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ADSORPTION OF HEAVY METALS FROM ELECTROPLATING WASTEWATER USING GUINEA CORN HUSK ACTIVATED CARBON

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ABSTRACT

This study details the removal of manganese and copper from electroplating wastewater using activated carbon made from Guinea corn husks. Activated carbon prepared from Guinea corn husks using a two-step activation process was characterized using standard analytical methods. The moisture content, ash content, bulk density and electrical conductivity of Guinea corn husk were estimated to be 10.00 %, 0.35 %, 0.33 g/cm^3 and 1.5 x 10^2 µmhos respectively. The adsorbent was used for the adsorption of Cu^{2+}, Zn^{2+}, Fe^{2+}, and Mn^{2+} from electroplating wastewater. Results obtained showed that manganese had the highest percentage removal at a dosage of 2g and copper had the lowest percentage removal at a dosage of 2g. The pseudo first-order, pseudo second-order kinetic models were used to evaluate adsorption kinetics for the removal of manganese and copper from electroplating wastewater. The results showed that the pseudo second-order kinetic model best described the adsorption kinetic process. Indicating that chemsorption (chemical adsorption) is the rate determining step during the removal of manganese and copper from electroplating wastewater. Thermodynamic parameters such as ΔH, ΔS and ΔG were studied, the result showed spontaneous and favourable reaction for all the heavy metals.

KEYWORDS: Activated Carbon, kinetics, entropy, enthalpy, guinea corn husk

INTRODUCTION

Metals are part of nature but exploitation of resources or other anthropogenic activities have added to the background concentration of metals in the soil and water bodies (Goudie, 2018). Electroplating wastewaters are highly enriched with heavy metals such as Zn, Fe, Mn, and Cu (Azimi *et al*., 2017). Electroplating wastewaters have contributed to the pollution of agricultural water and soil and the method of discharge of these wastewaters also pose pollution risks to the environment (Malik *et al*., 2019). Literatures have revealed however that nearly all human activities generate wastes and the way these waste are collected, stored, and disposed increase the concentration of heavy metals in the environment (Manzoor *et al*., 2019).

Electroplating wastewater consists of organic and inorganic pollutants such as heavy metals. Amongst the kinds of pollutants, heavy metals have attracted attention of scientific community because of serious health hazards associated with them (Kumar *et al*., 2018). Various methods such as chemical precipitation, reduction, electrolytic extraction, ion-exchange, membrane filtration, coagulation-flocculation and floatation has been used for the removal of these metals from electroplating wastewater (Nazari *et al*., 2015). The aforementioned methods have low efficiency in the removal of heavy metals (Gunatilake, 2015). adsorption is recognized as an alternative method for the removal of heavy metals due to its efficiency, low cost and environmental friendliness (Ruthiraan *et al*., 2019). adsorption has been the major research and application especially for those heavy metals that cannot be efficiently removed by other methods. Various materials such as polymer resins, mineral oxides and biological materials have been used as adsorbent for the removal of heavy metals among which adsorption using activated carbon from agricultural waste has been discovered to be very effective in treatment process such as heavy metal removal from industrial wastewater (Shaba *et al*., 2021). However other adsorbents such as waste straw, guinea corn husk, lignin, groundnut husk, agricultural wastes, zeolites, fly ash has been studied for the removal of heavy metals from wastewater so as to develop an industrially viable, cost-effective, and environmentally compatible adsorbent. For excellent review regarding the use of low-cost adsorbents, this research work is aimed at producing a low-cost activated carbon from guinea corn husk (an agricultural waste material) for the removal of some heavy metals from electroplating wastewater (Lakherwal, 2014). This research and its application would contribute immensely to reducing the heavy metal concentrations and reducing the risk posed by waste guinea corn husk to the environment.

MATERIALS AND METHODS

The two step activation process described by Reza *et al*. (2020) was used for production of activated carbon (AC) from waste guinea corn husk. Moisture content of the resultant activated carbon was determined by drying 5 g of the activated carbon in a Gellenkanp oven at 105 ^{o}C until constant weight was obtained (AOAC, 2006). Ash content was determined according to the method described by Ceirwyn (1998), which involves heating the AC in a furnace at 600 ^{o}C until grayish white ash was obtained. Bulk density was determined by packing 3 g of the sample into a graduated cylinder and its bottom was tabbed on bench top until the volume of the AC stopped decreasing (Niangoran *et al*., 2015). Conductivity was measured using conductivity meter as described by Ahmedna *et al* (2000).

Batch adsorption experiments with the activated carbon were used to determine the effect of variations in time, adsorbent dosage and temperature on the process. The interacted electroplating wastewater was digested before determining the concentrations of heavy metals. Concentrations of heavy metal ions were determined before and after interactions with activated carbon using Atomic Abadsorption Spectrophotometer and the removal efficiency (%) was calculated as follows:

$$RE\ (\%) = \frac{(C_o - C_f) \times 100}{C_o} \quad (1)$$

Where:

C_o is concentration of heavy metal ion before interaction with activated carbon

C_f is concentration of heavy metal ion after interaction with activated carbon

Adsorption capacity at time t (q_t) was calculated using equation (2):

$$q_t = \frac{(C_o - C_t)\, v}{m} \quad (2)$$

Where:

v is volume of electroplating wastewater used for interaction *m* is mass of adsorbent used (Javadian *et al*., 2015).

Adsorption Kinetics and Thermodynamics

Kinetics and thermodynamics parameters of adsorption were studied using the pseudo first order, pseudo second order, free energy, enthalpy and entropy of the system. The different models and their equations are presented in Table 1.

Table 1: Adsorption kinetic and thermodynamic models and their equations

Kinetics and Thermodynamic Model	Equation
Pseudo first order kinetic	$\log(q_e - q_t) = \log(qe) - \frac{k_t}{2.303}t$
Pseudo second order kinetic	$\frac{t}{q_t} = \frac{1}{k_2\, {q_e}^2} + \frac{t}{q_e}$
Thermodynamic parameters	$lnK = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$

The equations take the form of equation of straight line i.e y = mx +c

RESULTS

Tables 2-4 present the physico-chemical properties of activated carbon, pseudo-first order, pseudo-second order and thermodynamic parameters respectively while figures 1-3 present effects of time, dosage and temperature on the adsorption of copper, zinc, iron and manganese from the electroplating wastewater.

Table 2: Result of the Physico-chemical Properties of Activated Carbon

Parameters	Result
Ash content (%)	10
Moisture Content (%)	0.35
Bulk Density (g/cm^3)	0.33
Electrical Conductivity (µmhos)	1.5 x 10^2

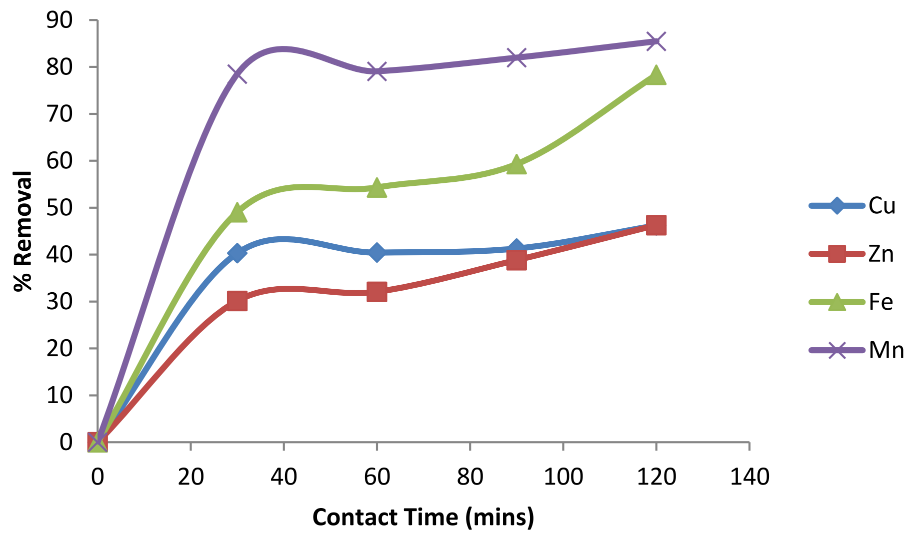

Fig 1: Effect of Contact Time on % removal of Cu, Zn, Fe, and Mn.

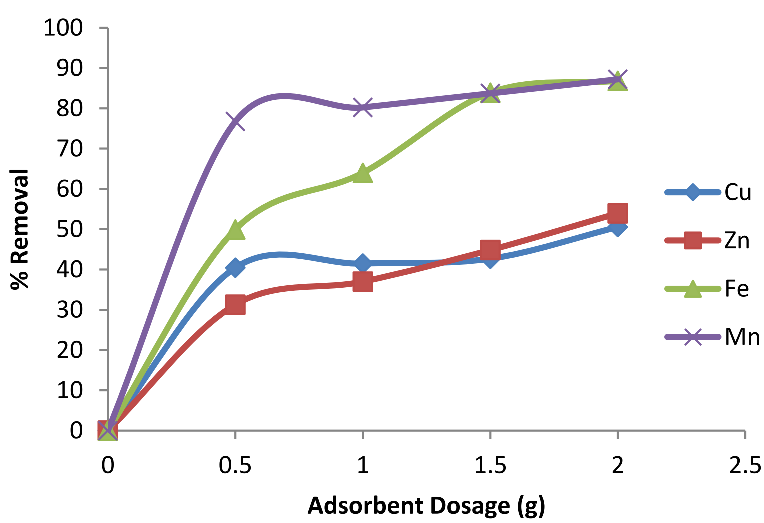

Fig 2: Effect of Adsorbent Dosage on % removal of Cu, Zn, Fe, and Mn.

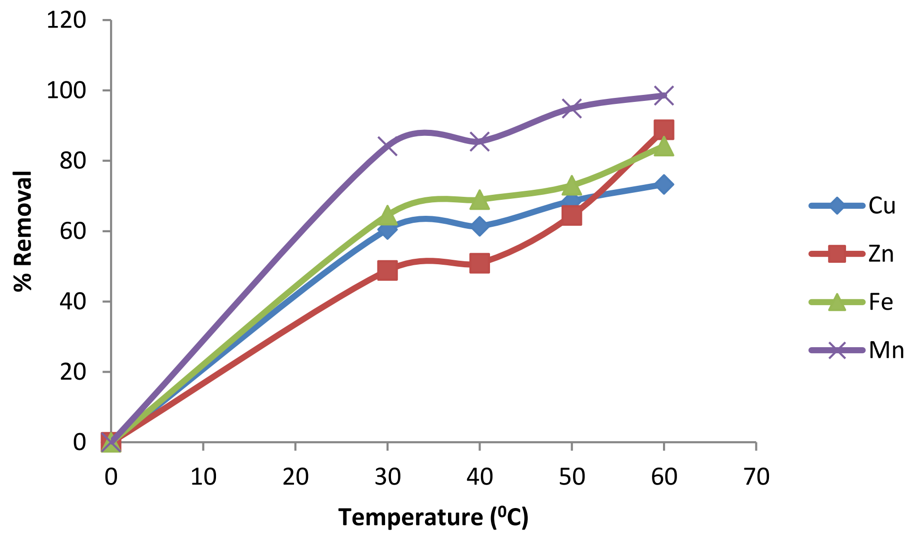

Fig 3: Effect of Temperature on % removal of Cu, Zn, Fe and Mn.

Table 3 Pseudo-first order and Pseudo-second order parameters for the adsorption of Copper, Zinc, Iron and Manganese

Metal ion	Pseudo-first order			Pseudo-second order		
	R^2	q_{e1}(m	k_1(g/mg/min)	R^2	q_e(mg/g)	k_2(g/
Copper	0.643	1.307	3.45 x 10^{-2}	0.985	1.205	0.47
Zinc	0.894	2.630	2.07 x 10^{-2}	0.935	2.240	3.94
Iron	0.819	4.931	1.61 x 10^{-2}	0.889	2.897	7.13
Manganese	0.229	1.694	2.30 x 10^{-3}	0.997	1.403	7.59

Table 4 Thermodynamic Studies of the adsorption of Cu^{2+}, Zn^{2+}, Fe^{2+} and Mn^{2+}

Metal ion	Temperature(K)	ΔG(kJmol)	ΔH (kJ/mol)	ΔS (J/molK)
Cu	303	-0.01		
	333	-0.75	6.91	22.99
	363	-1.44		
	393	-2.13		
Zn	303	-0.27		
	333	-2.95	32.85	107.51
	363	-6.18		
	393	-9.40		
Fe	303	-0.24		
	333	-2.37	21.29	71.04
	363	-4.50		
	393	-6.63		
Mn	303	-1.97		
	333	-8.82	67.21	228.32
	363	-15.67		
	393	-22.52		

DISCUSSION

Characteristics of Activated Carbon

From the result shown in Table 2, four properties (% moisture content, % ash content, bulk density and electrical conductivity) of the activated carbon were determined. The Table shows that the percentage moisture content of the guinea corn husk activated carbon was 0.35%. This value is significantly lower than the 4.60 % reported for saw dust activated carbon (Alzaydien, 2016). Percentage ash content was 10% a value considered low and an indication that guinea corn husk has a relatively small density and a high carbon content. This observation was found to correlate to the work reported by Jimoh *et al.*, (2017). Also, the electrical conductivity and bulk density of guinea husk activated carbon was obtained to be 1.5 x 10^2μmhos and 0.33g/cm^3 respectively.

Effect of Contact Time

The result of the effect of contact time on the adsorption of copper, zinc, iron and manganese ions by the activated carbon produced from guinea corn husk is shown in fig 1. The percentage removal of copper, zinc, iron and manganese ions from the wastewater increased as the contact time increased from 30 to 120 minutes; after which there was no further adsorption of ions. This implies that equilibrium was reached at 120 minutes and the adsorption site became saturated. The maximum percentage removal of copper, zinc, iron and manganese ions were 46.23%, 46.29%, 78.33% and 85.47% respectively at equilibrium time of 120 minutes. Similar optimum adsorption time was reported for the removal of Cr^{6+}, Mn^{2+} and Cd^{2+} respectively (Musah *et al.*, 2018). This study shows that Guinea corn husk activated carbon was efficient in the adsorption of zinc and copper ion from electroplating wastewater, and was corroborated by the work of Imamoglu *et al.,* (2018).

Effect of Adsorbent Dosage

The effect of adsorbent dosage on the adsorption of copper, zinc, iron and manganese ions by the activated carbon produced from guinea corn husk is presented in fig 2. The concentration of copper, zinc, iron and manganese ions in the wastewater decreased as the adsorbent dosage increased from 0.5 to 2.0g. This is a result of increase in the number of binding sites in the adsorbent, implying that equilibrium was reached at 2.0g. The maximum percentage removal of Copper, Zinc, Iron and Manganese ions were 50.54%, 53.95%, 86.82% and 87.21% respectively at equilibrium dosage of 2.0g adsorbent dosage. This study showed that guinea corn husk activated carbon was efficient for the adsorption of zinc and manganese ions from electroplating wastewater. This observation was found to correlate to the work reported by Zhang *et al.,* (2011).

Effect of Temperature

The result of the effect of temperature on the adsorption of copper, zinc, iron and manganese ions by the activated carbon produced from Guinea corn husk is showed in fig 3. From fig 3 the adsorption efficiency of the adsorbent increased as temperature increased from 30 ^oC reaching optimum adsorption at 60 ^oC indicating that equilibrium was reached at 60^0C. The maximum percentage removal of copper, zinc, iron and manganese ions were 73.30%, 88.81%, 84.19% and 98.55% respectively. This study shows that Guinea corn husk activated carbon was efficient for the adsorption manganese ion from electroplating wastewater.

Kinetic Studies

The values of the rate constant of the reaction processes and the correlation coefficient (R^2) values for the pseudo first and pseudo second order models for the removal of copper, zinc, iron and manganese ions from electroplating wastewater were shown in Table 3. Relatively high R^2 value is acceptable for a given model and indicates that the model successfully describes the adsorption kinetics. The optimum correlation coefficient (R^2) for pseudo first-order (0.894 for zinc ion) was lower than the corresponding 0.935 obtained in pseudo second. This indicates that the removal of copper, zinc, iron and manganese ions from electroplating wastewater followed the pseudo second order kinetic model.

Thermodynamic Studies

Thermodynamic parameters such as change in enthalpy, entropy and free energy were determined to understand the removal process of metal ions from electroplating wastewater by adsorption. The enthalpy values for the adsorption of copper, zinc, iron and manganese ions from electroplating wastewater were 6.91, 32.85, 21.29 and 67.21 kJ/mol respectively. This implies that the adsorption of these metal ions is endothermic in nature. The entropy values for the adsorption of manganese, zinc, iron and copper ions were 22.99, 107.51,71.04 and 228.32 kJ/molK respectively. From the results above, it can be interfered that the adsorption of these metal ions will be spontaneous at high temperatures and non spontaneous at low temperatures. The ΔG values were negative for all metals which is an indication that the removal processes feasible and favourable.

CONCLUSION

This research work is basically on the study of the adsorption potential of guinea corn husk activated carbon. The research established that guinea corn husk activated carbon could be used as an effective adsorbent for the adsorption of copper, zinc, iron and manganese. From the experimental results obtained, it can be recommended that guinea corn husk can be prepared as an activated for the removal of heavy metals and other organic contaminants from the wastewater. It can also be useful in the research laboratory for the removal of other pollutants in the environment.

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