



University of Science and Technology
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**Adsorptive Removal of Some Heavy Metals from Aqueous
Solutions by (*Hyphaene Thebaica*) Charcoal**

الإزالة بالإدمصاص لبعض العناصر الثقيلة من المحاليل المائية بواسطة الدوم

A Thesis Submitted in Partial Fulfillment for the Requirements of M.Sc.
in Chemistry

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الآية

بسم الله الرحمن الرحيم

قال تعالى: (قُلْ هَلْ يُسْتَوَى الَّذِينَ يَعْلَمُونَ وَالَّذِينَ لَا يَعْلَمُونَ إِنَّمَا

يَتَذَكَّرُونَ أُولَئِكَ أَلْبَابٌ)

صدق الله العظيم

سورة الزمر: ٩

DEDICATION

I dedicate this work to:

My beloved parents

My husband

My son and daughter

My Brothers and Sisters

ACKNOWLEDGMENT

My deep thanks and prayers to Almighty Allah for giving me health and desire to complete this work successfully.

My deep gratitude would go to my supervisor, Dr. Elfatih Ahmed Hassan, for his support, encouragement and valuable advice.

My thanks would be extended to all those who help me, taught me during the achievement of this work.

Abstract

The aim of the present study was to study the adsorption of the heavy metals (copper, zinc, lead and cadmium) using *Hyphaecene Thedaica* (Doum).

Doum palm charcoal was made by ignition of Doum palm into airtight metal tray slot for four hours, then the Doum palm charcoal was soaked in different solutions of heavy metal salts for half an hour. Atomic absorption Spectroscopic Technique was used to measure the heavy metals concentrations in their solutions before and after addition of Doum charcoal.

The atomic analyses showed that the Doum charcoal is a good adsorber of the metal ions in samples. The heavy metals concentrations of (copper, zinc, lead and cadmium) were decreased after Doum charcoal was added (copper: from 78.8 ppm to 7.34 ppm, zinc: from 40.11 ppm to 19.76 ppm, lead: from 15.28 ppm to 5.71 ppm, cadmium: from 38.32 ppm to 0.88 ppm).

مستخلص

تم جمع الدوم من أماكن مختلفة من ولاية الخرطوم. وتم أخذ هذه العينات وطحنها باستخدام هاون ومدقة إلى قطع صغيرة.

والهدف من هذه الدراسة هو دراسة امتزاز فحم الدوم بواسطة المعادن الثقيلة (النحاس والزنك والرصاص والكاديوم).

تكون فحم الدوم نتيجة لحرقة في صندوق حديدى ذو فتحة واحدة لمدة أربع ساعات، ثم بعد ذلك تم نقع فحم الدوم في المحاليل المحضرة المختلفة للمعادن الثقيلة لمدة نصف ساعة. وقد تم قياس امتصاص الذرية تركيزات المعادن الثقيلة قبل وبعد إضافة فحم الدوم.

وأظهرت التحليلات الذرية الأمتزاز الجيد لفحم الدوم بواسطة المعادن الثقيلة. وقد انخفض تركيزات المعادن الثقيلة (النحاس والزنك والرصاص والكاديوم) بعد إضافة فحم الدوم (النحاس: من 78.8 جزء في المليون إلى 7.34 جزء في المليون، الزنك: من 40.108 جزء في المليون إلى 19.76 جزء من المليون، والرصاص: من 15.28 جزء من المليون إلى 5.705 جزء في المليون، الكاديوم: من 38.32 جزء من المليون إلى 0.876 جزء في المليون).

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CHAPTER ONE
INTRODUCTION

1. INTRODUCTION

1.1 Charcoal

Charcoal is residue of solid non-agglomerating organic matter of vegetable or animal origin that result from carbonization by heat in the absence of air at temperature above 300degrees Celsius.

Charcoal is a highly recalcitrant by product of fire and has recently been shown to influence a variety of ecological processes and to enhance soil fertility (Zackrisson et al 1996).Charcoal is likely highly variable in natural ecosystems and may result in substantial variation in these ecological effects. Two factors that likely generate substantial variability in charcoal properties are formation temperature and the type of material from which charcoal is formed(Glaseretal,2002).Temperature may affect charcoal by volatilizing certain elements and organic molecules, while concentrating those that remain, resulting in a different chemical composition in high and low temperature charcoal. Source material may also influence properties of charcoal because lignified materials, such as wood and bark, likely have different chemistries and physical structures. Source material may also influence properties of charcoal because lignified materials, such as wood and bark, likely have different chemistries and physical structures. For instance, a simple difference in tracheid diameter between the wood of two species may determine the surface area, and thus sorption capacity, of charcoal generated from these substrates Differences in charcoal properties caused by temperature and source material may have important ecological significance. These changes in fire intensity and forest species composition may correspond with a shift in physical and chemical properties of charcoal generated in the system (Delouca et al, 2006).

Principal raw materials are medium to dense hardwoods such as beech, birch, hard maple, hickory, and oak. Others are softwoods (primarily long leaf and slash pine), nutshells, fruit outdoor cooking. In some instances, its manufacture may be considered as a solid waste disposal technique. Many raw materials for charcoal manufacture are wastes, as noted, when the Second World War began, the charcoal industry had in many countries a somewhat tactical task to sustain the war machinery, the products provided by carbonization century ago. Charcoal came to be utilized not only in metallurgy but also in chemical processes and the fabrication of plastics, it was the essential raw material for activated carbon with its numerous outlet in the filter industry, pharmaceuticals, catalysts, pollution control. Rapid pyrolysis is one of the most important achievements of charcoal technology.

1.1.1 Types of charcoal

1.1.1.1 Activated charcoal

A solid, porous, carbonaceous material, the surface area can be enlarged by special activation processes. Industries use gas, steam, or chemical activation. The internal spaces in activated charcoal trap chemicals.

1.1.1.2 Briquetted charcoal

Some industrial application and major barbeque markets demand char pieces with a particular shape. Known shapes and forms are spheres, cylinder, hexagonal, diamonds, pillow-shape and pellets.

1.1.1.3 Sugar charcoal

It is obtained from the carbonization of sugar and particularly pure.

1.1.1.4 Lump charcoal

It is charcoal in its most natural form, it has a lot of attractive qualities; it lights faster, burns hotter and leaves very little ash (Emerich 1985).

1.2 Doum palm tree

Doum palm fruit (*Hyphaenethebaica*) is a desert palm tree with edible oval fruit, originally native to the Nile valley (Fadele et al, 2011).



Figure (1): Doum palm (*Hyphaenethebaica*)

1.2.1 Taxonomy

Current name: *Hyphaenethebaica* (Hyphaene is derived from the Greek word ‘hyphaino’ referring to the fibers from the leaves, which are used for weaving).

Authority: (L.) Mart.

Family: *Areaceae*.

Synonym(s): *Coryphathebaica* L. and *Hyphaeneguineense* Schum. & Thonn.

Common names: Dom (Arabic), doum palm, Egyptian doum palm, gingerbread palm (English), zembaba (Amharic), mkoma (Swahili), arkobkobai and kambash (Tigrigna) (Orwa et al., 2009).

1.2.2 Botanic description

Hyphaenethebaica is a deciduous palm 5-7 m high, with a girth of 90 cm. Trunk is Y-shaped, and the tree is easily recognizable by the dichotomy of its stem forming up to 16 crowns. The bowl is fairly smooth but clearly showing the scars of the fallen leaves. Bark dark grey. Leaves 120 x 180 cm, fan shaped, in tufts at the ends of branches with the blade divided into segments about 60 cm long, margins entire; leaf stalk about 60 cm long, armed with curved thorns; petiole more than 1 m long, sheathing at the base with numerous upwardly curving hooks. Male and female flowers are on 6 separate trees (Orwa et al., 2009). The inflorescence is similar in both sexes, up to 1.2 m long, with short branches at irregular intervals and 2-3 spikes arising from each branch. Male flowers shortly stalked, solitary in pits of the spadix, spathebracts encircling the spadix, pointed. The female palm produces woody fruits that persist on the tree for a long time. They are 6-10 x 6-8 cm, smooth, rectangular to cubical, with rounded edges, shiny brown when ripe, about 120 g each when fresh, 60 g when dry, each containing a single seed. Seed 2-3.5 x 3 cm, ivory in colour, truncate at base, apex obtuse (Orwa et al., 2009).

Hermaphrodite trees do occur rarely, but their fruits are smaller and sterile. In the Sudan, flowering occurs from February to April and fruiting from November onwards. First fruiting is after 6-8 years. Fruit ripens after 6-8 months, and fruiting takes place at the end of the dry season. In Nigeria, fruit appears in March and persists until the following season's flowers appear (Orwa et al., 2009).

1.2.3 Distribution

Hyphaenethebaica is one of 11 species of this genus to be found in Africa. Widespread in the Sahel, it is known from Senegal to Egypt and the Sudan. East Africa records for this species usually refer to *H. compressa* H. Wendt. It is also found in parts of the Sahara where water occurs, in oases and wadis (Vogt, 1995). The tree is native to Benin, Burkina Faso, Cameroon, Central African Republic, Chad, Congo, Cote d'Ivoire, Democratic Republic of Congo, Egypt, Eritrea,

Ethiopia, Gabon, Gambia, Ghana, Guinea, Kenya, Liberia, Mali, Mauritania, Niger, Nigeria, Senegal, Sierra Leone, Sudan, Tanzania, and Togo. It is exotic to India (Vogt, 1995). In Sudan it is found mainly along river and stream banks on silty soil. It can, however, be found away from rivers on more stony sites (Vogt, 1995).

1.2.4 Functional uses

Tree: The doum tree is used in dune control and for shade.

Leaves: The leaves are probably the most important part of the palm, providing the raw material used in basketry, making mats, thatching, making string and in roofing (where the roots are also sometimes used). They are also browsed to a limited extent by livestock especially in dry periods (Vogt, 1995). Leaves may also be used as fuel.

Wood: The wood is occasionally used for firewood and charcoal but more often in construction, providing supports and rafters for houses, posts for fencing and for building rafts. It can be cut by axe but is very difficult to saw due to the many fibers which make up the wood. Timber from male palms is said to be better than that of female palms as it is wood-borer proof, termite proof, decorative and durable (Vogt, 1995). **Root:** Root fibers obtained after 2-3 days of soaking and beating of the roots are used for making fishing nets. In local medicine roots are used in treatment of schistosomiasis (Vogt, 1995).

Sap: The sap is used to make a black dye often applied on leather (Vogt, 1995).

Fruit: The covering of the fruits is edible and sharply aromatic (hence the name Gingerbread palm) and can either be pounded off to form a powder, or cut off in slices. The powder from it is often dried and then added as a flavoring agent to food. In Turkana, Kenya, the powder is also used to make a mild alcoholic drink by adding water and milk and leaving it to stand (Vogt, 1995).

Seed: The seed inside the fruit is very hard and known as (Vegetable Ivory) is having been used commercially for making buttons and small carvings, but since the introduction of plastic, demand for this has dropped virtually to nil. Also, the sprouted seed is edible (palm cabbage) and the charcoal from the seed kernel is traditionally used to treat sore eyes in livestock (Vogt, 1995).

Doum palm fruits also a source of potent antioxidants (Hsu et al., 2006). The fruit has a brown outer fibrous flesh which is normally chewed and spewed out. Doum palm kernel is edible when it is unripe but hard when it is ripe. Moreover, Doum Palm is also used for local craft, for construction and the root is also medicinal. The foliage is used to make mats, ropes ,baskets, and hats while the stem with the leaves are used for construction purpose (Moussa et al., 1998).Roots of doum palm are used for treatment of bilharziaswhile the fruit is often chewed to control hypertension (Orwa et al., 2009).

The hard seed inside the fruit, known as ‘vegetable ivory’, is used to treat sore eyes in livestock using charcoal from the seed kernel as well as making buttons and small carvings, and artificial pearls (Orwa et al., 2009). It has similar morphology with coconut except for the fact that it is not as big as coconut. However, the husk of this fruit is mostly eaten while the fleshy part of coconut is the only part that is edible. So also, the husk of doum palm is not as hard as that of coconut. Moreover, *H. thebaica* is a variety of doum palm which is dark to light brown in colour. The nut of this fruit with the kernel is very hard, closely similar to palm kernel nut (Fadele et al, 2011).

Doum palm fruit in its powder form was applied in some food products as a source of fiber, stabilizer and minerals as well as for its potential healthy effect. Aqueous doum palm extracts increased the viability and activity of some certain dairy starter cultures which used in the manufacture of some dairy products especially probiotics (Amira, 2015).

1.2.5 Chemical composition of doum fruit

The monocarp (pulp) of the fruits of *H. thebaica* was found to contain 12.65% ash, 89.25% carbohydrate, 0.95% oil, 316 mg/g glucose, very low protein content of 0.01% and calorific values of 3655.9 kcal/kg. The anti-nutritional factor, tannin, content was 8.30 mg/g. It also contains Ca (245.10 mg/100 g), Mg (236.45 mg/100 g), Fe (47.96 mg/100 g), Cu (0.38) and Zn (0.62). The minerals concentrations in the mesocarp seem to be adequate enough to provide livestock with the required metal essential for the biochemical activities. (Nwosu et al., 2008).

1.3 Atomic Absorption Spectroscopy

Atomic absorption spectroscopy (AAS) is a spectra-analytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state. In analytical chemistry the technique is used for determining the concentration of a particular element (the analyze) in a sample to be analyzed. AAS can be used to determine over 70 different elements in solution or directly in solid samples used in pharmacology, bio- physics and toxicology research.

Atomic absorption spectroscopy was first used as an analytical technique, and the underlying principles were established in the second half of the 19th century by Robert Wilhelm Bunsen and Gustav Robert Kirchhoff, both professors at the University of Heidelberg, Germany (Robert et al., 2014).

The modern form of AAS was largely developed during the 1950s by a team of Australian chemists (McCarthy, 2012). They were led by Sir Alan Walsh at the Commonwealth Scientific and Industrial Research Organization (CSIRO), division of chemical physics, in Melbourne, Australia. Atomic absorption spectrometry has many uses in different areas of chemistry such as clinical analysis of metals in biological fluids and tissues such as whole blood, plasma, urine,

saliva, brain tissue, liver, muscle tissue, semen, in some pharmaceutical manufacturing processes, minute quantities of a catalyst that remain in the final drug product, and analyzing water for its metal content (Koirtyohann, 1991).

1.3.1 Principles

The technique makes use of absorption spectrometry to assess the concentration of an analyze in a sample. It requires standards with known analyze content to establish the relation between the measured absorbance and the analyze concentration and relies therefore on the Beer-Lambert Law (Robert et al., 2014).

In short, the electrons of the atoms in the atomizer can be promoted to higher orbitals (excited state) for a short period of time (nanoseconds) by absorbing a defined quantity of energy (radiation of a given wavelength). This amount of energy, i.e., wavelength, is specific to a particular electron transition in a particular element. In general, each wavelength corresponds to only one element, and the width of an absorption line is only of the order of a few picometers (pm), which gives the technique its elemental selectivity. The radiation flux without a sample and with a sample in the atomizer is measured using a detector, and the ratio between the two values (the absorbance) is converted to analyze concentration or mass using the Beer-Lambert Law (Robert et al., 2014).

1.3.2 Instrumentation

In order to analyze a sample for its atomic constituents, it has to be atomized. The atomizers most commonly used nowadays are flames and electro thermal (graphite tube) atomizers. The atoms should then be irradiated by optical radiation, and the radiation source could be an element-specific line radiation source or a

continuum radiation source. The radiation then passes through a monochromator in order to separate the element-specific radiation from any other radiation emitted by the radiation source, which is finally measured by a detector (Robert et al., 2014).

1.3.2.1 Atomizers

The atomizers most commonly used nowadays are (spectroscopic) flames and electro thermal (graphite tube) atomizers. Other atomizers, such as glow-discharge atomization, hydride atomization, or cold-vapor atomization might be used for special purposes (Robert et al., 2014).

1.3.2.1.1 Flame atomizers

The oldest and most commonly used atomizers in AAS are flames, principally the air-acetylene flame with a temperature of about 2300 °C and the nitrous dioxide system (N₂O)-acetylene flame with a temperature of about 2700 °C. The latter flame, in addition, offers a more reducing environment, being ideally suited for analyses with high affinity to oxygen (Robert et al., 2014).

A laboratory flame photometer that uses a propane operated flame atomizer

Liquid or dissolved samples are typically used with flame atomizers. The sample solution is aspirated by a pneumatic analytical, transformed into an aerosol, which is introduced into a spray chamber, where it is mixed with the flame gases and conditioned in a way that only the finest aerosol droplets (< 10 µm) enter the flame. This conditioning process is responsible that only about 5% of the aspirated sample solution reaches the flame, but it also guarantees a relatively high freedom from interference (Robert et al., 2014).

On top of the spray chamber is a burner head that produces a flame that is laterally long (usually 5–10 cm) and only a few mm deep. The radiation beam passes through this flame at its longest axis, and the flame gas flow-rates may be adjusted to produce the highest concentration of free atoms. The burner height may also be adjusted, so that the radiation beam passes through the zone of highest atom cloud density in the flame, resulting in the highest sensitivity (Robert et al., 2014).

The processes in a flame include the stages of desolvation (drying) in which the solvent is evaporated and the dry sample Nano-particles remain, vaporization (transfer to the gaseous phase) in which the solid particles are converted into gaseous molecule, atomization in which the molecules are dissociated into free atoms, and ionization where (depending on the ionization potential of the analyte atoms and the energy available in a particular flame) atoms may be in part converted to gaseous ions (Robert et al., 2014).

Each of these stages includes the risk of interference in case the degree of phase transfer is different for the analyte in the calibration standard and in the sample. Ionization is generally undesirable, as it reduces the number of atoms that are available for measurement, i.e., the sensitivity (Robert et al., 2014).

In flame AAS a steady-state signal is generated during the time period when the sample is aspirated. This technique is typically used for determinations in the mg L⁻¹ range, and may be extended down to a few µg L⁻¹ for some elements (Robert et al., 2014).

1.3.2.1.2 Electro thermal atomizers

Electro thermal AAS (ET AAS) using graphite tube atomizers was pioneered by Boris V. L'vov at the Saint Petersburg Polytechnical Institute, Russia, since the late 1950s, and investigated in parallel by Hans Massmann at the Institute of

Electrochemistry and Applied Spectroscopy (ISAS) in Dortmund, Germany (L'vov, 1990).

Although a wide variety of graphite tube designs have been used over the years, the dimensions nowadays are typically 20–25 mm in length and 5–6 mm inner diameter. With this technique liquid/dissolved, solid and gaseous samples may be analyzed directly. A measured volume (typically 10–50 μL) or a weighed mass (typically around 1 mg) of a solid sample are introduced into the graphite tube and subject to a temperature program. This typically consists of stages, such as drying – the solvent is evaporated; pyrolysis – the majority of the matrix constituents are removed; atomization – the analyze element is released to the gaseous phase; and cleaning – eventual residues in the graphite tube are removed at high temperature (L'vov, 1990).

The graphite tubes are heated via their ohmic resistance using a low-voltage high-current power supply; the temperature in the individual stages can be controlled very closely, and temperature ramps between the individual stages facilitate separation of sample components. Tubes may be heated transversely or longitudinally, where the former ones have the advantage of a more homogeneous temperature distribution over their length. The so-called stabilized temperature platform furnace (STPF) concept, proposed by Walter Slaving, based on research of Boris L'vov, makes ET AAS essentially free from interference. The major components of this concept are atomization of the sample from a graphite platform inserted into the graphite tube (L'vov platform) instead of from the tube wall in order to delay atomization until the gas phase in the atomizer has reached a stable temperature; use of a chemical modifier in order to stabilize the analyze to a pyrolysis temperature that is sufficient to remove the majority of the matrix components; and integration of the absorbance over the time of the transient

absorption signal instead of using peak height absorbance for quantification(L'vov, 1990).

In ET AAS a transient signal is generated, the area of which is directly proportional to the mass of analyte (not its concentration) introduced into the graphite tube. This technique has the advantage that any kind of sample, solid, liquid or gaseous, can be analyzed directly. Its sensitivity is 2–3 orders of magnitude higher than that of flame AAS, so that determinations in the low $\mu\text{g L}^{-1}$ range (for a typical sample volume of 20 μL) and ng g^{-1} range (for a typical sample mass of 1 mg) can be carried out. It shows a very high degree of freedom from interferences, so that ET AAS might be considered the most robust technique available nowadays for the determination of trace elements in complex matrices (L'vov, 1990).

1.3.2.1.3 Specialized atomization techniques

While flame and electro thermal vaporizers are the most common atomization techniques, several other atomization methods are utilized for specialized use(L'vov, 1990).

A. Glow-discharge atomization

A glow-discharge device (GD) serves as a versatile source, as it can simultaneously introduce and atomize the sample. The glow discharge occurs in a low-pressure argon gas atmosphere between 1 and 10 torr. In this atmosphere lies a pair of electrodes applying a DC voltage of 250 to 1000 V to break down the argon gas into positively charged ions and electrons. These ions, under the influence of the electric field, are accelerated into the cathode surface containing the sample, bombarding the sample and causing neutral sample atom ejection through the process known as sputtering. The atomic vapor produced by this discharge is

composed of ions, ground state atoms, and fraction of excited atoms. When the excited atoms relax back into their ground state, a low-intensity glow is emitted, giving the technique its name(L'vov, 1990).

The requirement for samples of glow discharge atomizers is that they are electrical conductors. Consequently, atomizers are most commonly used in the analysis of metals and other conducting samples. However, with proper modifications, it can be utilized to analyze liquid samples as well as non-conducting materials by mixing them with a conductor (e.g. graphite).

B. Hydride atomization

Hydride generation techniques are specialized in solutions of specific elements. The technique provides a means of introducing samples containing arsenic, antimony, tin, selenium, bismuth, and lead into an atomizer in the gas phase. With these elements, hydride atomization enhances detection limits by a factor of 10 to 100 compared to alternative methods. Hydride generation occurs by adding an acidified aqueous solution of the sample to a 1% aqueous solution of sodium borohydride, all of which is contained in a glass vessel. The volatile hydride generated by the reaction that occurs is swept into the atomization chamber by an inert gas, where it undergoes decomposition. This process forms an atomized form of the analyze, which can then be measured by absorption or emission spectrometry (L'vov, 1990).

C. Cold-vapor atomization

The cold-vapor technique an atomization method limited to only the determination of mercury, due to it being the only metallic element to have a large enough vapor

pressure at ambient temperature .Because of this, it has an important use in determining organic mercury compounds in samples and their distribution in the environment. The method initiates by converting mercury into Hg^{2+} by oxidation from nitric and sulfuric acids, followed by a reduction of Hg^{2+} with tin (II) chloride. The mercury, is then swept into a long-pass absorption tube by bubbling a stream of inert gas through the reaction mixture. The concentration is determined by measuring the absorbance of this gas at 253.7 nm. Detection limits for this technique are in the parts-per-billion range making it an excellent mercury detection atomization method (L'vov, 1990).

1.3.2.2 Radiation sources

The distinguish between line source AAS (LS AAS) and continuum source AAS (CS AAS). In classical LS AAS, as it has been proposed by Alan Walsh, the high spectral resolution required for AAS measurements is provided by the radiation source itself that emits the spectrum of the analyze in the form of lines that are narrower than the absorption lines. Continuum sources, such as deuterium lamps, are only used for background correction purposes. The advantage of this technique is that only a medium-resolution monochromator is necessary for measuring AAS; however, it has the disadvantage that usually a separate lamp is required for each element that has to be determined. In CS AAS, in contrast, a single lamp, emitting a continuum spectrum over the entire spectral range of interest is used for all elements. Obviously, a high-resolution monochromator is required for this technique, as will be discussed later (Rakshit et al., 2016).

1.3.2.2.1 Hollow cathode lamps

Hollow cathode lamps (HCL) are the most common radiation source in LS AAS. Inside the sealed lamp, filled with argon or neon gas at low pressure, is a cylindrical metal cathode containing the element of interest and an anode. A high voltage is applied across the anode and cathode, resulting in an ionization of the fill gas. The gas ions are accelerated towards the cathode and, upon impact on the cathode, sputter cathode material that is excited in the glow discharge to emit the radiation of the sputtered material, i.e., the element of interest. Most lamps will handle a handful of elements, i.e. 5-8. A typical machine will have two lamps, one will take care of five elements and the other will handle four elements for a total of nine elements analyzed (Rakshit et al., 2016).

1.3.2.2.2 Electrodeless discharge lamps

Electrodeless discharge lamps (EDL) contain a small quantity of the analyze as a metal or a salt in a quartz bulb together with an inert gas, typically argon gas, at low pressure. The bulb is inserted into a coil that is generating an electromagnetic radio frequency field, resulting in a low-pressure inductively coupled discharge in the lamp. The emission from an EDL is higher than that from an HCL, and the line width is generally narrower, but EDLs need a separate power supply and might need a longer time to stabilize (Rakshit et al., 2016).

1.3.2.2.3 Deuterium lamps

Deuterium HCl or even hydrogen HCl and deuterium discharge lamps are used in LS AAS for background correction purposes. The radiation intensity emitted by these lamps decreases significantly with increasing wavelength, so that they can be only used in the wavelength range between 190 and about 320 nm (Rakshit et al., 2016).

1.3.2.2.4 Continuum sources

When a continuum radiation source is used for AAS, it is necessary to use a high-resolution monochromator, as will be discussed later. In addition, it is necessary that the lamp emits radiation of intensity at least an order of magnitude above that of a typical HCL over the entire wavelength range from 190 nm to 900 nm. A special high-pressure xenon short arc lamp, operating in a hot-spot mode has been developed to fulfill these requirements (Rakshit et al., 2016).

1.3.2.3 Spectrometer

As already pointed out above, there is a difference between medium-resolution spectrometers that are used for LS AAS and high-resolution spectrometers that are designed for CS AAS. The spectrometer includes the spectral sorting device (monochromator) and the detector (Rakshit et al., 2016).

1.3.2.3.1 Spectrometers for LS AAS

In LS AAS the high resolution that is required for the measurement of atomic absorption is provided by the narrow line emission of the radiation source, and the monochromator simply has to resolve the analytical line from other radiation emitted by the lamp. This can usually be accomplished with a band pass between 0.2 and 2 nm, i.e., a medium-resolution monochromator. Another feature to make LS AAS element-specific is modulation of the primary radiation and the use of a selective amplifier that is tuned to the same modulation frequency, as already postulated by Alan Walsh. This way any (unmodulated) radiation emitted for example by the atomizer can be excluded, which is imperative for LS AAS. Simple monochromators of the Littrow or (better) the Czerny-Turner design are typically used for LS AAS. Photomultiplier tubes are the most frequently used detectors in

LS AAS, although solid state detectors might be preferred because of their better signal-to-noise ratio (Rakshit et al., 2016).

1.3.2.3.2 Spectrometers for CS AAS

When a continuum radiation source is used for AAS measurement it is indispensable to work with a high-resolution monochromator. The resolution has to be equal to or better than the half width of an atomic absorption line (about 2 pm) in order to avoid losses of sensitivity and linearity of the calibration graph. The research with high-resolution (HR) CS AAS was pioneered by the groups of O'Haver and Harnly in the USA, who also developed the (up until now) only simultaneous multi-element spectrometer for this technique. The break-through, however, came when the group of Becker-Ross in Berlin, Germany, built a spectrometer entirely designed for HR-CS AAS. The first commercial equipment for HR-CS AAS was introduced by AnalytikJena (Jena, Germany) at the beginning of the 21st century, based on the design proposed by Becker-Ross and Florek. These spectrometers use a compact double monochromator with a prism pre-monochromator and an echelle grating monochromator for high resolution. A linear charge coupled device (CCD) array with 200 pixels is used as the detector. The second monochromator does not have an exit slit; hence the spectral environment at both sides of the analytical line becomes visible at high resolution. As typically only 3–5 pixels are used to measure the atomic absorption, the other pixels are available for correction purposes. One of these corrections is that for lamp flicker noise, which is independent of wavelength, resulting in measurements with very low noise level; other corrections are those for background absorption, as will be discussed later (Rakshit et al., 2016).

1.4 Some contaminated heavy metals

1.4.1 Copper

Copper is a major heavy metal contaminant that results from mining, metal processing, fertilizers, fungicides, agricultural and municipal wastes, sewage sludge dispersal, as well as traffic emissions (Ashish et al., 2013).

Although it is an essential micronutrient for normal plant metabolism, playing an important role in a large number of metalloenzymes, photosynthesis-related plastocyanin, and membrane structure, copper has been reported to be among the most toxic of heavy metals. Excess Cu inhibits plant growth and seed germination, induces chlorophyll degradation, and interferes with photosystem activity. At the molecular level, Cu ions generate reactive oxygen species such as O_2 , H_2O_2 , and OH. These reactive radicals cause oxidative damage of lipids, proteins, and nucleic acids. Cu ions also are responsible for alterations of membrane integrity in plant cells (Ashish et al., 2013).

Cu-mediated membrane lipid peroxidation causes membrane damage, thus changing membrane permeability and leading to electrolyte leakage.

It is generally accepted that heavy metal toxicity to plants is positively correlated to the concentration of the metals in plant tissues; higher metal concentrations in the tissues usually induce stronger damage to the plants (Ashish et al., 2013).

Copper (Tamba) is not poisonous in its metallic state but some of its salts are poisonous, especially the most common salts of copper are the Sulphate or the blue vitriol (NilaTutia) and the sub-acetate or Verdigris (Zangal) (Ashish et al., 2013).

Copper is also a vital dietary nutrient, although only small amounts of the metal are needed for well-being. It appears in several enzymes, facilitates the absorption of iron, and helps to transmit electrical signals in the body (Ashish et al., 2013).

In high doses, however, the metal can be extremely toxic. Copper can also saturate the water and soil, posing risks to wildlife. In a natural state, copper is rarely found pure. It is compounded with other elements, and the material must be treated before it can be sold. This can lead to serious environmental problems, especially

when mining companies engage in unsound practices. The chemicals used to extract the metal can be toxic, as can the discarded elements and runoff associated with its purification. Many countries attempt to regulate their copper industries to prevent widespread pollution and the problems associated with it (Ashish et al., 2013).

Copper is a reddish brown nonferrous mineral which has been used for thousands of years by many cultures. It is found in certain foods in greater quantity such as meats, eggs, poultry, nuts, seeds and grains, but certain foods are quite low in copper content such as fruits, vegetables, some nuts and grains. Those who are fast oxidizers require a lot more copper (Ashish et al., 2013).

The main foods that have high amounts of Copper are: Shellfish, Nuts and Seeds (except for pumpkin seeds), Soybeans (tofu, miso, etc.), Legumes, Wheat, Coconut, Avocado, Chocolate, Coffee, Leafy Greens.

Activated charcoal administration should be considered after a potentially dangerous ingestion. A dose of oral activated charcoal, responsible for chronic copper poisoning. The poison enters the system by absorption from the alimentary canal, by the lungs in the form of dust and partly by the skin in handling the metal or its salts. The places where copper accumulates are the liver first, then nervous system, the female and male reproductive system, connective tissues such as hair, skin and nails. Copper metallic poisoning depends upon the mode of administration, if copper is while of unproved benefit, is unlikely to be harmful and may have potential adsorptive capacity for copper. Usual dose is 25 to 100 gm in adults and adolescents and 25 to 50 gm in children aged 1 to 12 years (or 0.5 to 1 gram/kilogram body weight). Administer charcoal as aqueous slurry; most effective when administered within one hour of ingestion. Use a minimum of 240 ml of water per 30 gm charcoal. Chronic poisoning occurs due to continuous use of copper vessels for preparing and preserving food and prolonged use of water stored

in copper vessels over a long period of time is also swallowed as a metallic form is not poisonous but if taken as a vaporized form it acts as a poison. The formation of sub acetate on copper vessel, contamination of food stored in such vessels and prolonged use of water stored in copper vessels over a long period of time must be checked to control chronic copper poisoning (Ashish et al., 2013).

In freshwater environments, the toxic action of copper has been related to the disturbance of osmoregulation and waterborne silver and copper show very similar toxic actions, a recent review summarizes the role of developmental stage, size and salinity in Cu toxicity to estuarine and marine organisms (Boeck et al 2007). Copper is considered to be one of the most important pollutants of the air and is also a very significant pollutant of agricultural soils. Soil can be naturally rich in heavy metals or may be secondarily contaminated. Generally, clays and shale's have relatively high concentrations of many elements due to their ability to absorb metal ions. Alternatively, soil may be contaminated by fertilizers, pesticides, organic manures, urban and industrial wastes, atmospheric deposition, etc. (Filotheou et al., 2001).

1.4.2 Zinc

In the periodic table of the elements, zinc can be found in group Ib, together with the two toxic metals cadmium and mercury. Nevertheless, zinc is considered to be relatively non-toxic to humans. This is reflected by a comparison of the LD50 of the sulfate salts in rats. According to the Toxnet database of the U.S. National Library of Medicine, the oral LD50 for zinc is close to 3 g/kg body weight, more than 10-fold higher than cadmium and 50-fold higher than mercury.

Although consequences of zinc deficiency have been recognized for many years, it is only recently that attention has been directed to the potential consequences of excessive zinc intake. This is a review of the literature on manifestations of toxicity at several levels of zinc intake. Zinc is considered to be relatively

nontoxic, particularly if taken orally. However, manifestations of overt toxicity symptoms (nausea, vomiting, epigastric pain, lethargy, and fatigue) will occur with extremely high zinc intakes. At low intakes, but at amounts well in excess of the Recommended Dietary Allowance (RDA) (100-300 mg Zn/d vs. an RDA of 15 mg Zn/d), evidence of induced copper deficiency with attendant symptoms of anemia and neutropenia, as well as impaired immune function and adverse effects on the ratio of low-density-lipoprotein to high-density-lipoprotein (LDL/HDL) cholesterol have been reported. Even lower levels of zinc supplementation, closer in amount to the RDA, have been suggested to interfere with the utilization of copper and iron and to adversely affect HDL cholesterol concentrations. Individuals using zinc supplements should be aware of the possible complications attendant to their use (Gary, 1990).

1.4.3 Lead

Among the heavy metals, lead still remains the major toxic pollutant of the environment. Human exposure to lead can occur through numerous pathways including air, food, dust, soil, and water (Herman et al., 2011).

Lead is ubiquitous in human environment, because of its excellent physico-chemical properties, low cost and easy workability and is widely used in many industrial and domestic activities. The lead dispersed through gasoline exhausts, smelter emission, peeling paint, etc., never disappears completely from our environment. Human exposure to lead is from numerous sources and a myriad of pathways including air, food, dust, soil, and water. Exposure of the general population to lead mostly occurs through the ingestion of contaminated food and drinking water, and by the inhalation of particulate lead in ambient air. Exposure can also occur due to high lead levels in dust and soil in residential areas near high-

density traffic, smelters or refineries, and the consumption of vegetable, fruit and grains grown on high lead soils or near sources of lead emissions containing lead in excess as a result of direct deposition of lead onto plant surfaces apart from plant uptake of lead from soils. Gunshot wounds received through bullet injury either accidentally or due to reasons of crime act as long-term sources. Several times these type of lead poisoned cases go undiagnosed and untreated or may receive only symptomatic treatment because of lack of proper diagnosis. Screening and medical management of lead-exposed individuals is very important to identify and eliminate sources of lead (Herman et al., 2011).

1.4.4 Cadmium

Cadmium (Cd) is a naturally occurring metal situated in the Periodic Table of the Elements between zinc (Zn) and mercury (Hg), with chemical behavior similar to Zn. It generally exists as a divalent Cation, complexed with other elements (e.g., CdCl_2). Cd exists in the earth's crust at about 0.1 part per million, usually being found as an impurity in Zn or lead (Pb) deposits, and therefore being produced primarily as a byproduct of Zn or Pb smelting (Robin, 2013).

Cadmium toxicity has been demonstrated in several organs, as discussed later. Cadmium induces tissue injury through creating oxidative stress, epigenetic changes in DNA expression, inhibition or up regulation of transport pathways particularly in the proximal S1 segment of the kidney tubule. Other pathologic mechanisms include competitive interference with the physiologic action of Zn or Mg, inhibition of heme synthesis, and impairment of mitochondrial function potentially inducing apoptosis. Depletion of glutathione has been observed, as has

structural distortion of proteins due to Cd binding to sulfhydryl groups. These effects are magnified by interaction with other toxic metals such as Pb and As and possibly ameliorated by Zn or Se (Robin, 2013).

Clinical stigmata of cadmium toxicity depend on route, quantity, and rate of exposure. The chief organ of toxic impact in the humanism is the kidney, where the S1 segment of the proximal tubule is a major target of Cd deposition, with clinically observable defects in protein, amino acid, glucose, bicarbonate, and phosphate reabsorption (Fanconi syndrome) resulting from Cd-induced oxidative damage to transport proteins and mitochondria which may induce apoptosis of tubular cells. Effective antioxidant therapies are being sought, and there is *in vitro* evidence that selenium and zinc may at least partially antagonize the toxic effects of cadmium (Robin, 2013). About 30% of body cadmium is deposited in the kidney tubule region, as discussed earlier, with tubular damage being proportionate to the quantity of cadmium not bound to metallothionein. Diabetics are more susceptible to renal tubular damage from Cd exposure than controls (Robin, 2013).

Cadmium may also impair Vitamin D metabolism in the kidney, with deleterious impact on bone. This effect, coupled with direct Cd impairment of gut absorption of calcium and derangement of collagen metabolism, can produce osteomalacia and/or osteoporosis (Robin, 2013).

1.5 Objectives

1. Made the charcoal from Doum palm.
2. Purification some toxic heavy metals (Cu, Zn, Pb and Cd) by using Doum palm charcoal.
3. Determination of minerals contents after purify by using Atomic
4. Absorption instrument.

CHAPTER TWO
MATERIALS & METHODS

2. MATERIALS AND METHODS

2.1 Collection of samples

Different samples of Doum palm were collected from Khartoum state market. The palm seed coat was removed and smashed into suitable smaller sizes by using mortar and pestles and saved in dry, clean glass container for further handling.

2.2 Chemicals and materials

- Copper chloride.
- Zinc chloride.
- Lead chloride.
- Cadmium chloride.
- Distilled water

2.3 Instruments and apparatus

- Sensitive balance.
- Weight bottle.
- Glass bottle.
- Beaker.
- Measuring cylinder.
- Mortar and pestle.
- Filter funnel.

- Airtight metal tray slot.
- Atomic absorption spectrophotometer (GBC_ SavantAA).

2.4 Method of analysis

2.4.1 Samples preparation and treatment

The Doum palm seed coat (wooden seed cortex) was sorted out and broken into smaller size by applying mortar and pestles and left to dry at room temperature. The Samples were kept in clean, dry glass bottles.

2.4.2 Procedure

A number of Doum palms were collected, then the Doumbark was burned at a high temperature for four hours inside the airtight metal tray slot, until all the bark of Doum turned to charcoal, then the Doum charcoal was grinded into small parts by using mortar and pestle.

In different volumetric flasks, different solutions of CuCl_2 , ZnCl_2 , PbCl_2 and CdCl_2 were prepared by adding 0.1g of each salt to 100 ml distilled water.

In different volumetric flasks, 2g of Doum charcoal was soak into 50 ml of each prepared solutions for half an hour, then the mixture was filtered, and the concentration was measured after and before adding the Doum charcoal, using atomic absorption spectrometer.

CHAPTER THREE
RESULTS & DISCUSSION

3. RESULTS AND DISCUSSION

3.1 Results and Discussion

Table (3.1): Atomic absorption measurement of heavy metals adsorption by using Doum charcoal

Element	Concentration (ppm) before added Doum charcoal	Concentration (ppm) after added Doum charcoal	Adsorbed Cations (%)
Copper	78.80	7.34	90%
Zinc	40.11	19.76	50%
Lead	15.28	5.71	62%
Cadmium	38.32	0.88	97%

The use of low cost adsorbent has been studied as an alternative source of activated carbon for the removal of heavy metals. This study investigates the ability of using Hyphaene the baica, raw Doum palm seed coat, as an adsorbent. Results of adsorption of different Cations by Doum charcoal are show in Table (3.1), show that the concentration of Cu^{++} decreased from an initial value of 87 ppm to only 7% a reduction of 90%, Zn and lead also showed significant decrease in their concentration to the extend 50% and 62% respectively. The removal of cadmium was the most efficient among all the cations studies its concentration decreases from 38 ppm to only 0.8 ppm reacting as removed level of 97% which was remarkable performance. It clear from these results the Doum charcoal was an efficient absorber for the studied cations and it can be a cost effective alternative for charcoal imported in outside the country for Water treatment and other similar applications.

3.2 Conclusion

The present study indicates that new economic activated carbon developed from Doum palm seed coat is an effective adsorbent for the removal of heavy metal ions (Cu^{+2} , Zn^{+2} , Pb^{+2} and Cd^{+2}) from aqueous solutions.

The performance of Doum charcoal is especially remarkable in removed of Cd^{++} Ions.

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