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Adsorptive Removal of Heavy Metals from Refinery Waste Water Using Activated Carbon Produced From Palm Kernel Shell

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ABSTRACT: *In this study activated carbon produced locally from palm kernel shell (waste)was tested for the removal of target heavy metal contaminants ina mixed solution (refinery waste water).Batch adsorption experiments were performed to ascertain the effectiveness of the activated carbon in the removal of heavy metals (Cr, Cu^{2+}, Fe^{2+}, Pb^{2+}, Zn^{2+}) in the mixed solution of waste waterobtained from the Port-Harcourt Refinery Company. Batch adsorption experiments were also conducted to study the effects of adsorbent dosage, particle size of adsorbent and contact time. The activated carbon was found effective in the removal of heavy metals in the mixed solution. The optimum adsorbent dosage, particle size and contact time were found to be 1g, 75 μm and 120mins respectively. The study also showed that activated carbon prepared from palm kernel shell can be efficiently used as low cost alternative for metal ions removal.*

KEYWORDS: Activated carbon, heavy metals mixed solution adsorption.

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I. INTRODUCTION

Industrial processes produce various types of unwanted products (waste). These wastes could be gaseous, solid or liquid. These wastes most times contain substances dangerous to human health and the environment.These industrial wastes are discharged into the atmosphere for gaseous wastes, into water bodies such as streams, rivers and ocean for liquid wastesand on land for solid waste.Disposal of the wastes into these environments without treatment contaminates these environments[1].Therefore,these wastes have to be treated before they are discharged into the environments. To ensure the conservation of these environments, government enact laws and regulations that stipulate the allowable concentration limits of various components in wastes to be discharged into the environments. Industries therefore treat such waste streams to reduce the concentrations of variousharmful components in waste streamsand continually update its operational processes with modern procedures that generate less toxic elements.

Crude oil is converted in petroleum refineries into valuable products such as liquefied petroleum gas, naphtha, kerosene, gasoline, diesel oil, asphalt base and residual oil. However, the production process of these products also produces waste products.Most of these wastes are converted to liquid streams and generally termed waste water. These include: desalter water (water produced from washing the raw crude prior to topping operations), sour water (wastewater from steam stripping & fractionating operations, spent caustic (formed in extraction of acidic compounds from product streams), tank bottoms (the periodically removed bottom sediment and water that settles at the bottom of tanks used to store raw crude), condensate blow down (from boilers and steam generators to control buildup of dissolved solids), ballast water (water from product tankers), cooling tower blow down(to prevent buildup of dissolved solids in closed-loop cooling systems), source water treatment system, other process water (Wastewater from product washing, catalyst regeneration & dehydrogenation reactions) and storm water (Process area and non-process area runoff from storm events).A typical refinery waste water had been characterized [2] and found to contain crude oil products, polycyclic and aromatic

hydrocarbon, phenols, heavy metal derivatives (such as cadmium, iron chromium, copper, nickel, etc.), surface active substances, sulfides, naphthalene acids and other chemicals.

Various treatment methods abound for the removal of these components in a typical waste water stream [3]. This work focuses on the removal of the heavy metal derivatives in refinery waste water.Heavy metals are metallic elements such as cadmium (Cd), Lead (Pb), copper (Cu), mercury (Hg), arsenic (As), chromium (Cr), thallium (Tl) and metalloids with relatively high density (greater than $4g/cm^3$ or 5 times or more than that of water) [4], and toxic at low concentrations. Unlike organic contaminants, heavy metals do not undergo biological decay and are thus a challenge in the remediation of soils they contaminate. Heavy metals could reach human bodies through inhalation, ingestion and dermal absorption and have been reported to be dangerous to humans:Lead exposure has been associated with hypochromic anemia; Cadmium is highly toxic and is a possible cause of lung cancer [5]. Most chromium compounds are carcinogenic, long exposure may cause kidney, liver and nerve damage [6].Heavy metals are also dangerous to aquatic life when discharged to rivers and streams as they do not decompose by the self-purification capabilities of rivers and streams.

Treatment methods employed for the removal of heavy metals from waste water include precipitation, filtration, coagulation and flocculation, ion-exchange, ion flotation and adsorption [7] with each having its advantages and disadvantages.However, adsorptionon to activated carbon has been proven to be cost effective, with simple design of process, is less contaminated by toxic substances compared to conventional biological process, more efficient and has the capability of adsorbing a broad range of heavy metals efficiently [8].Adsorption is a process that collects or adsorbs dissolved substances in water to the surface of the materials being used known as adsorbent.

In the adsorption method, different materials may be used as the adsorbent which collects or adsorbs the heavy metals from the water.The current trend is in the use of industrial and agricultural waste products [9]with high carbon content in the production of activated carbon as adsorbents for adsorption.The carbon material is carbonized;then activated to produce activated carbon. Activated carbon is a form of carbon that has been processed to make it extremely porous and have a very large surface area available for adsorption.

The use of agricultural waste products for the production of activated carbon and subsequent use for adsorption processes had been reported in several works: activated carbon produced from rice hulls used for the removal of copper [10]; activated carbon produced from cotton stalks for the removal of nitrogen [11]; activated carbon produced from cotton stalks for removal of nitrogen [12]; silica used as an adsorbent for the removal of lead [13]; activated carbon from wood sawdust for the removal of heavy metals in electroplating waste [14]; activated carbon produced from palm kernel shell used for the removal of copper in aqueous solution [15]. The use of industrial and agricultural waste materials for the production of activated carbon had also been reported in several works;the use of: almond shells, olive stones, and peach stones [16]; recycled iron material [17]; apple pulp [18] and date pits, peach stones, almond shells, and olive stones [19].

In an earlier work [20], activated carbon was produced from three waste agricultural products: bamboo, coconut shell and palm kernel shell. The activated carbons were characterized and used for the adsorption of benzene in aqueous solution.In this study, activated carbon from palm kernel was chosen due to the availability of its raw material.Nigeria has been reported to be the third largest producer of palm fruit [21],thus the availability and abundance of palm kernel shell obtained after the processing of palm fruits is guaranteed. Hence this work investigates the possibility of using the activated carbon from palm kernel shell for the removal of heavy metals in typicalrefinery waste water.

II. MATERIALS AND METHODS

Materials

The activated carbon used were those produced [20]from palm kernel shell and obtained from the Unit Operations Laboratory of the Department of Chemical/Petrochemical Engineering, Rivers State University of Science and Technology, Port-Harcourt, Rivers State, Nigeria. The waste water was obtained from the waste water treatment unit of the Port-Harcourt Refining Company before treatment.

Methods

Characterization of Prepared Activated Carbon

The activated carbon had been characterized [20]with the properties as given in Table 1.

Table 1: Properties of Activated Carbon from Palm kernel Shell [20]

Activated Carbon Source	Parameter					
	Yield %	Bulk Density (g/dm^3)	Porosity	Water Content	Ash Content (%)	pH
Palm Kernel shell	50.5	0.65	0.96	2.35	6.44	6.1

Wastewater Preparation and Characterization

The waste water was collected in a plastic container and immediately taken to the laboratory for analysis.The heavy metals present in the waste water sample were analysed using the atomic-absorption spectrophotometer. The concentrations of the heavy metals detected were taken as initial values. The ability of the produced activated carbon to adsorb these heavy metals was investigated in the adsorption experiments. The characteristics of the waste water was also determined after treatment (adsorption experiments)

Adsorption Experiment

Batch experiments were conducted in a set of 100 ml capped conical flasks at 32^{o}C with all used apparatus thoroughly pre-cleaned with distilled water. A weighed amount (1.0g) of adsorbent was added to 20ml of waste water stock solution, the conicalflask was shaken at room temperature (32 ± 1^{o}C) continuously (agitated using a mechanical shaker) at different time intervals; the contents (activated carbon) were separated from the stock solution at each time interval by filtration using a Whatman filter paper number 41. The concentrations of the heavy metals ion in the filtrate were analysed at each time interval using an atomic absorption spectrophotometer (AAS). The experiment was continued until equilibrium (constant concentration of the heavy metals ion in the filtrate) was attained (the concentration of each metal ion became constant at different times). The Batch adsorption experiments were replicated trice.

Adsorption Capacity

The metal ions concentration-time data obtained from the adsorption experiments were used to calculate the uptake/amount of metal ions adsorbed by the adsorbent using the relationship:

$$q_t = \left[\frac{C_o - C_t}{W}\right] V \quad (1)$$

The adsorption capacity at equilibrium was also calculated using the formula:

$$q_e = \left[\frac{C_o - C_e}{W}\right] V \quad (2)$$

Where: C_o = Initial concentration of heavy metals present in waste water before adsorption

C_t = Final concentration of heavy metals present after adsorption at time t.

C_e = Concentration of heavy metals in waste water when equilibrium was attained

V = Volume of waste water used (ml)

W = Mass (g) of adsorbent used

The removal efficiency of the activated carbon expressed as percentage of heavy metal ions removed at each time interval was obtained using the relationship:

$$R\% = \left[\frac{C_o - C_t}{C_o}\right] x\ 100 \quad (3)$$

III. EFFECT OF PROCESS PARAMETERS

Theinfluence of several operating parameters such ascontact time, particle size of adsorbent and thedose of adsorbent on the uptake of metal ions from the wastewater were investigated.

Effect of Contact Time

The effect of contact time on adsorption was studied for a period of 120 minutes. 0.2g of the adsorbent was added to different conical flasks containing 20ml of waste water stock solution. The flasks were closed and the mixture was shaken at different contact time ranging from 20 to 120 minutes to ensure effective sample-chemical contact at intervals of 20 minutes and at a temperature of 30^{o}C. The contents were filtered and analysed after each agitation time.

Effect of Particle size

The activated carbon was sieved with different mesh sizes into different particle sizes of 75µm, 150µm, 212µm, 300µm and 400µm. 20ml of Waste water stock solution was added to 0.8g of each particle size adsorbent sample. Each mixture was shaken for 120 minute, the contents filtered and the resulting clarified mixture analysed using an atomic absorption spectrophotometer (AAS).

Effect of Adsorbent Dosage

Different dosages of adsorbent (0.2-0.8g) were placed into conical flasks; 20ml of waste water were added to each flask, themixtures were then shaken for 120 minutes, filtered and the filtrate analysed using an atomic absorption spectrophotometer (AAS).

IV. RESULTS AND DISCUSSION

Characterization of waste water

The analysis of the waste water showed that it contained the following heavy metals: copper (Cu^{2+}), iron (Fe^{2+}), zinc (Zn^{2+}), lead (Pb) and chromium (Cr) with concentrations as shown in Table 2.

Table 2: Initial Concentrations of Metal ions in Waste Water

Heavy Metal	Initial Concentrations (ppm)
Cu^{2+}	0.37
Fe^{2+}	0.70
Zn^{2+}	1.22
Pb	0.32
Cr	0.37

Effect of Contact time on amount of Heavy Metals adsorbed

The amount of heavy metals removed by adsorption on the activated carbon with contact time presented as a percentage of the initial concentration of each heavy metal in the waste water is shown in Fig. 1

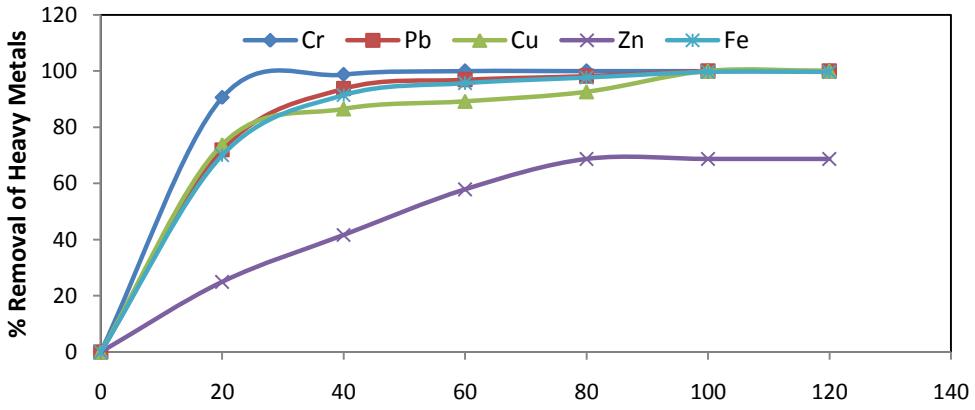

Fig. 1: Effect of Contact Time on Amount of Heavy Metals Adsorbed

From Fig. 1, it is evident that the removal of metal ions increased as the contact time increased for all heavy metals investigated.Equilibrium adsorption was attained within 60mins, 80mins for Cr and Zn ions; and 100minutes for Pb, Cu and Fe ions. Thus equilibrium was attained at different times for each metal ion and the heavy metals were completely removed at a contact time of 120minutes.At the minimum contact time for equilibrium; the adsorption capacity was:100%, 96.6%, 95.7%, 89.19% and 57.92% for Cr, Pb, Fe, Cu and Zn ions respectively. Hence Adsorption capacity for the heavy metals in increasing order was: Zn:Cu: Fe:Pb:Cr ions.

Effect of particle size on amount of Heavy metals adsorbed

Fig. 2 shows the effect of particle size on the percentage removal of heavy metals in the waste water.

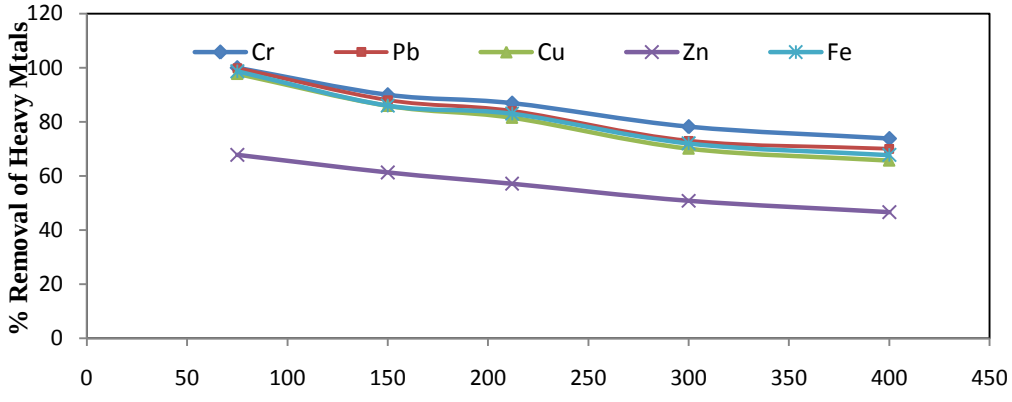

Fig. 2: Effect of Particle Size on Amount of Heavy Metals Adsorbed

Fig.2, shows that as the particle size of the adsorbent increases, the percentage removal of heavy metals decreases.The finer (smaller) the particle size of an activated carbon; the smaller the particle size distribution, the smaller the pore spaces and the better the access to the surface area of the activated carbon, hence the activated carbon retains more of the heavy metal molecules; however, large particle size distribution implies large pore spaces incapable of retaining heavy metal molecules seeping through. This trend is shown for each

heavy metal as adsorption capacity decreased with increase in particle size. Adsorption capacity for the heavy metals ions at each particle size in increasing order was: Zn: Cu: Fe: Pb: Cr.

Effect of Adsorbent Dosage on Amount of Heavy Metals Adsorbed

The effect of adsorbent dose on the waste water treatment is shown in Fig. 3

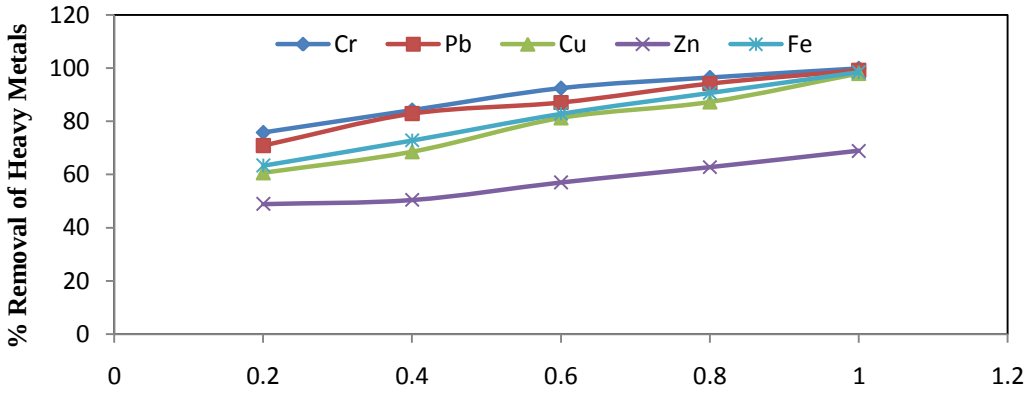

Fig. 3: Effect of Adsorbent Dosage on Amount of Heavy Metals Adsorbed

The dosage of activated carbon is the quantity of activated carbon used in the adsorption experiment. Hence the dose corresponds to the number of active sites of the activated carbon available for adsorption. An increase in activated carbon dose increases the active sites available for adsorption hence the rate of adsorption of the heavy metals increases and vice versa. This trend is seen in Fig. 3 where percentage removal of each heavy metal increased with increase in amount of activated carbon used (adsorbent dosage). It was also observed that the concentration of heavy metals ions in the refinery waste water was reduced by 100% (Cr), 100% (Pb) 98% (Cu), 95% (Zn) and 100% (Fe) after treatments with 1.0g. This revealed that the adsorption sites remained unsaturated during the adsorption reaction as the amount of heavy metal adsorbed increased continuously with increase in the adsorbent dosage (number of sites available for adsorption).

V. CONCLUSION

Activated carbon produced from palm kernel shell has been successfully used for the adsorption of heavy metals in refinery waste water containing Copper (Cu), Chromium (Cr), Iron (Fe), Zinc (Zn) and Lead (Pb) as adsorbates. The produced activated carbon showed potentials to adsorb heavy metals from a mixed solution (Refinery Waste Water). The effects of parameters such as contact time, adsorbent particle size and dose on the adsorption of the heavy metals in the waste water were investigated. Heavy metals adsorption increased with contact time, adsorbent dose and decreased with increase in particle size. The optimum values of these parameters are: contact time: 120 minutes, adsorbent particle size: 75 μm and adsorbent dose: 1g.The study also showed that activated carbon prepared from palm kernel shell can be efficiently used as low cost alternative for metal ions removal.

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