# PRELIMINARY STUDY ON THE USE OF UREA ACTIVATED MELON (*Citrullus colocynthis*) HUSK IN THE ADSORPTION OF CADMIUM FROM WASTE WATER

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## ABSTRACT

*Adsorption studies were carried out using urea activated melon (Citrullus colocynthis) husks as a low-cost potential adsorbent to remove cadmium from industrial effluents. Bioabsorption parameters considered were as contact time, adsorbent dosage and adsorbate concentration. Cadmium removal was found to be dependent on the three parameters with maximum removal attained at 50 minutes with 0.8 and 1.0g of urea activated melon husk. Cadmium ions were mostly removed at low adsorbate concentration. Maximum removal was attained at 20 minutes with 97.6% adsorption. Adsorption isotherms had positive correlation with both Langmuir and Freundlich isotherm models and their $r^2$ values ranged from 0.911 – 1.00. Experimental data were also evaluated to find out kinetic characteristics of the adsorption process. Adsorption process for the heavy metal ion was found to follow pseudo-second order adsorption kinetics with the $r^2$ value of 0.8309. Activated melon husk, a readily available adsorbent was found to be efficient in the uptake of Cd (II) ions in industrial effluents, thus, confirming it as an excellent alternative for the removal of heavy metals from water and waste water.*

**Keywords:** Bioadsorption, Cadmium removal, Waste water, Melon husk

## INTRODUCTION

Contamination of the environment; land, atmosphere and water which include streams, lakes, underground water, bays or oceans by substances harmful to living things has become a serious public health issue. The contamination of water seems to be more serious due to the place and importance of water to life. Water is necessary to life on earth. All organisms contain it; some live in it; some consume it. Plants and animals require water that is moderately pure and they cannot survive if their water is loaded with toxic chemicals or harmful microorganisms. If severe, water pollution can kill large numbers of fish, birds and other animals in some cases killing all members of a species in an affected area (Encarta, 2009).

Industrial effluents are one of the major causes of environmental pollutions. Effluents discharged from dyeing industries are highly coloured, of low biological oxygen demand (BOD) and high chemical oxygen demand (COD). Disposal of this coloured water into receiving waters can be toxic to aquatic life (Lee *et al.,* 1999). They also pose a problem because

they may be mutagenic and carcinogenic (Papic *et al.,* 2000) and can cause severe damage to human beings such as dysfunction of kidney, reproductive system, liver, brain and central nervous system (Menahan, 1994).

Industrial activities like mining, painting, car manufacturing, metal plating, tanneries and agricultural activities like intensive use of fertilizers and fungicides are the main sources of wastes containing heavy metals. The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous even at low concentrations. Heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl) and lead (Pb) (LENNTECH, 2004). Among these toxic heavy metals; mercury, lead and cadmium have been called "the big three" and are in the lime light due to their major impact on the environment (Volesky, 1994; Volesky and Holan, 1995).

Heavy metals are considered to be one of the most hazardous water contaminants. According to WHO (2006) among the most toxic heavy metals are cadmium, chromium, copper, lead, mercury and nickel. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological system over time, compared to the concentration in the environment. Heavy metals can enter our water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers and groundwater (Encarta, 2009).

The discharge of these waste containing heavy metals and other discharges which includes plastic wastes, such as polyethylene terephthalate (PET) and polyvinyl chloride (PVC), industrial wastes, such as oil combustion residues and fabrics, as well as the discharge of tires, sewages, sludge, fertilizers etc, constitutes a serious challenge in waste management strategies. It is therefore of relevance to find alternatives by which such materials can be handled in a more environmentally friendly or acceptable procedures (Hayashi *et al.,* 2005).

Many conventional methods such as chemical precipitation, chemical coagulation, chemical oxidation and biological techniques, solidification, electrolytic recovery, ion exchange have been used for removal of dyes and metal ions. The application of such method however, is sometimes restricted because of technical or economical constraints (Bossrez *et al.,* 1997; Yu and Kaewsarn, 1999). Hence, more economical means such as bioabsorption for the removal of metals have been utilized (Volesky, 1994; Volesky and Holan, 1995; Sun and Shi, 1998). Bioabsorption is non-polluting, and it can be highly selective, more efficient, easy to operate and hence cost effective. Also, adsorption using activated carbon has been reported (Ouki and Neufeld, 1997). The removal of heavy metals by activated carbon (AC) is economically favourable and technically easy (Khezani and Capart, 2005). Other advantage of AC over other methods of remediation of heavy metals from waste water is that, it is sludge-free. Activated carbons, therefore, are widely used to treat waters contaminated with heavy metals.

The use of non-conventional wastes as carbon source for the production of AC might be an efficient alternative for production of low-cost AC, adoption of waste and effective waste management practice. Plastic wastes, various industrials wastes like fly ashes, pitch, polymer residues, saw dust, old newspaper, tires and sewage sludge are good raw materials for AC production (Raji and Anirudhan, 1997; Igwe *et al.,* 2005). Several agricultural wastes products have also been found useful in AC production, like coconut shell, rise husk, groundnut husk, cassava peel, maize cob, banana pith, *Medicago sativa* (Alfalfa), sphagnum moss peat, sunflower stalks, fungal, bacteria and algae (Gardea-Torresdey *et al.,* 1998; Sun and Shi, 1998; Abia *et al.,* 2003).

Commercially available activated carbons are expensive. In a developing economy like Nigeria, it is better to find low-cost adsorbent to be use for removal of metallic ions from waste waters. There is therefore, a need to search for an effective, environmentally friendly and economical adsorbent for waste water treatment. This work therefore focuses on the use of activated carbon (AC) from melon

*Citrullus colocynthis* (Lloyd and Cincinnati, 1898) husk as low-cost adsorbent materials for the removal of cadmium from waste water discharged into a freshwater body.

The objective of the study was to convert the waste melon husk into usable material and use same in effecting the treatment of the industrial effluents containing cadmium. The study also assessed the efficiency of waste melon husk as an environmentally friendly material for metal remediation and finally ascertains the efficiency of urea activated melon husk in the treatment of cadmium contained in industrial effluents.

## MATERIALS AND METHODS

### Adsorbent

The melon husks were collected from the melon sellers at the main market in Ogbomoso town of Oyo State, Nigeria.

Debris and stones were separated from the melon husks by hand-picking. The husks were washed thoroughly with tap water and rinsed with distilled water before being sun-dried. The dried husks were hammer milled into flour (40 mm mesh screen). The grounded husks were sieved with kitchen sieve to achieve a more uniform particle sizes. The husk was now ready for modification.

**Urea activation:** 100 g of the melon husk flour was soaked in 0.6 M urea solution for 6 hours, drained with filter paper, dried overnight at $50^0$C and was further activated in Memmert oven at $120^0$C for 4 hours. It was washed with distilled water to remove excess urea. The husk was dried at $105^0$C overnight. 500µm particles size was achieved by further grounding and sieving. The urea activated melon husk was stored in an air-tight container pending use (Ola *et al.,* 2005).

### Cadmium Adsorption Assay

The urea activated melon husks were used to treat Cadmium (II) simulated waste water. The equilibrium time (contact time), adsorbent dosage effect and concentration effect of the adsorbates were studied.

**Preparation of stimulated wastewater (stock solution):** All the experimental containers were properly washed and rinsed with distilled water to avoid, any contamination. The stock solutions were prepared by measuring out 1000 ml of distilled water into a 2-litre container. One gram (1g) of the lead (II) was added to the container. Proper mixture was ensured. A stock solution was prepared, 1000 mg/L of lead.

**Treatment of the wastewater with the adsorbent:** The stock solution (250ml) was drawn and poured into 250ml Erlenmeyer flask. The adsorbent (3g) was measured out using electronic weighing balance and added into the 250ml of the stock sample and thoroughly shaken together for proper mixing. 20ml of this mixture (adsorbent and adsorbate) were immediately drawn and poured into eleven different 100 ml Erlenmeyer flasks. The first 20ml sample was immediately filtered into a sample container using Whatman filter paper. The other 20ml samples were placed on different magnetic stirrers and were stirred at different magnetic stirrers and were stirred at different time between 1 and 100 minutes using standard methods recommended for examination of water and waste water (Clesceri *et al.,* 1998). The stirring was to make adsorption more effective. The heavy metal ion concentration (Cd) of the treated wastewater was analyzed at the time interval of 10 minutes, between 1 and 100 minutes.

The concentrations of the stock solutions were determined to serve as control sample or initial concentrations. Residual metal ion concentrations in the filtrate (after adsorption) were measured by atomic adsorption spectrophotometry (AAS) model 9100, Philips, England.

The amount of cadmium (II) adsorbed qt, (mg/l) at time (t) were calculated by using the following equation: $q_{t(mg/L)} = (C_o - C_e)\ V\ /\ m$, where $C_o$ and $C_e$ are the metal ion concentration in mg/L initially and at given time t, respectively, V is the volume of the adsorbate

and M is the mass of the adsorbent in gram, while $q_{t(mg/g)} = (C_o - C_e) \times (V/1000)/m$. The percentage of the metal ion removed ($R_{metal}$ %) from solution was calculated by using the following equations: $R_{cd(ii)}$ [%] $= C_o - C_e /C_o \times 100$, $Rp_{b(iv)}$ [%] $= C_o - C_e / C_o \times 100$ and $q_e = C_o - C_e$.

**Sorption Isotherms:** Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. Equilibrium studies that give the capacity of the adsorbent and equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms which are usually the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium. Langmuir and Freundlich isotherms are the earliest and simplest know relationships describing the adsorption equation (Muhamad *et al.,* 1998; Jalali *et al.,* 2002). These two isotherm models were used to assess the different isotherms and their ability to correlate experimental data.

**Sorption Kinetics:** The rate of adsorption of a molecule unto a surface is an essential parameter when designing batch sorption systems, consequently it is essential to establish the time dependence of such systems under various process conditions. In an attempt to describe the sorption rate and confirm the reaction mechanism of $Cd^{2+}$ onto melon husk, two kinetic models were applied to the experimental data. The first model was based on the assumption that sorption of metal ions onto the melon husk was reversible and followed a first order rate kinetics (Vinod and Anirudhan, 2002).

The experimental data were further evaluated based on the pseudo-second order kinetic rate model (Ho *et al.,* 1995).

**Data Analysis**

Data obtained were analysed using Langmuir and Freundlich isotherm models and correlation coefficient and presented graphically.

**RESULTS AND DISCUSSION**

The result of the effects of contact time on cadmium sorption by the adsorbent is presented in Figure 1. The result of the adsorption of cadmium by urea activated melon husk showed that cadmium was slightly adsorbed.
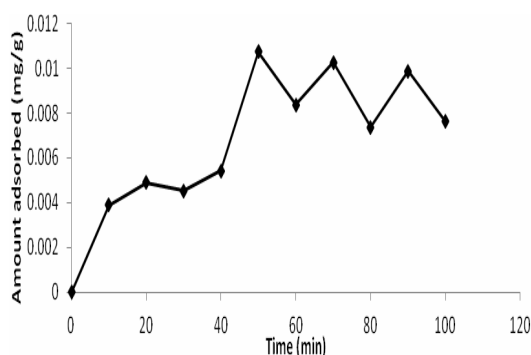


**Figure 1: Effect of contact time on adsorption of $Cd^{2+}$; using urea activated melon husk (adsorbent dose 3g, volume 250ml)**

There was increased sorption with increase in absorbent mass (Figure 2), but the increase in sorption with regards to increase in adsorbent mass dropped at the last increased dosage of 1.0g.

It is evident from Figure 3 that the sorption of cadmium was dependent on adsorbate concentration; the highest percentage removal was attained on the most dilute concentration of the adsorbate.

The negative values shown could be as a result of desorption. Adsorption isotherm models are widely employed to present the amount of solute adsorbed per unit of adsorbent, as a function of equilibrium concentration in bulk solution at constant temperature.
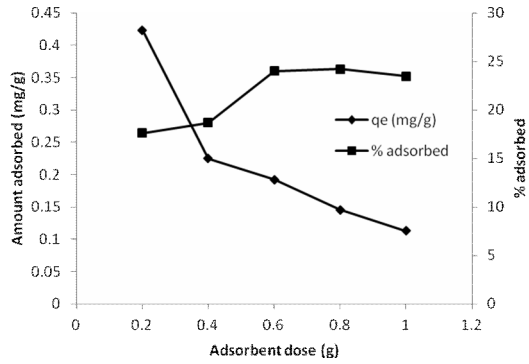
**Figure 2: Effect of adsorbent dose on adsorption of Cd$^{2+}$; using urea activated melon husk (adsorbent dose 3g, volume 250ml)**
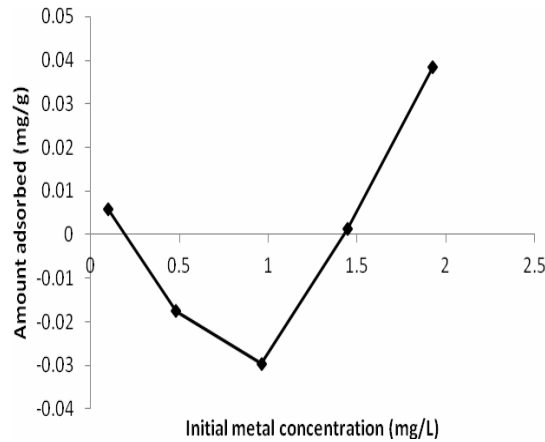


**Figure 3: Effect of initial metal concentration on adsorption of Cd$^{2+}$; using urea activated melon husk (adsorbent dose 3g, volume 250ml)**
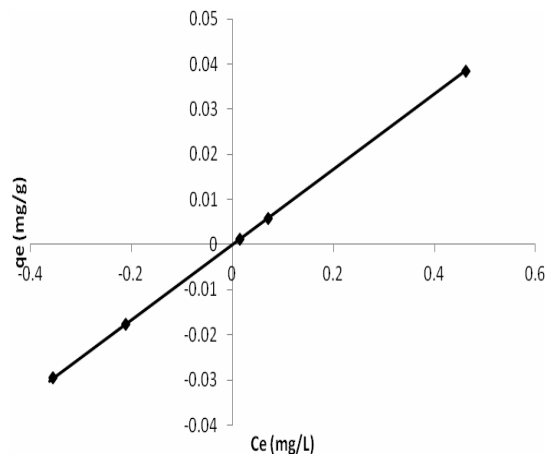


**Figure 4**: **Adsorption isotherm model for sorption of Cd$^{2+}$ using urea activated melon husk**

The equilibrium data obtained from Cd sorption capacity of the adsorbent were fitted to Langmuir and Freundlich isotherms. A plot of $q_e$ against $C_e$ in Figure 4 for urea yielded straight lines and indicated a good fit of the isotherm to the experimental data.

The linear plots of 1/ $q_e$ against 1/ $C_e$ showed that adsorption followed the Langmuir model (Figure 5).
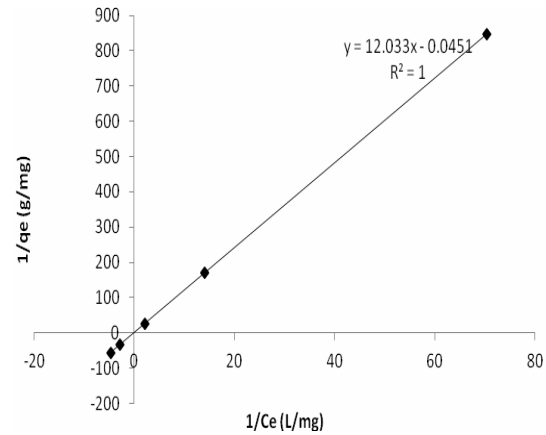


**Figure 5: Langmuir equilibrium isotherm model for sorption of Cd$^{2+}$ using urea activated melon husk**

The linearized form of Freundlich adsorption isotherm was used to evaluate the relationship between the concentration of Cd adsorbed by the adsorbent and Cd equilibrium concentration in wastewater. The plots of Log $q_e$ against Log $C_e$ showed that adsorption also followed the Freundlich model (Figure 6). The correlation coefficient ($R^2$) was 0.911 for sorption of Cd (II) by urea activated melon husk.
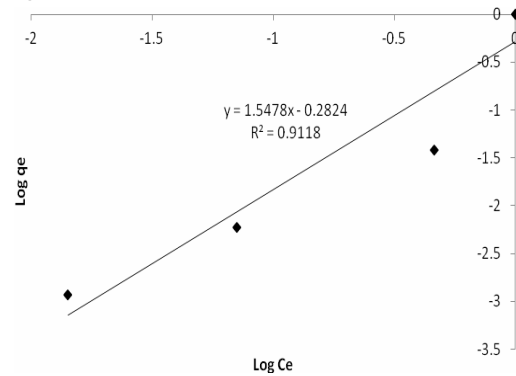


**Figure 6**: **Freundlich equilibrium isotherm model for sorption of Cd$^{2+}$ using urea activated melon husk**

The experimental data were fitted into pseudo-second order adsorption kinetics. The data showed that the urea activated melon husk enhanced the equilibrium sorption capacity of the melon husk towards the metallic ion. Figure 7 showed the pseudo-second order sorption kinetics of the metal ion by the adsorbent.

Results from this study indicated that urea activated melon husk has the potential of removing cadmium from wastewater like many other agricultural waste products. Nasim *et al.* (2004) in their study showed that agricultural waste products like sugarcane bagasse, rice husk, coconut husk, oil palm shell, neem bark, etc have great potential for the elimination of heavy metals from waste water.
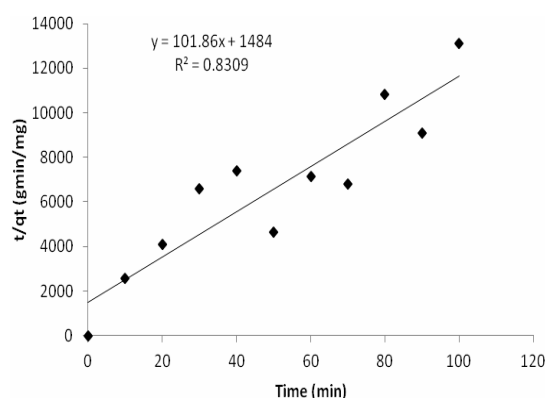


y = 101.86x + 1484
$R^2$ = 0.8309

**Figure** 7: **Pseudo-second order sorption kinetics of Cd$^{2+}$ using urea activated melon husk**

The sorption capacity depends on the contact time, adsorbent dosage and adsorbate concentration. Nasim *et al.* (2004) reported that though most agricultural waste product adsorbent have showed great potential for the elimination of heavy metals from waste water but the sorption capacity is dependent on the type of adsorbent used or investigated and the nature of the waste water treated. Results obtained from the analysis of filtrates while varying the contact time of the adsorbent with the adsorbate showed that the removal of cadmium from waste water increased with increasing contact time until equilibrium was achieved at 50 minutes. The results of the adsorption of cadmium by *Platanus orientalis* leaf (POL) indicated that cadmium adsorption increased with increasing time and became

almost constant after 60 min for POL and 60 min for its ash (Mahvi *et al.,* 2007). According to Iyagba and Opete (2009), the results obtained from varying the contact time of the adsorbent with the adsorbate showed that the removal of chromium and lead from drill cutting extract increased with increasing contact time and attained equilibrium at 90 and 120 min for both activated palm kernel shell (APKS) and activated palm kernel husk (APKH), respectively.

The amount of adsorbent employed was found to influence the efficiency of the adsorption process. The percentage removal of cadmium increased with increasing carbon dosage. Once the maximum adsorption sets in, even with further increase in the dose of adsorbent there was no further adsorption. This was in agreement with Ajmal *et al.* (2003) who reported that adsorption of Cd(II) was dependent on contact time, concentration, temperature, adsorbent doses and pH of the solution.

The percentage removal of cadmium by the adsorbent increased with decreasing adsorbate concentration. At lower concentration, cadmium ion in the solution interacted with the binding sites and higher percentage adsorption was facilitated. At higher concentration, more cadmium ions were left unabsorbed in solution due to the saturation of the binding site. Boucher *et al.* (2008) reported the sorption efficiency of Copper decreased with increase in adsorbate concentration.

**Conclusion:** Readily available agricultural waste like urea activated melon husk can be used as efficient sorbent for cadmium removal, representing an effective utilization of recycled wastes to solve an environmental problem. Melon husk is available abundantly and can be obtained for no price as agricultural waste in the country.

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