass, charcoal and ash biosorbent was 3.1696, 13.3352 and 173.6201 mg/g respectively. It is apparent that the Langmuir model explains the biosorption of lead (II) onto cactus ash residue better than the other models on the basis of correlation coefficients R^2 (0.887). The fitness of the biosorption data of lead ions to the Langmuir isotherm implies that the binding energy on the whole surface of the cactus ash residue on lead (II) ions was uniform. This also indicates that the adsorbed metal ions do not interact or compete with each other and that they are adsorbed by forming a monolayer. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies with no transmigration of adsorbate in the plane surface. Favorable biosorbent should have a low Langmuir constant b and a high q_{max} value. In the study, b and q_{max} values were found to be 0.105597 L/mg and 1000 mg/g respectively. This compares favorably with the adsorption of lead on *C. vulgaris* biomass where 0.0181 and 14.932 were reported for b and q_{max} respectively and the adsorption of lead on *S. cumini* L. where 0.075 and 322.47 were reported for b and q_{max} respectively^[2].

[1] Chijioke, A.J., Ibronke., Oluwafunke., Adedeji, L., Victor and Olafisoye O. Equilibrium and kinetic studies on the biosorption of heavy metals (Cadmium) on *cassiasamea* Bark. *Journal of scientific Research*, **2011**, *6*, 123-130

[2] King, P., Rakesh, N., Beenalahari, Y., Kumar, Y.P., Prasad, V.S.R.K. Removal of lead from aqueous solution using *syzygiumcumini*. Equilibrium and Kinetic studies. *Journal of Hazard mater.* **2007**, *142*, 340-347