Nanostructured Composite Based on Polyaniline and Rice Raw for Removal of Lead(II) and Cadmium(II) from Solution

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Composites based on polyaniline and raw rice were prepared by chemical method from acid medium containing aniline using ammonium persulfate as oxidation agent. The IR-spectrum confirmed the presence of polyaniline existed in composite which having morphological structure in nano scale by SEM and TEM images. Lead(II) and cadmium(II) ion concentrations in solution before and after adsorption process on absorbents were analyzed by atomic absorption spectroscopy. The favourable adsorption process of them was found by dimensionless Langmuir (R_L) and Freundich parameter (N_F). The maximum adsorption capacity obtained from the Langmuir isotherm model were 217.3913 and 138.8899 mg/g for Pb^{2+} and Cd^{2+}, respectively. The negative $\Delta G°$ values were found indicating the feasibility and spontaneous nature of the adsorption process for them.

Key Words: Polyaniline-rice raw composite, Langmuir isotherm adsorption, Nanostructure, Heavy metal ions removal.

INTRODUCTION

Many adsorbents based on zeolite, bentonite or conducting polymer composites, *etc.* have been using for removal of heavy metal ions from waste water[1-3]. In previous years, among conducting polymer, polyaniline (PANi) was mostly hybrided with agricultural waste or other materials to become composites using for environmental treatment because of their positive characteristics[4-6]. Vietnam is a land of rice export so a huge amount of raw rice from which as an agricultural waste goes into environment. The aim of this work was preparation of composite based on raw rice with polyaniline for removing Pb^{2+} and Cd^{2+} ions from solution. The thermodynamic study and adsorption mechanisms of above metal ions were also studied.

EXPERIMENTAL

Preparation of materials: Composite was prepared by chemical polymerizarion owing to oxidation of aniline in hydrochloric acid medium at presence of raw rice and ammonium persulfate. The reaction was occurred in 18 h under continuously stirring at 1-5 ℃. After purification and changing it into emeraldine base (EB) by treatment with 0.5 M ammonia solution, it was filtrated and dried under vacuum condition at 50℃ in 2 h and then kept in a sealed bottle for material properties and adsorption ability of heavy metal ions.

Detection method: The structure of materials was carried out by infrared spectrum on IMPACT 410-Nicolet unit. The surface morphology of them was examined by SEM on an equipment FE-SEM Hitachi S-4800 (Japan) and TEM on a Jeol 200CX (Japan). Their crystaline structure was analyzed by using an X-ray diffractometer D5000- Siemens (Germany). Their adsorption ability of heavy metal ions was characterized by atom adsorption spectroscopy (AAS) on an equipment Shimadzu AA-6800 (Japan).

Procedure of adsorption research: The mixture of absorbent and solution containing heavy metal ion were swinged at 300 rpm for 40 min and then filtered to remove solid parts. The filtrate was analyzed by AAS.

The amount of solute removed at equilibrium can caculate following equation:

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

where C_o is initial concentration, C is concentration after adsorption, V is amount of solution and m is adsorbent dose.

RESULTS AND DISCUSSION

SEM images: The images illustrated in Fig. 1 showed that obtained composite existed in nanostructural fibres having not uniform diameter (c) in comparision with which of polyaniline (b). Raw rice had spongy structure formed by
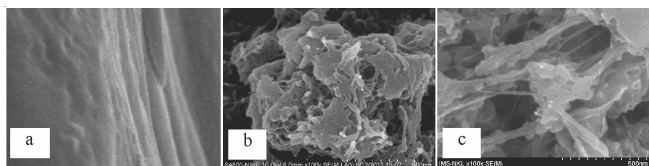
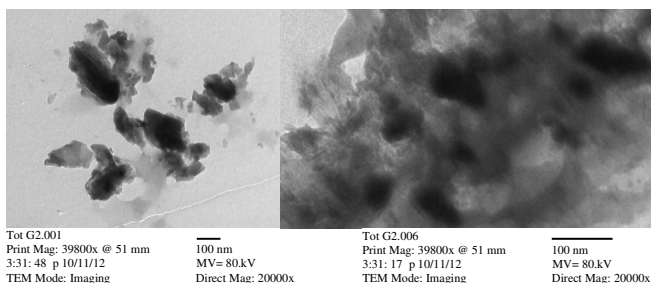Fig. 1. SEM images of raw rice (a), polyaniline (b) and composite prepared with ratio between monomer and raw rice of 1:2

mixing fibres of cellulose, hemicellulose and lignin containing materials.

TEM images: TEM images (Fig. 2) showed two clearly differrent colours the light one belonging to polyaniline enclosing the dark one belonging to raw rice. Both of them had size in nano range. The obtained results from SEM and TEM analysis explained that nanostructural composite based on polyaniline and raw rice were succesfully prepared in present research.


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Tot G2.001                                    Tot G2.006
Print Mag: 39800x @ 51 mm    100 nm          Print Mag: 39800x @ 51 mm    100 nm
3:31: 48  p 10/11/12                          3:31: 17  p 10/11/12
TEM Mode: Imaging    MV= 80.kV                TEM Mode: Imaging    MV= 80.kV
Direct Mag: 20000x                            Direct Mag: 20000x
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Fig. 2. TEM images of composite prepared with ratio between monomer and raw rice of 1:2

Infrared spectra: The results (Fig. 3) explained that polyaniline existed in composite owing to vibration signals of benzenoid and quinoid ring at 1590 and 1460 cm^{-1}, respectively. Some other signals were found at 3413-3300 cm^{-1} assigning N-H stretching mode, 2904 cm^{-1} (C-H) and 1125 cm^{-1} (C-N$^+$)[7]. Otherwise, the vibration signals of C=O group at 1740 cm^{-1} belonging to ester group in hemicellulose, C-O group at 1030 cm^{-1} belonging to cellulose, hemicellulose and lignin, which explained that the presence of raw rice in composite.

Adsorption ability of lead(II) and cadmium(II) ions onto materials

Influence of pH: The data (Fig. 4) explained that adsorption ability of Pb^{2+} and Cd^{2+} onto adsorbents depended strongly on pH medium of solution so that an optimal adsorption process for Cd^{2+} and Pb^{2+} ions can be occurred at pH of 5 and 6, respectively. The lower pH value is the worse uptake of Pb^{2+} and Cd^{2+} ions onto materials is because the presence of H$^+$ ion does make competing with them for the adsorption sites. Conversely, when pH values increase the metal ions are allowed to have a higher affinity for the adorption because H$^+$ ions were released from the imine groups[8]. The adsorption mechanism of metal ions on polyaniline may be as following equation:

$$-[B-N-Q-N-B-N-Q]_n- + 3nM(II) \longrightarrow$$
$$-[B-N(M)-Q-N(M)-B-N(M)-Q]_n \quad (2)$$

where B and Q are benzenoid and quinoid rings, respectively, M are Pb^{2+} and Cd^{2+} ions.

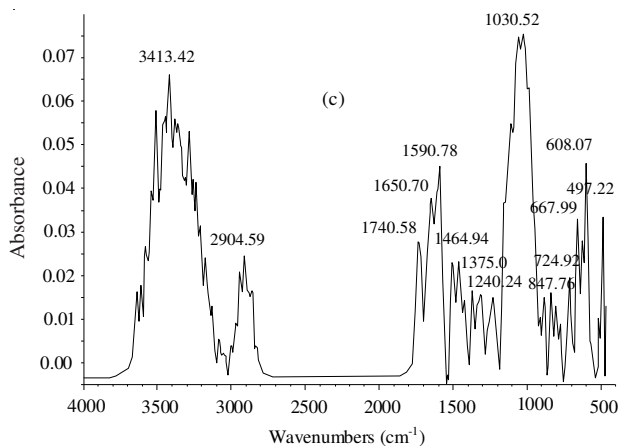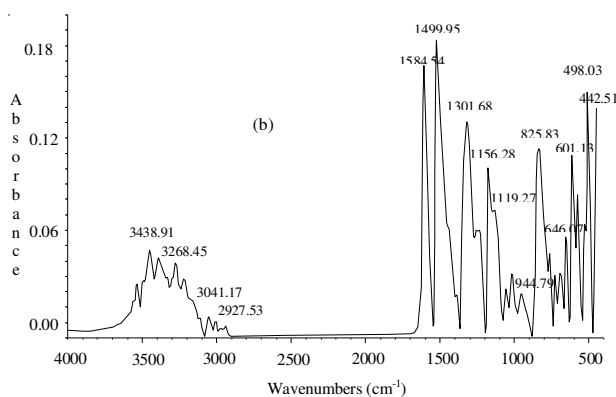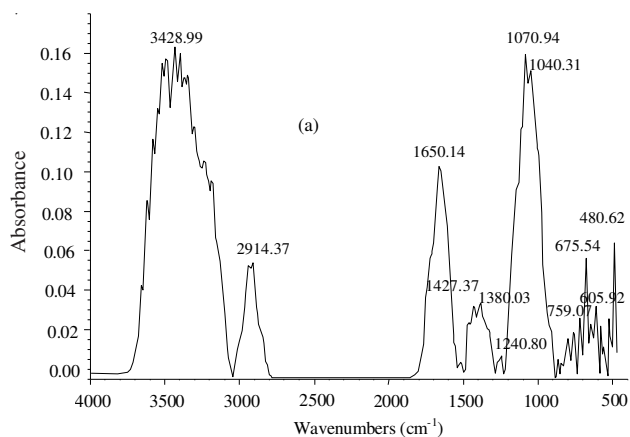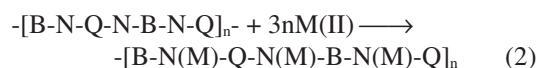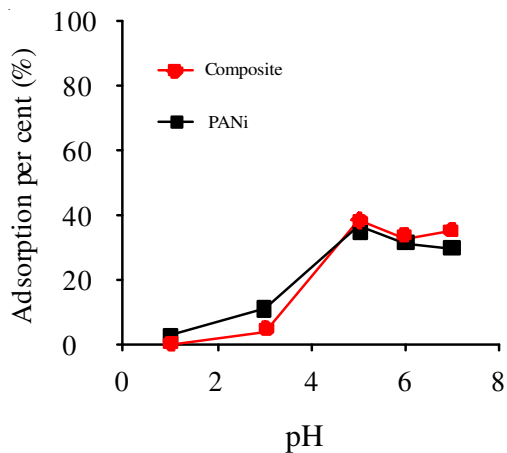| Signals ν (cm^{-1})			Binding
(a)	(b)	(c)	
3429		3413	ν_{O-H}
2914			ν_{C-H}
1739		1740	$\nu_{C=O}$ ester group in hemicellulose
1650		1650	ν_{H-O-H} in watr molecular
1427,1380			$\nu_{C=C}$ aromatic in lignin
1070,1040		1030	ν_{C-O} in cellulose, hemicellulose, lignin
	3438,3268	3413,3300	ν_{N-H}
	3041,2927	2904	ν_{C-H} aromatic
	1584	1590	Benzoid
	1499	1464	Quinoid
	1301	1375	–N=quinoid=N–
	1156	1125	C–N$^+$ group
	825	847	N-H group

Fig. 3. IR-spectra of (a) raw rice, (b) polyaniline and (c) polyaniline-raw rice composite prepared with ratio between monomer and raw rice of 1:2

Fig. 5. Influence of initial concentration of Pb^{2+} (above) and Cd^{2+} ions (below) on removal ability of them from solution by adsorbents

and 76.2667 mg/g for Cd^{2+} ions after contact time of 40 min, after which the removal effect was also optimal for both ions. However, the removal effect for Pb^{2+} was higher than that for Cd^{2+} in the same time (Fig. 6).
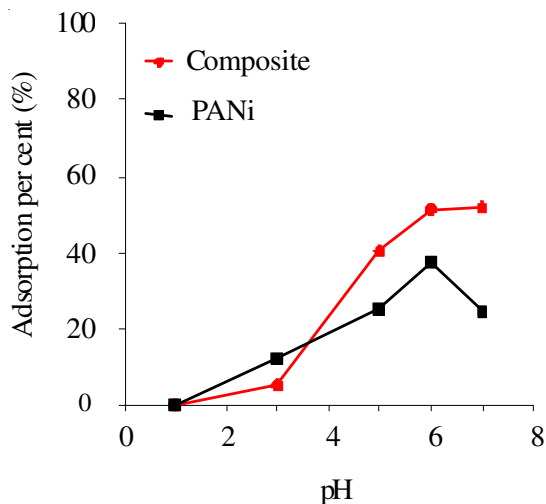

Fig. 4. Influence of pH on adsorption ability of Pb^{2+} (above) and Cd^{2+} ions (below) onto adsorbents. Initial concentration of Pb^{2+} = 20 mg/L and Cd^{2+} = 15 mg/L

Influence of initial concentration: The removal ability of metal ions from solution depended decreasingly on their initial concentration among them lead ion can be removed by composite better than that by polyaniline in comparision with cadmium ion (Fig. 5).

Effect of contact time: The adsorption capacity and removal per cent for Cd^{2+} and Pb^{2+} were evaluated following contact time at pH of 5 and 6 for Cd^{2+} and Pb^{2+} ions, respectively. It reached the maximum value of 130 mg/g for Pb^{2+}
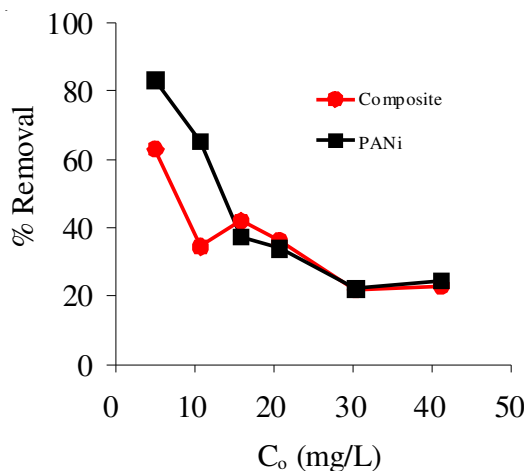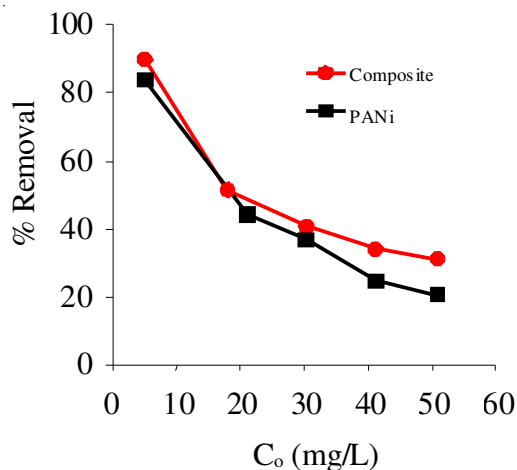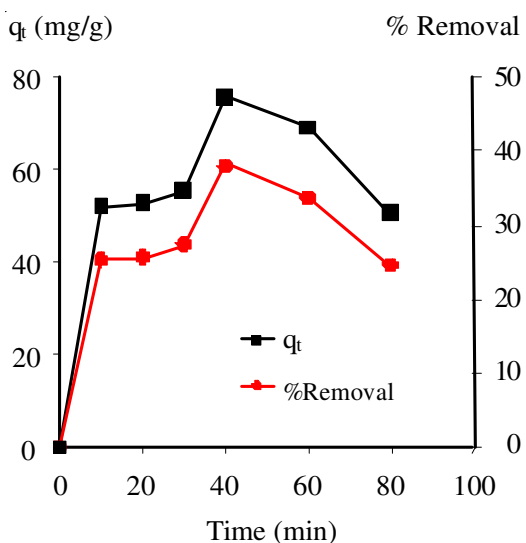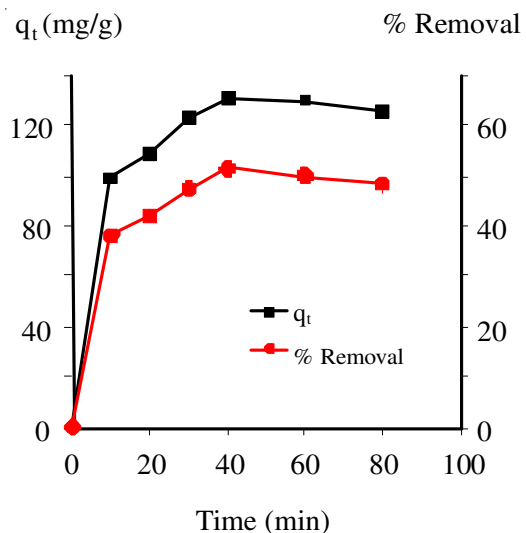

Fig. 6. Influence of contact time on adsorption capacity and removal per cent for Pb^{2+} (above) and for Cd^{2+} ions (below) onto composite. Conditions for Pb^{2+}: pH = 6 and C$_o$ = 18.5 mg/; for Cd^{2+}: pH = 5 and C$_o$ = 14.93 mg/L

Langmuir model: Langmuir model can be expressed by eqn. 3:

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

where q is the amount of solute removed at adsorbed equilibrium, C is concentration after adsorption, q_{max} is maximum adsorption capacity of absorbents, K_L is Langmuir parameter. Fig. 7 showed that the Langmuir isotherm parameters given in Tables 1 and 2 for Pb^{2+} and Cd^{2+} ions, respectively. It explained that the maximum adsorption capacity of composite better than that of polyaniline for both regarded ions among them the q_{max} of composite for Pb^{2+} ion (217.3913 mg/g) was much higher than that for Cd^{2+} ion (138.8899 mg/g).
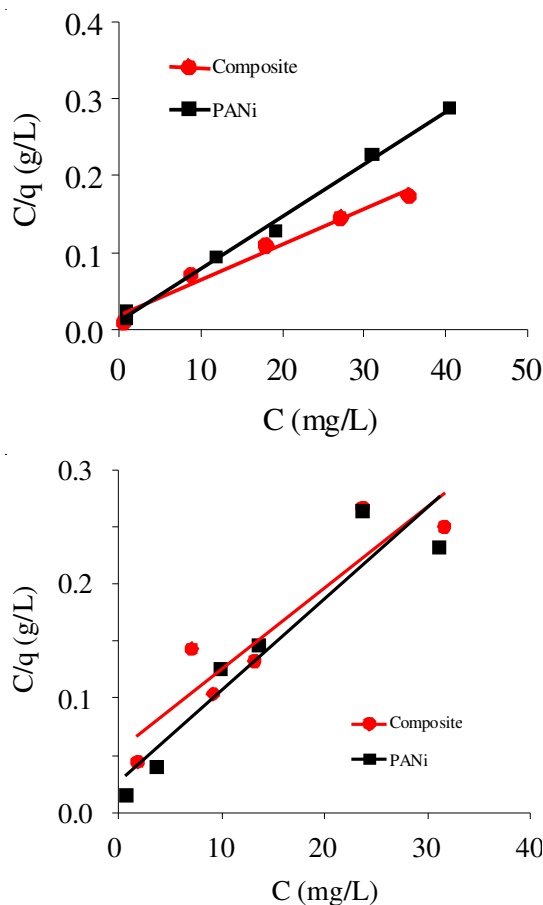

Fig. 7. Langmuir model of Pb^{2+} (above, pH = 6) and Cd^{2+} ions (below, pH = 5) onto adsorbents

TABLE 1
ADSORPTION PARAMETER FOR
Pb^{2+} ONTO MATERIALS (pH = 6)

Materials	q_{max} (mg/g)	R^2	K_L (L/mg)	Langmuir equation
PANi	147.6588	0.9958	0.623853	y=0.0068x+0.0109
Composite	217.3913	0.9738	0.235897	y=0.0046x+0.0195

TABLE 2
ADSORPTION PARAMETER FOR
Cd^{2+} ONTO MATERIALS (pH = 5)

Materials	q_{max} (mg/g)	R^2	K_L (L/mg)	Langmuir equation
PANi	123.4568	0.8946	0.321429	y=0.0081x+0.0252
Composite	138.8899	0.8569	0.134831	y=0.0072x+0.0534

By expressing of dimensionless Langmuir parameter R_L as the isotherm shape following eqn. 4 that can predict if an adsorption system is favourable or not[9,10]:

$$R_L = \frac{1}{1 + K_L \times C_0} \tag{4}$$

According to Ghorbani *et al.*[10] and Mamdouth *et al.*[11], if $R_L > 1$ the adsorption process is unfavourable, $R_L = 1$ it is linear, $R_L = 0$ it is irreversible and $0 < R_L < 1$, it is favourable. The parameter R_L given in Tables 3 and 4 indicated the adsorption process of Pb^{2+} and Cd^{2+} ions on mentioned adsorbents is favourable because of $0 < R_L < 1$.

TABLE-3
VALUES OF DIMENSIONLESS LANGMUIR PARAMETER R_L FOR Pb^{2+} ION ADSORPTION

C_o (mg/L)	R_L (L/mg)	
	PANi	Composite
5.04	0.293421	0.456846
21.19	0.241300	0.190616
30.31	0.070326	0.122699
41.16	0.050229	0.093375
50.87	0.037484	0.076923

TABLE-4
VALUES OF DIMENSIONLESS LANGMUIR PARAMETER R_L FOR Cd^{2+} ION ADSORPTION

C_o (mg/L)	R_L (L/mg)	
	PANi	Composite
5.070	0.380279	0.377259
10.808	0.223513	0.221294
15.858	0.164009	0.162257
20.682	0.130757	0.129305
30.377	0.092902	0.091826
41.114	0.070347	0.069512

Freundlich model: The Freundlich isotherm model can be expressed following eqn. 5:

$$q = K_F C^{1/N_F} \tag{5}$$

where q is the amount of solute removed at adsorbed equilibrium, C is concentration after adsorption, K_F and N_F are Freundlich parameters.

It was found the highest Freundlich parameter K_F for Pb^{2+} (71.1377 mg/g in Table-5) which was over two times as high as Cd^{2+} (32.0996 mg/g in Table-6) in the case of composite.

TABLE-5
ADSORPTION PARAMETER FOR Pb^{2+} ONTO MATERIALS (pH = 6)

Materials	K_F (mg/g)	N_F	R^2	Freundlich equation
PANi	51.0387	3.2300	0.9089	y=0.3096x+1.7079
Composite	71.1377	3.4662	0.9925	y=0.2885x+1.8521

TABLE-6
ADSORPTION PARAMETER FOR Cd^{2+} ONTO MATERIALS (pH = 5)

Materials	K_F (mg/g)	N_F	R^2	Freundlich equation
PANi	61.1787	5.777	0.6792	y=0.1731x+1.7866
Composite	32.0996	2.6674	0.7915	y=0.3749x+1.5065

The obtained results explained that adsorption of Pb^{2+} ions fitted into both Langmuir and Freundlich isotherm models better than that of Cd^{2+} onto materials because of higher R^2 values. It were found $1 < N_F < 5$ that confirmed the adsorption process was also favourable[8,10] (Fig. 8).
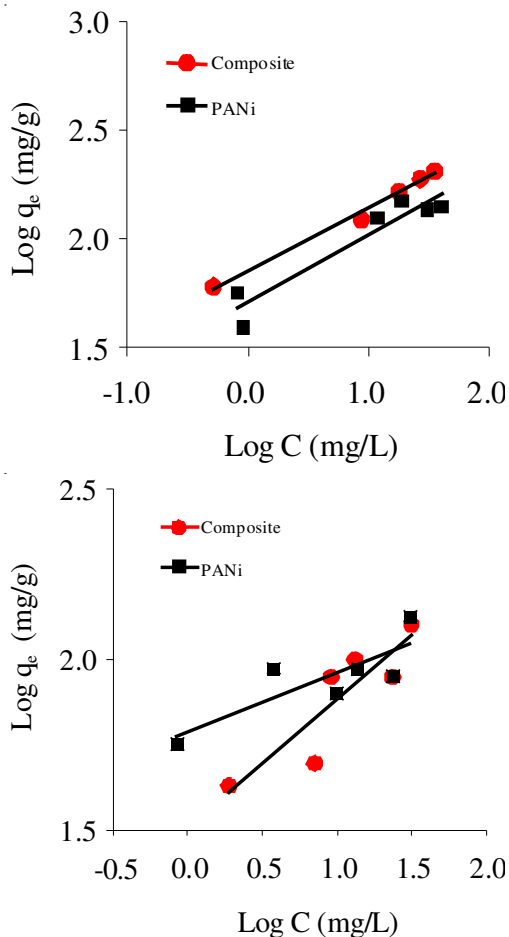

Fig. 8. Freundlich model of Pb^{2+} (above, pH = 6) and Cd^{2+} ion (below, pH = 5) onto adsorbents

Thermodynamic study: The thermodynamic parameters such as standard Gibbs free energy ΔG° (kJ/mol) can be calculated from thermodynamic equilibrium constant k_o following equation:

$$\Delta G^{\circ} = -RT \ln k_o \qquad (6)$$

The constant k_o was determined by plotting $\ln (C_s/C_e)$ versus C_s (Fig. 9) and extrapolating C_s to zero[12,13], where C_e is the equilibrium concentration in solution (mmol/L) and C_s is the solid-phase concentration at equilibrium (mmol/g). R is the gas constant (8.314 J/mol K) and T is absolute temperature (K).
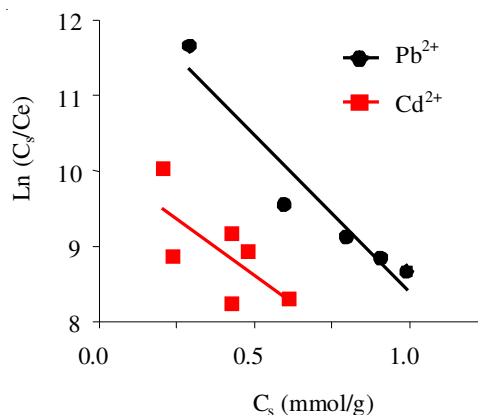

Fig. 9. Plots of $\ln (C_s/C_e)$ versus C_s at room temperature (30 ℃). Conditions: pH = 6 for Pb^{2+} and 5 for Cd^{2+} ions; absorbent: composite

At room temperature (30 ℃) the negative ΔG° values indicating the feasibility and spontaneous nature of the adsorption process for both involved metal ions among them Pb^{2+} ion can adsorb onto composite more easily than Cd^{2+} ion becauce of higher k_o and negativer ΔG° (Table-7).

TABLE-7 STANDARD GIBBS FREE ENERGY ΔG° AND THERMODYNAMIC QUILIBRIUM CONSTANT k_o FOR METAL ION ADSORPTION ONTO COMPOSITE AT ROOM TEMPERATURE (30 ℃)		
Metal ions	k_o	ΔG° (kJ/mol)
Pb^{2+}	12.57	-6.376
Cd^{2+}	10.11	-5.829

Adsorption mechanisms: The interaparticle diffusion equation is decribed as:

$$q_t = k_t t^{0.5} + B \qquad (7)$$

where k_i is the intraparticle diffusion rate constant (mg g^{-1} min$^{-0.5}$) and B is the intercept. The detailed understanding of adsorption rate can be expressed by following factors: (i) diffusion of the solute from the bulk solution to the external surface of particle, (ii) diffusion from the surface to the internal sites (surface diffusion or pore diffusion) and (iii) adsorption on the interior sites of the adsorbent[14-16].

According to this model, it were found three linear steps in Fig. 10 which illustrated the adsorption process of both Pb^{2+} and Cd^{2+} ions onto composite. The first stage is very sharp indicating the external surface adsorption. The second one is the gradual adsorption stage, where intraparticle diffusion is rate-controlled. Normally, the third one is the final equilibrium stage where intraparticle diffusion starts to slow down owing to extremely low adsorbate concentrations in the solution like in the case of Pb^{2+} ion, but, however, the desorption of Cd^{2+} ion may be occurred significantly after 40 min because of big negative slope of line appeared in this stage (Table-8).

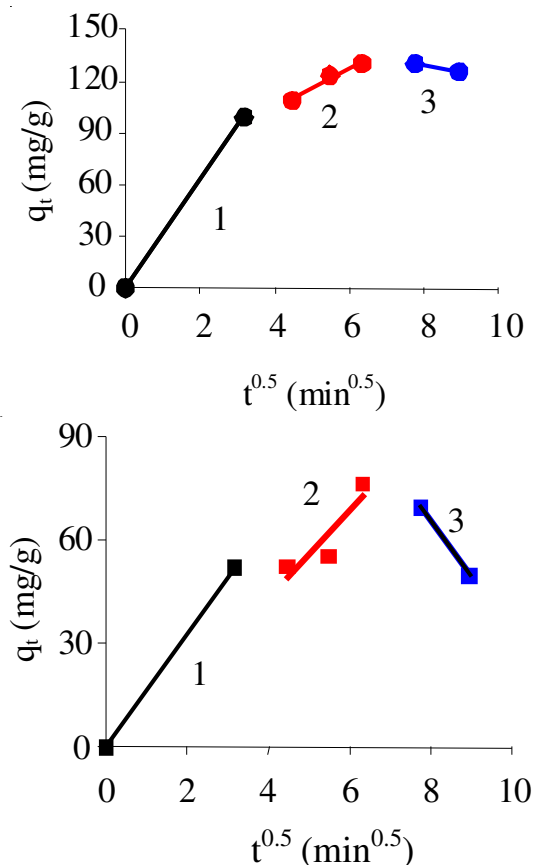| TABLE-8 INTRAPARTICLE DIFFUSION COEFFICIENTS AND INTERCEPT VALUES FOR Pb^{2+} AND Cd^{2+} ADSORPTION ONTO COMPOSITE AT ROOM TEMPERATURE (30 ℃)						
Diffusion stage	Pb^{2+}			Cd^{2+}		
	k_i (mg g^{-1} min$^{0.5}$)	B	R^2	k_i (mg g^{-1} min$^{0.5}$)	B	R^2
1	31.2850	131.67	1	16.4020	0	1
2	14.9140	45.454	1	12.5820	-0.6743	0.8074
3	-0.2474	1E-14	0.9981	-1.1702	78.398	1

Fig. 10. Intraparticle diffusion plots for Pb^{2+} (above) and Cd^{2+} adsorption (below) onto composite at room temperature (30 °C). Initial concentration of Pb^{2+} = 18.5 mg/L (pH = 6) and Cd^{2+} = 14.93 mg/L (pH = 5)

Conclusion

Nanostructured composite based on polyaniline and raw rice was successfully synthesized by chemical method. The adsorption ability of materials depended on pH medium which can receive values of 5 and 6 for an optimal adsorption process of both Cd^{2+} and Pb^{2+} ions, respectively. The adsorption of Pb^{2+} and Cd^{2+} ions onto present absorbents was favourable among them the adsorption of Pb^{2+} ion fitted into both Langmuir and Freundlich isotherm models better than Cd^{2+} ion. The maximum adsorption capacity were found 217.3913 and 138.8899 mg/g for Pb^{2+} and Cd^{2+} ions, respectively. The adsorption process of both ions onto composite is favourable among them the degree of spontaneity of Pb^{2+} is bigger than that of Cd^{2+} ion. The composite based on polyaniline and raw rice can use as adsorbent for above heavy metal treatment from solution.

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