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ADSORPTION OF LEAD AND MERCURY IONS ON CHEMICALLY TREATED DOUM PALM SHELLS

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ABSTRACT

Different sizes of 425µm and 850µm of the shell of Doum Palm (*Hyphaene thebaica*) were hydrolyzed with 7% v/v H_2SO_4 for 2 hours. Iodine method was used to determine the surface area. The hydrolyzed products were thiolated for 24 hours. The thiolated and unthiolated hydrolyzed shells were used to adsorb lead and mercury ions. The thiolated samples adsorbed 80-90% of the metals while the unthiolated samples adsorb 10-20%. This work has successfully shown that Doum palm shell with suitable chemical pretreatment has the ability of adsorbing heavy metal ions in solution. It is also clear from this work that the amount of metal ions removed from solution increases as the temperature of the solution and particle size of the adsorbent increases.

Keywords: Doum Palm, Thiolated, Unthiolated, Hydrolyzed, Pretreatment.

INTRODUCTION

Palms are extensively important to most of the world's population as providers of food and fiber, second only to the grasses that provide the grains [1]. Palms not only provide aesthetic beauty, but play an important role in the urban environmental diversity of plant materials. They are an important part of the landscape nursery in warmer areas of the world and an important part of the interior scaping industry in the Kingdom of Saudi Arabia. For many years, only a few palm species that were easily propagated were grown for both landscape and interior use.

Doum palm (*Hyphaene thebaica*) is a desert palm native to the Kingdom, sub-Saharan Africa and West India. It is known in the Kingdom which grows to 6 or 9 m and usually has forked stems with fan shaped leaves, 65-75 cm long. It is listed as one of the useful plants of the world [2]. The trunks of the palm are used as part of construction, as well as for manufacture of various domestic utensils and the leaves are used to make mats, packing and writing paper. The oblong, yellow-orange apple sized fruit has a red outer skin, a thick, spongy and rather sweet fibrous fruit pulp (mesocarp) that tastes like gingerbread and a large kernel. Dum palm seeds have a hard seed coat under the fleshy fibrous pericarp. The doum palm flourishes in hot dry regions where little else grows and the tree is appreciated for the shade it provides. All parts of the tree are useful, but probably the most important product is the leaves. The fibre and leaflets are used by people along the Niger and Nile Rivers to weave baskets, such as in the material culture of the Manasir. Other things made from the leaves are mats, coarse textiles, brooms, ropes, string and thatch (Factsheet, Hyphaene thebaica) [3]. The timber is used for posts and poles, furniture manufacture and beehives, and the tree provide wood for fuel. The leaf stalks are used for fencing and the fibre is used for textiles. Other products include fishing rafts, brooms, hammocks, carpets, buttons and beads [4].

The doum palm fruit-dates are also known in Eritrea as Akat, or Akaat in the Tigre language. The thin dried brown rind is made into molasses, cakes, and sweetmeats. The unripe kernels are edible. The shoots of the germinated seeds are also eaten as a vegetable [5]. In Egypt, the fruit is sold in herbalist shops, and is popular among children, gnawing its sweet yet sour hard fibrous flesh beneath the shiny hard crust. In Diu, Una and Saurashtra region of Gujarat (India), the tree is known as Hoka Tree and the red ripe edible fruit is known as Hoka. In northern part of Nigeria, among the Hausa people, it's known as "Goruba". Apart from the use of the fruit as food, juice is extracted from the young fruit and palm wine is prepared from the sap [6].

The fruit of the doum palm has been used in folk medicine to treat hypertension. In a trial, a group of patients with raised blood pressure were all given an antihypertensive drug but in half the individuals, this was supplemented with doum fruit extract. It was found that those receiving the supplement had lower systolic and diastolic pressures and lower total cholesterol, and the blood lipids and lipoproteins were changed in such a way as to decrease the risk of cardiovascular disease [7].

Doum palm was considered sacred by the Ancient Egyptians, and the seed was found in many pharaoh's tombs. On September 24, 2007, it was announced that a team of Egyptian archaeologists led by Zahi Hawass, discovered eight baskets of 3,000-year-old doum fruit in King Tutankhamun's tomb. The fruit baskets were each 50 centimetres high, the antiquities department said. The fruit are traditionally offered at funerals [8].

The Dum Palm is a tropical tree found in the savannah region of northern Nigeria. The tree resembles the coconut tree or the Dead Palm tree but not as tall as the two. The Dum Palm tree is of two types, the male and the female tree. The male tree normally does not produce fruit but has a rod-like substance representing the anther and behave as a normal flower. The female tree produces a fruit called Dum Palm [9]. The rod-like substance on the male tree has some traditional uses especially in the region where it is found. The substance is mixed with other herbs and is used as an aphrodisiac. The female tree unlike the male counterpart produces fruit which many people eat in the area where it is found. The fruit has sweet smell while eating and the seed inside contain a liquid or water that is sweet in taste like the coconut water. The “Gudduri” people in Azare, Bauchi state use the fruit when dry to construct a shield which they use during war. The shell can also be used to make whip for Donkeys and this whip is popularly known in Hausa as “Arandami”. The leaves of this plant are used to make local mat, hat, hut, local sack and “Azara” which is replaced by timber wood today though in the villages, it is still used in this 21st century. The fruit is no longer consumed as before only little children of the less privileged do eat the fruit and the bulk of it is thrown away as pollutant to the environment. The animals do not eat any part of the plant. Therefore this study is only considering the fruit which is the female part of the tree and to see how it can be put to proper use rather than just allowing it as a pollutant in the environment.

Materials and Methods

Sample collection

The Dum Palm fruit was obtained from the bush around Federal Polytechnic Bauchi-Nigeria. They were plucked from the tree still fresh.

Sample preparation

The Dum Palm fruit was broken open to remove the seed. It was washed, dried, divided into two and carbonized at 300^0C and 400^0C for 5 minutes and then grinded and sieved with a sieve of mesh sizes 425μm and 850μm [10]. Iodine method was used to determine the surface area of the crushed sample. The table below shows the particle size that was used [11].

Table 1: Particle size used

Sample	Carbonization temperature (^0c)	particle size (μm)
A	400	Between 425 and 850
B	400	Above 850
C	300	Between425 and 850
D	300	Above 850

The solutions of the metal ions Pb^{2+} and Hg^{2+} were prepared in varying concentrations of 10mg/l, 20mg/l, 30mg/l and 40mg/l using serial dilution from the standard stock of each metal ion. Equilibrium sorption of lead and mercury on the substrate was carried out by shaking 1g of the thiolated and unthiolated samples A, B, C and D. The contact time is 1.5 hour. The mixture was then filtered and the residual concentration was determined using spectrometer [12]. The difference between the initial and residual concentrations was recorded as the amount of metal ions removed from the solution. The amount of the metal ions bound to the modified and unmodified shells was studied and compared.

RESULTS AND DISCUSSIONS

Table 2: Effect of thiolation on surface area and iodine value

SAMPLE	UNTHIOLATED		THIOLATED	
	Iodine value (mg/g) shell sample	Surface area (g/mg) iodine	Iodine value (mg/g) shell sample	Surface area (g/mg) Iodine
A	79.80	$1.25x10^{-2}$	90.54	$1.10x10^{-2}$
B	112.04	$8.93x10^{-3}$	128.16	$7.80x10^{-3}$
C	51.85	$1.93x10^{-2}$	113.65	$8.80x10^{-3}$
D	67.97	$1.47x10^{-2}$	116.34	$8.60x10^{-3}$

From the above table, after thiolation, it was observed that the surface area decrease and the iodine value increased and this shows that certain spaces on the unthiolated sample after thiolation were taken up by the CS group of the thiourea.

Table 3: Effect of thiolation on adsorption of the heavy metal Pb from solution (RT) 425µm

Initial concentration of lead (Pb) (mg/l)	Unthiolated shell sample		Thiolated shell sample	
	Equilibrium concentration (mg/l)	Amount adsorbed (mg/l)	Equilibrium concentration (mg/l)	Amount adsorbed (mg/l)
10	7.20	4.50	5.00	6.00
20	13.00	8.00	7.00	14.50
30	18.30	13.10	12.20	20.60
40	22.20	19.50	16.10	26.00
50	27.40	24.30	18.00	34.20

It is evident from the information in table 2 that the thiolated (modified) shell sample adsorbed more than the unthiolated counterpart. This increased adsorbing property is due to the presence of CS groups incorporated in the modified sample during chemical treatment [13, 14].

Although this CS groups tend to be slightly reduce the number of available adsorption sites present before the treatment. The modified shell sample still adsorbed more than the unmodified ones. This shows that CS group (thiolation) plays important role in binding of the heavy metal ions.

Table 4: Adsorption of heavy metal (Hg) ion on thiolated shell samples of different sizes.

Initial concentration of Mercury (Hg).	Small particles (425-850)µm		Thiolated	
	Equilibrium concentration (mg/l)	Amount adsorbed (mg/l)	Equilibrium concentration (mg/l)	Amount adsorbed (mg/l)
10	7.8	3.2	10.2	2.8
20	12.5	9.4	15.0	7.0
30	19.0	13.0	19.4	12.2
40	21.6	20.0	24.2	17.2
50	26.2	26.0	31.0	20.0

In table 4, it was observed that the smaller the particle size of the adsorbent (treated dum palm shell) the greater the amount of metal ion adsorbed . This is because of the surface area of smaller particles compared to that of larger particles.

Table 5: Effect of thiolation on adsorption of heavy metal Lead (Pb) from solution 850µm

Initial concentration of Lead (Pb) (Mg/l)	Unthiolated shell sample		Thiolated shell	
	Equilibrium concentration (Mg/l)	Amount adsorbed (Mg/l)	Equilibrium concentration (mg/l)	Amount adsorbed (mg/l)
10	8.0	5.0	6.8	4.2
20	14.2	9.4	8.0	6.2
30	19.8	14.0	12.2	8.0
40	23.0	18.2	17.8	13.2
50	28.2	25.2	19.0	16.4

From the table above, the thiolated shell sample adsorb more than the unthiolated shell. This increased absorbing property is due to the presence of CS group incorporated in the modified sample during the chemical treatment [15, 16].

Although these CS groups tend to slightly reduce the number of available adsorption site as present before the treatment. The modified shell sample still adsorb more than the unmodified ones [17]. This shows that CS groups plays important role in binding of the heavy metal ion.

Table 6: Effect of thiolation on adsorption of heavy metal Mercury (Hg) from solution, 850μm

Initial concentration of Mercury (Hg) (mg/l)	Unthiolated shell sample		Thiolated shell sample	
	Equilibrium concentration (mg/l)	Amount adsorbed (mg/l)	Equilibrium concentration (mg/l)	Amount adsorbed (mg/l)
10	8.0	4.2	10.4	5.6
20	13.2	10.0	16.2	13.2
30	20.4	14.2	20.6	15.0
40	22.6	21.0	25.2	17.4
50	27.0	27.4	32.4	25.0

From the table above, the thiolated shell sample adsorb more than the unthiolated shell. This increased absorbing property is due to the presence of CS group incorporated in the modified sample during the chemical treatment.

Although these CS groups tend to slightly reduce the number of available adsorption site as present before the treatment. The modified shell sample still adsorb more than the unmodified ones [18]. This shows that CS groups plays important role in binding of the heavy metal ion.

Table 7. Logarithms of the amount adsorbed per unit mass of thiolated and unthiolated shell samples and equilibrium concentration after adsorption on thiolated and unthiolated shell mass.

Thiolated		Unthiolated	
Log a_T	Log c_T	Log a_{ut}	Log c_{ut}
0.778	0.699	0.653	0.857
1.161	0.845	0.903	1.114
1.314	1.086	1.117	1.262
1.415	1.207	1.290	1.346
1.534	1.255	1.386	1.438

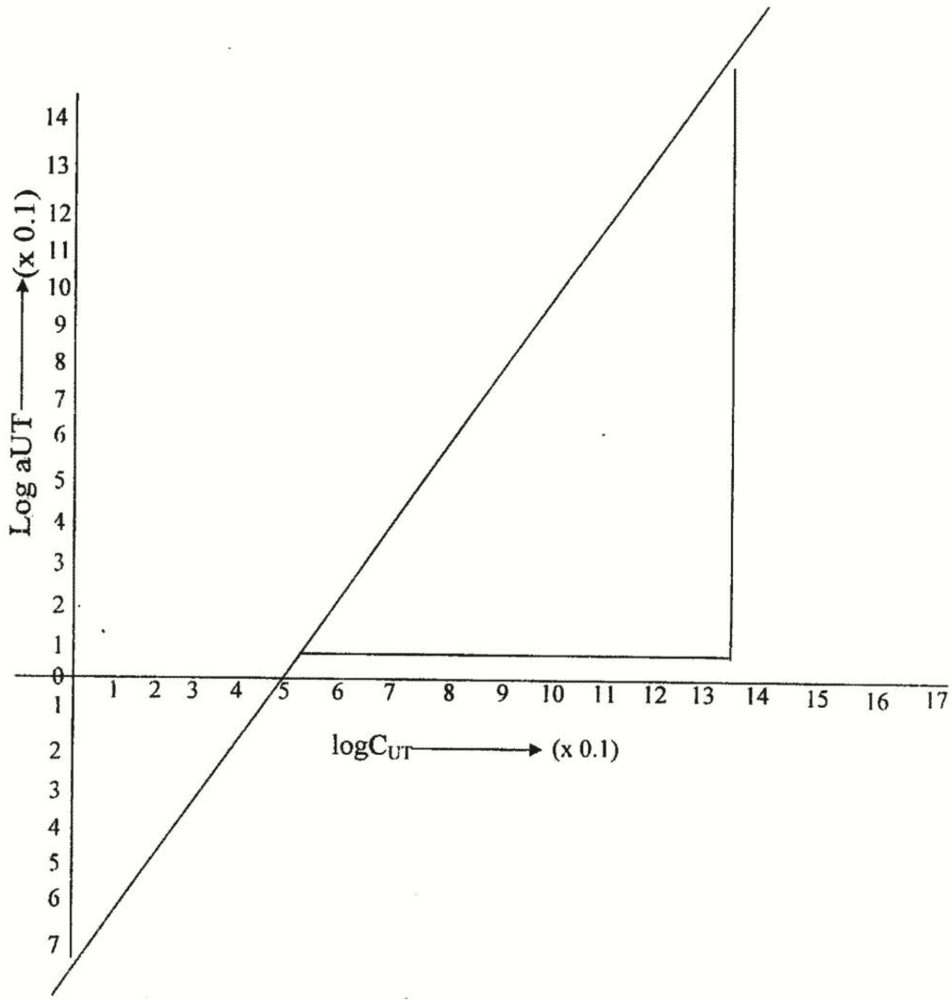
Key: a_T = amount adsorbed per unit mass of thiolated shell sample.

a_{uT} = amount adsorbed per unit mass of unthiolated shell sample.

C_T = equilibrium (residual) concentration after adsorption on thiolated shell sample.

C_{uT} = equilibrium (residual) concentration after adsorption on unthiolated shell sample.

Fig I: **FREUNDLICH ISOTHERM (UNTHIOLATED SHELL).**



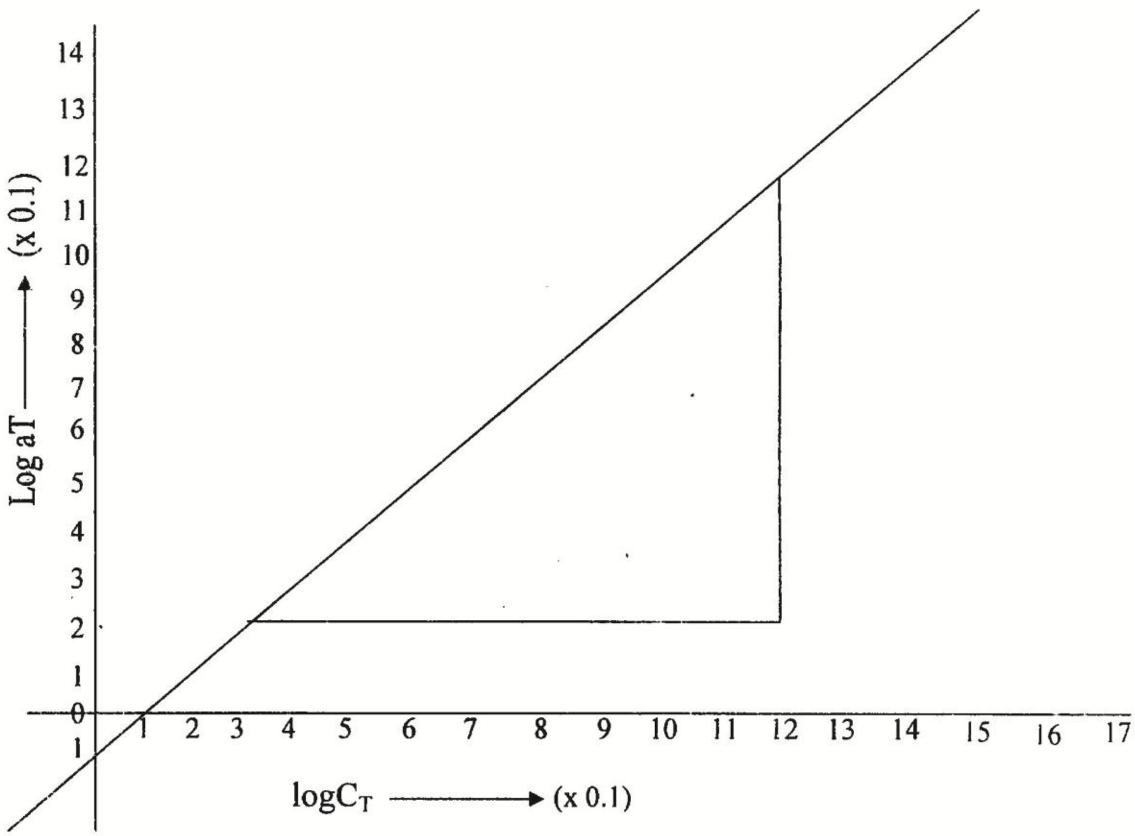
$$\text{Slope} = \frac{y_2 - y_1}{X_2 - X_1} = \frac{12.4-2}{12-2.6} = \frac{12.4}{9.4} = \underline{1.32}$$

$$n = \frac{1}{1.32} = \underline{0.76}$$

$$\text{intercept} = \log k = -1.432 \times 10^{-1}$$

$$K = 0.72$$

Fig.2: FREUNDLICH ISOTHERM (Thiolated shell).



$$\text{Slope} = \frac{y_2 - y_1}{X_2 - X_1}$$

$$= \frac{13.2 - 1}{14 - 5.8} = \frac{12.2}{8.2}$$

$$= \underline{1.49}$$

Freundlich isotherm gave approximate straight line which indicates that adsorption process followed the Freundlich isotherm. Freundlich isotherm takes the form

$$a = KC^n$$

This is found to be adequate for adsorption from solution over a considerable range of concentrations [19]. Where a = is the amount of solute adsorbed per unit mass of adsorbent from a solution of concentration C, K and n are constants for the given adsorbent and adsorbate. Taking the log of the above equation:

$$\log a = \log K + \log C$$

log a against log C should give a straight line. However the intercept K reveal that after thiolation the samples adsorbed approximately four times as they do before thiolation.

$$n = \frac{\log a - \log K}{\log C} = \frac{1}{1.49} = 0.67$$

Intercept = log K = -7.642×10^{-1}

$= 0.17$

CONCLUSION

Several works has been done to demonstrate adsorption by activated carbon. Samples such as hard wood, palm kernel, waste tyre, rubber and coconut has been used and reported to be rich in carbon content because they have one unit character that is the cellulose nature. This work has successfully shown that dum palm shell with suitable chemical pretreatment has ability of adsorbing heavy metals ions in solution. It is also clear from this work that the amount of metal ions removed from solution increases as the temperature of the solution and particle size of the adsorbent increases.

It is believed that utilization of dum palm shell in treatment of heavy metals waste from industrial effluent is an added advancement in researches involving chemists.

The freundlich coefficient and Langmuir constants obtained in this study show that dum palm shell are very effective in adsorbing lead and mercury ions from solution they may be found effective materials for treating waste water containing lead and mercury.

Due to its nature and properties, activated carbon has much individual application. They can use for adsorbing gases and vapour majorly.

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