



## Kinetics and equilibrium of desorption removal of copper from magnetic polymer adsorbent

Jyi-Yeong Tseng<sup>a</sup>, Ching-Yuan Chang<sup>a,\*</sup>, Chiung-Fen Chang<sup>b</sup>, Yi-Hung Chen<sup>c</sup>, Chia-Chi Chang<sup>a</sup>, Dar-Ren Ji<sup>a</sup>, Chun-Yu Chiu<sup>d</sup>, Pen-Chi Chiang<sup>a</sup>

<sup>a</sup> Graduate Institute of Environmental Engineering, National Taiwan University, 71 Chou-Shan Road, Taipei 106, Taiwan

<sup>b</sup> Department of Environmental Science and Engineering, Tunghai University, Taichung 407, Taiwan

<sup>c</sup> Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 106, Taiwan

<sup>d</sup> Department of Cosmetic Science and Application, Lan-Yang Institute of Technology, I-Lan 261, Taiwan

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### ABSTRACT

This study examined the desorption of copper ions, which were adsorbed on the magnetic polymer adsorbent (MPA) of polyvinyl acetate-iminodiacetic acid (M-PVAC-IDA), by ethylenediaminetetraacetic acid (EDTA). Stage-wise desorptions were applied to remove the Cu(II) ions from the Cu(II) adsorbed M-PVAC-IDA (A-M-PVAC-IDA). About seven desorption runs were needed to regenerate the A-M-PVAC-IDA. The Cu(II) desorbed M-PVAC-IDA (D-M-PVAC-IDA) was then reused to adsorb the Cu(II) ions from the Cu(II) ions-containing solution. The cyclic adsorption and desorption operations (CADOs) were performed to further elucidate the kinetics and equilibria of the desorption system of EDTA/A-M-PVAC-IDA and the adsorption system of Cu(II)-containing solution/D-M-PVAC-IDA. Two simple kinetic models, the pseudo-first-order equation and pseudo-second-order equation, were employed to simulate the kinetic behaviors of adsorption and desorption. With respect to the kinetics of adsorption behavior, the simulated results by both kinetic models exhibit good agreement with the experimental data. However, the adsorption capacities ( $q_e$ ) estimated by the pseudo-first-order equation are more accurate in comparison with those simulated by the pseudo-second-order equation. As for the desorption kinetics, the examination of correlation coefficients of model fittings of data shows that the pseudo-first-order kinetic model gives the better agreement for the cases with different initial solid-phase concentrations and can accurately compute the equilibrium concentrations of solid-phase. The values of  $q_e$  after CADOs are consistent with the predicted results via the previous work, evidencing that the adsorption behavior and the characteristics of the regenerated adsorbent of D-M-PVAC-IDA were not altered. In the experiments of desorbing copper ions and CADOs, the desorption isotherm was set up. The Freundlich and Langmuir adsorption (or desorption) isotherms were used to simulate the equilibrium of desorption. The results indicate that the Freundlich equation shows better agreement with the experimental data than the Langmuir equation. The information thus obtained is useful for the better use of M-PVAC-IDA on the removal of heavy metal ions of Cu(II) from the Cu(II) ion-containing water solution with the consideration of its regeneration.

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### 1. Introduction

Printed circuit board (PCB) is an important production item in electronic manufacturing industry. However, due to its complicated manufacturing with the use of a lot of chemicals and special substances, the wastewater produced during process leads to heavy pollution. The characteristics of pollution tend to become more complex with more requirements of products. The contents of the aged pickling solution contain primarily Cu(II) ion and some organ-

ics. At present, the heavy metals-containing wastewater of the PCB plant is commonly treated by chemical coagulation and precipitation [1]. The treatment uses alkaline compounds, such as sodium hydroxide or calcium hydroxide, to assist the formation of insoluble hydroxides with heavy metals. The heavy metal-containing sludge after stabilization or solidification to meet the regulation standards is then disposed in the landfill of hazardous materials. The organics in wastewater can be handled by the traditionally biological processes of the secondary treatment and/or the activated carbon adsorption [2–4] and advanced oxidation processes [5–7] of the tertiary treatment so as to meet the effluent standards. Nevertheless, either chemical precipitation or biological treatment can cause the sludge problem. Moreover, the solidification results in a

\* Corresponding author. Tel.: +886 2 23638994; fax: +886 2 23638994.  
E-mail address: [cychang3@ntu.edu.tw](mailto:cychang3@ntu.edu.tw) (C.-Y. Chang).

large volume of treated sludge which may also have potential risks of leaching of heavy metals. Therefore, better techniques are needed for treating the heavy metals of aged pickling solution in the PCB plant.

Recently, there have been growing interests in using adsorption materials with large specific external surface area, easy recycling, and high reusability [1,8–15]. Among them the synthesized magnetic polymer adsorbent (MPA) of micro-size has been used to recover heavy metal Cu(II) from the aged pickling solution in the PCB plant [1]. The MPA is essentially non-porous, thus preventing the clog problem and having good regeneration ability. Furthermore, it is easy to apply the chemical modification to change the chemical characteristics of the surface of polymer adsorbent. Therefore, the surface modified adsorbents can have high affinity to some specific substances. However, for the beneficial application of such tiny adsorbents, one should consider the recovery of adsorbents from the treated water after use. The tiny particles are too small to have good recovery efficiency via the conventional processes, such as gravity sedimentation, centrifugal separation, and filtration. Thus, the magnetic adsorbents were synthesized for the use so that a high gradient magnetic (HGM) force field can be applied to separate and recover them from the treated water after the adsorption process. Another advantage of the HGM separation is that the non-magnetic impurities can be excluded during the recovery of magnetic adsorbents [16–21].

Previous work had described the syntheses of MPA and magnetite-polyvinyl acetate-iminodiacetic acid (M-PVAC-IDA), and the chemical modification to enhance the affinity of adsorbent to adsorb Cu(II) ion of the aged pickling solution [1]. Meanwhile, the adsorption isotherms were set up for three different pH values of 1, 2, and 4.5. Due to the super-paramagnetic property of M-PVAC-IDA, it is convenient to recover the magnetic adsorbent from the treated solution via the HGM separator. The magnetically separated adsorbents can be regenerated via the desorption and then recycled for the reuse of adsorption again [1]. Thus the objective of this study is to examine the desorption of Cu(II) from the exhausted or Cu(II) adsorbed M-PVAC-IDA (denoted as A-M-PVAC-IDA) adsorbents, including the corresponding desorption isotherm, the prediction of the desorption equilibrium isotherm, and the kinetic models of adsorption and desorption of the system of Cu(II) ion and M-PVAC-IDA, which have not been reported. Ethylenediaminetetraacetic acid (EDTA) solution was used to desorb Cu(II) from the A-M-PVAC-IDA by stage-wise desorption operation. Furthermore, cyclic adsorption and desorption operations (CADOs) were performed. For the adsorption in CADOs, the regenerated or Cu desorbed M-PVAC-IDA (noted as D-M-PVAC-IDA) was used to adsorb the Cu(II) ion from the Cu(II) ion-containing solution. As for the desorption in CADOs, the A-M-PVAC-IDA adsorbent was desorbed using EDTA. The obtained desorption isotherm of EDTA/A-M-PVAC-IDA system was compared with the adsorption isotherm of D-M-PVAC-IDA adsorbent and Cu(II) ion loaded solution so as to assess the ability of EDTA for the removal of Cu from the A-M-PVAC-IDA. The information obtained in this study is useful for the rational operation and design of the system for the recovery of Cu from the Cu(II) ion-containing solution and the regeneration and reuse of M-PVAC-IDA adsorbent.

## 2. Experiments

### 2.1. M-PVAC-IDA adsorbent

The M-PVAC-IDA adsorbent used was synthesized via suspension polymerization using super-paramagnetic Fe<sub>3</sub>O<sub>4</sub> gel and other organics. The chemicals used for the synthesis included the follows. Ammonia, ferric chloride, ferrous chloride, and methanol were

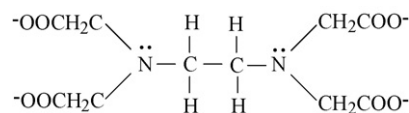


Fig. 1. The structural formula of ethylenediaminetetraacetic acid (EDTA).

supplied by Merck (Merck KGaA Co., Darmstadt, Germany). Oleic acid, epichlorohydrin, divinylbenzene, and vinyl acetate (VAC) were purchased from Aldrich. (Sigma–Aldrich Inc., St. Louis, MO, USA). Poly-vinyl alcohol (PVA) with molecular weight (MW) of 8000 was given by Nacalai Tesque (Nacalai Tesque Inc., Kyoto, Japan). Benzyl peroxide was purchased from Wako Pure Chemical Industries Ltd. (Wako Pure Chemical Industries Ltd., Osaka, Japan). Iminodiacetic acid (IDA) was obtained from Sigma (Sigma–Aldrich Inc., St. Louis, MO, USA). The M-PVAC-IDA is nearly non-porous with specific area of external surface of 12.9 m<sup>2</sup> g<sup>-1</sup> which is about 2.2 × 10<sup>3</sup> times larger than that of activated carbon of Calgon F-400 of mesh 12–40. The density of M-PVAC-IDA is about 1.63 g cm<sup>-3</sup>. The details of synthesis and other properties of M-PVAC-IDA can be referred to the previous study [1].

### 2.2. Stage-wise desorption of Cu(II) for regeneration of adsorbent

The Cu(II) adsorbed M-PVAC-IDA, A-M-PVAC-IDA, was recovered by magnetic separation. A 5 mM EDTA (Nacalai Tesque Inc., Kyoto, Japan) with initial pH value of 5.5 was used as regeneration solution and mixed with the A-M-PVAC-IDA in the completely stirred tank reactor (CSTR). The structural formula of EDTA is displayed in Fig. 1, showing four CH<sub>2</sub>COO<sup>-</sup> functional groups capable for attracting Cu(II) ions. The volume was controlled in 1 L and the CSTR was operated for 24 h. The atomic absorption spectrometer (AA) (model AA800, PerkinElmer Co., Norwalk, CT, USA) was used to measure the concentration of Cu(II) ion of the solution. The saturated EDTA solution was replaced by the fresh EDTA solution of 5 mM after the desorption process having reached the equilibrium. The above desorption steps were repeated until no signal of Cu(II) ion in the desorbent EDTA solution was detected. The resulted Cu(II) desorbed M-PVAC-IDA, D-M-PVAC-IDA, can then be reused for the adsorption again.

### 2.3. Digestion of D-M-PVAC-IDA

In order to correctly characterize the amount of Cu(II) remained on D-M-PVAC-IDA, the fusion method was employed to separate the metal and organics and the followed digestion method was applied to dissolve the remaining metallic compound for the measurement of Cu concentration [22,23]. It was revealed that the ultimate decomposition temperature ( $T_d$ ) of M-PVAC-IDA was 600 °C by the thermal gravity analysis (TGA) (model TGA51, Shimadzu Co., Kyoto, Japan) in the previous work [1]. Meanwhile, the melting point of Cu(II) oxide is 1326 °C. The temperature of 1000 °C was thus chosen for the fusion process to decompose the organics in D-M-PVAC-IDA. Thus, a 0.2 g dried D-M-PVAC-IDA was put in an alumina crucible and completely flamed at 1000 °C in a high-temperature oven (model muffle furnace DF 40, Deng Yng Co., Taipei, Taiwan). The fused solid containing iron oxide and Cu(II) oxide was cooled at room temperature. For digestion, a 120 mL of 16.67% hydrochloric acid (HCl) (Nacalai Tesque Inc., Kyoto, Japan) and the fused sample were put into a wide-mouth bottle followed by ultra-sonification (model Powerasonic 410, Hwashin Technology Co., Daegu, Korea) at 65 °C for 90 min until no residual samples existed in the alumina crucible. The concentration of Cu(II) ion in the digested solution was measured by AA.

#### 2.4. Cyclic adsorption and desorption operations (CADOs)

About 3.8 g D-M-PVAC-IDA was used to perform the experiments of CADOs. A 1 L buffer solution with the pH value of 4.5 was prepared by mixing acetic acid (CH<sub>3</sub>COOH) (Mallinckrodt Baker Inc., Phillipsburg, NJ, USA) and sodium acetate (CH<sub>3</sub>COONa) (Wako Pure Chemical Industries Ltd., Osaka, Japan). A solution with a specific Cu(II) ion concentration, say 997 mg L<sup>-1</sup>, was adjusted using CuSO<sub>4</sub>·5H<sub>2</sub>O (Nihon Shiyaku Industries Ltd., Tokyo, Japan) and subjected to the adsorption by the D-M-PVAC-IDA to reach the equilibrium state in the CSTR, resulting in an adsorbent of A-M-PVAC-IDA saturated with Cu(II). The resulted A-M-PVAC-IDA after adsorption at equilibrium was followed by the desorption process again, which was performed using regenerant solution in a 1 L of controlled volume containing 5 mM EDTA with initial pH value of 5.5 until the concentration of Cu(II) ion reaches the equilibrium in CSTR, yielding the regenerated D-M-PVAC-IDA. The adsorption and desorption cycles were performed 5 times, for which the adsorption were conducted at five different Cu(II) concentrations of 997, 792, 595, 294, and 97.3 mg L<sup>-1</sup>, respectively.

### 3. Kinetic models and equilibrium isotherms

Many adsorption kinetic models had been reported [24–39] with the pseudo-first-order and pseudo-second-order equations having been widely applied. Additionally, the Freundlich and Langmuir adsorption isotherms were often used to investigate adsorption mechanism and capacity [40–43]. These four models were elaborated in the following sections.

#### 3.1. Pseudo-first-order equation

The simplest model to analyze the adsorption and desorption kinetics is the pseudo-first-order equation, which can be formulated as below:

$$\begin{aligned} \frac{dq_{ta}}{dt} &= k_{1a}(q_{ea} - q_{ta}) \quad (\text{for adsorption}) \\ \text{or } \frac{dq_{td}}{dt} &= -k_{1d}(q_{td} - q_{ed}) \quad (\text{for desorption}) \end{aligned} \quad (1)$$

where  $k_1$  is the rate constant, and  $q_e$  and  $q_t$  are respectively the solid-phase-concentrations of metal adsorbed on the adsorbent ( $q$ ) at equilibrium and any time  $t$ . The subscripts  $a$  and  $d$  denote the processes of adsorption and desorption, respectively. Integrating Eq. (1) with the initial condition,  $q_{ta} = q_{0a}$  or  $q_{td} = q_{0d}$  at  $t = 0$ , for the adsorption or desorption, respectively, yields Eq. (2):

$$\begin{aligned} q_{ta} &= q_{ea} - (q_{ea} - q_{0a})\exp(-k_{1a}t) \quad (\text{for adsorption}) \\ \text{or } q_{td} &= q_{ed} + (q_{0d} - q_{ed})\exp(-k_{1d}t) \quad (\text{for desorption}) \end{aligned} \quad (2)$$

The value of  $q_t$  of adsorption or desorption is calculated according to Eq. (3):

$$\begin{aligned} q_{ta} &= \frac{[(C_{0a} - C_{ta})V_L a]}{m_B} + q_{0a} \\ \text{or } q_{td} &= q_{0d} - \frac{[(C_{td} - C_{0d})V_L d]}{m_B} \end{aligned} \quad (3)$$

where  $C_0$  is the initial concentration of Cu(II) ion in solution (mg L<sup>-1</sup>),  $C_t$  is the concentration of Cu(II) ion in solution (mg L<sup>-1</sup>) at  $t$ , and  $V_L$  is the volume of solution and  $m_B$  is the mass of the adsorbent or desorbent.

#### 3.2. Pseudo-second-order equation

The pseudo-second-order equation, which assumes that the adsorption behavior is controlled by a second-order reaction, is

expressed as below:

$$\begin{aligned} \frac{dq_{ta}}{dt} &= k_{2a}(q_{ea} - q_{ta})^2 \quad (\text{for adsorption}) \\ \text{or } \frac{dq_{td}}{dt} &= -k_{2d}(q_{td} - q_{ed})^2 \quad (\text{for desorption}) \end{aligned} \quad (4)$$

where  $k_{2a}$  and  $k_{2d}$  are the rate constants of the second-order kinetic models of adsorption and desorption, respectively. Integrating Eq. (4) with initial condition,  $q_{ta} = q_{0a}$  or  $q_{td} = q_{0d}$  at  $t = 0$  for the adsorption or desorption, respectively, then gives

$$\begin{aligned} q_{ta} &= q_{ea} + \frac{q_{0a} - q_{ea}}{k_{2a}t(q_{ea} - q_{0a}) + 1} \quad (\text{for adsorption}) \\ \text{or } q_{td} &= q_{ed} + \frac{q_{ed} - q_{0d}}{k_{2d}t(q_{ed} - q_{0d}) - 1} \quad (\text{for desorption}) \end{aligned} \quad (5)$$

Because Eqs. (2) and (5) are non-linear, therefore, the non-linear algorithms, such as Levenberg–Marquardt [9], were applied to compute the rate constants ( $k_1$  and  $k_2$ ) and theoretical capacity of adsorption in equilibrium state ( $q_e$ ).

#### 3.3. Adsorption isotherms

The Freundlich and Langmuir adsorption isotherms are often used to interpret the adsorption phenomenon at the interface between solid and liquid phases.

The Freundlich adsorption isotherm is an empirical equation proposed in 1906 [25]. It is hypothesized that the heat of adsorption decreases as a function of natural logarithm with the increase of surface coverage of adsorbent, indicating that adsorption sites on the surface of adsorbent possess different adsorption energies. The Freundlich isotherm equation in the linear form of  $\log q_e$  vs.  $\log C_e$  is expressed as:

$$\log q_e = \log k_F + \frac{1}{n_F} \log C_e \quad (6)$$

where  $q_e$  and  $C_e$  represent the solid-phase and liquid-phase concentrations of Cu(II) ion at equilibrium, respectively, and  $k_F$  and  $n_F$  are constants.

The Langmuir adsorption isotherm was reported in 1918 [34] to describe the adsorption phenomenon at the interface between solid and liquid phases for mono-molecular layer. The Langmuir model assumes that the surface of the adsorbent is homogeneous, adsorption energy is uniform for each adsorption site and solute uptake occurs by monolayer adsorption. The equation in the linear form of  $C_e/q_e$  vs.  $C_e$  is displayed as:

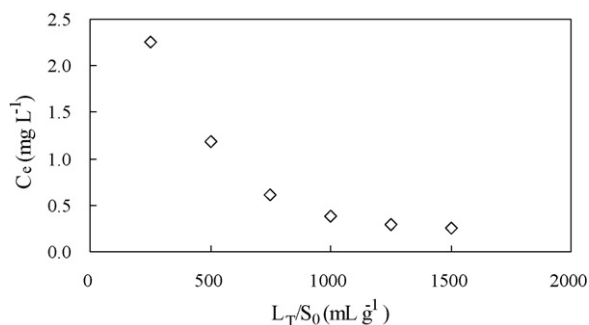
$$\frac{C_e}{q_e} = \left( \frac{1}{K_L q_L} \right) + \left( \frac{1}{q_L} \right) (C_e) \quad (7)$$

where  $q_L$  and  $K_L$  represent the monolayer adsorption capacity and equilibrium constant for the adsorption, respectively.

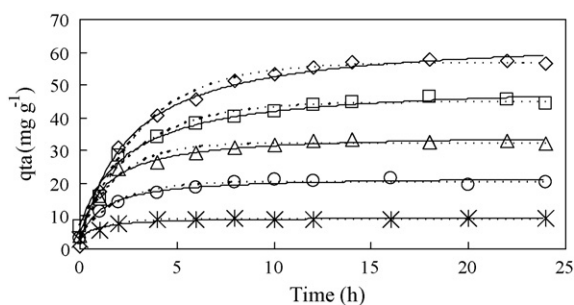
## 4. Results and discussion

#### 4.1. Stage-wise desorption of Cu(II) from A-M-PVAC-IDA for the regeneration

Fig. 2 shows the relationship between the equilibrium concentration  $C_e$  and dosage of desorbent liquid (in terms of the ratio of accumulated desorbent liquid used  $L_T$  to mass of adsorbent  $S_0$ ) after each desorption run. The  $C_e$  after each desorption stage decreases with increasing  $L_T/S_0$  as expected. The decrease of  $C_e$  is rapid up to the third desorption stage while slow after the fourth desorption stage. Consequently, further desorption of Cu(II) after six desorption runs is restrained by the low  $C_e$ . It is noted that the  $C_e$  after seven desorption runs is lower than the instrument detection limit as the value of  $L_T/S_0$  increases from 1500 to 1750 mL g<sup>-1</sup>. This thus confirms that the Cu(II) adsorbed on the A-M-PVAC-IDA is nearly



**Fig. 2.** Stage-wise desorptions of Cu(II) from A-M-PVAC-IDA using 5 mM EDTA as regenerant solution at initial pH value (pH<sub>0</sub>) 5.5. C: concentration of Cu(II) ion in solution (mg L<sup>-1</sup>); C<sub>e</sub>: equilibrium C; L<sub>T</sub>: accumulated regenerant solution used (sum of L<sub>i</sub>); S<sub>0</sub>: initial mass of adsorbent A-M-PVAC-IDA, =4 g; L<sub>i</sub>: volume of fresh regenerant solution used for i<sup>th</sup> desorption, =1000 mL; i: count number of desorption stage, i = 6 for this case; A-M-PVAC-IDA: exhausted or Cu(II) adsorbed M-PVAC-IDA.



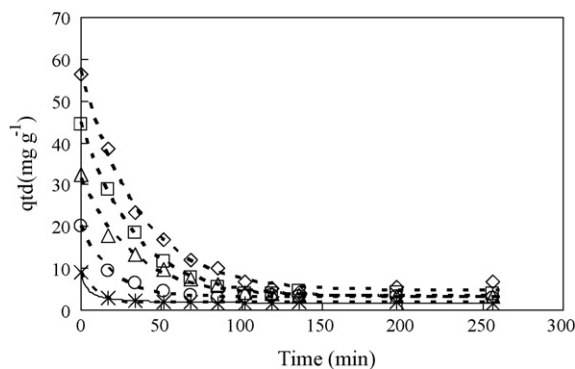
**Fig. 3.** Kinetics of adsorption of Cu(II) ion on the regenerated adsorbent D-M-PVAC-IDA during cyclic adsorption (CA) and desorption operations (CADOs) at fixed pH value of 4.5 with buffer solution. q: solid-phase concentration of Cu(II) (mg g<sup>-1</sup>); q<sub>ta</sub>: q during adsorption at any time t. Symbol, line: experiment, prediction. (◇, CA1), (□, CA2), (△, CA3), (○, CA4), (\*, CA5): initial C for CA (C<sub>0a</sub>) = 997, 792, 595, 294, 97.30 mg L<sup>-1</sup>. ---, - : pseudo-first-order model, pseudo-second-order model. CAi: The i<sup>th</sup> adsorption during CADOs; i = 1–5. D-M-PVAC-IDA: regenerated or Cu desorbed M-PVAC-IDA.

completely desorbed from the adsorbent. For further verification of this, the digestion of the desorbed adsorbent D-M-PVAC-IDA after seven desorption runs was implemented for the measurement of Cu(II) content on the D-M-PVAC-IDA, indicating a negligible amount of 0.16 mg g<sup>-1</sup>.

## 4.2. Cyclic adsorption and desorption

### 4.2.1. Adsorption kinetics

Fig. 3 depicts the time (t) variation of solid-phase concentration of Cu(II) (q<sub>ta</sub>) for the cyclic adsorption (denoted as CA) of Cu(II) ion on the regenerated adsorbent D-M-PVAC-IDA during CADOs. The results indicate that the lower initial concentration of Cu(II) ion in the solution for CA (C<sub>0a</sub>) is, the shorter the adsorption equilibrium time is. In the case at the lowest C<sub>0a</sub> of 97.3 mg L<sup>-1</sup>, the adsorption



**Fig. 4.** Kinetics of desorption of Cu(II) from the Cu(II) ion adsorbed adsorbent of A-M-PVAC-IDA during CADOs using 5 mM EDTA regenerant solution at pH<sub>0</sub> 5.5. q<sub>td</sub>: q during desorption at t. Symbol, line: experiment, prediction. (◇, CA1), (□, CD2), (△, CD3), (○, CD4), (\*, CD5): initial q for desorption (q<sub>0d</sub>) = 56.54, 44.43, 32.33, 20.22, 9.20 mg g<sup>-1</sup>. ---, - : pseudo-first-order model, pseudo-second-order model; CDj: the j<sup>th</sup> desorption during CADOs; j = 1–5.

reaches equilibrium with the shortest time of about 6 h as estimated at  $q_{ta} = q_{0a} + 0.95(q_{ea} - q_{0a})$ . On the other hand, at the highest C<sub>0a</sub> of 997 mg L<sup>-1</sup>, it takes about 12 h as estimated to reach the equilibrium state. However, the initial adsorption rate  $dq_{ta}/dt$  increases as C<sub>0a</sub> increases. This is contributed by the larger difference of q<sub>ea</sub> and q<sub>ta</sub> at t, which gives a larger driving force of (q<sub>ea</sub> - q<sub>ta</sub>). The trend is consistent with that for the other adsorption system [24].

The pseudo-first-order and pseudo-second-order equations were applied to describe the kinetics of adsorption for the cases with various C<sub>0a</sub>. The results of rate constants (k<sub>1a</sub> and k<sub>2a</sub>), equilibrium concentrations of solid-phase (q<sub>ea</sub>) and correlation coefficient (r<sup>2</sup>) are listed in Table 1. The value of k<sub>1a</sub> of the pseudo-first-order equation decreases with increasing C<sub>0a</sub>. Similar variation trend of the rate constant k<sub>2a</sub> with C<sub>0a</sub> obtained applying the pseudo-second-order kinetic model is also observed. The high values of r<sup>2</sup> (>0.97) of fittings using both pseudo-first-order and pseudo-second-order equations indicate good agreements. However, the q<sub>ea</sub> obtained using the pseudo-first-order kinetic model is more accurate than that using the pseudo-second-order kinetic model as compared with the experimental value. Therefore, the pseudo-first-order equation is more suitable than the pseudo-second-order equation for predicting the q<sub>ea</sub>.

### 4.2.2. Desorption kinetics

Fig. 4 displays the kinetics of desorption of Cu(II) from the Cu(II) ion adsorbed adsorbent A-M-PVAC-IDA during CADOs. In the case with the lowest initial the solid-phase concentration of Cu(II) at q<sub>0d</sub> = 9.20 mg g<sup>-1</sup>, the desorption reaches equilibrium with solid-phase concentration of q<sub>ed</sub> at the shortest time of about 50 min as estimated at  $q_{td} = q_{0d} - 0.95(q_{0d} - q_{ed})$ . On the contrast, the longest equilibrium time of about 100 min is needed for the case with the highest q<sub>0d</sub> of 56.54 mg g<sup>-1</sup>. The shorter desorption equilibrium time is due to the less amount of adsorbate of (q<sub>0d</sub> - q<sub>ed</sub>) to be des-

**Table 1**

Kinetic parameters for adsorption of Cu(II) ion on the regenerated adsorbent of M-PVAC-IDA (D-MPVAC-IDA) during cyclic adsorption and desorption operations (CADOs) at fixed pH value of 4.5 with buffer solution at 25 °C.

Run	Initial concentration C <sub>0a</sub> (mg L <sup>-1</sup> )	Experimental data		First-order kinetic			Second-order kinetic		
		C <sub>ea</sub> (mg L <sup>-1</sup> )	q <sub>ea</sub> (mg g <sup>-1</sup> )	k <sub>1a</sub> (h <sup>-1</sup> )	q <sub>ea</sub> (mg g <sup>-1</sup> )	r <sup>2</sup>	k <sub>2a</sub> (g mg <sup>-1</sup> h <sup>-1</sup> )	q <sub>ea</sub> (mg g <sup>-1</sup> )	r <sup>2</sup>
CA1	997	786	56.54	0.326	56.53	0.992	6.50E-03	64.90	0.994
CA2	792	649	44.43	0.329	44.69	0.986	9.40E-03	50.55	0.986
CA3	595	487	32.33	0.52	32.26	0.983	2.34E-02	35.26	0.988
CA4	294	229	20.22	0.526	20.46	0.977	4.13E-02	22.18	0.98
CA5	97.3	73.5	9.20	0.7	9.14	0.993	1.16E-01	9.65	0.975

C: concentration of Cu(II) in solution (mg L<sup>-1</sup>); C<sub>0a</sub>, C<sub>ea</sub>: Initial and equilibrium C for adsorption; q: concentration of Cu(II) on solid phase (mg g<sup>-1</sup>); q<sub>ea</sub>: equilibrium q for adsorption; r<sup>2</sup>: correlation coefficient.

**Table 2**  
Kinetic parameters for desorption of Cu(II) from the Cu(II) ion adsorbed adsorbent of M-PVAC-IDA (A-M-PVAC-IDA) during CADOs using 5 mM EDTA regenerant solution at initial pH value (pH<sub>0</sub>) 5.5 and 25 °C.

Run	Initial concentrate $q_{0d}$ (mg g <sup>-1</sup> )	Experimental data		First-order kinetics			Second-order kinetics		
		$C_{ed}$ (mg L <sup>-1</sup> )	$q_{ed}$ (mg g <sup>-1</sup> )	$k_{1d}$ (h <sup>-1</sup> )	$q_{ed}$ (mg g <sup>-1</sup> )	$r^2$	$k_{2d}$ (g mg <sup>-1</sup> h <sup>-1</sup> )	$q_{ed}$ (mg g <sup>-1</sup> )	$r^2$
CD1	56.54	198	4.36	1.74	4.70	0.995	3.48E-02	-4.093	0.975
CD2	44.43	154	3.86	1.80	3.23	0.996	4.86E-02	-3.409	0.975
CD3	32.33	111	3.11	1.98	3.55	0.991	8.40E-02	-0.565	0.995
CD4	20.22	65.7	2.93	3.30	3.22	0.996	3.09E-01	1.757	0.997
CD5	9.20	28.8	1.62	6.42	1.79	0.996	2.26E-00	1.528	0.997

$q_{0d}$ ,  $q_{ed}$ : initial and equilibrium  $q$  for desorption;  $C_{ed}$ : equilibrium concentration  $C$  for desorption;  $r^2$ : as specified in Table 1.

orbed. Similarly to the adsorption, the initial desorption rate  $dq_{td}/dt$  increases with increasing  $q_{0d}$ , also contributed by the larger driving force of  $(q_{td} - q_{ed})$ .

The kinetic parameters of desorption for the pseudo-first-order and pseudo-second-order equations are listed in Table 2. The values of  $r^2$  corresponding to the two kinetic equations display compatible features with  $r^2 > 0.97$ . However, the values of  $q_{ed}$  predicted using the pseudo-second-order equation are not accurate except for the case with  $q_{0d} = 9.20$  mg g<sup>-1</sup>. On the contrast, the pseudo-first-order model accurately predicts the values of  $q_{ed}$ , supporting its validity for all the examined cases with  $q_{0d}$  of 9.20, 20.22, 32.33, 44.43 and 56.54 mg g<sup>-1</sup>. The better applicability of the pseudo-first-order model may due to the strong affinity of EDTA to Cu, resulting that the desorption rate is mainly dependent on the amount of Cu on the surface remained to be desorbed (i.e.,  $q_{td} - q_{ed}$ ).

Further examination of the values of  $k_{1d}$  in Table 2 illustrates that  $k_{1d}$  decreases with increasing  $q_{0d}$ . The trend is similar to that of adsorption of Cu(II) ion from the solution. Moreover, comparing the values of  $k_{1d}$  in Table 2 with those of  $k_{1a}$  in Table 1 indicates that the values of rate constant of desorption are about one order of magnitude higher than those of adsorption. Thus, the use of EDTA to remove the Cu(II) from the A-M-PVAC-IDA is a fast desorption process.

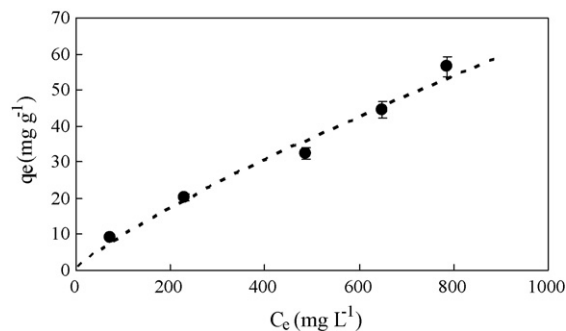
### 4.3. Isotherms and mechanism of adsorption

#### 4.3.1. Adsorption isotherm of Cu(II) ion in solution on D-M-PVAC-IDA

The adsorption isotherms of Cu(II) ion in solution with pH values of 1, 2 and 4.5 at 25 °C on the fresh M-PVAC-IDA were established in the previous work [1]. For the case with pH 4.5, the Freundlich adsorption isotherm  $q_e = k_F C_e^{1/n_F}$  gives  $n_F = 1.214$  and  $k_F = 3.53 \times 10^{-3}$  in unit (mmol g<sup>-1</sup>) (mg L<sup>-1</sup>)<sup>-0.8237</sup> with  $q_e$  in mmol g<sup>-1</sup> and  $C_e$  in mg L<sup>-1</sup>. With  $q_e$  in mg g<sup>-1</sup> and  $C_e$  in mg L<sup>-1</sup>, the  $k_F$  is equal to  $2.244 \times 10^{-1}$  in unit (mg g<sup>-1</sup>) (mg L<sup>-1</sup>)<sup>-0.8237</sup>. Besides, the Langmuir isotherm  $q_e = K_L q_L C_e / (1 + K_L C_e)$  gives  $q_L = 1.205 \times 10^{-1}$  mmol g<sup>-1</sup> and  $K_L = 4.029 \times 10^{-2}$  L mg<sup>-1</sup> with  $q_e$  in mmol g<sup>-1</sup> and  $C_e$  in mg L<sup>-1</sup>. With  $q_e$  in mg g<sup>-1</sup> and  $C_e$  in mg L<sup>-1</sup>, the  $q_L$  is equal to 7.657 mg g<sup>-1</sup>. As shown in Fig. 5, the Freundlich adsorption isotherm obtained from the previous work is compared with the  $q_e$  of the adsorption in the CADOs of the present study, indicating good agreement. The good agreement also supports that the adsorption equilibrium isotherm and the characteristics of the regenerated adsorbent D-M-PVAC-IDA were not altered by regeneration.

#### 4.3.2. The adsorption mechanism

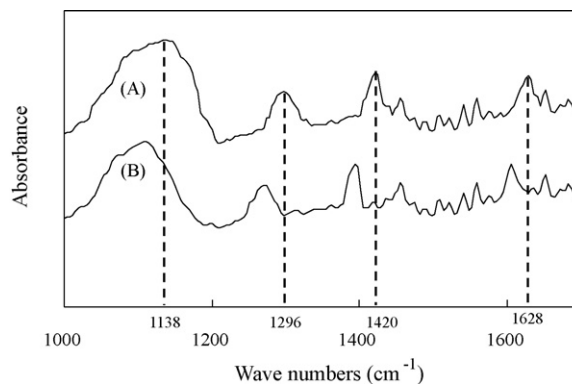
The mechanism of chelating reaction can be well interpreted by Crystal Field Theory [44]. As the electron pairs of ligand approach to metal ions along  $x$ ,  $y$  and  $z$  axis, two out of five d-orbitals of ions, namely  $d_{z^2}$  and  $d_{x^2-y^2}$ , directly come near the electron pairs, resulting in highly concentrated negative charges accompanied with the enhancement of energy level. The remaining d-orbitals, including



**Fig. 5.**  $q_e$  vs.  $C_e$  for adsorption of Cu(II) ion in solution onto D-M-PVAC-IDA with fixed pH value of 4.5 at 25 °C.  $q_e$ : equilibrium  $q$ . Symbol, line: experiments adsorption in CADOs, prediction [1]; ---: Freundlich.

$d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$ , are adversely away from the electron pairs, indicating lower energy level. The former and latter sets are called  $e_g$  and  $t_{2g}$  orbitals, respectively. The energy difference between  $e_g$  and  $t_{2g}$  is referred to as “octahedral crystal field splitting”, generally denoted as  $\Delta$ . It explains that if the complex is irradiated by a light wave with an energy of  $\Delta$ , the energy is absorbed to give rise the energy level of electrons from  $t_{2g}$  to  $e_g$ . In terms of ultraviolet or visible light spectrum, the absorption peak would shift to higher frequency or shorter wavelength which means the higher energy.

Fig. 6 illustrates the FT-IR spectra of A-M-PVAC-IDA (curve A) and M-PVAC-IDA (curve B) obtained [1]. The relative absorption peaks representing the carboxylic group ( $-\text{COO}^-$ ) of M-PVAC-IDA after adsorption shift from 1603 and 1393  $\text{cm}^{-1}$  of curve B to 1628 and 1420  $\text{cm}^{-1}$  of curve A, respectively. The phenomenon is induced by the formation of coordinate covalent bonds attributed to the electron pairs provided to copper ions by carboxylic group. In addition, the absorbances of tertiary amine and secondary alcohol at 1112 and 1265  $\text{cm}^{-1}$  of curve B shift to 1138 and 1296  $\text{cm}^{-1}$  of curve A, respectively. This is because the nitrogen atom of the tertiary



**Fig. 6.** Infrared absorption spectra of A-M-PVAC-IDA and M-PVAC-IDA. (A) A-M-PVAC-IDA with adsorption of Cu(II), (B) M-PVAC-IDA without adsorption of Cu(II) (free ligand).

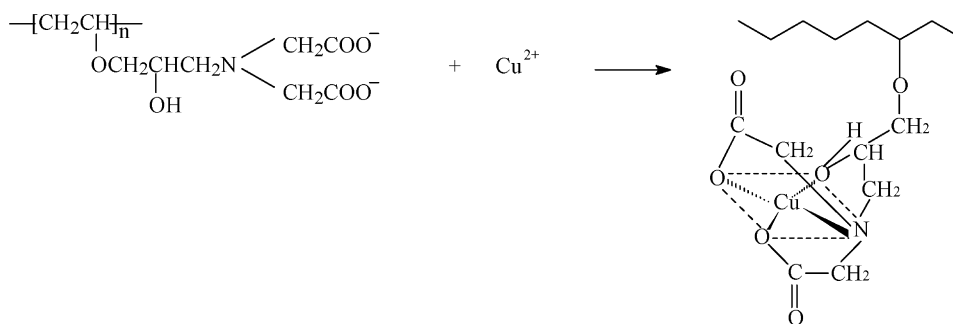


Fig. 7. Cu(II) ion reacts with M-PVAC-IDA forming a square planar complex.

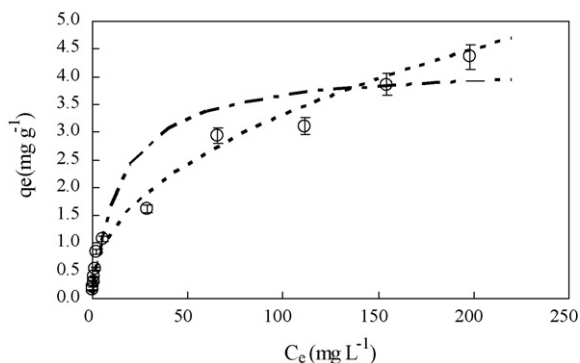


Fig. 8. Isotherms for desorption of Cu(II) from A-M-PVAC-IDA using 5 mM EDTA with pH0 of 5.5 at 25 °C. Symbol, line: experiment, prediction. ---, -.-: Freundlich ( $R^2 = 0.986$ ), Langmuir ( $R^2 = 0.907$ ).

amine as well as oxygen atom of the secondary alcohol individually offers electron pairs to Cu(II) ions to form coordinate covalent bond. In summary, the M-PVAC-IDA totally provides four coordination numbers to Cu(II) ions to form square planar complex. Based on Crystal Field Theory [44], this square planar complex arises from the d-orbitals,  $d_{x^2-y^2}$ , of Cu(II) ions approaching to electron pairs of M-PVAC-IDA, as displayed in Fig. 7.

#### 4.4. Isotherms and mechanism of desorption

##### 4.4.1. Desorption isotherm of Cu(II) from A-M-PVAC-IDA in EDTA regenerant

Fig. 8 depicts desorption of Cu(II) from the A-M-PVAC-IDA using EDTA regenerant. The parameters of desorption obtained from the regression of curve fitting applying the Freundlich adsorption isotherm in the form of Eq. (6) are listed in Table 3. The correlation coefficient  $r^2$  is 0.975, indicating that the desorption is satisfactorily fitted with the Freundlich model. The Freundlich constants  $k_F$  and  $n_F$  are 0.429 with unit of  $(\text{mg g}^{-1})(\text{mg L}^{-1})^{-1/n_F}$  (or  $6.77 \times 10^{-3}$  with unit of  $(\text{mmol g}^{-1})(\text{mg L}^{-1})^{-1/n_F}$ ) and 2.25, respectively.

On the other hand, analyzing the desorption results via the Langmuir adsorption isotherm using Eq. (7) gives the values of parameters of  $q_L$  and  $K_L$  in Table 3 with the regression line also plotted in Fig. 8. The correlation coefficient  $r^2$  is 0.953, implying that the Langmuir adsorption isotherm is also suitable to describe the desorption isotherm as well. The maximum adsorption capacity of mono-molecular layer  $q_L$  and equilibrium constant  $K_L$  are  $4.2 \text{ mg g}^{-1}$  (or  $6.62 \times 10^{-2} \text{ mmol g}^{-1}$ ) and  $6.81 \times 10^{-2} \text{ L mg}^{-1}$ , respectively. Comparing the value of  $q_L$  of  $6.62 \times 10^{-2} \text{ mmol g}^{-1}$  for the desorption using EDTA with that of  $0.121 \text{ mmol g}^{-1}$  for the adsorption of Cu(II) ion in the solution on D-M-PVAC-IDA indicates that former is lower than the latter. Thus, the EDTA is suitable to remove the Cu(II) form the A-M-PVAC-IDA for the desorption process to regenerate the adsorbent.

Further comparing the validities of the Freundlich and Langmuir adsorption models based on the correlation coefficients and determination coefficients ( $R^2$ ), one notes that the former is more suitable than the latter. Moreover, the acid dissociation of functional group of carboxylic acid on the surface of M-PVAC-IDA may not be homogeneous at the initial pH ( $\text{pH}_0$ ) of 5.5, indicating that the adsorption sites on the surface of M-PVAC-IDA may possess different potential energies to form surface complex. This also demonstrates that the Freundlich adsorption model is more appropriate to describe the desorption isotherm than the Langmuir adsorption model.

##### 4.4.2. The desorption mechanism

The desorbent EDTA, which can bind metals via the formation of covalent bonds by electron pairs in four acetate and two amine groups, is a chelator with six coordination sites (Fig. 1). In the aqueous solution containing Cu(II) ions, EDTA and M-PVAC-IDA are chelating agents or ligands competing with each other. According to Crystal Field Theory [44], the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals of Cu(II) ion can approach the electron pairs of EDTA, forming the octahedral structure (Fig. 9) [45] more stable than the square planar structure (Fig. 7). The affinity of EDTA to Cu(II) ion is stronger than that of M-PVAC-IDA with stability constant ( $K_{ML}$ ) of the former ( $K_{\text{CuEDTA}} = 10^{20.5}$ ) greater than that of latter ( $K_{\text{CuIDA}} = 10^{11.5}$ ) [46]. The

Table 3

Parameters of desorption isotherms of C(II) from A-M-PVAV-IDA using EDTA regenerant with pH<sub>0</sub> 5.5 at 25 °C.

Desorption isotherm	Equation	Parameter	This study	$r^2$	$R^2$
Langmuir	$q_e = (K_L q_L C_e) / (1 + K_L C_e)$	$K_L (\text{L mg}^{-1})$	6.81E-02	0.953	0.907
		$q_L (\text{L g}^{-1})$	4.20		
		or $q_L (\text{mmol g}^{-1})$	6.62E-02		
		$k_F = (\text{mg g}^{-1})(\text{mg L}^{-1})^{-1/n_F}$	0.43		
Freundlich	$q_e = k_F C_e^{1/n_F}$	or $k_F = (\text{mmol g}^{-1})(\text{mg L}^{-1})^{-1/n_F}$	6.77E-03	0.975	0.986
		$n_F = (\text{dimensionless})$	2.25		

$C_e$ : equilibrium concentration of Cu(II) in EDTA solution ( $\text{mg L}^{-1}$ ).  $q_e$ : equilibrium  $q$  ( $\text{mg g}^{-1}$  or  $\text{mmol g}^{-1}$ );  $r$ : as specified in Table 1;  $R^2$ : determination coefficient,  $= 1 - ((\sum (y_e - y_c)^2) / (\sum (y_e - y_m)^2))$  where  $y_e$  and  $y_c$ , and  $y_m$  are the experimental and predicted results, and average of experimental values, respectively.

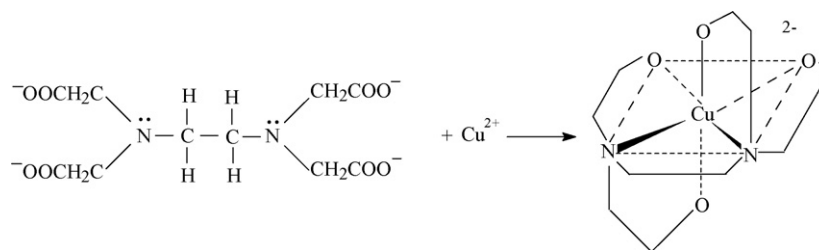


Fig. 9. Cu(II) ion reacts with EDTA forming an octahedral complex [45].

$K_{ML}$  is defined according to the follows. Thus, the EDTA is a good regenerative.

$$M + L \rightleftharpoons ML, K_{ML} = \frac{[ML]}{[M][L]} \quad (8)$$

where M and L are the metal and ligand, respectively.

## 5. Conclusions

In this study, EDTA was employed as a regenerant solution to desorb Cu(II) from the exhausted or Cu(II) loaded magnetic polymer adsorbent M-PVAC-IDA noted as A-M-PVAC-IDA. The regenerated or Cu desorbed M-PVAC-IDA denoted as D-MPVAC-IDA regaining its adsorption ability was reused to adsorb Cu(II) ion from the Cu(II) ion-containing solution. Some conclusions may be drawn as follows:

- (1) Stage-wise desorptions using EDTA for a certain runs, say 7 runs, satisfactorily remove the Cu(II) from the A-M-PVAC-IDA for the reuse.
- (2) The adsorption characteristics of the regenerated adsorbent D-M-PVAC-IDA were not altered by the regeneration process.
- (3) For cyclic adsorption and desorption operations, the pseudo-first-order kinetic model is suitable to describe the adsorption as well as desorption kinetics.
- (4) The kinetic results indicate that the value of rate constant of desorption is about one order of magnitude higher than that of adsorption, revealing that the use of EDTA to remove the Cu(II) from the A-M-PVAC-IDA is a fast desorption process.
- (5) The equilibrium behavior of desorption of Cu(II) from A-M-PVAC-IDA using EDTA regenerant can be well described by the Freundlich desorption isotherm, showing good agreement with the experimental data of stage-wise desorptions and desorptions of CADOS.
- (6) The adsorption and desorption mechanism analyses show that EDTA reacts with Cu(II) ion forming the octahedral complex more stable than square planar complex of M-PVAC-IDA with Cu(II) ion, suggesting that the EDTA is a good regenerant to remove the Cu(II) from the A-M-PVAC-IDA for the desorption process to regenerate the adsorbent.

## Acknowledgement

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