Equilibrium and Kinetic modelling Studies on Adsorption of Copper and Cadmium from Aqueous Solution by ground nut husk

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Abstract

Equilibrium and kinetic studies have been studied for adsorption of copper and cadmium from aqueous solution using ground nut husk and these results have been presented in this paper. Characterization of Ground nut Husk (GNH) showed the presence of –OH stretching, methylene C-H asymmetric stretching, Carboxylate group, P-O-C stretching in FTIR spectrum and indicated the porous, coarse and rough morphology in SEM image. Isothermal studies indicated the fitting of data into various models. Langmuir and Temkin model fits best for cadmium comparing with copper. DR isotherm model signifies that the adsorption is by physisorption as the mean sorption adsorption energy is < 8000 J/mole and fits better to copper metal with higher regression value as compared to cadmium. The error analysis for copper and cadmium shows that the maximum adsorption capacity is observed for Freundlich and Temkin models along with least values of χ^2, Sum of the square errors (SSE) and SAE in comparison with Langmuir model and Dubinin-Radushkevich models. The intra particle diffusion model was studied using Weber and Morris equation. The model parameters for copper and cadmium are found which signifies that the data fits for cadmium with higher R^2 values as compared to copper.

Key words: Ground nut husk, Freundlich isotherm, Langmuir isotherm, Temkin model, Dubinin-Radushkevisch model, Intra Particle diffusion model.

Introduction

Heavy metals like copper and cadmium enters the water bodies from industries such as electroplating, mining, and electrical manufacturing and electronics, iron and steel production, nonferrous metal production, the printing and photographic industries, as well as metalworking and finishing processes [1-2]. They are persistent and toxic in the environment than organic contaminants such as pesticides, fertilizers, and petroleum byproducts, for example. Their toxicity was caused by tainting of drinking water (ex. lead channels, mechanical and industrial waste) and spreads through the food chain or high ambient air conditions near emission sources. When these metals exceed tolerance levels, they have a negative impact on the human body, physiological systems, and other biological systems [3]. Exposition to these metals can cause liver disease, brain damage, kidney failure, and even death in the long run. Chronic exposure to these contaminants, even at low concentrations in the environment, has also been shown to be harmful to human health, and for the reasons stated above, heavy metals must be removed from industrial effluents [4].

Variety of methods can be used to remove these toxic metal ions from contaminated water but most of these cause number of issues, including unpredictable metal ion removal and the formation of toxic sludge, which is often difficult to de-water (remove the contaminants) and must be disposed of with extreme caution. Chemical precipitation, ion exchange, electrochemical deposition, solvent extraction, membrane filtration, and adsorption are all methods for removing heavy metal ions from water and wastewater. Adsorption is one of the most cost-effective and technically straightforward methods [11]. Activated carbon is widely recognized as one of the most effective adsorbents for heavy metal removal [12, 13]. However, the high cost of commercially available activated carbon and loss during regeneration make it unsuitable for use in developing countries. As a result, there is an increasing need for the development of alternative adsorbents to replace the costly activated carbon.

Furthermore, most of these methods have some limitations in that they are economically viable at high or moderate metal concentrations but not at low concentrations (1 to 100 mg/l) of dissolved metal. Among these conventional methods, adsorption and biosorption of metal ions is a very cheap, eco-friendly, and efficient method for removing heavy metals from industrial waste water [5-8]. The World Health Organization (WHO) recommended a maximum permissible concentration of copper (II)and cadmium in drinking water of 1.5 ppm and 5 ppm [9], but the acceptable limit in India is up to 3 ppm [9-10].

Several researchers have tested different variety of adsorbents such as sawdust [14], fly ash [15], baggase [16], activated carbon-zeolite composite [17], zeolite A [18], fertilizer plant waste slurry [19], modified clay [20], biosorbents like cassava waste [20], Areca [21], Lentil shell [22], Pine cone powder [23], Spent grain [24], crushed brick [25], alluvial soil of Bhagirathi river [26], Neem bark powder [27] etc. for the removal of copper and cadmium ions from aqueous medium.

Adsorption refers to the selective collection and concentration of a particular type of molecules contained in a fluid phase onto a solid surface [28]. The molecules of the adsorbate come from the fluid phase into the interface, where they remain for a period of time [29]. In a reversible process, the molecules go back to the phase from which they came or reversibly pass into another phase while other molecules replace them at the interface. On reaching the solid surface the adsorbed molecules exchange energy with structural atoms of the surface and if sufficient time was there for adsorption, the adsorbed molecules and the surface atoms reach thermal equilibrium and at equilibrium, the number of molecules arriving at the interface in a given time is equal to the number of molecules leaving the interface to go into the fluid phase [30-31].

Therefore, an attempt has been made to study the adsorption behavior of copper and cadmium on adsorbent and also to study the systematic parameters related to modelling of these metals in variety of complex solutions and these results are presented in this paper.

Materials and Methods: This section explains the adsorbent collection and its preparation, reagent preparation, procedure for Batch adsorption and different isothermal models have been discussed in this paper.

Preparation of adsorbent

The ground nut husk used in the present work was collected from local wood shop. The collected husk was initially washed with deionized water to remove dirt particles and water-soluble impurities. The washing process was continued till the wash water contains no colour. The washed husk was then initially sun dried for 10 days followed by drying in hot air oven at 240 -270 ^{o}C for 24 h. The dried husk was then cut into small pieces and powdered using local mixer grinder. The product was sieved to give a fraction of 150 mesh screen and finally stored in sterile, closed glass bottles until required. The developed powder is designated as Ground nut husk Powder (GHP) as shown in figure 1 [32].

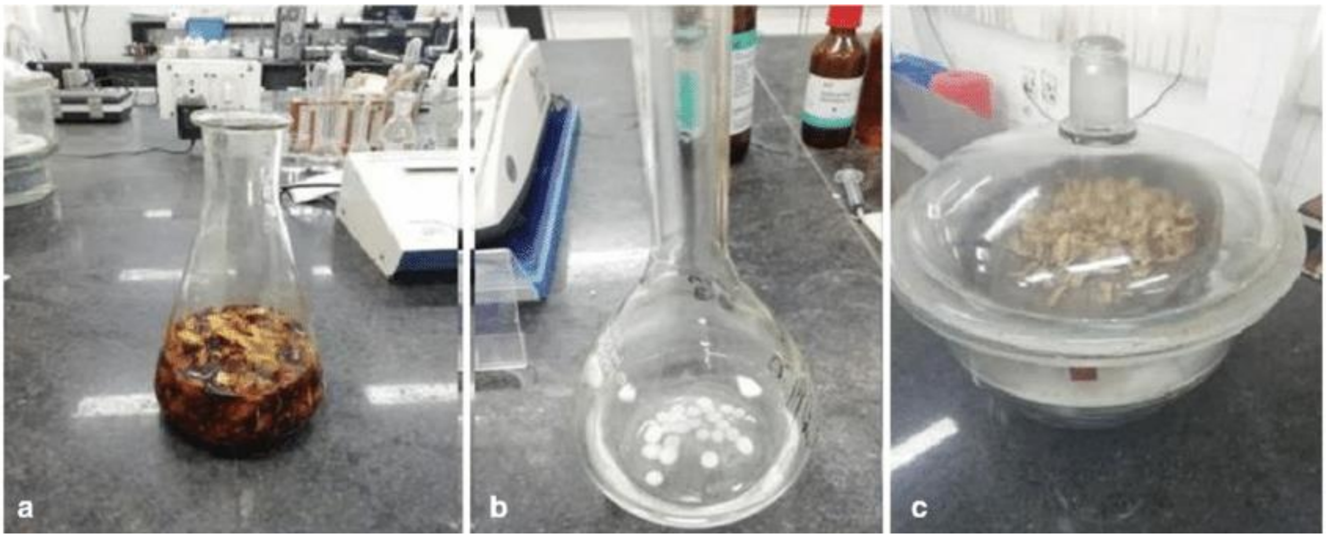

Fig 1: Different steps involved in preparation of coconut husk powder in laboratory

Reagents used for Chemical Treatment

All the chemicals used were of analytical reagent grade procured from E. Merck Ltd., India and double distilled water was used throughout this study for the preparation of different solutions. Stock solution of copper (II) ions (100 ppm) was prepared by dissolving 0.393 g of copper sulphate Penta hydrate in double distilled water and was suitably diluted as per the need. The range in concentrations of copper (II) and cadmium (II) ions were prepared from standard solution which varies between 25 and 100 mg/lit. Before addition of adsorbent, 0.1 M NaOH or 0.1 (M) HCl solutions were used for fixing the pH of each copper and cadmium solution to the desired pH [32]

Batch adsorption studies

Experiments were carried out to study the adsorption phenomenon through various batch parameters and also give the detailed procedure for preparation of adsorbent for the removal of Cd (II) and Cu (II) from synthetic solutions. The systematic procedure for the removal of heavy metal ions which is described below. Initially the pre-sterilizing flasks containing heavy metal ion solution of 50 mg/l of Cu (II) and Cd (II) were prepared and the mixed adsorbent of 0.5 to 5 g/L of Ground nut husk powder was added after maintaining the desired pH for all the flasks. All the pH used in the experiments were adjusted by adding 0.1 M NaOH or 0.1 M HCl. Adsorption process was carried out in the rotary shaker/agitator until the equilibrium was attained. The analysis was done for the filtered samples by U-V Visible Spectrophotometer (Thermo Scientific) to find the residual concentrations at various time intervals from the collected samples. After the analysis, equilibrium time and the residual concentration were reported. The data obtained in the present studies were used to calculate the % removal of the heavy metal ions and the equilibrium metal adsorptive amount/ quantity (mg/g) by using the mass balance relationship. Experiments were done thrice and the average values were reported for the adsorption system. **Figure 2** gives the adsorption procedure for batch studies. The equilibrium adsorptive quantity (capacity) of the metal ions **(q_e)** and % removal was evaluated by utilizing mass balance relationship given by the mathematical equations (Equations 1 and 2)

$$q_e = (C_0 - C_e) * \frac{V}{M} \quad (1)$$

$$\% \text{ removal} = \left(\frac{C_o - C_e}{C_O} \right) * 100 \quad (2)$$

Where q_e is the amount of heavy metal ion adsorbed per unit weight of adsorbent in mg/g, V is the volume of the solution treated in liter (s). C_o, C_e is the initial and equilibrium concentration of metal ions in mg/l, M is the mass of the adsorbent in g.

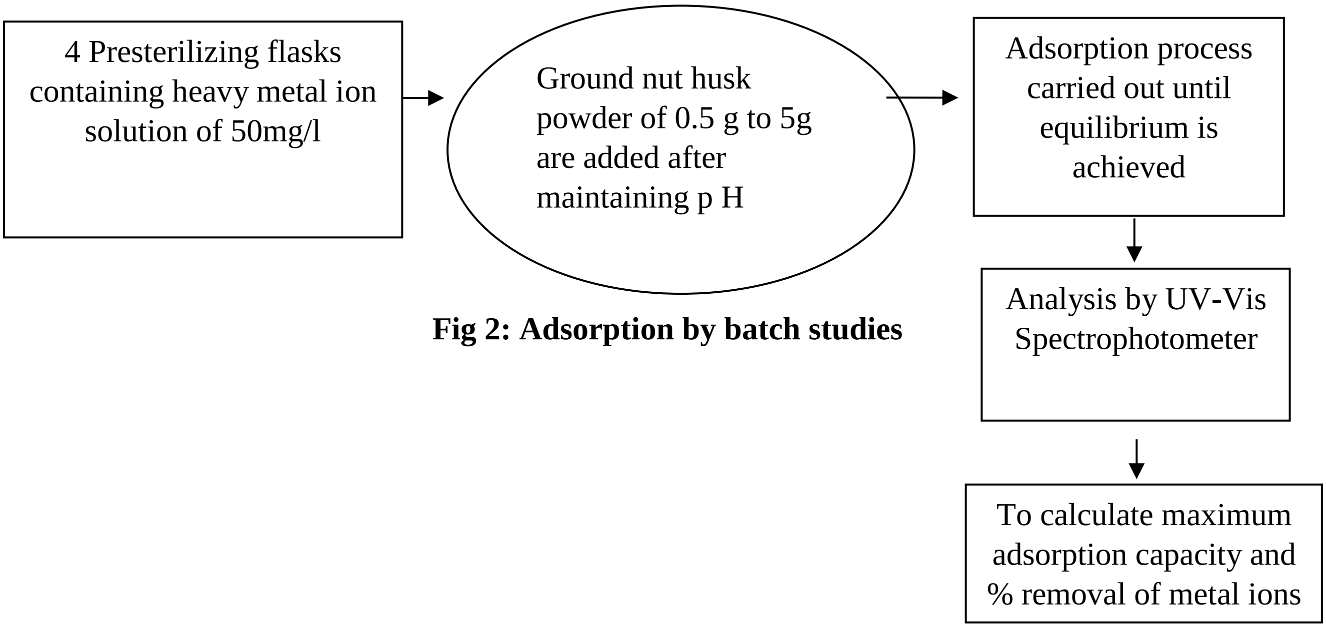

Fig 2: Adsorption by batch studies

Fitting of models for adsorption isotherms

To Investigate the relationship between adsorbate concentration in the aqueous phase and that on the adsorbent surface at a given equilibrium condition. For fitting the data, Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) models were used in this study.

Results & Discussion

Characterization of adsorbent

The physico–chemical properties of ground nut husk (GNH) are as follows- Ash content :14.36 %, Bulk density (g/cm^3): 0.671, pH$_{zpc}$: 4.3, Surface area (m^2 /g): 357.8, Volatile matter (%): 89.48, C (%): 47.22, H (%): 3.86, N (%): 0.74. The FTIR spectrum of GNH showed the presence of –OH stretching, methylene C-H asymmetric stretching, Carboxylate group, P-O-C stretching, C-O stretching and C-Cl stretching vibration [33]. The above results suggested that copper ions may interact with –O–H, carboxylate group and phosphate group that present on the GNH surface. Furthermore, SEM micrograph indicated the porous, coarse and rough morphology of the prepared GNH adsorbent [34] thus making it possible for the adsorption of copper (II) on different parts of the adsorbent.

Adsorption isotherms studies were most significant for the study of metal ion binding behaviour with adsorbent surface or in other words metal ion partition between the solid and liquid phase and to evaluate the adsorption capacity at equilibrium as a function of adsorbate concentration [35], and rate of change of temperature. Data obtained through such studies are useful in designing of batch process as well as continuous reaction columns [36, 37]. In present investigation adsorption isotherms namely Langmuir, Freundlich and Temkin model have been applied on Cu (II) and Cd (II) ion adsorption to predict the suitability of the process. The performance of isotherm curves was evaluated in-terms of linear regression coefficient R^2 obtained through linear regression analysis.

Freundlich isotherm model

Freundlich isotherm describes the non-ideal and reversible adsorption and is not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat affinities over the heterogeneous surface. In this perspective, the amount of metal ion adsorbed is the summation of adsorption on all sites (each having bond energy) with the stronger binding sites occupied first; until the adsorption energy are exponentially decreased upon the completion of ad- sorption process [38]. This model assumes the multilayer coverage of adsorbent surface by adsorbate species together with consideration of adsorbent surface as heterogeneous in character. The linear form of Freundlich isotherm model [39, 40] was given as

$$log(q_e) = log\ (K_f) + \frac{1}{n} \log (C_e) \qquad (3)$$

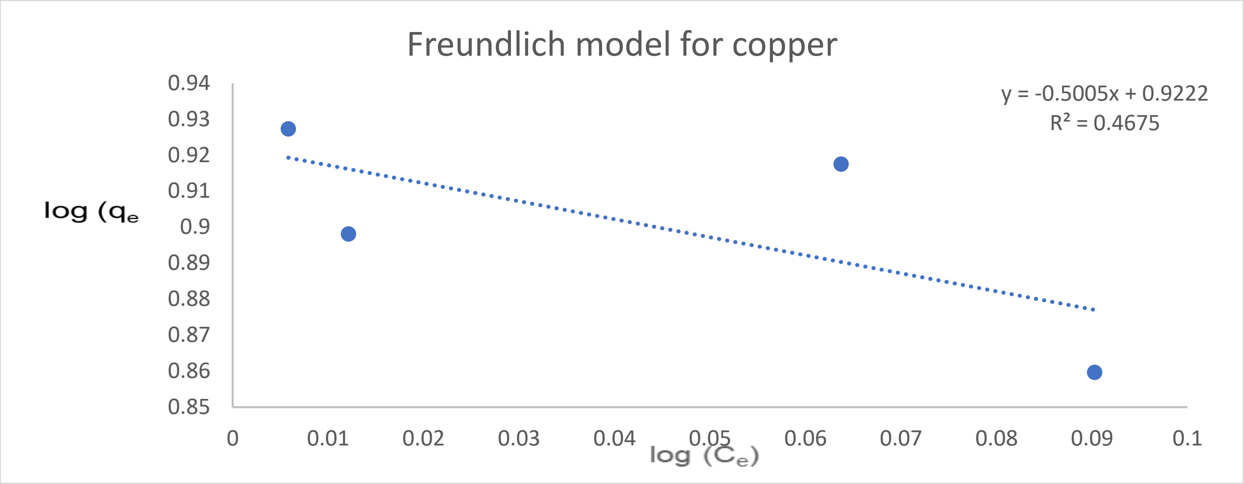

Fig 3: Freundlich model for copper at 25°C

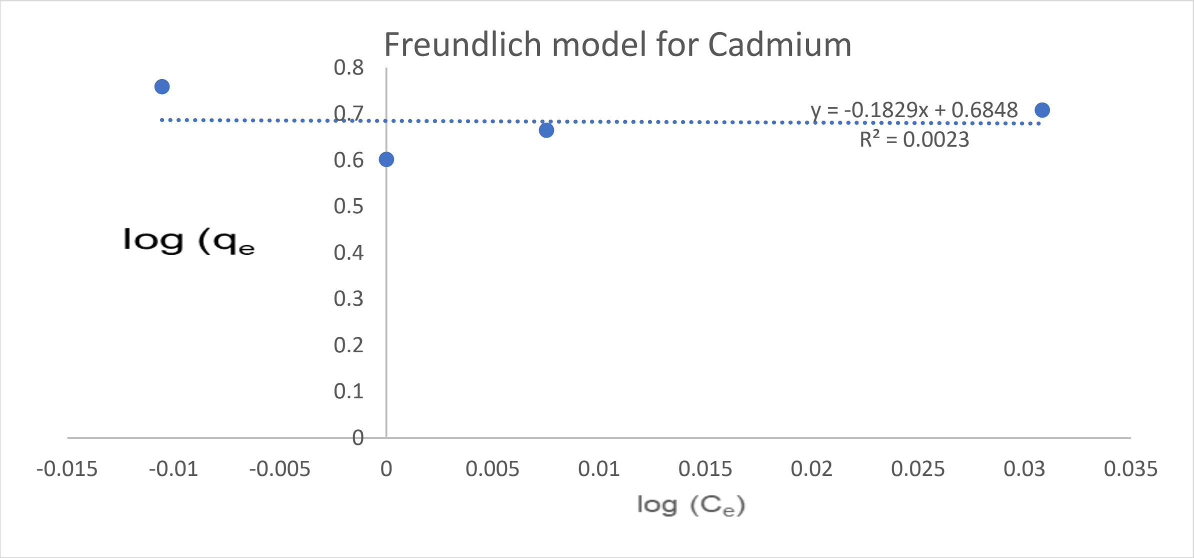

Fig 4: Freundlich model for cadmium at 25°C

Table 1: Freundlich model parameters for copper & cadmium at 25°C

Metals	Temperature(°C)	Slope (1/n)	Intercept (log K_f)	K_f	R^2
Cu	25	-0.5005	0.9222	8.36	0.4675
Cd	25	-0.1829	0.6848	4.84	0.0023

The Freundlich model constants are evaluated for copper and cadmium metals and shown in table 1. The Freundlich isotherm regression coefficient (R^2) for copper fits better than cadmium, which is close to 1 explains the fitting of adsorption data.

Langmuir isotherm model

This model assumes the monolayer coverage of adsorbent surface by adsorbate species, all energy sites are equally energetic, binding of adsorbate molecule at one site is independent of adjacent site occupancy, and dynamically metal ion adsorption rate is equal to the rate of desorption. Eq 4 represents the Langmuir isotherm model [41].

$$q_{eq} = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \tag{4}$$

The above equation 4 can be rearranged to the following linear form given by Eq 5, Where R_L is a dimensional less separation factor, C_o is the initial concentration (mg/L) and b is the Langmuir constant (L/mg). The parameter R_L indicates the shape of the isotherm accordingly as shown in Table 3 and the equation is given by Eq 4 (a). The R_L values for cadmium are > 1 which indicates unfavorable isotherm and the R_L values for copper is < 1, which indicates the favorable isotherm model

$$R_L = \frac{1}{(1+bC0)} \qquad [4\,(a)]$$

$$\frac{C_e}{q_{eq}} = \frac{1}{b q_{max}} + \frac{C_{eq}}{q_{max}} \tag{5}$$

Table 2: Suitability of isotherm model based on separation factor

(R_L))	**Types of isotherm**
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$R_L < 1$	Favorable
$R_L = 0$	irreversible

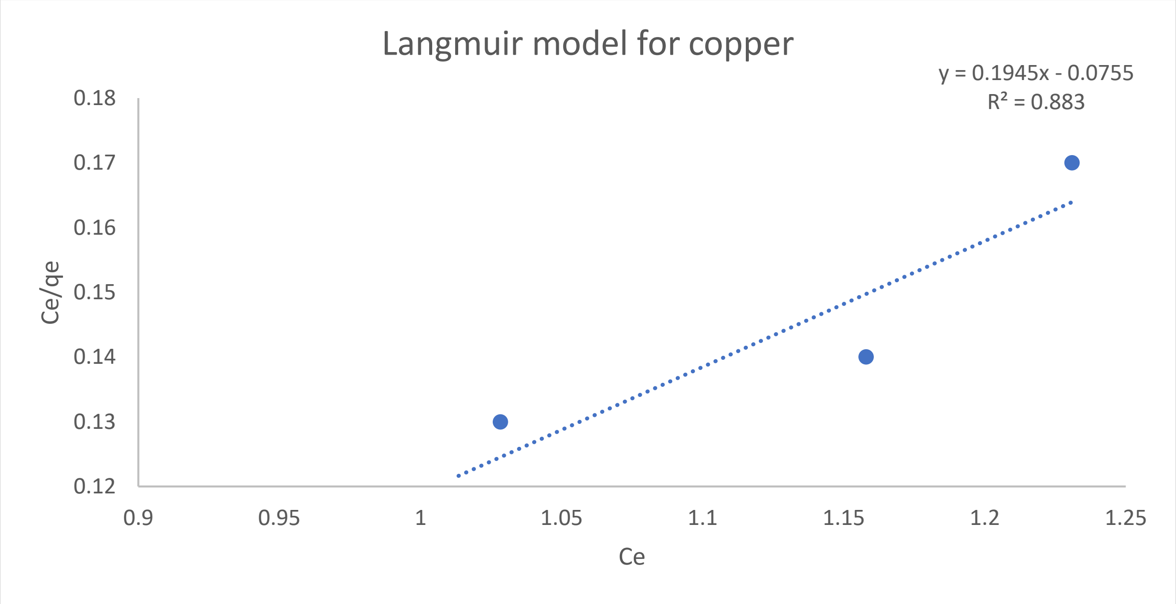

Fig 5: Langmuir model for copper at 25°C

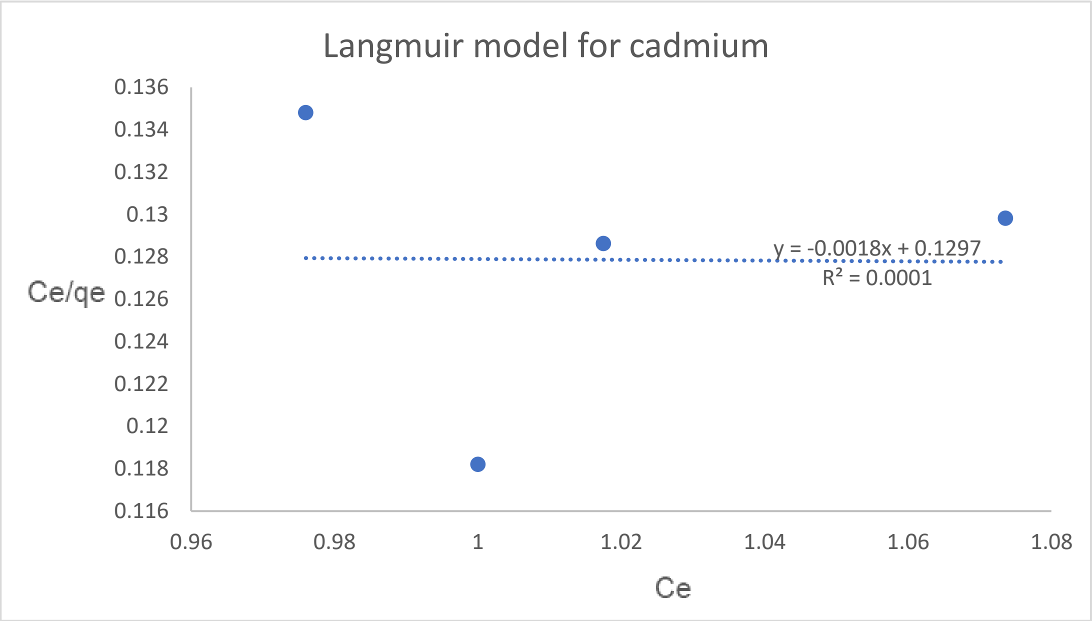

Fig 6: Langmuir model for cadmium at 25°C

Table 3: Langmuir model parameters for copper & cadmium at 25°C

Metals	Temperature (°C)	Slope ($1/q_{max}$)	Intercept ($1/bq_{max}$)	q_{max}	b (Langmuir constant)	R_L	R^2
Copper	25	0.1945	-0.0755	5.141	-2.576	-0.008	0.883
Cadmium	25	-0.0018	0.1297	-555.5	-0.0138	3.226	0.0001

The Langmuir model constants are evaluated for copper and cadmium metals and shown in table 3. The Langmuir isotherm model for copper fits better than cadmium based on linear regression coefficient (R^2) which is close to 1 explains the fitting of adsorption data.

Temkin model

Unlike the Langmuir and Freundlich isotherm, the Temkin isotherm considers the interactions between adsorbents and metal ions to be adsorbed and assumed that the free energy of sorption is a function of the surface coverage [42]. The Temkin isotherm assumes that the heat of adsorption of all the molecules in a layer decreases linearly due to adsorbent-adsorbate interactions and the adsorption was characterized by uniform distribution of binding energies [43]. The isotherm equation to find the adsorption capacity was given by Eq 6

$$q_e = B_t\,[ln(k) + ln(C_e)] \qquad (6)$$

$$\text{Where } B_t = \frac{RT}{b} \qquad (7)$$

where the constant B_t was related to the heat of adsorption, R is the universal gas constant (J/mole),
T is temperature (K), k is Temkin model constant. A plot of q_e versus ln C_e determines the isotherm constants B_t and k from the slope and the intercept respectively [44–46].

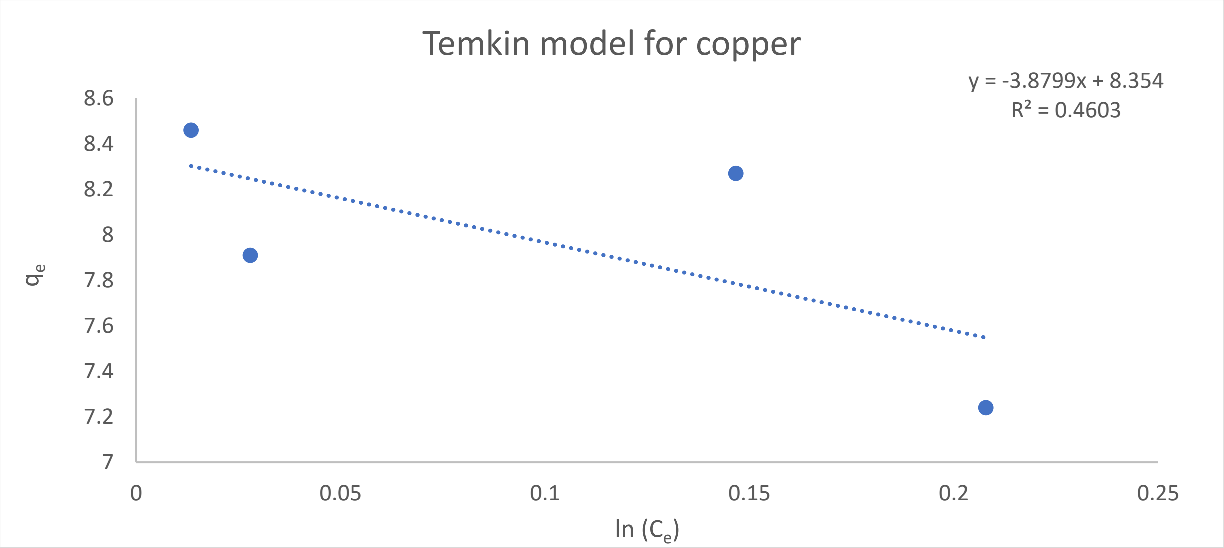

Fig 7: Temkin model for copper at 25°C

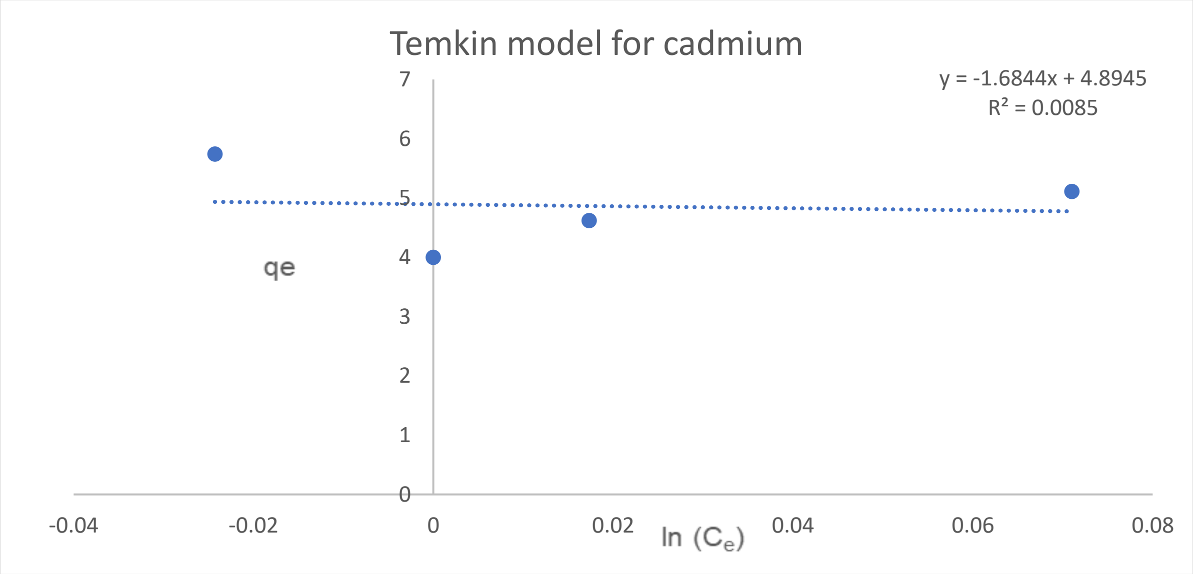

Fig 8: Temkin model for cadmium at 25°C

Table 4: Temkin model parameters for copper & cadmium at 25°C

Metal	Temperature (°C)	B_T	B_T ln (K_T)	ln (K_T)	Temkin constant (K_T)	R^2
Cu	25	-3.88	8.354	-2.153	0.116	0.4603
Cd	25	-1.685	4.895	-2.905	0.0547	0.0085

The Temkin model constants are evaluated for copper and cadmium metals and shown in table 4. The Temkin isotherm model constant for copper fits better than cadmium based on linear regression coefficient (R^2), which is close to 1 explains the fitting of adsorption data.

The Dubinin-Radushkevich isotherm model

The Dubinin-Radushkevich isotherm model: In order to get information about the energy needed for adsorption and mechanisms the Dubinin- Radushkevich isotherm model [30] is used. This model does not assume a homogeneous surface or a constant sorption potential. The linear form of D-R isotherm equation is represented as:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \qquad (8)$$

Where qm is the theoretical adsorption capacity (mol/g), β (mol^2 / J^2) is a constant related to the average energy of adsorption per mole of the adsorbate as it is transferred to the surface of the solid from infinity in the solution, and ε is the polanyi potential, which is expressed as:

$$\varepsilon = RT \ln \left(1+\frac{1}{C_e}\right) \qquad (9)$$

where, C_e (mg/L) is the equilibrium concentration of adsorbate in solution, R ($J\ mol^{-1}K^{-1}$) is the universal gas constant and T(K) is the absolute temperature. The DR isotherm constants q_m and β were calculated from the linear plots of ln (q_e) versus ε^2 .The mean sorption energy E (kJ/mol) of adsorption can be calculated from the following relationship [47] which was given by

$$E = \frac{1}{\sqrt{2\beta}} \qquad (10)$$

The mean adsorption energy (E) calculated from the D–R isotherm provides information about the adsorption mechanism. If the magnitude of E is between 8 and 16 kJ/mol, the sorption process is supposed to proceed via chemisorption, while for values of E < 8 kJ/mol, the sorption process is of physical nature [47].

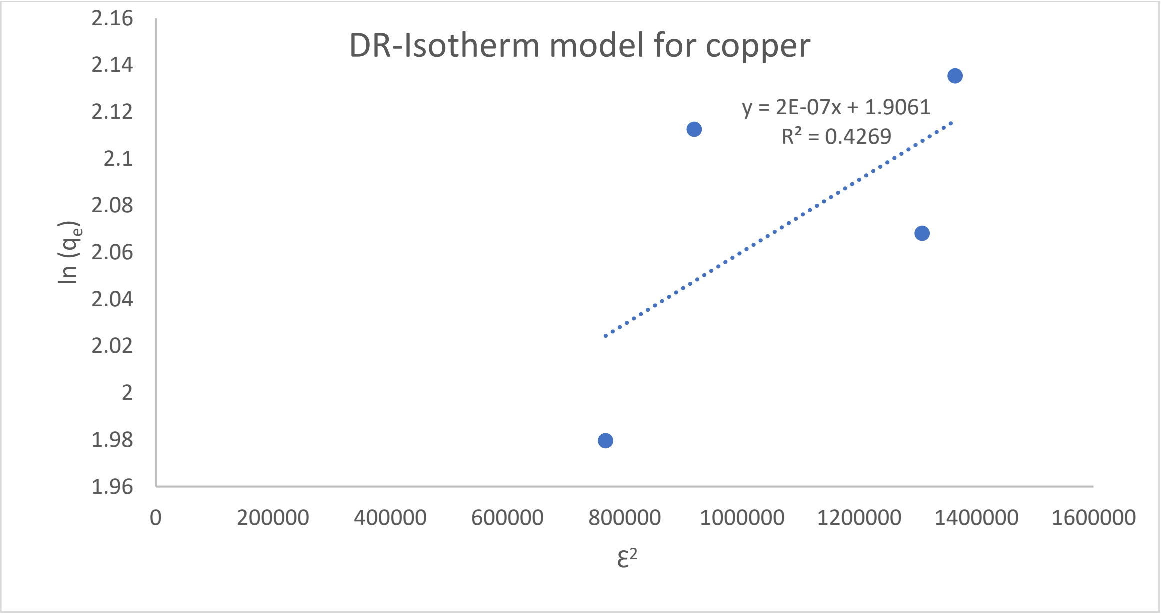

Fig 9: Dubinin-Radushkevich model for copper at 25°C

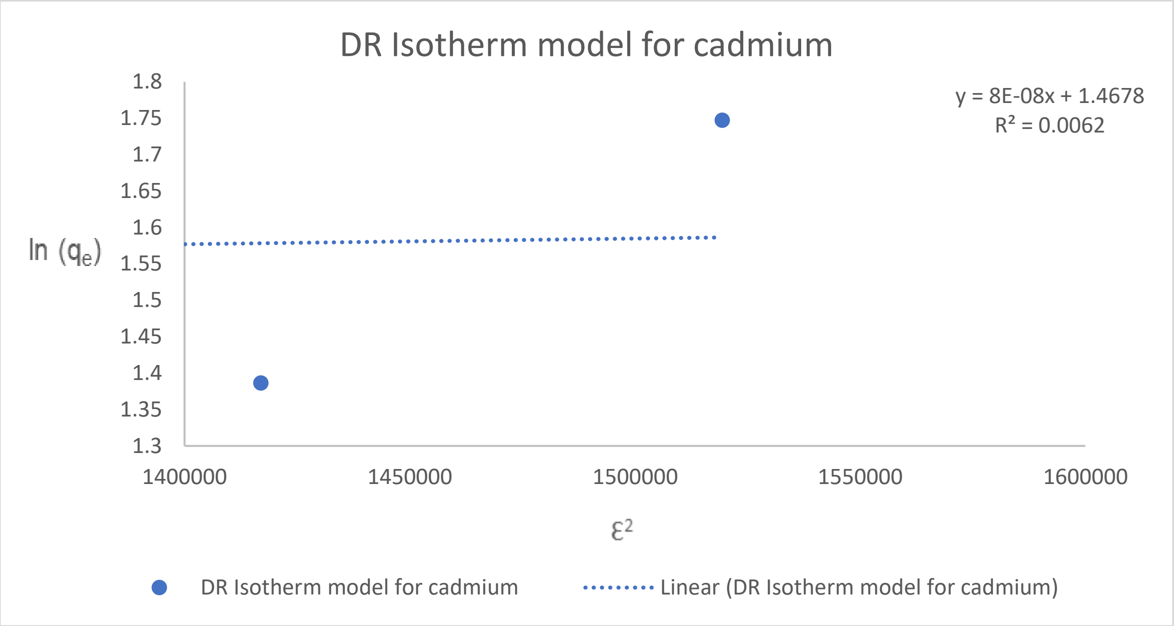

Fig 10: Dubinin-Radushkevich model for cadmium at 25°C

Table 5: Dubinin-Radushkevich model for copper at 25°C

ln (q_e)	ln (1+1/C_e)	[ln (1+1/C_e)]^2	RT	RT [ln (1+1/Ce)] 2	{RT [ln (1+1/Ce)]2}^2	Slope (m)	Intercept (ln q_m)	q_m	E = 1/(√2β) (J/mol)	R^2
2.13	0.687	0.4712	2478	1167.77	1363701.13	2 x 10^-7	1.91	6.73	1581.13	0.427
2.07	0.68	0.461	2478	1143.41	1307384.98					
2.11	0.622	0.3871	2478	958.65	919006.48					
1.98	0.595	0.3535	2478	876.05	767461.6					

Table 6: Dubinin-Radushkevich model for cadmium at 25°C

ln (q_e)	ln (1+1/C_e)	[ln (1+1/C_e)]^2	RT	RT [ln (1+1/C_e)]^2	{RT [ln (1+1/C_e)]}^{2}	Slope	Intercept (ln q_m)	q_m	E = 1/(√2β) [J/mol]	R^2
1.387	0.693	0.481	2478	1190.34	1416904.67	8 x10^{-8}	1.47	4.34	2500	0.006
1.53	0.685	0.471	2478	1160.98	1347878.81					
1.631	0.658	0.433	2478	1073.48	1152361					
01.75	0.705	0.505	2478	1232.61	1519331.6					

The DR isotherm model signifies that the adsorption is by physisorption as the mean sorption adsorption (E) is < 8000 J/mole and DR isotherm model for copper fits better than cadmium based on linear regression coefficient (R^2). Table 5 and 6 denotes the DR model constants for copper and cadmium metals along with R^2 value.

Error Analysis

In this study, four different nonlinear regression basin error functions [sum of square errors (SSE), sum of absolute errors (SAE), and chi-square (χ^2) were used to determine the best-fit isotherm model to the experimental equilibrium data.

SSE is denoted by

$$\text{SSE} = \sum_{i=1}^{n} (q_{e,estm} - q_{e,\exp})_i^2 \tag{11}$$

Here, $q_{e,estm}$ and $q_{e,exp}$ are respectively, the estimated and the experimental value of the equilibrium adsorbate solid concentration in the solid phase (mg/g), and n is the number of the data points.

SAE is given by:

$$\text{SAE} = \sum_{i=1}^{n} \left| q_{e,estm} - q_{e,\exp} \right|_i \tag{12}$$

Chi-square (χ^2) is given by

$$\chi^2 = \sum_{i=1}^{n} \left[\frac{(q_{e,\exp} - q_{e,estm})^2}{q_{e,estm}} \right]_i \tag{13}$$

The error analysis for copper and cadmium is shown in table 7 respectively along with R^2 values.

Table 7: Error analysis of copper (II) and cadmium (II) from solutions

Adsorption model	Metal ions	Max adsorption capacity (q_{max}) (mg/g)	R^2	χ^2	SSE	SAE
Freundlich	Copper	8.36	0.4675	0.044	0.37	0.44
	Cadmium	4.84	0.0023	0.084	0.41	0.5575
Langmuir	Copper	5.141	0.883	1.6	8.22	2.83
	Cadmium	-555.5	0.0001	565.28	314012	559.4
Temkin	Copper	8.354	0.4603	0.0436	0.364	0.437
	Cadmium	4.895	0.0085	0.083	0.41	0.558
Dubinin-Radushkevich	Copper	6.73	0.427	0.261	1.754	1.24
	Cadmium	4.34	0.006	0.158	0.687	0.698

The error analysis for copper shows that the maximum adsorption capacity is observed for Freundlich and Temkin models along with least values of χ^2, SSE and SAE in comparison with Langmuir model and Dubinin-Radushkevich as shown in table 7.

Similarly, the error analysis for cadmium shows that the maximum adsorption capacity is observed for Freundlich and Temkin models along with least values of χ^2, SSE and SAE in comparison with Langmuir model and Dubinin-Radushkevich as shown in table 7.

Intraparticle diffusion model

The agitation rate significantly effects the metal ion adsorption on its surface. The results obtained in Fig 11 and Fig 12 from the effect of agitation rate for copper and cadmium indicated that film/boundary diffusion and pore/ intra particle diffusions were involved in governing

reaction rate. The sorption rate is shown to be controlled by several factors including the following processes which involves [48, 49]
- Diffusion of the solute from the solution to the film surrounding the particle
- Diffusion from the film to the particle surface (external diffusion)
- Diffusion from the surface to the internal sites (surface or pore diffusion)
- Uptake which involves several mechanisms such as physico chemical sorption, ion exchange, precipitation or complexation

Due to rapid stirring during the batch experiments there was a possibility of transport of heavy metal ions from the bulk into pores of the adsorbent as well as adsorption at the outer surface of the adsorbent. The rate-limiting step may be either film diffusion or intra particle diffusion. As they act in series, the slower of the two will be the rate determining step [50]. The possibility of the heavy metal ions to diffuse into the interior sites of the particles of adsorbent was tested with Weber-Morris equation [51]. Hence the intra particle diffusion model was evaluated to determine the reaction rate limiting step. Eq 16 gives the intra particle diffusion model (Weber-Morris equation) as follows

$$q_t = K_p (t^{0.5}) \qquad (16)$$

Where, q_t is the amount of heavy metal ions adsorbed (mg/g), k_p is the intra particle diffusion rate constant and t is the agitation time in minutes. The rate constant k_p for intra particle diffusion for 180 rpm of agitation rate using the mixed adsorbent were determined from the slope of plot between the amount of heavy metals adsorbed (q_t) vs square root of time $\sqrt{t}$. The best fit of the intra particle diffusion model was calculated in terms of linear regression coefficient. The results of intra particle diffusion model have been shown in Fig 11, 12 and 13 respectively and table 8 indicates the parameters/ model constants for Cu (II) and Cd (II) respectively.

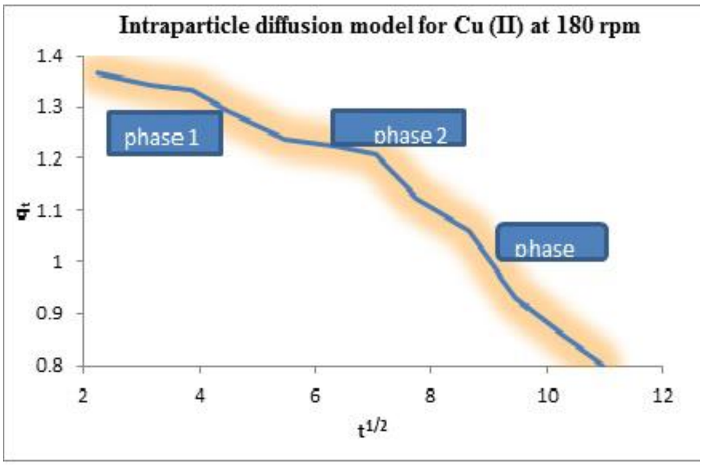

Fig 11: Intraparticle diffusion model for copper showing the phases at pH 6,120 min, T= 25°C, 5 g/L of ads dosage, 50 ppm IMC and 180 rpm.

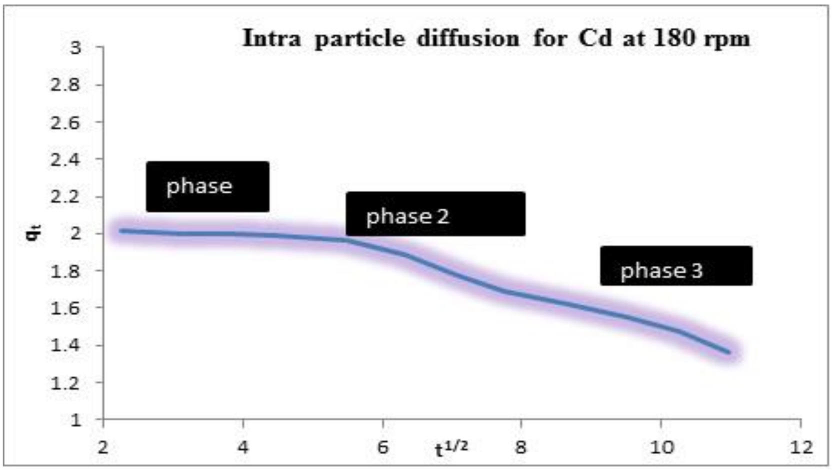

Fig 12: Intraparticle diffusion model for cadmium showing the phases at pH 6, 120 min, T = 25°C, 5 g/L of ads dosage, 50 ppm IMC and 180 rpm

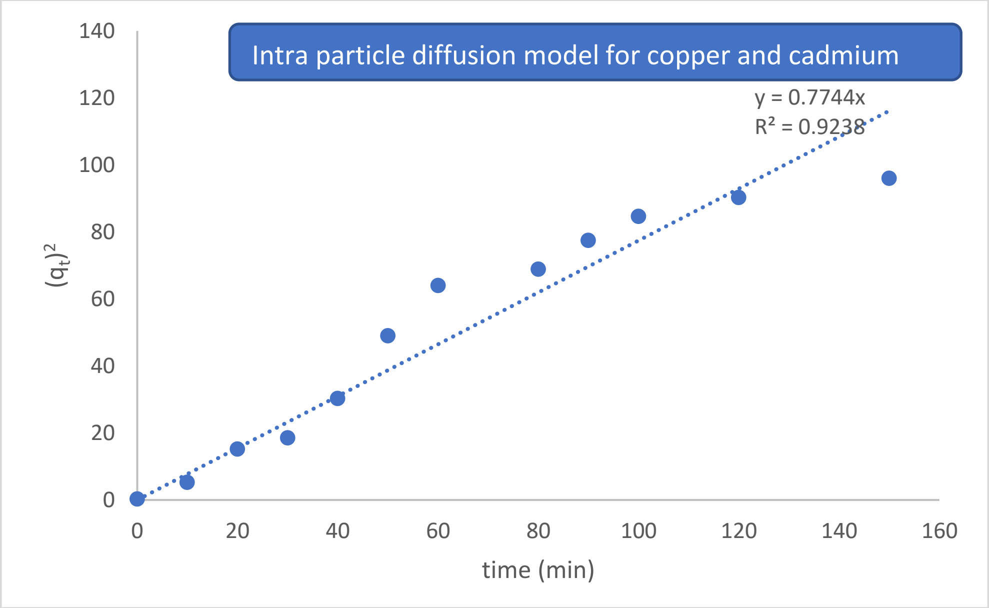

Figure 13 Intraparticle diffusion model for copper and cadmium showing the phases at pH 6, 120 min, T = 25°C, 5 g/L of ads dosage, 50 ppm IMC and 180 rpm

Table 8: Intra particle diffusion model parameters for copper and cadmium at T = 25ºC

Metal	Equation	Slope (m), $(K_p)^2$	K_p	R^2
Copper	y = 0.7744x	0.774	0.88	0.9238
Cadmium	y = 0.5002x	0.5002	0.707	0.9659

Table 8 denotes the intra particle diffusion model parameters for copper and cadmium, which indicates that the data fits for cadmium with higher R^2 values as compared to copper.

Conclusion

In this study, ground nut husk (GNH was tested and evaluated as a possible adsorbent for removal of copper and cadmium from aqueous solution using batch sorption studies. The maximum removal and adsorption capacity was found to be at pH 6, and temperature of 25ºC.

Equilibrium data fitted very well for Langmuir, Temkin, Freundlich and Dubinin Radushkevich isotherm model, which indicates that the adsorption of copper onto GNH seems to be physisorption. Intra-particle diffusion was not the sole rate controlling factor. Error analysis proved that the maximum adsorption capacity was found to be Freundlich and Temkin models along with least values of χ^2 , SSE and SAE.

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