



P-ISSN: 2349-8528

E-ISSN: 2321-4902

IJCS 2017; 5(2): 378-383

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Received: 23-01-2017

Accepted: 24-02-2017

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The kinetics of sorption of Cd (II), Co (II) and Cr (III) ions from aqueous solution using Orchid Malabar (*Piliostigma malabaricum*) Seed pod

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Abstract

Increased industrial activities have led to the generation of large amounts of wastewater polluted with heavy metals. Adsorption is recognized as one of the effective and economic methods for removal of low concentration of heavy metal ions from aqueous solution and industrial wastewater. In the present study, an agro-based adsorbent, orchid malabar seed pod was employed in the removal of Cr(III), Co(II) and Cd(II) ions from aqueous solution. The batch adsorption study was performed as a function of adsorbent dose and contact time. The dynamics of the process was investigated in order to establish the exact kinetics of the process and the likely mode of bonding of the metal ions to the adsorbent binding sites. Results obtained showed that optimum contact time of two hours was sufficient for the attainment of equilibrium for the adsorption process. The experimental adsorption data were analyzed using four sorption kinetic models viz; pseudo first-order, pseudo second-order, Elovich and intraparticle diffusivity models. Results obtained showed that the pseudo second-order gave the best description to the experimental adsorption data with correlation coefficients (R^2 values) ranging from 0.971 to 0.979 for the three metal ions. The calculated pseudo second-order kinetic rate constants k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) obtained from the plots gave 0.003, 0.011 and 0.011 for Cd(II), Cr(III) and Co(II) ions respectively. The calculated equilibrium sorption capacities, q_e for the three metal ions were found to agree very closely with experimentally determined values and are listed as 10.42 mg/g, 11.49 mg/g and 10.42 mg/g respectively for Cr(III), Cd(II) and Co(II) ions indicating that Cd(II) was best adsorbed among the three metal ions. Kinetic studies also show that the adsorption transport mechanism follows film-diffusion.

Keywords: Adsorbent, adsorption kinetics, heavy metals, Intraparticle diffusivity, Orchid malabar

1. Introduction

Our natural sources of potable water are rapidly depleting and are continually polluted due to extensive industrialization and urbanization. Pollution of the aquatic bodies by both organic and synthetic pollutants like polyaromatic hydrocarbons, fertilizers, pesticides, heavy metals, etc, have constituted serious menace to our ecological stability and have created an imbalance in the natural functioning of the ecosystem. Potential toxic metals such as cadmium, chromium, lead, copper, zinc, nickel, arsenic, mercury etc. have been identified as major causes of health hazards in aquatic animals and humans which consume them^[1,2]. Wastewater containing varying amounts of heavy metals are generated from residential and industrial activities such as mining, paint manufacturing, electroplating, refining, printing, dyeing *etc.* and these processes have been identified as major causes of heavy metal pollution in our water bodies^[3,4]. It is therefore imperative to treat industrial wastewaters before release into surface water bodies due to negative impacts of heavy metals contained in them.

Almost all heavy metals are toxic to living beings and excessive levels are known to cause both acute and chronic toxicities^[5]. Several health effects have been reported to be associated with the presence of heavy metals^[6-8]. In addition, some of these heavy metals have been found to have carcinogenic, mutagenic and teratogenic effects when being exposed to or taken orally through plants and aquatic animals that consume them^[9-12].

Some of these heavy metals once released are non-biodegradable and tend to bioaccumulate in higher trophic levels of the food chain. Moreover, the natural process of metal mineralization is very slow hence; their removal from water and wastewater is best accomplished by immobilization and concentration on suitable sorbents. A great number of biosorbents have been investigated on their potential to scavenge heavy metals from aqueous solutions.

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Some of these sorbents include but not restricted to the following: activated carbon, fly ash, chitosan, crab shell, *Luffa cylindrica* fibre, coconut shell, zeolite, groundnut husk, rice husk etc.

The present study investigates the potential of an agro-based material, the seed pod of orchid malabar in removing Cr(III), Cd(II) and Co(II) ions from aqueous solutions. The selection of the agro-based sorbent was due to their eco-friendliness, low cost, abundance in nature and ease of metal recovery when compared to conventional and costly adsorbents such as activated carbons, ion exchange zeolites, polymeric materials etc.

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 Nigeria. The uncooked 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. The sieved samples were soaked in 0.3 M HNO_3 , stirred for 30 min and 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 $^\circ\text{C}$ 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 to remove any debris or soluble bio-molecules that might interact with the metal ions during sorption.

Batch adsorption experiments

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. Batch adsorption studies of Co^{2+} , Cr^{3+} and Cd^{2+} onto Orchid malabar were investigated as a function of adsorbent dose and contact time. The effect of adsorbent dosage on the adsorption of the metal ions was studied at a fixed temperature of 30 $^\circ\text{C}$, pH 6.0 and at an initial metal ion concentration of 50 mg/L. The adsorption was carried out using varying masses of the adsorbent ranging from 0.05 g to 0.75 g. This was done by introducing 50 cm^3 of each metal ion solutions into different 100 cm^3 Erlenmeyer flasks containing 0.05, 0.15, 0.25, 0.50 and 0.75 g of the adsorbent of particle size 60 μm . The mixtures were 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 effect of contact time on adsorption of the metal ions was studied by carrying out the adsorption process at different time intervals, at a pH 6.0, temperature of 30 $^\circ\text{C}$ and at an initial concentration of 50 mg L^{-1} . Initial concentration of 50 mg L^{-1} of each of the metal ions Cr(III), Co(II) and Cd(II) used for the adsorption study was prepared from their individual metallic salts namely; $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2$ and $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ respectively. Exactly 50 cm^3 portions of 50 mg L^{-1} of each of the metal ion solution were introduced into different 100 cm^3 Erlenmeyer flasks containing 0.25 g of the adsorbent of particle size 60 μm . The mixtures were shaken intermittently in a thermostated mechanical shaker at different contact times (20, 40, 60, 90, 120, 150 and 180 min). At the end of each time, the content of each flask was filtered with a filter paper, centrifuged and the residual concentration of metal ion analyzed using the UNICAM Atomic Absorption

Spectrophotometer (Solar AAS 500). The procedure was carried out in triplicates and mean residual concentration of each metal ion taken. The amount adsorbed (mg/g) was calculated from the average residual metal ions in solution after adsorption.

3. Results and discussion

Effect of adsorbent dose on the adsorption process

The effect of biomass concentration on the uptake level of the metal ions Cr(III), Co(II) and Cd(II) is shown in figure 1. The plots show that the amount adsorbed decreased with increase in mass of adsorbent. With the increase in adsorbent mass, the amount adsorbed per gram decreases. This is because of the fixed concentration of metal ions in the system; and the more the biomass used, the less the adsorbate quantity adsorbed per unit gram of adsorbent. This Result shows that more active sites are utilized at lower adsorbent concentration, producing a higher adsorption capacity, while only part of the active sites are occupied by these metal ions at higher adsorbent concentration, leading to a lower adsorption capacity and this is in line with previous observations [9, 13]. The decrease in sorption capacity with increasing adsorbent dosage is mainly due to unsaturation of adsorption sites at higher dosage concentration of the adsorbent.

This trend therefore implies that at constant initial metal ion concentration, the amount adsorbed may decrease with biosorbent dose because of availability of unsaturated adsorbent sites. As the biosorbent dose increases, it reaches a point when the mass of biosorbent used is in excess of the initial concentration of metal ions, hence there will be no appreciable decrease in the amount adsorbed and a similar result has been reported [14].

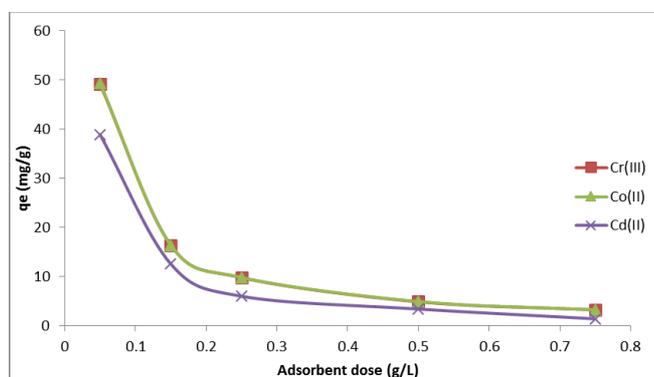


Fig 1: Effect of adsorption dose on the adsorption of metal ions onto orchid malabar

Effect of contact time

The sorption of heavy metals from aqueous solutions plays a significant role in water pollution control and it is therefore important to understand the optimum contact time required to achieve equilibrium. Figure 2 shows that the amount adsorbed increased with the exposure time until equilibrium was established. Optimum contact time for adsorption of the three metal ions by 0.25 g of the adsorbent was 120 min. It could be observed from the plots that there was an initial rapid increase in the rate of adsorption of Cd^{2+} for the first 40 min, then followed by a slower rate until after 120 min when the residual concentration at different times remained constant. The adsorption rates of Cr^{3+} and Co^{2+} were observed to follow faster kinetics and attaining equilibrium in less than 30 min. In could be observed in general that the three metal ions under study attended equilibrium in less than 120 min as observed by the flattening of the adsorption curves and this supports the

selection of the equilibration time of 2 h for the equilibrium adsorption study of the metal ions by the Orchid malabar.

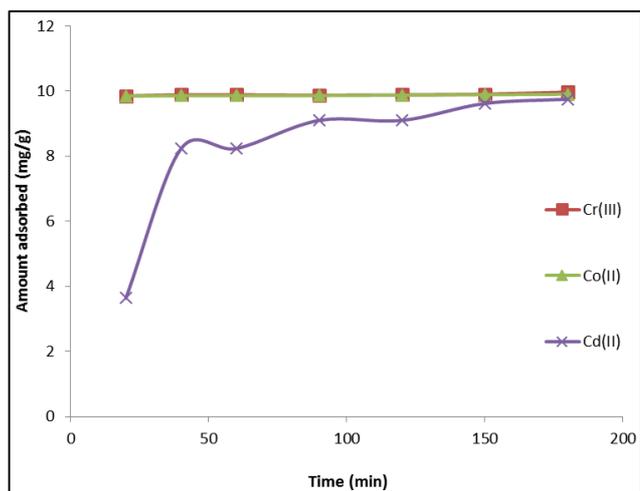


Fig 2: Variation of amount adsorbed with contact time for the adsorption of Cr^{3+} , Co^{2+} and Cd^{2+} onto Orchid Malabar seed pod.

Adsorption kinetics

1. Adsorption kinetics is an effective method of evaluating the rate and mechanism of metal ions adsorption onto adsorbents. In our present study, four different adsorption kinetic models viz; pseudo first-order, pseudo second-order, Elovich model and the intra-particle diffusion models [15-17] were applied to analyze the experimental data. The conformity between the experimental data and the model-predicted values is expressed by the correlation coefficients (R^2 values close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the kinetics of the metal ion adsorption. The different kinetic models are described as follows:

Pseudo first-order model

The pseudo first-order model assumes that the rate of metal ion adsorption is proportional to the number of free adsorption sites. The pseudo first-order equation is generally expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

Where q_e and q_t (mg/g) are adsorption capacities at equilibrium and at time, t respectively, k_1 is the rate constant for pseudo first-order adsorption process (min^{-1}). After integration and applying boundary conditions at $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of equation (1) becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

The plots of $\log(q_e - q_t)$ versus t yielded straight lines as shown in Figure 3. The values of the pseudo first-order rate constant, k_1 and the equilibrium sorption capacities, q_e were determined from the slopes and intercept of the linear plots respectively. The pseudo first-order parameters (k_1 and q_e) and R^2 values calculated from the linear plots are presented in table 1.

From table 1 it can be noted that there is a marked variation in the q_e values for the three metal ions from the experimental adsorption capacity, q_e values and this clearly reveals the non-fitting of the model to the experimental adsorption data. However, the R^2 values for all the three metal ions ranged from 0.844 to 0.968. The fairly high R^2 values obtained from

the kinetic pseudo first-order confirm that the model did not give perfect fitting to the experimental adsorption data.

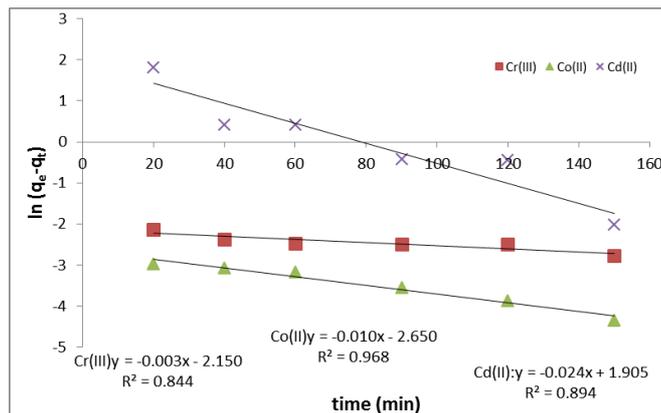


Fig. 3: Pseudo first-order plot of $\log(q_e - q_t)$ vs t for adsorption of the metal ions onto orchid malabar

Table 1: Kinetic rate constants for pseudo first-order reaction at 30 °C.

Constants	Adsorbent		
	Co(II)	Cd(II)	Cr(III)
q_e (mg g ⁻¹)	2.24×10^{-3}	80.35	7.08×10^{-3}
k_1 (min ⁻¹)	2.30×10^{-2}	5.53×10^{-2}	6.91×10^{-3}
R^2	0.968	0.894	0.844

Pseudo second-order model

The pseudo second-order kinetic model relies on the assumption that the rate-limiting step of an adsorption process may be chemical reaction involving valence forces resulting from sharing or exchanging of electrons between adsorbates and the adsorbent sites [13]. The pseudo second-order adsorption kinetic rate equation is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

Where k_2 is the rate constant for pseudo second-order adsorption process. After integration and applying boundary conditions at $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of equation (3) becomes;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

The initial adsorption rate, h_0 (mg/g min⁻¹) as t approaches zero is expressed as:

$$h_0 = k_2 q_e^2 \quad (5)$$

Equation (4) then becomes

$$\frac{t}{q_t} = \frac{1}{h_0} + \frac{t}{q_e} \quad (6)$$

The plot of $\frac{t}{q_t}$ versus t using equation (6) gave linear relationships as shown in Fig. 4 and from which q_e and k_2 were determined from the slope and intercept of the linear plots respectively.

From the pseudo second-order plot in Fig. 4, the pseudo second-order parameters k_2 , q_e and h_0 (the initial sorption rate) were computed and presented in table 2. The R^2 values were also determined and presented in table 2.

Examination of the values of the constants in table 2 and the high values of kinetic fitting parameter, *i.e.*, the coefficient of

determination (R^2), indicate that the pseudo second-order kinetic plots gave the best fit to the experimental adsorption data. And of course this assertion is based on the selection criterion which states that the closer the R^2 value is to unity, the greater the fitting pattern of that model to the experimental kinetic model. The R^2 values which ranged from 0.971 to 0.979 confirm this fitting. Therefore, the fitting of the adsorption data into pseudo second-order model means that the rate of occupation of active sites is proportional to the square of the number of the unadsorbed sites [18, 19]. The trend of kinetics of adsorption of the metal ions from the calculated initial sorption rate, h_0 follows the order: $Co^{2+} > Cr^{3+} > Cd^{2+}$ and this is also in line with the observation of the pseudo second-order rate constant, k_2 which follows a similar trend as observed in Table 2. The higher the k_2 values, the faster the kinetics of the adsorption process and this means that the sorption of Co^{2+} from solution was fastest among the three metal ions studied. The values of the equilibrium adsorption capacity, q_e , calculated from the slope of the pseudo second-order plots revealed that greater amount of Cd(II) ions was adsorbed than Cr(III) and Co(II) ions and their q_e values for the three metal ions are close to the experimentally determined values and this observation further buttresses the fitting of the model to the kinetic adsorption data.

It can be concluded from correlation coefficients (R^2 values) in table 2, that the pseudo second-order model provided the best description for the kinetics of the metal adsorption with R^2 values greater than 0.9700 and higher than those of the pseudo first-order.

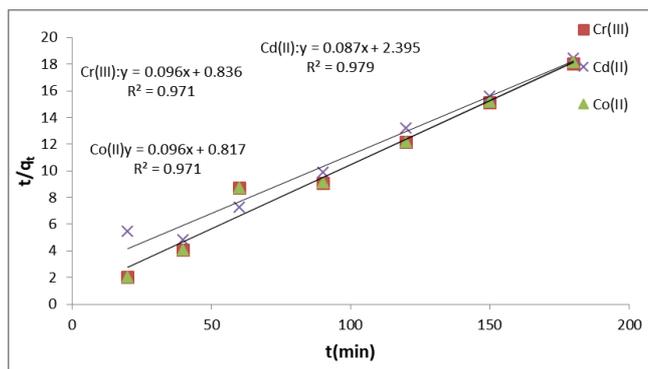


Fig 4: Pseudo-second order plot of t/q_t vs t for adsorption of the metal ions onto Orchid malabar.

Table 2: Kinetic rate constants for pseudo-second order reaction at 30 °C.

Constants	Metal ions		
	Cr(III)	Cd(II)	Co(II)
q_e (mg/g)	10.42	11.49	10.42
k_2 ($g \cdot mg^{-1} \cdot min^{-1}$)	1.10×10^{-2}	3.0×10^{-3}	1.13×10^{-2}
h_0 ($mg \cdot g^{-1} \cdot min^{-1}$)	1.194	0.396	1.224
R^2	0.971	0.979	0.971

Elovich model

The Elovich equation is another kinetic rate equation which describes the adsorbing surface as heterogeneous in nature [20]. The equation is generally expressed as:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{7}$$

Where α is the initial adsorption rate ($mg/g \cdot min$) while β is related to the extent of surface coverage and the activation energy for chemisorption (g/mg).

Integrating this equation for the boundary conditions $q_t = 0$ at $t = 0$ to $q_t = q_t$ at $t = t$, the equation becomes:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \tag{8}$$

The linear plots of q_t versus $\ln(t)$ (Figure 5) justifies the Elovich model from which the parameters β and α can be calculated from the slope and intercept of such plots. The plots are shown in Figure 5 while the Elovich parameters are displayed in Table 3. The relatively high correlation coefficient (R^2) values obtained showed that the model could not give a perfect description to the experimental kinetic data.

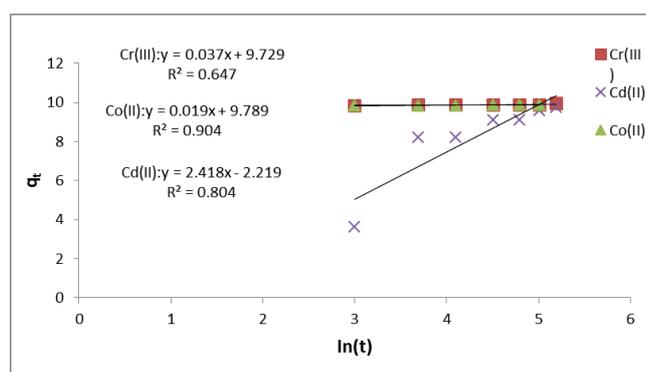


Fig 5: Elovich model for adsorption of Cr(III), Co(II) and Cd(II) ions by the orchid malabar.

Table 3: Elovich model constants for adsorption of Cr(III), Co(II) and Cd(II) ions by the adsorbent.

Constants	Metal ions		
	Co(II)	Cd(II)	Cr(III)
α ($mg/g \cdot min$)	-	-	0.965
β ($g/mg \cdot min$)	0.981	0.414	27.03
R^2	0.904	0.804	0.647

Intraparticle diffusion model

In order to identify the diffusion mechanism for the sorption process, the kinetic results were analyzed by the intraparticle diffusion model so as to aid in elucidation of the proper transport mechanism involved. A graphical method to prove the occurrence of intra-particle diffusion and to determine if it is the rate-limiting step in the adsorption process was introduced by Weber and Morris [17]. The intraparticle diffusion model can be expressed as [17, 21]:

$$R = k_{id} t^n \tag{8}$$

The logarithm of both sides of Equation (8) gives:

$$\ln R = \ln k_{id} + n \ln(t) \tag{9}$$

Where R is the per cent of metal ion adsorbed, t is the contact time (min), n is the slope of linear plots, which depicts the adsorption mechanism; k_{id} is the intraparticle diffusion rate constants (min^{-1}) which may be taken as a rate factor, i.e. per cent metal ion adsorbed per unit time. The plots of $\ln R$ versus $\ln t$ for adsorption of the metal ions by the adsorbent is shown in Figure 6. From the plots, n (the gradient of the linear plots) and k_{id} (the intraparticle diffusion rate constant in min^{-1}) were determined from the slope and intercept of the linear plots, respectively and are presented in Table 4. The correlation coefficients (R^2 values) are also presented in Table 4. The relatively high R^2 values obtained show non-fitting of the adsorption kinetic data into the Werber-Morris

intraparticle diffusion model. According to this model, if the plot $\ln R$ versus $\ln(t)$ gives a straight line, then the adsorption process is controlled by intraparticle diffusion, while if the data exhibit multi-linear plots, then two or more steps influence the adsorption process [22]. Therefore, it can be concluded that the rate of attainment of equilibrium for the sorption process may be mostly film-diffusion controlled.

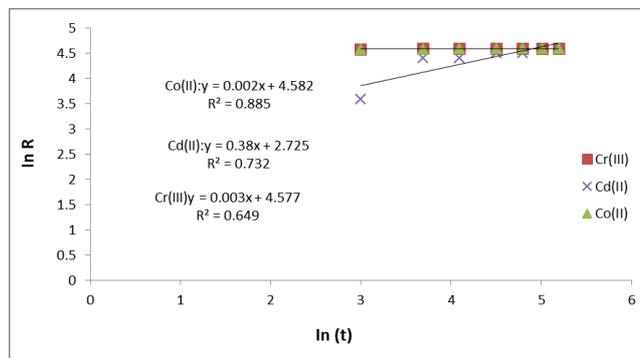


Fig 6: Werber-Morris Intraparticle diffusion model for the adsorption of the metal ions by orchid malabar

Table 4: Weber-Morris intra-particle diffusion parameters

Constants	Metal ions		
	Cr(III)	Co(II)	Cd(II)
n	0.003	0.002	0.380
k_{id}	97.222	97.710	15.256
R ²	0.649	0.885	0.732

The rate of attainment of equilibrium could also be explained in terms of adsorption being controlled by particle-diffusion or film-diffusion mechanism. In view of this, a linear driving force concept developed by Vinod and Anirudvan [23] for the rate equation was used to obtain the fractional attainment of equilibrium using the expression:

$$\ln(1 - \alpha) = k_p t \quad (10)$$

Where α is the fractional attainment of equilibrium and k_p is the rate constant or diffusion time constant. The fractional attainment of equilibrium, α is the ratio of the amount of metal ion adsorbed from solution after a certain time to that adsorbed when adsorption equilibrium is attained.

If the plot of $\ln(1 - \alpha)$ versus t gives a linear relationship, then adsorption is controlled by particle diffusion and the diffusion of the metal ions onto the adsorbent surface is independent of the extent of sorption while a non-linear plot indicates adsorbent film-diffusion controlled process, *i.e.*, the time of uptake is dependent on the initial metal ion concentration. The plots of $\ln(1 - \alpha)$ versus t for the metal ions are displayed in figure 7. The plots revealed that the relationship between metal ion diffusivity $\ln(1 - \alpha)$ and time, t are all non-linear as observed from the low R^2 values obtained indicating that the diffusion of the metal ions onto the adsorbent surface may mostly be film-diffusion controlled. The non-linearity of the plots obtained in Fig 7. Confirm that the rate of attainment of equilibrium for the sorption of the metal ions is film-diffusion controlled. This therefore reveals that the time for the metal ion uptake is dependent on the initial metal ion concentration and it can be concluded that in the adsorption process, the metal ions from the bulk solution must have to travel to the thin liquid film surrounding the adsorbent where the thin liquid may produce a diffusion barrier for the metal ions to penetrate before reaching the binding sites on the adsorbent.

This means that the metal ions must overcome this film barrier in order to adsorb onto the adsorbent sites and the ability of the metal ions to overcome this barrier must be dependent strongly on the initial metal ions concentration. Overall, this mechanism provides a measure of the diffusion rate and a similar conclusion had been drawn [18, 24].

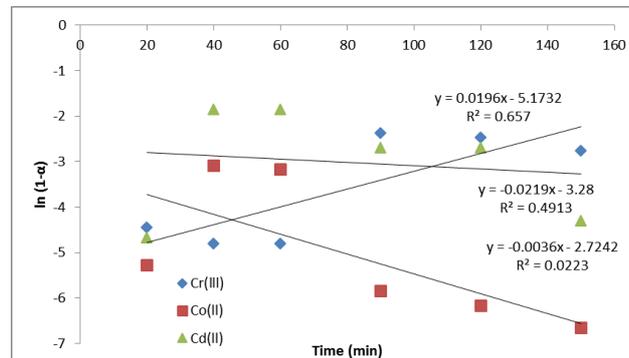


Fig. 7: Plot of $\ln(1 - \alpha)$ versus t for adsorption of the metal ions onto Orchid malabar

4. Conclusion

This work was designed to assess the possible use of orchid malabar seed pod as an adsorbent for the removal of Co(II), Cr(III) and Cd(II) ions from aqueous solution. Batch adsorption experiments were performed as a function of adsorbent dose and contact time in order to establish the proper kinetic model for the adsorption process. Results obtained show that the optimum contact time for adsorption of the three metal ions occurred within 120 min and after which there was no further increase in adsorption. The suitability of the pseudo first-order, pseudo second-order, Elovich and intraparticle diffusion kinetic models for the sorption process was assessed. Results showed that pseudo second order kinetic model was found to give the best description to the experimental kinetic data while the transport mechanism was found to follow film-diffusion mechanism. The values of the pseudo second-order rate constant calculated shows that the sorption of Co^{2+} from solution was fastest among the three metal ions studied. Results obtained showed that Cd^{2+} was best adsorbed at equilibrium by orchid Malabar as observed from their q_e values compared to Cr^{3+} and Co^{2+} . The marked variation in the values of the amount of the metal ion adsorbed at equilibrium, q_e (mg/g) for the three metal ions, Co^{2+} , Cr^{3+} and Cd^{2+} may be attributed to the differences in their ionic sizes and their affinities onto the surface.

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