

## The Adsorption of Divalent Metal Ions from Aqueous Media Using Unmodified Orange Peel (*Musa sapientum*) as Adsorbent

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### Abstract

Water is one of the world's most valuable resources, which is under constant threat due to climate change, drought, explosive population growth and waste. A wide variety of heavy metal species enters the aquatic compartment through atmospheric deposition, lixiviation of mining areas and cultivated fields, and industrial discharges. These activities follow an upward curve in response to the world's ever growing population and its needs. Therefore, there is need to discover non-toxic adsorbent from natural source to combat the menace of water pollution. Orange peel is a non-toxic and environmentally friendly fruit, adsorbent potentials. The present study investigates the adsorption of divalent metal ions from aqueous media using unmodified orange peel as adsorbent.

The orange peels for the adsorption experiment was cut, washed, dried and ground into fine powder. The powdered material was characterized using Fourier Transform Infrared (FT-IR) spectrophotometer and Scanning Electron Microscope (SEM). Determination of heavy metals adsorbed was performed on Perkin Elmer model 214 Atomic Absorption Spectrometry (AAS).

The effect of pH, contact time, initial metal ion concentration and adsorbent dosage in the removal of heavy metals from aqueous media were evaluated.

The Orange peel showed high metal uptake for the tested metal ions Co<sup>2+</sup> (97.8%), Cu<sup>2+</sup> (95.5%) and Zn<sup>2+</sup> (97.0%). The optimum pH for Orange peel was 3, the optimum contact time for the dehydration method of the orange peel was 150 min, and the optimum adsorbent dosage for the Orange peel was 2 g while the orange peel biosorbent optimum initial metal ion concentration was 40 ppm. Adsorption data fitted well with Freundlich and Langmuir equilibrium adsorption isotherms. The maximum adsorption capacity Q value for Langmuir model for the initial metal ion concentration were in the order Cu<sup>2+</sup>>Co<sup>2+</sup>>Zn<sup>2+</sup>. Conclusively, the effective adsorbent properties displayed by the orange peels in the removal of divalent ion from aqueous media studies indicate their potentials in the treatment of water pollution.

**Keywords:** Divalent metal ions; Aqueous media; Orange peel; Adsorption

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### Introduction

Divalent metals ions are group of undefined metals that include the transition metals, metalloids, the actinides and lanthanides. So many definitions have been propounded and put forward as regard to definition of heavy metals [1]. Heavy metals are toxics pollutants, released into the various water body through

different activities such as industries, mining and agriculture. The rapid pace of industrialization has led to severe problem of water pollution. Awareness about the menace of water pollution gives rise to the treatment of wastewater by industries and municipal authorities before discharging to the natural water bodies [2].

The accumulation of heavy metals in human body leads to several complication and organ impairments. Heavy metals

enter the human system through different means, which include contaminated food, water and air, industrial and domestic. Industrial exposure is common in adult while injection is the most common root in children. The toxicity of metals by some researchers has been stimulated by the increased concern on how to reduce environmental pollution that has plagued the existence of man for past centuries. Virtually all metals can produce toxicity when ingested in sufficient quantities but there are several metals which are especially important because they are either so pervasive or produce toxicity at even very low concentrations [1,2].

Many countries have regulatory guidelines for heavy metals presence and exposure as well as remediation and treatment options. The concentration limits to which these methods are economical and become ineffective or too expensive to treat wastes having metal ions in concentrations of 100 mg/L or below [3].

Water pollution from heavy metals such as cobalt, zinc, copper, nickel and lead emanated from industrial sources constituted major environmental problem. The treatment of large volumes of waste streams from industrial activities like mining operations required expensive processes. The discharging of heavy metals into the environment in the last three decades has been a case of major concern to the world. The adverse effects of metals on the population and existence of life have been a major point of study in the developing nations of the world [4]. Nigeria is not an exception to these trends. The release of industrial wastewaters to the environment causes several side effects. These waste water commonly contain heavy metals such as Cd, Pb, Cu, Co, Cr, and Zn and are not biodegradable and their presence in streams and lakes lead to bioaccumulation in living organisms, causing health problems in animals, plants and human beings. It is a known fact that most industries discharge their waste in liquid form which is the easiest way of waste disposal. Major industries involve in the discharge of these heavy metals containing waste include textile, paint, metallurgical, mining, electric appliances, fertilizers, pesticides, metal surface treating industries [5].

Many methods and sorbent materials have been introduced in the treatment of waste containing heavy metals. Among these are reverse osmosis, electro-dialysis, ion-exchange, precipitation, solvent extraction, phytoremediation and ultra-filtration. Chemical precipitation and electrochemical method are ineffective especially when the concentration of metal in aqueous solution is less than 50 mg/L. Ion exchange, electro-dialysis, ultra-filtration are reliable method of waste treatment [6]. However, these methods suffer several drawbacks such as high capital and operational cost, high reagent requirement, requirement of expensive monitoring system, unpredictable and incomplete metal ion removal and generation of toxic sludge. Conventional adsorbents such as activated carbon have been used widely in the treatment of wastewater [7]. However, the high cost manufacturing activated carbon limits its usage. Agricultural waste like are one of the rich sources of low-cost and environmental friendly adsorbent, due to its abundant availability. Agricultural waste such as peanut husk, rice husk, banana waste, wheat bran and sawdust offer little economic value, they also

create serious disposal problems. Activated carbons derived from peanut husk and rice husk have been successfully employed for the removal of heavy metals from aqueous solutions [8].

Adsorption methods are based on physical and chemical phenomena that occur when the adsorbate molecules accumulate on the adsorbent surfaces. Adsorption presents some advantages over others. Such as, low investment cost, as well as the possibility of using environmentally friendly natural adsorbents. Biosorption results from electrostatic interactions and also from the formation of complexes between the metallic ions and functionalities present in the cell surface which exhibits some chemical affinity for metallic ion [9-12].

In this work the utilization of orange residue was studied for metal adsorption ( $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$ ) from aqueous solution due to the great renewability production and low cost for these adsorbent.

## Experimental

The orange were bought from iyana-ipaja market of Lagos State. Synthetic stock solutions at different concentrations were prepared from analytical grade  $\text{CuSO}_4$ ,  $\text{ZnSO}_4$  and  $\text{COCl}_2$  were all supplied by sigma Aldrich (Johannesburg South Africa). All chemical used were analytical grade.

### Sample preparation

The orange peels for the experiment were repeatedly washed with distilled water and oven-dried for 24 h at 105°C to reduce the moisture content. The dried materials were then pulverized and sieved at 25  $\mu\text{m}$ .

### Method of adsorption

The batch adsorption studies were carried out in 100 mL flask, each containing 100 mL solutions of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  standards solutions. A mass of 2 g of the orange peel as shown in **Figure 1.0(b)** was introduced into the flask and agitated at 250 rpm in a thermostat shaker at 25°C for 150 min. After the addition of the adsorbent, the solution pH was adjusted to 4.0 in a minimum amount of dilute hydrochloric acid (HCl) at 60°C, room temperature. The solution was stored at 4°C for one month.

Working solutions of the desired  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  concentrations were prepared from the stock solution daily. The following concentrations of (10, 20, 30 and 40) ppm was each prepared from the 1000 ppm stock [13-25]. After the sorption, the orange peel were separated from the solution, using 0.45  $\mu\text{m}$  membrane filter briefly rinsed with distilled water to remove the residual solutions trapped among the orange peel and then prepared for other analysis. The initial and final  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  concentrations in the solutions in each of the flasks were quantified using atomic absorption spectroscopy (AAS) Perkin Elmer.

The percent removal can be calculated using the formula below:

$$Q_e = \frac{V(C_o - C_e)}{W}$$

Where  $C_o$ ,  $C_e$ ,  $W$  and  $V$  are the initial anion concentration, equilibrium anion concentration, dry weight of adsorbent and solution volume respectively.

### FT-IR spectroscopy

The Fourier transform infrared (FT-IR) spectra of orange peels before and after application were obtained using a Perkin Elmer Spectrum 100 FT-IR spectrometer with an AutoIMAGE System.

### Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) was used to determine the surface morphology of the orange peel. The orange peel was dusted onto a carbon sticker, then coated with gold using a sputter coater (Balzers Union, FL-9496) for 30 min. Images were recorded using INCAPentaFETx3 (Vega Tescan) SEM fitted with an Oxford ISIS EDS.

## Results and Discussion

### Characterization of orange peel

**FTIR studies:** The FTIR results before and after application of the unmodified orange peel as adsorbent is presented in **Figure 1.0A** and **Figure 1.0B** below.

The surface characterization of CH display a number of absorption peaks, indicating the complex nature of the material examined. In the spectrum (A) before application in **Figure 1.1** the characteristic band at  $3269\text{ cm}^{-1}$  and  $2918\text{ cm}^{-1}$  shows the O-H stretch and the C-H aliphatic stretch. The band at  $2850\text{ cm}^{-1}$  and the sharp peak at  $1075\text{ cm}^{-1}$  represent the C-H and the C-O stretch respectively. This type of functional group is likely to participate in metal binding. The band at  $1728\text{ cm}^{-1}$  assigned to C=O stretching vibration for the saturated for the saturated aldehyde.

**Figure 1.1** in spectrum (B) after application there was a decrease in the C-H stretch and binding vibration at bands  $2918\text{ cm}^{-1}$ . The absorption band at  $2850\text{ cm}^{-1}$  has been reduced from the spectrum B.

### Scanning electron microscopy (SEM)

**Figure 1.2A** and **Figure 1.2B** shows the surface morphologies of the orange peel particles before and after application. In **Figure 1.2A** before application, the surface morphology was not irregular while in **Figure 1.2B** after applications appear obviously diverse. Evidently, the surface of the morphology was irregular on the surface. Such irregularities are gainful for the heavy metal ions

that diffused into the adsorption sites of the adsorbent (**Figure 1.3**) [26].

In order to get more structural information and understanding on the adsorption mechanism of orange peel after adsorption, an energy dispersive x-ray spectrometer (EDS) was used to determine the mineral composition of the adsorbents as shown in **Figure 1.4**. The EDS detects X-rays from the sample when excited by the highly focused, high-energy, primary electron beam, penetrating into the sample. Comparing EDS images of orange peel after adsorption.

The Effect of Solution pH on the Removal of heavy metals from aqueous solution onto the orange peel. Operation Performed Thrice,  $n=3$ .

### Effect of pH

The pH is a controlling factor for any kind of metal adsorption process from aqueous solution. Effect of pH is a controlling factor for any kind of metal adsorption process from aqueous solution [27]. The pH dependent experiments were conducted and the result are shown in **Figure 1.5**. The copper, zinc and cobalt attained a maximum value (97.8%, 95.5% and 97%) at pH 4 (which was acidic).

### Effect of contact time

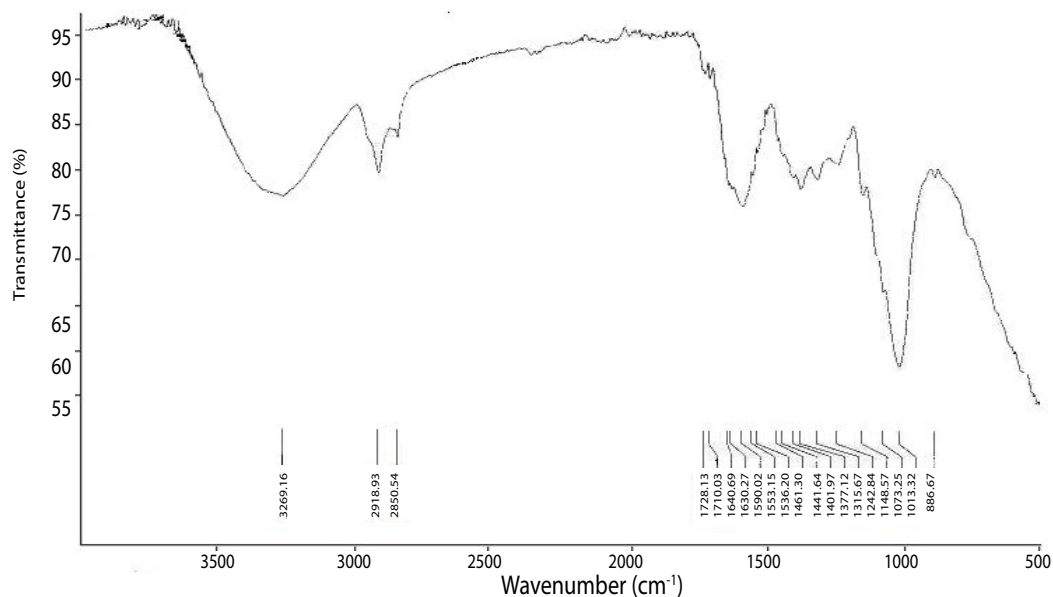
The percentage metal ions removal approached equilibrium within 150 minutes for all metals ( $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ) with  $\text{Co}^{2+}$  recording 97.8%,  $\text{Cu}^{2+}$  95.5% and  $\text{Zn}^{2+}$  97% removal, having a trend of  $\text{Co}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$ . The decrease in percentage removal is due to presence of some of the metal ions on the adsorbent surface. This experiment shows that the different metal ions attained equilibrium at different times.

### Initial concentration

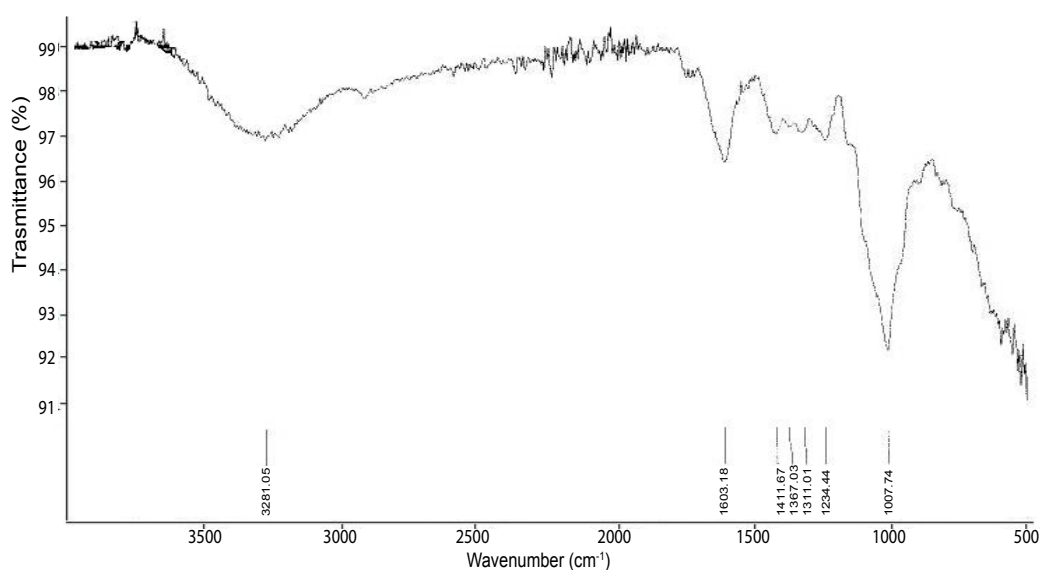
**Figure 1.6** shows the effect of Initial metal concentration on the percentage adsorption of the metals. There is a general increase in extraction percentage for all the metals. The effect of initial metal concentration was studied at a room temperature of  $25^\circ\text{C}$ , at varied concentration of 10, 20, 30 and 40 ppm respectively. From the result obtained it follows that there is increase in the percentage extraction of the metal ions as the



**Figure 1.0** (A) Shows the Orange were bought from Iyana-Ipaja Market of Lagos State and (B) The Pulverized Orange Peel.



**Figure 1.1A** FTIR Absorption Spectrum for the Orange Peel Before Application.



**Figure 1.1B** FTIR Absorption Spectrum for the Orange Peel after Adsorption.

initial concentration increases reaching equilibrium. The highest percentage extraction was achieved with  $\text{Co}^{2+}$  97.8%,  $\text{Cu}^{2+}$  95.5% and  $\text{Zn}^{2+}$  97%. This trend is similar to those results obtained in past work for metal adsorption by orange peel banana pith, and peanut hull carbon [27].

### Adsorption isotherm

Adsorption isotherms describe the equilibrium relationships between adsorbent and adsorbate. Two adsorption isotherms (Figures 1.7 and 1.8) were used to fit the equilibrium data namely Freundlich.

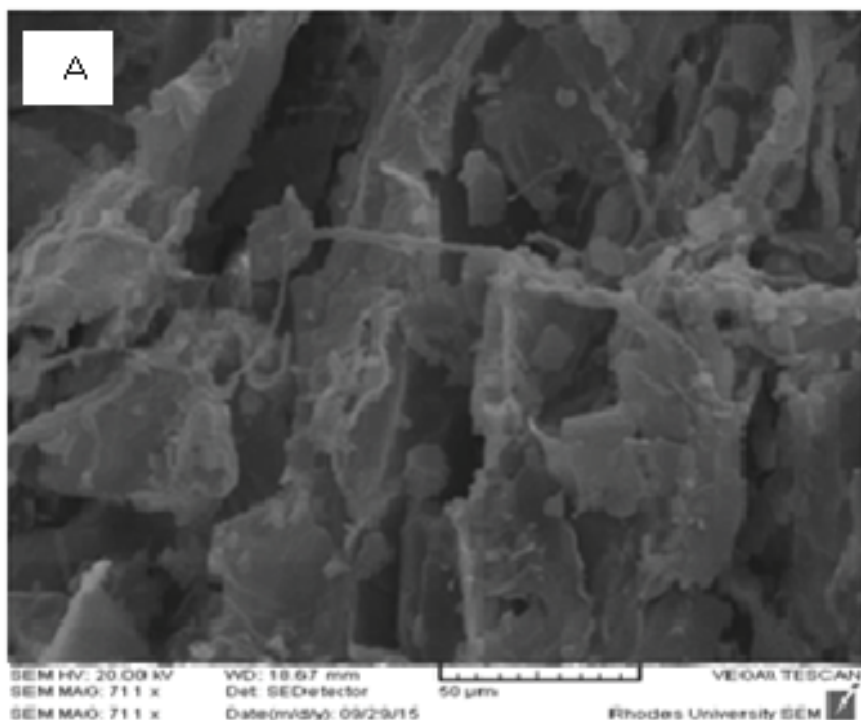
The Freundlich sorption isotherm describes the equilibrium on heterogeneous surfaces and the linear form of the isotherm, which can be represented by

$$\log Q_e = \log F + \frac{1}{n} \log C_e$$

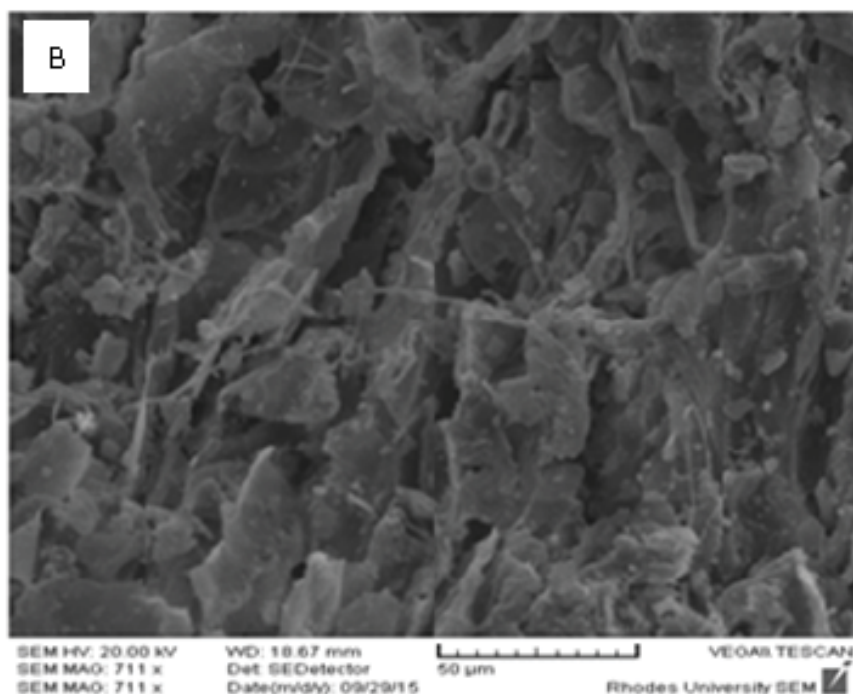
The Langmuir equation can be linearized by the following form

$$\frac{C_e}{Q} = C_e \times \frac{1}{Q_{\max}} + \frac{1}{K_L Q_{\max}}$$

where  $C_e$  [mg/L] and  $Q_e$  [mg/L] are concentration of anions and adsorption equilibrium,  $Q_m$  [mg/g] and  $K_a$  are the theoretical maximum adsorption capacity and Langmuir equilibrium constant



**Figure 1.2A** SEM Images (Scale Bar=50  $\mu\text{m}$ ) showing the morphology of orange peels before application.



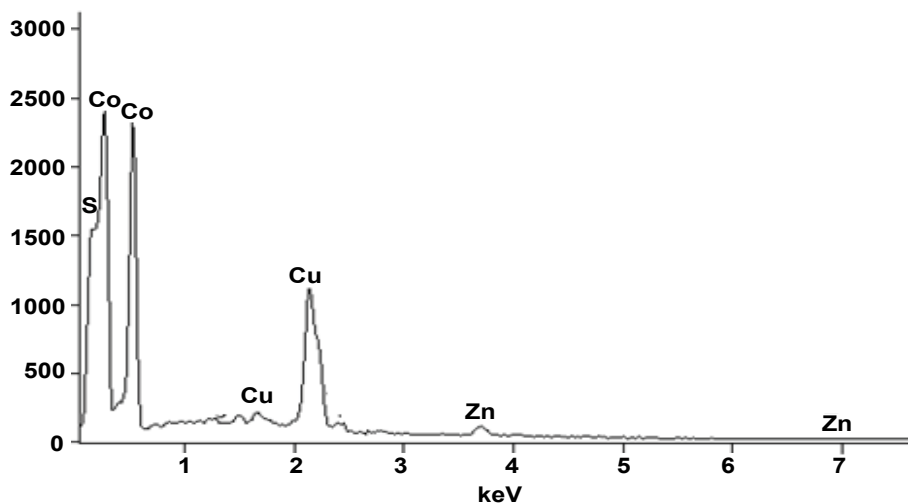
**Figure 1.2B** SEM Images (Scale Bar=50  $\mu\text{m}$ ) showing the morphology of orange peel after application.

related to the theoretical maximum adsorption capacity.

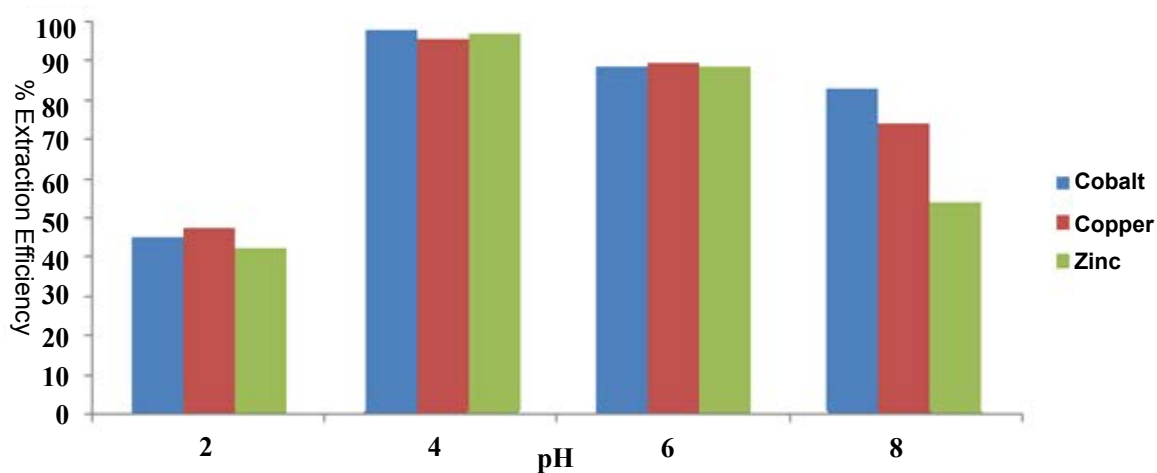
**Freundlich isotherm:** The Freundlich isotherm model fitted best with experimental data of the adsorption studies as it poses higher  $R^2$  values (0.914, 0.943, and 0.770). “n” shows the intensity between adsorbate and adsorbent (**Figures 1.9-2.2**).

## Conclusion

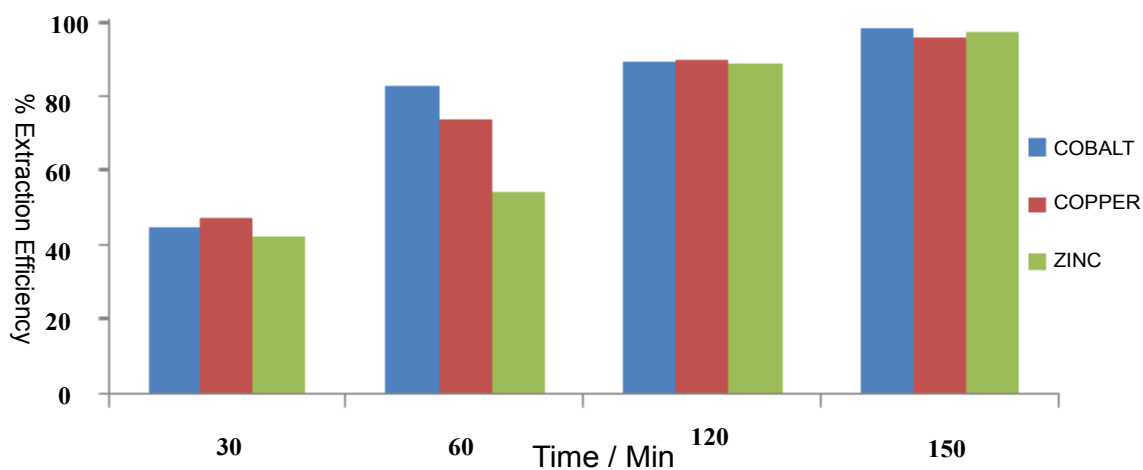
This study shows that it is feasible to use Orange peel as an adsorbent for  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ . The Orange peel bio sorbent showed high metal uptake making them more suitable for the adsorption process. The extraction percentage was controlled



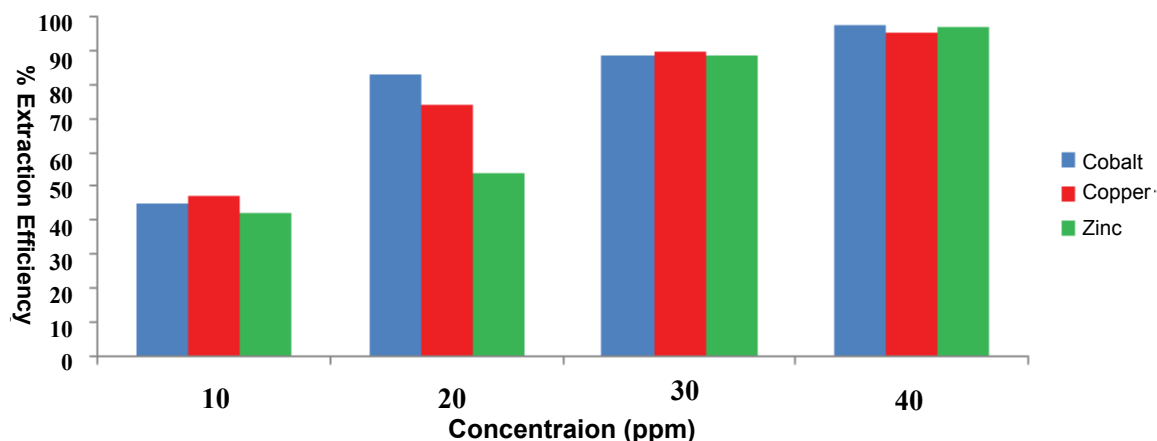
**Figure 1.3** Shows the spectra analysis of the orange peel after adsorption.



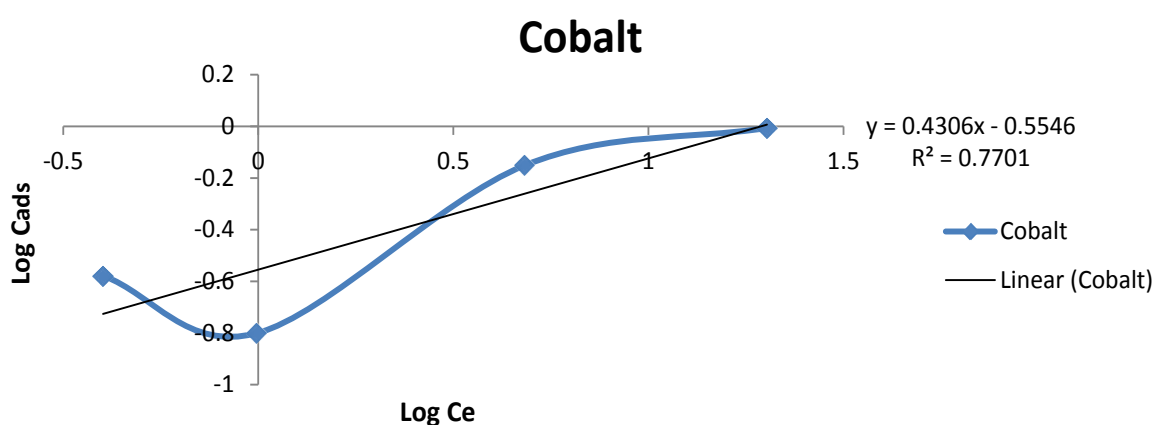
**Figure 1.4** Effect of pH on extraction percentage of  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  onto Orange peel (Experiment conditions employed: initial concentration 40 mg/L; Adsorbent dosage 2 g; Adsorption time 2 hours 30 min; Agitation speed 150 rpm)  $n=3$ .



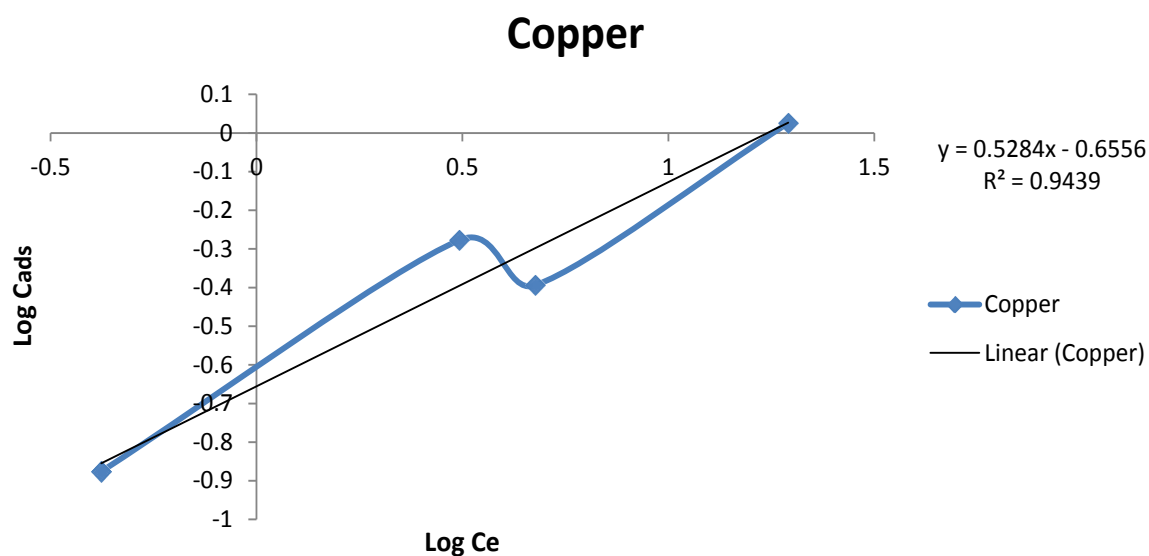
**Figure 1.5** Effect of Contact time on extraction percentage of  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  onto Orange peel. (Experiment conditions employed: initial concentration 40 mg/L; Adsorbent dosage 2 g, pH=4.0; Adsorption time 150 min; Agitation speed 150 rpm)  $n=3$ .



**Figure 1.6** Effect of Initial Concentration on extraction percentage of  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  onto Orange peel. (Experiment conditions employed: initial concentration 40 mg/L; Adsorbent dosage 2 g; Adsorption time 2 hours 30 min; Agitation speed 150 rpm)  $n=3$ .



**Figure 1.7** Freundlich adsorption isotherm for cobalt.



**Figure 1.8** Freundlich adsorption isotherm for copper.

by solution pH, initial metal concentration, contact time and adsorbent dosage. The Orange peel was characterized by the Fourier Transform Infrared (FT-IR), Scanning Electron Microscope (SEM) and X-Ray Fluorescence (XRF). The optimum pH of the solution for  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  was at pH 4. The optimum contact time attained at shaking speed of 150 rpm and the time taken was at 2 hours 30 minutes. The optimum initial metal

concentration was at 40 ppm and the optimum adsorbent dosage is 2.0 g. Adsorption of  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  onto Orange peel showed favourable correlation for the Freundlich isotherm more than the Langmuir Isotherm. Orange peel (waste) is inexpensive and readily available, thus this study provide a cost effective means for removing metal ions ( $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$ ) from aqueous solution.

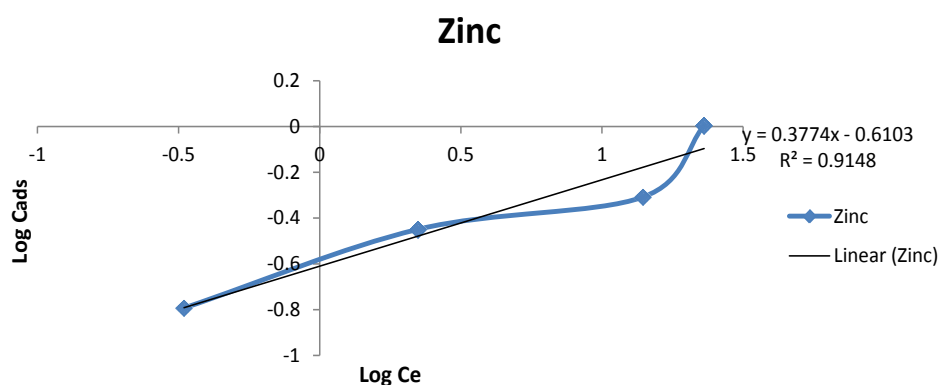


Figure 1.9 Freundlich adsorption isotherm for zinc.

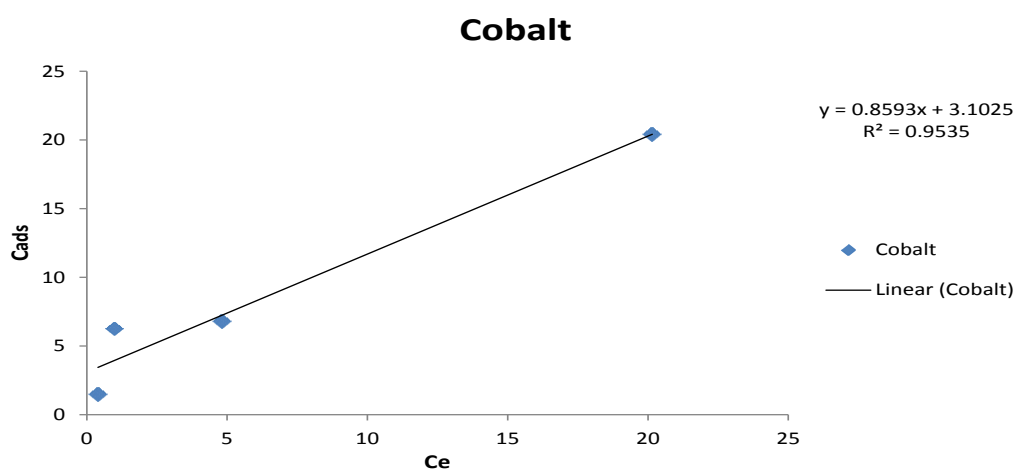


Figure 2.0 Linearized Langmuir adsorption isotherm for cobalt.

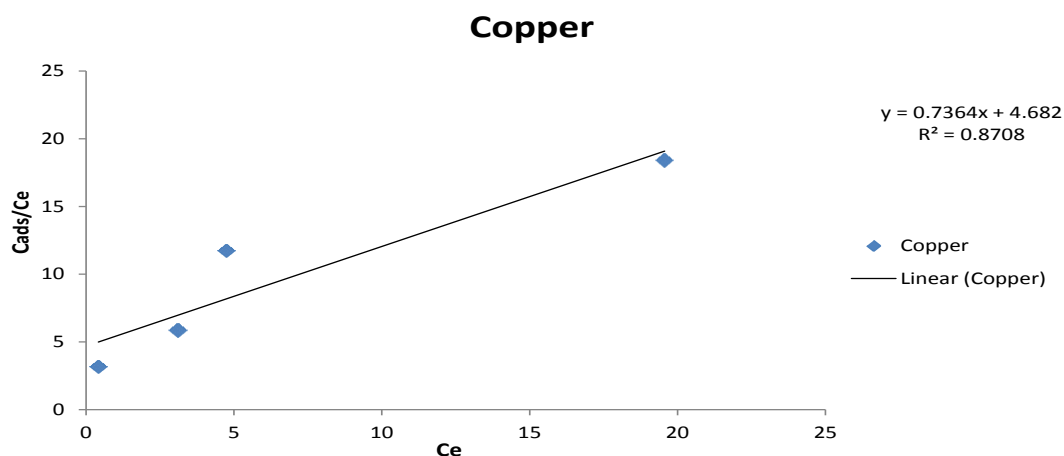
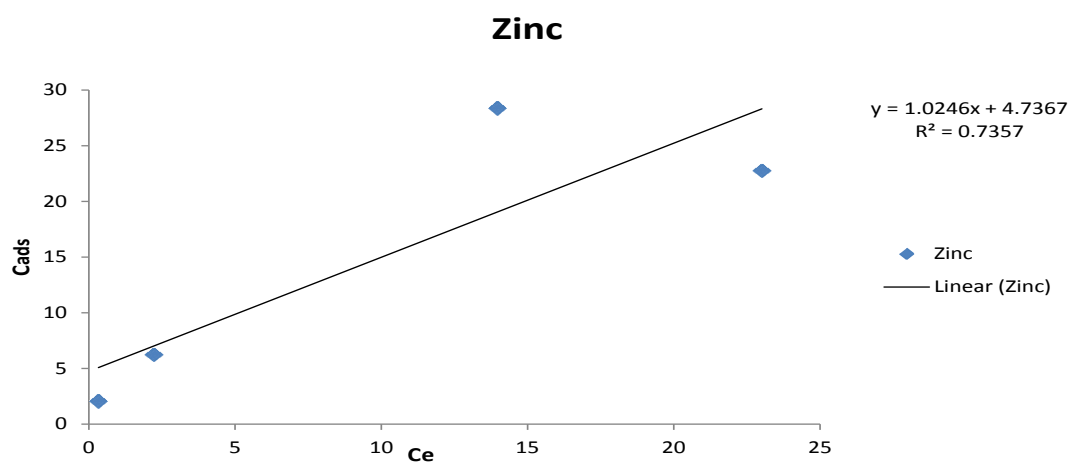


Figure 2.1 Linearized Langmuir adsorption isotherm for copper.





**Figure 2.2** Linearized Langmuir adsorption isotherm for zinc.

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