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Study of Chemical Activator in Preparation of Biochar Adsorbent from Patchouli Biomass for Removing Drug Contaminant

Tutik Setianingsih[*1], Masruri[1], Bambang Ismuyanto[2], Amaria[3]

[1]Department of Chemistry, Brawijaya University, Indonesia
[2]Department of Chemical Engineering, Brawijaya University Jl. Jl.Veteran 169 Malang 65145, Indonesia
[3]Department of Chemistry, Surabaya State University Jl. Ketintang Surabaya , Indonesia

Abstract : Biochar is a porous material prepared from pyrolisis of biomass. It has a potential application as adsorbent. In this research, biochar has been prepared from patchouli biomass. Purpose of the research is to study influence of activator types toward porosity and chemical surface of biochar prepared at relatively low pyrolisis temperature. Activated biochars were prepared using various activators ($ZnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $FeCl_3$, and $CrCl_3$)atpyrolisis temperature of 450 ^oC. Mass ratio of $ZnCl_2$/patchouli is 1:1. The other activators were added in the same mol amount of $ZnCl_2$. The products were characterized using nitrogen sorption method, FTIR spectrophotometry, X-ray diffraction and SEM. Characterization of the activated biochars confirmed that $CoCl_2$ activator created the highest porosity of the activated biochar, including pore volume of 0.2 cm^3 $g^{-1}$and specific surface area of 946.86 m^2 g^{-1}. All biocharsshowed –OH and C-O functional groups on their surfaces, except the biochars prepared using $CrCl_3$and without activator also showed C-H group of aliphatic hydrocarbon. The activated biochar has mixture of graphite and amorphous structures. The activated biochar revealed a surface morphology such as irregular squares separated by intersticies. Adsorption test gave adsorption capacity of 131.890 mg/g (based on Dubinin – Radushkevich) with mechanism indicates physical adsorption.
Key words : biochar, patchouli, activator, physicochemistry, adsorption.

Introduction

Biochar is a porous carbon obtained from the pyrolysis of organic matters which are provided abundantly and cheaply in our environment, such as plant materials, manure, sludge, etc[1,2].Usage of various plant waste as precursor of biochar have been reported, for example, paddy straw, maize stover, groundnut shell, coconut shell, coir waste, prosopis wood[3], rice husk[4], tea waste[5], corncob and miscanthus[6]. Patchouli biomass is chosen in this research because it is provided as large natural commodity in Indonesia which has field of patchouli plant about 9600 hectare[7].

Biochar also has various applications, including for energy storage, gas pollutant capture, catalyst support[8], biogas production, soil conditioner, compost, animal feed, adsorbent in waste water treatment, etc[9].As adsorbent, biochars, with[10-14]or without activation[15-18] in their production processes, have been used for removing various metals. Biochar has been also used for organic substance adsorption, such as tetracycline and naphthalene[19],paracetamol[20], dyes[21-23], tert-butyl ether and benzene[24], atenolol, benzophenone, and benzotriazole[25].

Adsorption performance of biochar is influenced by it's properties, including surface area[1,26,27], porosity[13], and surface functional groups[1,26], and modifications, such as sulphonation, amination, oxidation, and metal nanoparticle impregnation[8].Feedstock and condition of pyrolysis give influence toward its physicochemical characteristics[28,29].Some previousstudy of activator reported that salt chloride, such as $ZnCl_2$, has better performance in creating higher porosity of carbon than some acid and base activators, such as H_2SO_4, HNO_3, HCl, $NaHCO_3$[16], KOH[30],and H_3PO_4[31]. Compared to mixture of H_3BO_3- $ZnCl_2$- SiO_2, $ZnCl_2$ activator created higher pore volume in pore size range of 2 – 10 nm[32]. Other salt chloride type, $FeCl_3$, improved biochar yield, strength of biochar granule, and its adsorption of 4-chlorophenol[33]. The other previous researches also reported that different metal chlorides, $ZnCl_2$ and $FeCl_3$,createdthe different porosities of carbons[34,35]. Various chloride salts also showed different catalytic effect on conversion reaction of cellulose to HMF[36]. HMF is intermediete substance in pyrolysis of carbon[37] and cellulose is main part of lignocelulosic biomass[38], including patchouli biomass.

Purpose of this research is to study performance of various chemical activators in building physicochemical properties of biochar from patchouli biomass, especially porosity and surface functional groups. Result of this study will be very useful to recommend kind of activator salt chloride which can create high porosity of biochar at relatively low pyrolisis temperature. Adsorption test with 3 different structure and sizes of adsorbate in this research will support characterization of biochar, especially connected to porosity and polarity of biochar surface. This information will be useful for application of biochar as carrier of drug or adsorbent of drug wastewater.

Experimental

Preparation of biochar precursor

Patchouli biomass (stem and root) was washed and dried under sunrise. The clean biomass were crushed and sieved to obtain particle size of 60-100 mesh.

Preparation of biochar using various chemical activators

Biochar precursor, $ZnCl_2$, and distillated water (weight ratio of 1:1:6)were mixed and evaporated at 100 ^oC for 4 h under stirring, then, pyrolized at 450 ^oC for 2 h under nitrogen streaming. The composite of biochar-activator was washed using 1 M HCl solution and distillated water to remove activator. The biochar was sieved to obtain particle size of 100-120 mesh for characterization. The same procedures were applied for other activators,including$NiCl_2.6H_2O$, $CrCl_3.6H_2O$, $CoCl_2.6H_2O$, $CuCl_2.2H_2O$, and $FeCl_3$, each was added in the mixture at the same mole amount of $ZnCl_2$.All chloride salts and HCl which were used in this research are Merck productions.

Characterization of biochar

This research has used some instruments for characterization of biochars, including FTIR spectrophotometer (Shimadzu) using pellet KBr for characterization of surface functional group, Surface Area Analyzer (Quantachrome NovaWin2) for characterization of porosity through measurement of nitrogen adsorption-desorption isotherms at the temperature of –196 ^oC, X-ray diffractometer for characterization of crystal structure, and SEM for characterization of morphology.

Adsorption test

This adsorption test used paracetamol as adsorbate model. The biochar prepared using the best activator based on porosity was used as adsorbent in this test. The biochar (0.02 g) was mixed with paracetamol solution (25 mL) at various concentration (50, 100, 150 and 200 ppm), and were shaked at 175 rpm for 24h. Standart curve was made from absorbance data of paracetamol at concentration range of 10 – 50 ppm.Analysis of paracetamol was conducted using UV-Vis spectrophotometer at maximum wavelength of 243 nm. Both Freundlich and Dubinin-Raduskevich models were used to treat the adsorption data to determine adsorption parameters.

Results and Discussions

Effect of chemical activators on porosity of the patchouli biochar

Biochars have been prepared from patchouli biomass using various chemical activators. Before using it as precursor of biochar, the biomass was cleaned and treated to get the small size (30–60 mesh). The pictures of the biomass before treatment is reported in Figure 1, whereas the biomass after treatment and the biochars are reported in Figure 2.

Figure 1. Patchouli waste before treatment

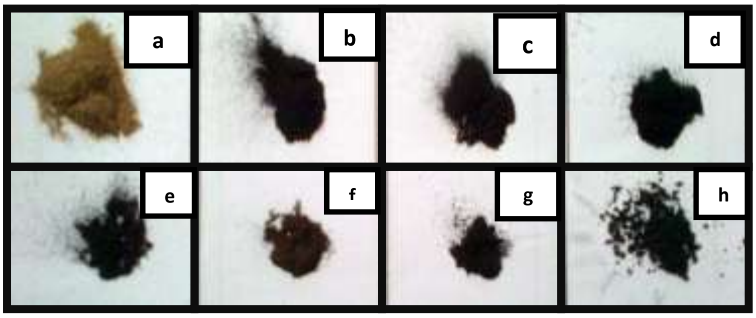


Figure 2 Patchouli biomass (a) and patchouli biochars prepared using various activators: b) no activator, c) $FeCl_3$, d) $NiCl_2$, e) $ZnCl_2$, f) $CrCl_3$, g) $CoCl_2$, h) $CuCl_2$

Figure 2 reveals relatively same colors of the biochar products, except the biochar prepared using $CrCl_3$ activator which shows the brownish black color. It indicates that Cr(III) created the incomplete pyrolis is reaction. Cr (III) has large cation charge so that it should be strong Lewis acid. The lowest performance of $CrCl_3$ in activation process may be connected to it's much higher melting point than pyrolisis temperature in this research, i.e 1152 ^oC[39]. It means that $CrCl_3$ was solid in the pyrolysis process. Whereas, the melt condition makes activators work easily as dehydrator in activation process[40].The other activators's melting points are 290, 735, 101, 300, and 498 ^oC for $ZnCl_2$, $CoCl_2$, and $NiCl_2$, $FeCl_3$, and $CuCl_2$, respectively[39].

Characterization of the patchouli biochars using gas sorption analysis method resulted in adsorption-desorption isotherm data as presented in Figure 3. The isotherm curve shows that all activators gave similar patterns of biochars' adsorption isotherm, i.e horizontal patterns of curves and short inflections of the curves at $P/P_o \approx 0.95$ which indicate small part of mesopore. However, the biochars prepared using $ZnCl_2$ and $CoCl_2$ showed much higher curves than the others. It indicates that both biochars have much higher pore volume than the others, as confirmed further in Table 1.Compared to $CrCl_3$, both $ZnCl_2$ and $CoCl_2$ have lower melting points than $CrCl_3$. This condition gives benefit in activation process as discussed in previous paragraph. $FeCl_3$ has relatively lower boiling point, i.e 316^oC[39], than temperature of pyrolisis, so that there is a possibility of evaporation during pyrolisis process.

Those pore volume values are confirmed further in Table 1 which reveals the same tendency. Isotherm curve of the biochar prepared without activator can't be reported because of too few adsorption data of the biochar to build isotherm curve. It indicates very poor porosity of the biochar due to low pyrolisis temperature.

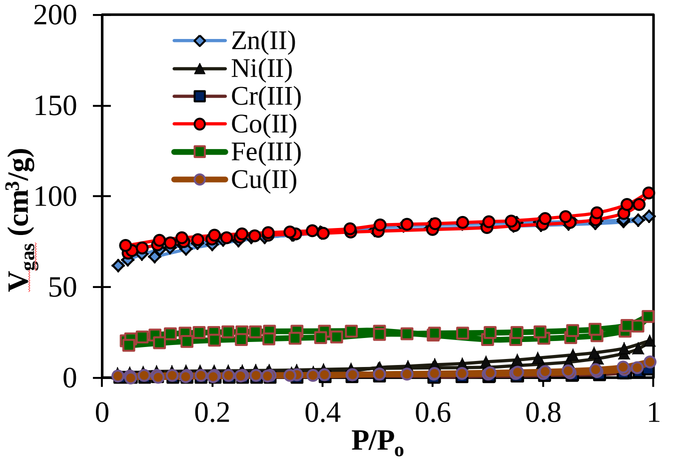


Figure 3 Adsorption-desorption isotherm of patchouli biochars prepared using various chemical activators

Table 1: Porosity data of patchouli biochar

activator	V_{tot} (cm^3/g)	S_{BET} (m^2/g)	D(Å)	V_{meso} (cm^3/g)	S_{meso}(m^2/g)
$CrCl_3$	0.01	3.80	78.91	0.01	6.02
$CuCl_2$	0.01	5.78	93.78	0.02	4.68
$NiCl_2$	0.03	14.56	85.99	0.03	15.32
$FeCl_3$	0.05	91.10	21.96	0.04	24.17
$ZnCl_2$	0.14	274.31	20.41	0.06	68.71
$CoCl_2$	0.16	946.87	6.64	0.07	51.86

Effect of chemical activators on surface functional groups of biochars

Characterization of biochars using FTIR spectrophotometry was conducted to identify functional groups of the biochar surface. Those functional groups can be used as indicator of pyrolisis reaction completeness and polarity of the biochar surface. Spectra of patchouli biomassa and the biochars are reported in Figure 4 and 5, respectively.

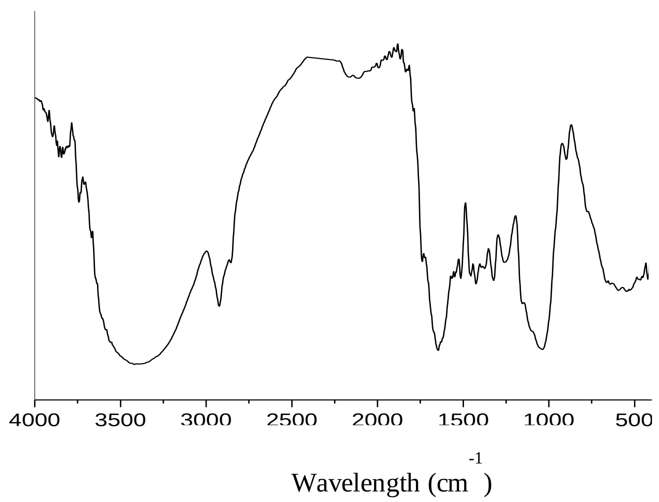


Figure 4. FTIR spectra of patchouli biomass

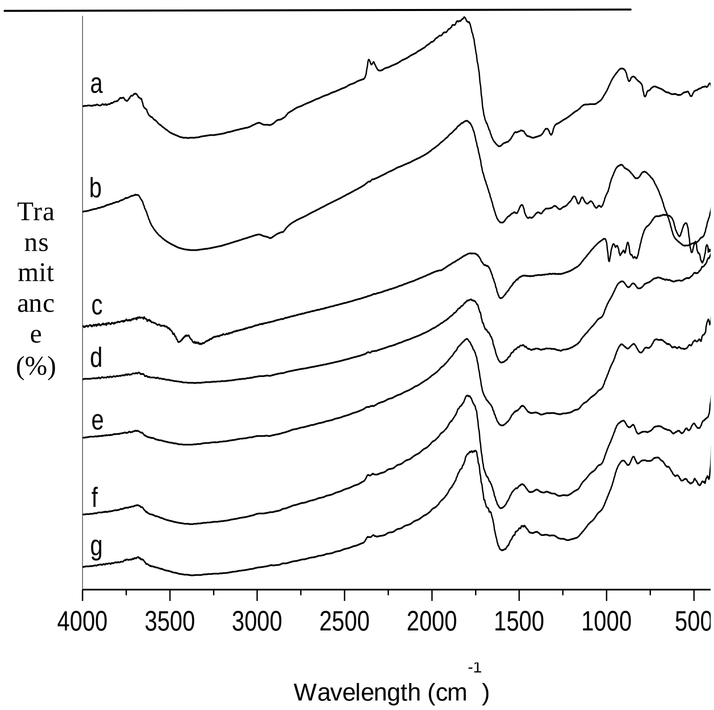


Figure 5. FTIR spectra of patchouli biochars prepared using various chemical activators :a) without activator, b) $CrCl_3$, c) $CuCl_2$, d) $CoCl_2$, e) $FeCl_3$, f) $NiCl_2$, g) $ZnCl_2$

Spectra of patchouli in Figure 4 shows bands on 3374 cm^{-1}, 2924 cm^{-1}, 1645 cm^{-1}, 1156 cm^{-1}, dan 1038 cm^{-1}. Based on checking it with FTIR spectra of cellulose and lignin[41], those bands may be connected to –OH, C-H of hydrocarbon, aromatic C=C, and C-O bonds, respectively. The –OH spectra of patchouli biomass is sharp enough because patchouli biomass is lignocellulosic material which contains lignin, cellulose, and hemicellulose. Those substances are rich of hydroxide functional groups[38]. The wide –OH spectra may be connected to hydrogen bond among the hydroxides in those substances. Difference of patterns between spectra of patchouli biomass and the biochars indicates change of chemical structure due to pyrolisis reaction, such as decomposition reaction of hemicellulose, cellulose, and lignin[41].

By comparing the biochar spectra in Figure 5 to spectra of activated carbons in previous researchs[41-44], the bands on 3410 cm^{-1}, 2997, cm^{-1}, 1614 cm^{-1}, and 1476 cm^{-1} may be connected to –OH of hydrate or surface hydroxide, C-H of aliphatic hydrocarbon, stretching vibration of C=O, and aromatic C=C.

Among all activators, only $CrCl_3$ shows spectra most similar with spectra of biochar prepared without activator, especially connected to C-H band of hydrocarbon aliphatics. It indicates that $CrCl_3$ gives lowest activation performance in preparation of biochar from patchouli biomass. In other side, $CoCl_2$, $FeCl_2$, $NiCl_2$, and $ZnCl_2$ give similar patterns of spectra, but $CoCl_2$ reveals the weakest band of C=O. It indicates the lowest content of C=O groups on the biochar surface.

Crystal structure of biochar

Crystal structure of biochar has been characterized using X-ray diffraction method and reported in Figure 6. The biochar prepared using $CoCl_2$ has been chosen for the characterization due to it's highest porosity. Figure 6 shows X-ray diffractogram of carbon which has broad peaks at $2\Theta \approx 22.55^o$($d = 0.394$ nm) and 45.55^o ($d = 0.199$ nm). The wide peaks indicate a predominantly amorphous structure[45]. The main peak of the carbon diffractogram has interlayer distance (d_{002}) of 0.394 nm, which suggests the larger interlayer distance than the d_{002} value of standart graphite data on JCPDS-ICDD card no 02-0456 ($2\Theta = 26.5^o$; $d_{002} = 0.335$ nm). Some difractogram peaks of biochar produced without activator may be connected to the inorganic impurities due to no washing treatment with HCl solution like biochar produced with activator.

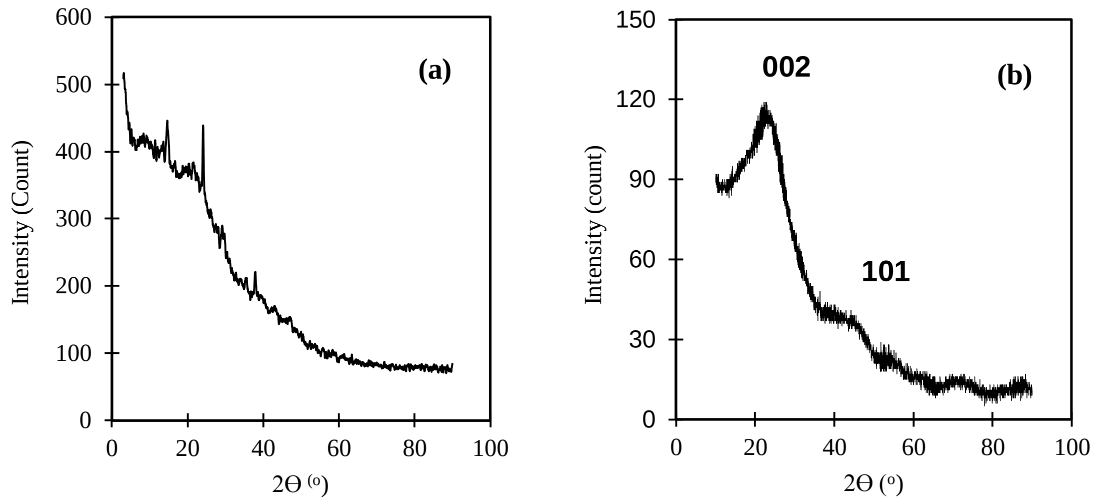


Figure 6 X-ray diffractogram of patchouli biochar prepared at pyrolisis temperature of 450 ^oC : a) without activator, b) using $CoCl_2$ activator

Surface morphology of biochar

Morphology of biochar has been characterized using SEM. The biochar prepared using $CoCl_2$ activator was chosendue to it's highest porosity. The SEM image of the biochar is reported in Figure 7.SEM image in Figure 7 reveals rough surface of biochar. There is pattern such as irregular squares which are separated by long holes (intersticies).

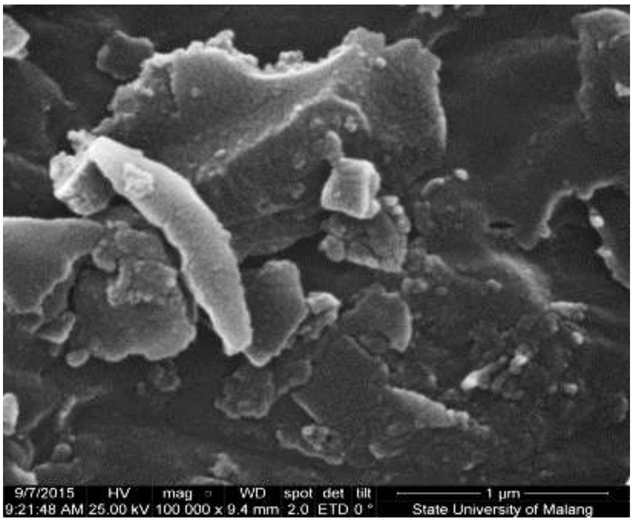


Figure 7. SEM image of patchouli biochar prepared using $CoCl_2$ activator

Adsorption test

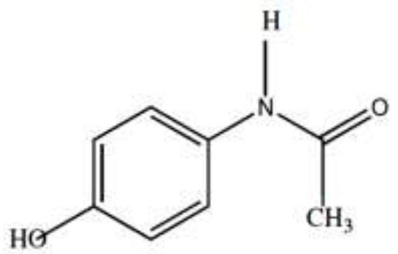
Adsorption test of paracetamol by the biochar has been conducted and reported in Table 2 and Table 3. The adsorption data shows that Freundlich model gives more correlation coefficient than Dubinin Radushkevichone. K_F is a constant of Freundlich model which is associated with adsorption capacity[46], whereas $q_D$is adsorption capacity calculated using Dubinin – Radushkevich, respectively[47].The other important constant of Freundlich is n, a measurement of adsorption intensity[48]. The n values between 1 and 10 describe beneficial/favorable adsorption[49], so that data of n in Table 2indicates the favorable adsorption for the adsorbate. Adsorption energy of the biochar toward the adsorbate was<8 KJ/mol. It indicates the physical adsorption, because chemical adsorption has adsorption energy of8-16 KJ/mol, whereas physical adsorption has the energy less than 8 KJ/mol[11].There are various interaction of adsorbate – adsorbate which support physical adsorption, such as ion – dipole, dipole – dipole, ion – induced dipole, and quadrapole interactions. Based on it's chemical structure (Figure 8), paracetamol has polar functional groups, such as hydroxyl (-OH) and (–NH), otherwise the biochar (based on FTIR spectra in Figure 5) indicates to have C=O, C-O, and O-H functional groups. So that, both dipole – dipole interaction and hydrogen bond may be responsible as the adsorption mechanism.

Table 2. Adsorption data of drugs by biochar prepared using $CoCl_2$ activator

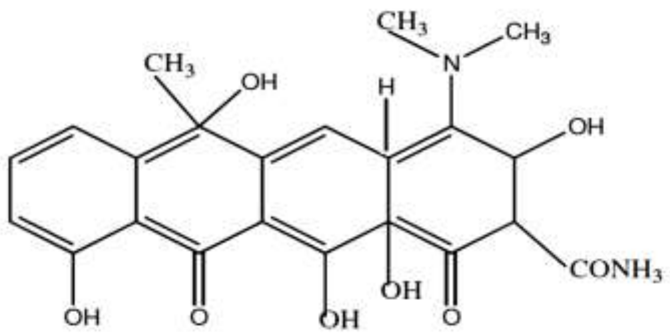
C_o (ppm)	q (mg/g)			
	q(1)	q(2)	q(average)	
50	34.740	35.077	34.91 ± 0.24	
100	59.296	58.075	58.69 ± 0.86	
150	116.301	114.280	115.29 ± 1.43	
200	175.515	175.599	175.56 ± 0.06	

Table 3. Adsorption of paracetamol by biochar prepared using $CoCl_2$ activator based on various adsorption isotherm models

Model	**parameter**	**paracetamol**
Freundlich	K(L/g)	5.242
	n	0.231
	R^2	0.998
Dubinin	q_s (mg/g)	131.890
Radushkevich	K_{DR}	5.00 X 10^{-5}
	R^2	0.630
	E (J/mol)	100.000



Paracetamol



Tetracycline

Figure 8.Chemical structure of drug [ ]

Conclusions

Biochars have been prepared using various activators of salt chlorides.$CoCl_2$ created the highest porosity of biochar from patchouli biomass, including S_{BET} of 946.87 m^2/g and V_p of 0.157 cm^3 g^{-1}, dominated by micropore. $CoCl_2$ gave the weakest FTIR spectra of the biochar, especially connected to C=O group. It has surface functional groups of C=O, C-O, and –OH. Patchouli biochar has crystal structure of amorph and graphite mxture and dominated by amorphous structure. $CrCl_3$ creates the lowest porosity and the most similar pattern of FTIR spectra with biochar without activator. Patchouli biochar has rough surface morphology, such as irregular squares separated by intersticies. Adsorption test gave adsorption capacity of 131.890 mg/g (based on Dubinin – Radushkevich) with mechanism indicates physical adsorption.

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References

1. Ferreiro, H.. Lu, S. Fu, A. Méndez, and Gascó, G., Phytoremediation and Biochar to Remediate Heavy Metal Polluted Soils: A Review, Agriculture, Ecosystems and Environment, Solid Earth, 2014,5: 65–75.
2. Gul, S., Whalen, J.K., Thomas, B.W., Sachdeva, V., Deng, H., Review Physico-chemical properties and microbial responses in biochar-amended soils: Mechanisms and future directions, Agriculture, Ecosystems and Environment,2015, 206: 46–59.
3. Shenbagavalli, S. and Mahimairaja, S., Production and Characterization of Biochar from different biological wastes, International Journal of Plant, Animal and Environmental Sciences, International Journal of Plant, Animal and Environmental Sciences, 2013, 2 (1): 197-201.
4. Prakongkep, N., Gilkes, RJ., Wiriyakitnateekul, W., Duangchan, A., Darunsontaya, T., The Effects of Pyrolysis Conditions on the Chemical and Physical Properties of Rice Husk Biochar, International Journal of Material Science, 2013, 3 (3):97-103.
5. Rajapaksha, A.U., Vithanage, M., Zhang, M., Ahmad, M., Mohan, D., Chang, S.X., Ok, Y. S., Pyrolysis Condition Affected Sulfamethazine Sorption by Tea Waste Biochars, Bioresour. Technol. , 2014,166: 303–308.
6. Budai, A., Wang, L., Gronli, M., Strand, L.T., Antal, M.J., Abiven, J.S., Dieguez-Alonso, A., Anca-Couce, A., Rasse, D.P., Surface Properties and Chemical Composition of Corncob and Miscanthus Biochars: Effects of Production Temperature and Method., J. Agric. Food Chem.,2014,62: 3791–3799.
7. Krismawati, A., Nilam dan Potensi Pengembangannya : Kalteng Jadikan Komoditas Rintisan,Tabloid Sinar Tani,Kalimantan Tengah, 2005, 1-4.
8. Liu, W.J., Jiang, H.,and Yu, H.Q., Development of Biochar-Based Functional Materials: Toward a Sustainable Platform Carbon Material, Chem. Rev., 2015, 115(22): 12251-12285.
9. Alamin, A.H., Kaewsichan, L., Adsorption of Zn(II) and Cd(II) ions from aqueous solutions by Bamboo biochar cooperation with Hydroxyapatite and Calcium Sulphate, International Journal of ChemTech Research, 2015, 7(5): 2159-2170.
10. Alamin, A.H., Kaewsichan, L., Adsorption of Zn(II) and Cd(II) ions from aqueous solutions by Bamboo biochar cooperation with Hydroxyapatite and Calcium Sulphate, International Journal of ChemTech Research, 2015, 7(5): 2159-2170.
11. Velumani, K., Kumar, P E, Sivakumar, V, Novel Adsorbent prepared from Passiflora foetida seeds for the adsorption of Nickel(II) in aqueous solution, International Journal of ChemTech Research, 2016, 9(07): 574-586.
12. Lima,I.M., Ro, K.S., Reddy, G.B., Boykin,D.L., and Klasson, K.T., 2015, Efficacy of Chicken Litter and Wood Biochars andTheir Activated Counterparts in Heavy Metal Clean upfrom Wastewater, Agriculture, 2015, 5: 806-825.
13. Li F, Shen K, Long X, Wen J, Xie X, ZengX, et al. (2016) Preparation and Characterization of Biochars from Eichornia crassipes for Cadmium Removal in Aqueous Solutions. PLoS ONE 11(2):e0148132. I:10.1371/journal.pone.0148132.

14. Komkiene1, J and Baltrenaite, E., Biochar as adsorbent for removal of heavy metal ions[Cadmium(II), Copper(II), Lead(II), Zinc(II)] from aqueous phase, Int. J. Environ. Sci. Technol. (2016) 13:471–482.
15. Sihabudeen, M.M., Ali, A.A., and Hussain, A.Z., Removal of Heavy Metals from Ground Water Using Eucalyptus Carbon as Adsorbent, International Journal of ChemTech Research, 2016, 9 (3): 254-257.
16. Kumari, H.J., Krishnamoorthy, P., Arumugam, T.K., Removal of Rhodamine B from aqueous solution by activated carbon prepared from the natural plant Typha latifolia by adsorption: Kinetic and Isotherm Studies, International Journal of ChemTech Research, 2015, 7 (7): 2867-2874.
17. Manivannan, P., Arivoli, R., Mohammed, R., Equilibrium and Thermodynamics Studies on the Removal of Iron (III) onto Activated Hibiscus Sabdariffa Stem Nano Carbon, International Journal of ChemTech Research, 2015, 8(10): 346-354.
18. Malathi, S., Srinivasan, K., and Gomathi, M., Studies on the removal of Cr (VI) from aqueous solution by activated carbon developed from Cottonseed activated with sulphuric acid, International Journal of ChemTech Research, 2015, 8(2): 795-802.
19. Lian, F., Song, Z., Liu, Z., Zhu, L., Xing, B., Mechanistic understanding of tetracycline sorption on waste tire powder and its chars as affected by Cu^{2+} and pH,Environmental Pollution, 2013,178: 264-270.
20. Setianingsih, T., Masruri, Ismuyanto, B., 2016, Effect of Calcination Temperature on Structural Properties ofBiochar-MCln Composite from Patchouli Biomass and Its Application for DrugAdsorption, International Journal of ChemTechResearch, 2016, 9(12): 610-621.
21. Yamuna.M and Kamaraj.M, Pineapple peel waste activated carbon as an adsorbent for the effective removal of methylene blue dye from aqueous solution,International Journal of ChemTech Research, 2016, 9(5): 544-550.
22. Agarwal, M., Tardio, J., and Mohan, S.V., Pyrolysis Biochar from Cellulosic Municipal Solid Wasteas Adsorbent for Azo Dye Removal: EquilibriumIsotherms and Kinetics Analysis, International Journal of Environmental Science and Development, 2015, 6 (1): 67-72.
23. Singh, V.K., Soni, A.B., Singh, R.K., Auramine ‘O’ dye adsorption onto de-oiled cotton seed cake biochar: process optimization using Response Surface Methodology for maximizing adsorbate removal, International Journal of ChemTech Research, 2016, 9(7): 340-353.
24. Xiao, L., Bi, E., Du, B., Zhao, X., Xing, C., Surface Characterization of Maize-straw-derived Biochars and Their Sorption Performance for MTBE and Benzene,Environ Earth Sci , 2014, 71:5195–5205.
25. Kim, E., Jung, C., Han, J., Her, N., Park, C.M., Son, A., Yoon, Y., Adsorption of selected micropollutants on powdered activated carbon and biochar in the presence of kaolinite, Desalination and Water Treatment,2016,1–13.
26. Rostamian, R., Heidarpour, M., Mousavi, S. F. and Afyuni, M., Characterization and Sodium Sorption Capacity of Biochar and Activated Carbon Prepared from Rice Husk, J. Agr. Sci. Tech.,2015, 17: 1057-1069.
27. Jindo, K., Mizumoto, H., Sawada, Y., Sanchez-Monedero, V, and Sonoki, T. , Physical and Chemical Characterization of Biochars Derived from Different Agricultural Residues,Biogeosciences, 2014, 11: 6613–6621.
28. Park, J., Hung, I., Gan, Z.,. Rojas, O.J., Lim, K.H., Park, S., Activated carbon from biochar: Influence of its physicochemical properties on the sorption characteristics of phenanthrene,Bioresource Technology,2013, 149: 383–389.
29. Gai X, Wang H, Liu J, Zhai L, Liu S,et al., Effects of Feedstock and Pyrolysis Temperature on Biochar Adsorption of Ammonium and Nitrate,2014, PloSONE, 9(12):1-19.
30. Ramakrishnan, K. and Namasivayam, C., Development and Characterstics of Activated Carbons from Jatropha Husk, An Agro Industrial Solid Waste by Chemical Activation Methods,J. Environ. Eng. Manage., 2009, 19(3) : 173-178.
31. Tawalbeh M., Allawzi, MA., dan Kandah, M., 2005, Production of Activated Carbon from Jojoba Seed Residue by Chemical Activation Using a Static Bed Reactor, Journal of Applied Sciences, 5(3): 482-487.
32. Setianingsih, T., Kartini, I., Arryanto, Y., 2014, Study of Structural Properties of Mesoporous Carbon FromFructose with Zinc Borosilicate Activator, J. Pure App. Chem. Res., 2014, 3 (3), 114-122.
33. Li, D.C., Ding, J.W., Qian, T.T., Zhanga, S., and Jiang, H., Preparation of High Adsorption Performance and Stable Biochar Granules by $FeCl_3$-catalyzed FastPyrolysis, RSC Adv., 2016, 6: 12226-12234.

34. Gimba, CE., Ocholi, O., Egwaikhide, PA., Muyiwa, T., and Akporhonor, EE., New Raw Material for Activated Carbon. I. Methylene blue Adsorption on Activated Carbon Prepared from Khaya Senegalensis Fruits, Cien. Inv. Agr., 2009, 36 (1): 107-114.
35. Guimaraes, L.C.E., Vallone, I.R., Pereira, A., Mesquita, M., Sapag, J.P., Preparation of Activated Carbons from Coffee Husks Utilizing $FeCl_3$ and $ZnCl_2$ as Activating Agents,J. Hazard Mater. , 2009, 165 (1-3): 87-94.
36. Peng, L., L Lin., J Zhang., J Zhuang., B Zhang., Y Gong., Catalytic Conversion of Cellulose to Levulinic Acid by Metal Chlorides, Molecules,2010, 15: 5258-5272.
37. Huang, Y., Hu, S., Zuo, S., Xu, Z., Han, C., Shen, J., Mesoporous carbon materials prepared from carbohydrates with a metalchloride template,J.Mater.Chem., 2009, 19: 7759 – 7764.
38. Fu, l., Scott A. McCallum, SA., Miao, J., Hart, C., Tudryn, GJ., Zhang, F., Linhardt, RJ., Rapid and accurate determination of the lignin content of lignocellulosicbiomass by solid-state NMR, Fuel,2015, 141:39–45.
39. Windolz, M., Budavari, S., Blumeti,RF., Otterbein, ES., 1983, The Merc Index : An Encyclopedia Of Chemicals, Drugs, and Biologicals, Merck & CO, Inc., 10th ed., USA.
40. Marsh H. dan Reinoso, R., 2006, Activated Carbon, Elsevier Sci., USA.
41. Song-Lin, Z., Shang-Yu, G., Xi-gen, Y., Bo-sen, X., Carbonization Mechanism of Bamboo (phyllostachys) by Means of Fourier Transform Infrared and Elemental Analysis,Journal of Forestry Research, 2003, 14(1): 75-79.
42. Sevilla, M., Fuertes, AB., The production of carbon materials by hydrothermal carbonization of cellulose, Carbon, 2009, 47: 2281 – 2289.
43. Lua,A.C., Yang, T., Characteristics of Activated Carbon Prepared From Pistachio-Nut Shell by Zinc Chloride Activation Under Nitrogen and Vacuum Conditions, Journal of Colloid and Interface Science,Journal of Colloid and Interface Science, 2005, 290: 505–513.
44. Chayande, Singha, SP., and Yenkie, MKN., Characterization of Activated Carbon Prepared From Almond Shells For Scavenging Phenolic Pollutants, Chem. Sci. Trans.,2013, 2(3):835-840.
45. Chen, J., Xia, N., Zhou, T., Tan, S., Jiang, F., Yuan, D., Mesoporous Carbon Spheres: Synthesis, Characterization and Supercapacitance, Int. J. Electrochem. Sci.,2009, 4:1063 – 1073.
46. Ismadji, S., Tong, D.S., Soetaredjo, F.E., Ayucitra, A., Yu, W.H., Zhou, C.H., Bentonite-hydrochar composite for removal of ammoniumfrom Koi fish tank, Applied Clay Science, 2015, 114: 467–475.
47. Kyzioł-Komosińska, J., Rosik-Dulewska, C., Franus, M., Antoszczyszyn-Szpicka, P., Czupioł, J., Krzyżewska, I., Sorption Capacities of Natural and SyntheticZeolites for Cu(II) Ions, Pol. J. Environ. Stud., 2015,24(3):1111-1123.
48. Chen , X., Modeling of Experimental Adsorption Isotherm Data, Information,2015, 6 : 14-22.
49. Igwe, J.C., Abia, A.A., Adsorption isotherm studies of Cd (II), Pb (II) and Zn (II)ions bioremediation from aqueous solution usingunmodified and EDTA-modified maize cob, Ecletica,2007, 32, 1:33-42.

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