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Removal of Cd (II) by polystyrene-base chelating resins: adsorption properties and experiences of industrial wastewater treatment

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ABSTRACT

This study involved the adsorption removal of Cd (II) by "green" chelating PS-DETA resins and its application in a column mode for industrial wastewater treatment. An initial factorial design of experiments showed that factors such as pH of the solution, agitation speed, and contact time were important. Competing adsorption of Cd (Ⅱ) and Zn (Ⅱ) onto the PS-DETA resins in binary system showed that the adsorption affinity may be in the following order: Cd (Ⅱ)>> Zn (Ⅱ). The adsorption kinetics for Cd (II) was found to follow pseudo-second-order reaction. Isotherm studies conducted at 5–500 mg/g of initial Cd (II) concentrations provided the maximum adsorption capacities of 92.1 mg/g for the PS-DETA resins. The Langmuir isotherm model was found to describe adsorption well indicating the monolayer adsorption process. It was evident from results of the desorption studies that desorption efficiency larger than 99.6% could be obtained for Zn (Ⅱ) and Cd (Ⅱ) with 0.1 M HCl or HNO_3. Data from a column study using PS-DETA resins for Cd (II) and Zn (II) from industrial wastewater showed that after approximately 760 BV, removal of Cd (II) achieved 50%. Hence, it was concluded that it was effective to remove Cd (II) from industrial wastewater with the column operation although the adsorption capacity of the PS-DETA resins for Cd (II) and Zn (II) was found to be less than the adsorption capacity obtained in the batch study.

Keywords: PS-DETA; Cd (Ⅱ) recovery; Column study; Selective adsorption; Industrial wastewater

1. Introduction

Cadmium is a toxicant mostly found in the effluent from manufacturing, construction, and chemical industries and considered as one of the most common heavy metal pollutants because of its numerous industrial applications [1,2]. On the other hand, Zn (II), as a trace element, is essential for nutrition and necessary for growth of animals and vegetation, especially in their infancy time [3]. Therefore, in the view of removal of toxic heavy metal and saving energy and resource for natural nutrients, it could be a win-win way to recover Cd (II) from cadmium bearing wastewater without

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cleaning of other trace metals such as Zn (II). Adsorption process has been considered as one of the most efficient and easy techniques for heavy metals treatment from aqueous solutions among many other methods and applied widely especially in the developing countries so that low-cost adsorbents have been attracted much attention recently [4,5]. Naiya et al. studied the adsorption of saw dust and neem bark from India towards Cd (II) with the maximum capacity of 26.73 and 25.57 mg/g, respectively by a batch mode [6]; Huang et al. found in a batch procedure the maximum amount of Cd (II) adsorbed (q_{max}) was 22.23 mg per gram of HACC–bentonite from China at pH 7.0 and 20˚C [7]. Batch adsorption experiments were conducted for the adsorption of Cd (II) ions from aqueous solution by Wang et al. using bamboo charcoal from China with the maximum capacity of 12.08 mg/g [8]; Farooq et al. reported the adsorption of Cd (II) onto wheat (*Triticum aestivum*) from Pakistan (maximum capacity: 39.22 mg/g) using batch mode [9]. However, it is evident that each adsorption capacity of these low-cost adsorbents is relatively low and almost all experiments are shortage of dynamic data which are important for industrial design. Another reason for the limited application of these reported adsorbents may be due to their natural properties such as low mechanical strength, unsuitable shape (powder) and weak stability in acid or alkaline solutions. Hence, to find cost-effective adsorbents with practical utility on commercial scale is still of significance currently.

So far, solid chelating resins with good selectivity and easy operation are usually on the top when the problems of regeneration and stability are addressed. Because it is inexpensive, readily available in different particle sizes and possesses high mechanical rigidity, polystyrene-base support material is of great advantage in environmental application [10]. On the other hand, the amino groups which can provide reactive sites for specific adsorption of various metal ions has been regarded as one of the most effective chelate functional groups for removal and recovery of heavy metal ions from wastewater [11–13]. While the high cost and hazardous organic solvents used during the process of modification limit their application further in terms of environmental friendly requirement. Recently, a series of chelating resins containing amino group were prepared in water phase and moderate conditions in our lab [14]. It was reported that because of C–N bond connected in these cheap and tractable resins are more stable than traditional EDTA chelating resins which connect with ester bonds. Hence, it would be much meaningful to apply these "green", versatile adsorbents to treatment of heavy metals from water and wastewater. In present study, adsorption and desorption of Cd (II) and Zn (II) from aqueous solutions onto PS-DETA resins from both single and binary systems were investigated in batch and column experiments for process design and optimization.

2. Materials and methods

2.1. Materials

PS-DETA resins as adsorbents were prepared from chloromethylated polystyrene beads by reacting with diethylenetriamine in aqueous phase according to the method previously reported [10]. The synthetic scheme and proposed mechanisms for metal ions combination were shown in Fig. 1 whereas the composition and some properties of PS-EDTA resin were shown in Table 1. The metal ion solutions were prepared by dissolving $Cd(NO_3)_2$ and $Zn(NO_3)_2$ with distilled water without pH adjustment, respectively. In several cases, the pH of the aqueous solution was controlled by the addition of 0.1 N HCl and NaOH solution. Industrial wastewater containing Cd and Zn ions was collected from electroplating industries in Lanzhou, Gansu, and China and characterized using standard methods as shown in Table 2 [15]. The wastewaters were diluted to the required concentration and used with the optimized pH value and adsorbent dosage obtained from batch experiments. The concentrations of Cd and Zn ions in solutions were determined using a GBC Avanta A 5450 atomic absorption spectrophotometer. The pH of solutions was determined using a HANNA pH meter.

2.2. Batch experiments

2.2.1. Adsorption in single system

Adsorption experiments were carried out in different standard joint-stoppered round-bottom conical flasks (capacity 250 mL) on a temperature-controlled shaker incubator. To investigate the optimum agitation speed, a fixed amount W (0.2 g) of dried PS-DETA resins and 100 mL Cd (II) or Zn (II) ions solutions were transferred into each flask. The flasks were then sealed and shaken at 50–150 rpm on a horizontal shaker for 24 h at constant temperature; in the pH studies, 0.2 g PS-DETA resins were added into 100 mL Cd (II) or Zn (II) ions solutions with a range of pH values 3.0–7.0 in a shaker at the optimum speed

In kinetic experiments, the effects of contact time on PS-DETA resins was studied by shaking 100 mL Cd (II) or Zn (II) ions solutions with 0.2 g of PS-DETA resins at 298 K. Samples of 0.1 mL were taken at predetermined time intervals for the analysis of the Cd (II) or Zn (II) ions in the solution.

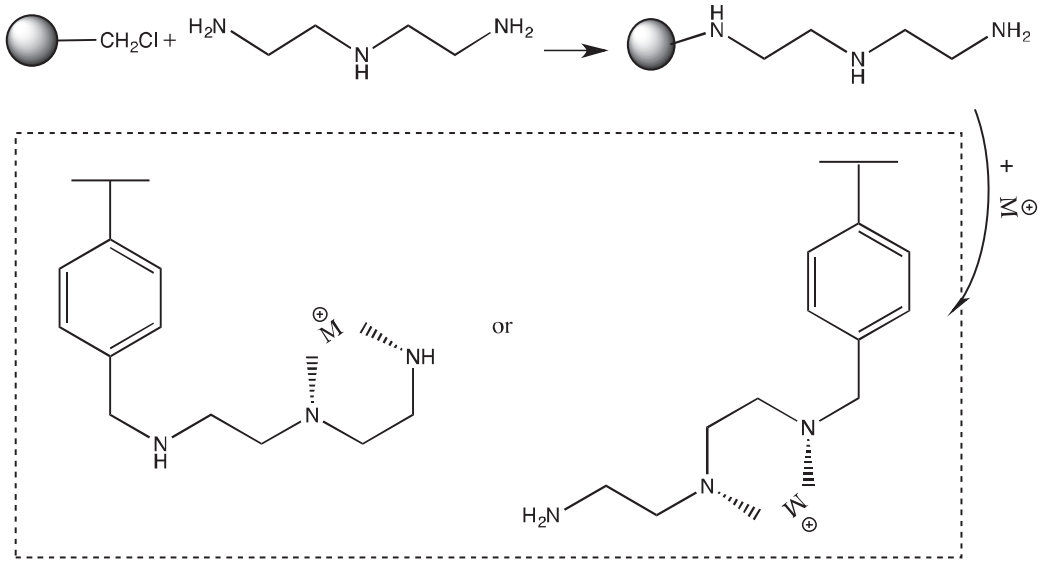

Fig. 1. Synthetic route of PS-DETA resins and possible chelating mechanisms (M: metal ions).

Table 1
Composition and some properties of PS-DETA resin [10]

N (%)	C (%)	H (%)	Amino (mmol/g)	BET surface area (m^2/g)	Exchange capacity (mmol/g)	
					For acid	For base
9.69	73.14	8.079	6.918	39.6	5.566	0.133

For determination of equilibrium adsorption isotherm and to study the effect of initial Cd (II) or Zn (II) ions concentration on PS-DETA adsorption, 0.2 g of PA-DETA resins and 100 mL of various concentrations (10–500 ppm) of Cd (II) or Zn (II) ion solutions were shaken for 2 h. Afterwards, the PS-DETA resin was filtered off and the concentration of metal ion in the filtrate is determined. The adsorption capacity of the PS-DETA resin and the percentage removal of Zn (Ⅱ) or Cd (II) are calculated using Eqs. (1) and (2), respectively:

$$q_t = \frac{(C_i - C_e)v/1,000}{W} \quad (1)$$

$$\%\ \text{Removal} = \frac{C_i - C_o}{C_i} \times 100 \quad (2)$$

where q_t is the adsorption capacity in $mg\,g^{-1}$ at time t; C_i,C_o and Ce are the initial, outlet, and equilibrium concentration of metal ions in mg L^{-1}; V is the volume of Zn (Ⅱ) or Cd (II) ion solution in mL; and W is the total amount of resins in g.

2.2.2. Adsorption in binary system

To examine the adsorption properties of Cd (II) and Zn (Ⅱ) onto PS-DETA resins in detail, competitive adsorption experiment was conducted in the binary systems. A 0.2 g of PS-DETA resins was added into a test solution (100 mL) containing both Cd (II) and Zn (Ⅱ) with the concentration of 50 mg/L. The adsorption conditions were kept at the optimum speed and contact time.

2.2.3. Desorption

In order to remove the loaded Cd (Ⅱ) and Zn (Ⅱ) ions and make the sorption process more economical through repeated use of the sorbent, desorption and

Table 2
Characterizations of wastewater of electroplating industry

pH	Conductivity ms/cm	Tds mg/L	Turbidity NTU	COD mg/L	Sodium mg/L	Calcium mg/L	Cadmium mg/L	Zinc mg/L	Sulfate mg/L	T ℃
5.6	19.87	10.233	6	73	329	42	50.84	41.5	143	16.4

regeneration experiments of PS-DETA resins were carried out as follows: after adsorption experiment with 200 mg/L Cd (II) and Zn (II) at 0.2 g of PS-DETA resins in 100 mL, the Cd (II) and Zn (II) loaded samples were separated by filtration and washed with distilled water to remove any unabsorbed Cd (II) and Zn (II). Five kinds of reagents including alkaline and acid solution (0.1 M NaOH, HCl, HNO_3, NaCl, and $NaNO_3$) were used as the desorbing agent for the recovery of Cd (II) and Zn (II) from metal-loaded PS-DETA resins. Following desorption experiments were performed with the process condition similar to the batch experiments.

2.3. Column experiments

This experiment was performed in small scale cylindrical fixed-bed columns with 8 mm internal diameter where the packing density was controlled at about 600 g L^{-1}. The PS-DETA resins were packed up to a desired bed height (30, 40 and 50 mm) in the column. The columns were mounted vertically and glass wool used at the bottom of the column acts as supporting materials of the adsorbent bed and also filters of the adsorbent particles. Then, the resins were pre-washed by flowing deionized water for 1 day to clean excess light metal ions that could leach out and interfere with the analysis. The column was operated in the downflow mode using a peristaltic pump with a solution of metal ions bearing industrial wastewater and influent flow rate (0.5, 1 and 2 mL min^{-1} (that is 0.99, 1.99 and 3.98 mL $min^{-1}cm^{-2}$)). The bed volume was equal to 2.01 mL (bed height 40 mm) and the empty bed contact time was 2 min. Initial pH of the metal solution was set at the optimum pH. The effluent was collected at a very short interval initially, and then the interval was extended. Samples were analyzed periodically to determine the ions concentration in the effluent. Once the ratio of effluent to influent concentration reached a value of approximately 0.5 or higher, the column study was terminated. At this point, the column was considered to have reached exhaustion.

3. Results and discussion

3.1. Adsorption of Cd (II) and Zn (II) in batch mode

3.1.1. Effect of the solution pH

The effect of pH on Cd (II) and Zn (II) removal was investigated in the pH range of 3.0–8.0 at 298 K for 1.5 h as shown in Fig. 2. From the corresponding data, at the beginning, an increase in pH corresponds to an increase in adsorption, reaching the maximum adsorption rate at pH 6.0. With the pH increased from 4.0 to 6.0, the adsorption capacity of Zn (II) and Cd (II) increased to 103.5 and 86.7 mg/g, respectively. On higher pH values, a decrease of adsorption for both Zn (II) and Cd (II) was observed. The generation of hydrolyzed species of Zn (II) and Cd (II) such as $Zn(OH)^+$ and $Cd(OH)^+$ at pH higher than 6.0 could promote a reduction of the adsorption capacity, due to the diminution of the formal charge of the metallic ion. They require acidification to prevent the formation of polynuclear hydroxo-bridged species or the precipitation of basic salts [16]. In general, adsorption of Zn (II) and Cd (II) was affected significantly by pH values. It should be stressed that, the maximum metal uptake at pH 6.0 allows this low-cost chelating resin to be used for Zn (II) and Cd (II) removal in a

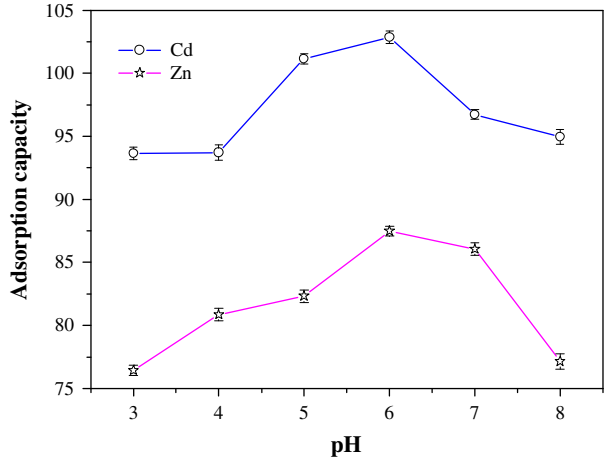

Fig. 2. Adsorption capacity of Zn (II) and Cd (II) onto PS-DETA resin as a function of pH.

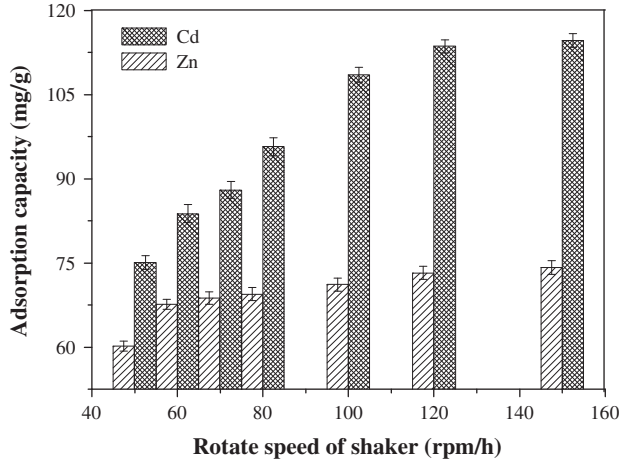

Fig. 3. Adsorption capacity of Zn (II) and Cd (II) onto PS-DETA resin as a function of agitation speed.

moderate condition and has less negative effect on the water environment in terms of acidity and alkalinity of solutions.

3.1.2. Effect of the agitation speed

To get the optimum operation conditions, different agitation speeds of shaker in the ranges of 50–150 rpm/h were applied in the batch mode. It can be seen from Fig. 3 that at the beginning, an increase in the agitation speed corresponds to an increase of both Zn (II) and Cd (II) in adsorption, reaching the maximum adsorption capacity at 120 rpm/h. However, with the speed increased from 120 to 150 rpm/h, the adsorption capacity of both Zn (II) and Cd (II) nearly kept instant. So, considering of the electricity cost-effective and protecting of the PS-DETA resins in the following experiments the speed of 120 rpm/h were set.

3.1.3. Effect of the contact time

The effect of contact time to the adsorption capacity of the PS-DETA resin was investigated in the time range of 2–120 min under natural pH at 30°C. The adsorption data for metal uptake vs. contact time for a fixed adsorbent amount are shown in Fig. 4. It was observed that the maximum capacity of adsorption of the PS-DETA resin for Zn (II) and Cd (II) was 66.64 and 92.55 mg/g, respectively. According to these data, equilibrium is achieved at around 100 min at 100 mg/L solutions. However, to be sure of the best adsorption conditions at higher concentration levels and to obtain equilibrium at the solid/liquid interface, all the experiments were carried out with 120 min of contact

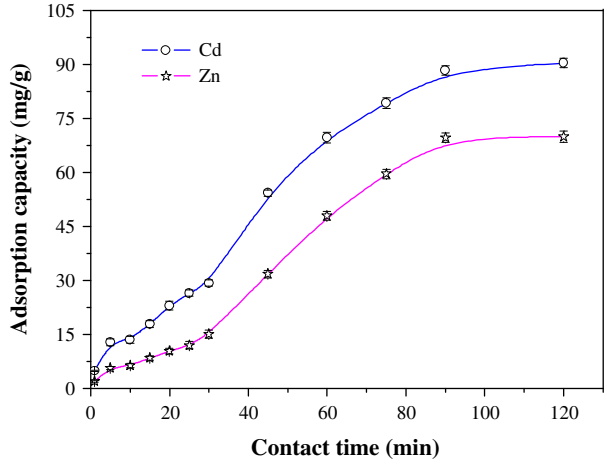

Fig. 4. Adsorption capacity of Zn (II) and Cd (II) onto PS-DETA resin as a function of contact time.

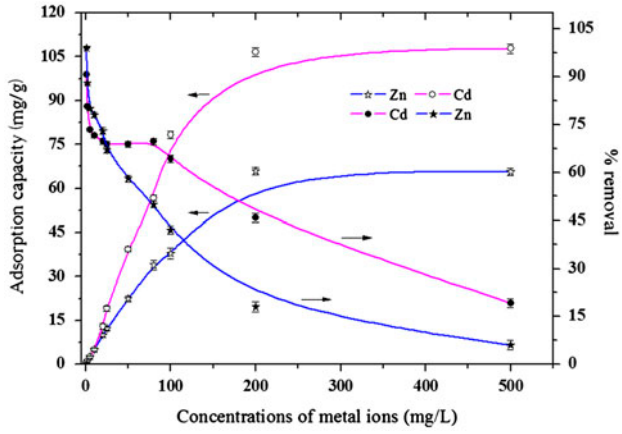

Fig. 5. Adsorption capacity of Zn (II) and Cd (II) onto PS-DETA resin as a function of initial concentration.

time. This short time period required to attain equilibrium suggests a good affinity of the adsorbent for Zn (II) and Cd (II) from aqueous solution.

3.1.4. Effect of the initial Zn (II) and Cd (II) concentrations

Initial Zn (II) and Cd (II) concentration was adjusted, respectively in the ranges of 1–500 mg/L for adsorption on the chelating resin under natural pH at 30°C for 120 min as shown in Fig. 5. The increasing initial metal ions concentration resulted in an increase in the metal ions on the resin. At the lower concentrations, Zn (II) and Cd (II) in the solution would interact with the binding sites and thus facilitated more than 90% adsorption for the adsorbent. With increasing metal ion concentration, there is an increase in the amount of metal ion adsorbed due to increasing driving force of the metal ions towards the active sites on the adsorbents. So, at higher concentrations, more Zn (II) and Cd (II) were left unadsorbed in solution due to the saturation of binding sites. However, there is a decrease in the active sites on the sorbents as more metal ions are adsorbed, when Zn (II) concentration reached 100 mg/L, adsorption capacity was only 34.1 mg/g, and the percentage removal was merely 17.2% while it was 36.7% when the concentration of Cd was 100 mg/L. As can be seen from Fig. 5, the adsorption capacity on the resin in 200 mg/L of both Zn (II) and Cd (II) solution reached the maximum while the percentage removal is much lower than that in 100 mg/L. It was observed that the percentage removal larger than 60% was obtained when the initial concentration of Zn (II) or Cd (II) was 50 mg/L and the higher percentage removal was observed as the concentration decreased. This

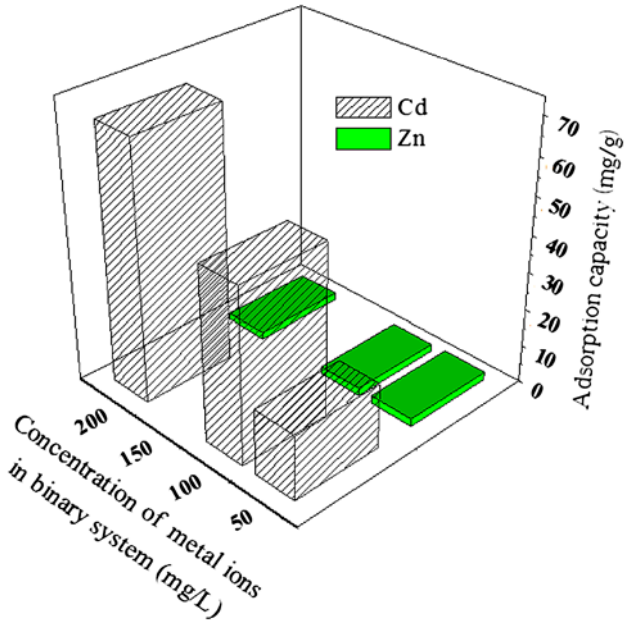

Fig. 6. Competitive adsorption of Zn (II) and Cd (II) onto PS-DETA resin in binary system.

indicates that this chelating resin was suitable for micro-polluted water with Zn (Ⅱ) and Cd (Ⅱ) of low concentrations (1–50 mg/L).

3.1.5. Competitive adsorption of Cd (Ⅱ) and Zn (Ⅱ) onto PS-DETA resins

Adsorption of co-existing metal ions i.e. Cd (Ⅱ) and Zn (Ⅱ) onto the PS-DETA resins was examined in binary system, and the results are presented in Fig. 6. As shown in Fig. 6, in general, the adsorption amount of Zn (Ⅱ) onto the PS-DETA resins decreased with the increases in the concentration of Zn (Ⅱ) and Cd (Ⅱ) varying from 50 to 200 mg/L. In the contrast, Cd (II) adsorption by PS-DETA resins showed the diverse trend and much higher adsorption capacity. It may be concluded that the adsorption affinity of metals onto the PS-DETA resins is in the following order: Cd (Ⅱ)>> Zn (Ⅱ). Initially, Cd (Ⅱ) and Zn (Ⅱ) were observed to be adsorbed onto the PS-DETA resins. After a few minutes, however, Cd (Ⅱ) started to be dominantly adsorbed on the PS-DETA resins attaining equilibrium after 120 min. Zn (Ⅱ) was slightly desorbed from the PS-DETA resins with time and negligible amounts of these metal ions (1.6–2.1 mg/g) had been removed by adsorption. The results were likely due to high adsorption affinity of Cd (Ⅱ) onto the PS-DETA resins which led to Cd (Ⅱ) substitution for Zn (Ⅱ) already adsorbed in the adsorption sites. Rengaraj et al. also reported that favored adsorption of a metal onto the adsorbent can result in desorption of other metals into solution if the adsorption capacity is not sufficient for the less-favored species [17]. These results are of significance in the practical treatment of Cd (Ⅱ) from drinking water or river water with a high removal of Cd (Ⅱ) but keeping the natural nutrient element Zn (Ⅱ) in the water.

3.2. Isotherm models for equilibrium data

Langmuir model has been widely applied to many metal ions sorption process. The basic assumption of the Langmuir theory is that all the adsorption sites have equal adsorbate affinity and that the adsorption at one site does not affect the adsorption at an adjacent site [18]. The model takes the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{3}$$

where q_m is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent (mg g^{-1}) and q_e is the amount adsorbed on unit mass of the adsorbent (mg g^{-1}) when the equilibrium concentration is C_e (mg L^{-1}) and b (L mg^{-1}) is Langmuir constant. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L, also known as the separation factor, given by Eq. (4) [19]:

$$R_L = \frac{1}{1 + bC_0} \tag{4}$$

The value of R_L lies between 0 and 1 for a favorable adsorption, while $R_L > 1$ represents an unfavorable adsorption, and $R_L = 1$ represents the linear adsorption, while the adsorption operation is irreversible if $R_L = 0$.

The Freundlich isotherm theory [20] describes the non-ideal and reversible adsorption, not restricted to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities on the heterogeneous surface [21]. The linear Freundlich isotherm is commonly expressed as follow:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{5}$$

where K_f ($mg^{1-1/n}$ $L^{1/n}$ g^{-1}) and n (g L^{-1}) are the Freundlich constants characteristics of the system, indicating the relative adsorption capacity of the adsorbent related to the bonding energy and the adsorption intensity, respectively.

The equilibrium data for the adsorption of Zn (II) and Cd (II) on PS-DETA resin were tested as shown in Fig. 7. The Langmuir isotherm model was applied to the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the resin surface. The linear isotherm parameters, q_m, and the coefficient of determinations are presented in Table 3. The values of q_m for Zn (II) and Cd(II) (66.7 and 93.1 mg/g) were close to the experimental data (66.64 and 92.55 mg/g) of adsorption capacity that indicated a good adsorption on the PS-DETA resin. The R_L values calculated were between 0.32–0.99 and 0.35–0.99 (Table 3), indicating highly favorable sorption of Zn (II) and Cd (II) on PS-DETA resins.

The regression coefficients of determining R^2 from the linearization of the two two-parameter isotherm models are listed in Table 3. The R^2 values suggest that the two isotherm models provide a good correlation for the sorption of Zn (II) and Cd (II). The good correlation of Langmuir model confirms the formation of a monolayer of Zn (II) and Cd (II) on the surface of the resin while the linear regression of the Freundlich isotherm provided a reasonable fit to the experimental data for Zn (II) and Cd (II) indicating a part of possible chemical reaction during the adsorption process. However, several studies showed that the linearization of a non-linear isotherm expression using data transformations would implicitly alter the error structure and could also violate the error squares [22,23]. To analyze the equilibrium data more accurately, a non-linear isotherm equation was fitted as shown in Fig. 7(c). From this figure, it was evident that the Langmuir isotherm model gave the best mathematical description confirming the monolayer adsorption.

3.3. Kinetic studies of Cd (II) and Zn (II) adsorption onto PS-DETA resins

Lagergren showed that the rate of adsorption of solute on the adsorbent is based on the adsorption capacity and followed a pseudo-first-order equation which is often used for estimating k_{ad} considered as mass transfer coefficient in the design calculations [24,25]. The non-linear form of the pseudo-first-order equation is described by Eq. (6):

$$\frac{dq_t}{d_t} = k_{ad}(q_e - q_t) \quad (6)$$

where q_e and q_t are the adsorbed amounts (mg g^{-1}) at equilibrium time and at any instant of time, t,

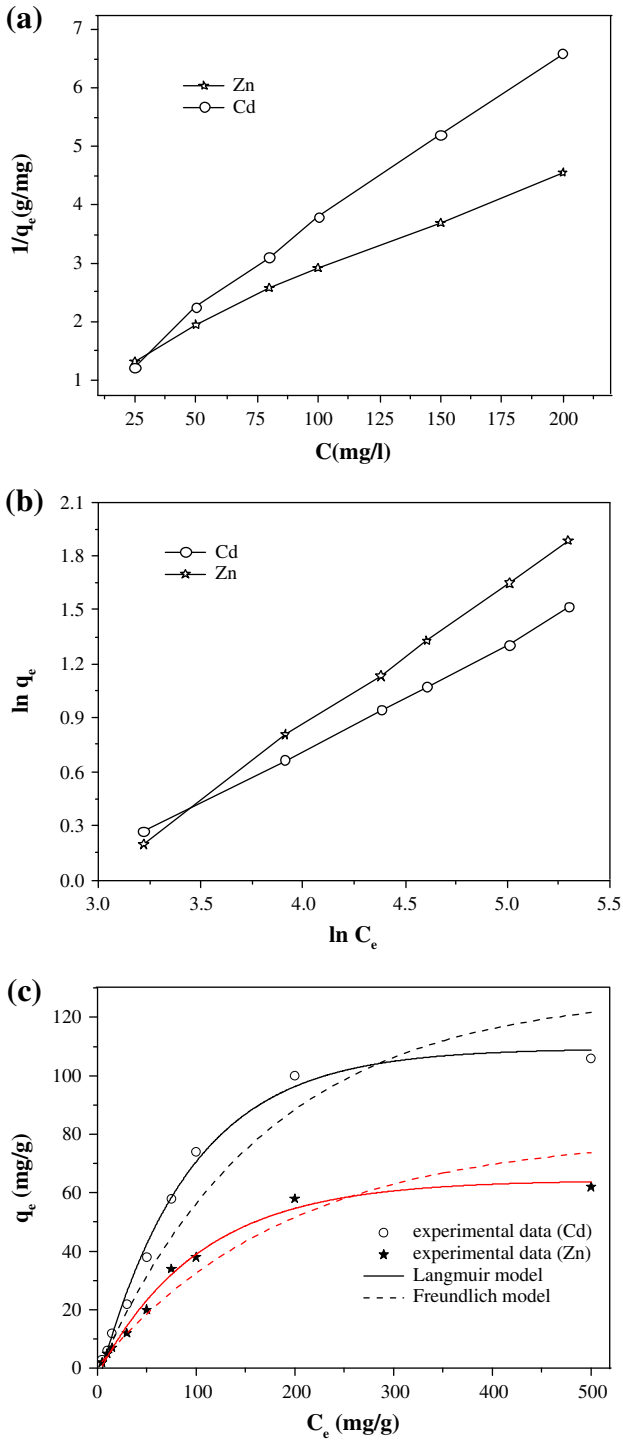

Fig. 7. Adsorption isotherm models ((a) Langmuir and (b) Freundlich models) of Zn (II) and Cd (II) onto PS-DETA resin under pH 6.0.

respectively, and k_{ad} (L min^{-1}) is the rate constant of the pseudo-first-order sorption. The integrated rate law after the application of initial condition of $q_t = 0$ at $t = 0$ becomes a linear equation as given by Eq. (7):

Table 3
Isotherm constants and regression data for various adsorption isotherms for adsorption of Cd (II) and Zn (II) using PS-DETA resins

Ions	Langmuir				Freundlich		
	q_m (mg/g)	b (L/mg)	R_L	R^2	K_f (mg/g)	n	R^2
Cd (II)	89.1	0.012	0.32–0.99	0.991	0.263	1.130	0.978
Zn (II)	63.8	0.015	0.35–0.99	0.99	0.0235	1.156	0.987

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}t}{2.303} \quad (7)$$

The plot of log $(q_e - q_t)$ vs. t gives a straight line for the pseudo-first-order adsorption kinetics, from the adsorption rate constant, k_{ad}, is estimated.

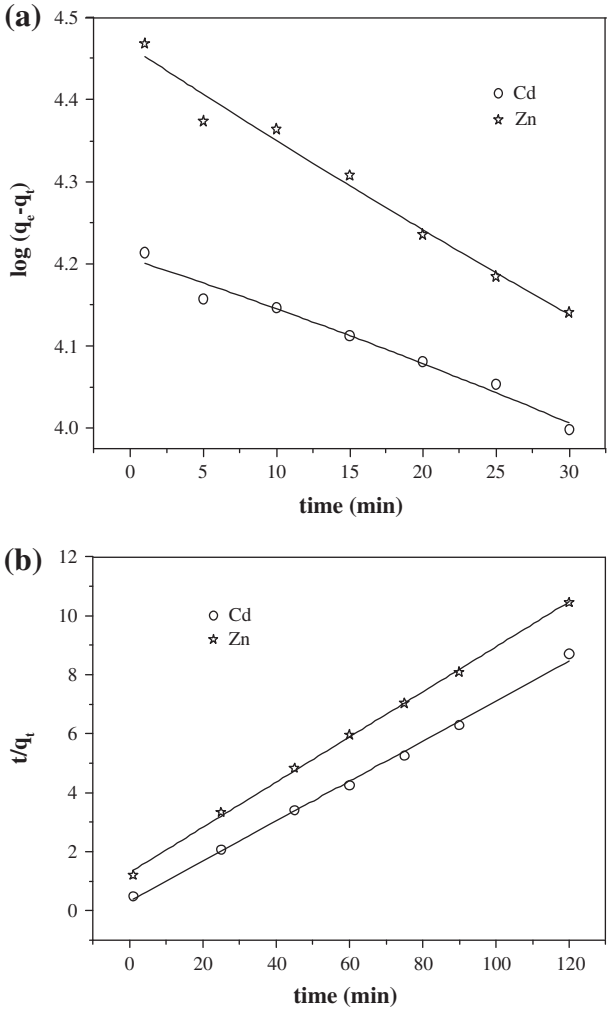

Fig. 8. Adsorption kinetics ((a) pseudo-first order and (b) pseudo-second order) of Zn (II) and Cd (II) onto PS-DETA resin under pH 6.0.

Ho developed a pseudo-second-order kinetic expression for the sorption system of divalent metal ions using sphagnum moss peat [26]. This model has since been widely applied to a number of metal/sorbent sorption systems. The second-order kinetics equation is described in the following form:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (8)$$

where k_2 (g mg^{-1} min^{-1}) is the second-order rate constant. From the boundary conditions, t = 0 to t and q_t = 0 to q_t, the integrated form of the equation becomes Eq. (9):

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (9)$$

Eq. (9) can be written in a linear form, as given by Eq. (10):

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{h} \quad (10)$$

where $h = k_2 q_e^2$ that can be regarded as the initial sorption rate as t approaches 0. Under such circumstances, the plot of t/q_t vs. t should give a linear relationship, which allows the computation of q_e and k_2.

The rate of metal sorption is an important factor and prerequisite for determining the reactor design and process optimization for a successful practical application. The rate kinetics of Zn (II) and Cd (II) adsorption on PS-DETA resin at initial metal ion concentration 200 mg/L, respectively were analyzed as shown in Fig. 8. Degrees of error between experimental and model predicted values were analyzed by employing chi-square test [27] (Eq. (11)):

$$\chi^2 = \sum \frac{(q_t - q_m)^2}{q_m} \quad (11)$$

where q_t and q_m (mg g^{-1}) are total adsorption capacity at time t using experimental data and

Table 4
Calculated kinetic parameters for pseudo-first-order and pseudo-second-order models for the adsorption of Cd (II) and Zn (II) using PS-DETA resins

Initial ions (mg/L)		First order kinetic model			Second order kinetic model			h (mg/gmin^{-1})
		k_1	R^2	χ^2	k_2	R^2	χ^2	
Cd	200	1.2089	0.9081	0.8675	0.4532	0.9973	0.0229	24.324
Zn	200	0.8796	0.9242	0.1978	0.3214	0.9981	0.4563	12.053

predicted model data, respectively. The correlation coefficients (R^2) of pseudo-first-order model are 0.9081 and 0.9242 (Table 4) whereas those of second-order kinetic order are 0.9973 and 0.9981. It also can be seen that χ^2 value for second order is much lesser than first-order kinetic model, suggesting Cd (II) adsorption on PS-DETA resin followed second-order kinetic model. The insufficiency of the pseudo-first-order model to fit the kinetics data could possibly be due to the limitations of boundary layer controlling the sorption process. The experimental data were observed to fit well to the second-order equation. The correlation coefficients (R^2) for the linear plots of t/q_t against t for the pseudo-second equation were observed to be close to 1. These observations suggest that metal sorption by PS-DETA resin followed the second-order reaction, which suggests that the process controlling the rate may be a chemical sorption.

3.4. Desorption and regeneration

The metal ion loaded on the adsorbent creates disposal problem as it is hazardous in nature. This problem may be overcome to some extent by using elution methods which allows recovery of the metal ions in the concentrated solution and the regenerated adsorbents so as to make the sorption process more economical and environmental friendly; and desorption and regeneration potential of PS-DETA resin was investigated. Various desorbing agents were used for the batch desorption studies from the Zn (II)- and Cd (II)-loaded PS-DETA resin. Desorption experiments were performed maintaining the process condition similar to the batch experiments. Results of batch desorption experiment studies were depicted in Fig. 9. It was evident that maximum desorption efficiency was both higher than 99.6% for Zn (II) and Cd (II) with 0.1 M HCl or HNO_3. It was found that adsorption/desorption cycle of PS-DETA resin decreases slightly as the number of cycle increases and more than 95% metal ion (Zn (II) and Cd (II)) removal is possible with 0.1 M HCl using 10 cycles (the data were no shown here).

3.5. Column adsorption of Cd (II) and Zn (II) and breakthrough curve

It was shown from Fig. 10 that the column was able to remove greater than 90% of Zn (II) and Cd (II) up to 1,420 min. The effluent volume at the breakthrough point (50% of the initial concentration) for Zn (II) and

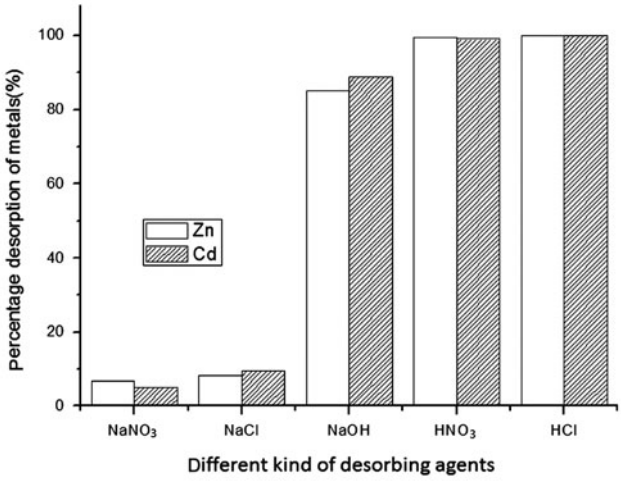

Fig. 9. Desorption of Zn (II) and Cd (II) from PS-DETA resins using various agents.

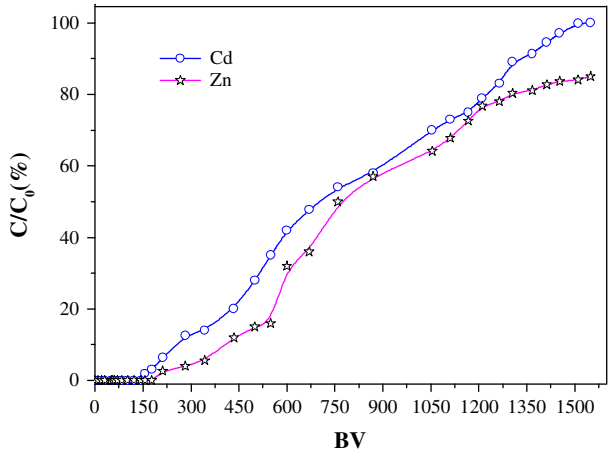

Fig. 10. Breakthrough curves for Zn (II) and Cd (II) removal by PS-DETA resins from industrial wastewater.

Table 5
Parameters for the column adsorption of Cd (II) and Zn (II) from real wastewater using PS-DETA resins

Heavy metal ions	Breakthrough time 50% (h)	Hydraulic loading rate ($m^3/(hm^2)$)	Bed height (m)	Adsorption column capacity (mg/g)
Cd (II)	27	2.5	0.15	37.74
Zn (II)	25	2.5	0.15	19.12

Cd (Ⅱ) was 710 BV (1427.10 mL) and 760 BV (1527.60 mL), respectively. The column reached exhaustion for both Zn (Ⅱ) and Cd (Ⅱ) > 95% of initial concentration) after 1,550 min. The column would need the second cycle at this stage. It was observed that from Table 5, the column adsorption capacity of Cd (Ⅱ) and Zn (Ⅱ) was 37.74 and 19.12 mg/g, respectively. However, when initial Zn (Ⅱ) and Cd (Ⅱ) concentration of 100 mg/L was used, the maximum solid phase concentration of Cd(Ⅱ) and Zn (Ⅱ) on PS-DETA resins in batch isotherm experiments at room temperature was 92.1 and 66.4 mg/g, respectively, much higher than that obtained in the column study. Reduced zinc and copper adsorption capacity of materials compared to that in batch studies was reported by Apiratikul et al. and Vijayaraghavan et al., respectively [28,29]. While, it is notable that the operation using the column of PS-DETA resins was effective for cadmium removal from real industrial wastewater.

4. Conclusions

A simple and "green" chelating PS-DETA resin was prepared as an adsorbent to remove Cd (Ⅱ) from synthetic and electroplating wastewater. The maximum adsorption capacity of PS-DETA resins for Cd (Ⅱ) was higher than rice husk (29.43 mg/g) and other biomasses (1.6–39 mg/g). From kinetic studies, it was found that the adsorption of Cd^{2+} was fast and it reached equilibrium around approximately 100 min. The adsorption kinetics of Zn (Ⅱ) and Cd (Ⅱ) were found to follow pseudo-second-order model, indicating the applicability of this kinetic equation for this system and the process controlling the rate may be a chemical sorption. The equilibrium adsorption data were tested and it was found that Langmuir isotherm models fit the experimental data better. It suggests that there may be two stages for Zn (Ⅱ) and Cd (Ⅱ) adsorption onto PS-DETA resins: a chemical adsorption stage where the functional groups as binding sites played the most important role during the initial 70 min; and the surface monolayer adsorption stage where the physical adsorption prevailed due to the pore structure on the surface of PS-DETA resin and the extremely few unoccupied sites of the adsorbent. In the column operation for clean of Cd (Ⅱ) from industrial wastewater, 50% of removal was found after about 760 BV. Based on the analysis, although the adsorption capacity of the resins for Cd (Ⅱ) and Zn (Ⅱ) was found to be 37.74 and 19.12 mg/g, which was less than the maximum adsorption capacity obtained in the batch mode, it is effective for Cd (Ⅱ) removal from complex industrial wastewater (> 95% after 1,440 BV) using PS-DETA resins.

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