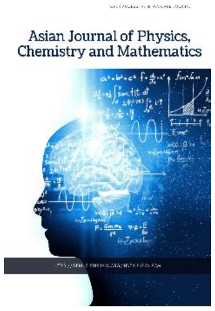

An Evaluation of The Adsorption Kinetics of Cd (Ii) Ions from Synthetic Solution Using Powdered Groundnut Shell as An Adsorbent

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ABSTRACT

The adsorption of Cd (II) from synthetic solution on powdered groundnut shell was investigated under laboratory conditions to assess its ability to remove the heavy metal. This synthetic route involved the grinding and sieving of the groundnut shell with a mesh size of 2.00mm, after washing and drying. The solid was employed as an adsorbent, in which the five kinetics model were tested. The results showed that the adsorption kinetics was best described by pseudo second order kinetic models with a linear regression coefficient R^2 = 1 and a rate content of 0.9950(mg/L) min^{-1}.

Keywords: Adsorption kinetics, Cd (II), powdered groundnut shell.

Introduction

A heavy mental is a member of loosely defined subset of element that exhibit metallic properties. It mainly includes the transition metals, metalloids, lanthanides and actinides. Many different definitions have been proposed, some based on density, some on atomic number or atomic weight and some on chemical properties or toxicity. (Duffus, 2002).

In modern times anthropogenic sources of heavy metals that is pollution, have been introduced to the ecosystem. Waste derived fuels are especially prone to contain heavy metals, so heavy metals are a concern in consideration of waste as fuel.

Relationship to living organism: living organism require varying amount of heavy metals. Iron, cobalt, copper, manganese, molybdenum and zinc are required by humans. Excessive levels can be damaging to the living organism. Other heavy metals such as mercury, platinum and lead are toxic metals that have no known vital or beneficial effect on organism and their accumulation over times in the bodies of animals that are normally toxic are for certain organisms or under certain conditions, beneficial. Examples include vanadium, tungsten and even cadmium. (Morel, 2000)

Cadmium has many application as it is a key component in battery production, is present in cadmium pigments (Buxbum, 2005), coating (Smith, 1999), and is commonly used in electroplating (Scoullos, 2001). Similarity cadmium compounds have various applications e.g. (CDO) is used in black and white television phosphors and the blue and green phosphors for color television picture tube (Lee, 1991). In PVC cadmium was used as heat, light and weathering stabilizers. [Jennings, 2005).

Cadmium has no known useful role in higher organisms (Michael, 2012). The highest concentration of cadmium has been found to be absorbed in the kidneys of humans and up to about 30mg of cadmium is commonly inhaled throughout childhood and adolescence (Perry *et al.,* 1976), cadmium can be used to block calcium channels in chicken neurons (Swandulla, 1989).

Acute exposure to cadmium fumes may cause flu like symptoms including chills, fever and muscle ache sometimes referred to as the cadmium blue". Inhaling cadmium laden dust quickly leads to respiratory tract and kidney problems which can be fatal (often from renal failure). Ingestion of any significant amount of cadmium causes immediate poisoning and damage to the liver and kidneys (ATSDR, 2010).

The most dangerous form of occupational exposure to cadmium is inhalation of fine dust and fumes, or ingestion of highly soluble cadmium compounds (Askoxford, 2010). Inhalation of cadmium containing fumes can result initially in metal fumes fever but may progress to chemical pneumonitis, pulmonary edema, and death. (Hayes *et al.,* 2007).

Considering the importance of water and adverse effect of heavy metals in both aqueous and non-aqueous media, a number of methods were developed for the removal of heavy metals in our environment. These includes a reduction process, sulfide treatment, chlorine treatment, magnetic ferrite treatment, ion exchange and ion-exchange followed by chelating resin (Ansari *et al.,* 2002). Adsorption, chemical oxidation, coagulation – flocculation, membrane processes are used for the removal of dyes and heavy metals.

Adsorption is one of the most effective physicochemical processes for the removal of colored pigment and heavy metals from industrial effluent (Kolleman, *et al.,* 1985). Activated carbon is the most widely used adsorbent due to its excellent adsorption capacity for heavy metals. However, the used of these methods is often limited due to the high cost, which makes it unfavourable for the needs of developing countries. Many reports have been published on the low-cost adsorbents for the removal of heavy metals from aqueous solutions (Badel *et al*., 2003). In recent years, the search for a new generation of low-cost adsorbents, such as clay minerals, (USGS, 2009) fly ash (Gdberg, 1969), activated slag (Jenning, 2005), and industrial waste products (Michael, 2010) has grown.

Therefore the purpose of this work is to study the kinetic adsorption of cadmium from synthetic solution using groundnut shell as an adsorbent

Materials And Methods

Preparation of 1000ml (1L) 0.1M HNO_3

Using the dilution formular: $C_1V_1 = C_2V_2$

Where C_1 = Initial concentration of the acid.
C_2 = Final concentration of the acid.
V_1 = Initial volume of the acid.
V_2 = Final volume of the acid.

C_1 = 15M HNO_3; V_1 =?; V_2 = 1000ml HNO_3; C_2 = 0.1M HNO_3

By substitution: $15MV_1 = 0.1M \times 1000ml$

$$\Rightarrow V_1 = \frac{0.1M \times 1000ml}{15M} = 6.7ml$$

6.7ml of 15M HNO_3 was added into 500mL distilled water, after through shaking it was made (1000mL) by adding de-ionized water. The acid solution was then 0.1M as expected.

Preparation of stock solution of 1000ppm (Cd)

The 1000ppm of (Cd) stock solution was prepared as follows:

i. Molar mass of cadmium Nitrate Cd $(NO_3)_2$ tetrahydrated $Cd(NO_3)_2 . 4H_2O$ = 308g/mol
ii. Relative atomic mass of cadmium Cd = 112g/mol

By definition: Mass Cd = $\frac{\text{Molar mass of Cd } (NO_3)_2 . 4H_2O}{\text{Relative atomic mass of Cd}}$

$$= \frac{308g/mol}{112gmol} = 2.75g$$

Since only 100mL of 1000ppm (Cd) is required, 0.275g was dissolved in 100mL of 0.1M HNO_3.

Preparation of an intermediate stock solution of (100ppm)

Using dilution formular: $C_1V_1 = C_2V_2$ (Dillution formular)

Where C_1 = 1000ppm; V_1 = ?; C_2 = 100ppm; V_2 = 100ml

By substitution: 1000ppm x V_1 = 100ppm x 100ml

$$V_1 = \frac{100\text{ppm} \times 100\text{ml}}{1000\text{ppm}} = 10\text{ml}$$

10ml of 1000ppm (Cd) was added in an empty conical flask and make it to the mark 100ml, using 0.1MHNO_3 solution after which 2ppm, 4ppm 6ppm, 8ppm and 10ppm were prepared with the used of dilution formular.

NB: The blank is purely 0.1MHNO_3 for the calibration curve.

Preparation of (0.1m) sodium nitrate $NaNO_3$

Preparation of (0.1M) $NaNO_3$ was carried out as follows:

Molar mass of $NaNO_3$ = 85g/mol

By definition: Mass = molarity x molar mass x V (dm^3) = 0.1M x 8.5 x 1dm^3

= 8.5g $NaNO_3$

The solution was prepared by dissolving 8.5g $NaNO_3$ in some amount of distilled water (double distilled), which was finally made up 1000ml with the same distilled water. The resulted solution was then 0.1M $NaNO_3$.

Preparation of 0.1M Cadmium Nitrate tetrahydrated Cd $(NaNO_3)_2 . 4H_2O$

The 0.1M cadmium nitrate tetrahydrated Cd $(NO_3)_2 . 4H_2O$ was prepared as follows;
Molar mass of Cd $(NO_3)_2 .4H_2O$ = 308g/mol
Total volume of solution = 200ml – 0.2L
Mass = molarity x molar mass x V (dm^3) = 0.1M x 308g/mol x 0.2L
= 6.16g Cd $(NO_3)_2 . 4H_2O$

Preparation of Groundnut shell powder:

The Groundnut shell used for this study was obtained from Osara market. The shells were washed and sundried. It was then grounded and sieved with a mesh size of 2.00mm.

Experimental

Kinetic Adsorption Study of Cadmium

This experiment is temperature sensitive; it was conducted differently at 25^{o}c, 30^{0}c, 40^{0}c and 50^{0}c all at a neutral pH of 7 respectively.

Initially 1.0g and 2.0g of the adsorbent were weighed and added into two (2) empty (250ml) conical flasks differently. Followed by the addition of (200ml) of 0.1M sodium Nitrate ($NaNO_3$) in each conical flask. The solid-liquid mixture was allowed to hydrate for a minimum of 24hrs, irrespective of temperature. The flasks were placed in an incubator shaker after 6.16g Cd $(NO_3)_2 .4H_2O$ was added in each conical flask. The incubator shaker was set at 150rpm and 25^{0}c for the first experiment. The solutions were shake until a period of 2min, 1minute for the first 5minutes, 20ml samples after each 5minutes for the first 25minutes and lastly 20ml samples after each 10minutes for next 30 minutes that is the samples were taken within a period of (1hr 2minutes). The same was repeated for the remaining samples at 30^{0}c, 40^{0}c. 50^{0}c and 60^{0}c while the number of rotation per minute was kept constant.

NOTE: The blanks were prepared for 1.0g and 2.0g adsorbent in 0.1M $NaNO_3$ differently without the metal of interest.

Preparation of the Calibration Curve:

The calibration curve was prepared after measuring the absorbance of 2mg/L, 4mg/L, 6mg/L, 8mg/L and 10mg/L of Cd respectively.

Concentration mg/L (x-axis)	Absorbance (y-axis)
2	0.024
4	0.042
6	0.063
8	0.085
10	0.113

The slope obtained from the calibration curve was used for the determination of new cadmium (Cd) concentration after the atomic absorption spectroscopic analysis was carried out, using the equation of a straight line.

Thus: Y = mx + c

Where c =0 which is the intercept

Y = Absorbance

X = Concentration

M = Slope

The equation becomes: Y =mx

$$x = \frac{Y}{m} \text{ (mg/L)}$$

Results And Discussion

Uptake Rate of Cd (II) on Powered Groundnut Shell

The uptake rate of Cd (II) on powered groundnut shell was studied at pH (7.0), by varying the amount of adsorbent from 1.0g to 2.0g and the temperature, 30^0C, 40^0C, 50^0C, 60^0C (Fig.1 to Fig. 8). Based on the data obtained from the conducted experiments, the results shown in Tables 1.0 and 2.0 showed that the adsorption process was best fitted by pseudo second order kinetic models with linear regression coefficient of 1 and a rate constant of 0.9950 while Fig. 1 to Fig. 8 showed that the adsorption efficiency increases with an increase in the contact time.

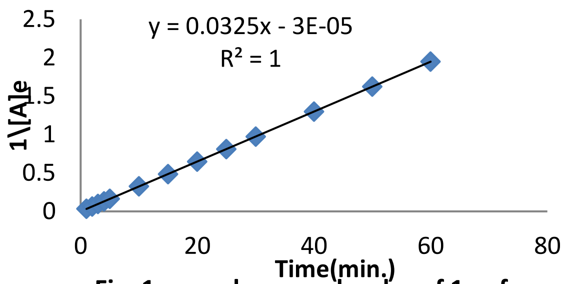

Fig. 1. pseudo second order of 1g of Adsorbent plot at 30^0c

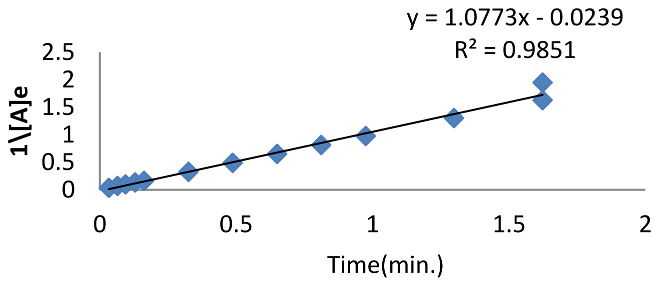

Fig. 2. pseudo second order of 1g of Adsorbent plot at 30^0c

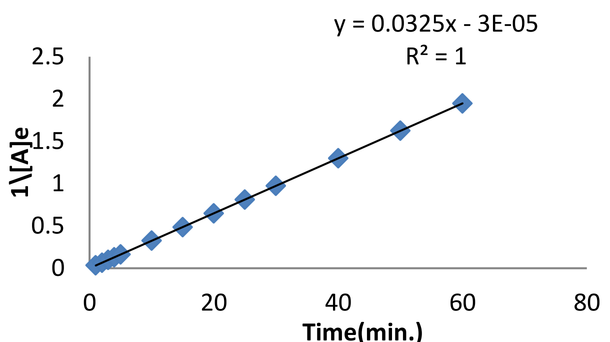

Fig. 3. pseudo second order of 1g of Adsorbent plot at 50^{0}c

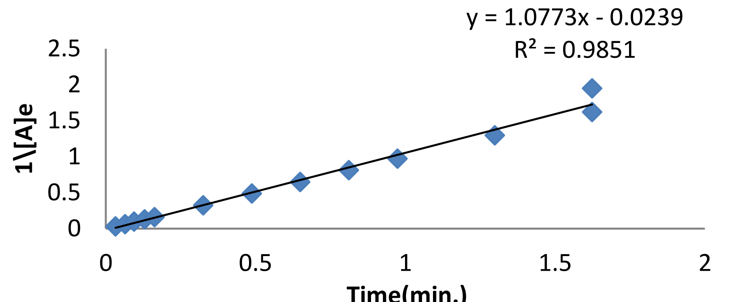

Fig. 4. Pseudo second order of 1g of Ad sorbent plot at 60^{0}c

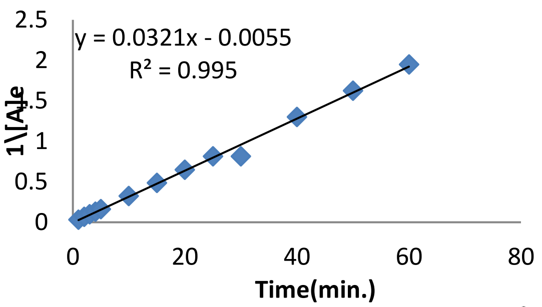

Fig. 5. pseudo second order of 1g of Adsorbent plot at 30^{0}c

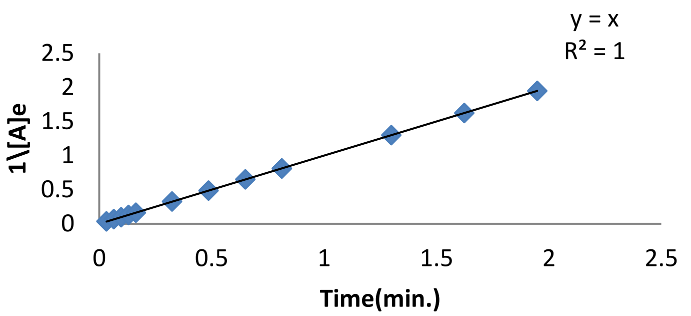

Fig. 6. PSeudo second Order of 2g of Adsorbent plot at 40°c

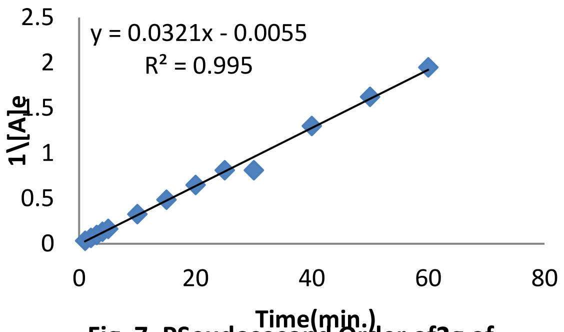

Fig. 7. PSeudosecond Order of2g of Adsorbent plot at 50°c

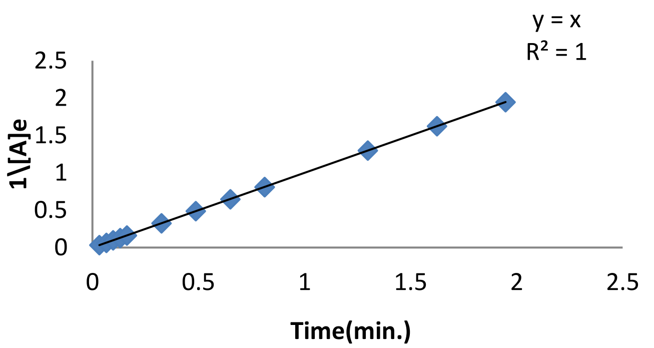

Fig. 8. PSeudo second Order of 2g of Adsorbent plot at 60°c

Effect of Adsorbent Dosage

The dependence of adsorption of cadmium on the amount of groundnut shell powered was studied at a neutral pH, by varying the amount of the adsorbent from 1.0g to 2.0g, while keeping the pH constant. The results in Table 1.0 and 2.0 shows that the rate of cadmium adsorption is independent of the adsorbent dosage.

Table 1.0: 1g of adsorbent

Temperature (^{0}C)	30		40		50		60	
	R^2	K(mg/L) min^{-1}	R^2	K(mg/L) min^{-1}	R^2	K(mg/L) min^{-1}	R^2	K(mg/L) min^{-1}
Pseudo second order	0.9950	0.0318	1	1	0.9950	0.0381	1	1

Table 2.0: 2g of adsorbent

Temperature ^{0}C	30		40		50		60	
	R^2	K(mg/L) min^{-1}	R^2	K(mg/L) min^{-1}	R^2	K(mg/L) min^{-1}	R^2	K(mg/L) min^{-1}
Pseudo second order	0.9950	0.0318	1	1	0.9950	0.0318	1	1

Effect of Temperature

Using 1.0g and 2.0g of the adsorbent, the same procedure was followed by varying the temperature of solution from 30^{0}C, 40^{0}C, 50^{0}C, 60^{0}C, and keeping the pH constant. From Table 3.0, the adsorption efficiency is independent of temperature but increases with increase in contact time.

Table 3.0: Pseudo Second Order of 1.0g and 2.0g of Adsorbent at all Temperatures

Time (mins.)	Temperature (^{0}C) 30	40	50	60
1	0.0325	0.0325	0.0325	0.0325
2	0.0649	0.0649	0.0649	0.0649
3	0.0974	0.0974	0.0974	0.0974
4	0.1299	0.1299	0.1299	0.1299
5	0.1624	0.1624	0.1624	0.1624
10	0.3247	0.3247	0.3247	0.3247
15	0.487	0.487	0.487	0.487
20	0.649	0.649	0.649	0.649
25	0.8118	0.8118	0.8118	0.8118
30	0.9742	0.9742	0.9742	0.9742
40	1.2988	1.2988	1.2988	1.2988
50	1.6236	1.6236	1.6236	1.6236
60	1.948	1.948	1.948	1.948

Effect of Cd (II) Concentration

The dependence of absorbance on the concentration of cadmium ion was studied at a neutral pH, by varying the concentration of the Cd(II) solution from 2mg/L, 4mg/L, 6mg/L, 8mg/L and 10mg/L while keeping the pH constant. The calibration curve shown in Fig.9 shows that the absorbance increases with increase in Cd (II) concentration with linear regression coefficient of 0.993

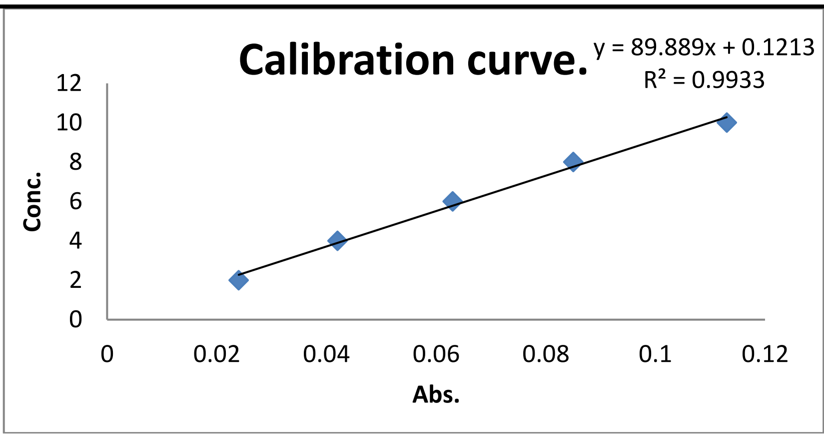

Fig.9: Absorbance calibration curve for various concentrations of Cd (II) solution

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