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Study on Removal of Heavy Metal from Water by Oxidized Agricultural Byproducts

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Abtract: In this article, hydrogen peroxide was used to modify jute and coir. IR spectrum of the materials showed the appearance of carboxyl groups on oxidized materials which enhances ion adsorption capacity for metals. Modified jute and coir was choiced to study the influential parameters such as initial metal ion concentration, contact time and pH of the solution on the adsorption process. The experimental data was well fitted by the pseudo-second-order kinetics model and Langmuir isotherm model. This study showed that under optimum conditions (pH = 5 and contact time of Ni and Pb experiment chosen at 30 and 120 minutes, repectively), modified coir had the highest potential of removal for metal ions, with maximum adsorption capacities were 48.54 mg/g and 19.34 mg/g for Pb(II) and Ni(II), respectively.

Keywords: Heavy metal, agricultural by-product, adsorption material.

1. Introduction

Over last a few decades, the rapid economic development and population growth has caused a negative impact on the environmental quality, in which, heavy metals are becoming one of the most serious environmental problems. Various toxic metals such as Cd, Cu, Ni, Cr, … from the industrial sources or human activities [1] are commonly associated with pollution and toxicity problems. In developing countries such as Vietnam [2], India [3], China [4] etc. heavy metal pollution becomes more serious because wastewater from household, hospital, smallscale industries discharge directly to the water sources without any treatment.

Numerous by-products of agricultural residues which represent a low cost and environmentally safe source of materials showed potential use as adsorbent materials that are useful for metal removal from water [5]. Chemical composition of common agricultural residues include cellulose (30 - 91%), hemicellulose (4 - 16%), lignin (0.6 - 26%), pectin, waxes and water soluble subtances [6,7]. The lignocellulosic or lignin have low cation adsorption capacity, therefore, chemical modification should be carried out for these materials to achieve efficient ion exchangers. An example of such processes is made biochar

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[8-11] from agricultural residues to such as adsorbent or copolymerizaion [12] or incorporation of certain groups to the lignocellulosic materials is used to increase their efficiency toward their cation-exchange ability, such as, phosphonic groups (-PO_3H_2) [13], sulfonic groups (-SO_3H) [14], and carboxylic groups (-COOH) [15,16].

Hydrogen peroxide is the simplest peroxide and finds use as a weak oxidizer. With the increasing of hydroxyl, carboxyl and carbonyl group, modified cellulosic materials by hydrogen peroxide can be used to remove heavy metal from wastewater. In oxidation of lignin by hydrogen peroxide, the mechanism has been extensively discussed by Ney et al. [17], whereby, the perhydroxyl anion, as a nucleophile, might attack carbon-carbon double bonds make diol group. In case of lignocellulosic [18], Paruvouri et al. [19] and Shukla et al. [20] showed the formation of carboxyl group and carbonyl group.

Therefore, this study aimed to modify cellulose agricultural hydrogen by hydrogen peroxide and examine the absorption capacity of the modified materials.

2. Materials and methods

2.1. Materials and instruments

All materials were collected at rural areas of Ha Noi, Vietnam. Materials were pretreated in running tap water for 1–2 h to remove coloration and dirt, after that washed with distilled water several times. The washed materials were transferred to an oven set at 60°C for 24 h to reduce the water content. The higher temperature may changed properties of materials. Materials were separated into fibers with diameter were less than 0.1 mm.

All other reagents utilized in the experiments were analytical grade and used without any further purification, and all solutions were prepared with deionized water.

Infrared spectra (FT-IR) of samples were reported in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} by Perkin Elmer Spectrum GX FT-IR. The surface properties of all the adsorbents were examined using scanning electron microscopy (SEM). FEI Nova Nanolab 200 has been used to study surface morphology of the adsorbents at 5 keV. Concentration of metal ions was performed with a flame atomic absorption spectrophotometer (AAS AAnalyst 400).

2.2. Modification of materials

Raw materials were washed in sodium hydroxide and 30% H_2O_2 solution for modified process with the ratio of 1 gram of absorbent with 10 ml of 30% H_2O_2 and 1M NaOH, and then the mixture was boiled for 2 h at 85°C. After 2 h, the adsorbent was taken out, and washed with distilled water repeatedly, until the pH of adsorbent is 7. Then it was dried at 80°C for 24 h.

2.3. Batch adsoption experiments

Experiments were carried out in batch mode and IKA HS 260 was used to equilibrate the solutions at 150 rpm. 1g of material was added to 100 mL solution of Ni(II) or Pb(II). The effect of solution pH was studied in the pH range of 1.0 - 5.0 and optimal of contact time was studied in 1 – 120 min with concentrations of Ni^{2+} and Pb^{2+} were 110 and 430 mg/L, respectively. Isotherm studies were accomplished by shaking 1 g of material in 50 mL of aqueous solution of metal ions at different initial concentrations (50–1333 mg/L) and at optimal of pH and contact time. All experiments were conducted at a constant temperature.

The removal efficiency (E) of heavy metals and blue methylene was calculated as follows:

$$E = \frac{C_i - C_e}{C_i} \times 100$$

where C_i and C_e are the initial and the final equilibrium concentration of heavy metals and blue methylene.

2.4. Kinetic model

The most popular kinetic models are the Lagergren pseudofirst-order and The pseudo-second order which describe how the metal interacts with the material. The Lagergren model equation [21] is given by:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

The linearised pseudo-first-order equation can be represented by the following equation

$$\ln(q_e - q_t) = \ln(q_e) - k_1t$$

where k_1 (in minute) is the pseudo-first-order adsorption rate constant and q_e and q_t are the values of the mass adsorbed per unit mass of adsorbent at equilibrium (capacity) and at time t, respectively. However, this model was found to be suitable for only the initial of 20 to 30 min of interaction time and not for the whole range of contact times. Additionally, it was found that k_1 depends on the initial concentration of the adsorbate and varies significantly depending on the adsorption system [22]. The pseudo-second order kinetic model as developed by Ho has the following form [23]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

And linear form:

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

Where k_2 is the second order rate constant (g/mg.min).

2.6. Adsoption isotherm

Adsorption isotherm models have been used to describe the interaction between metal ion in solution and adsorbents. In addition, the isotherm models can be used to explain the distribution of metal ion between the liquid and solid phase when equilibrium was reached. In this work, adsorption isotherm models were generated based on Freundlich and Langmuir models to evaluate the adsorption capacity of the material.

The Langmuir equation [24] is given by

$$q_e = q_mk_aC_e/(1+k_aC_e)$$

And linear form:

$$C_e/q_e = (1/q_m)C_e + 1/(k_aq_m)$$

Where q_e is the amount of ion adsorbed (mg/g) corresponding to C_e; Ce is the equilibrium concentration (mg/l); q_m is max adsorption capacity (mg/g); k_a is adsorption equilibrium constant.

The Freundlich equation [25] is given by

$$q_e = K_fC_e^{1/n}$$

Linear form

$$\ln q_e = \ln K_f + (1/n)\ln C_e$$

The constant K_f (mg/g (L/mg)$^{1/n}$) is related to the adsorption capacity of materials; and 1/n is related to the surface heterogeneity.

3. Result and discussion

3.1. Surface of the materials

The SEM images of the material (Fig. 1-2) showed the change in surface of the materials, whereby, surface of coir, jute become clean and more uniform, outer layer of the original material with shaped plate was disappeared, instead the fibrous layers, a part of wax and oil cover materials were removed and cellulosic fibers were transformed into crystalline forms. This surface acting like natural fibers are treated by sodium hydroxide at high concentration (0.8 to 8%)[26]. At that condition, lignin, pectin and waxy substances were removed from structure of cellulosic fiber (Fig. 3).

3.2. The changes of functional groups

The structure of the original and modified materials (jute and coir) analyzed via IR spectrum was showed in figure 4,5. Vibrations at 1596-1600 cm^{-1} (aromatic ring vibrations), 1502 cm^{-1} (aromatic rings vibrations), and 1234-1246 cm^{-1} (guaiacyl ring breathing with stretching C=O) can be seen in all the spectra proved the existence of aromatic ring in the original and modified materials. This fact indicates that the oxidation treatment only eliminated wax and oil layer but it did not affect lignin.

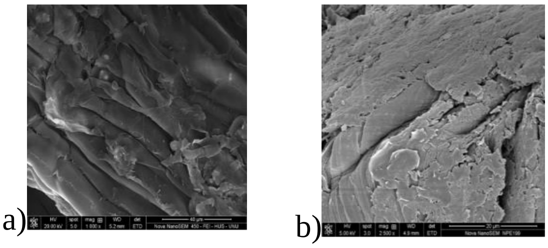

Figure 1. SEM image of original materials;

a) Coir; b) Jute.

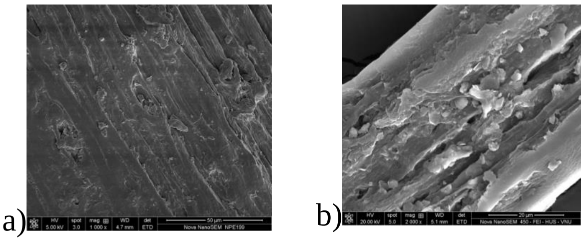

Figure 2. SEM image of modified materials,

a) Coir; b) Jute.

IR spectrum of the modified material had a new peak at 1728-1740 cm^{-1}, and this peak is characteristic by fluctuating valence of the carboxyl group. This proves, H_2O_2 has oxidized original materials to form carboxyl groups, increased cation adsorption capacity of the material for metal ions.

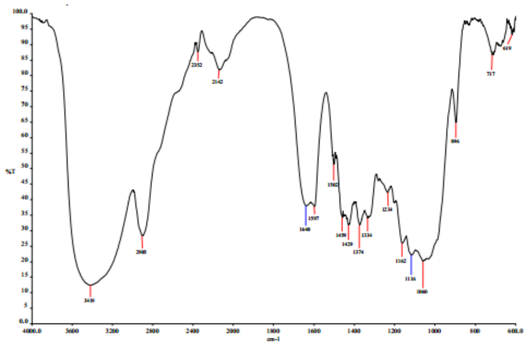

Figure 3. IR spectrum of original coir.

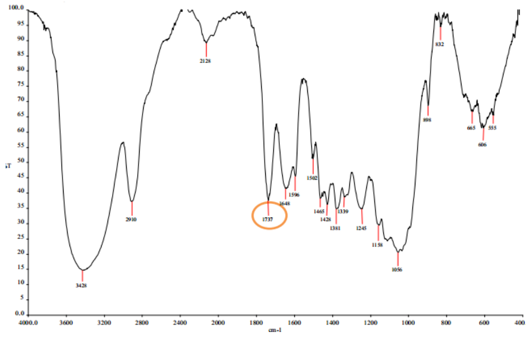

Figure 4. IR spectrum of modified coir.

3.4. The factors affecting adsorption process

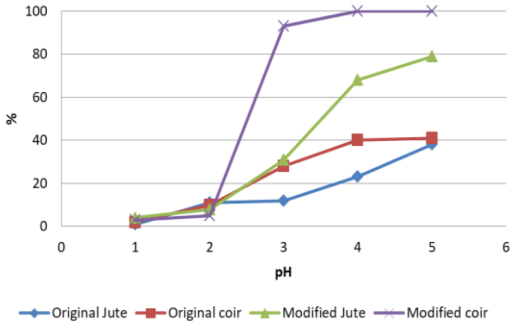

Figure 5. The effect of pH on the adsorption process

of Ni^{2+}.

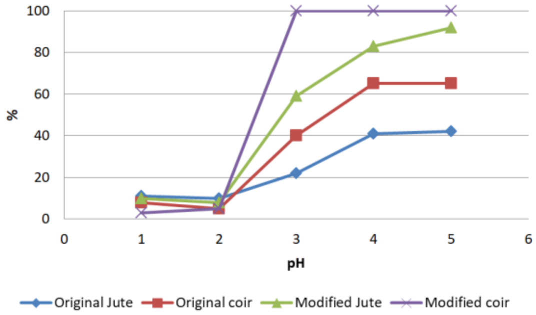

Figure 6. The effect of pH on the adsorption process of Pb^{2+}.

Fig.6-8 showed the effect of pH on the adsorption process of metal ions. The influences of pH on the cation adsorption of the 4 materials have similarities. At low pH values, the efficiency of heavy metal ions adsorption is very low because of competition of the H^+ ions with metal ions. When the pH increased, the efficiency of metal ion adsorption increased. The trend of increasing absorption capacity has been continued when pH increased. However, when considering the fact that metal ions could be precipitated by hydroxide formation, the optimal pH value of adsorption process was at 5.

Typical biosorption kinetics exhibit a rapid initial uptake, followed by a slower process. It has been observed that maximum removal rate took place within the first 30 min (Fig. 8). After this period, in the Ni ion case, the amount of bound metal ions did not change during the course of the process. Meanwhile, after the first 30 min, the adsorption process of Pb ion had continued however adsorption capacity changed not much and reached equilibrium in approximately 90-120 minutes. Thus, the contact time of Ni and Pb experiment was chosen at 30 and 120 min, repectively.

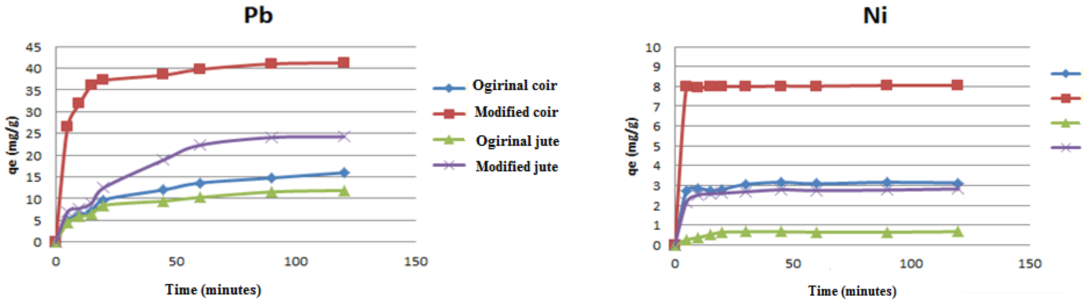

Figure 7. The effect of contact time on adsorption process.

Table 1. Kinetic model parameters

Pseudo-first order	Pb		Ni	
	K_1(g/mg.min)	R^2	K_1 (g/mg.min)	R^2
O. Coir	0.0262	0.9913	0.0454	0.832
M. Coir	0.0438	0.9411	0.0358	0.7074
O. Jute	0.0334	0.9582	0.0306	0.2715
M. Jute	0.0522	0.9515	0.0274	0.7062
Pseudo-second order	Pb		Ni	
	K_2 (g/mg.min)	R^2	K_2(g/mg.min)	R^2
O. Coir	0.0029	0.9935	0.21	0.9995
M. Coir	0.0075	0.9998	0.75	0.9999
O. Jute	0.0059	0.9957	0.27	0.9945
M. Jute	0.0012	0.9809	0.21	0.9998

The experimental results of the biosorption kinetics were compared to two kinetic models, allowing determining the parameters of these models (Table 1). The pseudo-first order model is poor in describing the experimental data of Ni(II), in case of Pb(II), the correlation coefficients exceed 0.95 to 0.99, which suggest good fitting, however, in the case of Ni, the correlation coefficients are lower (<0,85 in all case). The pseudo-second order model provides a better fitting with the correlation coefficient is always greater than 0.98. Comparison of the experimental results with model data confirmed a good correlation of the experimental results with the pseudo-second order model, which is proved to be the best for the description of biosorption kinetics.

3.5. Adsorption isotherm

The parameters of Langmuir and Freundlich equations for the adsorption capacity of two metals onto the four materials obtained as described above are given in Tab.2 and Fig.9-10.

This data indicated that heavy metal ions adsorbed onto the materials are described by the equation Langmuir more well-fitted than Freundlich model with correlation coefficients in the model Langmuir always > 0.91. From Langmuir equation, calculating the maximum adsorption capacity of each material, the maximum adsorption capacities of Pb and Ni onto modified coir were 48.54 mg/g and 10.76 mg/g, respectively, higher than the original materials. Modified jute has lower sorption capacity than coir, with the maximum adsorption capacities of Pb and Ni onto modified jute were 19.34 mg/g and 4.12 mg/g, respectively, however its adsorption capacity remains larger than the original jute. This data also indicated that selectivity of Pb higher than Ni in all case.

4. Conclusion

Agricultural by-product is an environmentally friendly biosorbent to remove heavy metals from wastewater. The study showed that coir and jute were modified by H_2O_2 to increase carboxyl group sites.

Several mathematical models were used to describe the equilibrium and kinetics of biosorption of heavy metals onto selected materials. Kinetic experiments proved that the biosorption process was rapid with Ni, with equilibrium achieved within 30 min. With the case of Pb, biosorption process was also rapid in fisrt 30 min, but this process was continued and reached equilibrium at 120 min. The kinetics of the process were best described using the pseudo-second order model. This study showed that under optimum conditions, modified coir had the highest potential for removal of metal ions, with maximum adsorption capacities were 48.54 mg/g and 19.34 mg/g for Pb(II) and Ni(II), respectively.

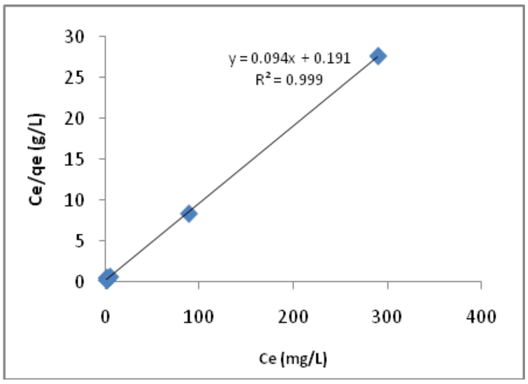

Figure 9. Langmuir isotherm for removal of Ni using modified coir.

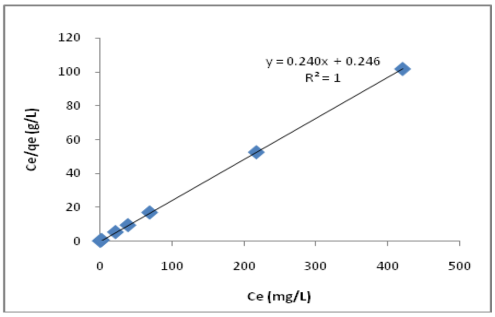

Figure 10. Langmuir isotherm for removal of Ni using modified jute.

Table 2. Adsorption isotherm parameters

Lang Muir	Pb			Ni		
	K_L	R^2	Q_{max}	K_L	R^2	Q_{max}
O. Coir	-0.02	0.985	12.48	0.03	0.991	3.98
M. Coir	0.25	0.999	48.54	0.17	0.995	10.76
O. Jute	0.01	0.918	12.92	0.13	0.996	2.20
M. Jute	-0.08	0.993	19.34	1.09	0.999	4.12

Freundlich	Pb			Ni		
	K_F	N_f	R^2	K_F	N_f	R^2
O. Coir	2.15	5.89	0.997	0.452	2.62	0.96
M. Coir	24.07	7.85	0.757	2.397	3.16	0.43
O. Jute	4.63	8.15	0.245	0.525	3.64	0.90
M. Jute	19.22	166.6	0.028	1.373	4.15	0.82

References

[1] Babich H, Devanas MA, Stotzky G (2014), “The mediation of mutagenicity and clastogenicity of heavy metals by physicochemical factors”. Environmental Research 37 (2), pp 253–286.

[2] Phuong N.M.,Yumei K., Katsutoshi S.,KōzōIwasaki, Kien C.N., Noi N.V., Son L.T. (2010), “Levels and Chemical Forms of Heavy Metals in Soils from Red River Delta, Vietnam”, Water Air Soil Pollut. 207, pp.319–332.

[3] Reddy M. V., Babu K. S., Balaram V., Satyanarayanan M. (2012), “Assessment of the effects of municipal sewage, immersed idols and boating on the heavy metal and other elemental pollution of surface water of the eutrophic Hussainsagar Lake (Hyderabad, India)”, Environ. Monit. Assess. 184, pp.1991–2000.

[4] Bai J., Xiao R., Cui B., Zhang K., Wang Q., Liu X., Gao H., Huang L. (2011), “Assessment of heavy metal pollution in wetland soils from the young and old reclaimed regions in the Pearl River Estuary, South China”, Environmental Pollution, 159 817-824.

[5] Laszlo J. A., Dintzis F. R. (1994), “Crop Residues as Ion-Exchange Materials. Treatment of Soybean Hull and Sugar Beet Fiber (Pulp) with Epichlorohydrinto Improve Cation-Exchange Capacity and Physical Stability”, Journal of Applied Polymer Science, Vol. 52,531-538.

[6] Mohanty A.K., Misra M., Drzal L.T. (2001), “Surface modifications of natural fibers and performance of the resulting biocomposites: An overview”, Compos Interfaces 8:313, pp313-343

[7] Rowell R.M., Young R.A., Rowell J.K. (1997) “Paper and composites from agro-based resources”. CRC Lewis Publishers, Boca Raton FL.

[8] Inyang M., Gao B., Yao Y., Xue Y., Zimmerman A.R., Pullammanappallil P., Cao X. (2012), “Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass”, Bioresource Technology, 110; 50–56

[9] Kılıc M., Kırbıyık C., Cepeliogullar Ö., Pütün A.E. (2013), “Adsorption of heavy metal ions from aqueous solutions by bio-char, a by-product of pyrolysis”, Applied Surface Science, 283; 856–862.

[10] Pellera F.M., Giannis A., Kalderis D., Anastasiadou K., Stegmann R., Wang J.Y, Gidarakos E. (2012), “Adsorption of Cu(II) ions from aqueous solutions on biochars prepared from agricultural by-products”, Journal of Environmental Management,96; 35-42.

[11] Krowiak A.W., Szafran R.G., Modelski S. (2011), “Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent”, Desalination, 265; 126–134.

[12] Feng N, Guoa Y., Lianga S., Zhub Y., Liu J. (2011), “Biosorption of heavy metals from aqueous solutions by chemically modified orange peel”, Journal of Hazardous Materials, 185; 49–54.

[13] Nada A.a.a., Eid M.a., Bahnasawy R.R.RL, Khalifa M.n. (2002), “Preparation and Characterization of Cation Exchangersfrom Agricultural Residues”, Journal of Applied Polymer Science, 85, 792–800.

[14] Fourest E., Volesky B. (1995), “Contribution of Sulfonate Groups and Alginate to Heavy Metal Biosorption by the Dry Biomass of Sargassum fluitans”, Environ. Sci. Technol. 30 (1), pp 277–282

[15] Anirudhan T.S., Senan P., Unnithan M.R. (2007), “Sorptive potential of a cationic exchange resin of carboxyl banana stem for mercury(II) from aqueous

solutions", Separation and Purification Technology, 52,; pp. 512–519

[16] A. M. A. Nada, M. D. Badry & K. N. Abd EI-Nour (1992), "Grafting of cellulose and carboxymethylated cellulose with methyl methacrylate and the dielectric properties of the products", Polymer Degradation and Stability, 36,; pp.201-205.

[17] Ney, P. (1982) Melliand Textilber. 63, 443-450.

[18] Eiichi M., Tetsuo K. (1984), "Properties of 2,3-Dicarboxy Cellulose Combined with Various Metallic Ions", Journal of Applied Polymer Science, 29, pp. 2289-2297

[19] Parovuori P., Hamunen A., Forssell P., Autio K., and Poutanen K. (1995), "Oxidation of Potato Starch by Hydrogen Peroxide", Starch vol. 47 Nr. 1. S, pp. 19-23.

[20] Shukla S.R., Roshan S. P., Amit D. S. (2006), "Adsorption of Ni(II), Zn(II) and Fe(II) on modified coir fibres", Separation and Purification Technology, 47;pp., 141–147.

[21] S. Lagergren, K. Sven (1989), "Zur theorie der sogenannten adsorption gelöster stoffe", Vetenskapsakad, 24 ; pp., 1–39.

[22] McKay G., Ho Y.S., Ng J.C.Y. (1999) "Biosorption of copper from waste waters: a review". Sep Purif Methods, 28; pp., 87–125.

[23] Ho Y.S., McKay G. (1999), "Pseudo-second order model for sorption processes". Process Biochem. 34; pp., 451–465

[24] I. Langmuir (1916), "Constitution and fundamental properties of solids and liquids", J. Am. Chem. Soc. 38; pp. 2221–2295.

[25] H.M.F. Freundlich (1906), "Uber die adsorption in losungen", Z. Phys. Chem.,57 (A); pp. 385–470

[26] Leonard Y. Mwaikambo, Martin P. Ansell (2002), "Chemical Modification of Hemp, Sisal, Jute, and Kapok Fibers by Alkalization", Journal of Applied Polymer Science, 84, pp. 2222–2234

Nghiên cứu xử lý kim loại nặng trong nước bằng các phụ phẩm nông nghiệp được oxi hóa

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Tóm tắt: Nghiên cứu này sử dụng hydropeoxit để biến tính đay và sơ dừa. Phổ IR của vật liệu cho thấy các vật liệu oxy hóa đã xuất hiện nhóm carboxyl, tăng cường khả năng hấp phụ ion của kim loại. Các nghiên cứu thực nghiệm đã. Nghiên cứu này cho thấy trong điều kiện tối ưu (pH = 5 và thời gian phản ứng của Ni (II) và Pb (II) là 30 và 120 phút), sơ dừa biến tính có khả năng loại bỏ ion kim loại cao nhất, với khả năng hấp phụ tối đa là 48,54 mg / g và 19,34 mg / g đối với Pb (II) và Ni (II) tương ứng.

Từ khóa: Kim loại nặng, phụ phẩm nông nghiệp, vật liệu hấp phụ.