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Removal of copper, cobalt and zinc from aqueous solution using *Musa sapientum* (Plantain Peel) as bioadsorbent

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Abstract

Heavy metals are group of metals and metalloids with atomic density that are five times more than water. The most toxic form of these heavy metals is when in the ionic species. In the environment, the heavy metals are generally more persistent than organic contaminants such as pesticide or petroleum by-products. The Fourier transform Infrared spectroscopy (FTIR) was used for the characterization of the plantain peel. The FTIR spectrum showed broad and intense absorption band obtained at a range of 3311 cm^{-1} indicating the presence of intra- and inter-molecular hydroxyl groups. The bands at 2917 cm^{-1} and 1375 cm^{-1} showed the presence of aliphatic C-H stretching and bending vibrations respectively. The band at 1629 cm^{-1} is indicative of an aromatic C=C stretching. The strong absorption band of C-O stretching vibration got disappeared from the spectra and these indicate that there was a difference between the two spectra used for the removal of these heavy metals from aqueous solution. Atomic Absorption Spectrometer (AAS) was used for the quantification of cobalt, copper and zinc and the highest removal was 97.7% (Co), 70% (Cu) and 60% (Zn) at pH 4 using 40 ppm.

Keywords: Copper, Cobalt, Zinc, *Musa sapientum*

1. Introduction

The heavy metals definition is based on densities and atomic weights (Fu and Wang, 2011) [1] and toxicities (Boran and Altmok 2010) [2]. The term is therefore used for a loosely-defined subset of elements that exhibits metallic properties. These include transition metals, metalloids, lanthanides and actinides (Duffus 2002) [3]. They are generally classified as elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Srivastava and Majumder 2008) [4]. The heavy metals can neither be degraded nor destroyed unlike their organic counterparts. They are stable and persistent environmental contaminants (Fu and Wang 2011) [1]. They are widespread, typically in concentrations less than 1 mg/L in surface water resources (Zolotov *et al*., 1987) [5]. Although their concentrations in natural water sources are low (mg/L range), metal ions tend to bio-accumulate through the food chain (Gundacker 2000; Pourang 1995) [7, 6] and exert various health effects on humans and animals. The impact of heavy metals on human health is becoming a challenge to public health (Demirbas 2008; Muhammad *et al*. 2011) [8]. There is therefore the need for a regular, quick and accurate determination of the heavy metal ion in water resources. The direct quantification of metals in natural water samples has, however, proven to be a challenge as their concentrations are usually below the detection limits of many analytical instruments (Muhammadi *et al*., 2010) [9]. Hence, the need for an efficient sample pre-concentration step to bring their concentrations to detectable levels for accurate measurements.

Heavy metals in water could originate from natural sources (such as weathering and erosion of bed rocks and ore deposits) or anthropogenic sources such as mining, industries, wastewater irrigation and agriculture activities (Chanpiwat et aI., 2010) [10]. Industrial waste constitutes the major source of metal pollution in natural water (Celik and Demirbas 2005; Demirbas *et al*., 2006; 2005; Pastircakova, 2004) [11, 13]. Heavy metals are found in the wastewater from several industrial processes such as electroplating, metal finishing, metallurgy, tanning, mining and chemical manufacturing (Acar and Malkoc 2004; AI-Rub 2006) [14, 12]. Heavy metals from these sources leach into surface and underground water reserves and eventually become their major pollutants (Kang *et al*., 2007).

The presence of some toxic heavy metals such as Zinc, Copper and Cobalt in the body has a potentially damaging effect on human physiology (Demirbas 2008) [8]. These metals exceeding their critical level in the human system may cause lung and kidney failure, gastrointestinal distress, pulmonary fibrosis and skin dermatitis (Borba el al" 2006). Nickel is also known to be a human carcinogen (Fu and Wang 2011) [1]. Mercury is a neurotoxin and can impair the functions of the kidney (Namasivayam and Kadirvelu, 1999) [15]. Exposure to high levels of mercury has also been established to result in death (Godt *et al*. 2006). Cadmium exposes human health to several risks. Chronic exposure to cadmium results in kidney dysfunction, mucous membrane destruction, diarrhea and vomiting as well as bone damage. It also impedes the production of progesterone and testosterone. Lead is one of the most toxic heavy metals that have latent long-term negative impacts on human health; causing diseases such as anaemia, encephalopathy, hepatitis and nephritic syndrome (Deng *et al*. 2006). Lead has also been reported to cause irrevocable damage to the brain, kidneys and liver as well as the nervous and the reproductive systems (Naseem and Tahir, 2001) [16]. In view of their high toxicities, the exact concentrations of heavy metals in water samples ought to be known. Also, effort ought to be made to reduce their concentrations in water to the minimum or possibly remove them totally.

Owing to the toxic effects of heavy metals, industries are advised to treat their wastewater systematically to remove or minimize the metal contents before disposal. A number of methods are already in constant use to achieve this feat. Adsorption by activated carbon is the most efficient of the classical methods. It has been reported to be responsible for the removal of more than 99% of certain metal ions however, the method has been impeded by the cost of production of activated carbon and its inability to be regenerated and recycled. Apart from the use of highly expensive materials, this method mostly treats metal ions as "wastes" thus eliminating the recycling of materials. Some other methods such as precipitation and coagulation produce concentrated and further toxic wastes, creating yet another disposal problem. Moreover, there are detection limits to which these methods are economical. They become ineffective or too expensive for waste treatment containing metal ions in concentrations of 100 mg/L or below (Nomanbhay and Palanisamy 2005). Hence, there is a constant need to search for an optimal technology that is favoured by cost, materials and efficiency.

Environmental pollution is currently one of the most important issues facing humanity. It has increased exponentially in the past few years and reached alarming levels in terms of its effects on living creatures. Toxic heavy metals are considered one of the pollutants that have direct impact on man and animals. Industrial wastewater containing lead, copper, cadmium and chromium is capable of contaminating groundwater resources and thus leads to a serious groundwater pollution problem (Schiewer and Patil 2008).

Many bioadsorbents used for heavy metals removal from aqueous solutions are developed from agro-wastes such as rice straw, seaweed, wood and bark, tea-waste, maize corn cob, jatropha oil cake, sugarcane bagasse, tamarind hull, sawdust, rice husk, saltbush, marine algal biomass, olive pomace, activated sludge, sugar beet pulp, wool, olive cake, sawdust, pine needles, almond shells, cactus leaves, and charcoal, seafood processing waste sludge and pine bark [Gao *et al*., 2008.; Basha *et al*., 2008.; Mohan *et al*., 2007.; Malkoc *et al*., 2007.; Garg *et al*., 2007.; Verma *et al*., 2006.; Memon *et al*., 2005.; Kumar *et al*., 2006.; sawalha *et al*., 2005.; Sheng *et al*., 2004.; Pagnanelli *et al*., 2003.; Kim *et al*., 2002.; Reddad *et al*., 2002.; Dakiky *et al*., 2002.; Lee SM and Davis AP *et al*., 2001.; Al-Asheh *et al*., 2000] [17, 19-32].

Therefore, this paper aims at investigating the effects of varying time, pH and adsorbent dosage on the adsorption of zinc, copper and cobalt on peels (waste) from plantain. This study also looks into the kinetics of adsorption using Langmuir and Freundlich isotherm models in order to have insight into the equilibrium data.

2. Materials and methods

2.1 Preparation of the adsorbent

Plantain peels were purchased from a local market in Egbeda, Lagos State. The collected biomaterial was extensively washed under tap water to remove trapped solid particles and further rinsed with distilled water. The sorbent was cut into small pieces, oven-dried at 100 °C, crushed and sieved through a 1.80 mm size before its use in adsorption experiments without any further treatment.

2.2 Adsorption Studies

The batch adsorption experiments were carried out by using 2.0 g of the plantain peel with 50 ml solution of Cobalt, Copper and Zinc standards solutions. The effect of pH was studied between 2.0 and 8.0 using 1 M H_2SO_4 or 1 M NaOH solution for adjusting. The Cobalt, Copper and Zinc concentrations of (10, 20, 30 and 40 ppm) were prepared from 1000 ppm stock solution. The samples were withdrawn from the shaker at pre-determined time. After the sorption, the plantain peel were separated from the solution using 0.45 µm membrane filter briefly rinsed with distilled water to remove the residual solutions trapped among the plantain peel and then prepared for other analysis. The initial and final Cobalt, Copper and Zinc 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:

$$q = \frac{(Ci - Ce)V}{W}$$

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

3. Results and Discussion

Surface Characterization

3.1 FTIR

An FTIR spectrum of minced plantain peel (with carbohydrates, proteins, lipids, and fibers as constituents) was recorded to identify functional groups responsible for coordination to the metal ions. Figure 1 shows the FTIR spectrum of dried plantain peels with a particle size of about 1.80 mm size mesh. The bands in the region range of 3311-3000 cm^{-1} were assigned to OH stretching, while those at 2817 and 2917 cm^{-1} to C-H stretching, and the band absorbing at 1735 cm^{-1} was attributed to the C=O bond of carboxylic acids (Memon *et al*., 2008) [33]. The weak band in the region of 886 cm^{-1} was attributed to amine groups.

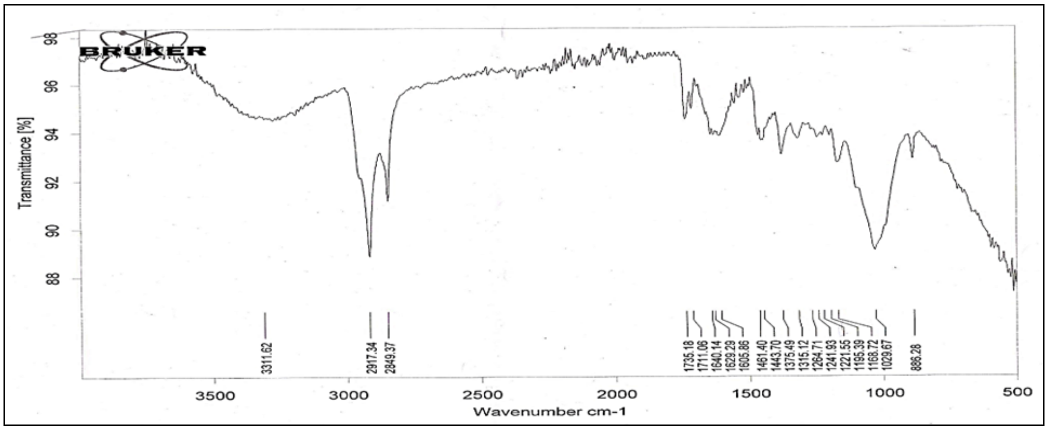

Fig 1: FTIR analysis of plantain peels before adsorption.

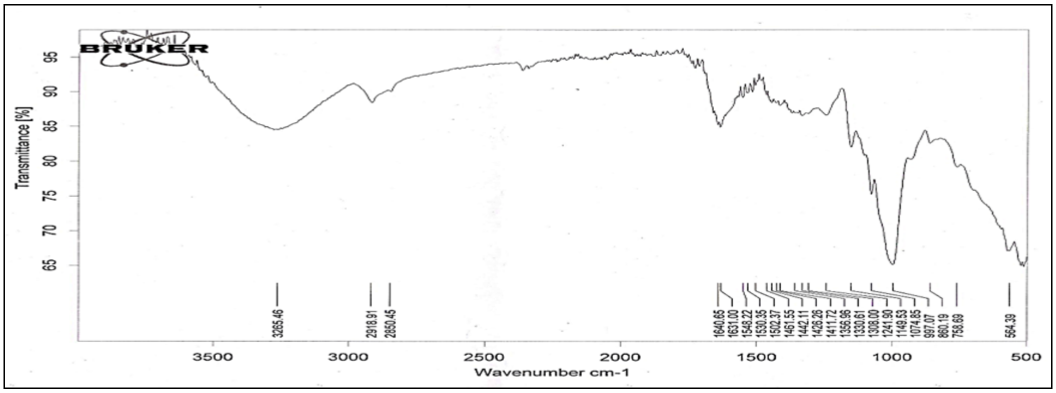

Fig 1.2: FTIR analysis of plantain peels after adsorption

3.2 Surface Morphology

The images of the biomass of the plantain peel surfaces was studied and represented in Figures 3.0 and 3.1 using a scale bar of 50 µm. In Figure 3.0 before application of the removal of heavy metals was smooth while in figure 3.1 which was after application, it appears obviously that the surface was rough. Evidently, that gainful of the heavy metal ions has diffused to the adsorption sites located in the inner portion of the adsorbent.

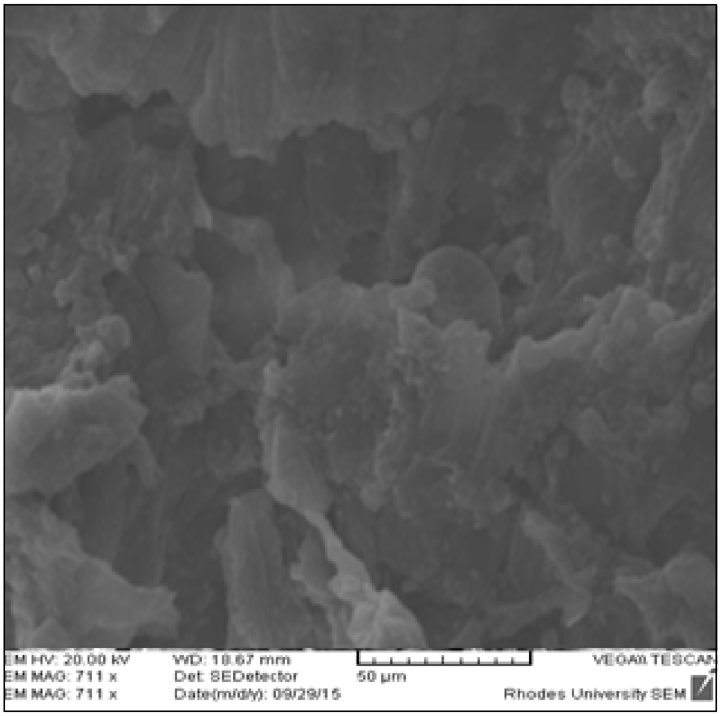

Fig 3: SEM images (scale bar = 50 µm) showing the morphology of plantain peels before application

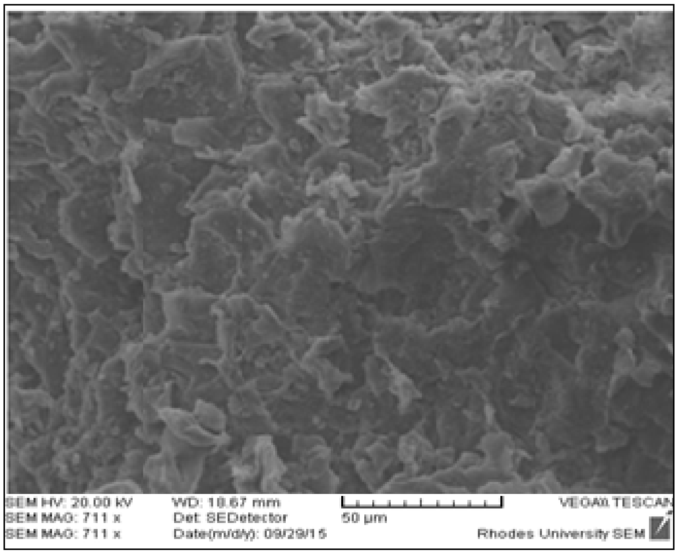

Fig 3.1: SEM images (scale bar = 50 µm) showing the morphology of plantain peel after application

3.3 Effect of Metal Concentration

The effect of initial metal concentration was studied at room temperature at a varied concentration of 10, 20, 30, and 40 ppm respectively. From the result obtained, it follows that there was an increase in the percentage extraction of the metal ions 45.9 - 60.31 %, 53.0 - 70.9 % and 93.5 - 97.7 % in adsorption of zinc, cobalt and copper ions respectively.

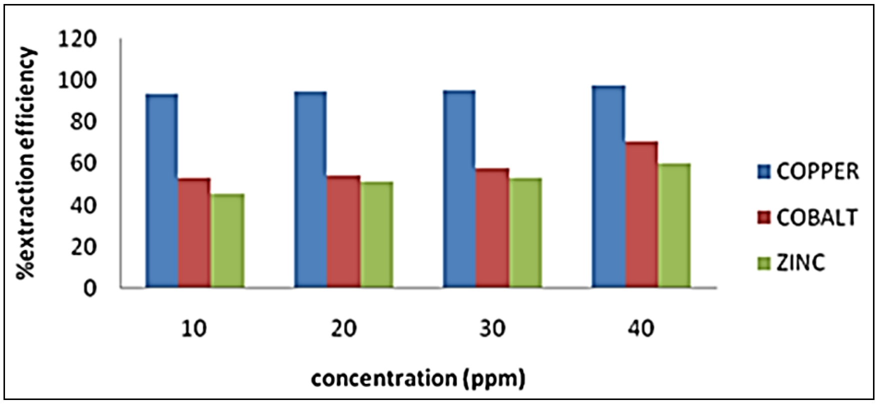

Fig 3.2: Effect of solution concentration on the adsorption of Co^{2+} Cu^{2+}, Zn^{2+}onto plantain peel. (Experiment conditions employed: initial metal ions concentration 40 ppm, adsorbent dosage 2. 0 g, adsorption time 2hrs 30 min, agitation speed 150 rpm/min). n = 3

3.4 Effect of ph

The effect of pH is a controlling factor for metal adsorption from aqueous solution (Gundacker 2000) [7]. The surface properties of adsorbents, ionic state of functional groups and species of metals are dependent on pH condition. The pH dependent experiments were conducted and the results are shown in Figures 3.3

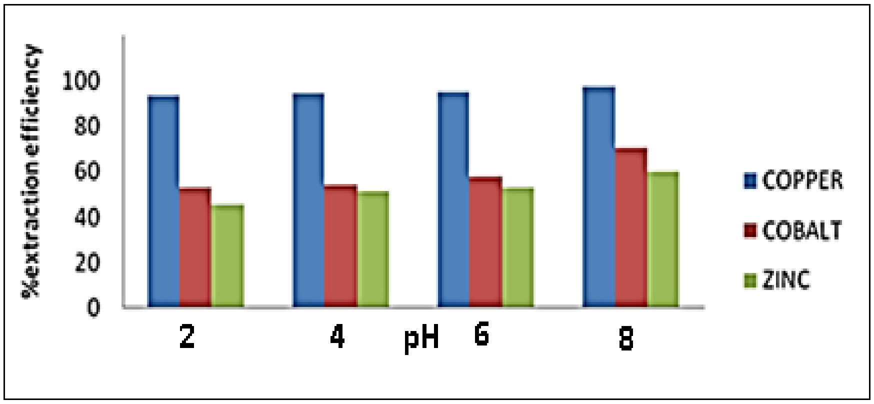

Fig 3.3: Effect of solution pH on the adsorption of Co^{2+}, Cu^{2+}, Zn^{2+} onto plantain peel. (Experiment conditions employed: initial metal ions concentration 40 ppm, adsorbent dosage 2.00 g, adsorption time 2 hrs 30 min, agitation speed 150 rpm / min). n = 3

The Effect of pH on the removal of cobalt, copper and zinc ions from aqueous is shown in Figures 3.3. The percentage of cobalt, copper and zinc ions removed via adsorption increased from 2 to 4, and thereafter drops slowly, the maximum percentage of cobalt, copper and zinc was

Effect of adsorbent dosage

The removal efficiency of zinc, cobalt and copper considerably increased with the increase of adsorbent dosage. The increase in adsorbent dosage from 0.5 – 2.0 g/L resulted in an increase of 53.0-70.9 %, 45.9-60.31 % and 93.5-97.7 % in the adsorption of cobalt, zinc and copper ions respectively.

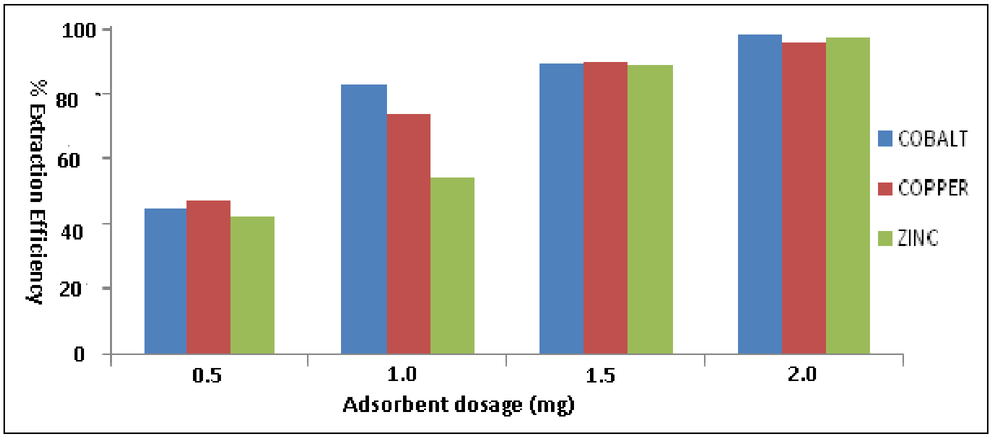

Fig 3.4: Effect of adsorbent dosage on the adsorption of Co^{2+}, Cu^{2+} and Zn^{2+} onto plantain peel. (Experiment conditions employed: initial metal ions concentration 40 ppm, adsorbent dosage 2. 00 g, adsorption time 2hrs 30 min, agitation speed 150 rpm/min). n = 3

This may be due to the greater availability of the exchangeable sites or surface area at higher concentrations of the adsorbent. On the other hand, the increase in the efficiency of removal may be attributed to the fact that an increase in the adsorbent dosage created more adsorbent surfaces or adsorption spots that were readily available for the adsorption of the solute. (Nomanbhay, S. and Palanisamy, K. 2005).

3.5 Effect of contact time

The main purpose of the study was to establish the ideal conditions of the adsorbent capacity, by considering the contact time of the solution at the solid / liquid interface. Contact time is one of the effective factors in batch adsorption process. The effect of contact time on zinc, cobalt and copper ions adsorption efficiency was shown in Figure 3.5. The removal efficiency copper, cobalt and zinc ions onto the plantain peel composite adsorbent significantly increases during the initial adsorption stage (30-120 minutes) and then continued to increase at a relatively slow speed with contact time until a state of equilibrium was attained after 150 min.

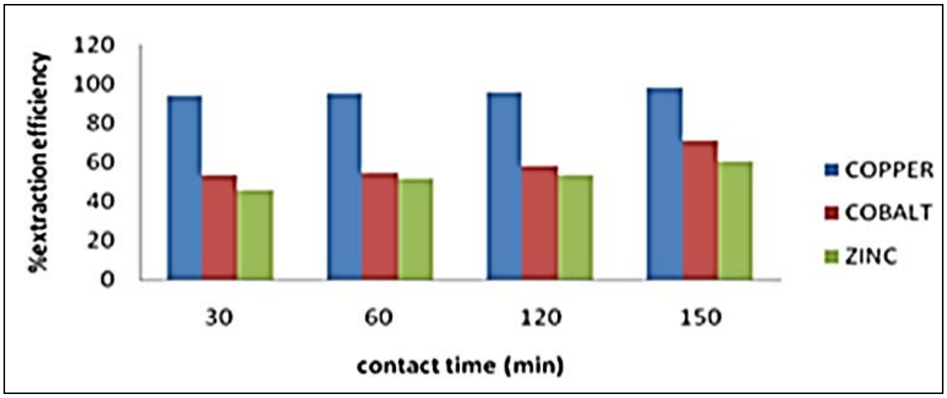

Fig 3.5: Effect of contact time on the adsorption of Co^{2+}, Cu^{2+} and Zn^{2+} onto plantain peel. (Experiment conditions employed: initial metal ions concentration 40 ppm, adsorbent dosage 2. 00 g, adsorption time 2hrs 30 min, agitation speed 150 rpm/min). n = 3

3.6 Adsorption Isotherm

Langmuir Isotherm

The Langmuir adsorption isotherm describes how uptake occurs on a homogeneous surface by a monolayer sorption without interaction (Langmuir, 1916; Singh *et al.*; 2004). The linear form of the Langmuir isothermal is represented by the equation below:

$$\frac{Ce}{Qe} = \frac{Ce}{Qm} + \frac{1}{(kaQm)} \qquad \text{Eqn. (5)}$$

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 related to the theoretical maximum adsorption capacity.

Freundlich Isotherm

The Freundlich adsorption isotherm describes the equilibrium on heterogeneous surfaces and the linear form of the isotherm can be represented by the equation below

$\text{Log } Q_e = \log_F + \frac{1}{n} logCe$ (Freundlich isotherm)

Table 1: Estimated Freundlich Adsorption Parameters for Co^{2+}, Cu^{2+} and Zn^{2+} adsorption.

S/N	Metal Ions	Freundlich Isotherm Parameters For Adsorption		
		K_f	N	R^2
1	COBALT (II)	0.2793	2.3256	0.770
2	COPPER (II)	0.2213	1.894	0.943
3	ZINC (II)	0.2455	2.6525	0.914

Table respectively. The Freundlich isotherm model was found best fitted with experimental data as it poses higher R^2 values (0.770, 0.943, and 0.914). K_f is a Freundlich constant that shows adsorption capacity on heterogeneous sites with non-uniform distribution of energy level and "n" shows the intensity between adsorbate and adsorbent. The calculated value of "n" (Table 1.1) prove that the adsorption of Co^{2+}, Cu^{2+} and Zn^{2+}onto plantain peel is favorable as the magnitude lies between 1 and 3.

Table 1.1: Estimated Langmuir Adsorption Parameters for Co^{2+}, Cu^{2+} and Zn^{2+}

S/N	Metal Ions	Langmuir Isotherm Parameters For Adsorption		
		K_L	Q_{max}	R^2
1	COBALT (II)	0.277	1.1641	0.953
2	COPPER (II)	0.1572	1.3587	0.870
3	ZINC (II)	0.2162	0.9766	0.735

4. Conclusion

The batch experimental results show that, the adsorption of zinc, cobalt and copper on plantain peels was very fast, efficient because of its simplicity, ease of separation and handling and low cost and pH-dependent

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