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Isotherm studies on biosorption of some heavy metal ions from aqueous solution onto orchid Malabar *(Piliostigma malabaricum)* seed pod

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Abstract
The adsorption of the following heavy metals; Cd(II), Co(II) and Cr(III) from aqueous solution using Orchid Malabar has been investigated with the aim of assessing the potential of the adsorbent in detoxifying industrial effluents before their safe disposal into land or water bodies. The study involves the application of different isotherm models to assess their suitability to the observed equilibrium adsorption data. Effect of pH on the adsorption process was investigated and results obtained show that the optimum pH for adsorption of the metal ions: Cr(III), Co(II) and Cd(II) occurred at pHs 4.0, pH 7.0 and pH 4.0 respectively. The equilibrium experimental data were tested using five different isotherm models, namely; the Langmuir, Freundlich, Dubinin-Radushkevich, Harkins-Jura and Halsey isotherms. The correlation coefficients (R^2 values) obtained from the five isotherm plots were used to assess their suitability to the experimental adsorption data. Results obtained from the isotherm plots show that Halsey and Freundlich isotherms provided best fits to the adsorption data. Comparison of the maximum amount of each of the metal ions adsorbed onto the adsorbent shows that Cr(III) and Cd(II) were better adsorbed onto the adsorbent than Co(II) ions. The trend of adsorption of the metal ions generally follows: Cr(III) > Cd(II) > Co(II). The results from this study indicate that the biosorbent could be employed as a low cost alternative for the removal of the studied metal ions from dilute aqueous solutions.

Keyword: Adsorbent, Adsorption, Adsorption Isotherms, Metal ions, Orchid Malabar

1. Introduction

Heavy metal ions have been ranked as priority pollutants due to their toxicity, accumulation in the food chain and mobility in natural water ecosystems [1]. The increasing rise in the use of heavy metals and their compounds in our industries present a possible human health risk. The pollutants of utmost concern include: lead, cadmium, nickel, chromium, zinc, and copper. These Heavy metals have important applications in basic engineering works, paper and pulp industries, leather tanning, petrochemicals, fertilizers, battery manufacturing, electroplating etc. and effluents from these processes which contain varying degrees of the heavy metals are deposited into water bodies without treatment thereby causing toxic effects to our aquatic plants and animals. Toxic metal compounds coming from the earth's surface not only reach the earth's waters (seas, lakes, ponds and reservoirs), but also contaminate underground water in trace amounts by leaking through the soil. Therefore, the earth's waters may contain various toxic metals [2]. Since most of heavy metal ions are non-biodegradable, their effective removal from aqueous solutions and waste effluents through various technologies (physical or chemical) is important in the protection of environmental quality and public health.

Various chemical and physical methods have been used to remove metal ions from solutions in the last few decades. These methods include: chemical precipitation, solvent extraction, ion exchange, evaporation, reverse osmosis, electrolysis and adsorption. Among these methods, chemical precipitation, solvent extraction, ion exchange and adsorption are most commonly used [3]. Chemical precipitation has traditionally been used to remove heavy metal ions from wastewater with relatively high concentrations of metals. The operation of chemical precipitation is simple but generates large quantities of sludge, which require further disposal. In addition, chemical precipitation is usually not effective in removing trace levels of metal ions from aqueous solutions. Solvent extraction has widely been used in organometallic removal. Although the process may have fast kinetics and high capacity, solvent extraction is often costly due to the quantity and specific types of solvents needed. Ion exchange method has commonly been used to remove metal ions from water or wastewater, but the process has

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slow kinetics, consumes additional chemicals, generates hazardous streams and is not well applied to heavy metal ions due to the possible problem of resin pollution [3, 4].

Biosorption of heavy metals from aqueous solutions has proven to be an efficient and a relatively new technology for the treatment of industrial wastewater. Adsorbent materials derived from low cost agricultural wastes have been employed for the effective removal and recovery of heavy metal ions from wastewater streams. Biosorption, a passive non-metabolically mediated process that removes metals or metalloid species, compounds and particulates from solution, with materials of living or dead biomass is currently being considered as an important means of purifying industrial wastewaters containing toxic heavy metal ions [5]. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and involving inexpensive, abundant biosorbent materials [6-8]. The application of biosorption in environmental treatment of waste effluents has become an important area of research in the past few decades. There is therefore an urgent need to explore all possible sources of agro-based inexpensive adsorbents and their feasibility for the removal of heavy metals be studied in detail. The current study involves the assessment of the potential of an agricultural waste, Orchid Malabar pod in the adsorption of Co(ll), Cd(ll) and Cr(lll) ions from aqueous solutions.

2. Materials and methods
Preparation of the adsorbent
The adsorbent, Orchid malabar seed pod was obtained at Michael Okpara University of Agriculture, Umudike, Abia state. The shells were carefully removed, washed with deionized water, dried and crushed with a blender. The crushed samples were sieved through to obtain 60 μm mesh size, soaked in 0.3 M HNO_3, stirred for 30 min and then left undisturbed for 24 h. They were then filtered through Whatman no. 41 filter paper and rinsed thoroughly with de-ionized water until a pH of 7.4 was obtained. The adsorbent was kept in an oven at 100 °C for 12 h and finally stored in a tight plastic container. The treatment of the adsorbent with 0.3 M HNO_3 helps to oxidize the adhering organic materials and the removal of any debris or soluble bio-molecules that might interact with the metal ions during sorption.

Preparation of the metal ion solutions
All the reagents used were of analytical grades and were used without further purification. De-ionised water was used in the preparation of all sample solutions. Stock solutions of 1000 mg/L of each of chromium, cobalt and cadmium were prepared from their salts, $Cr(NO_3)_3.9H_2O$, $Co(NO_3)_2$ and $CdSO_4.8H_2O$ respectively. This was done by dissolving appropriate amount of each salt in 1000 cm^3 of de-ionized water, and made up to the mark of volumetric flask with de-ionized water. From the stock solutions, working concentrations of 10 to 50 mg/L of each of the metal ions were prepared by serial dilution.

Batch adsorption experiments
Equilibrium sorption of Co(ll), Cr(lll) and Cd(ll) ions onto Orchid malabar was studied as a function of pH and initial metal ion concentration. The effect of pH on the adsorption of the metal ion was studied at a temperature of 30 °C and at a fixed metal ion concentration of 50 mg/L. The pH of the solutions was adjusted to 2, 4, 6, 7 and 8 using 0.1M HCl or

0.1M NaOH solution as the case may be. Exactly 50 ml of each metal ion solution of different pH were introduced into 250 ml different Erlenmeyer flasks containing 0.25 g of the adsorbent. The mixture was agitated intermittently for 2 h in a thermostated shaker and then filtered. The metal ion content of each filtrate was finally determined using UNICAM Atomic Absorption Spectrophotometer (Solar AAS 500).

The isotherm studies were investigated by studying the influence of initial metal ion concentrations on the equilibrium sorption of the metal ions by Orchid Malabar. It involved introducing 50 ml of various concentrations (10, 20, 30, 40, and 50 mg/L) of the metal ions into 250 ml Erlenmeyer flasks containing 0.25 g of the adsorbent of particle size 60 μm while maintaining the study temperature and pH at 30 °C and 6.0 respectively. The flasks were agitated intermittently for 2 h and at the end of the contact time, the mixtures were filtered rapidly into separate sample bottles. The metal ion concentration of the filtrate was determined using Atomic Absorption Spectrophotometer (Solar AAS 500).

Data analysis
The amounts of Cr(lll), Co(ll) and Cd(ll) adsorbed by the adsorbents during the batch adsorption studies were determined using a simplified mass balance equation:

$$q_e = (C_0 - C_e)\frac{V}{m} \tag{1}$$

Where q_e is the equilibrium sorption capacity (mg/g), C_o and C_e are the initial and the equilibrium concentrations of metal ions in mg/L, V is the volume of adsorbate solution in L and m is the dry mass of the adsorbent in g.

3. Results and discussion
Effect of pH on adsorption of the metal ions onto Orchid Malabar
The amounts of Cr(III), Co(II), Cd(II) ions adsorbed as a function of initial pH are shown in Figure 1. The pH of an aqueous solution is an important factor affecting both the availability of metal ions in solution and the number of binding sites on the adsorbent[9,10]. This implies that the dependence of metal adsorption on pH is related to both the metal chemistry in solution and the ionization state of the functional groups of the adsorbent, which will in turn affect the availability of binding sites. The range of pH values 2.0 to 8.0 selected in our study were chosen to avoid the precipitation of these metal ions in solution at higher pH. Results show that the amount of metal ions adsorbed from the solutions by the adsorbent increased as the pH of the metal ion solution increased from pH 2.0 to pH 6.0 and pH 7.0 and then decreased as the pH is increased above 6.0 and 7.0 in the different metal solutions. At low pH, the protons are likely to compete with the metal ions for the binding sites on the adsorbent surface which may ultimately lead to a decrease in metal ion adsorption by the adsorbent as a result of electrostatic repulsion. Also at higher pH, the proton concentration will decrease thereby creating more binding sites on the adsorbent surface thus leading to enhanced metal removal. From Figure 1, it can be observed that the adsorption of Cr(lll), Co(ll), Cd(ll) ions onto the Orchid malabar depends on pH and maximum adsorption occurred at pH 4.0 for Cr(lll) and Cd(ll) and pH 7.0 for Co(ll) ions.
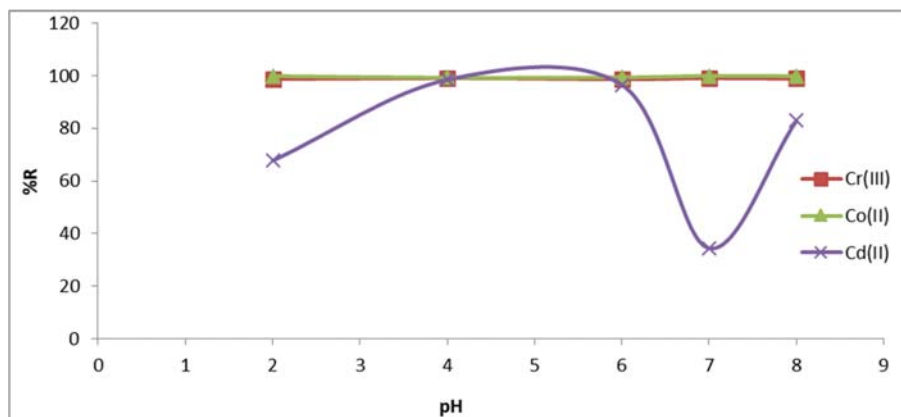
Fig 1: Effect of pH on the adsorption of the metal ions by orchid Malabar

Adsorption Isotherms

Adsorption isotherm is established when the concentration of an adsorbate (metal ion) in a bulk solution (C_e) is in dynamic balance with that at the interface. In this study, the adsorption process was evaluated using different isotherm models viz; the Langmuir, Freundlich, Dubinin– Radushkevich, Harkins-Jura and Halsey isotherm models.

Langmuir isotherm

The Langmuir isotherm represents the equilibrium distribution of metal ions between the adsorbent and liquid phases. This isotherm predicts monolayer coverage of the adsorbate (metal ions) on the outer surface of the adsorbent and assumes that there is no lateral interaction between the adsorbed molecules[11, 12]. The isotherm had been used to assess the adsorption properties of metal ions on the surfaces of a number of solid materials and is generally expressed as Equation 2 [13-15].

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \, K_L} + \frac{C_e}{q_{max}} \tag{2}$$

Where q_e is the adsorption capacity in mg of adsorbate per gram of adsorbent, C_e is the residual (equilibrium) metal ion concentration in solution, q_{max} is the maximum adsorption capacity corresponding to sites saturation and K_L is the Langmuir isotherm constant, which expresses the intensity of the adsorption process. The results obtained from the Langmuir plots indicate that Langmuir isotherm fairly gave good description to the experimental adsorption data especially for Co(ll) and Cr(lll) adsorption onto the adsorbent while the negative slope obtained for adsorption of Cd(ll) ions onto the adsorbent indicate poor fitting of the adsorption data into the Langmuir model. The Langmuir parameters are shown in Table 1 while the plots are shown in Figure 2. The Langmuir isotherm parameters and the R^2 values obtained from the plots indicate the non-suitability of the isotherm to the equilibrium adsorption data.
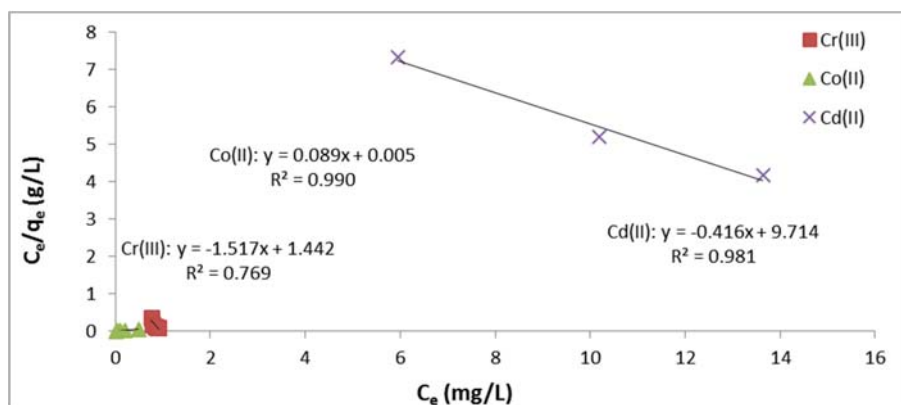

Fig 2: Langmuir Isotherm plot of C_e/q_e vs C_e for adsorption of the metal ions onto orchid malabar

Table 1: Langmuir Isotherm Constants for adsorption of Cr(lll), Co(ll), and Cd(ll) ions by the adsorbent.

Parameters	Metal ions		
	Cr(lll)	Co(ll)	Cd(ll)
K_L (L/mg)	-1.0520	17.8001	-0.0428
q_{max} (mg/g)	-0.6592	11.2359	-2.4038
R_L at diff conc.			
10	-0.1050	0.0055	1.748
20	-0.0499	0.0028	6.944
30	-0.0327	0.0019	-3.521
40	-0.0243	0.0014	-1.404
50	-0.0193	0.0011	-0.877
R^2	0.769	0.990	0.981

Freundlich isotherm

The Freundlich isotherm is generally applied to adsorption occurring on a heterogeneous surface. The linearized form of Freundlich adsorption isotherm is represented as [16]:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \tag{3}$$

Where K_F and n are Freundlich constants describing both the intensity and capacity of the adsorption process, respectively. Figure 3 represents linear plots of ln q_e vs ln C_e according to Freundlich isotherm equation. The constants K_F and 1/n were calculated from the intercept and slope of the linear Freundlich isotherm plots. The values of the Freundlich parameters calculated from the linear plots are presented in
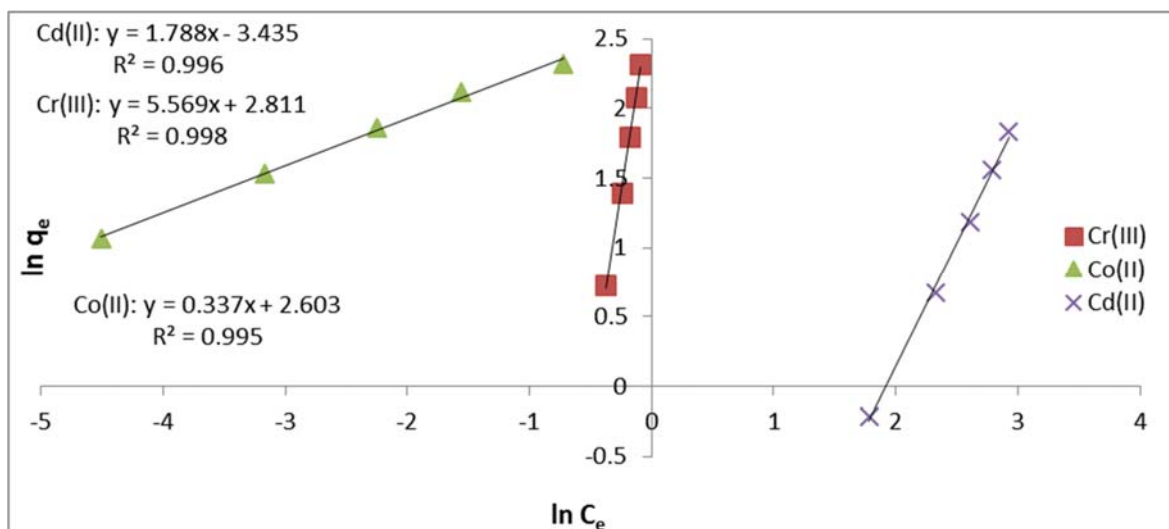
Table 2. Assessment of the correlation coefficients (R^2 values) obtained from the plots shows that the equilibrium adsorption data were best described by the Freundlich model. The R^2 values were generally greater than 0.994 for the three metal ions and this indicates that the Freundlich isotherm clearly describes the adsorption of the metal ions onto the adsorbent. Anusiem *et al* [17] had reported that 'n' values between 1 and 10 represent favourable adsorption conditions. In the present study, the range of the values of n was within 0.1796 to 2.9674 for the adsorption process, indicating beneficial adsorption for the present study. The fit of experimental adsorption data to Freundlich model indicates that the forces of adsorption by the adsorbents are likely to be governed by physisorption.

Fig 3: Freundlich isotherm plot of ln q_e vs ln C_e for adsorption of the metal ions onto orchid Malabar seed pod.

Table 2: The Freundlich isotherm parameters for the adsorption process

Parameters	Metal ions		
	Cr(lll)	Co(ll)	Cd(ll)
K_F	16.6265	13.5042	0.0322
n	0.1796	2.9674	0.5593
R^2	0.998	0.995	0.996

Dubinin-RadushKevich isotherm

The Dubinin-RadushKevich (D-R) model was applied to the equilibrium data to assess the nature of the adsorption process, *i.e.* whether it is physical or chemical adsorption. The linearized D-R adsorption isotherm is represented as [18]:

$$\ln q_e = \ln q_D - B_D \varepsilon^2 \tag{4}$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{c_e}\right) \tag{5}$$

Where q_D is the theoretical saturation capacity (mg g^{-1}) and B_D is a constant relating to adsorption energy (mol^2 K J^{-2}), R is the gas constant (kJ mol^{-1} K^{-1}) and T is the temperature (K). The constant B_D gives an idea of the mean energy of adsorption E (kJ mol^{-1}).

The plots obtained (Figure 4) show that the Dubinin-Radush Kevish isotherm provides good description to the adsorption

of Cr (III) and Co (II) ions onto the adsorbent and this suggests that the characteristic sorption of these metal ions may be related to the porous structure of the adsorbent. The coefficients of correlation (R^2 values) were all high with the exception of Cd (ll) ions indicating that the D-R isotherm model could not provide a good description to Cd(ll) ion adsorption by the adsorbent.

The constant B_D gives an idea of the mean energy, E (kJ mol^{-1}) of adsorption per mole of the adsorbate as it is transferred to the surface of the adsorbent from infinite distance in the solution and this energy is usually evaluated using equation 6.

$$E = \frac{1}{\sqrt{2B_D}} \tag{6}$$

It has been reported [19, 20] that when the value of E_D is below 8 kJ mol^{-1}, the adsorption process can be considered as physical adsorption and when it is within the range of 9–16 kJ mol^{-1}, it is chemical adsorption (chemisorption). The Dubinin-Radush Kevich Isotherm parameters were all calculated from the linear plots and presented in Table 3. From Table 3, it can be observed that the obtained E_D values are within the range of 0.3829 - 7.0711 kJ mol^{-1}, indicating that physisorption may have played a dominant role in the adsorption process.
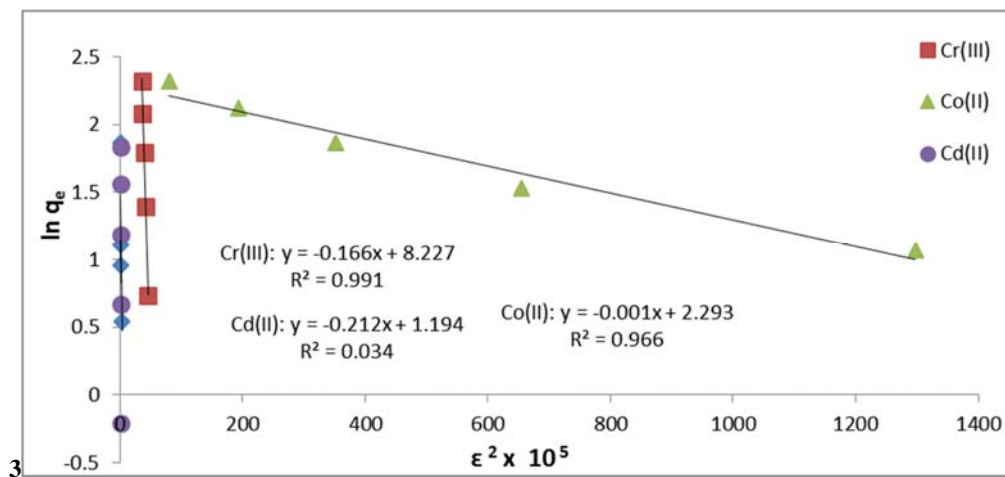
Fig 4: Dubinin-Radushkevich (D-R) Isotherm plots for adsorption of Cr(lll), Co(ll) and Cd(ll) ions by orchid malabar

Table 3: Dubinin-Radushkevich Isotherm Parameters for the adsorption process.

Parameters	Metal ions		
	Cr(lll)	**Co(ll)**	**Cd(ll)**
q_D (mg g^{-1})	3740	9.9046	3.3003
B_D(mol^{2}kJ^{-2})	1.660×10^{-6}	1.000×10^{-8}	2.120×10^{-6}
E_D (kJ mol^{-1})	0.5488	7.0711	0.4856
R^2	0.9209	0.966	0.034

Harkins-Jura isotherm
It is reported [19, 21] that Harkins-Jura isotherm model mainly describes the multilayer adsorption and the existence of the heterogeneous pore distribution on the surface of adsorbents and is expressed as:

$$\left[\frac{1}{q_e^2}\right] = \left[\frac{B_{HJ}}{A_{HJ}}\right] - \left[\frac{1}{A_{HJ}}\right] \log (C_e) \quad (7)$$

Where B_{HJ} and A_{HJ} are the Harkins-Jura constants which are calculated from the slope and the intercept of the linear plots of $1/q^2e$ versus log (C_e), respectively. The plots are displayed in Figure 5 while the calculated isotherm parameters are presented in Table 4. The fairly high R^2 values obtained from the plots show that the isotherm could not present a perfect description to the experimental equilibrium adsorption data and further show that the adsorption process did not involve multilayer formation on the surface of the adsorbent.
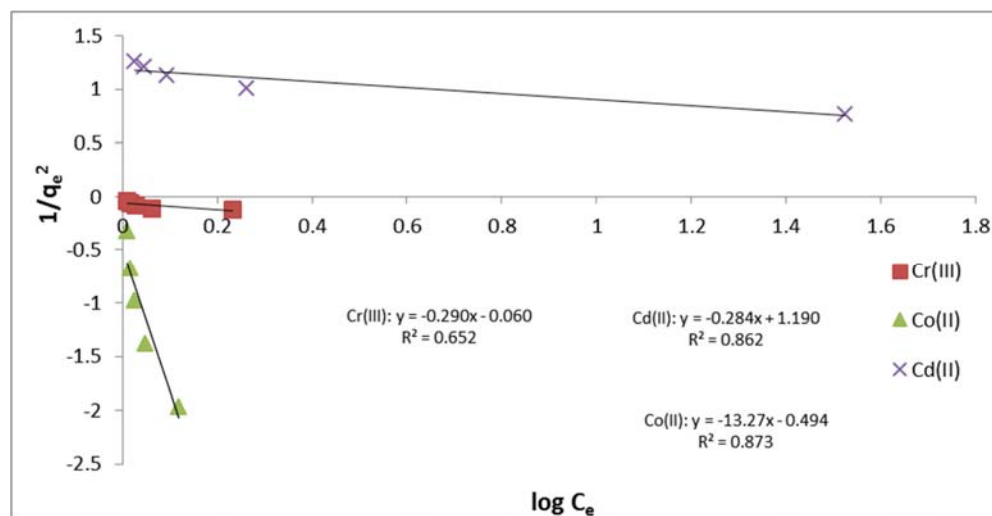

Fig 5: Harkins-Jura Isotherm for the adsorption of the metal ions onto orchid malabar

Table 4: Harkins-Jura Isotherm Constants for the adsorption process

Constants	Metal ions		
	Cr(III)	**Co(II)**	**Cd(II)**
A	-3.4482	-0.0754	-3.5211
B	-0.2069	-0.0372	4.1899
R^2	0.652	0.873	0.862

Halsey isotherm
Halsey isotherm model can be used to evaluate the multilayer adsorption system for metal ion adsorption at a relatively large distance from the surface[21, 22], and is expressed as:

$$\ln(q_e) = \left[\left(\frac{1}{n_H}\right)\ln(K_H)\right] - \left(\frac{1}{n_H}\right)\ln\left(\frac{1}{C_e}\right) \quad (8)$$

Where K_H and n_H are the Halsey constants, which are calculated from the slope and the intercept of the linear plots of $\ln(q_e)$ versus $\ln\left(\frac{1}{C_e}\right)$ respectively. Figure 6 gives the Halsey isotherm plots for Cr(lll), Co(ll) and Cd(ll) ions adsorption onto orchid malabar. The Halsey isotherm parameters were calculated from the plots and tabulated in Table 5. It can be observed from Table 5 that the R^2 values ranged from 0.935–0.996, which show very good fit to the experimental adsorption data.

Analysis of the adsorption data using R^2 values of the five isotherm models revealed that the Freundlich and Halsey isotherms provided the best description to the experimental equilibrium adsorption data. The Dubinin-RadushKevich isotherm provided good description for adsorption of Cr(III) and Co(II) ions onto the Orchid Malabar adsorbent while Harkins-Jura isotherm showed a fairly good fit for data.
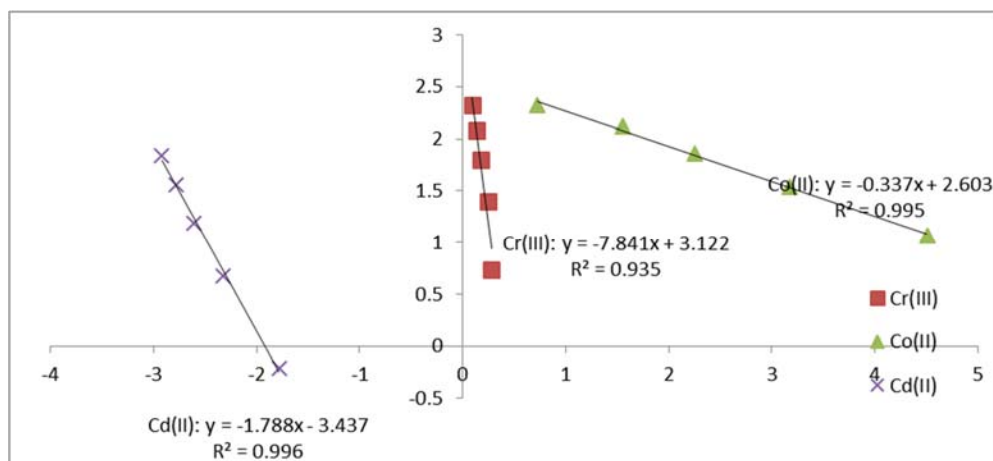

Fig 6: Halsey Isotherm for adsorption of metal ions onto orchid malabar

Table 5: Halsey Isotherm Constants for adsorption of Cr(lll), Co(ll) and Cd(ll) ions by the adsorbent.

Constants	Metal ions		
	Cd(II)	Co(II)	Cr(III)
n_H	0.1269	0.7479	0.1275
K_H	0.6465	2261.98	1.4797
R^2	0.996	0.995	0.935

4. Conclusion

This study investigates the potential of an agricultural waste, the seed pod of orchid malabar as an adsorbent in removing three heavy metal ions: Cr (lll), Co (ll) and Cd (II) from aqueous solution. The suitability of five different isotherm models namely; the Langmuir, Freundlich, Dubinin-RadushKevich, Harkins-Jura and Halsey in interpreting the adsorption data was assessed. The correlation coefficients (R^2 values) obtained from the different isotherm show that Halsey and Freundlich isotherms provided the best description to the experimental adsorption data. Assessment of the maximum amount of metal ions adsorbed onto the adsorbent shows that Cr(lll) and Cd(ll) ions were better adsorbed onto the adsorbent compared to Co(II) ions. The affinity of the adsorbent for the metal ions also follows the trend: Cr(III) > Cd(II) > Co(II). Effect of pH on the adsorption process showed that the optimum pH for adsorption of the metal ions; Cr(lll), Co(ll) and Cd(ll) occurred at pHs 4.0, pH 7.0 and pH 4.0 respectively. Results obtained showed that the adsorbent is fairly good substrate for the removal of these metal ions from aqueous solution.

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