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ORIGINAL ARTICLE

Baobab fruit shell (*Adansonia digitata*) as a Natural Adsorbent for Copper and Lead Removal from Industrial Effluent

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ABSTRACT
Water the most abundant and natural resource is extremely essential for the survival of all organisms. But today clean water has become a precious commodity and its quality is threatened by numerous sources of pollutants. Water pollution is a major problem around the world. The main source of polluted water is the industry and domestic wastewater. Industrial wastewater is polluted with hazardous substances such as heavy metals (Arsenic, Lead, Mercury, Cadmium, Chromium, Copper, Nickel, Zinc) and petroleum products. Wastewater technology is various, one of them – the biological sorption. In this study, removal of copper (Cu) and lead (Pb) from industrial effluent has been investigated by using baobab fruit shell (Adansonia digitata) as a natural adsorbent. The research is a bench scale experiment type and analysis have performed by using different fractions (>200 µm and 200 µm fraction of baobab fruit shell (Adansonia digitata) for copper removal the treatment efficiency is 86.1% when the metal concentration is 0.5 mg/L, while the lead is 86.9%. Increasing metal concentration in the solution of the adsorbent treatment efficiency decreases to 71.76% for Cu and 86.76 % for Pb. When the smaller fractions (>200 µm) are used in baobab fruit shell (Adansonia digitata) treatment efficiency increases by 6–1 1% for copper, and 8–9% for lead. Baobab fruit shells can be used as a cost effective adsorbent for the removal of lead(II) and copper(II) ions from wastewater in the treatment of industrial effluent.
***Keywords**: Adsorbtion, Adansonia digitata, copper, lead, Effluent, Water pollution, Heavy metal*

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INTRODUCTION

Industrial activities generate a variety of waste products which are generally discharged into water steam. The nature of industrial waste depends upon the process in which these are generate.

Heavy metal sources

Heavy metal pollution of water is a serious threat to the globe ecosystem. Many industries such as metal plating, mining operation, battery manufacturing processes, the production of paints and pigments, ceramic and glass industries, release wastewaters, Pharmaceutical Industrial Waste polluted with heavy metals into the environment [1, 2, 3]. And Industrial sources: e.g. Printed board manufacturing, metal finishing and plating, semiconductor manufacturing, textile dyes, Street runoffs, Landfills, Industrial wastewater includes Cu, Pb, Zn, Ni, Cd and Cr [4]. Toxic metals are most affected by natural ecosystems. Toxic metals are added in aquatic system from industrial process, domestic sewage discharge, street dust, land run off and fossil fuel burning. Metal ions to accumulate in human and other animal bodies occur through trial direct intake or food chains. Many heavy metals are essential trace elements for humans, animals and plants in small amounts. In larger amounts cause acute and chronic toxicity. Linked to learning disabilities, cancers and even death Heavy metals have inhibitory effects on the biological treatment process at the wastewater treatment plants Limit the use of biosolids as fertilizer and may inhibit the digestion process in biogas plant.

Copper.

Copper is a transition metal which belongs to period 4 and group IB of the periodic table with atomic number 29, atomic weight 63.5, density 8.96 g/cm3 , melting point 1083 °C and boiling point 2 595 °C [5].

Copper ions can be found in many wastewater sources, including printed circuit board manufacturing, electronics plating, plating, wire drawing, copper polishing, paint manufacturing, wood preservative using and printing operations. Typical concentrations vary from several thousand mg/1 from plating bath waste to less than 1 ppm from copper cleaning operations [6].

Copper is an essential trace element necessary for plant and animal growth. Copper ion in small amounts is used in agriculture and is an essential element for health of plants, animals and humans. In humans, it helps in the production of blood hemoglobin. High concentration of copper creates a kind of disease, which is similar to flu. It has been proved that drinking water, including 30 grams of copper ion is fatal and the concentration of 1.3 mg/l of this ion could be a reason for the relatively common diarrhea, abdominal cramps and nausea [5, 6].

Lead

Lead is a metal that belongs to the group IV elements and period 6 of the periodic table. Pb atomic number is 82, atomic mass 207.2, density 11.4 g/cm3 , melting point 327.4 °C and boiling point 1 725 °C.

It is a naturally occurring; bluish-gray metal usually found as a mineral contaminated with other elements (such as sulphur or oxygen) [5]. Lead is a cumulative poison. Natural waters contain upto 20 ppb of lead.

Lead intensive use in industries such as storage-battery manufacture, printing, pigment manufacturing, petrochemicals, fuel combustion and photographic materials. The current annual worldwide production of Pb (II) is approximately 5.4 million tons and continues to manufacturing of batteries (automobile batteries, in particular), while the remainder is used in the production of pigments, glazes, solder, plastics, cable sheathing, ammunition, weights, gasoline additive, and a variety of other products [7]. Lead is a highly toxic metal and has the ability to accumulate in living organisms. Assimilation in the human body of relatively small amounts of Pb over a long period of time can lead to malfunctioning of certain organs and chronic toxicity. It can damage practically all tissues, particularly the kidneys and the immune system. Intense exposure to high Pb levels (from 100 to 200 g/day) causes encephalopathy with the following symptoms: vertigo, insomnia, migraine, irritability, and even convulsions, seizures, and coma [5, 7].

Copper as lead can damage the health of all living organisms; therefore heavy metals should be prevented from reaching the natural environment [8] People in Europe and North America are beginning to realize that Baobab Fruit Pulp (*Adansonia digitata*) is among the most nutrient dense food in all of creation. A few realize that the leaves are also a very rich vegetable. Many parts of the plant are also used in traditional medicine. In traditional African Medicine, Baobab Fruit Pulp, leaves, bark, roots, seeds and oil are commonly used to treat a wide variety of ailments. Although natural medicine is a growing sector in the health care industry, many botanical remedies are not very well proven, or approved by regulatory agencies, leading to consumer skepticism. Certainly, there is also a good amount of snake oil on the market as well! Baobab as a food product is relatively new to the market, and its medicinal uses are virtually unknown outside of Africa . [David Goldman Aug 6,2012,]. This study is aimed to use low cost natural adsorbent which consist of Baobab (*Adansonia digitata*)as plant fruit waste in treatment of industrial waste water by bench scal experiment type and analysis have performed by using different fractions for Cu and Pb removed.

(b) Adsorption

Adsorption is the phenomenon of accumulation of large number of molecular species at the surface of liquid or solid phase in comparison to the bulk.

Various technologies exist for the removal of such metals, such as filtration, evaporation, precipitation, electro precipitation, chemical precipitation, electro coagulation, cementing and separation by membrane, the solvent extraction and the exchange of ions on resins [3, 9, 10]. But these methods are enough expensive. Therefore, recently have been sought a cheaper metal removal from aqueous solution's technology. One of these technologies is adsorption. Adsorption is a fundamental process in the physiochemical treatment of contaminated solutions. Adsorption is a separation process in which certain components of the fluid phase are transferred to the surface of the solid adsorbents. When a solid surface is exposed to a fluid phase, the molecules from the bulk of the fluid phase have a tendency to accumulate or concentrate at the surface of a solid. Separation occurs because differences in molecular weight, shape, or polarity cause some molecules to be held more strongly on the surface than others or because the pores are too small to admit the larger molecules. The adsorption operation can be batch; semi-batch and continuous batch operations are generally conducted when small amounts are to be treated [11, 12]. The equilibrium distribution depends on the contact time in batch operation.

Types of adsorption.

At molecular level, adsorption is due to attractive interactions between a surface and the species being adsorbed.

Physical adsorption or Physisorption :

It is a result of intermolecular forces of attraction between molecules of the adsorbent and the adsorbate. In this case, the molecular attractive forces that retain the adsorbent on the surface are purely physical are called Vander Walls forces. This is a readily reversible phenomenon. The energy of interaction between the adsorbate and adsorbent has the same order of magnitudes as, but is usually greater than the energy of condensation of the adsorptive. Therefore, no activation energy is needed.

Chemical adsorption or Chemisorption :

It is a result of chemical interaction between the solid and the adsorbed substance. It is also called activated adsorption. It may be exothermic or endothermic processes ranging from very small to very large magnitudes. The elementary step in chemisoption often involves large activation energy [11, 12].

Variety of adsorbents

There are various types of adsorbent for heavy metal removal from aqueous solutions. Most popular are activated carbon, chitosan, zeolites and silica gel.

Activated carbon.

Activated carbon is a highly porous, amorphous solid consisting of micro crystallites with a graphite lattice, usually prepared in small pellets or a powder. Activated carbon have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption [12].

Chitosan.

Chitosan and its derivatives are examples of value-added materials. They are produced from chitin, which is a natural carbohydrate polymer found in the skeleton of crustaceans, such as crab, shrimp. Chitosan is a polymer obtained from deacetylation of chitin [13].

Zeolites.

Zeolites are micro porous crystalline solids with well defined structures. Naturally-occurring zeolites are hydrated aluminosilicate materials with high cation exchange capacity [14]. Adsorption in zeolites is actually a selective and reversible filling of crystal cages, so surface area is not a pertinent factor [12].

Silica gel.

This is a chemically inert, nontoxic, polar and dimensionally stable (<400 °C or 750 °F) amorphous form of SiO_2. It is prepared by the reaction between sodium silicate and acetic acid, which is followed by a series of after-treatment processes such as aging, pickling, etc. These after treatment methods result in various pore size distributions [12].

Also metal removal can be used peat moss, clay, activated alumina, activated charcoal, polymeric adsorbents, calcite and hydroxyapatite, modified cement and others.

Adsorption of heavy metals on conventional adsorbents such as activated carbon had been used widely in many applications as an effective adsorbent, and the activated carbon produced by carbonizing organic materials is the most widely used adsorbent [15]. However, need a lot funds for the preparation of adsorbents, so its price is high and it is limits its use in polluted solution treatment applications. There is a lot of research to find cheaper materials to be used as adsorbents for heavy metal removal. The literature showed that the industrial waste (such as tea wastes, sawdust, rice husk and etc.) can be used for removal of heavy metals. In Tables 1 and 2 show various adsorbents treatment efficiencies for copper and lead [8, 14–21].

Table 1. Various adsorbent for Cu removal from polluted solutions

Adsorbents	**Treatment efficiency(%)**	**References**
Cocoa shells	95	(21)
Sawdust	98.1-93.6	(8)
Activated charcoal	45-50	(16)
Papaya wood	97.8	(18)
Waste fruit residues	96	(20)
Wheat shell	99	(19)
Coffee ground	72-97	(26)

Table 2. Various adsorbent for Pb removal from polluted solutions

Adsorbents	**Treatment efficiency(%)**	**References**
Sawdust	98.6-95.4	(8)
Waste fruit residues	96	(20)
Cocoa shells	70	(21)
Coffee ground	72-78	(26)
Indigenous clay	80.3-51.3	(14)

In this study baobab fruit shell (*Adansonia digitata*) as heavy metal adsorbent has been used. baobab fruit shell (*Adansonia digitata*) treatment efficiency in removing metals from aqueous solutions has been determined. Heavy metals studied were copper and lead.

MATERIAL AND METHODS

Preparation of adsorbents

In this study, baobab fruit shell (*Adansonia digitata*) has been used for adsorption experiments. baobab fruit shell (*Adansonia digitata*) were been washed and rinsed with distilled water. After drying in 80°C, a part of the baobab fruit shell (*Adansonia digitata*) were sieved (sieve mesh size 200 μm) [22]. Fractions of baobab fruit shell (*Adansonia digitata*) were put in sealed polyethylene for preservation so that it not reacts with neighboring environment [23]. The baobab fruit shells (BFS) were rinsed with distilled water to remove dust and impurities deposited on the surface. The BFS were air-dried and then oven dried at 80 C to constant mass. The dried shells were pulverized and sieved to obtain particle sizes less than 300 μm. The baobab shell powder was soaked in 0.1 M HNO3 for 24 h. Acid treatment was done to remove or mask functional groups and to expose more ion binding sites. The mixture was filtered and the powder residue washed with distilled water several times to remove any acid contents. The filtered biomass was dried in an oven at 105 C. The dried biomass was preserved in air-tight glass bottles to protect it from moisture [25].

Preparation of heavy metal solutions

Cu and Pb with 4 different concentrations of 0.5 mg/L, 1.0 mg/L, 1.5 mg/L and 3.0 mg/L were prepared using standard metal solutions (conc. 1000 mg/L).

Procedure

12 flasks are taken each containing 0.5 g (a particle size >200 μm) of baobab fruit shell (*Adansonia digitata*) used as an adsorbent, 100 ml solution with known concentration of Cu were added, thereupon we had 3 similar concentration of each experiment. All these flasks were places into a shaker with 120–130 rpm. After 1-hour contact time, the contents of flasks were filtered through "VWR Qualitative filter paper 413" filter paper so that turbidity does not interference in this result. Copper concentration of the filtered solution after contact time was determined by atomic adsorption spectroscopy. The same procedure has been done 4 J. Seniūnaitė et al. / The 9th Conference Environmental Engineering. Selected Papers, Article number: enviro.2014.052 for another coffee grounds particle size (< 200 μm) and Cu solutions, and both baobab fruit shell's (*Adansonia digitata*) fractions with lead solutions [22, 23].

Data analysis

The removal percentages (R, %) were calculated according to equation (1):

$$R(\%) = C_o - C_e / C_0 \times 100. \qquad (1)$$

where C_0 – metal concentration before adsorption, mg/L; C_e – metal concentration after adsorption, mg/L [24].

RESULT AND DISCUSSION

Effects of adsorbent particle size

Tables 3 and 4 show the residual heavy metal (Cu and Pb) concentrations in solution after 1.30-hour contact time using different adsorbent fractions.

Table 3. Concentration of residual copper after adsorption by baobab fruit shell (*Adansonia digitata*)

Baobab(*Adansonia digitata*) fraction	Concentration of Cu (mg/L)			
	0.5	1.0	1.5	3.0
Particle size<200μm	0.0705	0.1439	0.3170	0.847
Particle size>200μm	0.0141	0.0739	0.1578	0.6655

Table 4. Concentration of residual lead after adsorption by baobab fruit shell (*Adansonia digitata*)

Baobab(*Adansonia digitata* fraction)	Concentration of Pb (mg/L)			
	0.5	1.0	1.5	3.0
Particle size<200μm	0.0190	0.0387	0.0584	0.1335
Particle size>200μm	0.0613	0.1289	0.1978	0.3968

Tables 3 and 4 present the removal percentages from the initial concentration for various initial concentrations of the metals, with different fractions of adsorbent baobab fruit shell (*Adansonia digitata*)). The adsorption rate is dependent on the adsorbent particle size as well as the initial concentration of metal in the synthetic solutions. The percentage of heavy metal removal increased with the decreased adsorbent baobab fruit shell (*Adansonia digitata*) adsorbent particle size. Copper removal from aqueous solution efficiency increased 6–1% when it was used in smaller fractions (<200 μm) adsorbent baobab fruit shell (*Adansonia digitata*). Lead treatment efficiency increased by 8–9%. The results show that lower residual concentrations obtained when the adsorbent baobab fruit shell (*Adansonia digitata*) have a smaller particle size (<200 μm).The adsorption capacity for Cu was lower than for Pb metals.

Effects of initial concentration

Metal adsorption is influenced by the initial concentration of metal ions in aqueous solutions. In the present study, the initial metal concentration is varied from 0.5 to 3.0 mg/L for each of the adsorbent fractions. The result show the effect of initial concentration on the removal percentage of metal ions. The removal efficiency of Cu decreases from 85.2 (for 0.5 mg/L) to 71.8% (for 3.0 mg/L), baobab fruit shell (*Adansonia digitata*) particle size is >200µm and contact time is 1.30 hour, when used for smaller adsorbent fraction of copper removal efficiency decreased from 97.2 (metal conc. 0.5 mg/L) to 77.8% (metal concentration = 3.0 mg/L).

Lead removal efficiency with >200 µm particle size of adsorbent baobab fruit shell (*Adansonia digitata*), at 0.5–3.0 mg/L of metal concentrations remained almost unchanged, and were 86–87%. With lower adsorbent fraction (<200 μm) lead removal efficiency is 95–96% .The results show that the adsorbent baobab fruit shell (*Adansonia digitata*) cleaning efficiency is also dependent on the metal the removed. By comparing the copper and lead in treatment efficiency using adsorbent baobab fruit shell (*Adansonia digitata*) with adsorbents whish are presented in results we can conclude that the adsorbent baobab fruit shell (*Adansonia digitata*) are an effective and suitable adsorbent to remove heavy metals from aqueous solution.

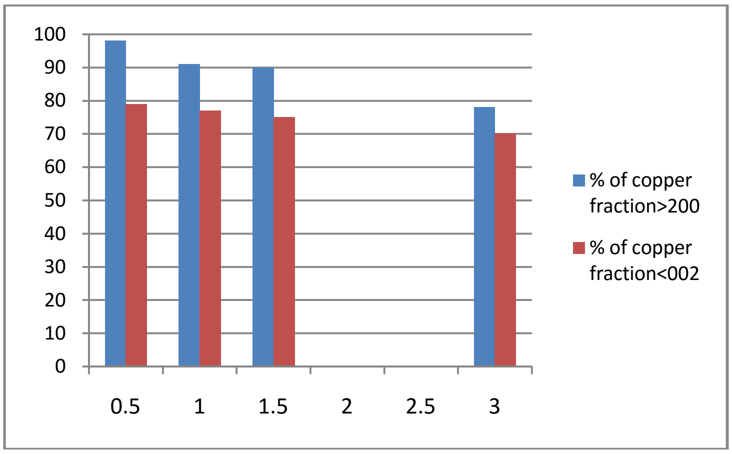

Fig1. Plot of adsorbent % of copper by two fractions of baobab fruit shell (*Adansonia digitata*))

Result that the copper adsorption efficiency is of 88% (particle size >200 µm) and 98% (particle size <200 µm) using baobab fruit shell (*Adansonia digitata*)), while Cu concentration is 0.5 mg /L. When Cu concentration amounted 3.0 mg/L; adsorption efficiency decreased from 70 to 79%.

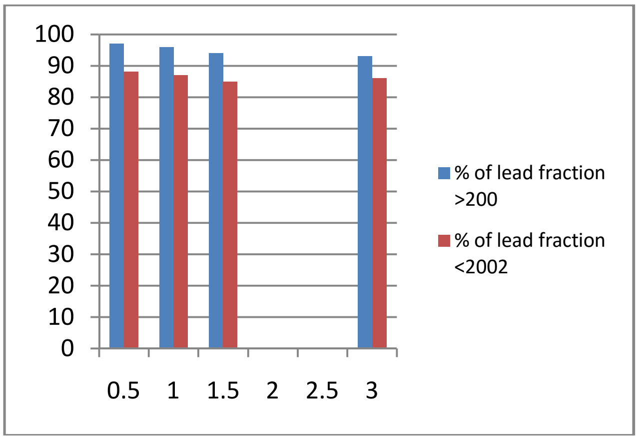

Fig 2. Plot of adsorbent % of copper by two fractions of baobab fruit shell (*Adansonia digitata*))

Result that the baobab fruit shell (*Adansonia digitata*) from industrial effluent eliminate 88% (particle size >200 μm) and 97% (particle size <200 μm) lead, when metal concentration is 0.5 mg/L. With increasing in Pb concentration the adsorption efficiency almost unchanged. Experimental results have indicated that baobab fruit shell (*Adansonia digitata*) can be excellent natural adsorbent for heavy metal removal from industrial effluent, like wastewater of landfill leachate.

CONCLUSION

Studies showed that using smaller fraction's baobab fruit shell (*Adansonia digitata*) treatment efficiency increases by 6–11%. Therefore, in order to obtain an even higher cleaning efficiency, baobab fruit shell (*Adansonia digitata*) should be additional crushed. The copper adsorption efficiency of 86% (particle size >200 μm) and 97% (particle size <200μm) using baobab fruit shell (*Adansonia digitata*), when Cu concentration is 0.5 mg /L. When Cu concentration reached 3.0 mg/L adsorption efficiency decreased from 72 to78%. Experiments show that the baobab fruit shell (*Adansonia digitata*) from aqueous solution eliminate 87% (particle size >200 μm) and 96% (particle size <200 μm) lead, when metal concentration is 0.5 mg/L. With increasing concentration of Pb adsorption efficiency almost unchanged. Experiment and result analysis indicated that baobab fruit shell (*Adansonia digitata*) can be excellent natural adsorbent for heavy metal removal from aqueous solutions, like wastewater of landfill leachate.

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