

Equilibrium studies for Cadmium (II) ions from Water Using Activated Carbon Derived from Macadamia *Intergrifolia* Nutshell Waste Powder

Abstract

Heavy metals have continued to be of great concern in research as major pollutants of water. Adsorption using low cost adsorbent is a low cost method of the removal heavy metal ions from aqueous solution. In this study activated carbon derived from macadamia *intergrifolia* nutshell powder was considered as an alternative low cost adsorbent for the removal of Cd(II) ions from aqueous solution. Various physicochemical parameters which included sorbent mass, and initial metal ions concentration isotherms using sorption models were determined. Results from the experiment indicated the optimum values for sorbent mass as 0.3 grams, and initial metal ions concentration as 8mg/l. Adsorption isotherms were found to fit well in Langmuir model ($R^2=0.9935$), Javanovic model ($R^2 =0.9857$) and Freundlich model ($R^2=0.9911$). Additionally, for Langmuir model the value of separation factor (K_L) was in the range of 0 to 1 indicating a favorable reaction. For Jovanovic model adsorption energy was found to be 1.00334 l/mg thus an indication of binding vibrations during Cd(II) ions adsorption. FTIR spectrum revealed that the presence of O-H at V_{max} 3389 cm^{-1} , COO- at V_{max} 2367 cm^{-1} , C=O at V_{max} 1593 cm^{-1} , C-O at V_{max} 1344 cm^{-1} , P-O at V_{max} 1206 cm^{-1} and POO-H at V_{max} 1110 cm^{-1} functional group in activated carbon enhanced Cd(II) ions removal. The study revealed that activated carbon derived from macadamia *intergrifolia* nutshell can be used to remove Cd(II) ions from water.

Keywords: Adsorbent, isotherm, Adsorption, chemisorption

1.0 Introduction

Adsorption is a separation process. In adsorption fluid, liquid and gaseous substances usually adhere to the inside or the outside surface of the material called the adsorbent [1]. There are various

mechanisms which are involved in metal ions adherence onto the surface of the adsorbent, and such mechanism includes; ion exchange and physical adsorption [2] and chemisorption (Mohamed *et al.*, 2014). Ion exchange, mechanism involves exchange of metal ions in aqueous solution with ions of the same charge which is found in the immobilized solid [4]. Physical adsorption involves the formation of weak van der Waals forces between the metal ions and the adsorbent, no exchange of electrons takes in this mechanism (Tripathi and Ranjan, 2015). Chemisorption involves interaction between the metals ions and the organic functional groups present in the adsorbent, in this mechanism there is exchange of electrons between the adsorbate and the adsorbent leading to the formation of a chemical bond (Kakoi *et al.*, 2016).

Water pollution is a very serious problem in both the developing and the developed countries, many citizens lose their lives daily (Chaudry and Malik, 2017). Some of the water pollutants includes; agricultural pollutants [8]; atmospheric pollutants [9]; Pathogens (Payment and Locas, 2011); Pesticides (Agarawal *et al.*, 2010); herbicides [12]; sediments [13]; salt water pollution [14] and chemical pollutants (Wang and Yu, 2013). Non-essential heavy metals are among the chemical pollutants which are of great concern globally due to their toxicity in human body [16]. Industrial activities and human activities are the major source of heavy metal pollution in water (Ghadimi and Ghomi, 2013).

There are various regular methods which have been extensively used to remove heavy metal ions from aqueous solutions. Such methods includes; chemical precipitation [18]; electrocoagulation [19]; ion exchange [20], and membrane separation (Barakat and Schmidt, 2010). However, these methods have drawbacks of high cost of buying and maintenance of the equipment, formation of a chemical sludge, and inefficiency at low concentrations (Rao *et al.*, 2011). This has therefore lead to the search for the low cost and effective method for the removal of the heavy metal ions from aqueous solution. Studies have shown that various adsorbents have been used to remove metal ions from water, such includes; nanochitosan and chitosan (Seyed *et al.*, 2013), multiwalled carbon nanotubes modified by diphenylcarbazide [24], lemon peel [25], esterified spent grain (Li *et al.*; 2012), polyacrylic acid-

grafted *Macadamia* nutshell powder (Ntuli and Pakade, 2020) olive stone [28], banana pith (Kakoi *et al* 2016) among others.

Cadmium as a metal has a very wide range of applications in industry which includes in the manufacture of batteries, manufacture of alloys and also coating and plating industries (Sharma *et al.*, 2015). The most common method of cadmium exposure to humans is through consumption of a cadmium containing substance, various sources of cadmium exposure includes; smoking cigarettes, burning of wastes and also during the burning of fossils fuels (Newbigging *et al.*; 2015). High concentration of cadmium in human body leads to infertility, mental disorders leading to the abnormality of the mind, damage of the immune system and it may also lead to stomach pain (Mohod and Dhote, 2013).

Using low cost activated carbons as a method of heavy metal removal from aqueous solution have proved to be cost efficient and eco-friendly [28]. The feasibility of the activated carbon in the removal of heavy metal ions from aqueous solutions can best be described by the adsorption isotherms. Adsorption isotherms provides relationships between the metal ions which have adhered to the adsorbent surface and the amount of metal ions remaining in the aqueous solution after the equilibrium is established (Reddy *et al.*; 2014). When metal ions interact with the activated carbon, metal ions get attached at the active sites of the activated carbon and this process continues until equilibrium is attained between the aqueous solution and the adsorbent surface. When the equilibrium is attained there will be no more increment in the amount of metal ions which are attached to the surface of the adsorbent [34]. Adsorption isotherm will therefore provide us with information on the relationship between the metal ions which have adhered to the activated carbon surface and the metal ions remaining in the aqueous solution after the equilibrium is attained as a function of the initial metal ion concentration [35].

The objective of this study was to characterize the low cost activated carbon derived from *Macadamia intergrifolia* nutshell powder, study the effect of adsorbent dosage and initial metal ion concentration on Cd(II) ions removal and then fit the data in adsorption isotherms.

2. Materials and methods

2.1 Instrumentation

Flame atomic absorption spectrophotometer (FAAS) (AA 7000- shimadzu Japan) using air-acetylene flame was used for cadmium ions determination before and after adsorption. To determine the effect of pH on Cd(II) ions adsorption, pH measurement was done using pH meter (pH 211, Hanna instruments). The organic functional groups present in activated carbon which were responsible for heavy metal ions adsorption were determined using Fourier transform infrared spectrophotometer (FTIR) (8400 CE, Shimadzu, Japan).

2.2 Chemicals and reagents

All the chemicals used in this study were of analytical grade purchased from PY-REX EAST AFRICA LTD with its branch located in Nairobi Kenya. Cadmium ions stock solution was prepared by dissolving 1.855 grams of cadmium nitrate in distilled water and then topping up the solution to 1000 mls with distilled water. Working solutions were made by making the appropriate dilutions from the stock solutions by using distilled water.

2.3 Sample collection, preparation and pretreatments

Macadamia intergrifolia nutshells were purchased from Kenya nut company in Kiambu county. They were then transported to the laboratory and washed with deionized water. Thereafter they were oven dried at 105°C for 48 hours. Dried *macadamia intergrifolia* nutshells were grounded to a fine powder and then sieved using a st

andard sieve of 90 μm to 150 μm . Part of the raw *macadamia intergrifolia* nutshell powder was soaked in 50 % phosphoric acid for 24 hours at 105°C and then oven dried for 48 hours at 105°C. Dried sample was charred using a heating mantle at 300°C for 24 hours followed by ignition in an electric muffle furnace at 550°C for 24 hours. The sample was left to cool and washed with 0.1M HCl to remove ash content and then washed with 0.1M NaOH to raise the pH of the activated carbon to 7. The sample was then oven dried at 105°C for 24 hours and kept in a stoppered bottle ready for use.

2.4 FTIR Characterization

FTIR spectrum for activated carbon was done as follows; approximately 1.0 mg of activated carbon was mixed with 5.0 mg of potassium bromide. Mixtures were ground to a fine powder and then pressed under vacuum forming pellets which were then analysed using FTIR.

2.5 Adsorption studies

Batch tests were carried out to evaluate removal of cadmium from aqueous solutions using activated carbon. The main parameters affecting bio-sorption such as adsorbent dosage and initial metal concentration were evaluated for these materials. The equilibrium studies of the removal of heavy metal from solution using adsorbent were carried out by fitting the data into adsorption isotherms. A 1000 mg/l cadmium metal standard was used as the stock solution. All working solutions were prepared by diluting the stock solutions with distilled water to the desired concentration.

To determine the percentage Cd(II) ions removal after adsorption, the following equation was used

$$\% \text{ Removal} = \left(\frac{C_0 - C_e}{C_0} \right) * 100 \dots\dots\dots 1$$

Where C_0 is the initial concentration, and C_e is the equilibrium concentration.

Amount adsorbed at equilibrium was determined using the following equation

$$q_e = \frac{V(C_0 - C_e)}{W} \dots\dots\dots 2$$

Where q_e is amount adsorbed at equilibrium in mg/g, V is the volume of the solution in litres, C_0 and C_e are the initial and equilibrium concentration in mg/l respectively and W is the weight of the adsorbent in grams.

3. Results and discussion

3.1 Analysis of functional groups in the activated carbon

The FT-IR spectrum of activated carbon is shown in figure 1 below. The absorption bands at V_{\max} 3856 cm^{-1} and V_{\max} 3747 cm^{-1} was due to the presence of the isolated OH groups in the activated carbon (Huang, *et al*; 2015). The broad absorption bands at V_{\max} 3389 cm^{-1} was attributed to the presence of OH stretching vibration of hydroxyl groups. The absorption band at V_{\max} 2922 cm^{-1} was attributed to CH stretching vibrations which is indicative of the presence of methyl or methylene groups (Shamsuddin, *et al* 2016). The presence of band at V_{\max} 2367 cm^{-1} was ascribed to the presence of COO-. Additionally, the band at V_{\max} 1593 cm^{-1} was attributed to the presence of C=O stretching vibrations in acids, alcohols and phenols [38]. The band at V_{\max} 1395 cm^{-1} was associated with the aliphatic -CH₃- bend while the peak at 1344 cm^{-1} was indicative of C-O stretching vibrations which may be assigned to ethers, phenols, esters, acids or alcohols (Gupta *et al.*, 2013). The band at 1206 cm^{-1} was associated with the stretching mode of the hydrogen bonded P-O and O-C which are found in P-O-C and P-OOH (Amorim Filho and Gomes Neto, 2009). The band at V_{\max} 1110 cm^{-1} was associated with the ionized linkage P-O- which is found in phosphate esters it was also assigned to symmetric vibration in P-O-P. The band at V_{\max} 979 cm^{-1} depicted the C-O bending vibrations associated with acids and alcohols whereas the peak at V_{\max} 687 cm^{-1} was associated with in-plane ring deformation (Tongpoothorn *et al.*, 2011).

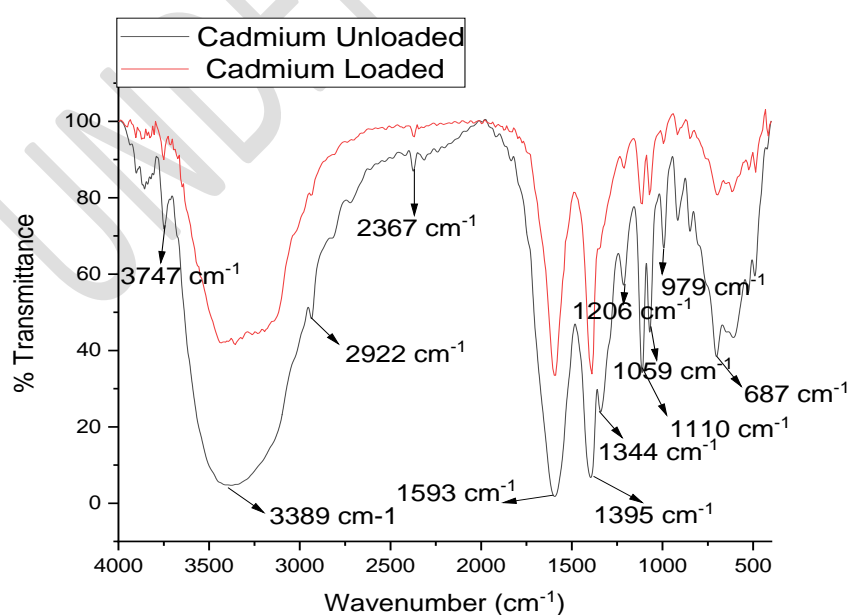


Figure 1: FTIR Spectrum for cadmium loaded and unloaded activated carbon

The comparison of FTIR spectrum for loaded and unloaded activated carbon indicates that the stretching vibrations of O-H, COO-, C=O, C-O, P-O and P-OOH shifted from V_{\max} 3389, 2367, 1593, 1344, and 1206 and 1110 cm^{-1} respectively after Cd(II) adsorption. This therefore reveals the chemical interaction between the above functional groups and the cadmium ions.

3.2 Effect of sorbent mass on Cd(II) ions removal

Accumulation of Cd(II) ions in the activated carbon as a function of the sorbent mass is shown in figure 2. The effect of sorbent mass on cadmium ions accumulation using activated carbon derived from macadamia *intergrifolia* nutshell powder was done while increasing the sorbent mass from 0.1 to 0.7 grams. Accumulation of Cd(II) ions onto activated carbon increased with increase in sorbent mass from 97.49 to 98.90 and 99.36 percent at a mass of 0.1, 0.2 and 0.3 grams respectively. Increment in the sorbent mass leads to a corresponding increase in the surface area and also increase in the number of binding sites which are responsible for Cd(II) ions accumulation onto activated carbon (Sahu *et al*; 2018). Beyond sorbent mass of 0.3 grams, there was a slight reduction in metal ion removal which was found to be 99.31, 99.15, 99.13 and 99.15 percent at the sorbent masses of 0.4, 0.5, 0.6 and 0.7 respectively. This is because, of the oversaturation of the activated carbon attachment sites which was as a result of the overcrowding of Cd(II) ions on the binding sites (Malakahmad *et al*; 2016). Additionally, greater sorbent masses leads to screening effect on the outer layers of the adsorbents and consequently this leads to shielding effect in the adsorbent binding sites from the metal ions (Edris *et al*; 2012). ANOVA test revealed that the value of F calculated was greater than the value of F critical. This therefore showed that there was significance difference between the mean at different values of adsorbent dosages. The optimum dosage obtained was used in the subsequent experiment.

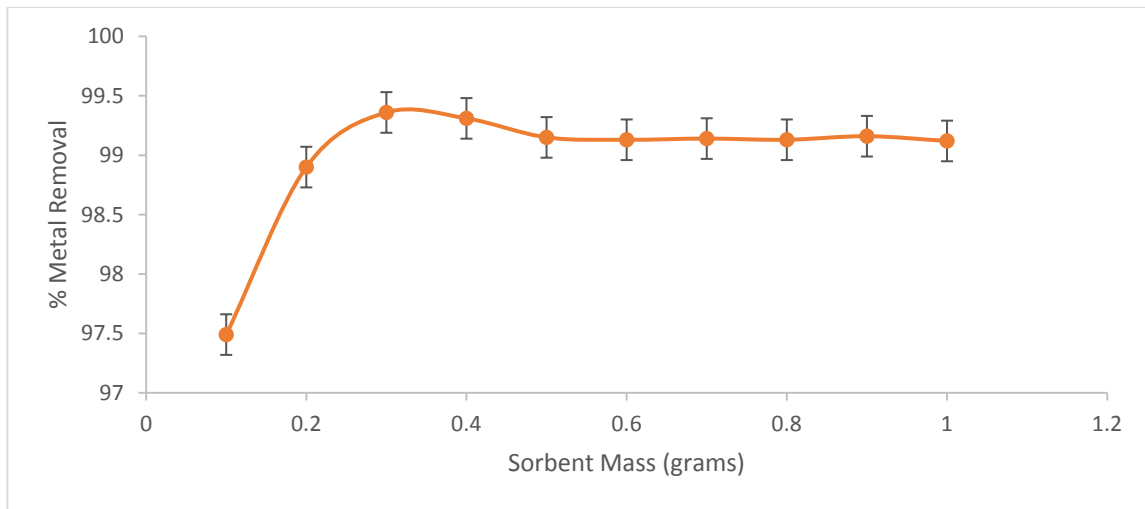


Figure 2. Effect of sorbent mass on Cd(II) ions removal using activated carbon at pH of 5, contact time of 60 minutes and initial metal ion concentration of 8 mg/l

3.3 Effect of initial metal ion concentration Cd(II) ions removal using activated carbon

Effect of Cd(II) ions concentration on its rate of adsorption in activated carbon is shown in Figure 3. There was an increment in percentage Cd(II) ions accumulation when initial concentration of Cd(II) ions was increased from 4mg/l to 8 mg/l from 96.15 % to 99.49%. This is because increment in Cd(II)

ions concentration is the driving force to be able to overcome mass transfer resistance between the aqueous solution and the superficial layer of the activated carbon [45]. At optimum initial metal ions concentration of 8mg/l, the ratio of the number of attachment sites to the number of Cd(II) ions was so high such that nearly all the Cd(II) ions reacted with the active sites of the activated carbon (Al Bsoul *et al*; 2014). At 12, 16, 20, 24, 28 and 32 mg/l percentage removal was 98.20, 97.95, 97.63, 97.22, 97.08 and 96.01 respectively. Therefore, further increment in Cd(II) ions concentration led to the reduction in percentage adsorption. This is because the ratio of the number of unattached binding sites to the ratio of the number of Cd(II) ions in solution decreased and therefore this leads to the reduction in the Cd(II) ions removal (Zewail and Yousef, 2015). Additionally, all the adsorption sites which had higher affinity for Cd(II) ions are saturated at high concentration and therefore there was increased mutual electrostatic interaction between the lower affinity adsorption sites and the unabsorbed Cd(II) ions (G. Sharma *et al*; 2017). ANOVA test revealed that the value of F calculated was greater than the value of F critical. This therefore showed that there was significance difference between the mean at different values of initial metal ions concentration. Adsorption capacities however increased with increase in initial concentration and were f

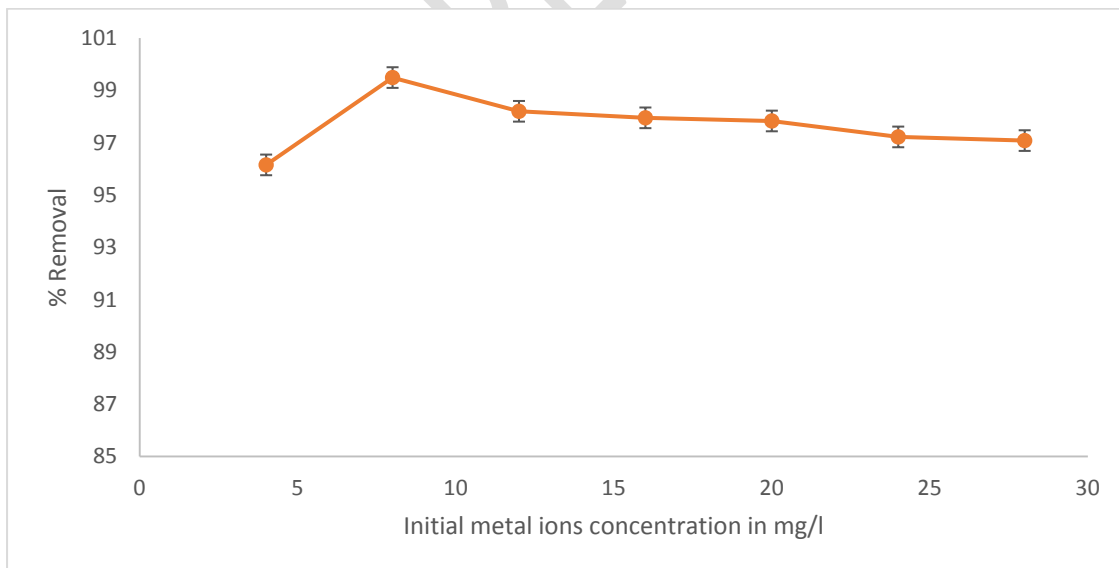


Figure 3: Effect of Cd(II) ions concentration in Cd(II) removal using activated carbon at pH of 5, adsorbent dosage of 0.3 grams and contact time of 75 minutes.

itted in adsorption isotherms.

3.4 Adsorption isotherms

Various definitive surface adsorption isotherms have been used to describe the equilibrium created between the metal ions accumulated in the adsorbent and the concentration of the metal ions remaining in the solution at a constant temperature.

3.4.1 Langmuir Isotherm

Langmuir isotherm is based on the fact that metal ions adsorbed in the adsorbent are in contact with the adsorbent superficial layer a phenomenon referred to as monolayer adsorption. Langmuir model is expressed by the following linear equation

$$\frac{c_e}{q_e} = \frac{1}{k_L q_{max}} + \frac{c_e}{q_{max}} \dots\dots\dots 3$$

Where c_e is the equilibrium concentration of the metal ions remaining in solution after the adsorption is complete with the units of mg/l, q_e is the amount of metal ions adsorbed and has the units of mg/g, q_{max} is the maximum holding power of the adsorbent when the adsorbent superficial layer is saturated by the adsorbate which has the units of mg/g and k_L is a constant related to the Langmuir equilibrium, K_L is dependent on the adsorbed energy and has the units of L/mg and the plot of c_e/q_e vs c_e gives a straight line in which $\frac{1}{q_{max}}$ and K_L are computed (Onyancha *et al*; 2008).

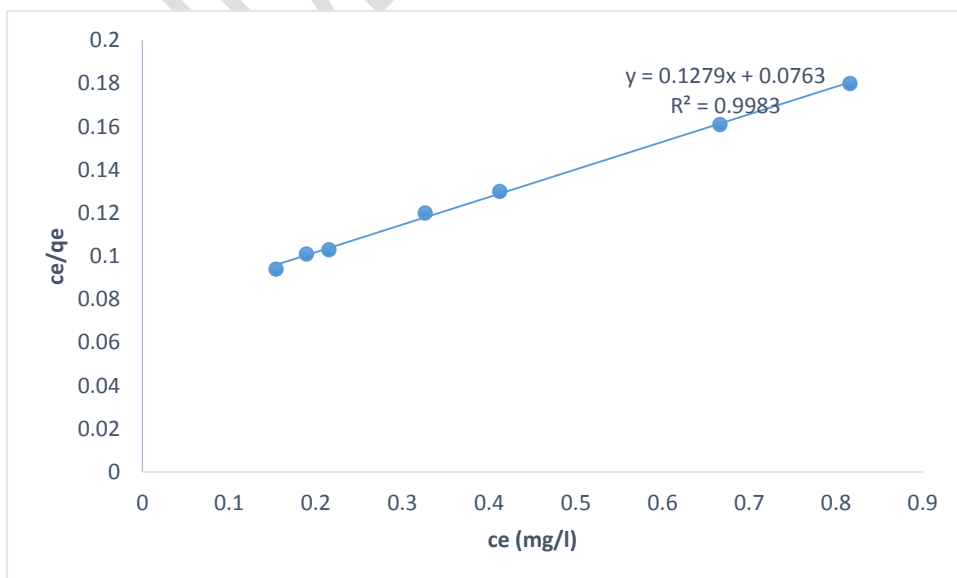


Figure 4: Linearized Langmuir isotherm for Cd(II) ions adsorption unto activated carbon

3.4.2 Freundlich isotherm

Freundlich isotherm assumes that the adsorption of the adsorbate towards the adsorbent is through the multiple surfaces located at both the interior and exterior layers of the adsorbent which is generally referred to as heterogeneous distribution, the linear form of the Freundlich isotherm is;

$$\ln q_e = \ln k_f + \frac{1}{n} \ln c_e \dots\dots\dots 4$$

q_e is the adsorbed amount and has the units of mg/g, K_f is the Freundlich isotherms constant and has the units of mg/g, C_e is the concentration of the adsorbate at equilibrium in units of mg/l, and $\frac{1}{n}$ is a function of the potential of the adsorbate to adhere to the adsorbent surfaces, a plot of $\ln q_e$ vs $\ln c_e$ is plotted in which the values of $\frac{1}{n}$ and K_F are computed from slopes and intercepts respectively (Rao *et al*; 2010).

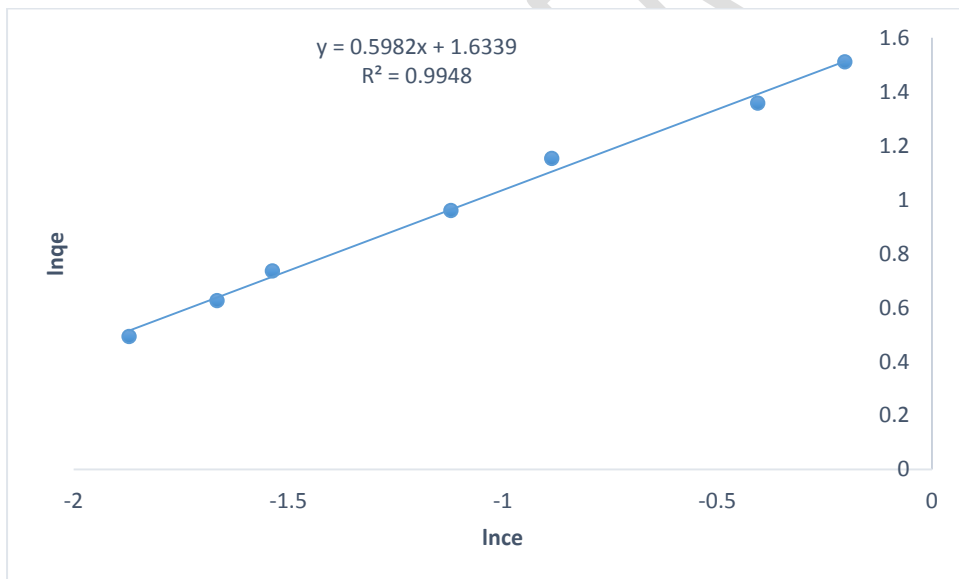


Figure 5: Linearized Freundlich isotherm for Cd(II) ions adsorption unto activated carbon

3.4.3 Temkin Isotherm

Temkin adsorption isotherms is based on the assumption that the heat of adsorption decreases with reference to the increase in adsorbent coverage [51]. The linear form of Temkin isotherm is

$$q_e = B \ln A + B \ln C_e \dots \dots \dots 5$$

where $B = \left(\frac{RT}{b}\right)$, b is temkin constant which is linked to the heat of sorption, A is Temkin isotherm constant, T is absolute temperature in kelvins and R is molar gas constant and a plot of $\ln q_e$ vs $\ln C_e$ was drawn and the values of B and A were computed from slopes and intercepts respectively (Can *et al*; 2016).

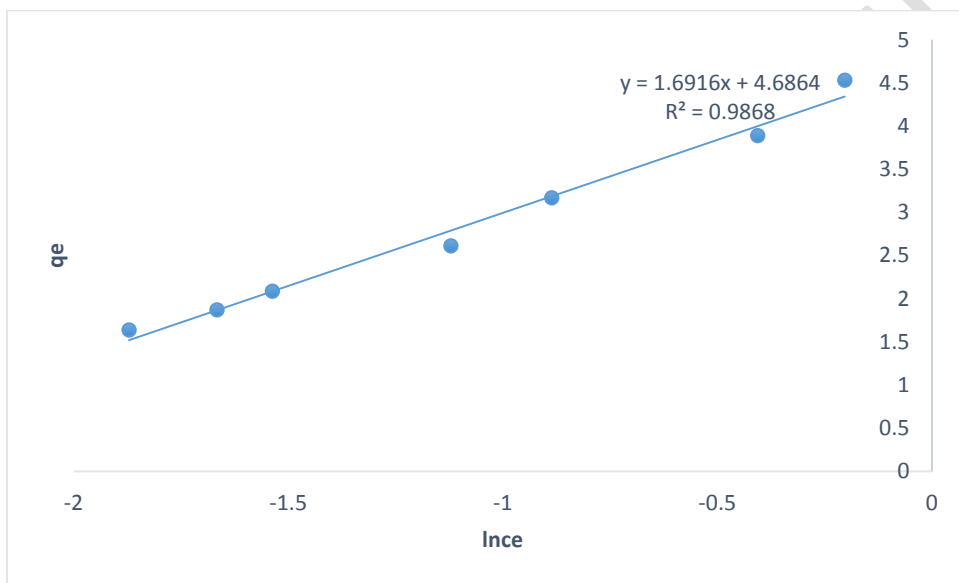


Figure 6: Linearized Temkin isotherm for Cd(II) ions adsorption onto activated carbon

3.4.4 Javanovic Isotherm

It is identical to the Langmuir isotherm with the exception of the binding vibrations experienced by the adsorbed species (Rangabhashiyam and Selvaraju, 2015). The linearized form of Javanovic equation is

$$\ln q_e = \ln q_{\max} - K_J C_e \dots \dots \dots 6$$

q_{\max} is the maximum amount of adsorbate adsorbed per unit mass of the adsorbent and K_J is Jovanovic constant which is associated with energy of adsorption, a plot of $\ln q_e$ vs C_e was plotted where K_J and q_{\max} were obtained from the slope and intercept respectively (Yousef *et al*; 2016).

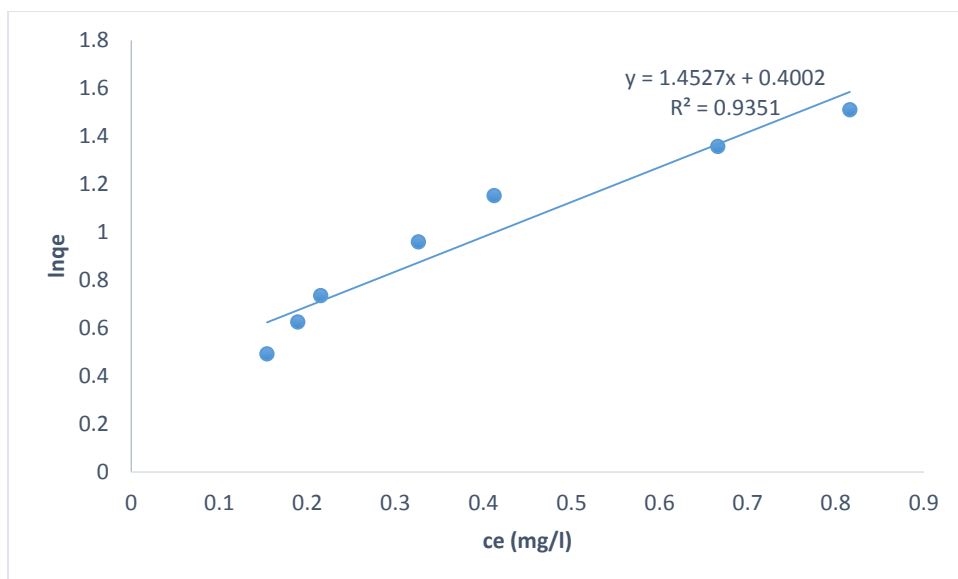


Figure 7. Linearized Cd(II) ions adsorption Jovanovich isotherm for Cd(II) ions adsorption onto activated carbon

From the comparison of the regression coefficients it was found that Langmuir > Jovanovic > Freundlich > Temkin. Therefore, adsorption of Cd(II) ions using activated carbon can best be described by Langmuir model and consequently an indication that single layer adsorption was predominant. Additionally, since the value of K_L for Langmuir was 0.08934 lies between 0-1 thus an indication of a favourable reaction. Jovanovic adsorption isotherm gave a good correlation coefficients of 0.9911 and the value of energy of adsorption was found to be 1.0034 l/mg, thus there was binding vibrations experienced during the adsorption of Cd(II) ions onto activated carbon. Temkin isotherm had a very low value of R^2 which was 0.78352 thus could not describe well Cd(II) ions adsorption onto activated carbon.

Table 1: Contrast of predicted parameters obtained from various adsorption isotherm

Langmuir	$1/q_{\max}$ 0.1279	K_L 0.0763	R^2 0.9983
Freundlich	K_F 1.6349	$1/n$ 0.5982	R^2 0.9949
Temkin	A 4.6864	B 1.6916	R^2 0.9868
Jovanovic	K_J 1.4527	q_{\max} 0.4002	R^2 0.9351

3.8 Recovery of activated carbon during Cd(II) ions adsorption

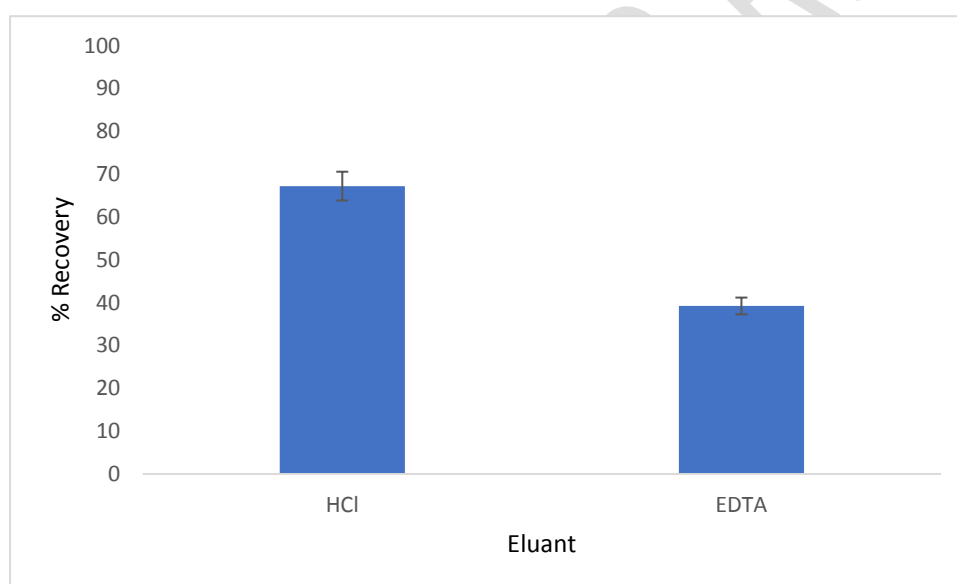


Figure 8: Percentage recovery efficiency of different desorption agents on Cd^{2+} adsorbed onto activated carbon

Desorption is a term which is used to describe the removal of heavy metal ions from the adsorbent surfaces. Recovery of the adsorbent is important since it lowers the cost, which leads to the reduction in dependence on the continuous supply of the adsorbent [49]. Application of acids as desorbing agents have been used since most adsorption have ion exchange mechanism for metal ions leading to

the increase in the acidity of the metal loaded adsorbent, which consequently leads to leaching of metal ions from the adsorbent surface (Kariuki *et al*; 2017). Figure 7 above shows the desorption of Cd(II) ions using 0.1M HCl and 0.1M EDTA. It was found that activated carbon recovery using 0.1M HCl was relatively high compared to 0.1M EDTA. However, 100% recovery was not achieved. This was attributed to other mechanisms taking place apart from ion exchange mechanism.

4. Conclusions

Based on the results obtained, the following results were obtained

1. The optimum dosage was 0.3 grams while the optimum initial concentration was 8mg/l.
2. Adsorption of Cd(II) onto activated carbon was described by various adsorption models and they order of prevalence in relation to their correlation coefficient was as follows; Langmuir>Jovanovic>Freundlich>Temkin thus suggesting that single layer adsorption was prevalent.
3. FTIR analysis revealed that O-H, COO-, C-O and P-O and P-OOH groups are believed to be the main binding sites responsible for metal ions adsorption onto the adsorbent through chemisorption.
4. The study revealed low cost activated carbon derived from macadamia *intergrifolia* nutshell powder as an efficient and reliable adsorbent for the removal of Cd(II) ions from aqueous solutions

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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APPENDICES

Appendix 1: Variation (ANOVA) for the effect of sorbent mass on Cadmium

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.608552	1	1.608552	67.96673	5.46E-10	4.098172
Within Groups	0.899337	38	0.023667			
Total	2.507889	39				

Appendix 2: Variation (ANOVA) for the effect of initial metal ions concentration and adsorption isotherms on Cadmium

Source of Variation	SS	df	MS	F	P-value	F crit
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Between Groups	1282.058	1	1282.058	74.16535	4.32E- 09	4.225201
Within Groups	449.4485	26	17.28648			
Total	1731.506	27				

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