

Study on Mass Transfer, Kinetic Parameters and Rate Determining Step with Statistical Analysis in Adsorption of Pb ions onto Coir Pith

B.M.W.P.K. Amarasinghe*, A.A.K.T. Amarasinghe

Department of Chemical and Process Engineering, University of Moratuwa, Sri Lanka

ABSTRACT

Adsorption of Pb ions onto coir pith from aqueous solutions was studied. Adsorption kinetic data were fitted to second order kinetic equation and equation parameters were determined. Overall liquid phase mass transfer coefficients, K_L , were calculated from first principles using experimental kinetic data and Freundlich isotherm parameters. This method overcomes the errors due to assumption of linear isotherm parameters and the K_L the values varied from 1.3284×10^{-05} to 2.7927×10^{-05} m/s. Pore diffusion coefficient values were calculated and found to be in the range 1.6273×10^{-11} to 3.3547×10^{-11} m²/s. Statistical analysis of mass transfer coefficients and kinetic parameters showed that for all the parameters tested, the variation of the parameters are significant with initial Pb ion concentration in the solution. Intra particle diffusion model and Boyd plots confirmed that the adsorption of Pb onto coir pith is controlled not only by intra-particle diffusion but film diffusion also plays an important role.

Key words: Heavy metal, Adsorption, Mass Transfer Coefficients, Statistical Analysis

*Corresponding Author: +94716558759, padma@uom.lk

1. INTRODUCTION

Contamination of water resources by heavy metal ions has become a severe problem due to rapid industrialization over the past. Several methods are available for the removal of heavy metal ions from wastewater streams, among them adsorption is proven to be a reliable technique. Presence of lead ions in water consumed by humans can cause many health issues (Malik & Khan, 2016). Industrialists are reluctant to use costly adsorbents for wastewater treatment due to economical reasons. Numerous researchers have investigated on various types of adsorbents for the separation of heavy metal ions from wastewater. Low cost adsorbents such as tea waste, coir pith, rice husk, plant leaves, peanut husks have been tested for heavy metal ion removal from aqueous solutions (Amarasinghe and Williams 2007; Bhatnagar et. al. 2010; Bhatnagar et. al. 2015; Dai et.al. 2018; da Silva et. al. 2018; Demirbas 2008). Adsorption kinetics and equilibrium isotherms have been determined in many investigations. Adsorption is a mass transfer operation and the mass transfer coefficient and diffusion coefficient through the porous solid are important parameters to understand the transfer process. The objectives of this study are to investigate on removal of Pb ions from aqueous solutions using coir pith as an adsorbent, to determine the mass transfer coefficient and diffusion coefficient for the process, to determine the rate limiting step and to analyze the results statistically.

2. THEORY ON MASS TRANSFER COEFFICIENT CALCULATIONS

Adsorption of a solute onto a porous solid adsorbent from a aqueous phase involves several stages namely; Movement of the solute in the bulk solution to the solid particles, Transfer of solute through the fluid film around the solid adsorbent particle, Diffusion of solute from the solid surface through the pores to internal active sites, Adsorption of solute on the active sites of the solid (Girish & Murthy 2016; Seader et. al., 1998; Uzun & Guzel 2004). Fig 1 gives pictorial presentation of film transport and intra particle transport. For agitated systems first step is rapid and adsorption onto the active sites is also known to be fast. Therefore transfer of the solute through the fluid boundary and diffusion through solid become rate determining steps. Theories on mass transfer and adsorption rate limiting stages are discussed below.

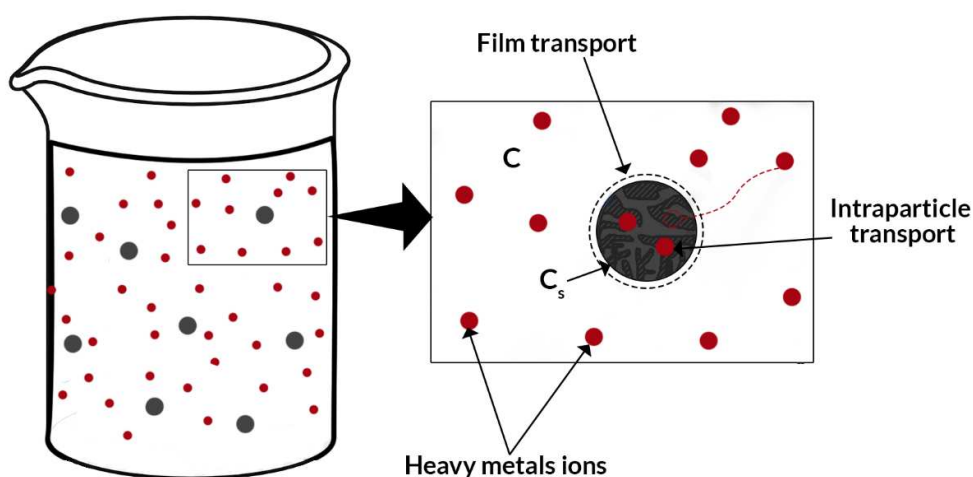


Fig. 1: Schematic diagram of liquid film transfer and intra particle diffusion when Pb ions adsorbed onto coir pith.

2.1 Overall mass transfer coefficient

Rate of change of metal ion concentration in the solution can be expressed in terms of the overall mass transfer coefficient (K_L) as per equation 1 (McCabe et. al., 1967; Nurbas et. al. 2002; Seader et. al., 1998; Treybal, 1980; Wankat, 2009).

$$\frac{dC}{dt} = -K_L S (C - C^*) \quad [1]$$

Where, K_L is liquid phase overall mass transfer coefficient in m/s, S is surface area of the adsorbent per unit volume of particle free solution in m^{-1} , C is the solute concentration in the solution at time t in mg/L, C^* is the solute concentration in the solution in equilibrium with the adsorbent at time t in mg/L.

Overall mass transfer coefficient can be determined from the equation (2) obtained by rearranging and integrating the equation 1 between the boundary conditions; when $t = 0$, $C = C_0$, $q = 0$, $C^* = 0$ and when $t = t$, $C = C$, $q = q$, $C^* =$ equilibrium concentration of solution with q . q is the solid phase solute concentration (mg/g) at time t .

$$\int_0^t S K_L dt = \int_C^{C_0} \frac{dC}{C - C^*} \quad [2]$$

The relation between q and C at a given time can be obtained by the material balance. Applying the material balance for the solute (metal ion) at $t = t$ equation 3 is obtained.

$$C = C_0 - qw \quad [3]$$

Where w is the weight of adsorbent in the solution (g/L)

Solute uptake (q) and C^* are related by the equilibrium isotherm equations (Amarasinghe & Williams, 2007; Kennedy et. al., 2007; Uzun et. al., 2004). In this study Freundlich isotherm given by equation 4 was observed as the best fit and hence used for the calculations.

$$q = k C^{*1/n} \quad [4]$$

Hence, the C^* value corresponding to any C value can be determined from equations 3 and 4 and the integral on the right hand side of the equation 2 can be determined graphically or analytically and K_L can be calculated. Expressing C^* in terms of C from equations 3 and 4, equation 2 can be modified as given by equation 5 which can be used to determine K_L when experimental data is available.

$$K_L = \frac{1}{S t} \int_C^{C_0} \frac{dC}{\left[C - \left(\frac{C_0 - C}{kw} \right)^n \right]} \quad [5]$$

2.2 Intra-particle diffusion rate constant

Intraparticle diffusion model can be used to determine the rate limiting step in the adsorption process. Morris and Weber intraparticle diffusion model is given by the equation 6.

$$q = k_d t^{1/2} + \delta \quad [6]$$

Where q is the solid phase solute concentration (mg/g) at time t , k_d is the intra particle diffusion rate constant in ($\text{mgg}^{-1} \text{min}^{-1/2}$) and δ is the boundary layer effect mg/g. The plots of q vs $t^{1/2}$ are usually multi linear corresponding to three stages in adsorption namely; external mass transfer, intra particle diffusion and final equilibrium stage. The regression line of the second linear portion can be used to determine intra particle diffusion rate constant (k_d) and the boundary layer effect (δ). Values of intercept give an idea about the thickness of boundary layer, i.e., the larger the intercept the greater will be the boundary layer effect (Nethajiet. al., 2013; Yakub et. al., 2019).

2.3 Pore diffusion coefficient

Diffusion coefficients for the intra-particle transport of a solute within the pores of an adsorbent; the Pore diffusion coefficient ($D \text{ m}^2/\text{s}$); is given by the equation 7.

$$D = \frac{0.03 r^2}{t_{1/2}} \quad [7]$$

Where r is the particle radius (m), $t_{1/2}$ (s) is the time required for the adsorption to take up half as much what the adsorbent can take at its equilibrium value which can be calculated from second order kinetic parameters (Girish & Murty, 2016; Kennedy et. al., 2007; Khezami & Capart, 2005; Onganer & Temur, 1998; Yakout & Elsherif, 2010).

Second order kinetic equation (Amarasinghe & Williams 2007; Chakrapani et. al., 2010; Ho & McKay, 2002; Kennedy et. al., 2007; Wang et. al., 2017; Yakout & Elsherif, 2010) and equation to determine $t_{1/2}$ (min) are given by equations 8 and 9 respectively (Girish & Murty, 2016; Khezami & Capart, 2005; Nethaji et. al., 2013).

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad [8]$$

$$t_{1/2} = 1/k_2 q_e \quad [9]$$

Where k_2 is the second-order rate constant ($\text{g mg}^{-1} \text{ min}^{-1}$), q and q_e are the solid phase solute concentration (mg/g) at time t and at equilibrium respectively.

2.4 Boyd Plot

Boyd plots given by equation 10 can be used to investigate on the rate determining step in the adsorption process.

$$B_t = -\ln \frac{6}{\pi^2} - \ln \left[1 - \left(\frac{q}{q_e} \right) \right] \quad [10]$$

B_t , which is a mathematical function of q , versus time plots are used to determine the rate determining step of the adsorption process. If the B_t versus time (t) plot is a linear regression fit that passes through the origin, then the adsorption rate is governed by the particle diffusion mechanism (Banerjee et. al., 2013; Nethaji et. al. 2013; Teixeira & Raimundo, 2013; Tsibranska & Hristova, 2011; Yakubu & Owabor, 2018).

3. METHODOLOGY

3.1. Wastewater solution preparation

Synthetic wastewater samples were prepared by dissolving analytical grade $\text{Pb}(\text{NO}_3)_2$ in distilled water. 1000 mg of Pb ions /L solutions were prepared and diluted using distilled water to the required concentrations; 150 ppm, 100 ppm and 50 ppm. The solution pH was measured and found to be 5.5 ± 0.5 and no chemicals were added to change the pH. Previous studies on the Pb adsorption onto waste materials has shown that the adsorption is maximum at pH 5-6 range (Amarasinghe & Williams, 2007).

3.2 Adsorbent Preparation

Coir pith obtained from coir mills in Sri Lanka was used for the experiments. The material was washed with hot water at 80 °C and distilled water several times until the water is colorless. The adsorbent was dried in the oven at 85 °C for 12 hr. The fraction between 350-850 μm was separated using a sieve shaker and the material was stored in sealed containers.

3.3 Batch Adsorption Experiments

Adsorption kinetic experiments were conducted at room temperature 25 °C using a agitated vessel. A measured weight of adsorbent (0.5 g) was mixed with a known volume of synthetic wastewater samples (200 ml) of selected Pb ion concentrations (50, 100 and 150 ppm). Samples were withdrawn from the container at known time intervals and analyzed for the metal ion concentration. Atomic absorption spectrophotometer with an air-acetylene flame and hollow cathode lamps for Pb was used for metal ion analysis. Adsorption isotherm experiments were conducted by mixing the same weight of adsorbent in equal volumes of synthetic wastewater samples of varying concentrations. The samples were kept while mixing for 9 hrs until the mixture reaches equilibrium and the solution concentrations were measured.

The adsorption experiments were performed in duplicate to observe the reproducibility.

3.4 Adsorbent characterization

True and bulk densities of adsorbents were determined using the specific gravity bottle method. The particle size was measured by sieve analysis. The surface area of coir pith was measured using BET surface area analyzer (Quantachrome). Scanning electron microscope photographs were obtained for coir pith using Field emission SEM S4700 (Hitachi corporation).

4. RESULTS AND DISCUSSION

4.1 Physical properties of coir pith

Physical properties of the adsorbent coir pith, mean particle size, bulk density and true density were observed as 513 μm , 116 kg/m^3 and 799 kg/m^3 respectively. The surface area of the particles were found to be 1.56 m^2/g and pore size was 45.2 \AA . The SEM of coir pith is shown in Fig. 2.

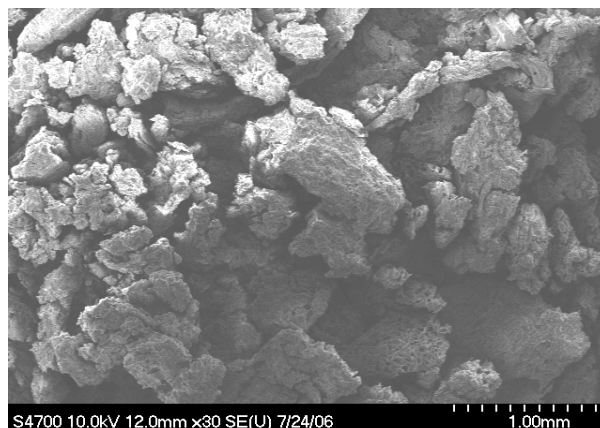


Fig 2: Electron microscopy (SEM) of coir pith

4.2 Adsorption Equilibrium and Kinetics

Metal ion concentrations obtained from adsorption experiments were converted to mg of metal ion adsorbed per gram of adsorbent (q) values. Percentage removal values were calculated as a function of time and presented in Fig3. Kinetic data for adsorption of Pb ions onto coir pith were fitted to second order kinetics given by equation 8. Adsorption kinetic parameters obtained from data fitting to the second order kinetic equation, k_2 and $q_{e,pre}$ are summarized in Table 1.

Equilibrium data fitted to Freundlich isotherm with coefficient of determination (R^2) values above 0.9 and the equation 11 was obtained for Pb adsorption onto coir pith. The kinetic and isotherm parameters will be used to determine the diffusion coefficient and mass transfer coefficients in the subsequent sections. Adsorption kinetics and isotherms are not discussed in detail in this paper as the main objective of this work is to determine the mass transfer coefficients.

$$q_e = 21.14C_e^{1/3.12} \quad [11]$$

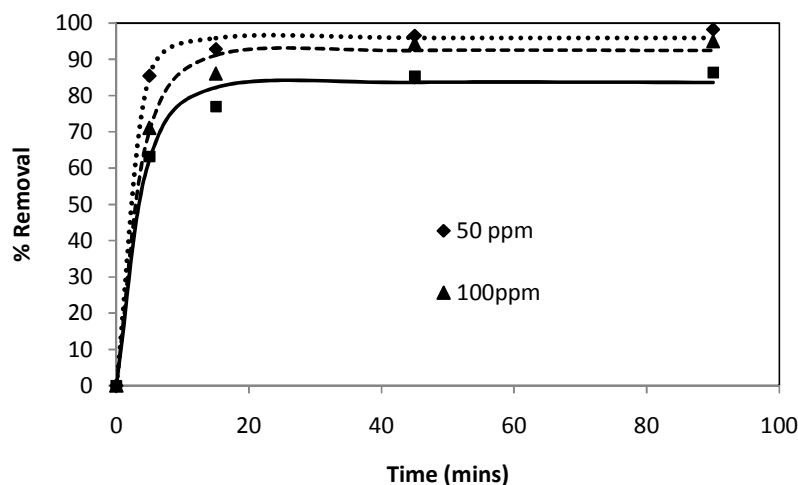


Fig. 3: Percentage removal of Pb ions as a function of time onto coir pith at 25 °C at different initial solution concentrations, adsorbent dose =2.5 g/L

Table 1: Second order kinetic parameters and Intra particle diffusion model parameters for adsorption of Pb onto coir pith at 25 °C

Initial Solution conc. (mg/l)	Second order rate equation			Intra particle diffusion model		
	k_2 (g mg ⁻¹ min ⁻¹)	q_{pre} (mg/g)	R ²	k_d mg/g min ^{1/2}	δ mg/g	R ²
150	0.0093	53.19	1	1.001	43.04	0.8411
100	0.0147	38.75	0.9999	0.6396	32.42	0.8176
50	0.0514	19.84	1	0.1917	17.89	0.9561

4.3 Mass Transfer and Diffusion coefficient Determination

4.3.1 Overall Mass transfer coefficient

Overall liquid phase mass transfer coefficient (K_L) values were calculated for Pb adsorption at various initial solution concentrations using equation 5 as follows. Solute concentration, C , as a function of time was obtained from the experiments. Solute uptake onto the adsorbent (q) values were calculated from the material balance and the Freundlich isotherm equation was used to obtain the relation between q and C^* . Integral on the right hand side of the equation 5 was evaluated using the trapezoidal rule. Overall liquid phase mass transfer coefficients thus calculated are given in Table 2. Nurbas et. al.(2002) has obtained values of K_L , similar range for Cu adsorption onto Ca-Alginate. The overall liquid phase mass transfer coefficient (K_L) values thus obtained can be used to determine the time required for a given degree of adsorption for a given adsorbent dose (w).

Table 2: Mass transfer parameters for adsorption of Pb ions onto coir pith at 25 °C

Initial Concentration (C ₀)(mg/L)	50	100	150
Overall liquid phase mass transfer coefficient K _L (m/s) eq ⁿ 5	2.7927 x 10 ⁻⁵	2.2015 x 10 ⁻⁵	1.3284 x 10 ⁻⁵
Pore diffusion coefficient, D (m ² /s) eq ⁿ 7	3.3547 x 10 ⁻¹¹	1.8738 x 10 ⁻¹¹	1.6273 x 10 ⁻¹¹

4.3.2 Pore diffusion coefficient

Pore diffusion coefficient values were calculated from the equation 7. The half time (t_{1/2}) values in equation 7 were obtained from second order kinetic model parameters as per equation 9. Pore diffusion coefficient values are shown in Table 2. The values are in agreement with the pore diffusion coefficient values obtained by Kennedy et. al (2007) for adsorption of phenol onto mesopores carbon and Onganer and Temur (1998) for adsorption of Fe(III) onto activated carbon.

4.4 Statistical analysis

Mass transfer parameters determined based on experimental data can be critically analyzed using statistical techniques. Overall liquid phase mass transfer coefficient K_L, Pore diffusion coefficient D and adsorption kinetics parameter k₂ values calculated from batch adsorption experiments were analyzed statistically (Kaushal & Singh, 2017; Selimet. al., 2019).

Spearman's correlation coefficient, (ρ) given by equation 12, measures the strength and direction of association between two ranked variables, in this study, initial solution heavy metal concentration, C₀, and the mass transfer parameter.

$$\rho = 1 - \frac{6 \sum d_i^2}{n(n^2 - 1)} \quad [12]$$

where d_i = difference in paired ranks and n = number of cases.

Statistical significance test namely p-test, was performed to find the significance of initial solution concentration, C₀, on the mass transfer and kinetic parameters namely; Overall liquid phase mass transfer coefficient, K_L; Pore diffusion coefficient, D; second order rate constant, k₂ and intra particle diffusion rate constant k_d.

Null Hypothesis; H₀; Variation of the parameter value with C₀ is not significant.

Alternate Hypothesis; Variation of the parameter value with C₀ is significant.

Results of the Spearman correlation test and the p-test are shown in Table 3.

Table 3: Spearman correlation and p-value for statistical analysis of parameters for for adsorption of Pb ions onto coir pith at 25 °C

Second order rate equation k_2 (g mg ⁻¹ min ⁻¹)		Intra particle diffusion model k_d (mg/g min ^{1/2})		Overall liquid phase mass transfer coefficient K_L (m/s)		Pore diffusion coefficient D (m ² /s)	
ρ	P value	ρ	P value	ρ	P value	ρ	P value
-1.0	0.0	1.0	0.0	-1.0	0.0	-1.0	0.0

Statistical analysis results show that for Pb adsorption onto coir pith, Spearman correlation coefficient for the parameters K_L , k_2 and D is -1.0, which indicates perfect negative association between the C_0 and the parameter. However, for k_d spearman correlation coefficient is +1.0 indicating perfect positive association. Results of the p-test further confirm the above result; that p value of zero, indicating variation of the parameter value with C_0 , is significant.

4.5 Determination of the rate limiting step

Adsorption of a solute onto the solid is controlled either by the film diffusion or by the intra particle diffusion. Understanding the rate controlling step is important to understand the adsorption process. Intra-particle diffusion model and the Boyd plots were used to determine the rate limiting step for adsorption of Pb and Cd ions onto coir pith.

4.5.1 Intra-particle diffusion model

Plots of solute uptake (q) versus $t^{1/2}$ were produced to identify the rate limiting step. q vs $t^{1/2}$ plots for Pb adsorption are shown in Fig.4. The plots of the intra particle diffusion did not pass through the origin indicating that the adsorption processes not only followed the intra particle diffusion but the film diffusion also played an important role in Pb adsorption processes. Many previous researchers have observed a similar result for the systems they have experimented. (Chakrapani et. al., 2010; Nethaji et. al., 2013; Teixeira et. al., 2013; Wang et. al., 2019). Intra particle diffusion rate constant (k_d) and boundary layer effect (δ) were determined from the second linear portion of the plots and the values are presented in Table 1. Both parameters k_d and δ increases with the initial heavy metal ion concentration. The value of δ gives an indication of the boundary layer effect. High values of δ obtained for Pb adsorption further confirms the effect of film diffusion on mass transfer. The values are in agreement with the k_d and δ values obtained by Pap et. al. (2017) for the adsorption of Pb Cd and Ni onto fruit processing industry waste and by Khezami & Capart (2005) for Cr(VI) removal by activated carbons.

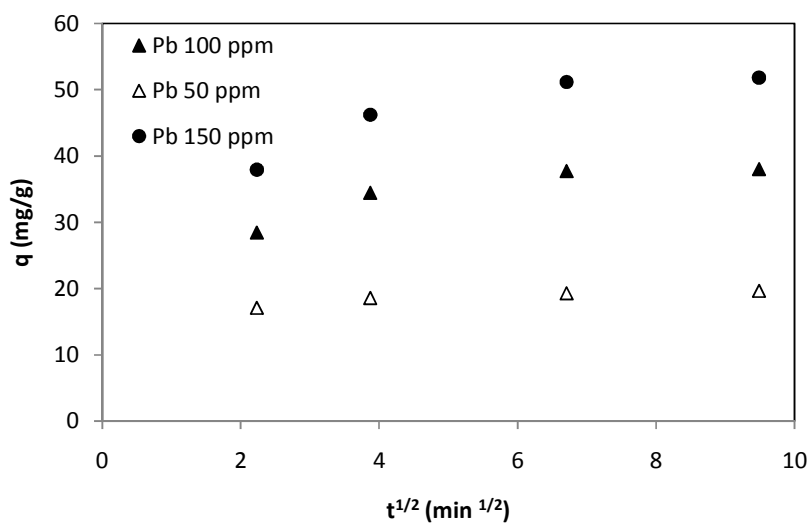


Fig. 4: Intra-particle diffusion model plots for adsorption of Pb ions onto coir pith at 25 °C, adsorbent dose =2.5 g/L

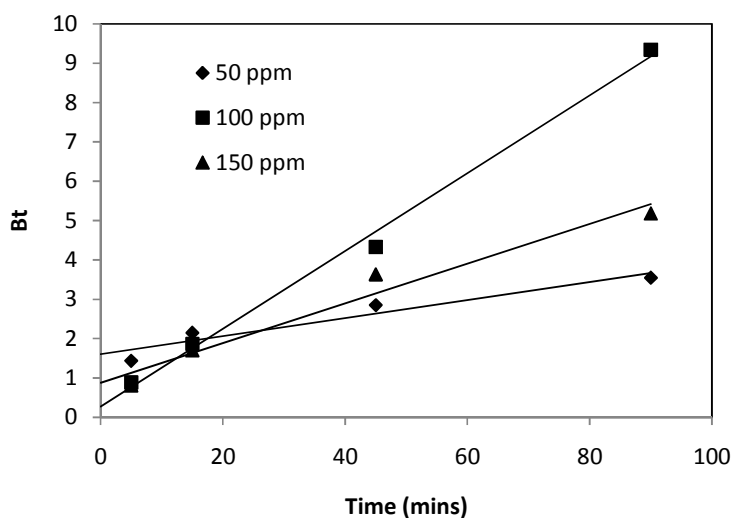


Fig 5: Boyd plots for adsorption of Pb ions onto coir pith at 25 °C, adsorbent dose =2.5g/L

4.5.2 Boyd Plot

Kinetic data for adsorption of Pb onto coir pith was further studied using the Boyd model given by the equation 10. Boyd plots (B_t verses time) are shown in Fig 5. According to the Boyd model if B_t verses time plots are linear and pass through the origin intra-particle diffusion is the rate controlling step in adsorption of the heavy metal onto coir pith. If the plot does not pass through the origin then the film diffusion is also significantly contribute the adsorption rate. Hence, the presence of an intercept in all B_t verses time suggested that the adsorption rate is not only governed by the particle diffusion mechanism for adsorption of Pb onto coir pith. Many researchers have obtained similar results for the adsorption systems investigated namely; heavy metals Pb, Cd, Cu and Zn from aqueous solutions with activated carbon from apricot stones (Tsibranska & Hristova, 2011), phenol by sand and clay sediments (Yakub et. al., 2019). Yakub et. al., 2018) cationic and anionic dyes onto carbonaceous particles prepared from Juglansregia shell biomass (Nethaji et. al., 2013), Phenol from Aqueous Solution Using *Lantana camara*, Forest Waste (Girish & Murty, 2014), chlorhexidinegluconate onto GAC (Banerjee et. al., 2013).

5. CONCLUSION

Adsorption of Pb ions from aqueous solutions onto coir pith was studied. Experimental results show that the adsorption capacity of Pb onto coir pith is high and 98% removal was achievable with 5 g of adsorbent/L of solution. Study on the variation of heavy metal ion concentration in the solution with time shows a rapid drop at the initial stages of the adsorption process leading to an exponential decay. Overall liquid phase mass transfer coefficient was determined by the graphical method and the method overcomes the errors due to assumption of linear isotherm equation. Analysis based on the intra particle diffusion and the Boyd model show that the intra particle diffusion is not the only rate limiting step in adsorption of Pb and Cd onto coir pith. Mass transfer coefficients and the pore diffusion coefficients calculated are in the same order of magnitude as the values obtained by other workers for similar materials. The Statistical analysis of the mass transfer coefficients and pore diffusion coefficient show that the variation of the parameters with the initial solution concentration is significant for Pb adsorption onto coir pith.

6. REFERENCES

- Amarasinghe, B. M. W. P. K., and Richard A. Williams. (2007), "Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater." *Chemical Engineering Journal* 132, no. 1-3: 299-309.
- Banerjee, Debasree, Ujjaini Sarkar, and Debasri Roy (2013), "Multicomponent adsorption of chlorhexidine gluconate in presence of a cationic surfactant: Role of electrostatic interactions and surface complexation." *Journal of Environmental Chemical Engineering* 1, no. 3: 241-251.
- Bhatnagar, Amit, Mika Sillanpää, and Anna Witek-Krowiak (2015), "Agricultural waste peels as versatile biomass for water purification—A review." *Chemical Engineering Journal* 270: 244-271.
- Bhatnagar, Amit, Vítor JP Vilar, Cidália MS Botelho, and Rui AR Boaventura (2010), "Coconut-based biosorbents for water treatment—a review of the recent literature." *Advances in colloid and interface science* 160, no. 1-2: 1-15.
- Chakrapani, C. H., Babu, C., Vani, K. N. K., & Rao, K. S. (2010), Adsorption kinetics for the removal of fluoride from aqueous solution by activated carbon adsorbents derived from the peels of selected citrus fruits. *Journal of Chemistry*, 7(S1), S419-S427.
- Da Silva Correia, Ives Krishna, Pitágoras Fonseca Santos, Caroline Santos Santana, Jordan BriziNeris, Francisco HM Luzardo, and Fermin G. Velasco (2018), "Application of coconut shell, banana peel, spent coffee grounds, eucalyptus bark, piassava (*Attalea funifera*) and water hyacinth (*Eichornia crassipes*) in the adsorption of Pb²⁺ and Ni²⁺ ions in water." *Journal of Environmental Chemical Engineering* 6, no. 2: 2319-2334.
- Dai, Yingjie, Qiya Sun, Wensi Wang, Lu Lu, Mei Liu, Jingjing Li, Shengshu Yang (2018), "Utilizations of agricultural waste as adsorbent for the removal of contaminants: A review." *Chemosphere* 211: 235-253.
- Demirbas, Ayhan. (2008), "Heavy metal adsorption onto agro-based waste materials: a review." *Journal of hazardous materials* 157, no. 2-3: 220-229.
- Girish, C. R., & Murty, V. R. (2016), Mass transfer studies on adsorption of phenol from wastewater using Lantana camara, forest waste. *International Journal of Chemical Engineering*, 2016.
- Girish, C. R., and V. Ramachandra Murty (2014), "Adsorption of phenol from aqueous solution using Lantana camara, forest waste: kinetics, isotherm, and thermodynamic studies." *International Scholarly Research Notices* 2014.
- Ho, Y. S., & McKay, G. (2002). Application of kinetic models to the sorption of copper (II) on to peat. *Adsorption Science & Technology*, 20(8), 797-815.
- Kaushal, Achla, and S. K. Singh, (2017), "Critical analysis of adsorption data statistically." *Applied Water Science* 7, no. 6: 3191-3196.
- Kennedy, L. J., Vijaya, J. J., Kayalvizhi, K., & Sekaran, G. (2007), Adsorption of phenol from aqueous solutions using mesoporous carbon prepared by two-stage process. *Chemical Engineering Journal*, 132(1-3), 279-287.
- Khezami, L., & Capart, R. (2005), Removal of chromium (VI) from aqueous solution by activated carbons: kinetic and equilibrium studies. *Journal of hazardous materials*, 123(1-3), 223-231.

- Malik, Q. A., & Khan, M. S. (2016), Effect on human health due to drinking water contaminated with heavy metals. *J. Pollut. Eff. Cont*, 5(1).
- McCabe, Warren Lee, Julian Cleveland Smith, and Peter Harriott (1967), *Unit operations of chemical engineering*. Vol. 5. New York: McGraw-hill.
- Nethaji, S., Sivasamy, A., & Mandal, A. B. (2013), Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from Juglans regia shell biomass. *International Journal of Environmental Science and Technology*, 10(2), 231-242.
- Nurbas, M., Kaçar, Y., & Kutsal, T. (2002), Determining the overall mass transfer coefficient for adsorption of Cu²⁺ ions onto Ca-Alginate in fixed bed column. *Eur. J. Miner. Process. Environ. Prot*, 2, 55-60.
- Onganer, Y., & Temur, Ç. (1998), Adsorption dynamics of Fe (III) from aqueous solutions onto activated carbon. *Journal of Colloid and Interface Science*, 205(2), 241-244.
- Wanket, P.C. (2009), *Separation Process Engineering*, 2nd Edition, Prentice Hall.
- Pap, Sabolč, Tatjana Šolević Knudsen, Jelena Radonić, Snežana Maletić, Saša M. Igić, and Maja Turk Sekulić (2017), "Utilization of fruit processing industry waste as green activated carbon for the treatment of heavy metals and chlorophenols contaminated water." *Journal of Cleaner Production* 162 : 958-972.
- Seader, Junior D., Ernest J. Henley, and D. Keith Roper (1998) *Separation process principles*. Vol. 25. New York: Wiley.
- Selim, Ali Q., Lotfi Sellaoui, Sayed A. Ahmed, Mohamed Mobarak, Essam A. Mohamed, Abdelmottaleb Ben Lamine, Alessandro Erto, Adrián Bonilla-Petriciolet, and Moaaz K. Seliem (2019), "Statistical physics-based analysis of the adsorption of Cu²⁺ and Zn²⁺ onto synthetic cancrinite in single-compound and binary systems." *Journal of Environmental Chemical Engineering* 7, no. 4 : 103217.
- Teixeira, Raimundo NP, Vicente O. Sousa Neto, Juliene T. Oliveira, Thalles C. Oliveira, Diego Q. Melo, Marcos AA Silva, and Ronaldo F. Nascimento (2013), "Study on the use of Roasted Barley Powder for Adsorption of Cu²⁺ Ions in Batch Experiments and in Fixed-bed Columns." *Bioresources* 8, no. 3: 3556-3573.
- Treybal, Robert E. (1980), "Mass transfer operations." *New York* 466.
- Tsibranska, I., & Hristova, E. (2011), Comparison of different kinetic models for adsorption of heavy metals onto activated carbon from apricot stones. *Bulgarian Chemical Communications*, 43(3), 370-377.
- Uzun, İlhan, and Fuat Güzel (2004), "External mass transfer studies during the adsorptions of some dyestuffs and p-nitrophenol onto chitosan from aqueous solution." *Turkish Journal of Chemistry* 28, no. 6 : 731-740.
- Wang, F., Pan, Y., Cai, P., Guo, T., & Xiao, H. (2017), Single and binary adsorption of heavy metal ions from aqueous solutions using sugarcane cellulose-based adsorbent. *Bioresource technology*, 241, 482-490.
- Yakout, S. M., & Elsherif, E. (2010), Carbon—science and technology. *Applied science innovations Pvt. Ltd. India*, 1, 144-153.

- Yakub, E., Agarry, S. E., Omoruwou, F., & Owabor, C. N. (2019), Comparative study of the batch adsorption kinetics and mass transfer in phenol-sand and phenol-clay adsorption systems. *Particulate Science and Technology*, 1-11.
- Yakubu, Eugene Ehidihamhen, and Chiedu Owabor (2018), "The Effect of Mass Transfer Resistance on the Adsorption Rate of Phenol in Soil Sediments." *American Journal of Environmental Science and Engineering* 2, no. 4: 56-64.