

Adsorption of Ni(II) and Cd(II) Ions from Aqueous Solutions by Modified Surface of *Typha latifolia* L. Root, as an Economical Adsorbent

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ABSTRACT

The modified surface of *Typha latifolia* L. root (MSTL), as an alternative economical adsorbent, was used for the removal of Ni (II) and Cd(II) ions from aqueous solutions. The effect of initial pH, initial concentration of metal ion, and contact time was investigated in a batch system at room temperature. The kinetics data could be fitted well by pseudo-second-order model with correlation coefficient values greater than 0.99. The mechanism of adsorption process was tested by fitting the experimental data by intraparticle diffusion kinetic and Boyd kinetic equations. The adsorption data could be fitted well by Langmuir and Freundlich adsorption isotherms. The maximum adsorption capacity of MSTL was determined to be 37.31 mg g⁻¹ for Ni²⁺ and 28.90 mg g⁻¹ for Cd²⁺ at room temperature when the initial concentration of both metal ion was 100 mg/L, and the pH of the solution was 5.00 and 4.00 for Ni²⁺ and Cd²⁺, respectively. It has been suggested that the MSTL can be successfully applied for the removal of toxic heavy metal ions such as Ni²⁺ and Cd²⁺ from aqueous solutions.

Keywords: Adsorption; *Typha latifolia* L.; Ni (II); Cd (II); Kinetic model; Isotherm model

INTRODUCTION

Heavy metals such as lead, copper, zinc, nickel, cadmium, etc., are the most important pollutants throughout the world, which threaten aquatic ecosystems, agriculture, and human health [1]. Some of these heavy metals such as copper and zinc are necessary for living organisms, but many of them are toxic even at very low concentration. Therefore, remediation of contaminated aquatic resources is important for healthy living. Many scientists have focused on accumulation of heavy metals by aquatic macrophytes. Among aquatic macrophytes, *Typha*

latifolia L. is a common plant that grows widely in wetlands and has a high capacity for taking heavy metals into its tissue [2, 3]. It has been reported that the uptake of metal ions by this plant is highest in the root section [4, 5]. Already, some cheaper macrophytes such as algae, fungi, moss, fern, and *Carex* were used as an adsorbent rather than activated carbon for removal of heavy metal ions and dyes from polluted water [6-8]. In this work we used fine powder of *T. latifolia* L. root for removal of heavy metal ions such as Ni (II) and Cd (II) ions from aqueous solutions. Nickel

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and cadmium is released to the environment by municipal and industrial wastewater, fertilizers and local air pollutants. Also, nickel and cadmium are used mainly in the production of stainless steels, metal plating, coating operations, non-ferrous alloys, and super alloys. Other uses of nickel and cadmium are in electroplating, as catalysts, in nickel-cadmium batteries, in coins, in welding products, and in certain pigments and electronic products [9]. According to the World Health Organization (WHO), the favorable level of nickel and cadmium in drinking-water supplies must be below $2\mu\text{g/liter}$ and the maximum acceptable level can be about $5\mu\text{g/liter}$ [10]. Some people who drink water containing nickel and cadmium well in excess of the maximum contaminant level for many years could experience kidney damage [11]. So, it is important to find new treatment technologies for removing heavy metals from wastewater. Adsorption is one of the simplest and most effective treatment technologies for treating wastewater containing heavy metal ions rather than other expensive techniques such as chemical precipitation, electrolysis, ion exchange, membrane filtration, oxidation/reduction, electroplating, electro-winning, electro-coagulation, cementation, solvent extraction, and evaporation [12-14]. A survey of the literature shows that no work has been done on the kinetics and isotherms of sorption of nickel and cadmium by *T. latifolia* L. biomass. Therefore, we were interested in researching this topic. In this study, the pseudo-first-order and pseudo-second-order kinetic models were applied for determining of the adsorption kinetics. To further investigate the adsorption behaviours, intraparticle diffusion and Boyd kinetic equations were used to describe the adsorption mechanism. Also, the experimental data were fitted by

Langmuir and Freundlich isotherm models to find the best adsorption isotherm for removal of Ni (II) and Cd(II) ions by MSTL from aqueous solutions.

EXPERIMENTAL

Biomass preparation

T. Latifolia L. biomass was collected from Baliqly Chay River sediments, located in Ardabil City, Iran. This river is one of the main feeder channels of Khazar Lake in the north of Iran. This biomass is one of the aquatic plants that grows widely along this river. The root section of collected biomass was separated from other tissues, and was thoroughly washed with tap water to remove impurities from their surfaces, followed by distilled water. The washed root section was dried under sunlight and then ground into a fine powder using mixer grinder. A certain amount of dried biomass was soaked in 2 L of 0.01 M H_2SO_4 solution to remove probably inherent metals, and subsequently in 0.02 M NaOH solution to activate functional groups on the cell wall of the biomass, for 2 h with a rotating shaker for each reagent. Thereafter, the biomass was removed from solution using a grating and washed with generous amounts of distilled water until the pH of the filtered solution remained constant near the neutral range (6.8–7.2). Finally, the materials were dried in hot air oven at 40°C for 4 h, cooled, ground, and passed through a no. 45 mesh sieve to obtain fine particles with homogeneous size of 0.354 mm and stored in airtight plastic box for further use. The prepared material was abbreviated as the modified surface of *Typha latifolia* L. root (MSTL) and this material was used as an adsorbent for the removal of Ni(II) and Cd(II) ions from the aqueous solutions.

Materials and instrument

Double-distilled water was prepared using a water purification system from BiBBY

Company (Aquatron, UK). Nickel and cadmium solutions were respectively prepared using anhydrous NiCl_2 and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ salt from Sigma Aldrich Company by dissolving exact quantities of these salts in double distilled water. pH measurements were performed by pH meter (model 691; Metrohm, Swiss). The pH of the solutions was adjusted to the required value with standard acid and base solutions (0.1 M HCl and 0.1 M NaOH), obtained from Merck Company. The concentration of metal ions was determined using an atomic absorption spectrophotometer (Analyst 300; Perkin Elmer, USA). Standard solutions of Ni^{2+} and Cd^{2+} (1,000 mg L^{-1}) for atomic absorption calibration were obtained from Merck Company.

Batch adsorption experiments

Batch adsorption experiments were performed by placing 25 mg MSTL in contact with 25 mL Ni(II) or Cd(II) solution with known initial concentrations (25, 50, 75, and 100 mg L^{-1}) in 100-mL screw-top conical flasks. All adsorption studies were performed at room temperature with fixed MSTL dose of 1 g L^{-1} . To investigate the influence of the aqueous solution pH on metal removal, the initial pH of the metal ion solutions was adjusted in the 2–6 pH range, using dilute HCl or NaOH and it was not controlled after the initiation of the experiment. The mixtures of MSTL and the metal ions solution were shaken in an orbital incubation shaker at 150 rpm for a period of 180 min. After the target contact time was reached, the MSTL–metal mixture was filtered for analysis of unadsorbed metal ions in the mixture, using an atomic absorbance spectrophotometer with air–acetylene flame. All the batch adsorption experiments were carried out in duplicate and mean results are reported. The removal

percentage of metal ions was calculated by the following equation:

$$\text{Removal percentage} = \frac{C_o - C_e}{C_o} \times 100, \quad (1)$$

where C_i and C_e are the initial and equilibrium metal ions concentrations in the solution (mg L^{-1}), respectively.

Metal adsorption capacity at equilibrium time (q_e) and time t (q_t) were calculated using the following expressions, respectively:

$$q_e = \frac{(C_o - C_e) V}{1000 W}, \quad (2)$$

$$q_t = \frac{(C_o - C_t) V}{1000 W}, \quad (3)$$

where q_e and q_t (mg g^{-1}) are the amount of total adsorbed heavy metal ions at equilibrium time and time t , respectively, C_o (mg L^{-1}) the initial metal ion concentration, C_e (mg L^{-1}) the equilibrium metal ion concentration, C_t (mg L^{-1}) the metal ion concentration in solution at time t , V (L) the solution volume and W (mg) is the mass of the MSTL.

RESULTS AND DISCUSSION

Effect of contact time and initial concentration

The adsorption of Ni (II) and Cd(II) ions onto the MSTL was carried out at four different initial concentrations of both metal ions in separate. The maximum amount of adsorption was observed at pH 5.00 and 4.00 for solutions of Ni(II) and Cd(II), respectively. The adsorption data indicated that the amount of Ni^{2+} adsorbed on the MSTL is higher than Cd^{2+} , in all cases. The effect of initial concentration of metal ion on the adsorption capacity and removal percentage was investigated at room temperature and the results are summarized in Table 1.

Also, the effect of contact time and initial concentration on adsorption of Ni(II) and Cd(II) onto MSTL are shown in Fig. 1. These curves indicate that the adsorption process is reach equilibrium in 60 min. After 60 min contact time with

fixed biomass dose of 1 g L^{-1} and initial metal ion concentration of 100 mg L^{-1} , up to 37.31 mg g^{-1} of nickel ions and 28.90 mg g^{-1} of cadmium ions were adsorbed onto MSTL.

Table 1. Effect of metal ion concentration on adsorption capacity and removal percentage (s/l ratio 1.0 g L^{-1} ; contact time 180 min)

Metal ion	Initial concentration (mg L^{-1})	q_e (mg g^{-1})	Removal percentage (%)
(pH = 5.00)			
Ni^{2+}	25	14.22	56.90
	50	25.60	51.20
	75	30.19	40.26
	100	37.31	37.31
(pH = 4.00)			
Cd^{2+}	25	12.42	49.70
	50	19.48	38.95
	75	25.10	33.47
	100	28.90	28.90

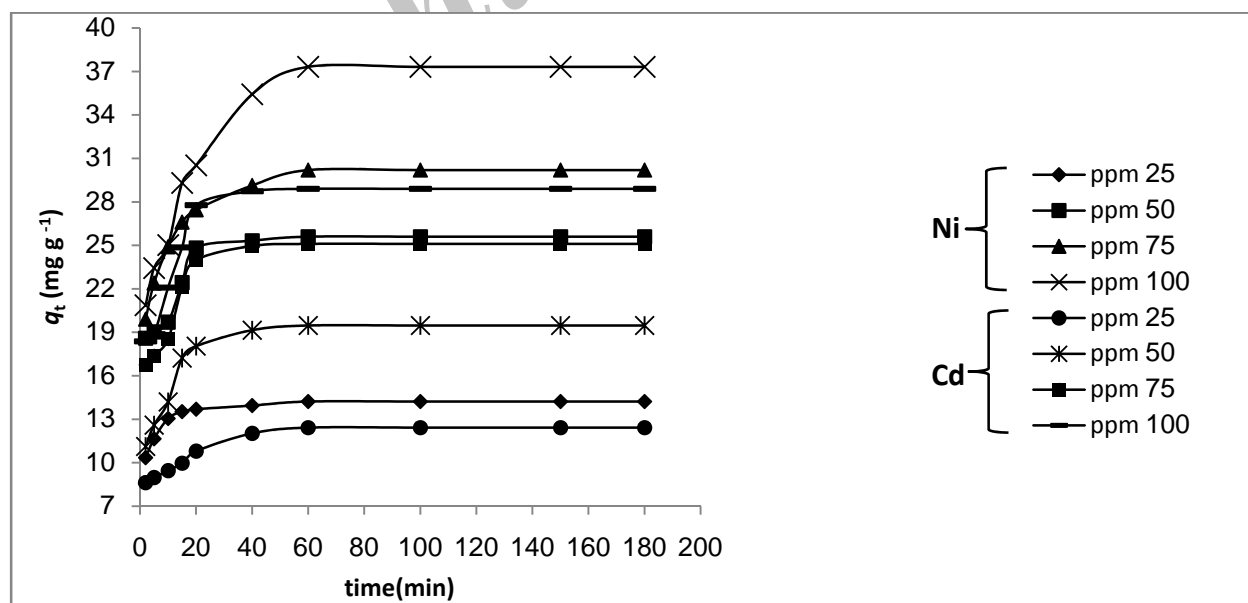


Fig. 1. Effect of contact time and initial concentration on adsorption of Ni(II) and Cd(II) onto MSTL.

Adsorption kinetics

There are different kinetic models to explain the removal of metal ions from aqueous solution. Some of them that were used frequently are Lagergren pseudo-first-order and pseudo-second-order kinetic models. In this study, we also fitted the adsorption kinetic data to the pseudo-first-order and pseudo-second-order kinetic equations [15].

The pseudo-first-order kinetic model assumes that the rate of occupation of adsorption site is proportional to the number of unoccupied sites. The linear form of the pseudo-first-order kinetic model is shown by the following equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (4)$$

where q_e is the adsorption capacity at equilibrium (mg g^{-1}), q_t is the adsorption capacity at time t (mg g^{-1}), k_1 is the pseudo-first-order kinetic rate constant (min^{-1}) and t is the time (min).

The pseudo-second-order kinetic model assumes that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. The linear form of the pseudo-second-order kinetic model is shown by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (5)$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of pseudo-second-order adsorption [16].

The rate constants of pseudo-first-order and pseudo-second-order adsorption at different initial concentrations of Ni(II) and Cd(II), the correlation coefficients, and the experimental and calculated values of adsorption capacity were evaluated, and the results are gathered in Tables 2 and 3.

The plots of $\ln(q_e - q_t)$ and t/q_t versus t are shown in Figs. 2 and 3.

Table 2. Pseudo-first-order adsorption kinetic constants

Metal ion	Initial concentration (mg L^{-1})	$q_{e, \text{exp}}$ (mg g^{-1})	$q_{e, \text{cal}}$ (mg g^{-1})	$k_1 \times 10^2$ (min^{-1})	R^2
Ni^{2+}	25	14.22	2.88	6.70	0.859
	50	25.60	10.01	9.30	0.916
	75	30.19	9.84	5.80	0.978
	100	37.31	19.51	5.70	0.990
Cd^{2+}	25	12.42	5.03	6.00	0.974
	50	19.48	10.12	8.80	0.982
	75	25.10	13.85	11.30	0.974
	100	28.90	17.05	16.60	0.972

Table 3. Pseudo-second-order adsorption kinetic constants

Metal ion	Initial concentration (mg L^{-1})	$q_{e, \text{exp}}$ (mg g^{-1})	$q_{e, \text{cal}}$ (mg g^{-1})	$k_2 \times 10^2$ ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
Ni^{2+}	25	14.22	14.49	6.71	0.999
	50	25.60	27.03	1.82	0.998
	75	30.19	31.25	1.55	0.999
	100	37.31	40.00	0.59	0.995
Cd^{2+}	25	12.42	12.99	2.68	0.996
	50	19.48	20.41	1.72	0.998
	75	25.10	26.32	1.57	0.998
	100	28.90	30.30	1.29	0.995

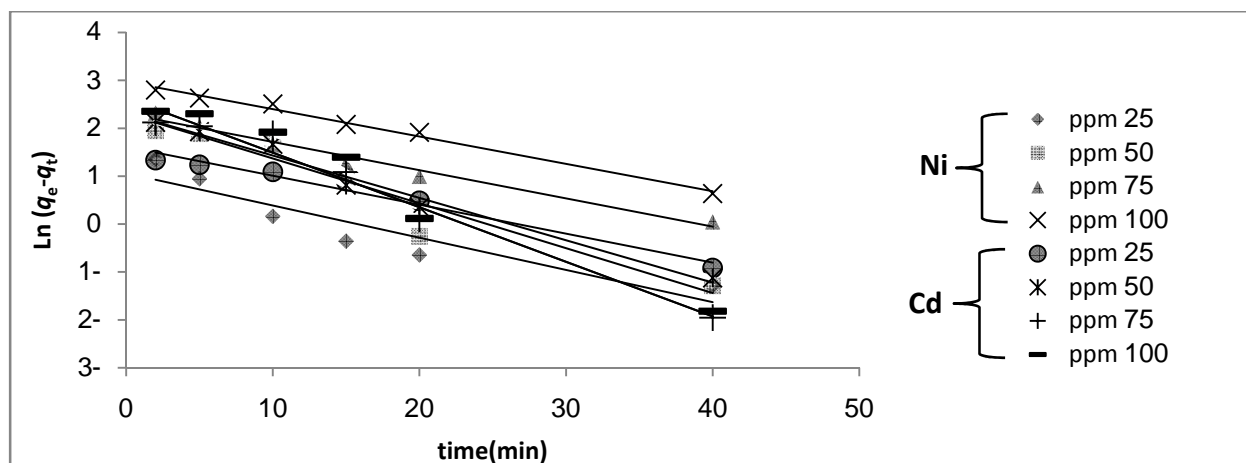


Fig. 2. Pseudo-first-order adsorption kinetics of Ni^{2+} and Cd^{2+} at different initial concentrations.

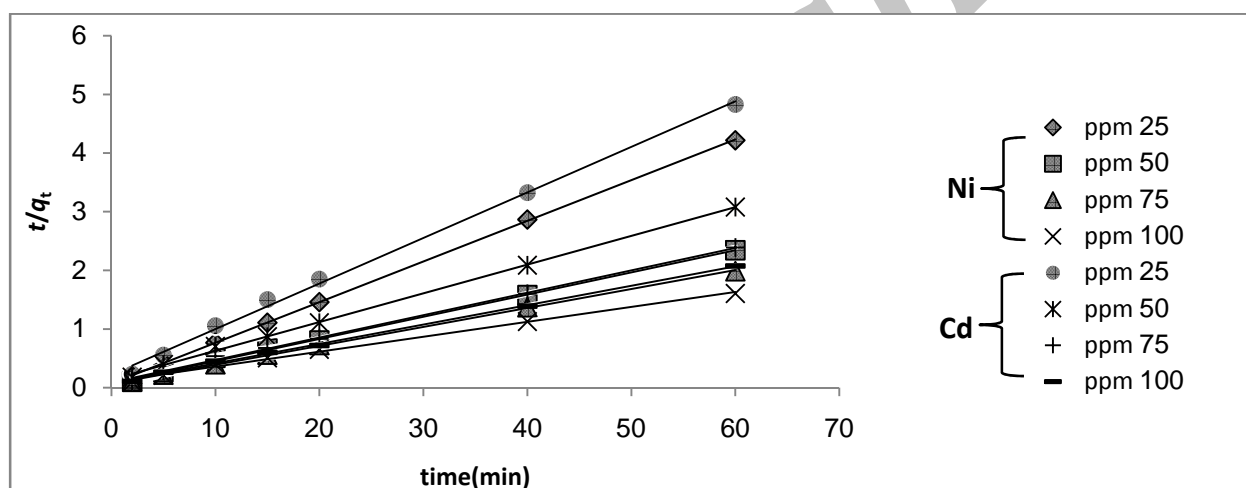


Fig. 3. Pseudo-second-order adsorption kinetics of Ni^{2+} and Cd^{2+} at different initial concentration.

The pseudo-second-order adsorption kinetic plots indicate higher correlation coefficient (R^2) and the adsorption kinetic data have better conformity with the pseudo-second-order kinetic model than pseudo-first-order one.

The values of the correlation coefficient for the pseudo-second-order kinetic model are greater than 0.995, and the adsorption capacities calculated by this model are also close to those determined experimentally. So, the pseudo-second-order adsorption model is more suitable than pseudo-first-order one to describe the adsorption kinetics of $\text{Ni}(\text{II})$ and $\text{Cd}(\text{II})$ onto MSTL.

Adsorption isotherms

Adsorption process depends strongly on experimental conditions such as metal ion concentration, pH, competing ions and particle size [17]. Cadmium ions are found to be adsorbed to a lesser extent than nickel ions, due to the formation of their complexes with ligands bearing amino and hydroxyl groups existing at MSTL. In the other hand, the ionic radius of $\text{Cd}(\text{II})$ is greater than $\text{Ni}(\text{II})$. So, nickel ions have a high charge density compared with cadmium ions and were adsorbed to a higher extent on the MSTL. In this study, we applied Langmuir and Freundlich

isotherm models to interpret of collected data in Table 4. The non-linear form of Langmuir isotherm model is given as following expression:

$$q_e = \frac{q_m b C_e}{1 + b C_e}, \quad (6)$$

and the separation parameter from the Langmuir equation can be obtained using the following equation:

$$R_L = \frac{1}{1 + b C_0} \quad (7)$$

where q_e is the adsorption capacity at equilibrium time (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (mg L^{-1}), C_0 is the initial concentration of metal ions (mg L^{-1}), q_m the ultimate capacity (mg g^{-1}), b the intensity of adsorption (L mg^{-1}), also known as binding constant.

The Langmuir model was linearised to obtain the parameters q_m and b from experimental data by plotting inverse of the adsorption capacity versus inverse of the equilibrium concentrations.

The non-linear form of Freundlich

adsorption isotherm model is given as follows:

$$q_e = k_F C_e^{1/n}, \quad (8)$$

where k_F is the Freundlich adsorption constant and $1/n$ is the Freundlich exponent, which can be calculated from plotting logarithm of the adsorbent loading versus logarithm of the equilibrium concentrations.

Data collected for nickel and cadmium were fitted well by both Langmuir and Freundlich models with higher correlation coefficient, and it mainly confirms the presence of a monolayer adsorption. The values of separation parameter which can be calculated by the Eq. (7) are in the range of 0.55–0.21 for both metal ions an initial concentration of 25–100 mg L^{-1} , respectively. Separation parameter in the range of 0–1 indicates that the adsorption process is favourable. The isotherm simulations using the Langmuir and Freundlich models for Ni(II) and Cd(II) adsorption are shown in Figs. 4(a) and (b), respectively.

Table 4. Adsorption isotherm coefficients obtained from Langmuir and Freundlich models (pH 5.00 for Ni^{2+} and 4.00 for Cd^{2+} solutions; s/l ratio 1.0 g L^{-1} ; contact time 180 min)

Models	Metal ion	q_m	b	R^2
Langmuir	Ni^{2+}	55.55	0.033	0.991
	Cd^{2+}	38.46	0.038	0.993
Freundlich	Ni^{2+}	k_F	n	R^2
	Cd^{2+}	4.27	1.90	0.968
		3.59	2.03	0.998

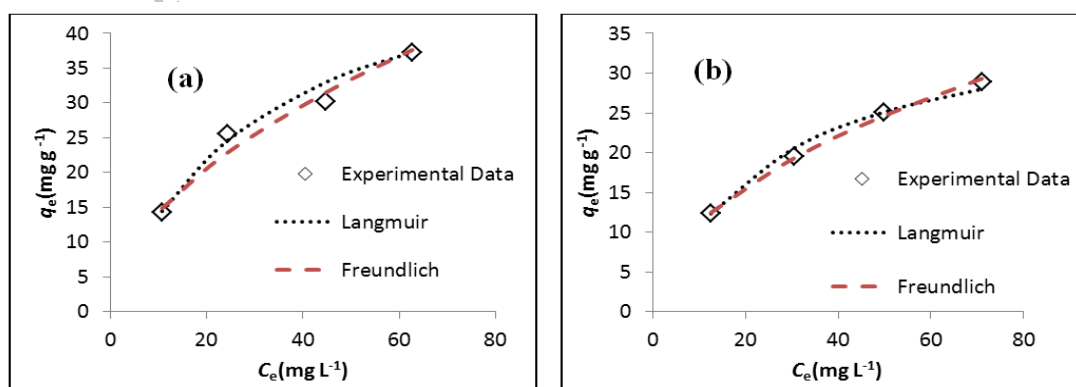


Fig. 4. Comparison of estimated Langmuir and Freundlich isotherms with experimental data for (a) Ni^{2+} and (b) Cd^{2+} adsorption onto MSTL.

Adsorption mechanism

In order to interpret the mechanism of adsorption Ni (II) and Cd(II) onto MSTL, the experimental data are further analyzed by the models named intraparticle diffusion and Boyd kinetic model. The formation of these models is as follows:

$$q_t = k_i t^{0.5} + C \text{ (Intraparticle diffusion model),} \quad (9)$$

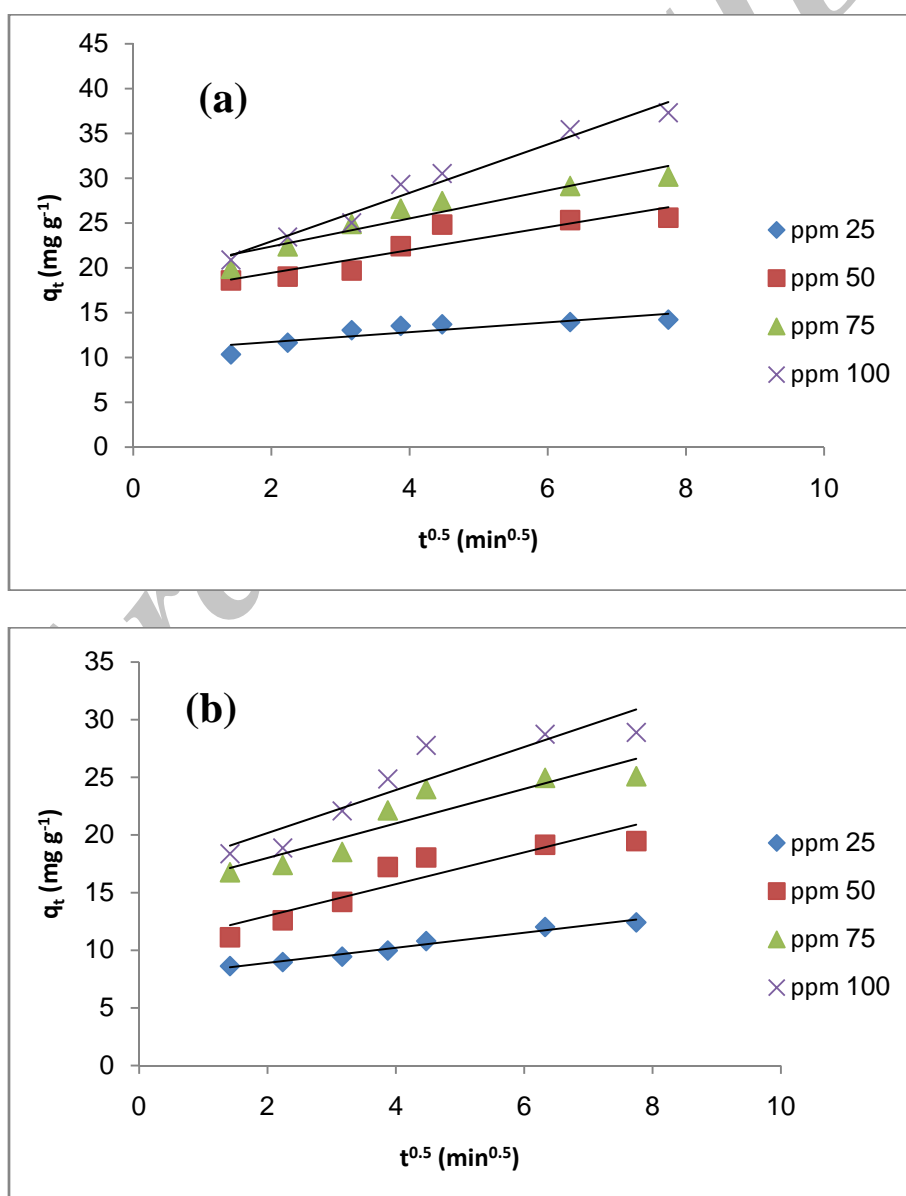
$$F = 1 - \frac{6}{\pi^2} \exp(-Bt) \text{ (Boyd kinetic model),} \quad (10)$$

where k_i ($\text{mg g}^{-1} \text{ min}^{-0.5}$) is the rate

constant of the intraparticle diffusion model and C is the intercept [18]. Since F is equal to q_t/q_e , Bt could be represented as follows:

$$Bt = -0.4977 - \ln(1 - F), \quad (11)$$

where F is the fraction of metal ions adsorbed at any time t , and Bt is a mathematical function of F . The plots of intraparticle diffusion model for removal of Ni(II) and Cd(II) ions from aqueous solution by MSTL are shown in Figs. 5(a) and (b), respectively. The plots in relation to Boyd kinetic model are also shown in Figs. 5(c) and (d).



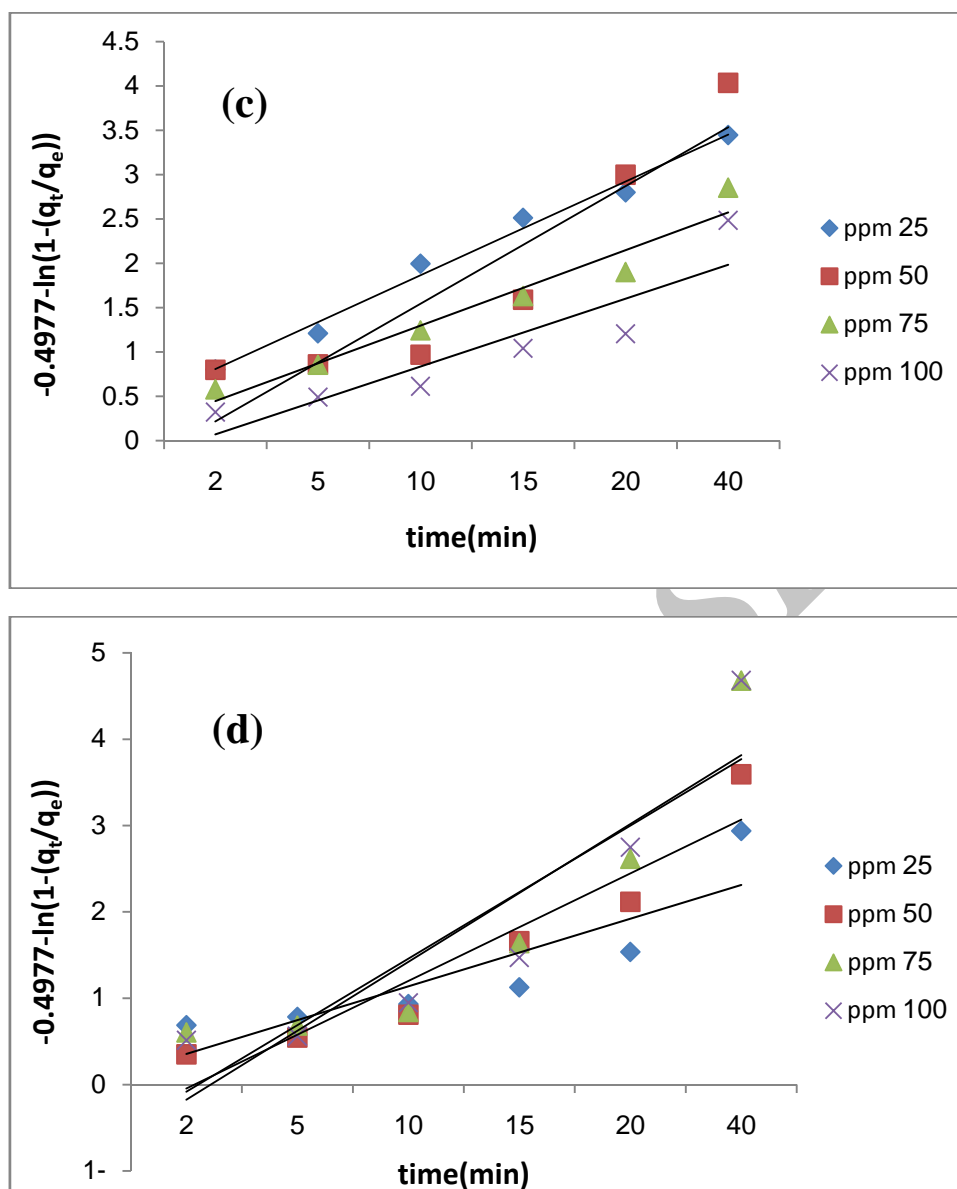


Fig. 5. Adsorption mechanism for the removal of Ni(II) ions (a,c) and Cd(II) ions (b,d) in relation to intraparticle diffusion and Boyd kinetic models by MSTL.

It is shown that all the plots are linear but do not pass through the origin, signifying that external mass transfer is the main rate-controlling step at the initial stages of adsorption process. This indicates that some degree of film diffusion controls the rate of adsorption process and this is further confirming that the intraparticle diffusion is not only the rate-controlling step. When the amounts of metal ions which have reached external of MSTL increase to a certain degree, the sorption

process becomes intraparticle diffusion-controlled [19]. The effective diffusion coefficient, D_i (m^2/s) values were estimated using the following expression:

$$B = \frac{\pi^2 D_i}{r^2}, \quad (12)$$

where D_i is the effective diffusion coefficient and r is the radius of the MSTL particles. The rate constants of the intraparticle diffusion and effective diffusion coefficient values are listed in table 5.

Table 5. Intraparticle diffusion constant and effective diffusivity at different initial metal ion concentration

Metal ion	Initial concentration (mg L ⁻¹)	K_i (mg g ⁻¹ min ^{-1/2}) (pH = 5.00)	D_i (x 10 ⁻⁹) (m ² /s)
Ni ²⁺	25	0.545	1.68
	50	1.275	2.10
	75	1.565	1.35
	100	2.706	1.21
			1.58 (Average)
Cd ²⁺		(pH = 4.00)	
	25	0.654	1.24
	50	1.378	1.98
	75	1.498	2.44
	100	1.867	2.53
			2.05 (Average)

Table 5 shows that k_i increases with increasing initial metal ions concentration. According to Eq. 9, it can be seen that k_i is proportional to q_e . On the other hand, the adsorption capacity at equilibrium (q_e) increases with increasing initial metal ions concentration. So, it is clear that k_i must be increase with increasing initial metal ions concentration.

CONCLUSIONS

The adsorption kinetics, equilibrium and mechanism of Ni(II) and Cd(II) ions onto MSTL have been investigated in the present study. Lagergren pseudo-first-order and pseudo-second-order kinetic models have been applied to fit the experimental data. The results indicate that pseudo-second-order kinetic model is in good agreement with the experimental data. The equilibrium data could be fitted by both Langmuir and Freundlich isotherm models which reflected the monolayer adsorption process. The adsorption mechanism was evaluated by fitting the kinetic data with the intraparticle diffusion and Boyd kinetic models. It is revealed that the intraparticle diffusion is not only the rate-controlling step and there is some degree of film diffusion that controls the rate of adsorption process.

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