Surface properties characterization of local *Eichornia crassipes* biosorbent

Cite as: AIP Conference Proceedings **2120**, 050018 (2019); https://doi.org/10.1063/1.5115694
Published Online: 03 July 2019

Himmatul Barroroh, Faris April Liansah, and Tri Kustono Adi

Surface Properties Characterization of Local *Eichornia crassipes* Biosorbent

Himmatul Barroroh[1, a)], Faris April Liansah[1, b)] and Tri Kustono Adi[1, c)]

[1]*Chemistry Department, Faculty of Science and Technology, Universitas Islam Negeri Maulana Malik Ibrahim Jl. Gajayana No.50 Malang, East of Java, Indonesia.*

[a)]Corresponding author: himmatul.b@kim.uin-malang.ac.id
b)ayizchemy@gmail.com
c)tk.adi@kim.uin-malang.ac.id

Abstract. *Eichornia crassipes* is potentially used as biosorbent of high metal. There are still incomplete data about the surface properties of local *Eichornia crassipes* biomass. The objective of this research is to obtain surface acidity, specific surface area, and pore structure of *Eichornia crassipes* biosorbent. *Eichornia crassipes* plant obtains form Selorejo belly Ngantang District area of Malang, East Java, Indonesia. Samples characterized were root, stem and leaf part. Surface acidity characterization was carried out on unwashed and washed samples by variation of HCl. Surface acidity was determined by acid-base titration, the specific surface area was measured by methylene blue and stereological analysis method and pore structure were analyzed by optical and SEM. The results showed that surface acidity of unwashed biosorbent on the root, stem, and leaf was small compared to surface acidity of washed biosorbent. The specific surface area of root, stem and leaf measured by methylene blue method seemed alike. Stereological analysis of specific surface area showed a more varying number. Pore structure described by SEM for root was in the form of a round hole, trilateral and spasmodic, whereas the stem pores were resembling to a piece of broken pipe while leaf pores were a coral stone-like.

INTRODUCTION

Eichornia crassipes is not a weed because *Eichornia crassipes* has millions of potential which is still explored yet. Nowadays, *Eichornia crassipes* was developed as a biomass sorbent, fiber, phytoremediation, hydrochar and biochar. This biomass were used to adsorb and treat metal pollutant such as Cd, Cr, Pb, Cu, Zn, Co, Ni, Se, Cs, As and Hg, as well as dyes, small organic molecules, fluoride [1–6]. Those advance development of *Eichornia crassipes* biomass form is based on natural characteristics of plant properties self, ultimately on its surface properties for sorbent aplication. Optimal material engineering only can achieve by knowing the precise natural characteristic.

Research about the surface properties characterization of *Eichornia crassipes*absorbenthas been done by several researchers [7-8]. There is some variation of *Eichornia crassipes* biosorbent surface properties obtained from different locations. Certainly, it is important to know the natural surface properties of each plant originally grow in different areas. Until now still no deep information about characterization the surface properties of local *Eichornia crassipes* [9]. This investigation reports surface properties of local *Eichornia crassipes* absorbent to obtain from Selorejo belly Ngantang District area of Malang, East Java, Indonesia. The research collects information related to surface acidity, specific surface area, the biomass solid texture and pore and specific surface area uses stereological analysis of SEM data.

International Conference on Biology and Applied Science (ICOBAS)
AIP Conf. Proc. 2120, 050018-1–050018-7; https://doi.org/10.1063/1.5115694
Published by AIP Publishing. 978-0-7354-1860-8/$30.00

EXPERIMENTAL DETAILS

Equipment and Materials

The equipment of this research is some glasses, mortar, the sieve of 120-150 mesh, magnetic stirrer, hot plate, analytical scale, pH meter, suction ball, shaker, calorimetry instrumentPhywe Systeme GmbH & Co. KG. D-37070 Gottingen, Du Nouy instrument of Phywe Systeme GmbH & Co. KG. D-37070 Gottingen, UV-Vis spectrophotometer Varian, optical microscopy of Olympus SMZ 1500 and Nikon CX 31, and Scanning Electron Microscopy (SEM) of FEI Type: Inspect-S50.

The material of this research is *Eichornia crassipes* from Selorejo bellyNgantang District area of Malang, East Java, Indonesia, methylene blue p.a., NaOH p.a., HCl p.a. by E-Merck, aquadest, and cube ice made in a laboratory freezer.

Preparation of Sample

The sample is *Eichornia crassipes*, which consist of root, stem and leaf. All samples are rinsed in water, then separated and dried uses the oven on 90 °C to reach constant weight. The sample is cut and crushed until smooth and then sieved on 100-250 mesh.

Determination of Root, Stem and Leaf of *Eichornia crassipes* Biomass Surface Acidity uses Acid-Base Titration Method.

Surface acidity was identified for an unwashed sample and washed sample by 0.005 M, 0.01 M, 0.05 M, 0.1 M, 0.5 M, and 1 M of HCl. Erlenmeyer of 100 mL is filled with 0.2 g of sample, then 25 mL of NaOH 1 M is added. The mixture was stirred using a magnetic stirrer for 15 min and filtered by filter paper. Blanco prepared by the same steps with no sample. Each filtrate are added by 2-3 drops of phenolphthalein indicator and then titrated by HCl 1 M until color changing occurs. This procedure was performed for root, stem and leaf, performed in triplicate. Surface acidity is calculated using the equation below:

$$K\ al = \frac{\text{mmol of NaOH}^{1st} - \text{mmol NaOH}^{free}}{\text{Weight of Sample}} \quad (1)$$

Determination of Specific Surface Area of Root, Stem, and Leaf of *Eichornia crassipes* Biomass uses Methylene Blue Method

Determination of the maximum wavelength used 5 ppm of methylene blue solution in 20.0 mL. Then the absorbance is measured on 500-700 nm use UV-Vis spectrophotometer. The standard curve of methylene blue used the concentration of 2, 4, 6, 8, 10 ppm.

Determination of biomass specific surface area performed by varying adsorption contact time. A biomass sample of 0.1 g adds into 100 ppm of 20 mL of methylene blue solution, shake on 120 rpm in various contact times of 5, 10, 15, 20, 25, 30, 35, 40 min. The solutions were then filtered and the absorbance measured using UV-Vis spectrophotometer. The mass of adsorbed adsorbate (mg/g) was calculated using the Langmuir equation:

$$Xm = \frac{(C_0 - C_e)V}{m} \quad (2)$$

Where Xm = Mass of adsorbed adsorbate (mg/g); C_0= Initial dye concentration of liquid phase (mg/L), C_e= Liquid phase dye concentration at equilibrium (mg/L), V= Volume of dye solution (L) and m= Mass of adsorbent (g).

The specific surface area was calculated by:

$$S = \frac{Xm.N.a}{Mr} \quad (3)$$

Where S = Spesific surface area (m^2/g), N= Avogadro's number (6.022.1023 mol^{-1}), Xm= Mass of adsorbate (mg/g), a= Closing wide of methylene blue (197.10-20 m^2) and Mr= Molecule mass of methylene blue (320.5 g/mol).

Determination of Biomass Solid Texture by Optical Microscopy

Determination of solid texture is determined by Optical Microscopy, those are Olympus CX 31 and Nikon SMZ 1500. A spatula of the sample was placed on object glass and close by object glass casing then observe by microscope. Magnification performed on 100× by Olympus CX 31 and 120× by Nikon SMZ 1500. Then the picture analyzed descriptively.

Determination of Biomass Pore Structure uses Scanning Electron Microscopy (SEM)

A few samples of *Eichornia crassipes* biomass were placed in the sample holder. Observation uses SEM with a magnification of 500-30,000×. Pore structure was observed by SEM figure descriptively by average radius value. To determine the pore average radius, the average diameter calculated uses this equation:

$$\Sigma = \frac{TotalNumberof\lambda}{n} \quad (4)$$

The average of the pore is determined by:

$$r_{average} = \frac{\Sigma}{2} \quad (5)$$

Where Σ= Average pore (nm), λ = Pore diameter (nm), r = Pore radius (nm) and n = Number of lines.

The specific surface area was determined using stereological analysis method. The protocol is included to measure the pore diameter in the SEM picture, choose these as the test line λ. This line is measured using a ruler manually, then place the test line randomly on several pores picture. A number of times of the test line λ which is in the pore is donated as T_p, whereas the number of times of the test line which is crossed the pore is donated as X_{pm}. E is the porosity value of biomass, then use this equation to determine the specific surface area (Σ):

$$\Sigma = 4\ \varepsilon\ Xpm\ \lambda^{-1}\ Tp^{-1} \quad (6)$$

Then the result of the specific surface area of methylene blue was compared to the stereological analysis one and then explained descriptively.

RESULT AND DISCUSSION

Surface Acidity

Eichornia crassipes biomass has some surface, functional groups, Infrared spectra analysis has been found O-H, v_{as} CH_2,C=O, C-H, and C-O as the functional groups [9]. The surface acidity of biosorbent is caused by proton dissociation from hydroxyl groups (OH) on biosorbent.

Table 1 showed that the highest surface acidity of unwashed biomass by HCl is on leaf sample and the lowest surface acidity is on the root one. The differences of surface acidity can be detected by a number of metals which are bonded to an active group. The more metals are bonded to an active group, the more active sites are capped by metals causing surface acidity decrease. Conversely, the fewer metals are bonded to active groups, the less active sites are capped by metals, causing an increase in surface acidity. To increase the surface acidity, need to perform an activation procedure with an acid activator such as washing by HCl.

TABLE1. Surface Acidity of Eichornia crassipes biomass

No	HCl Concentration (M)	Surface Acidity (mmol/g)			Annotation
		Root	Stem	Leaf	
1	0	5.497	7.831	9.160	Unwashed
2	0.005	33.932	40.78	42.920	
3	0.01	33	44.768	43.967	
4	0.05	33.949	45.448	44.224	
5	0.1	35.264	43.328	46.080	
6	0.5	34.448	42.607	41.294	
7	1	33.983	42.421	47.624	

The activation procedure is to obtain better chemical and physical properties such as surface acidity. Before activation, it finds a little active group on biomass as confirmed by the little surface acidity number before activation. Acid activation makes higher biosorption capacity by acquiring the change of metal cations on biosorbent with H^+ cations from HCl. Acid activation increases active group ability to bond the high number of metals. Acid is used to soluble high metal cap on biosorbent and opens the pores, therefore the biosorption capacity will increase [10]. Generally, the root has less surface acidity compare to stem, and the highest is leaf surface acidity. Activation by HCl increases the surface acidity about five times. It seems no significant surface acidity differences between HCl concentration variation used to activate.

Determination of *Eichornia crassipes* Biomass Specific Surface Area of Methylene Blue Method

The specific surface area of *Eichornia crassipes* biomass is shown in Table 2. It seems no differences on specific surface area values between the three parts of the biomass.

TABLE 2. Specific surface area of *Eichornia crassipesbiomass*

Sample	Optimum Interaction Time (min)	Specific Surface Area (m^2/g)
Root	20	73.609
Stem	30	73.597
Leaf	20	73.609

Based on the result, it can be analyzed that different value of optimum time is caused by the natural structure of the sample, which stem contains of fiber [11] then need a more time to reach the optimum interaction time. Besides, it is related to methylene blue molecular size, which is adsorbed on the pore. Methylene blue is a foursquare shape molecule with volume dimension about 17.0 ×7.6 × 3.25 Å [12]. It is predicted that methylene blue located at the suits pore with its size, and pore volume located on the same size.

Eichornia crassipes has cellulose, which contains a hydroxyl group (OH). Hydroxyl has an H atom that able to interact with atoms on methylene blue. The hydrogen bond is occurring to a hydrogen atom and it is bonded to two or more other atoms which have a high electronegativity like N, O and F atom. Based on the structure, methylene blue contains H, C, N, S and Cl atoms, therefore the hydrogen bond may occur between H on cellulose and N on methylene blue. The hydrogen and nitrogen atoms have an electronegativity value of 2.1 and 3.0 respectively

Determination of *Eichornia crassipes* Biomass Solid Structure by Optical Microscopy

Biomass solid structure is determined by optical microscopy. It Uses Nikon SMZ 1500 and Olympus CX 31. Olympus CX 31 has a higher solution than Nikon SMZ 1500 because it has maximum magnification up to 1000× and Nikon SMZ 1500 up to 400× magnification.

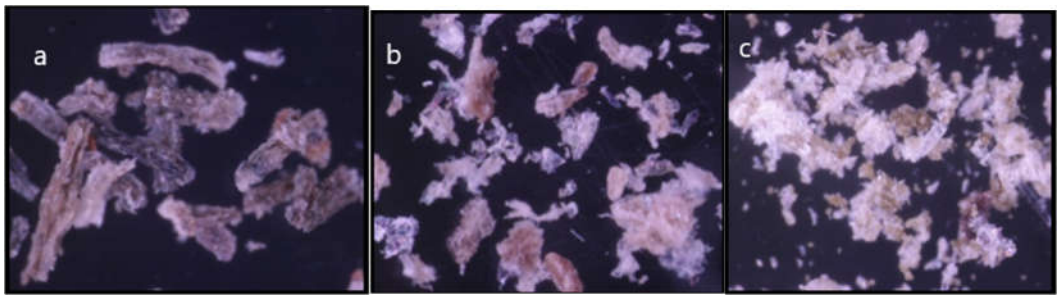

FIGURE 1. Nikon SMZ Optical microscopy pictures of (a) root powder, (b) stem powder and (c) leaf powder with a magnification of 120×

According to Fig. 1, the root of *Eichornia crassipes* mostly has equal shape, long and which is like crystalline. The stem has variation in shape, there are square, trilateral, and another shape which was like crystal. The crystal phase of the biomass fiber as confirmed by Asrofi *et al.* [13]. The leaf has a different shape, which is like something clot and crystal. From this observation, the pore structure cannot be observed.

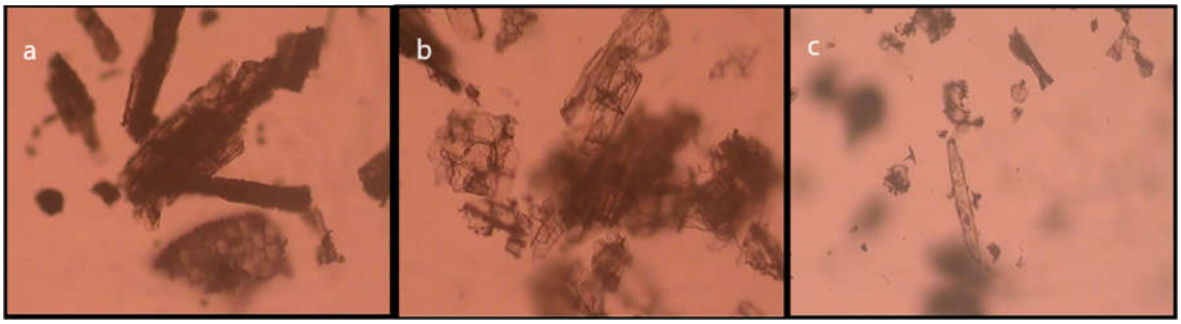

FIGURE2. Olympus CX 31 Optical microscopy picture of (a) root powder, (b) stem powder and (c) leaf powder with a magnification of 100×

Based on Fig. 2, the morphology of biomass cannot be observed clearly by Olympus CX 31. The root has equal shape, it is long and like a sponge. The stem has the unequal shape, long and hexagonal, besides, it looks like cube ice. The leaf has unequal shape, long and small circle. The best figure is shown by Nikon SMZ 1500, but the best quality is shown on Olympus CX 31 because it has higher resolution than Nikon SMZ 1500.

Determination of *Eichornia crassipes* Biomass Pore Structure by Scanning Electron Microscopy (SEM)

SEM is electron microscopy, which uses an electron beam to capture a surface picture of solid materials. The SEM principal procedure is to shoot a surface by a high energy electron. SEM picture clearly describes the structure of biomass solid pore. Fig. 3. give some information about the pore structure of *Eichornia crassipes* biomass. The root is like a hole, trilateral, and spasmodically. The stem looks like a piece of the broken pipe and the leaf looks like a coral stone.

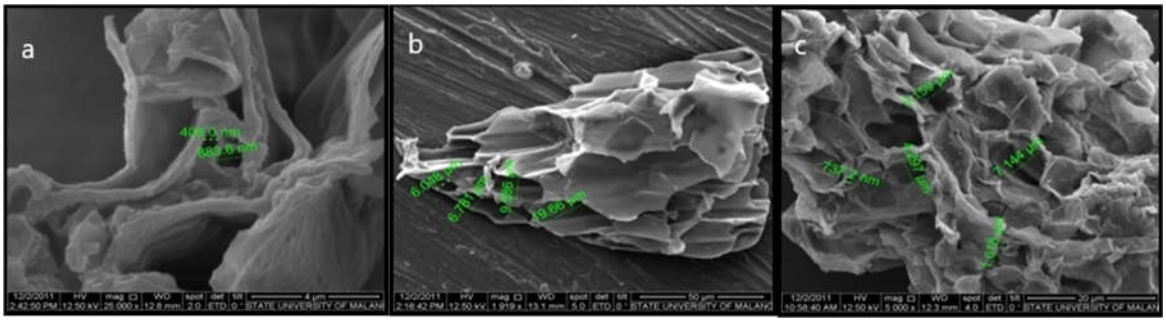

FIGURE 3. SEM picture of (a) root powder with magnification 25,000×, (b) stem powder with magnification 1,919×, (c) leaf powder with magnification 5,000×.

The average pore radius of each sample was calculated based on SEM data showed in Table 3. According to the SEM picture, the pore size is on the thousands nanometer scale. Based on data, it can be concluded that the pore of *Eichornia crassipes* was categorized as macropore with diameter more than 50 nm. These findings are rather different compared to Asrofi's findings that the diameter and length of nanocellulose WHF were 15.61 and 147.4 nm, respectively [13]. This can be thought that the differences caused by the different treatment for both samples [14]. Three parts of root, stem and leaf have little differences on the average pore radius, but the leaf still has the highest average pore radius value.

TABLE 3. The average pore radius of *Eichornia crassipes* biomass

No	Sample	The average pore (nm)
1	Root	2875.56
2	Stem	3441.9
3	Leaf	3500

Determination of *Eichornia crassipes* Biomass Specific Surface Area

Determination of specific surface area using 5 hits of line test λ. The length of line test picks from pore radius that exists in the SEM pictures which represents the radius variation. The length of the line test range from 883.6 nm until 20.129 μm. Table 4 showed that specific surface area value which is determined by stereological analysis method has variation in value. The root part has more variations of specific surface area value, means that is found many variations on surface topology and more variation on the opportunities of adsorption mode and adsorption force. Stem and leaf have a relatively uniform specific surface area, generally, stem has a less specific surface area compared to leaf. The specific surface area which is determined by the methylene blue method has relatively equal value for the three parts of the biomass body.

TABLE 4. Comparison of specific surface area between stereological analysis and methylene blue method

Sample	Specific Surface Area (m2/g)					
	Stereological Analysis				Methylene Blue	
Root	150	24.76	320	1640	230	73.609
Stem	2.319	6.276	0.7898	7.224	4.279	73.597
Leaf	9.921	8.228	3.456	2.314	9.125	73.609

Based on the result of the stereological analysis, the root has the highest specific surface area than the stem and leaf. The specific surface area of stem and leaf is confirmed by S_{BET} data for biochar [15]. It shows that the pore size is relatively small as confirm by pore radius data. The higher specific surface area, leads to a higher adsorption capacity. This fact is not confirmed linearly by surface acidity data, where the root has lowest surface acidity compared to stem and leaf. It seems that surface acidity not only determined by pore size and specific surface area value but more likely influenced by the natural properties of the functional group constituted the surface.

SUMMARY

The results show that the surface acidity of unwashed biosorbent on the root, stem, and leaf are small compared to surface acidity of washed biosorbent. The specific surface area value of root, stem and leaf by the methylene blue method seems alike. Stereological analysis of specific surface area shows more vary number. We have more detail topological information of surface by stereological analysis on SEM data. Pore structure described by SEM for root is in the form of a round hole, trilateral and spasmodic, whereas the stem pore is resemble pieces of the broken pipe while leaf pores are a coral stone alike.

REFERENCES

1. J. B. Neris, F. H. M. Luzardo, P. F. Santos, O. N. de Almeida and F. G. Velasco, J. Environ. Chem. Eng. **7**, 102885 (2019).
2. A. E. Ramírez and Instituto Politécnico Nacional, Rev. Mex. Ing. Quím. **17**, 1121 (2018).
3. R. H. Mahmoud and A. H. M. Hamza, in *Phytoremediation*, edited by A.A. Ansari, S. S. Gill, R. Gill, G. R. Lanza, and L. Newman (Springer International Publishing, Cham, 2017), pp. 405–422.
4. M. K. Mahapatra and A. Kumar **7**, (2018).
5. S. Manna, D. Roy, B. Adhikari, S. Thomas and P. Das, Environ. Prog. Sustain. **37**, 1560 (2018).
6. Q. Li, L. Tang, J. Hu, M. Jiang, X. Shi, T. Zhang, Y. Li and X. Pan, R. Soc. Open Sci. **5**, 180966 (2018).
7. E. T. Romero-Guzmán, L. R. Reyes-Gutiérrez, M. J. Marín-Allende, Z. I. González-Acevedo and M. T. Olguín-Gutiérrez, Chem. Ecol. **29**, 459 (2013).
8. M. M. Netai, K. Jameson and F. Z. Mark, Afr. J. Biotechnol. **15**, 897 (2016).
9. F. Rahmawati, P. Pranoto and N. I. Aryunani, Alchemy **2**, 10 (2003).

10. R. K. Gautam, A. Mudhoo, G. Lofrano and M. C. Chattopadhyaya, J. Environ. Chem. Eng. **2**, 239 (2014).
11. S. Punitha, K. Sangeetha and M. Bhuvaneshwari, Int. J. Adv. Res. **3**, 290 (2015).
12. P. T. Hang and G. W. Brindley, Clays Clay Miner **18**, 203 (1970).
13. M. Asrofi, H. Abral, A. Kasim and A. Pratoto, J. Metastable Nanocrystalline Mater. (2017).
14. M. T. Sundari and A. Ramesh, Carbohydr. Polym. **87**, 1701 (2012).
15. F. Li, K. Shen, X. Long, J. Wen, X. Xie, X. Zeng, Y. Liang, Y. Wei, Z. Lin, W. Huang and R. Zhong, PLOS ONE **11**, e0148132 (2016).