

## **Equilibrium and Isotherm studies of the biosorption of potentially toxic elements from aqueous solution by *Blighia sapida* (Akee apple) seeds**

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### **ABSTRACT**

The possibility of using *Blighia sapida* seeds to remove  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cd}^{2+}$  ions from aqueous solutions was explored in this study. The effects of pH, contact time, concentration of metal solution and adsorbent dosages were monitored using Multi-metal batch adsorption technique at  $32^{\circ}\text{C}$ . The residual concentrations of the potentially toxic elements were determined using atomic absorption spectrophotometer. The results of the uptake level of the metal ions were found to be dependent on pH of the solution, metal ions type and adsorbent dosage. The adsorption mechanism indicated that biosorption of  $\text{Co}^{2+}$  and  $\text{Cd}^{2+}$  ion fitted better for Freundlich isotherm while the biosorption of  $\text{Cu}^{2+}$  ion was observed to fit well to the Langmuir isotherm. The maximum sorption uptake of the studied metal ions by *Blighia sapida* seeds was in the order of  $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+}$  ions. This study justifies that *Blighia sapida* seeds might serve as a viable low cost agricultural waste to remove potentially toxic elements from aqueous solution.

**Keywords:** Biosorptive, simulated wastewater, *Blighia sapida*

### **INTRODUCTION**

The tremendous increase in the number of industries coupled with the technological advancement over the past few decades has inevitably been responsible for an increased influx of potentially toxic elements in terrestrial and aquatic environments [1]. Hence, these increases pose significant risks to soil, water and human health. These potentially toxic elements enter into the water bodies through wastewater from metal plating industries and industries of Cd- Ni batteries, phosphate fertilizer, mining, pigments, tannery, textiles and

stabilizers alloys [2]. Potentially toxic elements are of special concern because of their toxicity, non-degradation and continual accumulation in the food chain [3]. The choice of these potentially toxic elements were made as a consequence of their industrial and potential pollution impact. Numerous technologies such as precipitation, filtration, oxidation-reduction, ion exchange and liquid membrane separation were developed over the years to remove toxic elements from industrial effluents, but these methods were reported to be generally ineffective or rather expensive [4] [5]. Therefore, there is a need for the development of a low cost technique to remove potentially toxic elements economically.

Biosorption method has been proved to be an excellent way of treating industrial waste effluents, offering significant advantages like low-cost, availability, profitability, easy operation and efficiency [6]. Several researchers had used agricultural wastes to sequester potentially toxic elements from wastewater [7] [8] [9] [10] [11] [12].

*Blighia sapida* otherwise known as Akee apple considered in this study is an evergreen dense crown tree of about 25 m. It is widespread in the equatorial region and found in West Sudan domain. The fruit is a three-valved, more or less pear-shaped capsule that is round and bright red. At maturity the valve opens by reflex to expose 1-3 shiny black seeds with a yellow or white edible aril round the base [13]. This whitish fruit is edible and the black seeds are thrown away which constitute environmental pollution. The annual production of these fruits continues to increase and as such large quantity of waste is generated. Nigeria like any other developing country is facing the problem of solid waste disposal. It was on this basis that this readily available, affordable agricultural waste was used to treat wastewater containing potential toxic elements, so as to remedy our environment from the toxic metal pollution as well as improving our water quality.

## **Experimental**

### **Materials and Methods**

#### **Sample collection**

*Blighia sapida* seeds were randomly collected at Oja-Oba in Ilorin, Kwara State, Nigeria. The seeds were rinsed with de-ionised distilled water, sun-dried and ground using mortar and pestle. A composite sample was made from where the representative sample was collected for the sorption studies.

#### **Preparation of sample**

The representative sample was again washed thoroughly with deionised water to remove colouring material, sun dried and grounded using mortar and pestle. The samples were sieved with 300 $\mu$ m mesh to obtained the smallest particle sizes. The sieved sample was then kept in an air tight container for sorption studies.

#### **Simulated wastewater preparation**

Simulated wastewater samples containing  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Co}^{2+}$  ions were prepared from their salts  $\text{CuCl}_2$ ,  $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  and  $\text{CoCl}_2$  respectively. 1000 mg/L stock solutions of each of the salts were prepared. Other concentrations (10 to 50 mg/L) were obtained from this stock solution by serial dilution.

#### **Effect of contact time on metal ion**

0.5 g of the pre-treated powdered samples were taken in each case in 250  $\text{cm}^3$  conical flasks and shaken with 30  $\text{cm}^3$  of a metal ion solution whose concentration was 5  $\text{mgdm}^{-3}$ . The flasks were shaken at various time intervals of 20 to 120 minutes at room temperature in a magnetic shaker. At the end of each contact period, the mixture was filtered using Whatman filter paper No. 42 and the filtrate was stored in sample bottles before analysis. The residual

concentration of the metal ion in the filtrate was determined by atomic absorption spectrophotometer, Perkin Elmer; Analyst 200.

### **Effect of the initial metal ion concentration**

The equilibrium sorption was carried out at  $34\pm 2^\circ\text{C}$  over a concentration range of 10 - 30  $\text{mgdm}^{-3}$ . 0.5 g of the substrates were weighed into  $250\text{ cm}^3$  conical flasks and  $50\text{ cm}^3$  of the metal ion solution was measured into each conical flask containing the substrates. The flasks were shaken for 40 minutes on a magnetic shaker. The substrates were removed from the mixture by filtration and the concentrations of the residual metal ions in the solutions were determined. The amounts of metal ions adsorbed from solution were analysed using atomic absorption spectrophotometer, Perkin Elmer; Analyst 200.

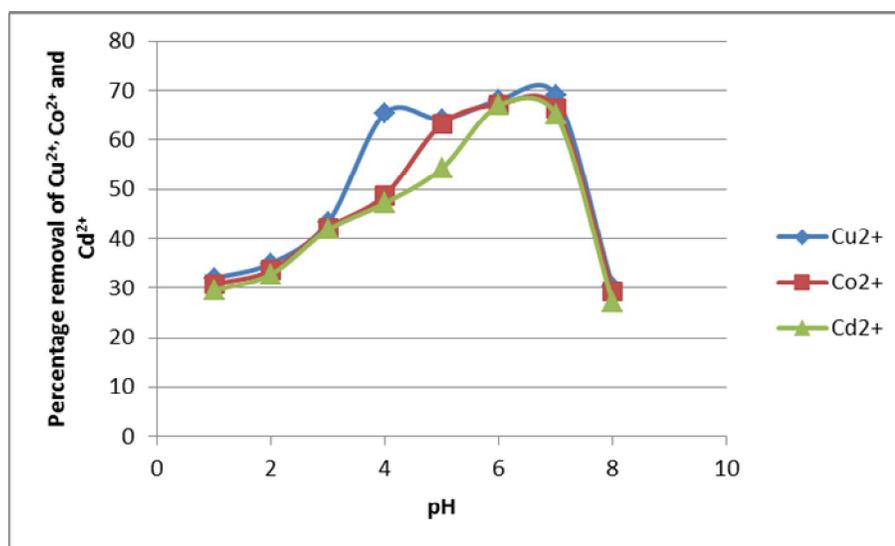
### **Effect of pH**

The experiments were conducted at  $34\pm 2^\circ\text{C}$  to study the effect of pH on the adsorption of the metal ions by contacting 0.5 g of the substrates with  $30\text{ cm}^3$  of  $5\text{ mgdm}^{-3}$  of the metal ion in a boiling tube. The pH of each of the metal solutions was adjusted to the desired value with 0.1 M HCl or 0.1 M NaOH. The pH values were varied from 1-8. The sorbent was removed from the solution by filtration and the residual metal ion concentration in the solution was analysed.

### **Effect of dosage on removal of metal ions**

0.5 g, 1 g, 1.5 g, 2 g, 2.5 g of the pre-treated powdered samples were mixed with  $30\text{ cm}^3$  of  $5\text{ mgdm}^{-3}$  solution in different conical flasks and were shaken for 40 minutes. After the contact time, the samples were filtered and the amounts of metal ions adsorbed from solution were determined.

## RESULTS AND DISCUSSIONS

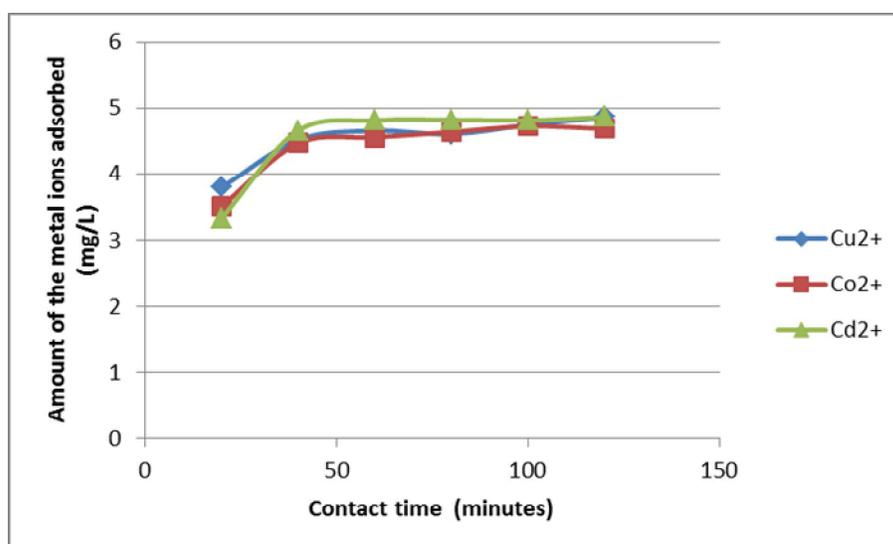


**Figure 1:** Effect of pH on the biosorption of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cd}^{2+}$  using *Blighia sapida* seeds

### Effect of pH on adsorption of $\text{Cu}^{2+}$ , $\text{Co}^{2+}$ and $\text{Cd}^{2+}$ ions

Figure 1 above shows the effect of pH on adsorption of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cd}^{2+}$  ions. At low pH 1-3, the rate of metal uptake was low which could be as result of the seed cell wall closeness associated to hydroxonium ion ( $\text{H}_3\text{O}^+$ ) as such access of metal ions to cell walls was restricted as a result of repulsive forces [14]. With increase in pH from 3 – 5, the rate of metal uptake increased. This may be due to increasing exposure of negative ligands with the subsequent increase in attraction sites to positively charged metal ions [15]. Beyond this point there was not much increase in the percentage of metal ion recovered. After pH 6 the

efficiency of the biosorption process increased drastically due to the formation of metal hydroxides with their respective metal ions [15]. This could also have resulted from the metal ions being precipitated as hydroxides which sometimes depend on the pH and ion concentration [16]. It was initially thought that, at higher pH values, metals may accumulate inside the cells or cell walls by a mechanism known as combined sorption-micro precipitation [7]. When the pH increased to 8, the effect of competition from  $H^+$  ions decreased and the positively charged ions replaced them place on the surface [7]. This might be responsible for the rapid decline in percentage recovery of the metal ions at pH 8.

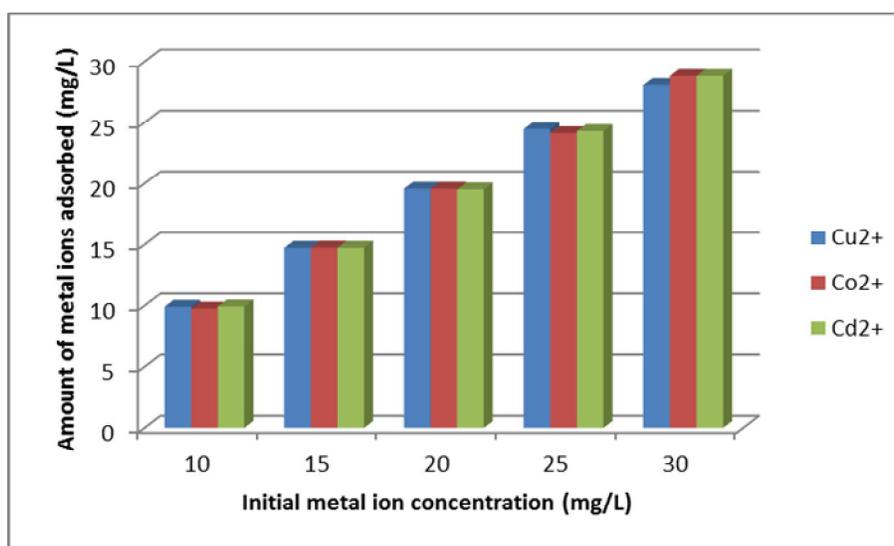


**Figure 2. Effect of contact time on adsorption of  $Cu^{2+}$ ,  $Co^{2+}$  and  $Cd^{2+}$  ions on *Blighia sapida* seed**

### Effect of contact time on adsorption

The contact time was evaluated as one of the important parameters affecting the biosorption efficiency. The results of the influence of contact time on the biosorption capacity for different metal ions was shown in Figure 2 above. The amount of the metal ions increased for a while and later declined as the contact time increased from 20 to 120 minutes. The biosorption rates for Cu, Co and Cd ions were rapid within contact time of 40 minutes, and beyond this, the amount adsorbed by the substrates decreased. These initial fast biosorption rate was attributed to the sufficient surface binding sites on the substrates while further shaking resulted in desorption [1]. This was not surprising because in a mixture of metal ions

and substrates, the metal ions competes for the adsorption sites on the adsorbent. This competition could affect the diffusion properties of the metal ions and hence the adsorption capacity of the metal ions. Maximum removals were attained at 40 minutes of contact between the adsorbate and adsorbent, from this, the equilibrium time was deduced to be 40 minutes for the three metal ions. It was observed that at each contact time,  $\text{Cu}^{2+}$  ions was the most adsorbed by the adsorbents. The plausible reason for this could be that copper with smaller ionic radius was able to diffuse through the cell wall of the seeds than cobalt and cadmium, although they both reached equilibrium at the same time of 40 minutes [17].



**Figure 3. Effect of variation of initial metal ion concentration on adsorption of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Cd}^{2+}$  on *Blighia sapida* seed**  
**Effect of initial metal ion concentration on the adsorption**

The rate of biosorption is also a function of the initial concentration of metal ions and it is considered as an important factor for effective sorption [18]. The variation in the amount of metal ion on the *Blighia sapida* seed with increasing metal ion concentration is illustrated in Figure 3. The result of the study of the effect of increasing the initial metal ion concentration on the biosorption of Cu (II), Co (II) and Cd(II) ions indicated that the sorption capacity increased with increase in initial metal ion concentration. At the lower concentrations, all metal ions present in the solution would interact with the binding sites and thus facilitated 100% biosorption [19]. The feasibility and efficiency of a biosorption process depends not only on the properties of the biosorbents, but also on the concentration of the metal ion solution [20]. Also, it was observed that the amount of metal ion bound increases with respect to adsorbate concentration. This was similar to the report of [14] that used saw

dust and [21] that worked on kale plants. There are many factors which can contributed to the adsorbate concentration effect. The first and most important one is that adsorption sites remain unsaturated during the adsorption reaction. The second cause is the aggregation/agglomeration of adsorbent particles at higher concentrations. This aggregation leads to a decrease in the total surface area of the adsorbent particles available for adsorption and an increase in the diffusional path length [22].

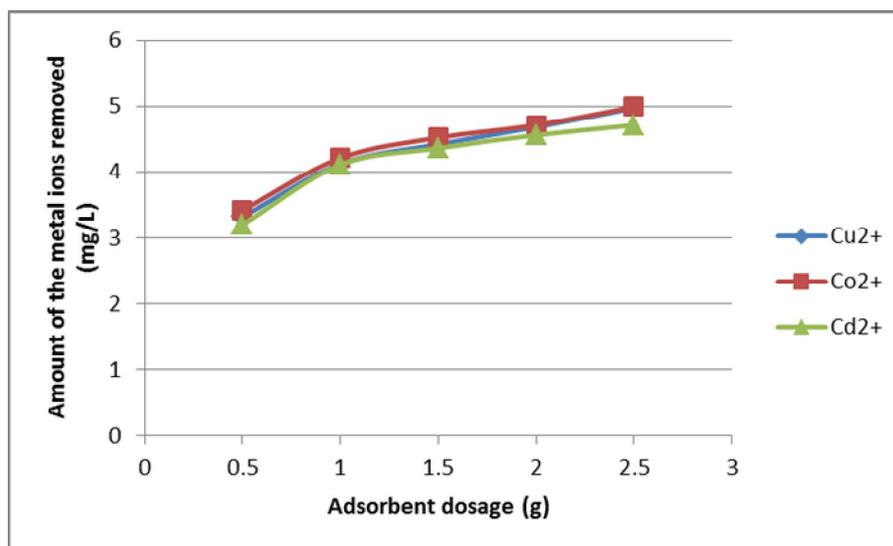


Figure 4. Effect of *Blighia sapida* dose on adsorption of Cu<sup>2+</sup>, Co<sup>2+</sup> and Cd<sup>2+</sup> on *Blighia sapida* seed

### Effect of dosage on adsorption

The concentration of the metal ions and the biosorbent dosage is a significant factor to be considered for effective biosorption because it determines the sorbent/sorbate equilibrium of the system [19]. The results of biosorption of the metal ions in this study with varying biosorbent dosage are shown in the Figure 4. These three potentially toxic elements uptake increased with increase in biosorbent concentration from 0.5g - 2.5g. The plausible reason might be due to increase in the number of active sites available for the metal ions. This could also have been due to increase in electrostatic interaction between the substrate and the adsorbate. The higher the electrostatic interaction between the adsorbent and the metal ions, the higher the metal uptake level. In this study, it was found that *B. sapida* seed was more effective in removing copper ion than cobalt and cadmium ions. This could be due to the fact that copper with smaller ionic radius was able to diffuse through the pores of the seeds than cobalt and cadmium. Thus the trend of adsorption was Cu > Co > Cd and this results therefore showed that the adsorption of cations with large ionic radii would be less than that of metal

ions with smaller ionic radii. A similar trend in metal uptake with variations in biosorbent concentration has been reported for lead biosorption from its synthetic aqueous solutions by *Spirulina maxima* [23].

**Table 1: Freundlich isotherm of the *Blighia sapida* seed on Copper, Cobalt and Cadmium adsorptions**

Metals	$K_f$	Slope (1/n)	N	$R^2$
Copper	0.076	0.7942	1.259	-16.8
Cobalt	0.135	0.7415	1.349	0.9381
Cadmium	0.120	0.7499	1.334	0.9476

**Table 2: Langmuir isotherm of the *Blighia sapida* seed on Copper, Cobalt and Cadmium adsorptions**

Metals	$q_{max}$	$K_L$	$R^2$
Copper	0.231	0.058	0.6193
Cobalt	1.605	0.020	0.8333
Cadmium	0.134	0.061	0.9114

### Adsorption isotherm

The Freundlich model is used to estimate the adsorption intensity of the sorbent towards the adsorbate. The constants  $K_f$  and  $1/n$  indicate the adsorption capacity and the adsorption intensity [9] [11]. The linearity of the plot showed that the adsorption of the three metal ions by *Blighia sapida* seed fits well to Freundlich Model. The Langmuir adsorption isotherm has been used traditionally to quantify and contrast the performance of different biosorbents. The

affinity between the biomass and the different metals was quantified by fitting the obtained sorption values to the Langmuir isotherm. Comparing Table 1 and 2, it could be observed that the correlation regression coefficient  $R^2$  for the biosorption of the Co and Cd ions fitted Freundlich isotherm while data generated for Cu ions fitted Langmuir isotherm. The values obtained from this study were comparable, except for copper with adsorption of the previous studies by [10] [11] and [12]

### **Conclusion(s)**

Based on the experimental results from this work, the following conclusions were drawn

- (i) *Blighia sapida* seed could be applied as a cheap adsorbent for potentially toxic elements removal
- (ii) pH, sorption time, adsorbent dosage and initial metal ion had a clear influence on the sorption capacity of *Blighia sapida* seed for removal of toxic elements.

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