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REMOVAL OF Pb^{2+} FROM AQUEOUS SOLUTION BY ADSORPTION ONTO COMPOSITE BASED ON EUCALYPTUS LEAF AND POLYANILINE

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ABSTRACT

Composite based on eucalyptus leaf and polyaniline (EL-PANi) was prepared by chemical polymerization method. It showed that the function groups belonging to polyaniline and eucalyptus leaf were found through IR analysis and the nanostructure of composite was explained by SEM images. The adsorption of Pb^{2+} was carried out onto composite in aqueous solution via varying pH, contact time, and its initial concentration. The experimental adsorption data fitted well into Freundlich adsorption isotherm model (R^2 ~ 0.99). The adsorption process followed pseudo-second order kinetic with R^2 ~ 1. The maximum adsorption capacity q_{max} of Pb^{2+} onto that composite was 172.41 mg/g by Langmuir equation and Freundlich constant K_F was 53.75 mg/g by Freundlich one.

Keywords: EL-PANi composite, adsorption isotherms, adsorption kinetics, Pb^{2+} ion adsorption.

1. INTRODUCTION

Removal of heavy metal ions from aqueous solution has been regarding intensively by scientists on the world because of human health was damaged by pollution from many industrial branches such as metallurgy, electroplating, trade village and so on. All of them are resulting to critical environmental pollution in air or groundwater due to heavy metals among them lead belongs to a group of very toxic [1]. Because lead poisoning can lead to many serious diseases difficult to treat, therefore, many methods as well as adsorbents have been investigated for removing it from aqueous medium [2 - 5]. The adsorption method is used mostly for environmental treatment with relatively low metal ion concentration because of inexpensiveness and sample treatment process. Nowadays, polyaniline (PANi) was composited with many organic, inorganic agents as well as agriculture waste for widely application in many areas such as battery materials [6], supercapacitor [7], removal of heavy metal ions [8 - 10] and so on. Among them their composites with agriculture waste as adsorbents that have some advantages over the others rest ones because of sample preparation and easy regeneration.

The main objective of this work was to evaluate the adsorption isotherms and kinetics for Pb^{2+} ion onto EL-PANi composite which was prepared by chemical method.

2. EXPERIMENTAL

2.1. Synthesis procedure of EL-PANi composite

EL-PANi composite based on eucalyptus leaf (EL) and PANi was prepared by chemical method from chlorhydric acid medium containing aniline using ammonium persulfate as an oxidation agent [9]. The reaction occurred in 18 h under continuous stirring at temperature of 1 ÷ 5 ^{0}C. After purification and changing it into emeraldine base (EB) by treatment with 0.5M ammonia solution, it was dried in vacuum at 50 ÷ 60 ^{o}C for 4 ÷ 5 h and kept in a sealed bottle for adsorption of Pb^{2+} ion.

2.2. Pb^{2+} ion adsorption

The pH effect was considered by varying it from 1 to 8 while initial Pb^{2+} ion concentration (C_0) and contact time (t) were kept 1 mg/L and 40 min, respectively. The contact time was varied from 10 to 120 min under condition of C_0 of 1 mg/L and pH of 6 to consider its effect. C_0 was changed from 1 to 15 mg/L to examine its effect by keeping t of 40 min and C_0 of 1 mg/L. The concentration of Pb^{2+} ion before and after adsorption were analyzed by Atomic Absorption Spectroscopy (AAS) for determining the adsorption amount and other adsorption parameters.

The adsorption capacity (q_t, mg/g) and the removal efficiency (H, %) were calculated from the following equations:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

$$H = \frac{(C_0 - C_t)}{C_0}.100\% \tag{2}$$

where C_0 and C_t are the concentration (mg/L) of Pb^{2+} ion at starting time (t = 0) and any time t, respectively; V is the volume of the solution, m is the mass of adsorbent (g).

The pseudo – first and second order kinetic models [2] were applied to examine kinetics and rate of Pb^{2+} ion adsorption onto materials following equation 3 and 4, respectively.

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where q_e and q_t are the adsorption capacity (mg/g) of Pb^{2+} ion at equilibrium and time t. The equilibrium rate constants of pseudo- first and second order adsorption are k_1 and k_2, respectively.

The Langmuir (5) and Freundlich (6) adsorption isotherm equations [11,12] were used for calculating adsorption parameters of that ion.

$$\frac{C}{q} = \frac{1}{q_{max} K_L} + \frac{C}{q_{max}} \tag{5}$$

$$\log q = \log K_F + \frac{1}{N_F} \log C \tag{6}$$

where, C is Pb^{2+} ion concentration in solution after adsorption, q is adsorption capacity, K_L is Langmuir isotherm constant (L/mg), q_{max} is maximum adsorption capacity (mg/g), K_F (mg/g) and N_F are Freundlich isotherm parameters.

3. RESULTS AND DISCUSSION

3.1. SEM image

The SEM images on Figure 1 showed that morphological structure of EL-PANi composite was in fibre form with diameter of 40÷50 nm, bigger than that of PANi alone (~ 30 nm). Both of them were found in nanofibre structure while eucalyptus existed in small slice.

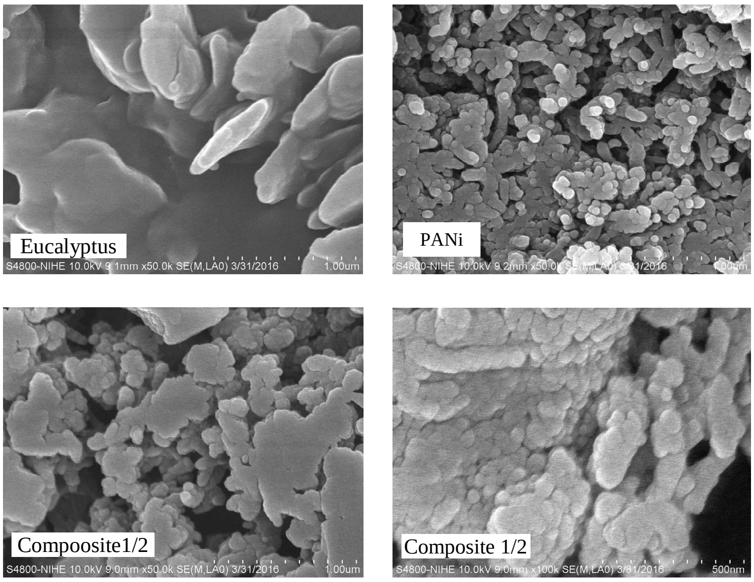

Figure 1. SEM images of EL-PANi composite compared with Eucalyptus and PANi.

3.2. IR-spectrum

The IR-spectrum on Figure 2c indicated that PANi coexisted in composite matrix because of vibrations of benzoid and quinoid rings at 1645 & 1590 cm^{-1} and 1530 cm^{-1}, respectively [13]. The signal at 3533 cm^{-1} shows a vibration of hydroxyl group, 2911 cm^{-1} (saturated C-H) and 1682 cm^{-1} (C=O) due to the presence of EL in composite. Compared with spectra of EL (a) and PANi (b) it can be observed that not only the peak position but also their intensity were changed indicating an existence of composite.

Additionally, other main groups of PANi were found such as the band from 3430 cm^{-1} to

3390 cm^{-1} assigned to the N-H stretching mode, from 3078 cm^{-1} to 3046 cm^{-1} (aromatic C-H), 1305 cm^{-1} (-N=quinoid=N-), 1145 cm^{-1} ($C-N^+$). It explained that EL-PANi composite was successfully synthesized because of containing structures of both of PANi and EL.

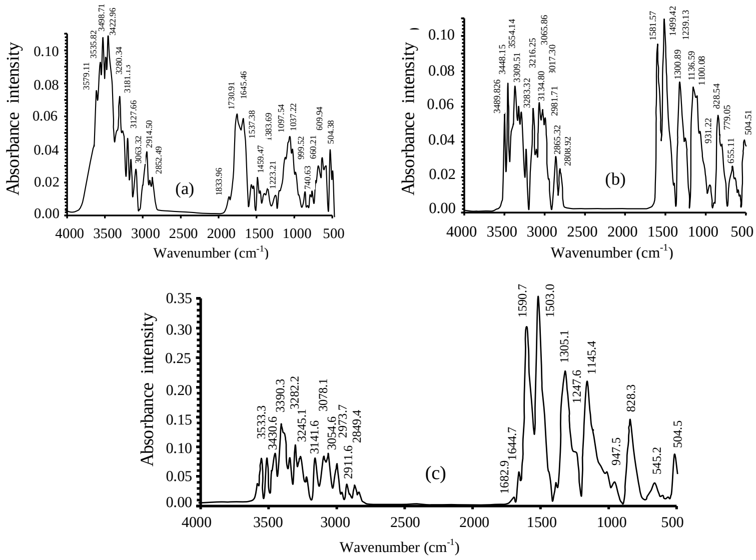

Figure 2. IR-spectra of EL (a), PANi (b) and EL-PANi composite (c).

3.3. Effect of pH

The results presented in Figure 3 showed that the adsorption efficiency of Pb^{2+} ion which depended strongly on solution medium. It was very badly if pH of 1÷2, but significantly increased when pH over 3. A maximum was observed at pH of 6. It may be explained that at low pH Pb^{2+} ion can not adsorb on EL-PANi composite because of protonation state of -N groups of PANi resulted to no ligand or chelating agent appeared. Conversely, in high pH medium PANi existed in undoped form, then its free amine or imine groups will be available for metal chelating, resulting to significantly increase of Pb^{2+} ion adsorption [8].

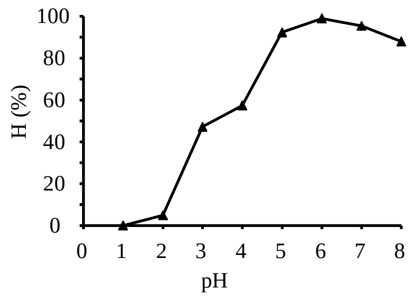

Figure 3. The effect of pH on the removal efficiency of EL-PANi composite (C_0 = 1 mg/L; t = 40 min).

The data on Table 1 indicated that Pb^{2+} ion was removed 94.48% from solution by EL-PANi composite, higher than that by EL and PANi alone at the same condition. However, adsorption ability of Pb^{2+} ion onto EL and PANi significantly also very good, 87.17 and 93.14%, respectively.

Table 1. Adsorption efficiency of EL-PANi composite compared with EL and PANi at pH of 6, contact time of 40 min and initial concentration of 1 mg/L.

Materials	C (mg/l)	H%
EL	0.13	87.17
PANi	0.07	93.14
EL-PANi composite	0.06	94.48

It explained that from the nature of EL due to IR-analysis (Fig. 2) a possible mechanism of ion exchange could be considered as a divalent heavy metal ion (Pb^{2+}) attaches itself to two adjacent hydroxyl groups and two oxyl groups which could donate two pairs of electrons to metal ions, forming four coordination number compounds and releasing two hydrogen ions into solution following schema shown in Figure 4 [14].

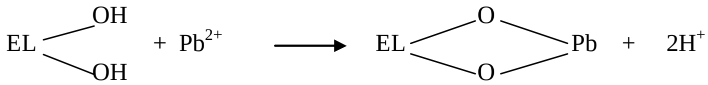

Figure 4. Schema for Pb^{2+} ion adsorption onto EL.

3.4. Effects of contact time and adsorption kinetic model

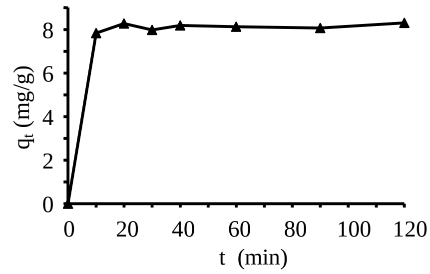

Figure 5. Plot of adsorption capacity versus time for initial Pb^{2+} ion concentration of 1 mg/L at pH of 6.

The Figure 5 explained that the adsorption capacity of Pb^{2+} ion depended strongly on the contact time during twenty initial minutes, then it seems to be stable.

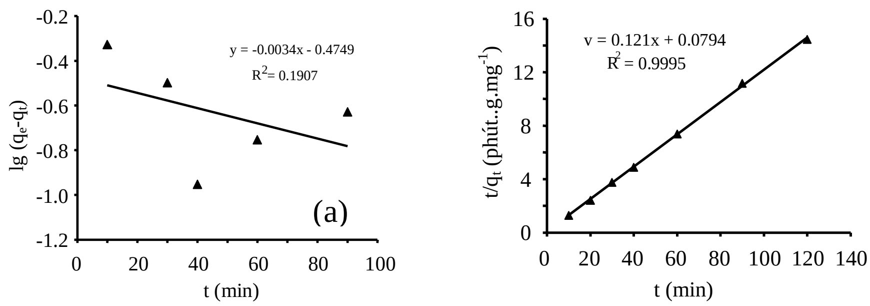

Figure 6. The first-order (a) and second-order (b) adsorption kinetic models of Pb^{2+} ion onto EL-PANi composite (C_0 = 1 mg/L, pH = 6).

The data given in Figure 6 and Table 2 confirmed that the adsorption process fitted very well into the second order adsorption kinetic model as the correlation coefficient R^2 ~ .1 and the suitability between theoretical and experimental equilibrium capacities ($q_{e,th}$ = 8.26 mg/g; $q_{e,exp}$ = 8.30 mg/g). Contrary to that, the very poor fitting, of R^2 (~0.2) and $q_{e,th}$ (0.34 mg/g), from the first-order kinetic model compared with $q_{e,exp}$ indicating that an unsuitability was found.

Table 2. Kinetic parameters for adsorption of Pb^{2+} ion onto EL-PANi composite calculated from Figure 6 (C_0 = 1 mg/L; pH = 6).

First-order adsorption kinetic model			Experimental $q_{e,exp}$ (mg/g)	Second - order adsorption kinetic model		
y = -0.0034x – 0.4749				y = 0.121x + 0.0794		
$q_{e,th}$ (mg/g)	k_1 (min^{-1})	R^2		$q_{e,th}$ (mg/g)	k_2 (g/mg.min)	R^2
0.34	~ 0.00	~ 0.20	8.30	8.26	0.12	~ 1.00

3.5. Effect of initial Pb^{2+} ion concentration

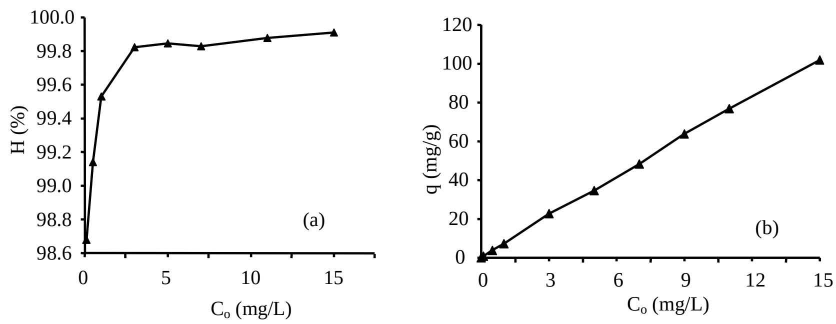

Figure 7. The influence of initial concentration on Pb^{2+} ion removal efficiency (a) and adsorption capacity (b). Contact time of 40 min at pH = 6.

Figure 7 showed the effect of initial Pb^{2+} ion concentration on its adsorption efficiency (a) and adsorption capacity (b) of EL-PANi within 40 min contact time at pH of 6. It was found an excellent removal of Pb^{+} ion until over 98% in chosen C_0, especially near 100% if C_0 over 3 mg/L. The Pb^{2+} ion adsorption capacity of that composite is increased linear with C_0 indicating an advantage for removing Pb^{2+} from aqueous solution.

3.6. Adsorption isotherms

The Langmuir dimensionless parameter (R_L) can be calculated from equation (7):

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

where K_L is Langmuir constant and C_0 is initial concentration of Pb^{2+} ion. The obtained values of R_L (Table 3) and N_F (Table 4) indicated that the adsorption process of Pb^{2+} ion was favourable because of $0 < R_L < 1$ and $1 < N_F < 10$ [15]. The data given on Figure 8 and Table 4 explained the adsorption of Pb^{2+} ion on regarded material has made more consistent with Freundlich model (R^2 ~ 0.99) compared with Langmuir one (R^2 ~ 0.72) because of higher correlation coefficient. The maximum adsorption capacity q_{max} of Pb^{2+} ion was 172.41 mg/g following Langmuir isotherm line, while Freundlich constant K_F from Freundlich one was 53.75 mg/g.

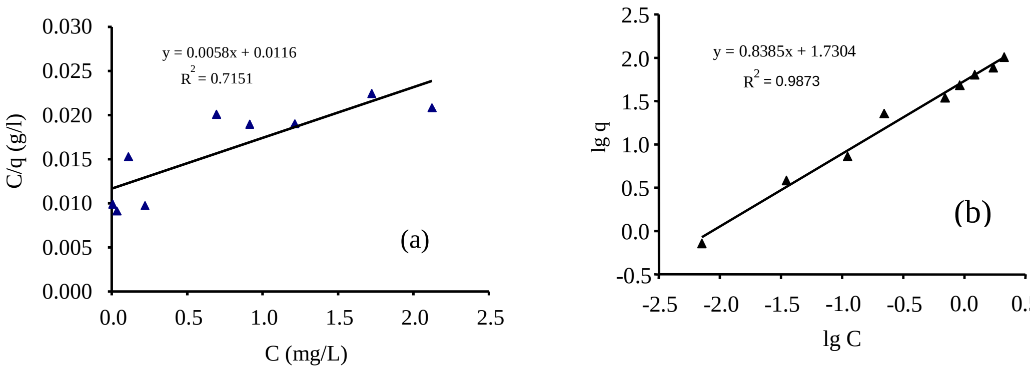

Figure 8. Langmuir plot (a) and Freundlich plot (b) for the adsorption of Pb^{2+} ion onto EL-PANi.

Table 3. Values of dimensionless Langmuir parameter R_L for Pb^{2+} ion adsorption.

C_0 (mg/L)	0.10	0.50	1.00	3.00	5.00	7.00	9.00	11.00	15.00
R_L	0.95	0.80	0.67	0.407	0.29	0.229	0.189	0.159	0.12

Table 4. Langmuir and Freundlich adsorption iso-therm constants for Pb^{2+} ion onto EL-PANi calculated from Figure 8.

Langmuir constants		Freundlich constants	
q_{max} (mg/g)	172.41	K_F (mg/g)	53.75
K_L (L/mg)	0.50	N_F	1.20
R^2	0.72	R^2	0.99

The Table 5 indicated that the maximum adsorption capacity was found 172.41 mg/g in our research, much higher than that in other publications.

Table 5. Comparison of maximum adsorption capacity of EL-PANi composite with some other adsorbents.

Materials	q_{max} (mg/g)	Conditions	References
EL-PANi composite	172.41	pH = 6; t = 40 min	This study
Sawdust	15.90	25 °C	[14]
pine cone	27.53		[16]
Untreated orange barks	112.36	pH = 3÷4.6	[17]
Activated carbon/iron oxide magnetic composite	18÷19	pH = 4÷6	[18]
Bentonite clay	51.19	20 °C	[19]
Activated carbon from cashew nut shell	28.90		[20]
Activated carbon from coconut shell	26.60		[21]
Activated carbon from apricot stone	21.38	pH = 6; t = 20 min	[22]
Nanostructured CuO	115.00	pH = 6.5; t = 240 min	[23]
PANi-RH	131.58	pH = 6; t = 40 min	[24]

4. CONCLUSION

EL-PANi nanocomposite based on eucalyptus leaf and polyaniline was successfully synthesized by chemical method. It could be useful for the removal of Pb^{2+} ion from aqueous solution. The optimum conditions for Pb^{2+} ion removal were found at pH of 6 and contact time of 40 min. The adsorption of Pb^{2+} ion onto EL-PANi fitted very well into the pseudo-second order kinetic model, it followed the Freundlich adsorption isotherm equation better than Langmuir one. The maximum adsorption capacity q_{max} was 172.41 mg/g following Langmuir model and Freundlich constant K_F was 53.75 mg/g for Pb^{2+} ion adsorption onto EL-PANi.

REFERENCES

1. Hepple P. - Lead in the environment. Institute of Petroleum, Lodon, 1972.
2. Ayyappan R., Sophia A. C., Swaminathan K., and Sandhya S. - Removal of Pb(II) from aqueous solution using carbon derived from agricultural wastes. Process Biochemistry **40** (3-4) (2005) 1293–1299.
3. Yu X. Y., Luo T., Zhang Y. X. et al. - Adsorption of lead(II) on O_2-plasma-oxidized multiwalled carbon nanotubes: thermodynamics, kinetics, and desorption. ACS Applied Materials and Interfaces **3** (7) (2011) 2585–2593.
4. Murat Erdem, Suat Ucar, Selhan Karagöz, and Turgay Tay - Removal of Lead (II) Ions from Aqueous Solutions onto Activated Carbon Derived from Waste Biomass, The Scientific World Journal **2013** (2013) 7 pages. doi: 10.1155/2013/146092.
5. Zahra Saadi, Reyhane Saadi and Reza Fazaeli – Fixed bed adsorption dynamics of Pb (II) adsorption from aqueous solution using nanostructured γ-alumina, Journal of Nanostructure in Chemistry **3** (48) (2013) 1-8.
6. He Ze-qiang, Xiong Li-zhi, Chen Shang, Wu Xian-ming, Liu Wen-ping, Huang Ke-long – Insitu polymerization and characterization of $Li_4Ti_5O_{12}$-polyaniline anode material. Trans. Nonferrous Met. Soc. China **20** (2010) 262-266.
7. Park K. I., Dinh H. C., Kim J. S., Yeo I. H. and Mho S. I. - Impedance monitoring of the anodic dissolution of PANi during the V_2O_5 deposition step for the PANi/V_2O_5 composite film preparation ECS Transactions **28** (8) (2010) 179-186.
8. Ansari R., Raofie F. - Removal of lead ions from aqueous solution using sawdust coated by polyaniline. E – Journal of Chemistry **3** (1) (2006) 49-59.
9. Phan Thi Binh, Pham Thi Tot Mai Thi Thanh Thuy, Bui Minh Quy and Nguyen The Duyen - Nanostructured Composite Based on Polyaniline and Rice Raw for Removal of Lead(II) and Cadmium(II) from Solution, Asian Journal of Chemistry **25** (14) (2013) 8163-8168.
10. Bui Minh Quy, Vu Quang Tung, Hoang Thi Huong, Nguyen Thi Ngan, Phan Thi Binh, Vu Duc Loi- Pseudo-isotherms for lead(II) ion onto bean shell-polyaniline composite, Vietnam Journal of Chemistry **51** (5A) (2013) 130-133.
11. Langmuir I. - The adsorption of gases on plane surfaces of glass, mica and platinum, The Journal of the American Chemical Society **40** (9) (1918) 1361-1403.
12. Freundlich H. M. F. - Over the adsorption in solution, The Journal of Physical Chemistry **57** (1906) 385–471.

13. Vivekanandan J., Ponnusamy V., Mahudeswaran A. and Vijayanand P. S. - Synthesis, characterization and conductivity study of polyaniline prepared by chemical oxidative and electrochemical methods, Arch. Appl. Sci. Res. **3** (6) (2011) 147-153.
14. Bulut Yasemin, Tez Zeki - Removal of heavy metals from aqueous solution by sawdust adsorption, Journal of Environmental Sciences **19** (2007) 160-166.
15. Ghorbani M., Eisazadeh H. and Ghoreyshi A. A. - Removal of Zinc Ions from Aqueous Solution Using Polyaniline Nanocomposite Coated on Rice Husk, Iranica Journal of Energy & Environment **3** (1) (2012) 83-88.
16. Milan Momčilović , Milovan Purenović, Aleksandar Bojić, Aleksandra Zarubica, Marjan Ranđelović - Removal of lead(II) ions from aqueous solutions by adsorption onto pine cone, Activated Carbon **276** (1–3) (2011) 53-59.
17. Naima Azouaou,Mohamed Belmedani, Hassiba Mokaddem, Zahra Sadaou - Adsorption of Lead from Aqueous Solution onto Untreated Orange Barks, The Italian Association of Chemical Engineering **32** (2013) 55-60.
18. Sguhua Yao, Shuyu Sun, Shuo Wang, and Zhongliang Shi - Adsorptive removal of lead ion from aqueous solution by activated carbon/iron oxide magnetic composite, Intiaan Journal of Chemical Technology **23** (2016) 146-152.
19. Saad A. Al-Jlil - Chgaracterization and application of bentonite clay for lead ion adsorption from wastewater: equilibrium and kinetic stufy. Research Journal of Environmental Sciences 2015, doi: 10.3923/rfes.2015.
20. Tangjuank S., Insuk N., Tontrakoon J., Udeye V. -Adsorption of lead (II) and cadmium (II) ions from aqueous solutions by adsorption on activated carbon prepared from cashew nut shell, Wordl Academy of Science, Engineering and Technology **52** (2009) 110-116.
21. Sekar M., Sakthi V., Rengaraj S. - Kinetics and equilibrium adsorption study of lead (II) onto activated carbon prepared from coconut shell, J. Coll .Interf. Sci. **279** (2004) 307-313.
22. Lotfi Moun et al. - Adsorption of Pb (II) from aqueous solutions using activated carbon developed from Apricot stone, Desalination **176** (2011) 148-153.
23. Farghali A. et al. - Adsorption of Pb (II) ions from aqueous solutions using copper oxide nanostructures, Sci.Verse Science Direct **2** (2013) 61-71.
24. Thi Tot Pham, Thi Thanh Thuy Mai, Minh Quy Bui, Thi Xuan Mai, Hai Yen Tran and Thi Binh Phan - Nanostructured polyaniline rice husk composite as adsorption materials synthesized by different methods, Adv. Nat. Sci.: Nanosci. Nanotechnol. **5** (2014) 015010 (5 pp).

TÓM TẮT

LOẠI BỎ Pb^{2+} KHỎI DUNG DỊCH NƯỚC BẰNG HẤP PHỤ TRÊN COMPOZIT TỪ LÁ CÂY BẠCH ĐÀN VÀ POLIANILIN

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Vật liệu hấp phụ trên cở sở polianilin và lá cây bạch đàn được tổng hợp bằng phương pháp hóa học. Kết quả phân tích hồng ngoại (IR) đã xác định được các nhóm chức đặc trưng thuộc về PANi và lá cây bạch đàn có mặt trong thành phần compozit. Vật liệu có cấu trúc dạng sợi với đường kính 40÷50 nm nhờ phân tích ảnh SEM. Sự hấp phụ Pb^{2+} được nghiên cứu ở các điều kiện thay đổi pH, thời gian tiếp xúc và nồng độ ban đầu. Kết quả xác định quá trình hấp phụ Pb^{2+} tuân theo động học bậc 2 (R^2 = 0,9995) và phù hợp với mô hình hấp phụ đẳng nhiệt Freundlich (R^2 = 0,9873) tốt hơn so với Langmuir (R^2 = 0,7151). Dung lượng hấp phụ cực đại theo mô hình Langmuir đạt q_{max} là 172,41 mg/g và hằng số Freundlich K_F là 53,75 mg/g theo mô hình Freundlich.

Từ khóa: compozit EL-PANi, hấp phụ ion Pb^{2+}, đảng nhiệt hấp phụ, động học hấp phụ.