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Effect of Calcination Temperature on Structural Properties of Biochar-MCl_n Composite from Patchouli Biomass and It's Application for Drug Adsorption

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Abstract : Patchouli biomass is a abundant and potensial plant waste to produce biochar by pyrolisis. Biochar is a porous black carbon. It is useful for adsorbent of organic substances due to it's porosity. In this research, biochar - $ZnCl_2$ and biochar - $CrCl_3$ composites are synthesized to study influence of both calcination temperature and metal type on structural properties and drug adsorption of the composites. Paracetamol was used as adsorbate model. Research was performed at some steps, i.e pyrolisis of patchouli biomass using $CoCl_2$ activator, impregnation of biochar using metal chloride solutions, calcination of the biochar - metal chloride composites at various temperatures (400, 600, 800 ^{o}C), characterization of the composites using X-ray diffraction and FTIR spectrophotometry, and adsorption test at various concentration of paracetamol. Paracetamol concentration was determined using UV-Vis spectrophotometry at 243 nm. Langmuir and Dubinin-Radushkevich models were used to determine adsorption capacity, whereas Freundlich model was used to determine adsorption intensity. Result of this research showed that temperature of 600 and 800 ^{o}C gave change of impregnant structure for each metal types. Temperature of 600 and 800 ^{o}C gave the highest adsorption capacities for each composite using $CrCl_3$ and $ZnCl_2$, respectively with adsorption intensities indicating the favourable adsorptions.

Keywords: biochar, patchouli biomass, metal chloride, pyrolisis, impregnation, adsorption.

Introduction

Patchouli is the abundant plant in Indonesia. It provides abundant biomass waste in environment. Patchouli is a hard woody waste, so that it is rich of organic components and can be categorized as lignocellulosic material. Patchouli biomass can be pyrolized to produce biochar. Biochar is type of a porous black carbon material[1]. Biochar has various applications in human life, including as a soil amendment[2], supercapacitor[3], adsorbent[4], and carrier/support[5]. As adsorbent, biochar showed good performance for removing various metals, suc as lead, copper, chromium, zinc and cadmium[6], ammonium[7], and organic contaminants, for example methyl tert-butyl ether and benzene[8], azo dyes[4], tetracycline[9]. Biochar can be also used as support or adsorbent. Porous carbon can be an effective support due to its some characteristics, including its high surface area, its resistance toward both acid and base, its surface which can be functionalized to provide the metal loading sites, its pore structure which can be engineered to improve adsorption, its stability at high temperatures in anoxic environment, and its easiness to be separated by combustion to recover spent catalysts[10].

Adsorption is a relatively low cost and highly efficient method, even connected to the low concentration pollutant[11]. Adsorption is also flexible, simple, and inactive towards toxic pollutants[12]. Adsorption capacity of the carbon can be increased by chemical impregnation treatment[13]. For example, impregnation of carbon nanotubes (CNTs) with iron oxide nanoparticles has improved the removal of benzene from 53% to 61% compared to raw CNT at same experimental condition[14]. Composites of Cu(II)- and Ni(II)-impregnated activated carbon (Cu/PAC and Ni/PAC) had more than 2.5 times adsorption capacity of cyanide than Cu(II)- and Ni(II)-impregnated clay (Cu/clay and Ni/clay)[15]. The other research reported that after Fenton regeneration, adsorption of the pharmaceutical diclofenac on ferryhidrite impregnated activated carbon (Fe/PAC) was higher than on powdered activated carbon (PAC)[16].

Composite of the chemical impregnated carbon can be prepared in 3 steps, i.e impregnation process of carbon in salt solution, drying process of the impregnated carbon, and calcinations process to obtain final impregnant compound[17]. The previous researchers reported that calcinations temperature gave effect on impregnant's structure and composite's adsorption capacity. For example, carbon – CuO, carbon – Cu_2O, and carbon – Cu were formed by calcination of carbon – $Cu(NO_3)_2$ at 400, 530, and 800 ^oC respectively under nitrogen gas streaming. Carbon was obtained from pyrolisis of palm seed. In other side, carbon – NiO and carbon – Ni were formed by calcination of carbon – $Ni(NO_3)_2$ at 550 and 800 ^oC respectively in nitrogen gas streaming The Cu(I) and Ni(II) impregnated carbons improved thiophenate adsorption of 40 – 53%[18].

In this research, composites of biochar from patchouli impregnated by metal chlorides, $ZnCl_2$ and $CrCl_3$, were calcined at various calcination temperatures. Purpose of this research to investigate effect of those temperature on physicochemistry and adsorption capacity of those composites, especially for adsorption of drug pollutant. Result of this research will be a recommendation about usage of metal compound – biochar composite adsorbent to minimize the drug wastewater.

Experimental

Preparation of biochar and composites

There were 3 main steps in this research, including preparation of biomass, synthesis of biochar by pyrolysis of biomass using $CoCl_2.6H_2O$ activator, and impregnation of biochar using chloride salts. Preparation of patchouli biomass were conducted by washing it using water and dried under sunrise. Then, the clean biomass was crushed to produce precursor size of 60 - 100 mesh. The precursor (10 g) was mixed with $CoCl_2.6H_2O$ salt (52 g), and distillated water (60 mL), then the mixture was evaporated at 100 ^oC for 4 h under stirring. The $CoCl_2$ impregnated biomass was pyrolized at 450 ^oC for 2 h under nitrogen gas stream. Activator was removed from product by washing the product with 1 M HCl solution and distillated water. The biochar product was sieved for conditioning the size of 100-120 mesh. The obtained biochar (6 g) was mixed with each 0.1 M of $ZnCl_2$ and $CrCl_3$ solution (100 mL), then was shaked for 24 h at 200 rpm. The mixture finally was filtered and residue (composite) was dried at 100 ^oC for 1 h. Each composite product of biochar - MCl_n was calcined at 400, 600, and 800 ^oC for 1 h in the closed ceramic crucible.

Characterization of biochar

Characterization of surface functional groups was conducted using FTIR spectrophotometer (Shimadzu) and pellet KBr technique. Characterization of crystal structure was performed using X-ray powder diffraction (XRD) in 2θ range of 10–90°. Surface Area and pore characterizations were calculated usimg measurement data of nitrogen adsorption-desorption isotherms at the temperature of –196 ^oC using Surface Area Analyzer (Quantachrome NovaWin2). Isotherm data was treated using Bruanuer Emmet Teller (BET) and Pierce Orr Dalla Vale (POD) methods.

Adsorption test

For adsorption test, this research has used paracetamol as adsorbate model. Paracetamol solution (500 ppm) was prepared by dissolving a paracetamol tablet which contains 500 mg of paracetamol in distillated water. Residue was filtered before dilution of the filtrate to get 500 ppm paracetamol solution. Then, a serie of of paracetamol solution (10, 20, 30, 40, and 50 ppm) was mixed with biochar and was shaked for 24 h at 200 rpm. The drug solution was analyzed using UV-Vis spectrophotometer at maximum wavelength of 243 nm.

Results and Discussions

Functional groups of composites

Biochar has been prepared from pyrolisis patchouli biomass and the product has been impregnanted using $CrCl_3$ and $ZnCl_2$. The composites of biochar – $CrCl_3$ and biochar – $ZnCl_2$ were calcined at various temperatures. Characterization of the calcined composites using FTIR spectrophotometry gave spectra as reported in Figure 1.

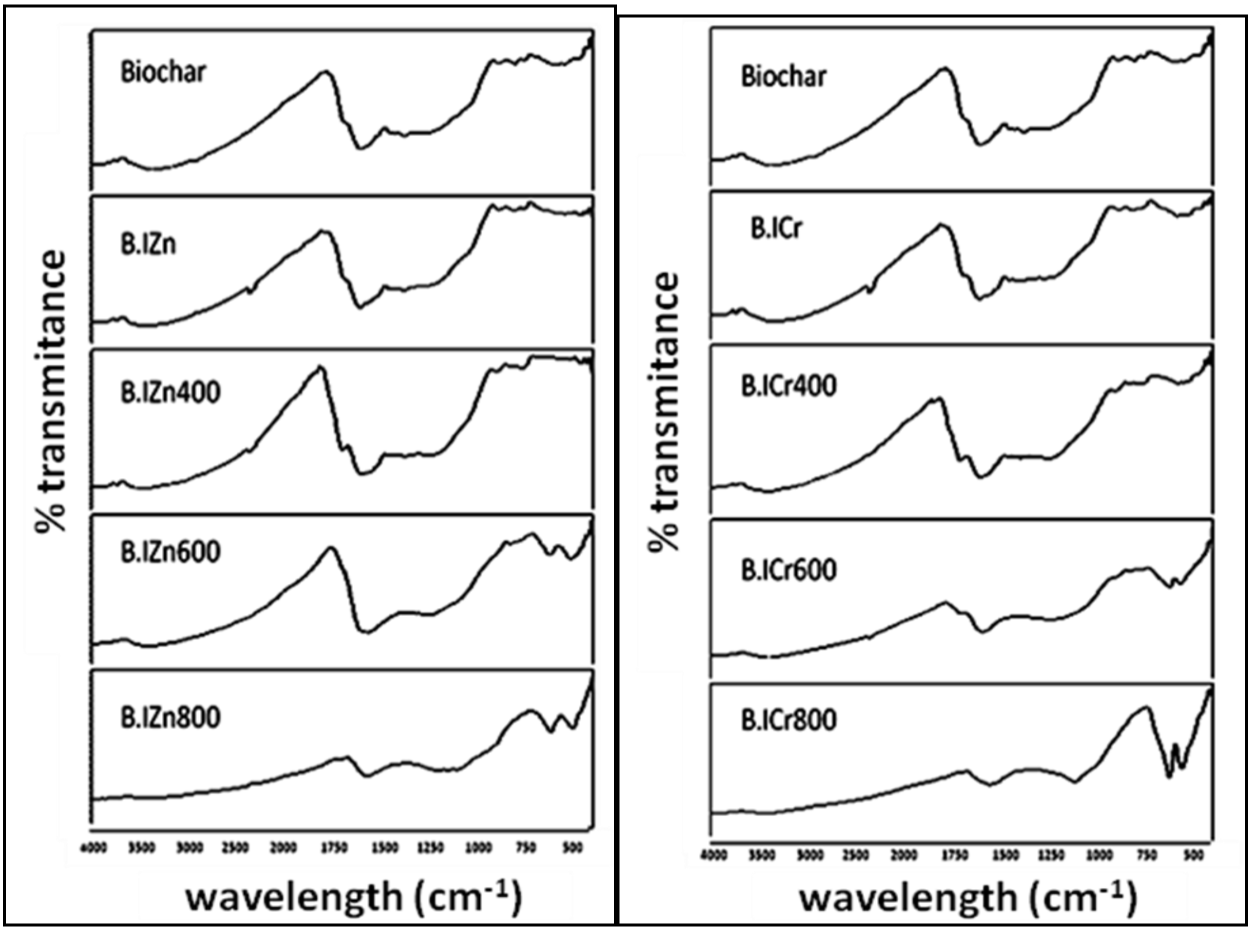

Figure 1. FTIR spectra of the calcined composites of biochar-$ZnCl_2$ (BIZn) and biochar – $CrCl_3$ (BICr) at various temperatures

Figure 1 showed that the spectra of biochar, the MCl_n impregnated biochar, and the calcined impregnant at 400 ^oC are relatively same. Based on the previous research, strong band around 1736, 1643, and 1332 cm^{-1} refers to the stretching vibrations of C = O, C=C, and C-O bonds[19]. So that, bands of the biochars at about 1700, 1600, and 1250 cm^{-1} may refer to stretching of C=O, C=C, and C-O, respectively.

Calcination at temperature of 600 ^oC gives different pattern of spectra, i.e weaker bands of C-O, C=C, -OH for both composites than without calcinations and after calcination at 400 ^oC. It indicates that biochar experienced the decomposition reaction. This decomposition may be effect of reaction between functional groups on biochar surface and gas emited by decomposition reaction of the impregnant salt. Lost of C=O band for the calcined composite – $ZnCl_2$ indicated that $ZnCl_2$ is more effective as dehydrator than $CrCl_3$. It may be connected to it's less melting point than $CrCl_3$. Change of spectra is also signed by emerging 2 bands of spectra between 500 and 650 cm^{-1}. By referring to previous research connected to bands of Cu-O[20], those bands may be connected to CrO and ZnO stretching vibrations.

Crystal structure of composites

Characterization of composites using X-ray diffraction method has been conducted to study effect of calcination temperature on crystal structure of the composites. Diffractograms of the composites are reported in Figure 2.

Figure 2 shows that increasing of calcination temperature from 400 to 600 ^{o}C gave no change of diffractogram patterns. Those diffractograms have 2 wide peaks at around 22^{o} and 44^{o}. Those patterns are similar to activated carbon previous researchs, connected to (002) and (100) planes of turbostratic graphic structures, respectively[21]. No peak of impregnants detected in those diffractograms may be due to low concentration of impregnant on surface of biochars.

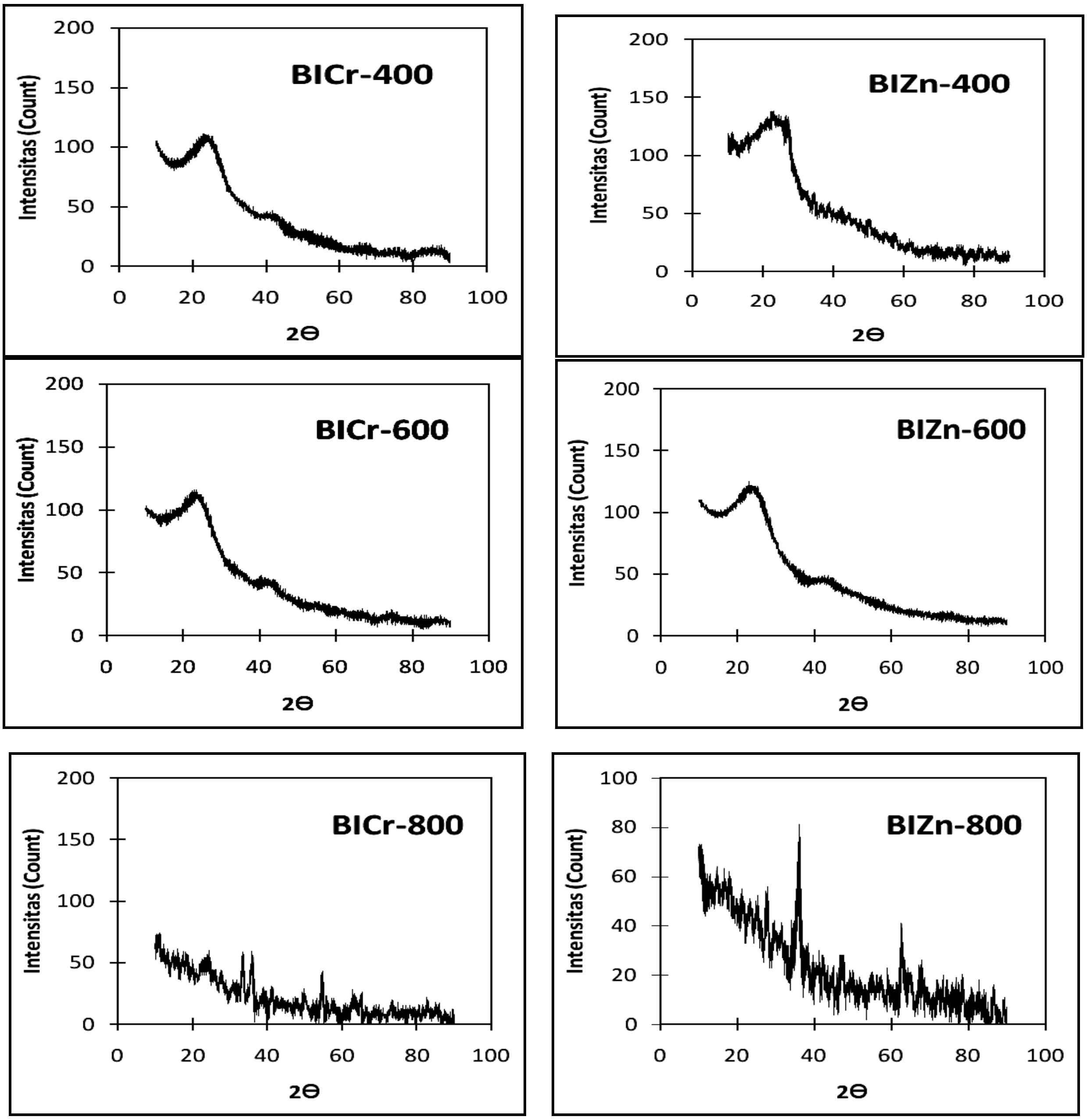

Figure 2. Diffractograms the calcined composite of biochar – $ZnCl_2$ and biochar – $CrCl_3$ at various temperatures

In other side, the calcined composites at 800 °C show new patterns of difractograms. By reffering to the standart data of JCPDS-ICDD (Table 1), the composites formed by calcination indicate biochar – ZnO and biochar – Cr_2O_3. No wide peak of difractograms are appeared by the composites which were calcined at 800 °C. It indicates lower structure of biochars due to thermal decomposition.

Table 1. Diffractogram data biochar - $ZnCl_2$ and biochar – $CrCl_3$ calcined at 800 °C

Sample Code	2Θ sampel	d-spacing sampel	2Θ standar	Standart
BIZ-800	35.96	2.50	36.25	ZnO JCPDS no. 36-1451
	47.20	1.93	47.53	
	62.77	1.48	62.86	
BICr-800	33.45	2.68	33.62	Cr_2O_3 JCPDS no. 381-479
	35.89	2.50	36.25	
	50.11	1.82	50.28	
	54.66	1.68	54.89	
	57.64	1.60	58.48	
	64.89	1.44	65.19	
	78.21	1.22	79.14	

Porosity of composites

Pore texture is one of carbon's characteristics which affects the adsorption process. This is connected to size of adsorbate which determines it's accessibility to the inner surface of the adsorbent[22]. Porosity data of biochar and composites are reported in Table 2.

Data in Table 2 shows that impregnation of biochar to form .composites of biochar – $CrCl_3$ (BICr) and biochar – $ZnCl_2$ (BIZn) decreased pore volume and specific surface area. It indicates that some impregnant particles stayed in the pore of the biochar. Calcination of the composites seems to give different impact, i.e reducing of porosity for usage of $ZnCl_2$ impregnant, but increasing of porosity for usage of $CrCl_3$, probably due to different melting point of impregnants which influence activation of biochar by impregnant along calcination process.

Table 2. Porosity data of biochar and composites of biochar – $CrCl_3$ and biochar – $ZnCl_2$ before and after calcination

Biochar and composite	S_{BET} (m^2/g)	V_p (cm^3/g)	D (nm)	S_{mm} (m^2/g)	V_{mm} (cm^3/g)	%V (micro)	%S (micro)
BICr	22.15	0.02	4.3	1.11	0.001	95	96
BICr-600	1455.30	2.85	7.8	49.38	0.043	97	98
BIZn	10.27	0.21	82.8	0.93	0.001	91	100
BIZn-800	2.54	0.12	185.1	0.71	0.002	72	98
Biochar	471.69	0.33	2.8	161.59	0.250	66	24

Notes :

S_{mm} = mesoporous and macroporous specific surface area, calculated from N_2 adsorption data using Pierce Orr Dalla Vale method, refering to Lowell and Shields[23]

V_{mm} = mesoporous and macroporous volume, calculated from N_2 adsorption data using Pierce Orr Dalla Vale method, refering to Lowell and Shields[23]

S_{BET} = BET specific surface area, calculated using BET equation at range of $0.05 \leq P/P_o \leq 0.35$, refering to Lowell and Shields[23]

V_{micro} and S_{micro} were calculated by substracting each V_p and S_{BET} with V_{mm} and S_{mm}, respectively

D. Adsorption test

Adsorption test of paracetamol by the composites calcined at various temperatures has been conducted. Adsorption data was treated using 3 kinds of adsorption models, i.e Langmuir, Freundlich, and Dubinin – Radushkevich models. The Langmuir model assumes that adsorption occurs on a homogenous surface. The Freundlich isotherm is used to show the surface heterogeneity, which shows the multilayer adsorption properties of the adsorbent[242315]. Langmuir model is based on the assumption that number of adsorption sites is fixed and each site will hold only one adsorbate molecule[25]. Dubinin – Radushkevich model generally expresses the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface[26].

Freundlich, Langmuir, and Dubinin – Radushkevich isotherm adsorptions of paracetamol by the composites are reported in Figure 3, Figure 4, and Figure 5, respectively.

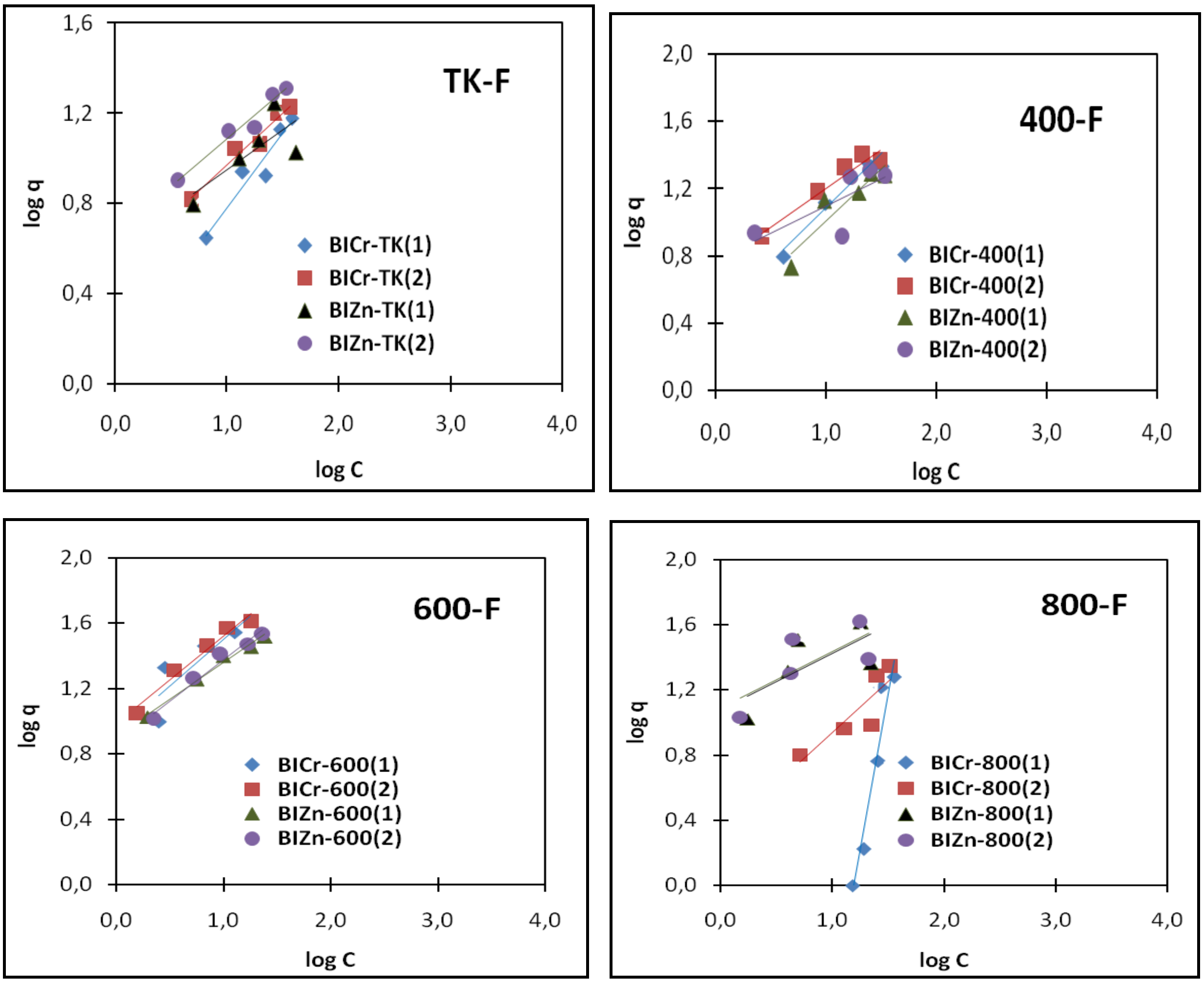

Figure 3. Freundlich isotherm adsorptions of biochar – $CrCl_3$ and biochar – $ZnCl_2$ composites before (with code of TK) and after calcination at various temperatures

Correlation coefficient of those curves are reported in Table 3. Data in Table 3 shows that generally the highest correlation coefficients is achieved by application of Langmuir model forbiochar – $ZnCl_2$ by sequence of Freundlich < Dubinin – Radushkevich < Langmuir. In other side, the highest one is obtained by Dubinin – Radushkevich model for biochar – $CrCl_3$ by sequence of Freundlich < Langmuir < Dubinin – Radushkevich. It indicates that surface of the biochar – $CrCl_3$ tends to be heterogenous but still contain homogenous part. In other hand, the biochar – $ZnCl_2$ tends to have homogenous surface with containing heterogenous part.

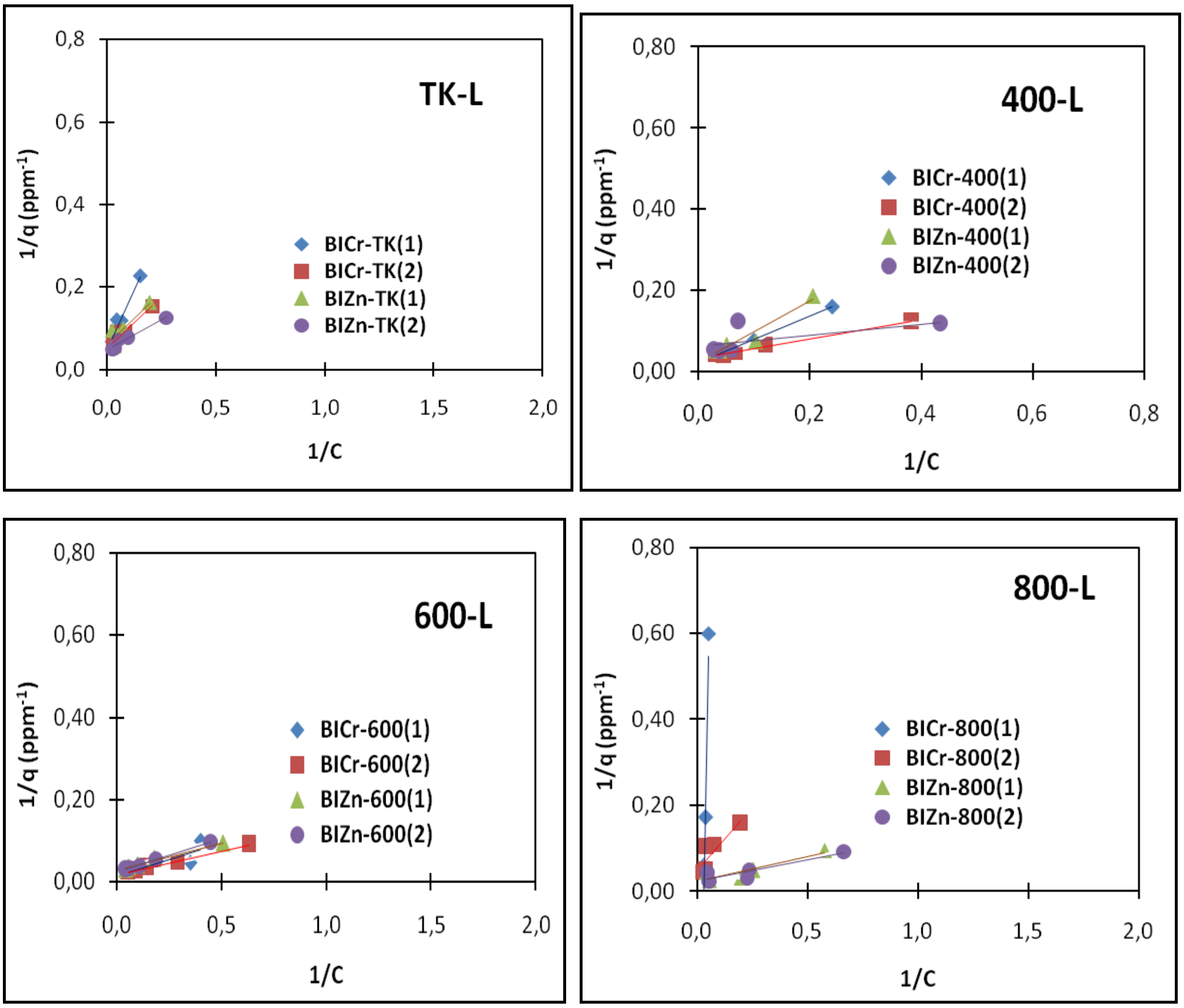

Figure 4. Langmuir isotherm adsorptions of biochar – $CrCl_3$ and biochar – $ZnCl_2$ composites before (with code of TK) and after calcinations at various temperatures

Process efficience and affinity of adsorbent - adsorbate can be predicted from value of R_L, i.e Langmuir separation factor. Based on the R_L, isotherm type can be classificated as follows : $R_L > 1$ (unfavorable), $R_L=1$ (linier), $0 < R_L < 1$ (favorable), $R_L = 0$ (irreversible) [24,27]. The R_L data of the composites are reported in Table 4. All those data, except for biochar – $CrCl_3$ calcined at 800 ^oC (> 1), show values in range of R_L between 0 and 1. It indicates that adsorption of paracetamol by those composites are favorable, except biochar – Cr_2O_3 gives unfavorable adsorption.

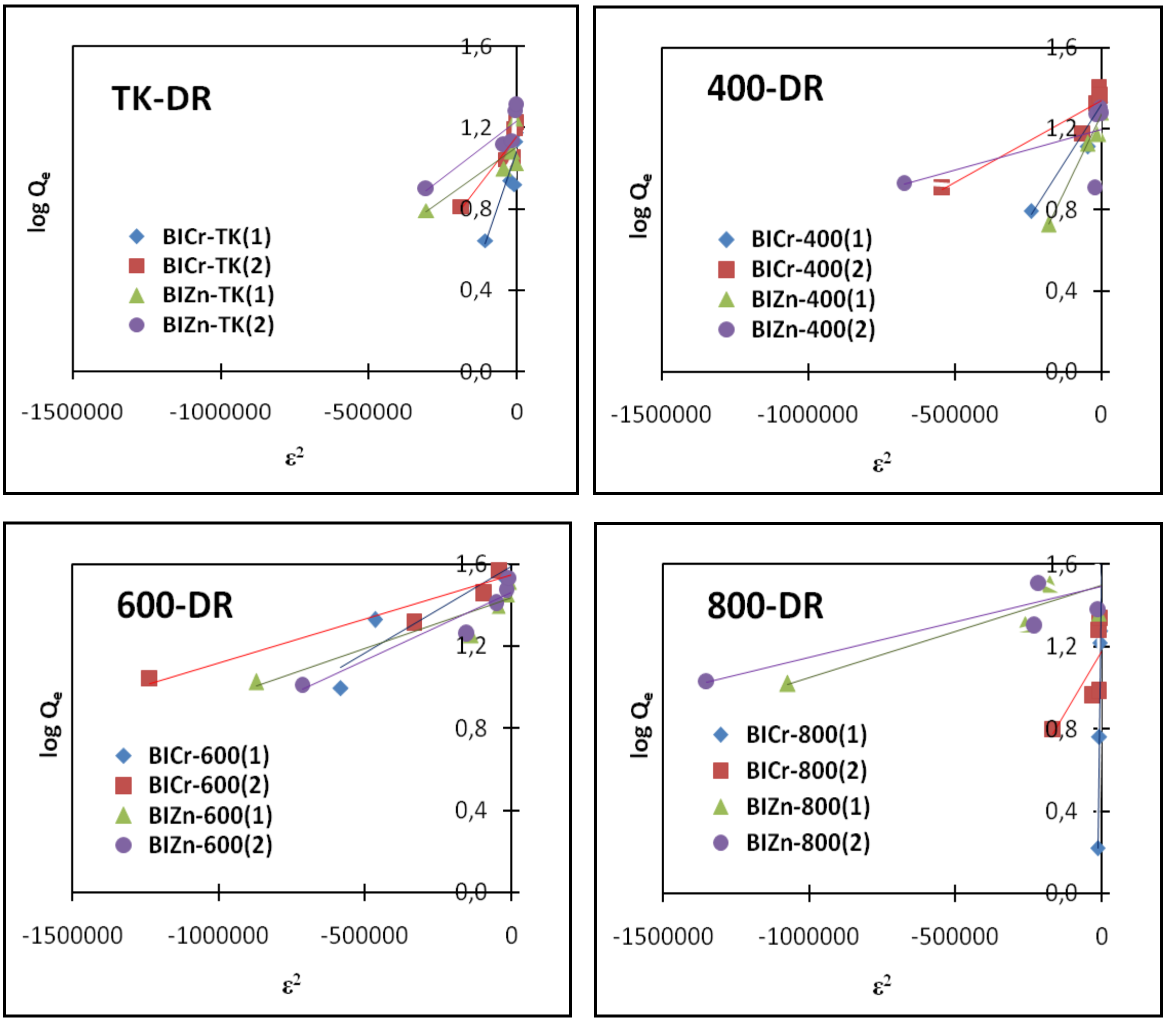

Figure 5. Dubinin - Radushkevich isotherm adsorptions of biochar –$CrCl_3$ and biochar – $ZnCl_2$ composites before (with code of TK) and after calcinations at various temperatures

Constant of n is a Freundlich constant which is an indicator of adsorption intensity[12,28]. Value of n between 1 and 10 describes favorable adsorption[29]. The n value is also an indicator of adsorbent's heterogeneity. The higher n value, the more heterogenous adsorbent is[7] . The high 1/n value indicates weak bonding of adsorbent and adsorbate[30]. The value of 1/n close to 1 indicates the high adsorption capacity at high equilibrium concentration which will be rapidly reduced at lower equilibrium concentrations, whereas the value less than 1 indicate the adsorption capacity which is only slightly reduced at lower equilibrium concentrations[31]. The n values of the composites are presented in Table 5.

Table 3. Correlation coefficient (R^2) of isotherm adsorption of paracetamol by composites of biochar – MCl_n composites before (TK) and after calcination at various temperatures

Model	M	TK	400 °C	600 °C	800 °C
Freundlich	Cr	0.910	0.939	0.878	0.810
	Zn	0.742	0.708	0.976	0.530
Langmuir	Cr	0.959	0.986	0.858	0.829
	Zn	0.893	0.965	0.944	0.839
Dubinin-Radushkevic	Cr	0.933	0.914	0.952	0.811
	Zn	0.915	0.983	0.881	0.767

Table 4. R_L data of the biochar – $ZnCl_2$ and biochar – $CrCl_3$ composites before and after calcination at various temperatures

Komposit	TK	400 °C	600 °C	800 °C
Biochar –$CrCl_3$	0.42	0.40	0.17	1.10
Biochar – $ZnCl_2$	0.29	0.35	0.21	0.22

Table 5. n data of the biochar – $ZnCl_2$ and biochar – $CrCl_3$ composites before and after calcination at various temperatures

Komposit	TK	400 °C	600 °C	800 °C
Biochar – $CrCl_3$	5.91	1.86	1.80	3.17
Biochar – $ZnCl_2$	6.48	2.70	2.12	2.89

Data in Table 5 shows that all adsorptions gave value of n between 1 and 10, indicating the favorable adsorptions. Those values decrease by calcination treatment, meaning that the calcined composites are more homogenous than the uncalcined composites.

Adsorption process works physically or chemically can be predicted from adsorption energy (E). The energy is calculated using Dubinin Radushkevich's contant, K_D. Isotherm adsorption which gives value of E between 8 and 16 KJ/mol indicates chemical adsorption, whereas less than 8 KJ/mol indicates physical adsorption[32]. Data of the composites's adsorption energy are reported in Table 6.

Table 6. Adsorption energy (J/mol) of the biochar – $ZnCl_2$ and biochar – $CrCl_3$ composites before and after calcinations at various temperatures

Komposit	TK	400 °C	600 °C	800 °C
Biochar – $CrCl_3$	408.11	375.00	912.57	237.83
Biochar – $ZnCl_2$	478.55	362.24	922.58	1204.51

All data in Tabel 6 show E values less than 8 KJ/mol. It indicates that adsorption last physically. According to Lowell dan Shield[23], physical adsorption works through 4 kinds of adsorbate – adsorbent interactions, including ion – dipole, dipole – dipole, ion – induced dipole, and quadrapole interactions. In this research, adsorption of paracetamol may be lasted through dipole – dipole interaction, i.e paracetamol's polar functional group, such as hydroxyl (-OH) and –NH with carboxyl (C=O) and hydroxyl of the composites. Adsorption energy of biochar – $CrCl_3$ increased by increasing the temperature to 600 °C, then decreased again. In other side, adsorption energy of biochar – $CrCl_3$ improved by improving the temperature to 800 °C.

Adsorption performance of adsorbents can be determined from adsorption capacity. Parameters of q_m and q_s are adsorption capacities calculated using Langmuir and Dubinin – Radushkevich models, respectively[30]. Based on Langmuir model, q_m is related to complete coverage monolayer of adsorbent surface[32].The adsorption capacities of the composite are reported in Figure 6.

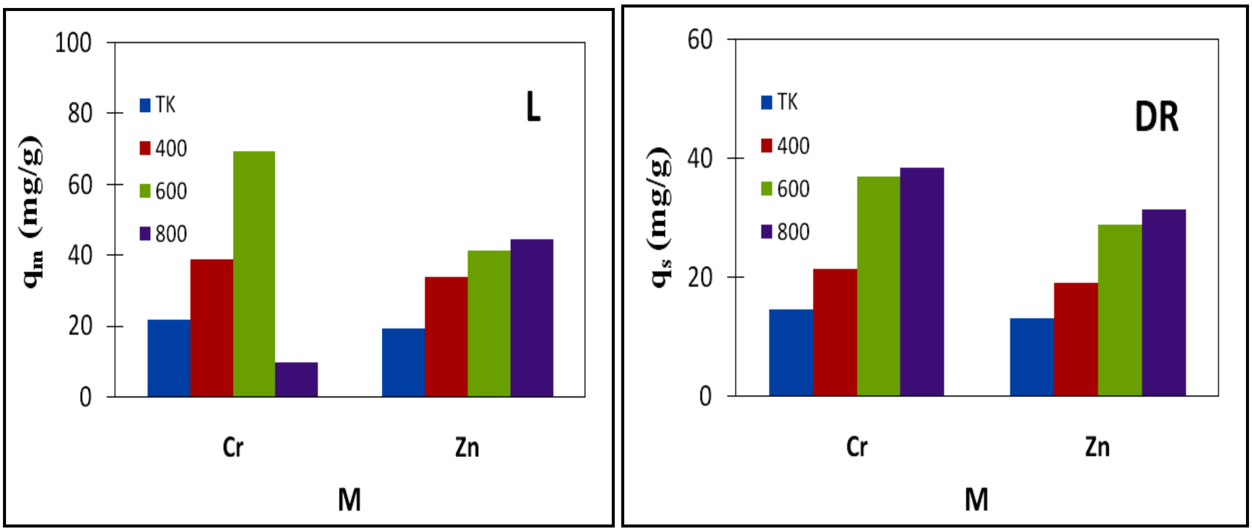

Figure 6. Paracetamol adsorption capacities of biochar – MCl_n composites (M = Cr, Zn) before and after _calcination at various temperatures calculated using Langmuir model (L) and Dubinin – Radushkevich (DR)

Figure 6 shows that based on Langmuir model, the highest capacities are achieved by both composites calcined at 600 and 800 ^oC, respectively. In other side, by using Dubinin – Radushkevic model, both composites give relatively same pattern of curves with the similar highest capacities obtained by the composites calcined at 600 and 800 ^oC, respectively.

Conclusion

The composites of biochar – $ZnCl_2$ and biochar – $CrCl_3$ have been synthesized and calcined at various temperatures. Based on X-ray diffraction, both composites formed biochar – ZnO and biochar – Cr_2O_3 at 800 ^oC, repectively. Characterization using FTIR spectrophotometry indicated the significant change of spectra at 600 ^oC. Adsorption test of paracetamol shows that temperature gave effect on parameters of adsorption. The highest capacity was achieved by biochar – $CrCl_3$ calcined at 600 ^oC, with adsorption capacity of 69.44 mg/g (based on Langmuir model), adsorption energy of 912.57 J/mol (physical adsorption), R_L value of 0.17 and n value of 1.80 (favorable adsorption).

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References

1. Ernsting, A., Biochar – A Climate Smart Solution? Climate Change and Agriculture, Report, Bischöfl iches Hilfswerk Misereor e.V., 2011, 1: 1-20.
2. Uchimiya, Lima, IM., Klasson, KT., Wartelle, L.H., Contaminant immobilization and nutrient release by biochar soil amendment: Roles of natural organic matter Minori Chemosphere, 2010, 80: 935–940.
3. Jiang, J., Progress of Biochar Supercapacitors , 1st Midwest Biochar Conference , Illionis Sustainable Technology Center, 2013, June 14.
4. Agarwal, M., Tardio, J., and Mohan, S.V., Pyrolysis Biochar from Cellulosic Municipal Solid Waste as Adsorbent for Azo Dye Removal: Equilibrium Isotherms and Kinetics Analysis, International Journal of Environmental Science and Development, 2015, 6 (1): 67-72.

5. Domingues, M.T., Bueno, C.C., Watanabe, C.H., Fraceto, L.F., Joyola-licea, J.C., Crowley, D., Rosa, A., Polymeric alginate microspheres containing biochar to immobilize phosphate ions, Chemical Engineering Transactions, 2014, 37:109-114.
6. 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.
7. Ismadji, S., Tong, D.S., Edi, F., Soetaredjo, Ayucitra, A., Yu, W.H., Zhou, C.H., Bentonite-hydrochar composite for removal of ammonium from Koi fish tank, Applied Clay Science, 2015, 114: 467–475.
8. 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 Environmental Earth Science, 2014, 71: 5195–5205.
9. 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 and pH Environmental Pollution, 2013, 178 : 264-270.
10. Atkinson, D.J., Fortunato, M.E., Dastgheib, S.A., Rostam-Abadi, M., Rood, M.J., K.S., Suslick, Synthesis and Characterization of Iron-impregnated Porous Carbon Spheres Prepared by Ultrasonic Spray Pyrolysis, Carbon, 2011, 49: 587 –598.
11. Zhu, J., Wei, S., Chen, M., Gu , H., Rapole, S.B., Pallavkar, S., Ho, T.C., Hopper , J., Guo , Z., Magnetic nanocomposites for environmental remediation, Advanced Powder Technology, 2013. 24: 459–467
12. 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 [Relevant].
13. Srivastava, A.K., Saxena, A., Singh, B., and Srivas, S.K., Development and Evaluation of Impregnated Carbon, Systems Against Iodine Vapours, Carbon Letter, 2007, 8 (4): 274-279.
14. Abbas, A., Abussaud, B.A., Ihsanullah, Al-Baghli,N.A.H., Khraisheh, M., and Atieh, M.A., Benzene Removal by Iron Oxide Nanoparticles Decorated Carbon Nanotubes, Journal of Nanomaterials, 2016: 1-10.
15. Mbadcam, J.K., Ngomo, A.M., Tcheka, C., Rahman, A.N., Djoyo, A.S., and Kouotou, D., Batch Equilibrium Adsorption of Cyanides from Aqueous Solution onto Copper- and Nickel-impregnated Powder Activated Carbon and Clay, Journal of Environmental Protection Science, 2009, 3: 53 – 57.
16. Plakas K.V. and Karabelas A.J., A Study on Heterogeneous Fenton Regeneration of Powdered Activated Carbon Impregnated with Iron Oxide Nanoparticles, Global NEST Journal, 2016, 18: 1-10.
17. Halász, L., Vincze, A., Solymosi, J., Use of The Microwave Impregnation of Active Carbon, Aarms Technology, 2008, 7(3): 533–550.
18. Moosavi, E., Dastgheib, S., and Karimzadeh, R., Adsorption of Thiophenic Compounds from Model Diesel Fuel Using Copper and Nickel Impregnated Activated Carbons, Energies, 2012, 5: 4233-4250.
19. Lua, A.C and 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, 2005, 290: 505–513.
20. Praba, L.K., Jayashree M., Banu, B.K., Kurian, G.A., Green and Chemically Synthesized Copper Oxide Nanoparticles-A Preliminary Research Towards Its Toxic Behavior, International Journal of Pharmacy and Pharmaceutical Sciences, 2015, l7 (1): 154-160.
21. Li, D., Tian, Y., Qiao, Y., Forming Active Carbon Monoliths from H_3PO_4 – loaded Sawdust with Addition of Peanut Shell Char, BioResources , 2014, 9(3): 4981-4992.
22. Moreno-Castilla , C., Adsorption of Organic Molecules from Aqueous Solution on Carbon Materials, Carbon, 2004, 42: 83–94.
23. Lowell, S., and Shields, J.E., Powder Surface Area and Porosity, 2nd ed., Chapman and Hall Ltd, New York, 2004, 10.
24. Hamid, S.B.A., Chowdhury, Z.Z., and Zain, S.M., Base Catalytic Approach: A Promising Technique for the Activation of Biochar for Equilibrium Sorption Studies of Copper, Cu(II) Ions in Single Solute System, Materials, 2014, 7: 2815-2832.
25. 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

26. **.** Kyzioł-Komosińska, J., Rosik-Dulewska, C., Franus, M., Antoszczyszyn-Szpicka, P., Czupioł, J., Krzyżewska, I., Sorption Capacities of Natural and Synthetic Zeolites for Cu(II) Ions, Polish Journal of Environmental Study, 2015, 24 (3): 1111-1123.
27. 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.
28. Mohammed, R.R., Decolorisation of Biologically Treated Palm Oil Mill Effluent (POME) Using Adsorption Technique, International Refereed Journal of Engineering and Science, 2013, 2(2): 01-11.
29. Igwe, J.C., Abia, A.A., Adsorption isotherm studies of Cd (II), Pb (II) and Zn (II) ions bioremediation from aqueous solution using unmodified and EDTA-modified maize cob, Ecletica Químico, 2007, 32(1): 33-42.
30. Ismail, M.G.B.H., Weng, C.N., Freundlich Isotherm Equilibrium Equastions in Determining Effectiveness a Low Cost Absorbent to Heavy Metal Removal In Wastewater (Leachate) At Teluk Kitang Landfill, Pengkalan Chepa, Kelantan, Malaysia, Journal of Geography and Earth Science, 2013, 1(1): 01-08.
31. 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.
32. 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.

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