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Nanostructured polyaniline rice husk composite as adsorption materials synthesized by different methods

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Abstract

Composites based on polyaniline (PANi) and rice husk (RH) were prepared by two methods: the first one was chemical method by combining RH contained in acid medium and aniline using ammonium persulfate as an oxidation agent and the second one was that of soaking RH into PANi solution. The presence of PANi combined with RH to form nanocomposite was clearly demonstrated by infrared (IR) spectra as well as by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images. Lead(II) and cadmium(II) ion concentrations in solution before and after adsorption process on those composites were analysed by atomic adsorption spectroscopy. Of the above preparation methods, the soaking one provided a composite onto which the maximum adsorption capacity was higher for lead(II) ion (200 mg g⁻¹), but lower for cadmium(II) ion (106.383 mg g⁻¹) in comparison with the chemical one. However, their adsorption process occurring on both composites also fitted well into the Langmuir isotherm model.

Keywords: nanostructured PANi–RH composite, adsorption isotherms, heavy metal ion removal, synthesis method Classification number: 5.00

1. Introduction

Currently there are many methods to treat heavy metal ions from waste water, such as electrochemical technology, biotechnologyy and adsorption process [1–3]. Among them, the adsorption method is very useful because of very cheap cost and easy processing. Some authors have researched adsorbents which were prepared by chemically combining conducting polymer and agriculture wastes to remove heavy metal ions from solution [4, 5]. However, there has been very little work on soaking methods for preparing them. In this research we would like to report some results about composites based on polyaniline and rice husk (PANi–RH) as

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. adsorbents which are prepared by both chemical and soaking methods.

2. Experimental

2.1. Preparation of materials

The chemical method was carried out by taking 100 ml of 1 M HCl containing 0.1 M aniline into a triangle glass vessel that was placed in an ice basin, adding an amount of RH (double for amount of aniline) under stirring and then dropping ammonium persulfate in ratio to monomer of 1 : 1 into it. The procedure was similar to that reported in [6]. The second one was done by soaking 2 g of RH into 20 ml of formic acid PANi solution (5 g l⁻¹) under stirring for 3 h and then stirred was continued overnight. The product was dried under vacuum condition at 70 °C for 8 h.



Figure 1. SEM images of RH (a), PANi-RH composite prepared by chemical (b) and soaking (c) methods.



Figure 2. TEM images of PANi-RH composite prepared by chemical (a) and soaking (b) methods.

2.2. Detection method

The structure of material was studied by infrared spectroscopy on IMPACT 410-Nicolet unit. The surface morphology was examined by SEM on equipment FE-SEM Hitachi S-4800 (Japan) and by TEM on a Jeol 200CX (Japan). Adsorption ability of heavy metal ions on prepared material was characterized by atom adsorption spectroscopy (AAS) on equipment Shimadzu AA-6800 (Japan).

2.3. Procedure of adsorption research

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

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

where C_0 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.

3. Results and discussions

3.1. SEM images

The images in figure 1 show that both preparation methods provided composites in nanostructure; among them, the one obtained from the chemical way (b) appeared in longer fibres than that from soaking method (c), while RH was in nanograin form (a).

3.2. 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 RH showing structure of both kinds of composite in nano range. The obtained results from SEM and TEM analysis explained that nanostructured composite based on PANi and RH were successfully prepared by both the above methods in our research.

3.3. Infrared spectra analysis

The results given in figure 3 explain that PANi existed in composite owing to vibration signals of benzoid and quinoid ring at 1584 and 1492 cm⁻¹ (b) and 1511 and 1461 cm⁻¹ (c), respectively [6, 7].

Some other signals were found at 3385 and 3300 cm^{-1} (b) and 3379 cm^{-1} (c) assigning N–H stretching mode, 2932 cm⁻¹ (b) and 2928 cm⁻¹ (c) (C–H), 1310 cm⁻¹ (b) and 1329 cm⁻¹ (c) (–N=quinoid=N–), 1159 cm⁻¹ (b, c) (C–N⁺). Otherwise, the vibration signal of Si–O–Si group at 1025 cm⁻¹ (b) and 1043 cm⁻¹ (c) belonging to cellulose, hemicellulose and lignin containing in RH [8, 9] which explained their presence in PANi–RH composites. The vibration signals of IR-spectra from figure 3 are given in table 1.



Figure 3. IR-spectra of RH (a), PANi-RH composite by chemical (b) and soaking (c) methods, PANi (d) [6].

	Signals ν (cm ⁻¹)			Binding		
Figure 3(a) 3422	Figure 3(b) 3450	Figure 3(c)	Figure 3(d) [6]	v_{O-H} stretching, v_{Si-OH}		
2927	2932	2928		v_{C-H} stretching in cellulose		
1725, 1641		1659		$\nu_{C=O}$ stretching of hemicelluloses and lignin		
1465				$\nu_{\rm C-H}$ asymmetric bending of		
				CH_3 and methoxy ($-OCH_3$)		
				groups present in lignin		
1150				v_{C-O} group in lactone		
1057	1025	1043		$v_{Si-O-Si}$ stretching		
815	830	892		v_{Si-H} group		
	3385, 3300	3379	3438, 3268	$\nu_{\rm N-H}$		
	2932	2928	30 412 927	$v_{\rm C-H}$ aromatic		
	1584	1511	1584	Quinoid		
	1492	1461	1499	Benzoid		
	1310	1329	1301	-N=quinoid=N-		
	1159	1159	1156	$C-N^+$ group		

 Table 1. Vibration signal of IR-spectra from figure 3.

3.4. Adsorption study

3.4.1. Effect of contact time. In order to establish the equilibration time for maximum uptake of metal ions onto regarded composites the contact time was varied from 10 to 80 min. The results showed that both metal ions were rapidly removed by composites after 15 min, but, a slightly significant desorption of Cd^{2+} ion can be observed in continuing contact time (figure 4) in the case of chemical method.

3.4.2. Effect of initial concentration. Figure 5 shows the effect of varying initial metal concentration on the adsorption under contacting time of 40 min. The removal percentages of both metal ions are decreased with increasing their initial concentration. However, the removal degree was better



Figure 4. Effect of contact time on adsorption capacities of Pb^{2+} (a) and Cd^{2+} (b) ions.

for lead(II) ion (a), but worse for cadmium(II) ion (b) if comparing composite prepared by soaking method to that by chemical one.

Table 2. Langmuir parameters for Pb²⁺ and Cd²⁺ adsorption onto PANi–RH composites prepared by different methods.

Methods	Metal cations	$q_{\max} \ (\mathrm{mg}\mathrm{g}^{-1})$	$\frac{K_{\rm L}}{(\rm lmg^{-1})}$	R^2	Langmuir equation
Chemical	Pb ²⁺	131.5789	19.0000	0.9724	y = 0.0076x + 0.0004
	Cd ²⁺	158.7302	0.2250	0.8895	y = 0.0063x + 0.028
Soaking	Pb ²⁺	200.0000	0.4098	0.9714	y = 0.005x + 0.0122
	Cd ²⁺	106.3830	0.4123	0.9700	y = 0.0094x + 0.0228

Table 3. Dimensionless Langmuir parameter R_L for Pb²⁺ and Cd²⁺ adsorption onto PANi–RH composites prepared by different methods.

	Pb ²⁺		Cd ²⁺			
	R_{1}	L	RL			
$C_0 \;(\mathrm{mg}\mathrm{l}^{-1})$	Chemical	Soaking	$C_0 \;(\mathrm{mg}\mathrm{l}^{-1})$	Chemical	Soaking	
3.860	0.0135	0.4025	5.070	0.4981	0.3236	
5.040	0.0103	0.3403	10.808	0.3177	0.1833	
21.190	0.0025	0.1093	15.858	0.2409	0.1327	
30.310	0.0017	0.0790	20.682	0.1957	0.1050	
41.160	0.0013	0.0594	30.377	0.1421	0.0739	
50.870	0.0010	0.0486	41.114	0.1090	0.0557	

Table 4. Freundlich parameters for Pb^{2+} and Cd^{2+} adsorption onto PANi–RH composites prepared by different methods.

Methods	Metal cations	$\frac{K_{\rm F}}{({\rm mgg}^{-1})}$	$\frac{N_{\rm F}}{(\rm lmg^{-1})}$	R^2	Freundlich equation
Chemical	Pb ²⁺	53.1007	3.3422	0.8835	y = 0.2992x + 1.7251
	Cd^{2+}	53.9186	3.5638	0.6244	y = 0.2806x + 1.7259
Soaking	Pb ²⁺	61.4328	2.9533	0.9586	y = 0.3386x + 1.7884
-	Cd ²⁺	45.2064	4.0193	0.7156	y = 0.2488x + 1.6552



Figure 5. Effect of initial concentration on removal percentage of Pb^{2+} (a) and Cd^{2+} (b) ions from solution.

3.4.3. Langmuir isotherm model. We have formula

$$\frac{C}{q} = \frac{1}{K_{\rm L}q_{\rm max}} + \frac{1}{q_{\rm max}}C,\tag{2}$$

where *C* is metal ion concentrations $(mg l^{-1})$ and *q* is adsorption capacity $(mg g^{-1})$ at equilibrium, K_L is the Langmuir constant $(l mg^{-1})$ and q_{max} is the maximum adsorption capacity $(mg g^{-1})$ [10].

The data given in figure 6 and table 2 showed that the maximum adsorption capacity q_{max} of lead(II) ion onto PANi–RH composite obtained by soaking method (200 mg g⁻¹) was half as much again as that by chemical one (131.5789 mg g⁻¹), while it was reduced about one-third for the case of cadmium(II) ion adsorption. However, their adsorption process fitted relatively well into the Langmuir model.

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



Figure 6. Langmuir model of Pb^{2+} (a) and Cd^{2+} (b) onto PANi–RH composites.

as below:

$$R_{\rm L} = \frac{1}{1 + K_{\rm L} C_0},\tag{3}$$

where K_L is Langmuir constant $(l mg^{-1})$ and C_0 is initial concentration $(mg l^{-1})$.

The calculated $R_{\rm L}$ values given in table 3 indicating that adsorption of Pb²⁺ and Cd²⁺ ions onto both PANi–RH composites is favourable because of $0 < R_{\rm L} < 1$ [11], however, favourable degree is cut down with increasing initial metal ion concentration due to decreasing $R_{\rm L}$ values.

3.4.4. Freundlich isotherm model. We have formula

$$\log q = \log K_{\rm F} + (1/N_{\rm F}) \log C, \tag{4}$$

where *C* is metal ion concentrations (mgl^{-1}) and *q* is adsorption capacity (mgg^{-1}) at equilibrium, K_F is Freundlich constant (mgg^{-1}) and N_F is Freundlich parameter [12].

Table 5. Temkin parameters for Pb^{2+} and Cd^{2+} adsorption onto PANi–RH composites prepared by different methods.

Methods	Metal cations	$\frac{K_{\rm T}}{(\lg^{-1})}$	b (kJ mol ⁻¹)	R^2	Temkin equation
Chemical	Pb ²⁺	9.730	0.099	0.8338	y = 58.374x + 57.746
	Cd ²⁺	15.670	0.118	0.6329	y = 58.751x + 49.108
Soaking	Pb ²⁺	1.998	0.073	0.9614	y = 79.563x + 69.125
	Cd ²⁺	12.864	0.747	0.7063	y = 39.375x + 43.731



Figure 7. Freundlich model of Pb^{2+} (a) and Cd^{2+} (b) adsorption onto PANi–RH composites.



Figure 8. Temkin model of Pb^{2+} (a) and Cd^{2+} (b) adsorption onto PANi–RH composites.

As shown in figure 7 and table 4, the obtained results explained that adsorption of lead(II) ion fitted into Freundlich isotherm model better than that of cadmium(II) one because of higher R^2 values, however, it was worse than that in comparison with Langmuir model (table 2). Otherwise, it was found $1 < N_F < 5$ confirming that the adsorption process was also favourable [13].

3.4.5. Temkin isotherm model. We have formula

$$q = \frac{RT}{b} \ln K_{\rm T} + \frac{RT}{b} \ln C, \qquad (5)$$

where *C* is metal ion concentrations (mgl^{-1}) and *q* is adsorption capacity (mgg^{-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 (lg^{-1}) and *b* is Temkin isotherm constant $(kJ mol^{-1})$ [13] (figure 8).

The smaller Temkin correlation coefficients (R^2) for cadmium ion (0.6329 and 0.7063) in comparison with

those for lead(II) ion (0.8338 and 0.9614) in table 5 indicate that Temkin equation cannot be used to model the adsorption of Cd^{2+} ion onto above PANi–RH composites correctly.

4. Conclusion

PANi–RH composites can be used as inexpensive effective adsorbents for removing lead(II) and cadmium(II) ions from solution by adsorption following Langmuir isotherm model, however, Freundlich and Temkin isotherm models can be used to model only for lead(II) but not for cadmium ion adsorption. The PANi–RH composite prepared by soaking method can better remove lead(II) ion, but, less well remove cadmium(II) ion from solution in comparision with that by the chemical one.

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