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Synthesis of adsorbent materials based on polyaniline and agriculture waste by soaking method for removal heavy metal ions from solution

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Abstract : Composites based on polyaniline (PANi) and agriculture waste (peanut shell (PS), rice raw (RR)) prepared by soaking method for removal Cd^{2+} and Pb^{2+} ions from solution. It was found by IR-spectroscopy a clearly presence of PANi in composites. Their mophorlogical structure was shown in nano range due to SEM and TEM images. Cd^{2+} and Pb^{2+} ion concentrations in solution before and after adsorption process on those composites were analysed by atomic adsorption spectroscopy. The maximum adsorption capacities of Pb^{2+} (185.1852 mg/g) and Cd^{2+} (131.5789 mg/g) ions onto PANi-PS were higher than those onto PANi-RR (158.7302 mg/g and 93.4579 mg/g for Pb^{2+} and Cd^{2+} ions, respectively). Their adsorption process occurred onto both composites fitted well into Langmuir isotherm model also.

Keywords : Nanocomposite; Adsorption isotherm model; Heavy metal ion removal.

INTRODUCTION

Removal heavy metal from water by adsorption method is useful over the other such as biotechnology or electrochemistry because of low cost and simple implementation. Thus, many adsorbent materials have been developing for waste water treatment, which are prepared not only by chemical method[1-3], but also by soaking one[4]. Among them the materials based on polyaniline (PANi) and some agriculture waste such as sawdust, rice raw, rice husk, *etc.* are mentioned in recently literatures[5-7], but, there are a lack of peanut shell (PS) and rice raw (RR) which may become composite by soaking them into PANi solution. In this research, PANi-RR and PANi-PS will be compared with each other in the adsorption effect for Pb^{2+} and Cd^{2+} ions.

EXPERIMENTAL

Preparation of materials

Clean RR and PS were dried before grinded and sieved (0.27 mm). Their powder grains were ultrasonically washed by acetone, then fitrated and dried at 50°C for 1 day. The soaking method for preparing materials was done following as 2 g of RR or PS powder grain soaked into 20 ml of formic acid PANi solu-

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tion (5 g L^{-1}) under stirring of 3 h and then still of the night. The product was dried under *vacuum* condition at 70 ^{o}C in 8 h.

Detection method

The structure of material 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). Adsorption ability of heavy metal ions on research material was characterized by atom adsorption spectroscopy (AAS) on an equipment Shimadzu AA-6800 (Japan).

Procedure of adsorption research

The mixtures of materials and solution containing mono heavy metal ion with different initial concentrations were swinged at 300 rpm for 40 min and then filtered to remove solid parts. The filtrate was analysized by AAS. The adsorption capacity (mg metal ion per g composite material) was determined by mass balance, as follows:

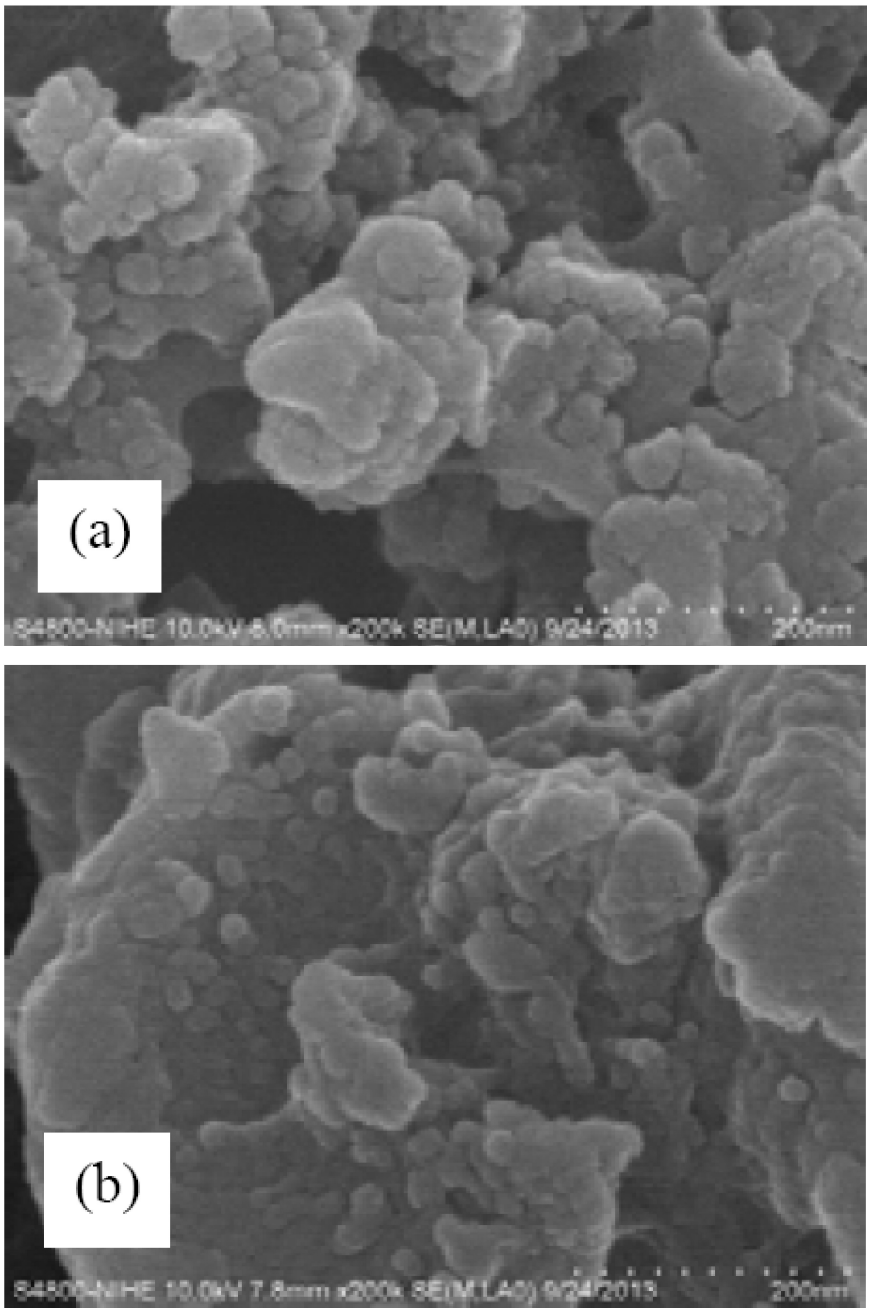
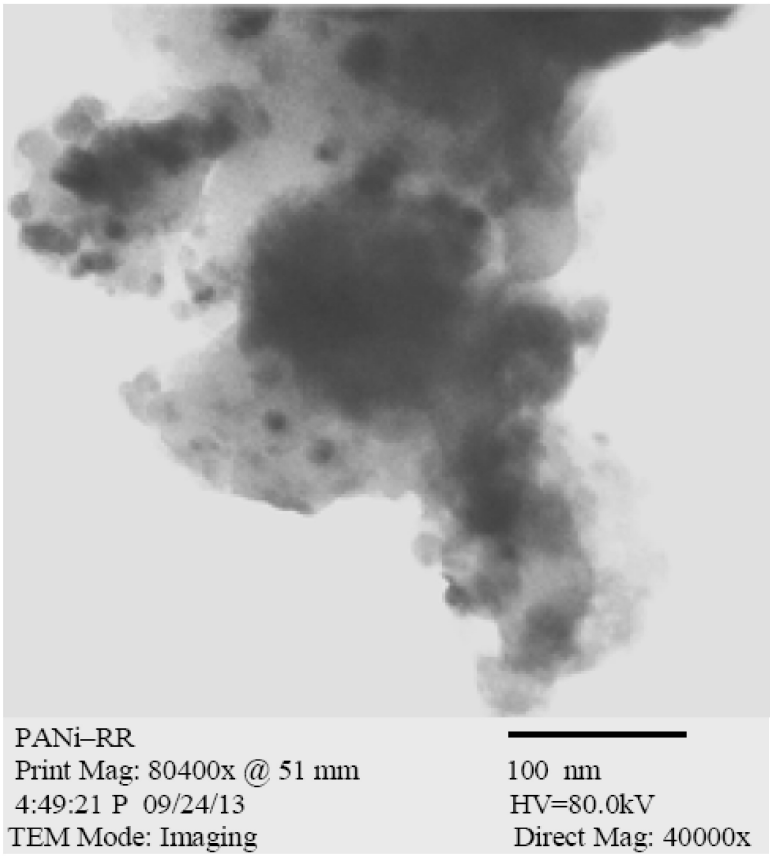


Figure 1 : SEM images of PANi-RR (a) and PANi-PS (b)



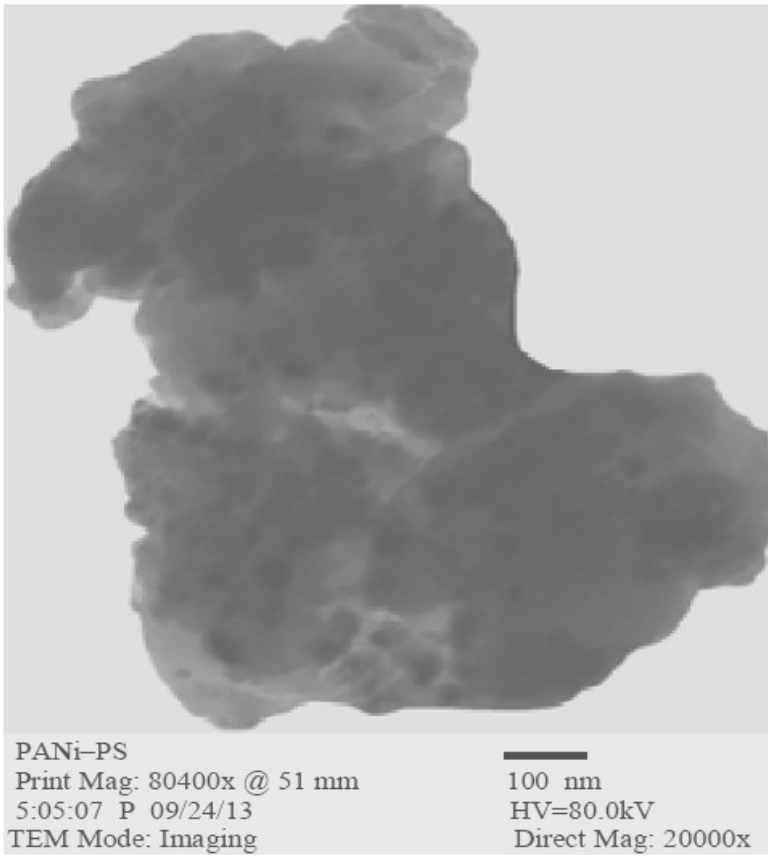


Figure 2 : TEM images of PANi-RR (a) and PANi-PS (b) composites

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$$q = \frac{(C_o - C)\,V}{m} \quad (1)$$

where C_o and C are metal ion concentrations (mg L^{-1}) before and after adsorption, respectively, V is the volume of the solution (mL) and m is the mass of adsorbent.

RESULTS AND DISCUSSIONS

Characterization of materials

SEM images

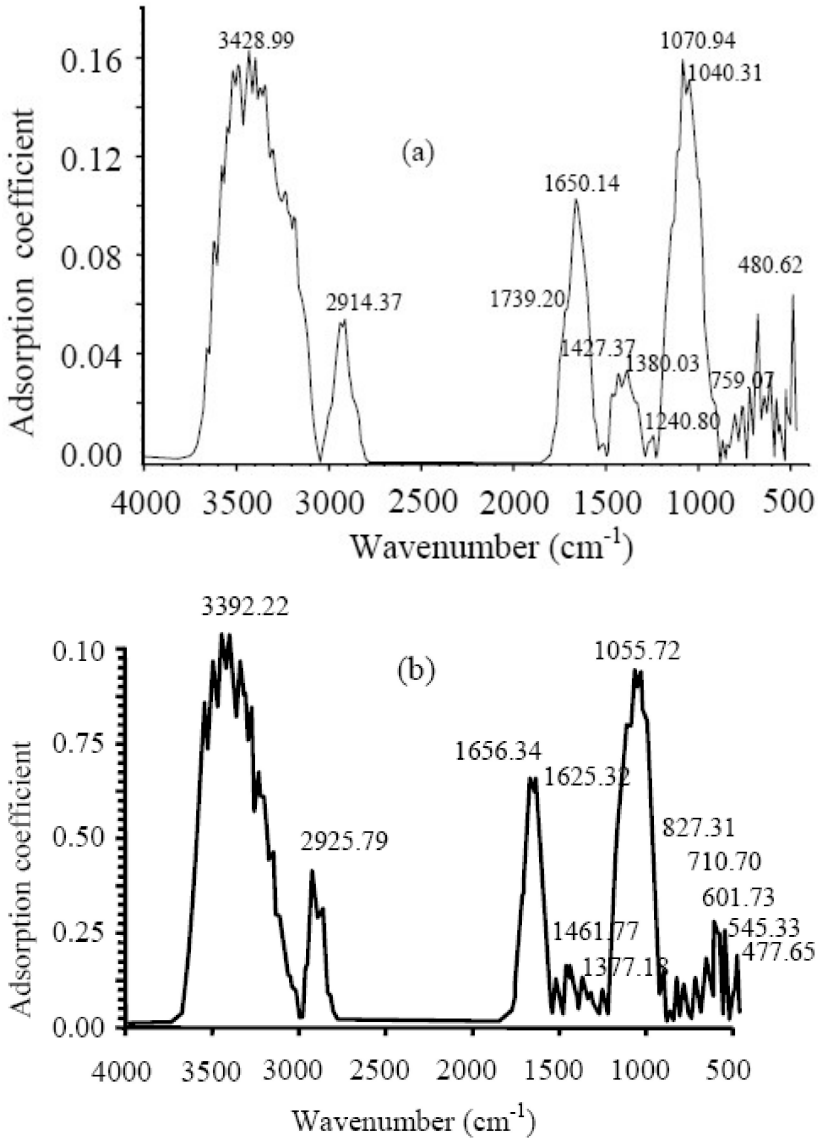
The images in Figure 1 showed that the both composites existed in nanostructure among them the fiber size of PANi-PS (b) was bigger than that of PANi-RR (a).

TEM images

There were found on TEM images (Figure 2) two different colours among them the light one belonging to PANi enclosing the dark one belonging to RR (a) or PS (b) which showing structure in nano range of both regarded composites. The obtained results from SEM and TEM analysis explained that nanostructured composites based on PANi and RR or PS were succesfully prepared by soaking method in our research.

Infrared spectrum analysis

The results given in Figure 3 and TABLE 1 explained that PANi existed in composites owing to vibration signals of benzoid and quinoid ring at 1625 cm^{-1} and 1461 cm^{-1} (b), 1628 cm^{-1} and 1428 cm^{-1} (d), respectively[6]. Some other signals were found at 3392



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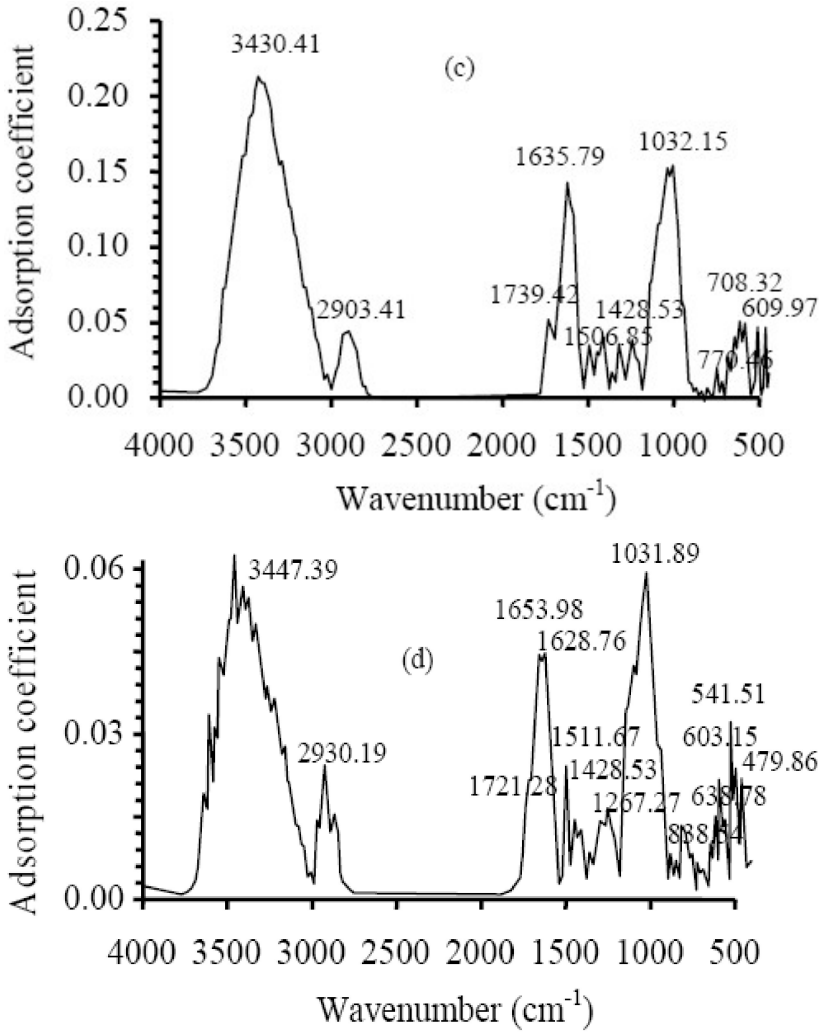

Figure 3 : IR-spectra of RR (a), PANi-RR (b), PS (c), and PANi-PS (d)

TABLE 1 : Vibration signal of IR-spectra from figure 3

Signals ν (cm^{-1})		Binding	Signals ν (cm^{-1})		Binding
a (RR)	b (PANi-RR)		c (PS)	d (PANi-PS)	
3429		ν_{O-H}	3430		ν_{O-H}
2914	2925	ν_{C-H} aromatic	2903		ν_{C-H-O}
1739		$\nu_{C=O}$ ester group in hemicellulose	1739	1721	$\nu_{C=O}$ ester group in hemicellulose
1650	1656	ν_{H-O-H} in water molecular	1636	1653	$\nu_{C=C}$
1427, 1380		$\nu_{C=C}$ aromatic in lignin	1032	1032	ν_{C-O}
1070, 1040	1055	ν_{C-O} in cellulose, hemicellulose and lignin		3447	ν_{N-H}
	3392	ν_{N-H}		2930	ν_{C-H} aromatic
	1625	Benzoid		1628	Benzoid
	1461	Quinoid		1511	Quinoid
	1377	–N=quinoid=N–		1267	–N=quinoid=N–

cm^{-1} (b), 3447 cm^{-1} (d) assigning N-H stretching mode, 2925 cm^{-1} (b) and 2930 cm^{-1} (d) (C-H), 1377 cm^{-1} (b) and 1267 cm^{-1} (d) (-N=quinoid=N-). Otherwise, the vibration signal of C=O group at 1721 cm^{-1} (d) belonging to ester group in hemicellulose containing in PS, C-O group at 1055 cm^{-1} (b) belonging to cellulose, hemicellulose and lignin in RR, which explained that the presence of RR and PS in their composites[8,9].

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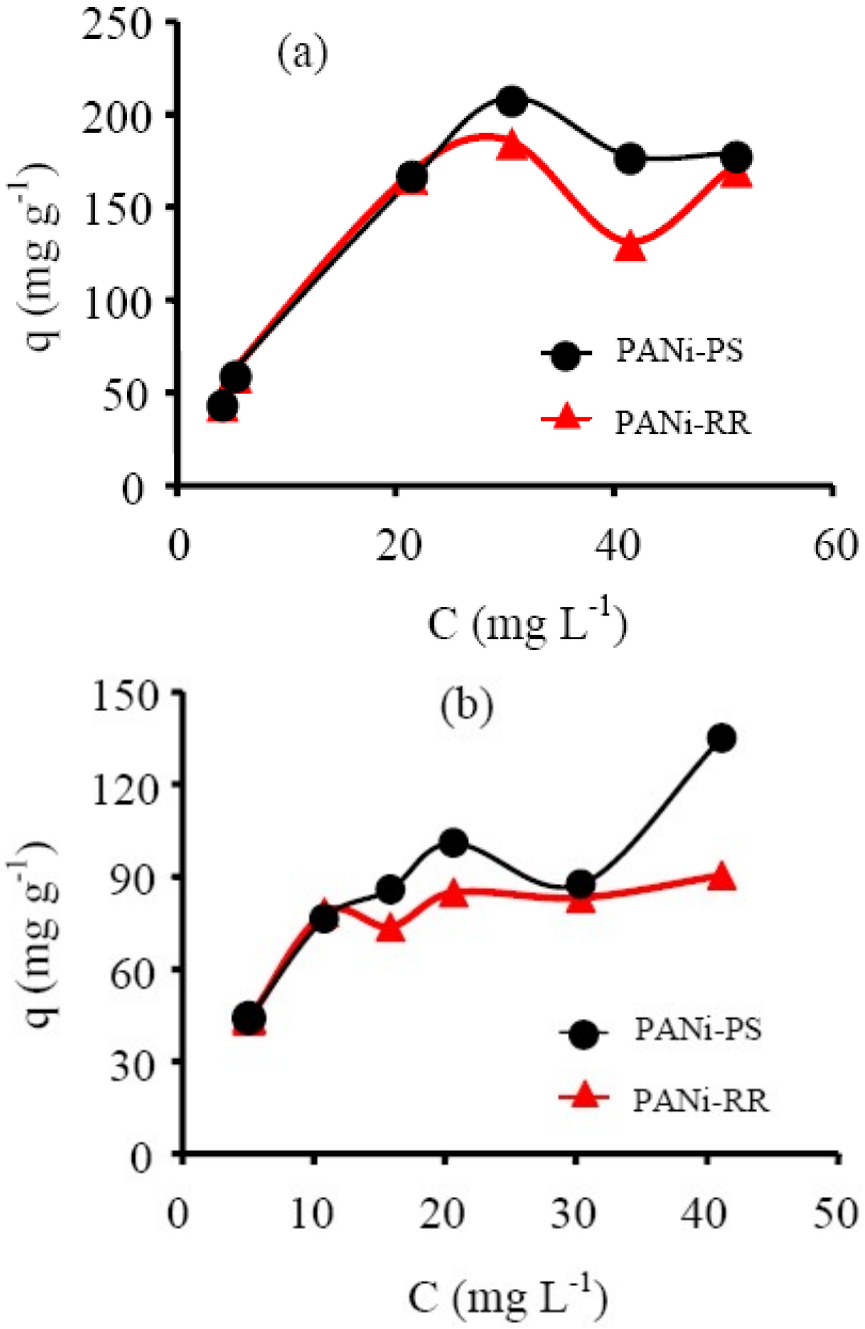

Figure 4 : Equilibrium adsorption isotherm for Pb^{2+} (a, pH = 6) and Cd^{2+} (b, pH = 5) onto composites (contact time of 40 min) following their initial concentration.

TABLE 2 : Langmuir parameters for Pb^{2+} and Cd^{2+} adsorption onto composites

Composites	Metal cations	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	Langmuir equation
PANi-RR	Pb^{2+}	158.7302	2.6250	0.9572	y = 0.0063x + 0.0024
	Cd^{2+}	93.4580	0.5245	0.9952	y = 0.0107x + 0.0204
PANi-PS	Pb^{2+}	185.1852	1.2857	0.9936	y = 0.0054x + 0.0042
	Cd^{2+}	131.5789	0.2203	0.8804	y = 0.0076x + 0.0345

Adsorption models

The data given in Figure 7 showed that the adsorption capacity of both metal ions increased with increase of their initial concentration, however, an maximum

reached at C of 30 mg g^{-1} and 41 mg g^{-1} for Pb^{2+} and Cd^{2+}, respectively. Their adsorption capacity on PANi-PS was higher than that on PANi-RR among them Pb^{2+} can adsorb better than Cd^{2+} as well. This might be due to the high affinity of those adsorbents for Pb^{2+} in comparision with Cd^{2+}.

Langmuir isotherm model[10]

$$\frac{C}{q} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} C \quad (2)$$

where C is metal ion concentrations (mg L^{-1}) and q is adsorption capacity (mg g^{-1}) at equilibrium, K_L is the

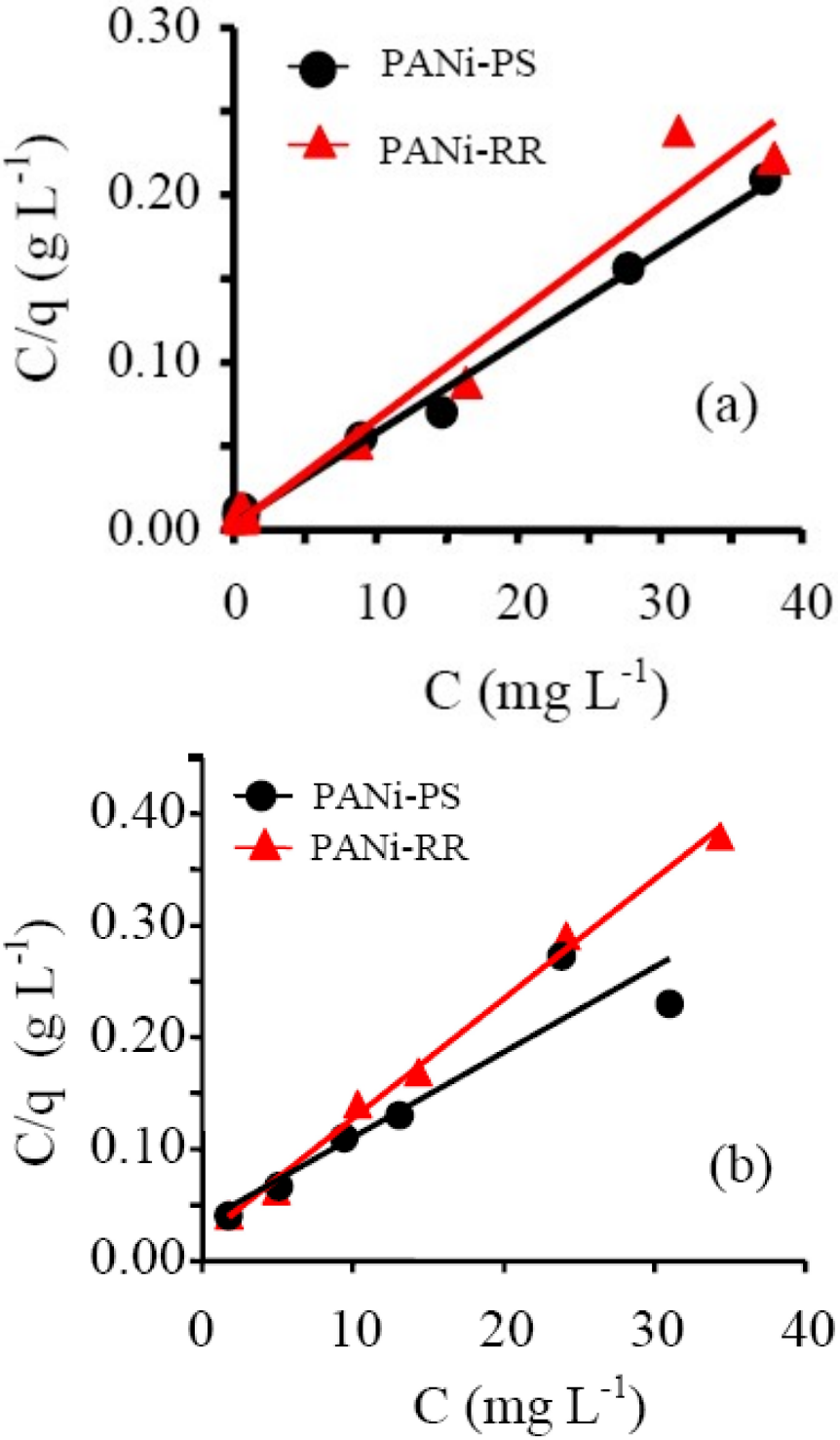

Figure 5 : Langmuir model of Pb^{2+} (a) and Cd^{2+} (b) onto composites

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Langmuir constant, q_{max} is the maximum adsorption capacity (mg g^{-1}).

The data given on TABLE 2 resulted from Figure 5 due to eqn. 2 showed that a maximum adsorption capacity q_{max} of Pb^{2+} and Cd^{2+} ions onto PANi-RR were 158.7302 mg g^{-1} and 93.2580 mg g^{-1}, less than that onto PANi-PS (185.1852 mg g^{-1} and 131.5789 mg g^{-1}), respectively. However, their adsorption process fitted into Langmuir model due to relatively high R^2 values.

The dimensionless Langmuir parameter R_L, which represents for characteristics of adsorption process, can

TABLE 3 : Dimensionless Langmuir parameter R_L for Pb^{2+} and Cd^{2+} adsorption onto composites

Pb^{2+}			Cd^{2+}		
C_o (mg L^{-1})	R_L		C_o (mg L^{-1})	R_L	
	PANi-RR	PANi-PS		PANi-RR	PANi-PS
3.860	0.0898	0.1677	5.070	0.2733	0.4069
5.040	0.0703	0.1337	10.808	0.1500	0.2435
21.190	0.0177	0.0354	15.858	0.1073	0.1799
30.310	0.0124	0.0250	20.682	0.0844	0.1440
41.160	0.0092	0.0185	30.377	0.0591	0.1028
50.870	0.0074	0.0151	41.114	0.0443	0.0780

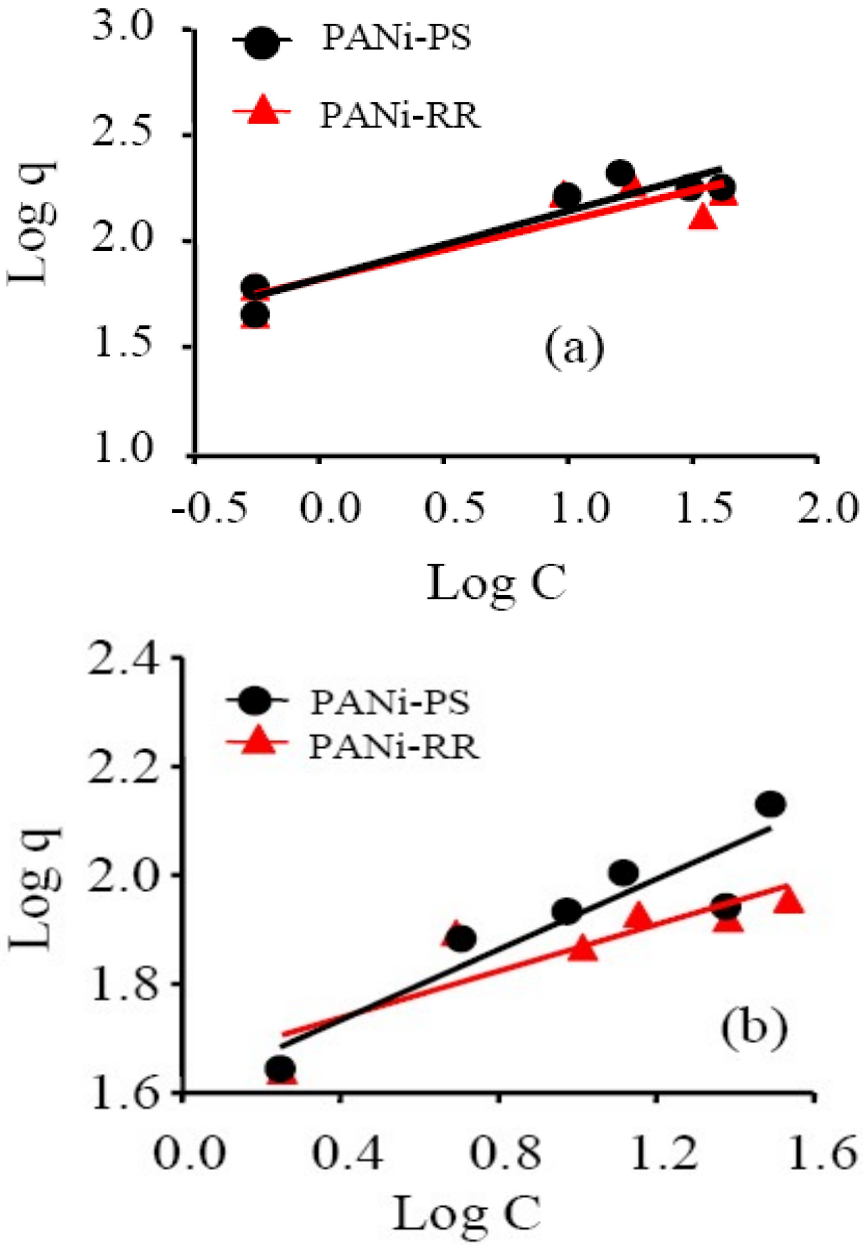

Figure 6 : Freundlich model of Pb^{2+} (a) and Cd^{2+} (b) adsorption onto composites

TABLE 4 : Freundlich parameters for Pb^{2+} and Cd^{2+} adsorption onto composites

Composites	Metal cations	K_F (mg g^{-1})	N_F (L mg^{-1})	R^2	Freundlich equation
PANi-RR	Pb^{2+}	67.6239	3.5638	0.8393	y = 0.2806x + 1.8301
	Cd^{2+}	44.8642	4.6620	0.7700	y = 0.2145x + 1.6519
PANi-PS	Pb^{2+}	68.4542	3.1133	0.9093	y = 0.3212x + 1.8354
	Cd^{2+}	40.0682	3.0826	0.8503	y = 0.3244x + 1.6028

TABLE 5 : Temkin parameters for Pb^{2+} and Cd^{2+} adsorption onto composites

Composites	Metal cations	K_T (L g^{-1})	b (kJ mol^{-1})	R^2	Temkin equation
PANi-RR	Pb^{2+}	18.1946	0.0928	0.7906	y = 62.42x + 78.734
	Cd^{2+}	24.0737	0.1829	0.8039	y = 31.671x + 43.804
PANi-PS	Pb^{2+}	11.2809	0.0754	0.8962	y = 76.858x + 80.972
	Cd^{2+}	3.3962	0.0996	0.7966	y = 58.161x + 30.918

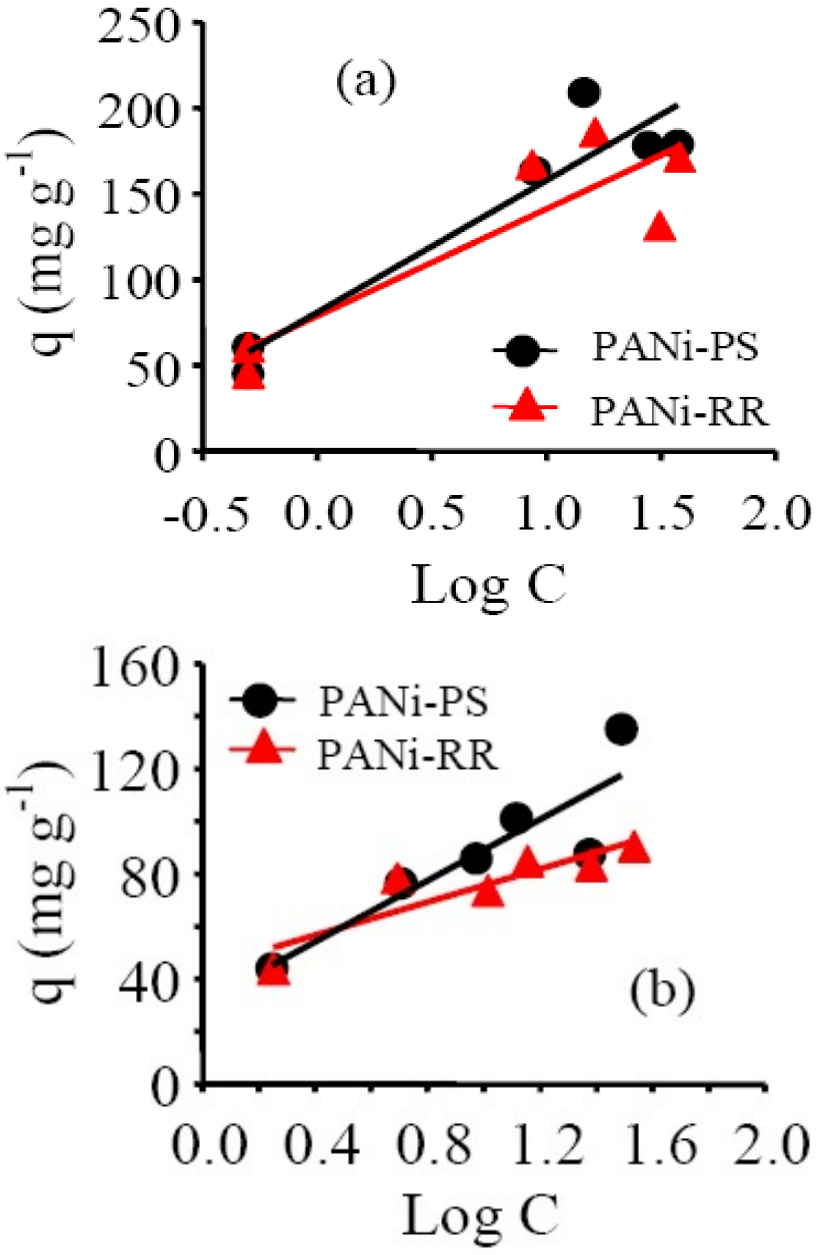

Figure 7 : Temkin model of Pb^{2+} (a) and Cd^{2+} (b) adsorption onto composites

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be defined as below:

$$R_L = \frac{1}{1 + K_L C_o} \quad (3)$$

where K_L is Langmuir constant (g L^{-1}), C_o is initial concentration (mg L^{-1}).

According to Foo *et al.*[11], the calculated R_L values given on TABLE 3 indicating that adsorption of Pb^{2+} and Cd^{2+} ions onto both composites is favourable because of $0 < R_L < 1$, but however, favourable degree is cut down with increasing initial metal ion concentration due to decreasing R_L values.

Freundlich isotherm model[12]

$$\textbf{Log q = log } K_F \textbf{ + (1/}N_F\textbf{) log C} \quad (4)$$

where C is metal ion concentrations (mg L^{-1}) and q is adsorption capacity (mg g^{-1}) at equilibrium, K_F is Freundlich constant, N_F is Freundlich parameter.

As shown in Figure 6 and TABLE 4, the obtained results explained that adsorption of Pb^{2+} and Cd^{2+} ions onto both composites fitted not well into Freundlich isotherm model because of low R^2 values (0.77÷0.91), however, according to Dada *et al.*[13], the adsorption process was also favourable because $1 < N_F < 5$.

Temkin isotherm model[14]

$$q = \frac{R\,T}{b} \ln K_T + \frac{R\,T}{b} \ln C \quad (5)$$

where C is metal ion concentrations (mg L^{-1}) and q is adsorption capacity (mg g^{-1}) at equilibrium, R is universal gas constant (8.314 J mol^{-1} K^{-1}), T is Kelvin temperature (K), K_T is the Temkin isotherm equilibrium binding constant (L g^{-1}), b is Temkin isotherm constant (kJ mol^{-1}).

The less Temkin correlation coefficients (R^2) for Cd^{2+} ion (0.8039 and 0.7966) and Pb^{2+} ion (0.7906 and 0.8962) in TABLE 5 resulted from Figure 7 indicating that Temkin equation can not be good used to model the adsorption of above ions onto both PANi-RR and PANi-PS as well.

CONCLUSION

Composites based on PANi and agriculture waste such as RR and PS can be used as inexpensive adsorbents for removing Pb^{2+} and Cd^{2+} ions from solution by adsorption among them PANi-PS composite is more effective one than PANi-RR. The adsorption process of both metal ions fitted into Langmuir isotherm model better than Freundlich and Temkin isotherm models, which occurred favourable with decreased degree by increasing initial metal concentration.

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