# Effect of polyaniline maize tree-trunk composite on adsorption of lead (II) and cadmium (II) ions from solution

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#### ABSTRACT

Hybrid nanostructured composite by polyaniline (PANi) and maize tree-trunk (MTT) was prepared by chemical polymerization method. Its structural morphology was nano range through SEM and TEM images. The decomposition temperature of PANi-MTT composite for 61.9% was about 341°C, less than that of PANi (about 507°C) for 46.6% through thermal analysis. It means this composite is less thermal stable than pure PANi because of MTT presence in composite matrix. The conductivity of PANi-MTT in salt form was 0.597 mS cm<sup>-1</sup>, much smaller than that of pure PANi (35 mS cm<sup>-1</sup>) in the same state. The adsorption isotherm process of lead (II) and Cd (II) on PANi-MTT followed by Freundlich model better than by Langmuir one thanks to higher correlation coefficients (~1). It occurred spontaneously and fitted into the second order reaction. The maximum capacities were 121.951 mg  $g^{-1}$  and 54.645 mg  $g^{-1}$  for Pb<sup>2+</sup> and Cd<sup>2+</sup> ions, respectively.

Keywords: Adsorption of lead (II) and Cd (II); PANi-MTT composite

#### 1. Introduction

Lead (II) and cadmium (II) are very toxic [1,2] which can disperse into aqueous environment by wastewater from some industrial branches such as battery manufacture, metallurgy, petrochemicals, and so on. Both of them belong to heavy metal group that can damage body health. Only a small amount of them, if accumulated in the human body over a long time leading to cancer or damaging to certain organs and chronic toxicity [3]. There are many conventional methods to remove them from aqueous solution including precipitation, electroplating, chemical coagulation, ion exchange and membrane separation. Among these methods, using adsorption technique for reducing the level of heavy metals in wastewater has been a simpler treatment and quite popular [4]; especially the hybrid materials. They based on conducting polymers with agriculture wastes as low cost absorbents, which can be very easily regenerated by controlling pH [5]. Maize tree-trunk (MTT) is one of agriculture waste that is used normally for doing it on fire, additionally, there is no publication about it as composite with polyaniline (PANi) for adsorption of lead (II) and cadmium (II). Besides, there is a large amount of it in Vietnam, an agricultural country, so it can be used to hybrid with PANi to form an effective adsorbent for removing heavy metal ions. The main objective of this work is preparation of nanostructured PANi-MTT composite as adsorbent based on PANi and MTT for removing lead (II) and cadmium (II) ions from solution.

# 2. Experimental

#### 2.1. Materials and methods

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First, MTT was dried and then grinded in micro size ( $<100 \mu m$ ). Then it was untrasonic for 20 min in acetone,

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then filtrated and washed by distilled water. Then, it was dried under vacuum at 50°C until completely dry before being used as carrying agent. Ammonium persulfate, acetone, methanol and HCl were provided by Merck (Germany) and aniline by Kanto Chemical (Japan) which was freshly distilled under vacuum at 120°C before use. The preparation procedure of composite was reported in the previous work [6].

# 2.2. Detection method

The surface morphology of materials was examined by SEM and TEM on an equipment FE-SEM Hitachi S-4800 (Japan) and a Jeol 200CX (Japan), respectively. Thermal analysis was done on Thermal Detector (LABSYS Evo, France) until 800°C with heat flow of 10°C min<sup>-1</sup> under nitrogen gas. The conductivity of materials was determined by cyclic voltammetry (CV) using two-pointelectrode method on an electrochemical workstation IM6 (Zahner-Elektrik, Germany). Adsorption ability of heavy metal ions on regarded material was characterized by atom adsorption spectroscopy (AAS) on an equipment Shimadzu AA-6800 (Japan).

# 2.3. Procedure of adsorption research

The mixtures of adsorbent and solution containing mono heavy metal ion at different initial concentrations were swung at 300 rpm within 40 min and then filtered to remove solid parts. The filtrate was used for analysis of metal ion. The adsorption capacity (mg metal ion per g adsorbent) was determined by following equation:

$$q = \frac{(C_0 - C) V}{m} \tag{1}$$

where  $C_0$  and C are metal ion concentrations (mg L<sup>-1</sup>) before and after adsorption, respectively, V is the volume of the solution (mL) and m is the mass of adsorbent.

The adsorption efficiency H (removal per cent of metal ion from solution) can be written following equation:

$$H = \frac{(C_0 - C)}{C_0} \times 100$$
 (2)

#### 2.4. Procedure of desorption and regeneration

The metal loaded composite was immersed in 0.5 M HCl and shaked in 40 min to release  $Pb^{2+}$  and  $Cd^{2+}$  ions. The solid part from filtration process was washed by distilled water until pH of 7 and converted into emeraldine base (EB) by immersing in 0.5 M ammonia solution. They were spreaded by mix of acetone/methanol (volume ratio of 1:1) after washing with distilled water, and dried under vacuum condition at 50°C for 2 h. The generated material was reused for the adsorption process of  $Pb^{2+}$  and  $Cd^{2+}$  ions similar to the initial PANi-MTT composite.

#### 3. Results and discussion

# 3.1. Material characterization

# 3.1.1. Morphology study

The SEM images on Fig. 1 explains that morphological structure of PANi-MTT composite (b) was in fibre form with diameter of about 50 nm while PANi (a) existed in bundle of small fibres. Both of them were found in nanofibre structure while MTT existed in mix of grain and fibre with different sizes. The seeding materials had much larger sizes (c), however, in the procedure for synthesis of composite they were broken in much smaller sizes because of stirring that their sizes were being nano-range resulting to prepared composite was also in nano-range.

Two different colors were observed by TEM images (Fig. 2) due to the dark color of MTT and the other bright one indicating the presence of PANi.

#### 3.1.2. Thermal analysis

The Fig. 3 shows thermal decomposition temperature of materials resulting to a comparison of thermal stability between PANi-MTT and PANi. From TG curves we can see that the initial stage of weight loss was the elimination of water molecules adsorbed on the both materials in the temperature range of  $50 \div 150^{\circ}$ C. The main loss was degradation of the polymer backbond observed at the temperatures were found about 341°C and 507°C corresponding to mass lost of 61.9% and 46.6% for PANi-MTT and PANi, respectively. It indicated that the composite was less thermal stable than pure PANi because of MTT in composite matrix.



Fig. 1. SEM images of PANi (a), PANi-MTT (b), MTT (c).



Fig. 2. TEM images of PANi-MTT composite.



Fig. 3. Thermal plots of PANi-MTT composite (a) and PANi (b).

# 3.1.3. Conductivity measurement

The data given in Table 1 indicates the conductivity of pure materials (MTT or PANi) and their composite in base state compared with it in salt form. According to the published procedure [6], the salt form was formed before it changed into base state. Its conductivity was found 0.597 S cm<sup>-1</sup>, much smaller than that of pure PANi (35 mS cm<sup>-1</sup>) because of the presence of non-conductive MTT dispersed in composite matrix. However, the prepared composite in base state was also non-conductive.

#### 3.2. Effect of pH on adsorption

The adsorption efficiency (H) of lead (II) and cadmium (II) ions were found to strongly depend on pH medium of solution. pH affected solubility of metal ions in solution and active sites at adsorbent surface. In our study, the effect of pH on the adsorption of  $Pb^{2+}$  and  $Cd^{2+}$  ions was examined in pH range of  $1 \div 7$  because the metal precipitation as hydroxides is dominant at pH above 7 resulting to misunderstanding for adsorption capacity during the metal removal process. On





the other hand, if pH is above 7, PANi will change into base form so adsorption process of these ions will strongly inhibit. Their optimal adsorption ability was found at pH from 5 to 7 (Fig. 4) due to no precipitation of these ions was observed. But, at pH below 3 the metal ion uptake was limited because the presence of H<sup>+</sup> ion competed with them for the adsorption sites [7]. The results indicated that adsorption ability of Pb<sup>2+</sup> ion was higher than that of Cd<sup>2+</sup> one.

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Conductivity data of materials

Materials	Conductivity (mS/cm)
MTT	Non-conductivity
PANi in base state	Non-conductivity
PANi in salt state	35
PANi-MTT composite prepared in base state	Non-conductivity
PANi-MTT composite prepared in salt state	0.597



Fig. 4. Effect of pH on adsorption efficiency of  $Pb^{2+}$  and  $Cd^{2+}$  ions at initial concentration of 1 mg  $L^{-1}$  and contact time of 40 min onto PANi-MTT composite.

#### 3.3. Effect of initial concentration on adsorption

The Fig. 5 shows the effect of initial concentration in the range of 0.5–5 mg L<sup>-1</sup> for both regarded ions on adsorption efficiency onto research composite. It was found that removal per cent of both above metal ions decreased with increasing initial concentration. It decreased lightly from 96.81% to 95.40% for Pb<sup>2+</sup>, but significantly from 96.81% to 78.58% for Cd<sup>2+</sup>. In short, the removal ability of Pb<sup>2+</sup> was better than that of Cd<sup>2+</sup> because the hydrated ionic radius of Pb<sup>2+</sup> is smaller than Cd<sup>2+</sup> (4.01 Å for Pb<sup>2+</sup> and 4.26 Å for Cd<sup>2+</sup>) [8]. It can be explained that the greater ionic radius at the same valence, the weaker the ion adsorbed by farther from the adsorbing surface.

#### 3.4. Effect of contact time on adsorption

The adsorption ability of  $Cd^{2+}$  and  $Pb^{2+}$  ions depended also on contact time. In order to determine the equilibrium time for their adsorption process onto PANi-MTT composite in solution, the adsorption capacity and removal efficiency were investigated at pH of 6 and initial concentration of 1 mg L<sup>-1</sup> which is shown in Fig. 6. It indicated clearly that Pb<sup>2+</sup> and Cd<sup>2+</sup> ions were rapidly removed by this composite during initial 10 minutes resulting to the removal efficiency



Fig. 5. Effect of initial concentration of  $Pb^{2+}$  and  $Cd^{2+}$  ions at pH = 6 and contact time of 40 min onto PANi-MTT composite.



Fig. 6. Effect of contact time on adsorption efficiency of  $Pb^{2+}$  and  $Cd^{2+}$  ions at pH of 6 and initial concentration of 1 mg  $L^{-1}$  onto PANi-MTT composite.

of 97.6% and 92.3% for both of them, respectively. The removal per cent of them was changed very lightly for the rest time and so to ensure that equilibrium was really achieved, the contact time of 40 min was necessary for following researches.

# 3.5. Effect of adsorbent dose on adsorption

The influence of adsorbent dose on adsorption ability of the metal ions was investigated by varying the adsorbent dose from 1 to 20 mg (Fig. 7). The removal per cent of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions increased lightly from 98.69% to 99.66% and sharply from 83.7% to 94.4% when the adsorbent dose was used from 1 to 3 mg, respectively. It was found stable for Pb<sup>2+</sup>, but unstable for Cd<sup>2+</sup> if adsorbent dose increased from 3 to 20 mg. The initial rapid rise of the removal efficiency could be explained that the adsorption of the ions were quite easy due to the increasing active sites and contact surface area. When equilibrium was reached, the removal of these ions was changed insignificantly with increasing adsorbent dose.

# 3.6. Adsorption isotherms

# 3.6.1. Langmuir model

Langmuir model can be presented by the below Eq. (3) [9], where *q* is the solute mass adsorbed per unit adsorbent one at equilibrium (mg g<sup>-1</sup>), *C* is concentration after adsorption (mg L<sup>-1</sup>),  $q_{max}$  is maximum adsorption capacity of absorbents (mg g<sup>-1</sup>),  $K_L$  is Langmuir parameter (L mg<sup>-1</sup>).

$$\frac{C}{q} = \frac{1}{q_{\max}K_L} + \frac{C}{q_{\max}}$$
(3)

The fundamental characteristics of Langmuir isotherm model can be presented by dimensionless parameter  $R_L$  which determined the adsorption system is favourable or not [10], where  $K_L$  is the Langmuir parameter (L mg<sup>-1</sup>) and  $C_0$  as initial concentration (mg L<sup>-1</sup>).



Fig. 7. Effect of adsorbent dosage on adsorption capacity and removal per cent of  $Pb^{2+}$  (a) and for  $Cd^{2+}$  (b) at pH of 6 and initial concentration of 1 mg  $L^{-1}$  onto PANi-MTT composite.

$$R_{L} = \frac{1}{1 + K_{L} \times C_{0}} \tag{4}$$

The Fig. 8 shows that the adsorption of  $Cd^{2+}$  ( $R^2 = 0.9312$ ) fitted into the Langmuir isotherm model better than that of  $Pb^{2+}$  ( $R^2 = 0.815$ ) due to higher correlation coefficient. It was found that the  $q_{max}$  value of PANi-MTT composite (Table 2) for lead ion (121.951 mg g<sup>-1</sup>) was over two times as high as for cadmium ion (54.645 mg g<sup>-1</sup>). Both of them were presented again in Table 3 for comparison of their adsorption ability on different adsorbents reported previously [11–28]. It indicated that the most of them could adsorb Pb<sup>2+</sup> and Cd<sup>2+</sup> less than our obtained composite (PANi-MTT), except PANi-RH [18]. However, the  $q_{max}$  value for Cd<sup>2+</sup> in this study was smaller than those of PANi-chitosan and thermal activated hyroxyapatite [12,24]. The result given in Table 4 shows  $R_L$  value (0 <  $R_L$  <1) for a favourable adsorption process of both Pb<sup>2+</sup> and Cd<sup>2+</sup> ions [10].

#### 3.6.2. Freundlich model

The Freundlich isotherm model can be expressed in Eq. (5) [9,21], where q is adsorption capacity at adsorbed

equilibrium, *C* is concentration after adsorption,  $K_F$  and  $N_F$  are Freundlich parameters.

$$q = K_{\rm F} C^{1/\rm NF} \tag{5}$$

It can also be written in another form:

$$\log q = \log K_r + 1/N_r \log C \tag{6}$$

where the constants  $K_F$  and  $N_F$  could be obtained owing to experimental data from Freundlich plots shown in Fig. 9. It was found the Freundlich parameter  $K_F$  of 180.302 mg  $g^{-1}$  for Pb<sup>2+</sup> which was over six times higher than that for Cd<sup>2+</sup> (28.820 mg g<sup>-1</sup>). The  $N_F$  values were 1.354 and 2.552 for the Pb<sup>2+</sup> and Cd<sup>2+</sup> adsorption process, respectively. It confirmed that this adsorption process was also suitable [21].

Comparing the results given in Tables 2 and 5, we found out that the experimental data for adsorption of both Pb<sup>2+</sup> and Cd<sup>2+</sup> ions fitted into Freundlich isotherm model ( $R^2 = 0.9924$  and 0.9921, respectively) better than into Langmuir equation ( $R^2 = 0.815$  and 0.9312, respectively). According to the Langmuir and Freundlich isotherm models the adsorption ability of Pb<sup>2+</sup> on PANi-



Fig. 8. Langmuir plots for the adsorption of  $Pb^{2+}$  (a) and  $Cd^{2+}$  (b) ions at pH of 6 and contact time of 40 min.

Table 2

The Langmuir constants for the adsoprtion of $Pb^{2+}$ and $Cd^{2+}$ ions	onto PANi-MTT composite at pH of 6 and contact time of 40 min
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Metal ions	$q_{max} ({ m mg \ g^{-1}})$	R <sup>2</sup>	$K_L$ (L mg <sup>-1</sup> )	Langmuir equation
Pb <sup>2+</sup>	121.951	0.815	4.316	y = 0.0082x + 0.0019
Cd <sup>2+</sup>	54.645	0.9312	5.719	y = 0.0183x + 0.0032

Table 3

Comparison of Langmuir adsorption capacity  $q_{\rm max}$  of  $Pb^{2+}$  and  $Cd^{2+}$  ions

Adsorbent	Maximun adsorption capacity $q_{\scriptscriptstyle max}$ (mg g^-1) of adsorbed ions		Ref.
	Pb <sup>2+</sup>	Cd <sup>2+</sup>	
Heat treated bentonite		16.50	[11]
Themally activated hydroxyapatite		64.30	[12]
Activated carbon from coconut shell	26.60		[13]
Natural calcite	19.92 (25°C)	18.52	[14]
Activated carbon from cashew nut shell	28.90	14.29	[15]
Activated carbon from apricot stone	21.38 (pH=6; <i>t</i> = 20 min)		[16]
Nanostructured CuO	115.00 (pH = 6.5; <i>t</i> = 240 min)		[17]
PANi-RH	131.58 (pH = 6; <i>t</i> = 40 min)	158.73 (pH = 6; <i>t</i> = 40 min)	[18]
Bentonite clay	51.19 (20°C)		[20]
Activated carbon/iron oxide magnetic composite	18–19 (pH = 4÷6)		[21]
PANi-M.B (Maize brand)	18.75		[22]
PANi-W.B (Wheat brand)	28.93		[22]
PANi-R.B (Rice brand)	30.11		[22]
PANI/ML (Madhuca longifolia)	3.891		[23]
PANI/JL (jambolana)	5.917		[23]
PANi-chitosan	92.9	98.4	[24]
PANi-Chitin	7.03 (25°C)	6.05 (25°C)	[25]
PAn/Al <sub>2</sub> O <sub>3</sub> -HPC		13.7741	[26]
Romania peat	41.4 (20°C)	43.84 (20°C)	[27]
Lignin	89.01 (20°C)	25.85	[28]
PANi-MTT	121.95 (pH = 6; <i>t</i> = 40 min)	54.65 (pH =6; <i>t</i> = 40 min)	Present study

Table 4

The value of dimensionless Langmuir parameter  $R_{_L}$  for the adsorption of  $\rm Pb^{2+}$  and  $\rm Cd^{2+}$  ions

$C_0 ({ m mg \ L^{-1}})$	$R_{L}$ (L mg <sup>-1</sup> )		
	$Pb^{2+}$	Cd <sup>2+</sup>	
0.5	0.317	0.259	
1.0	0.188	0.149	
2.0	_	0.080	
3.0	0.072	0.055	
4.0	0.055	0.042	
5.0	0.044	0.034	

MTT composite was better than that of Cd<sup>2+</sup> due to higher  $q_{max}$  and  $K_F$  values.

# 3.7. Thermodynamic study

The thermodynamic parameter such as standard Gibbs free energy  $\Delta G^0$  (kJ mol) can be calculated from thermodynamic equilibrium constant  $k_0$  following Eq. (7) which demonstrates that the adsorption process will occur favourably and spontaneously or not.

$$\Delta G^0 = -R_T \ln k_0 \tag{7}$$



Fig. 9. Freundlich plots for the adsorption of  $Pb^{2+}$  (a) and  $Cd^{2+}$  (b) ions at pH of 6 and contact time of 40 min.

Table 5 The Freundlich constants for the adsorption of  $Pb^{2+}$  and  $Cd^{2+}$  ions onto PANi-MTT composite at pH of 6 and contact time of 40 min

Metal ions	$K_F (\mathrm{mg g}^{-1})$	$N_F$	<i>R</i> <sup>2</sup>	Freundlich equation
Pb <sup>2+</sup>	180.302	1.354	0.9924	y = 0.7388x + 2.256
Cd <sup>2+</sup>	28.820	2.552	0.9921	y = 0.3918x + 1.6634



Fig. 10. Plots of ln (Cs/Ce) versus Cs at room temperature ( $30^{\circ}$ C) at pH of 6 and contact time of 40 min.

The constant  $k_0$  is determined by plotting ln ( $C_s/C_s$ ) versus  $C_s$  (Fig. 10) and extrapolating  $C_s$  to zero [14,29], where  $C_s$  is the equilibrium concentration in solution (m mol mL<sup>-1</sup>) and  $C_s$  is the solid-phase adsorbed concentration at equilibrium (mmol g<sup>-1</sup>). R is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and *T* is absolute temperature (K).

At the room temperature of 30°C the negative  $\Delta G^0$  values were found (Table 6) indicating the feasibility and spontaneous nature of the adsorption process for both metal ions.

# 3.8. Adsorption kinetics

In order to study the mechanism of adsorption, the pseudo first order, the pseudo second order and intraparticle diffusion models were used to examine the Table 6

Standard Gibbs free energy  $\Delta G_0$  and thermodynamic equilibrium constant  $k_0$  for metal ion adsorption onto PANi-MTT at room temperature (30°C)

Metal ions	K <sub>0</sub>	$\Delta G_0$ (kJ mol <sup>-1</sup> )
Pb <sup>2+</sup>	13.22	-7.019
Cd <sup>2+</sup>	13.63	-7.102

kinetics experimental data. The pseudo first order kinetic equation is represented in Eq. (8) where  $q_e$  and  $q_t$  are the adsorption capacities of ions onto adsorbent (mg g<sup>-1</sup>) at equilibrium and at time  $t_r$  respectively,

 $k_1$  is the rate constant of the pseudo first-order adsorption (min<sup>-1</sup>). The kinetic parameters are obtained from the plot of log  $(q_e - q_i)$  vs. *t*.

$$lg (q_e - q_t) = lgq_e - k_1/2.303 t$$
(8)

The pseudo second order model is expressed as equation (9), where  $k_2$  is the rate constant of the pseudo second-order adsorption (g mg<sup>-1</sup> min<sup>-1</sup>). The kinetic parameters are calculated based on the plots of  $t/q_t$  vs. t.

$$t/q_{t} = 1/k_{2}q_{e}^{2} + t/q_{e}$$
(9)

The obtained data in Table 7 illustrates that the adsorption processes of  $Pb^{2+}$  and  $Cd^{2+}$  ions on researched composite fitted into the pseudo second order kinetics because the coefficient  $R^2$  almost equal to 1. Also, plots given in Fig. 11 shows linear relationship what indicated

Table /							
Kinetic param	eter for adsorption	on of Pb <sup>2+</sup> and C	Cd <sup>2+</sup> ions follow	ving the pseudo first a	and pseudo secc	ond order models	
Metal ion	The pseudo fi	rst order		Exprimental	The pseudo se	econd order	
	$q_{e'}t_h ({ m mg g}^{-1})$	$k_1 (\min^{-1})$	$R^2$	$q_{e'}\exp(\mathrm{mg}\mathrm{g}^{-1})$	$q_{e'}t_h ({\rm mg \ g^{-1}})$	$k_2 ({ m g mg^{-1} min^{-1}})$	$R^2$
Pb <sup>2+</sup>	0.279	0.039	0.976	13.233	13.333	0.345	1.000

12.680



0.277

Fig. 11. The pseudo first order plots (a) and the pseudo second order plots (b) of Pb<sup>2+</sup> and Cd<sup>2+</sup>.

that the pseudo second order kinetics is applicable. It was found that the rate constant of the pseudo second order adsorption of  $Cd^{2+}$  ion was higher than that of  $Pb^{2+}$  one, but, the equilibrium capacity adsorption of  $Cd^{2+}$  was lower.

# 3.9. Intraparticle diffusion model

The rate parameters for intraparticle diffusion ( $k_i$ ) at different initial concentrations are determined using the following Eq. (10), where  $k_i$  is the intraparticle diffusion rate constant (mg g<sup>-1</sup> min<sup>-1/2</sup>) and *B* is the intercept describing the thickness of the boundary layer [30].

$$q_t = k_t t^{1/2} + B \tag{10}$$

0.446

12.658

0.999

According to some papers reported [31,32], the overall rate of adsorption process occurs in three steps: the first one is film or surface diffusion where the metal ion as adsorbate is transported from the bulk solution to the external surface of sorbent, describing a shaper portion, the second one is intraparticle or pore diffusion, where metal ion move into the interior of adsorbent particles, illustrating the gradual adsorption stage, where intraparticle diffusion is ratecontrolled, and the third one is adsorption on the interior sites of the adsorbent, where intraparticle diffusion starts to



Fig. 12. Intraparticle diffusion plots for  $Pb^{2+}$  (a) and  $Cd^{2+}$  adsorption (b) onto composite at room temperature (30°C). Initial concentration of  $Pb^{2+}$  and  $Cd^{2+} = 1 \text{ mg } L^{-1}$  (pH = 6).

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Table 7

 $Cd^{2+}$ 

0.270

0.009

Table 8

Intraparticle diffusion coefficients and intercept values for  $Pb^{2+}$  and  $Cd^{2+}$  adsorptions onto PANi-MTT composite at room temperature (30°C)

Diffusion	Pb <sup>2+</sup>			Cd <sup>2+</sup>		
stage	$k_i (\mathrm{mg}  \mathrm{g}^{-1}  \mathrm{min}^{-1/2})$	В	$R^2$	$k_i (\mathrm{mg}  \mathrm{g}^{-1}  \mathrm{min}^{-1/2})$	В	R <sup>2</sup>
1	4.3019	0.4090	0.9692	4.0910	0.4127	0.9653
2	0.0254	12.9760	0.9344	0.0251	12.2040	0.9222

slow down due to extremely low adsorbate concentrations in the solution.

We can find only two linear steps in Fig. 12 which illustrates the adsorption process of both  $Pb^{2+}$  and  $Cd^{2+}$  ions onto regarded composite. The first stage was very sharp, which completed only in the first 10 min, indicating the external surface adsorption that is the movement of metal ions from aqueous phase through the hydrodynamic boundary layer film of the solid. The second one was the final equilibrium stage. It is clear that the intraparticle diffusion was not the rate controlling step because of the absent of intraparticle or pore diffusion. The results from Table 8 indicate the intraparticle diffusion rate constant ( $k_i$ ) and the intercept (B) of both metal ions were nearly similar.

# 3.10. Desorption and regeneration of adsorbent

The received data in Fig. 13 and Table 9 shows that the maximum adsorption capacities were found 123.457 and 57.143 mg  $g^{-1}$  for Pb<sup>2+</sup> and Cd<sup>2+</sup> on the regenerated PANi-MTT composite, respectively. The values were a little higher than those of the PANi-MTT composite presented in Table 2. It can be explained that the material after regeneration could be trained from desorption resulting to a deeper adsorption for both above ions.

# 3.11. Treatment of wastewater from the electroplating factory in *Hung Yen province*

Using the wastewater sample (pH = 6) from the electroplating factory in Hung Yen province for removing some heavy metal ions. The data given in Table 10 shows that the Cu<sup>2+</sup>, Ni<sup>2+</sup> and Cd<sup>2+</sup> ions which presented in this wastewater could be good adsorbed on the prepared composite with removal efficiency of 81.36, 76.84 and 97.05%, respectively. It explained that the same time their adsorption ability depended not only on their initial concentration but also on kind of metal ion.

Table 10

Treatment result of wastewater from the electroplating factory in Hung Yen province (pH = 6)

Cation	$C_0 ({ m mg \ L^{-1}})$	<i>C</i> (mg L <sup>-1</sup> )	H (%)
Cu <sup>2+</sup>	5.330	0.993	81.36
Ni <sup>2+</sup>	4.885	1.131	76.84
Cd <sup>2+</sup>	0.340	0.010	97.05



Fig. 13. Langmuir plots for the adsorption of  $Pb^{2+}$  and  $Cd^{2+}$  ions on regenerated composite at pH of 6 and contact time of 40 min.

Table 9

The Langmuir constants for the adsoprtion of  $Pb^{2+}$  and  $Cd^{2+}$  ions onto regenerated composite at pH of 6 and contact time of 40 min

Metal ions	$q_{max}$ (mg g <sup>-1</sup> )	R²	$\frac{K_L}{(\mathrm{L}\mathrm{mg}^{-1})}$	Langmuir equation
Pb <sup>2+</sup>	123.457	0.84	0.0014	y = 0.0081x + 0.0014
$Cd^{2+}$	57.143	0.96	0.0059	y = 0.0175x + 0.0059

## 4. Conclusion

PANi-MTT nanocomposite based on PANi and MTT was successfully synthesized by chemical polymerization method. It could be useful for the removal of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions from aqueous solution. The optimum conditions for removal of both ions were found at pH of 6 and contact time of 40 minutes. The adsorption of them onto regarded composite fitted very well into the pseudo-second order kinetic model, it followed by the Freundlich adsorption isotherm equation better than by Langmuir one. The maximum adsorption capacities were 121.951 mg g<sup>-1</sup> and 54.645 mg g<sup>-1</sup> for Pb<sup>2+</sup> and Cd<sup>2+</sup> ions, respectively. The material could be regenerated for reusing in treatment process of Pb<sup>2+</sup> and Cd<sup>2+</sup> from solution.

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