

The influence of activating agents on the performance of rice husk-based carbon for sodium lauryl sulfate and chrome (Cr) metal adsorptions

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Abstract. This research aims to study the influence of activating agents to produce rice husk based-carbon with high adsorption capacity and efficiency for either hazardous organic molecules or heavy metals which are unfriendly for the environment. Firstly, rice husk was burned by pyrolysis at different temperatures to produce rice husk-based carbon. To improve its ability as an adsorbent, carbon was treated with activating agents, namely, H_3PO_4 and KOH at room and high temperature (420°C). The performance of carbon was then tested by contacting it with surfactant (SLS). Finally, the surfactant-modified active carbon was applied for chrome metal removal. The result shows that activation of carbon using phosphate acid (H_3PO_4) was more effective than potassium hydroxide (KOH) conducted at high temperature to adsorb sodium lauryl sulfate (SLS) and chrome metal with the adsorption capacity 1.50 mgg^{-1} and 0.375 mgg^{-1} , respectively.

1. Introduction

Rice husk is a by-product of rice milling. It is normally used for red rock production as a fuel, for cooking and sometimes it is thrown away as waste resulting in pollution to the environment. However, recently, rice husk has been applied as an adsorbent in the form of carbon for environmental treatments such as treatment of waste water caused by hazardous heavy metals [1, 2] and dye molecules [3]. To produce carbon, rice husk must be burned at a certain temperature. Furthermore, an abundant carbon can be generated in very limited oxygen condition since if oxygen is excess, carbon will not be produced perfectly, otherwise carbon monoxide and water are produced; this is called perfect combustion. After getting carbon, carbon is treated with activating agents to obtain activated carbon with the aim to produce carbon with high performance as an adsorbent [4]. The activating agents used for carbon activation are H_3PO_4 , ZnCl_2 , K_2CO_3 , KOH , etc. [4, 5]. The use of activating agents is to eliminate the impurities such as alcohol, acids, aldehyde, etc. contained in the pores so that the pores of carbon become opened and the diameter of the pores and surface area of adsorbent increase. In addition to activation of carbon using activating agents, the performance of carbon can be improved by modifying the surface with the surfactant. This modification changes the surface properties of the activated carbon becoming more hydrophilic so that increasing its wettability and adsorption efficiency [6]. Therefore, this present work aims to investigate the influence of different activating agents to the performance of carbon as adsorbent for surfactant and chrome metal adsorptions.

2. Experimental Methods

2.1 Materials

Rice husk obtained from Semarang, Indonesia, phosphoric acid, potassium hydroxide, sodium lauryl sulfate (SLS) powder, sodium hydroxide, sulfuric acid, aquadest, chloroform, phenolphthalein,



methylene blue, monosodium phosphate monohydrate, and potassium dichromate. All the reagents were of analytical grade purchased from Sigma Aldrich.

2.2 Rice Husk Carbonization

Rice husk-based carbon was produced by several steps. Firstly, rice husk was washed using water and then dried under the sun. Subsequently, the dried rice husk had been burned by pyrolysis at different temperature 300, 350 and 400 °C for 10 minutes. The obtained carbon was then sifted using the top ending 100 mesh sieve.

2.3 Carbon Activation

20 gram rice husk-based carbon had been contacted with H₃PO₄ and KOH at different concentration for 1.5 hours at room temperature. The concentration used in each activating agent was 30, 40, 50, 60 and 70% for H₃PO₄ and 40, 50, 60, 70, 80 % for KOH. After that, the mixture was filtered. The residue, activated carbon, was then washed with aquadest until constant pH was achieved. Furthermore, the activated carbon had been dried in an oven at 105 °C for 1 hour and then being smoothed using a mortar and sifted using 100 mesh sieve. The optimum concentration of activating agents indicated by high adsorption capacity for SLS adsorption was then used to activate carbon at high temperature (420 °C) for 1 hour.

2.4 Determination of the Adsorption Efficiency and Capacity of Activated Carbon

1 gram rice husk-based activated carbon had been contacted with 100 mL surfactant (SLS) 60 ppm for 1.5 hours. Subsequently, the mixture was filtered. The obtained filtrate was then treated using MBAS method [7] to separate surfactant (SLS) unabsorbed by activated carbon. Finally, the obtained surfactant was then analyzed using UV-Vis spectrophotometer.

2.5 Characterization of Activated Carbon

Characterization of activated carbon was conducted using FTIR (Prestige 21 Shimadzu), SEM (JEOL-JSM-6510LV) and SAA (Quantochromenove - AsiQwin 1200e) to identify the functional groups on activated carbon surface, morphology, pore size, pore volume, surface area, which are of important on the adsorption process.

2.6 Adsorption of Chrome (Cr) by Activated Carbon Adsorbing Surfactant (SLS)

1 gram activated carbon adsorbing surfactant had been contacted with 25 mL of 20 ppm potassium dichromate (as a model pollutant) for 4 hours. Then, the mixtures were filtered and the obtained filtrate was analyzed using AAS (Shimadzu AA-640IF) to calculate the concentration of chrome metal not adsorbed by activated carbon.

3. Results and Discussion

3.1 Carbonation of Rice Husk

Carbonization process aims to eliminate the components of volatile organic compounds so that it can form carbon which also has pores [4]. Carbonization of rice husk was carried out using pyrolysis method. Using this method, oxygen was conditioned very limited, so that the carbon generated was optimal. Carbon generated is also influenced by temperature applied during pyrolysis.

Based on Figure 1, it can be observed that by increasing the carbonization temperature during the pyrolysis, the color of the resulting carbon is a mixture between black and gray. The difference of carbon in color was caused by the ash content. The presence of ash resulted from the oxidation process of carbon from oxygen coming from burning of organic molecules in the carbonization process. The black carbon was achieved at 300 °C with the carbon content of 63.51%.



Figure 1. Carbon resulting from pyrolysis of rice husk at (a) 300 °C (b) 350 °C (c) 400 °C

3.2 Carbon Activation using H_3PO_4 and KOH

It can be seen from Table 1 that the adsorption capacity of activated carbon in H_3PO_4 - and KOH-activated carbons (CA- H_3PO_4 and CA-KOH, respectively) changed insignificantly when the concentration of activating agents increased. Furthermore, in comparison to the adsorption capacity of both samples, H_3PO_4 is little more effective than KOH to produce activated carbon applied to adsorb SLS. We suggest that H_3PO_4 is more effective to open up the layer of the carbon structure even though it has been reported that KOH as an activating agent enables to generate mesoporous and microporous carbons [8].

Table 1. Adsorption capacity of carbon after being activated using different concentration of H_3PO_4 and KOH at room temperature

[H_3PO_4]	Adsorption capacity (mg g^{-1})	[KOH]	Adsorption capacity (mg g^{-1})
30%	1,496	40%	1.432
40%	1,499	50%	1.493
50%	1,494	60%	1.491
60%	1,498	70%	1.485
70%	1,486	80%	1.482

Phosphoric acid (H_3PO_4) is an activating agent to open the pores and enlarge the surface area of activated carbon so that the adsorption power will increase. H_3PO_4 removes impurities contained in the carbon [9] as a result of carbonization process of biomass (rice husk) such as ketones, alcohols, acids, aldehydes. Moreover, H_3PO_4 also helps to form a bridge that connects the fragments of biopolymers (layer of carbon structure) by forming phosphate bonds that make pores more open and enlarge surface area. Further we used 60% H_3PO_4 and 50% KOH to activate carbon at 420 °C.

Figure 2 shows that carbons activated using H_3PO_4 both at room temperature and high temperature have higher % adsorption efficiency than that of using KOH. It can be said that H_3PO_4 is more effective than KOH as an activating agent even though at 300 °C, KOH is more effective to activate carbon but the difference is insignificant.

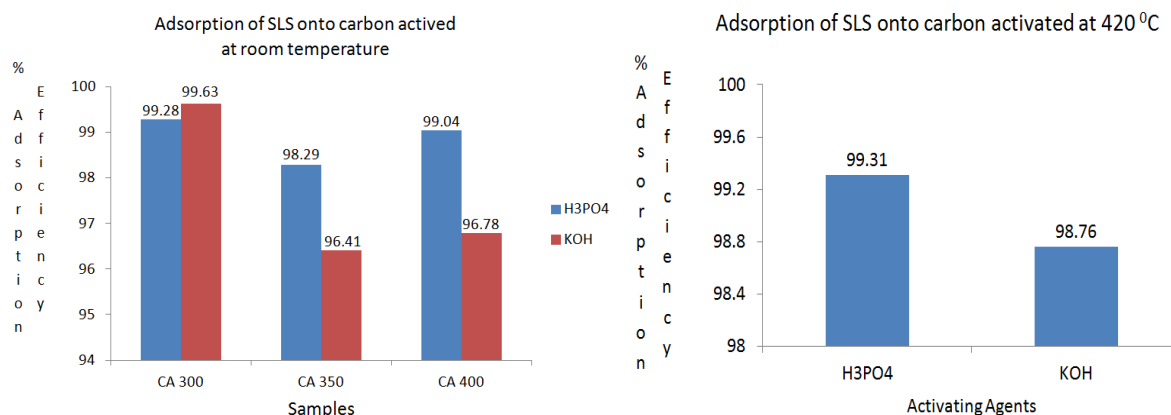


Figure 2. The adsorption of SLS surfactant onto carbon activated using H₃PO₄ and KOH at room temperature and high temperature (420 °C)

3.3 Characterization of Active Carbon and active carbon adsorbed SLS

As seen in figure 3, after activation using KOH (b), the vibration mode of –OH (3200-3800 cm⁻¹) [10] was higher than that of carbon. Si-O-Si vibration mode observed at 1097 cm⁻¹ [10] almost disappeared after treating using KOH (b). Vibration mode of Si-H was also observed at 800 cm⁻¹ [11]. The vibration mode at 1169-1173 cm⁻¹ observed in CA-H₃PO₄ attributed to P=O vibration [12]. After adsorption of SLS surfactant, there is no significant change in the FTIR spectra of both samples as seen in figure 4 except for Ca-H₃PO₄. The appearance of S=O vibration mode was observed at 1110-1182 cm⁻¹ [13]. It indicates that SLS has been well adsorbed on H₃PO₄-activated carbon.

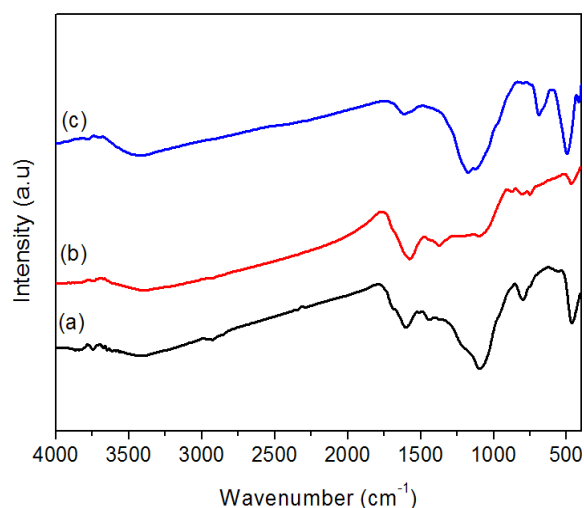


Figure 3. FTIR spectra of (a) carbon, (b) CA-KOH and (c) CA-H₃PO₄

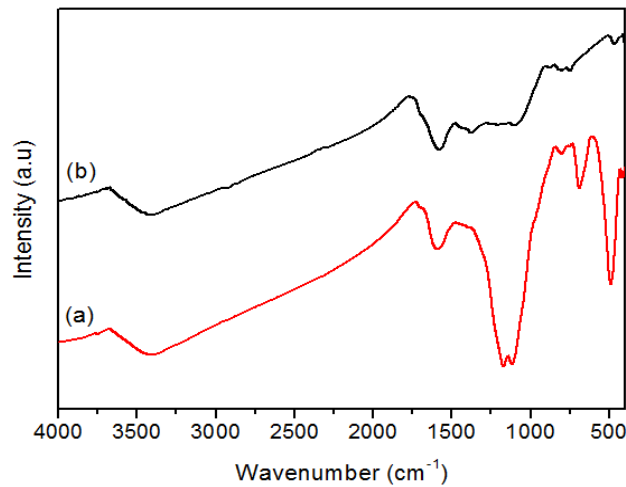


Figure 4. FTIR spectra of activated carbon adsorbed SLS coming from (a) CA-H₃PO₄ and (b) CA-KOH

SEM was applied to identify the morphology of resulting activated carbon. Because CA-H₃PO₄ gave better adsorption, SEM analysis was conducted for samples using H₃PO₄ as an activating agent. It can be seen in figure 5, before activation, carbon has heterogeneous pores (a) and after activation using H₃PO₄ at room temperature, the pores is more homogeneous and it looks brittle (b). After adsorption of SLS, the pores are still conserved. However, activation at high temperature made the carbon more rigid with the small pores below 1 μm .

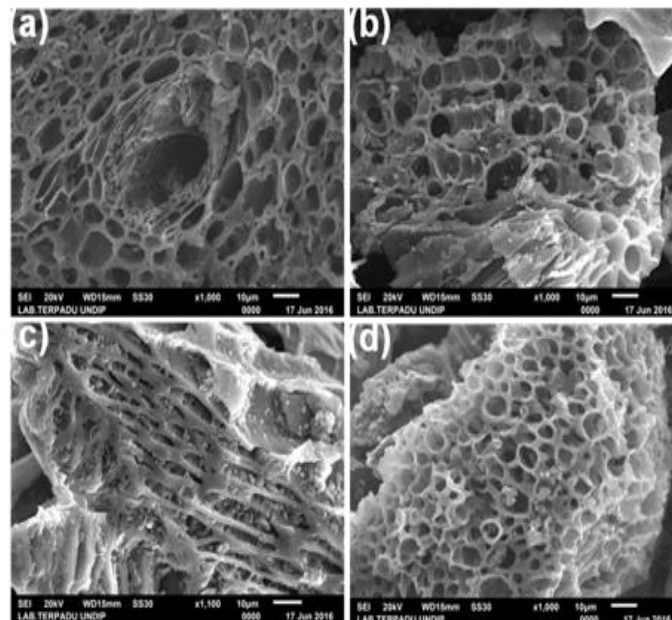


Figure 5. SEM images of (a) carbon, (b) activated carbon using H₃PO₄ at room temperature and high temperature and (d) H₃PO₄-activated carbon adsorbed SLS.

3.4 Adsorption of Cr^{2+} by Activated Carbon Adsorbing SLS

Carbons activated using both H_3PO_4 and KOH were then applied for synthetic chrome (Cr) waste metal removal with the aim to investigate the adsorption capacity of both samples. The result of Cr removal of both samples is presented in table 2. It can be seen that CA- H_3PO_4 modified with SLS adsorbed Cr (0.375 mgg^{-1}) higher than that of CA-KOH modified with SLS (0.113 mgg^{-1}). Therefore, it can be said that H_3PO_4 is more effective than KOH as an activating agent to produce surfactant-modified active carbon and to remove Cr as pollutant model.

The adsorption mechanism of ionic metals is generally due to exchange ions or electrostatic interaction on the hydrophilic surface of the adsorbent. The hydrophilic surface results from surfactant adsorbed on activated carbon surface so that the surface properties of activated carbon changes from hydrophobic into hydrophilic and becomes more negative. Consequently, the adsorption of Cr increases [6].

Table 2. Adsorption capacity of SMAC to adsorb Cr^{2+}

Activating Agent	Adsorption Capacity (mgg^{-1})
KOH	0,113
H_3PO_4	0,375

4. Conclusion

Carbon activated using H_3PO_4 is more effective to produce surfactant modified activated carbon than using KOH. Moreover, CA- H_3PO_4 adsorbing SLS is more effective for removal of Cr as pollutant model.

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References

- [1] Mehdinia S M, Khalilollah M, Tayyabeh R 2014 Rice husk silica adsorbent for removal of hexavalent chromium pollution from aquatic solutions *Iranica Journal of Energy & Environment* **5** 218-223
- [2] Ali I O, Mostafa H A, Salah M S, Karam S S 2011 Synthesis and characterization of ZSM-5 zeolite from rice husk ash and their adsorption of Pb^{2+} onto unmodified and surfactant modified zeolite *Separation and Purification Technology* **83** 38-44
- [3] Cheenmatchaya A, Kungwankunakorn S 2014 Preparation of activated carbon derived from rice husk by simple carbonization and chemical activation for using as gasoline adsorbent *International Journal of Environmental Science and Development* **5** 171-175.
- [4] Soltani N, Bahrami A, Pech-Canul M I & González L A 2015 Review on the physicochemical treatments of rice husk for production of advanced materials *Chemical Engineering Journal* **264** 899-935
- [5] Al-Latief D N, Arnelli and Astuti Y 2015 Synthesis of sodium lauryl sulfate (SLS)-modified activated carbon from risk husk for waste lead (Pb) removal *AIP Conference Proceedings* **1699** 060017
- [6] Agustinus E T S, Mursito A T, Sembiring H 2013 Peningkatan daya serap karbon aktif terhadap ion logam hexavalent chromium (CrVI) melalui modifikasi dengan cationic surfactant (ethylenediamine) *Jurnal Riset Geologi dan Pertambangan* **23** 15-26.
- [7] ASTM., Standart Test Method for Methylene Blue Active Substance, ASTM international, West Conshohocken, 2002

- [8] Utama S, Kristianto H, Andreas A 2016 Adsorpsi ion logam kromium (Cr (Vi)) menggunakan karbon aktif dari bahan baku kulit salak *Prosiding Seminar Nasional Teknik Kimia "Kujangan"*, ISSN 1693-4393 1-6
- [9] Yaman S 2004 Pyrolysis of biomass to produce fuels and chemical feedstocks *Energy Conversion and Management* **45** 651-671.
- [10] Lambert J B, Herbert F S, David A L, Graham R C, *Introduction to Organic Spectroscopy*, 1987 Macmillan Publ. New York
- [11] Nakbanpote W, Goodman B A, Thiravetyan P 2007 Copper adsorption on rice husk derived materials studied by EPR and FTIR *Colloid Surface A* **304** 7-13
- [12] Myglovets M, Poddubnaya O I, Sevastyanova O, Lindstrom M.E, Gawdzik B, Sobiesiak M, Tsyba M M, Sapsay V I, Klymchuk D O, Puziy A M 2014 Preparation of carbon adsorbents from lignosulfonate by phosphoric acid activation for the adsorption of metal ions *Carbon* **80** 771-783
- [13] Abidin A Z, Lukman O W, Christian 2014 Konversi sampah plastic styrofoam menjadi bahan pembersih sulfur light diesel oil *Jurnal Sains Materi Indonesia* **16** 25-31