REMOVAL OF COPPER AND CADMIUM FROM WASTEWATER USING CHEMICALLY ACTIVATED WATERMELON PEELS

ABSTSRACT

Activated Carbon of high adsorption efficiency and highly active surface properties were prepared from water melon fruits peels by physical and chemical processes such as carbonization using muffle furnace, chemical activation with 1M H_2SO_4 solution, followed by activation at 300^oC for 30 minutes. The adsorption capacity of the activated carbon is considered on the following; the effect of concentration, adsorbent dosage, and contact time. The physicochemical characteristics such as ash content (18.7%), pH(6.72),moisture content (1.82), bulk density(0.36) and conductivity (32.4) were investigated to understand the adsorptive capacity of activated carbon prepared from water melon peels. The adsorptive efficiency of the adsorbent in removing Cadmium and Copper ions from wastewater were compared with Langmuir and Freundlich adsorption isotherm, which proved effective removal efficiency within the range of 91.80 – 99.98 %. On the whole chemically activated watermelon peels should be used in treating our wastewaters, for a cleaner and healthier environment.

KEYWORDS: ***wastewaters, activated carbon, Removal efficiency, adsorbent, watermelon***

1.0 INTRODUCTION

Lack of clean water for drinking is an enormous challenge in most of the developing countries of the world due to daily contamination by excessive release of heavy metals into the environment due to industrialization and urbanization (Agbaire *et al*., 2014; Ikpe *et al*., 2022). Industrial uses of metals and other domestic processes have introduced substantial amounts of potentially toxic heavy metals into the atmosphere and into the aquatic and terrestrial environments. Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Ubong *et al*., 2023). They generally refers to the elements such as Cd (cadmium), Cr (chromium), Cu (copper), Hg (mercury), Ni (nickel), Pb (lead), Fe (iron) and Zn (zinc) which are commonly associated with pollution and toxicity problems. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless final products (Ikpe *et al*., 2017). They occur naturally in rock formation and ore minerals and so a range of normal background concentration is associated with each of these elements in soils, sediments, waters and living organisms(Ukpong and Okon,2013 ; Uwanta *et al*., 2023). In small quantities, certain heavy metals are nutritionally essential for healthy life (Ikpe *et al*., 2017), some of these are referred to as the trace elements (e.g., iron, copper, manganese, and zinc). These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products (Imoisi *et al*., 2020). Heavy metals are also common in industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel, mining, refining ores, fertilizers industries, and paper industries (Ubong *et al*., 2020). Many of these products are in our homes and actually add to our quality of life when properly used. Water pollution by heavy metals is one of the most important environmental problems today because they do not degrade into harmless products, tend to accumulate and are toxic to human beings. Among the heavy metals, cadmium is one of the extremely toxic and has been classified as a human carcinogen and teratogen impacting lungs, liver and kidney (Ikpe *et al*., 2020). The main contamination sources of this element are anthropogenic: industry wastewaters, mining operations, waste incineration as well as the combustion of some coals and oils. Increasing global emission of cadmium compounds into the atmosphere, together with aqueous and solid emission lead to local contamination problems. An additional problem of Cd(II) toxicity is its accumulative character. The US Environmental Protection Agency (USAEPA) has established a maximum contaminant level of 0.005 mg/L for cadmium in drinking water, while the World Health Organization (WHO) has set a maximum guideline concentration of 0.003 mg/L (Krystyna, 2019).

Given widespread cadmium contamination and the low drinking water guideline, there is considerable interest to remove it before discharge wastewaters. Several treatment methods can be used for this purpose, such as filtration, chemical precipitation, coagulation, solvent extraction, ion exchange, adsorption, membrane process, and bioremediation (Akpakpan *et al*., 2018). Among these techniques, adsorption has been recognized as one of the most popular methods due to its simplicity of operation, high efficiency, easy recovery and cost-effectiveness. An ideal adsorbent for this purpose should have high surface area, high adsorption capacity, mechanical stability and be easily regenerated. The process parameters such as solution pH, temperature, contact time and dosage of adsorbent also have significant impacts on the adsorption effectiveness. The aim of the study is to determine the adsorption capacity of chemically activated water melon peels.

2. MATRIALS AND METHOD

Sixty (60) fruits of Water melon were purchased from Oluku and New Benin,Benin City Edo State vegetable markets respectively. Thereafter, the water melons were washed and the peels collected. The water melon peels were then sun dried for 2 - 5 weeks to remove the moisture using standard analytical method described by Othman and Mohd 2013; Ikpe *et al.* (2017) .The water melon peels were ground into smaller bits using an electronic blender. The water melon peels were then carbonized using a muffle furnace at 300°C. The carbonized water melon peels were then activated with 1M conc. H_2SO_4. Thereafter, it was washed till the pH was brought to 7 using deionized water. The adsorbent was then dried at 105°C using an oven for 3 hours in order to evaporate the water used in washing the water melon peels.

2.1 ADSORBATE PREPARATION

Copper (Cu^{2+}) solution was prepared from its salt of Copper nitrate Cu (NO3)2 and Cadmium (Cd2+) solutions was as well prepared from its salt of Cadmium chloride ($CdCl_2$.21/2H_2O). The stock solutions were prepared taking 3 g of (Cu(NO_3)2 and 2.03 g of $CdCl_2$.21/2H_2O respectively were weighed and dissolved in 1000 ml volumetric flasks separately and then diluted with deionized water to the mark which gave a concentration of 1000 ppm. Thereafter, Serial dilution was prepared from the stock solutions of Cu^{2+} and Cd^{2+} where concentrations of 50 ppm, 75 ppm, 90 ppm, 115 ppm and 140 ppm were prepared by diluting 5 ml, 7.5 ml, 9 ml, 11.5 ml and 14 ml in 100 ml of deionized water respectively(Ikpe *et al*.,2017)

2.2 Effect of Concentration: 2.5 g of absorbent was placed into several 100 ml polyethylene bottles, 50 ml solutions with concentrations of 50, 75, 90, 115 and 140 ppm of Cu^{2+} and Cd^{2+} obtained from 1000 ppm stock solutions was added and shake for 20 min using Mechanical Orbital Shaker. An atomic adsorption spectrophotometer was used to analyze the filtrate obtained from the mixture (Haung, 2007; Ubong *et al*., 2023)

2.3 Effect of Adsorbent Dosage: Adsorbent Dosage of 1 g, 1.5 g, 2 g, 2.5 g and 3g were placed into different 100 ml polyethylene bottles with 50 ml of 50 ppm of the solutions of copper nitrate and Cadmium chloride respectively. The solution was shaken using a Mechanical Orbital Shaker for 20 min, then the filtrate of the mixture was analyzed using Atomic Adsorption Spectrophotometer according to Ikpe *et al*. (2020)

2.4 Effect of Contact Time: Varying time of 20, 25, 30, 35 and 40 min was used during the study of the effect of contact time on adsorption of the heavy metals. A fixed mass of 2.5 g of adsorbent was placed into several bottles of 50 ml of 50 ppm of solutions added. Mechanical Orbital Shaker was used in shaking the solutions for various times of 20, 25, 30, 35 and 40 min before they were filtered and the filtrate analyzed using the Atomic Absorption Spectrophotometer (Ikpe *et al.*, 2022)

3.0 RESULTS AND DISCUSSION

3.1 PHYSIOCHEMICAL PROPERTIES OF ACTIVATED CARBONIZED WATER MELON PEEL

The following physicochemical properties were obtained from the carbonized water melon peels;

Table 1: Result for the characterization

Ash content(%)	18.7
pH	6.72

Moisture content (%)	1.82
Bulk density	0.36
Conductivity	32.4

3.2 RESULT FOR THE ADSORPTION OF COPPER AND CADMIUM ION BY THE CHEMICALLY ACTIVATED WEAR MELON PEEL

The following values were obtained as result from the Atomic Adsorption Spectrophotometer (AAS) carried out on the sample filtrate using activated carbonized water melon peel on the adsorption of copper and cadmium ion.

3.2.1 EFFECT OF CONCENTRATION

With reference to both table below, showing the effect of different concentration of 50 to 140 mg/1 on the adsorption of the heavy metals of copper and cadmium respectively. At constant time of 20 minutes and adsorbent dosage of 2.5 g

Table 2: Effect of chemically activated water melon peel of initial concentration on adsorption of copper ion

Initial concentration (mg/)	Equilibrium concentration (mg/1)	Amount Adsorbed (mg/1)	% removal efficiency
50	0.02	49.98	99.96
75	0.04	74.96	99.95
90	0.17	89.83	99.81
115	1.33	113.67	98.84
140	1.67	138.33	98.81

Table 3: Effect of chemically activated water melon peel of initial concentration on adsorption of cadmium ion

Initial concentration (mg/)	Equilibrium concentration (mg/1)	Amount Adsorbed (mg/1)	% removal efficiency
50	0.05	49.95	99.90
75	0.32	74.68	99.57
90	0.50	89.50	99.44
115	1.65	113.35	98.57
140	1.90	138.10	98.64

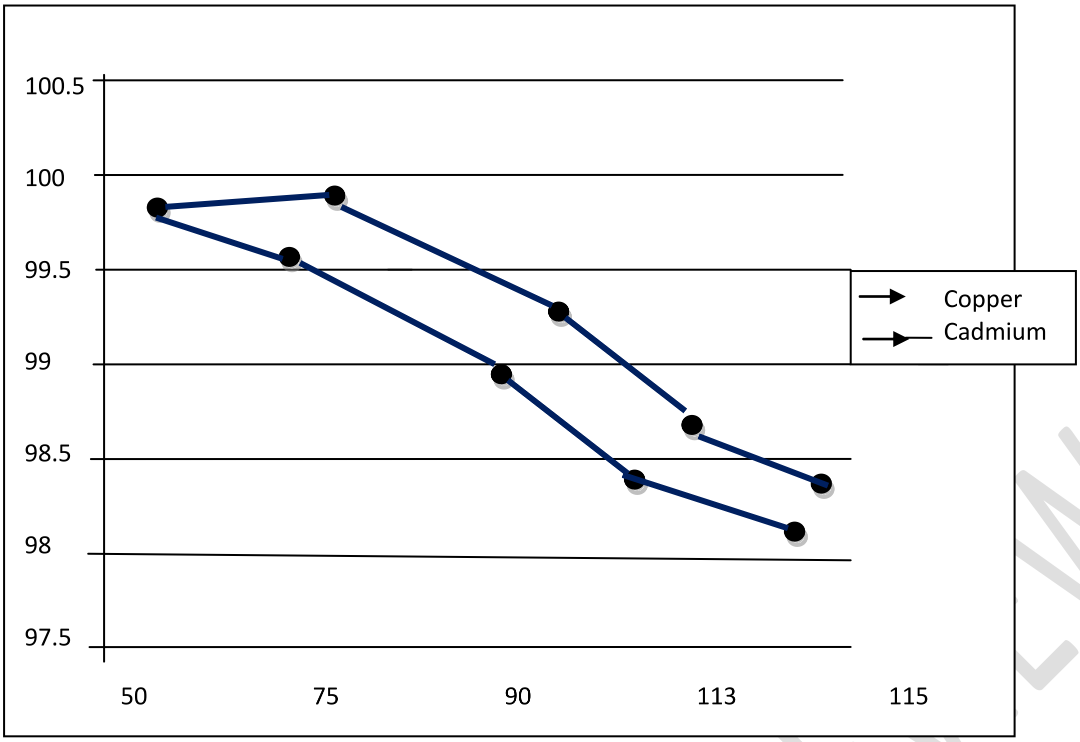

Figure 1: Plot of % removal efficiency against concentration

Figure 1: is a graphical representation of initial metal ion concentration against removal efficiency.

The efficiency of metal uptake by an adsorbent is highly dependent on the initial metal ion concentration of the solution. Figure 1 is a graphical representation of initial metal ion concentration against removal efficiency. The initial metal ion adsorbed onto the chemically activated carbon decreases as the initial metal ion concentration increases. The reason for the decrease in adsorption efficiency is due to the relatively smaller number of active sites available on adsorbent. The decrease in % removal efficiency can be explained by the fact that as the concentration of the adsorbate increases so does the metal loading on the adsorbent (Mckay,1995), so when the concentration is higher, more ion will be competing for the same adsorption sites and go through without being adsorbed. The result tell how there is a great interaction between the adsorbent and adsorbate in solutions of lesser initial concentration as

99.96% and 99.90% are the % removal efficiency for Cu (II) respectively at 50 mg/1 compared to 98.81% and 98.64% with 140 mg/1

3.2.2 Effect of Adsorbent Dosage

With reference to both table below, the effect of different adsorbent dosage of 1 to 3g respectively on the adsorption of the heavy metals of cooper and cadmium respectively. At constant initial concentration of 50 mg/1, a constant time of 20 minutes. The rate of adsorption was found to increase with increase in the adsorbent dosage from 1 to 3 g for each of the test carried out. The availability and accessibility of adsorption site is controlled by adsorbent dosage (Othman and Mohd, 2013).

Table 4: Effect of chemically activated water melon peel of adsorbent dosage on copper ion.

Time: 20mins		Concentration: 50mg/1	
Adsorbent Dosage (g)	Equilibrium concentration (mg/1)	Amount Adsorbed (mg/1)	% removal efficiency
1.0	2.70	47.30	94.60
1.5	1.20	48.80	97.60
2.0	0.22	49.78	99.98
2.5	0.08	49.92	99.98
3.0	0.06	49.94	99.98

Table 5: Effect of chemically activated water melon peel of adsorbent dosage on cadmium ion

Time: 20 mins		Concentration: 50mg/1	
Adsorbent Dosage (g)	Equilibrium concentration (mg/1)	Amount Adsorbed (mg/1)	% removal efficiency
1.0	3.41	46.59	93.15
1.5	2.85	47.15	94.30
2.0	2.74	47.26	94.52
2.5	2.57	47.43	94.80
3.0	2.30	47.70	95.40

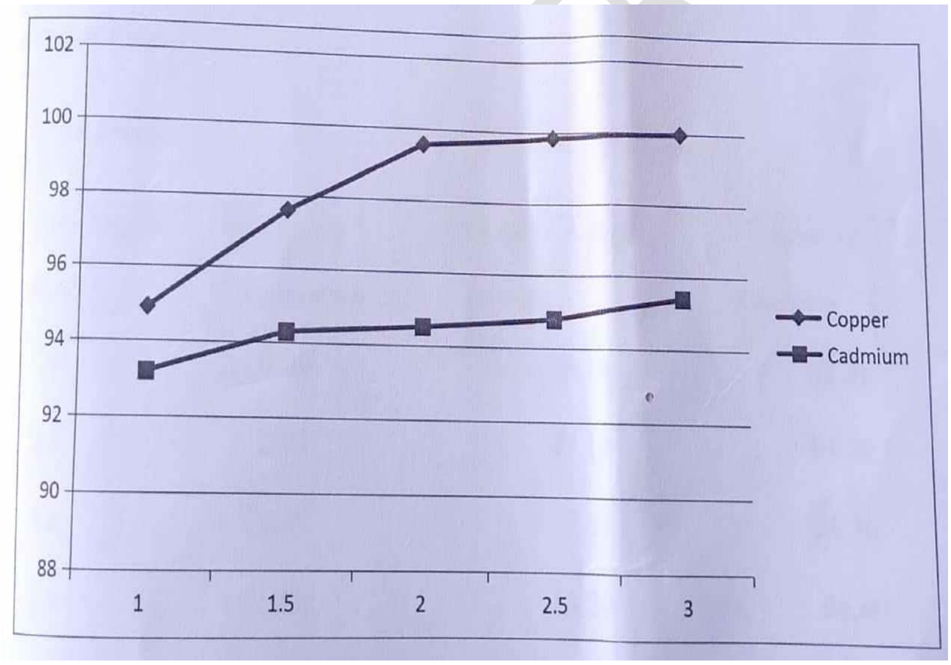

Figure 2: Plot of % removal efficiency against adsorbent dosage

The figure 2 above shows, that the removal efficiency of both copper and cadmium increases with increase in adsorbent dosage as a result of the availability of more sorption sites for adsorption. With a higher adsorbent dosage, there would be a greater number of exchangeable sites for metal ions (Agbaire *et al.*, 2014). The results from the experiment show that Cu (II) adsorbed more efficiently than Cd (II) with chemically activated water melon peel as adsorbent with their maximum % removal efficiency being 99.98% for Cu^{++} respectively.

3.2.3 Effect of Contact Time

With reference to both table below, showing the effect of different contact time of 30 to 40 minutes on the adsorption of the heavy metals of copper and cadmium respectively. At constant time of 20 minutes and initial concentration of 50 mg/1.

Table 6: Effect of chemically activated water melon peel of contact time on copper ion

Time: 20 mins		Concentration: 50 mg/1	
Time Elapsed (min)	Equilibrium concentration (mg/1)	Amount Adsorbed (mg/1)	% removal efficiency
20	3.86	46.14	92.28
25	2.90	47.10	94.20
30	2.65	47.35	94.70
35	1.80	48.20	96.40
40	1.60	48.20	96.80

Table 7: Effect of chemically activated water melon peel of contact time on cadmium ion

Time: 20 mins		Concentration: 50 mg/1	
Time Elapsed (min)	Equilibrium concentration (mg/1)	Amount Adsorbed (mg/1)	% removal efficiency
20	4.10	45.90	91.80
25	3.55	46.45	92.90
30	3.25	46.75	93.50
35	2.60	47.40	94.80
40	2.30	47.70	95.40

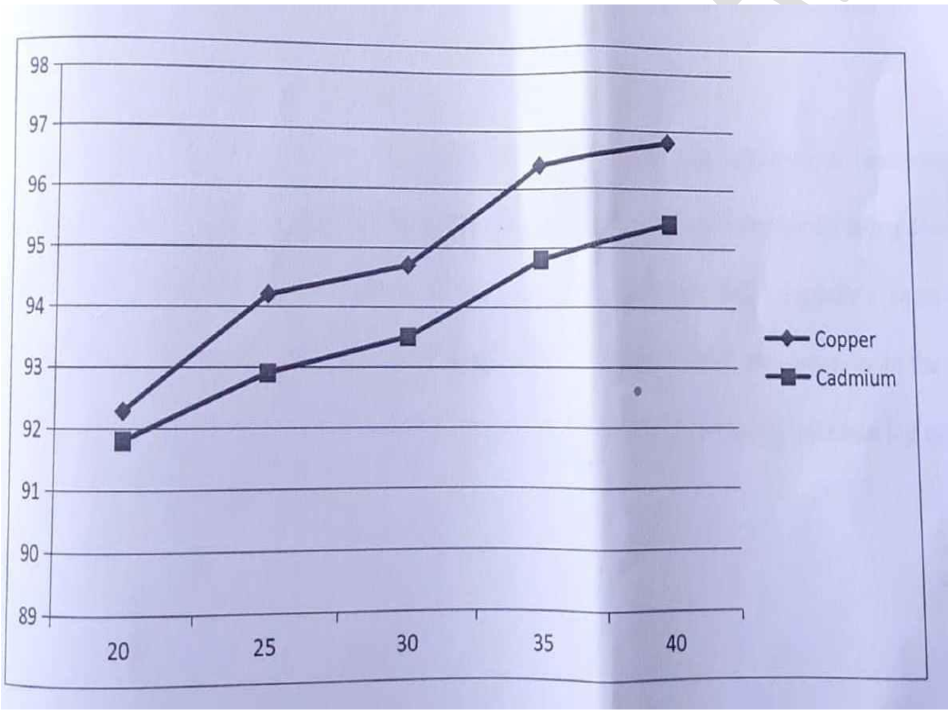

Figure 3: Plot % removal efficiency against contact time

The figure 3 above shows, with increasing contact time the amount adsorbed increases, as there is enough time for interaction and efficient contact time between the adsorbent ad adsorbate. The patterns of the curve established that the adsorption is time dependent in which adsorption capacity was proportionally related to time (Ukpong and Okon, 2013). The result indicates that Cu (II) % removal efficiency increased from 92.28% with a contact time of 20 min to a maximum point of 96.80% with a contact time of 20 mins to 95.40% when the contact time was 40 mins.

3.3 ADSORPTION ISOTHERM

In successful representation of equilibrium adsorption behaviour, it is important to have a satisfactory description of the equation between the various phases composing the adsorption systems. The equilibrium data obtained for copper and cadmium for their adsorption using chemically activated water melon peel was analyzed using the Langmuir and Freundlich Adsorption Isotherm (Akpakpan *et al*., 2018)

Adsorption isotherm studies were carried out to determine an approximate estimation of adsorption capacity of an adsorbent and the intensity of heavy metal ions uptake using adsorbent dosage at constant concentration of 50 mg/1 of metal ion. With the Langmuir's equation to analyze copper adsorption isotherm, the graph shows the relationship between c_o/q_o in the y-axis and c_o in the x-axis while the Freundlich equation shows the relationship between log c_c on the x-axis and log q_o on the y-axis

3.3.1 LANGMUIR ADSORPTION ISOTHERM FOR COPPER AND CADMIUM METAL ION

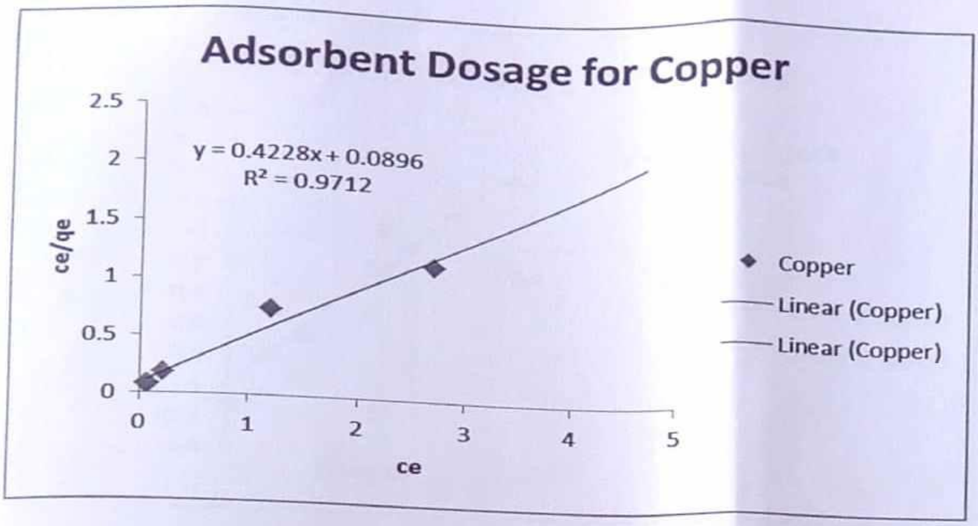

Figure 4: Langmuir adsorption isotherm for Cu (II) ion.

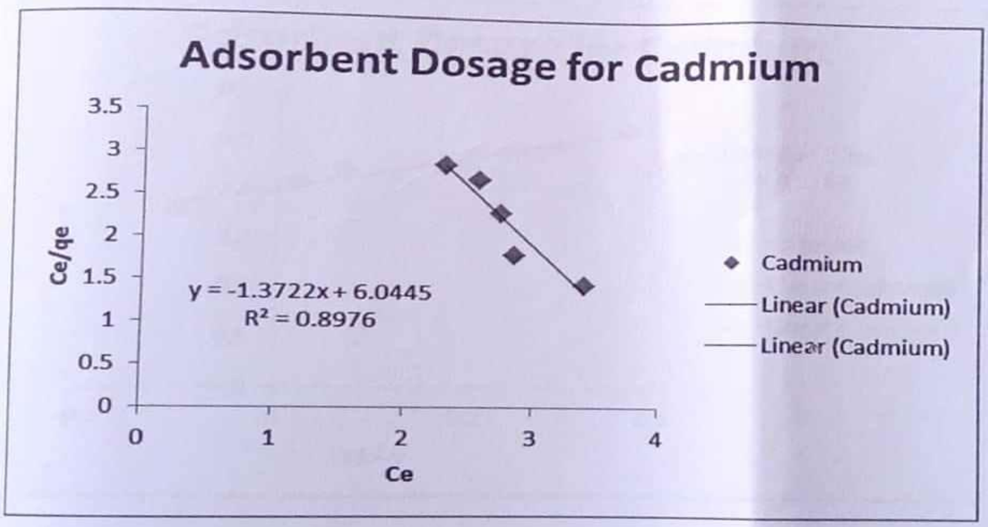

Figure 5: Langmuir adsorption isotherm for Cd (II) ion

3.3.2 Freundlich Adsorption Isotherm for Copper and Cadmium Metal Ion

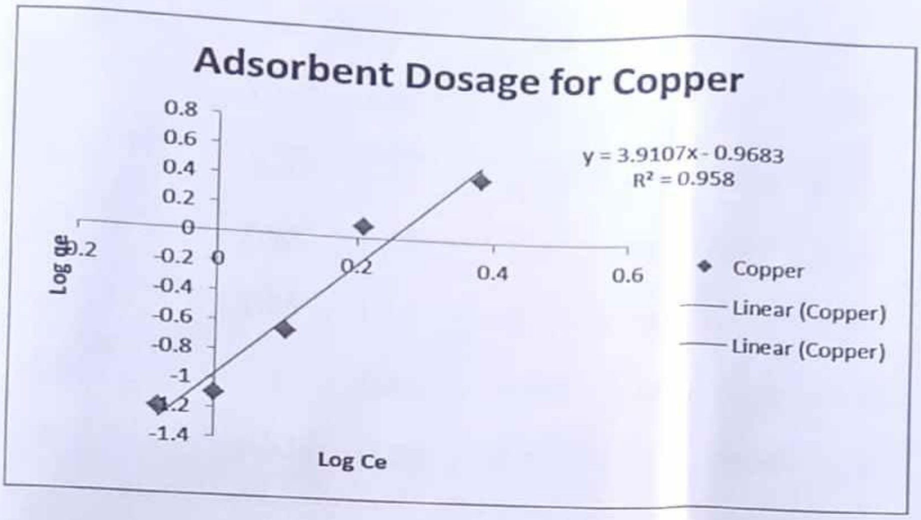

Figure 6: Fruendlich adsorption isotherm for Cu (II) ion.

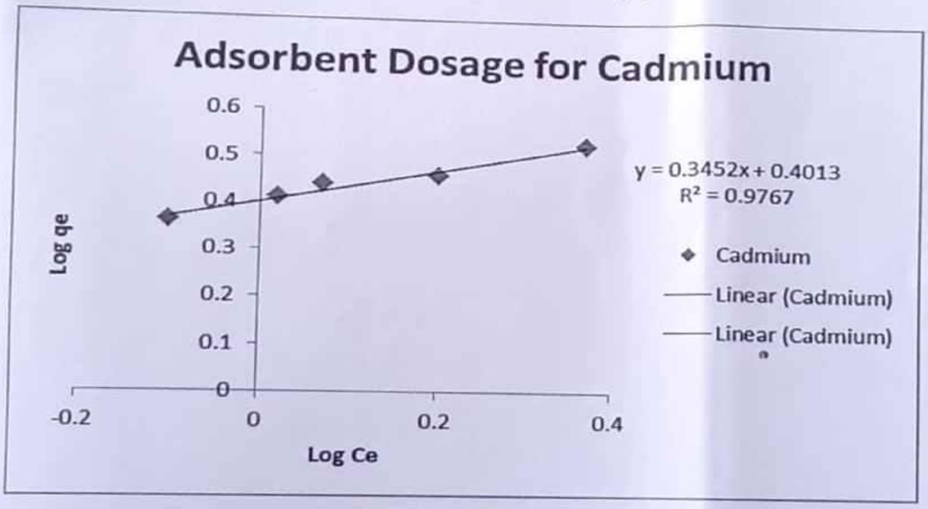

Figure 7: Freundlich adsorption isotherm for Cd (II) ion

Table 8: Estimated parameters for Cu^{2+} and Cd^{2+} ion adsorption using chemically activated water melon peel

Dosage (g)	**Qe**		**Ce**		**Log Qe**		**Log Ce**	
	Cu^{2+}	**Cd^{2+}**	**Cu^{2+}**	**Cd^{2+}**	**Cu^{2+}**	**Cd^{2+}**	**Cu^{2+}**	**Cd^{2+}**
1	2.37	2.33	2.70	3.41	0.38	0.37	0.43	0.53
1.5	1.63	1.57	1.20	2.85	0.21	0.20	0.079	0.46
2	1.25	1.18	0.22	2.74	0.10	0.07	-0.66	0.44
2.5	1	0.95	0.080	2.57	0	0.02	-1.097	0.41
3	0.83	0.80	0.062	2.30	-0.08	-0.10	-1.208	0.36

Table 9. Adsorption Isotherm Constant

LANGMIUR	
Cu^{2+}	Cd^{2+}
K = 8141.4	K = 2.21
N = 1.03	N = 2.49
R^2 = 0.958	R^2 = 0.9767
FRUENDLICH	
Cu^{2+}	Cd^{2+}
K = 8141.4	K = 2.21
N = 1.03	N = 2.49
R^2 = 0.958	R^2 = 0.9767

CONCLUSION

From the result and discussion of this research work, it can be inferred that the chemically activated water melon peel used as activated carbon is a good alternative source for activated carbon production. It is effective in the adsorption of both heavy meals – copper and cadmium and the adsorption process is dependent on contact time, adsorbent dosage and the concentration of the solution

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