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Preface to The Conference Proceedings

On behalf of the Scientific Committee, we would like to thank all participant of the 5th International Seminar on New Paradigm and Innovation on Natural Sciences and Its Application who already submitted their papers. We are very fortunate this year to begin our program with the keynote address from Iran, South Korea, Germany and Indonesia.

We are extremely grateful to all the reviewers for giving up their time so generously and providing constructive feedback to authors. Your hard work ensured that we maintained the high quality of work being presented.A note on the refereeing process, the work presented at this year's conference spans multiple disciplines, range from the area of fundamental research up to the area of applied research. The 5th ISNPINSA provides also a forum for starting researchers and PhD students by offering seminars and discussion groups.

Last but not least we would like to ask your apology for waiting this proceeding published. We highly appreciate your consistently to support us in finishing this proceeding.

Rully Rahadian

Scientific Committee Chair

Board of Reviewers

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Modification of Rice Husk-Based Activated Carbon using Sodium Lauryl Sulfat (SLS) for Lead (Pb) Ions Removal

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Abstract. A rice husk-based active carbon modified using SLS surfactant showed an increase on Pb ionic metal removal with the efficiency of 99.96%. Activated carbon is commonly applied as adsorben in waste water treatment, in particularly, waste water containing heavy metals and dye molecules. Even though it is commonly used, the adsorption efficiency of activated carbon to the heavy metal waste is still low. Therefore, in the present work, carbon from rice husk was modified using surfactant which further it is called surfactant modified active carbon (SMAC). Firstly, rice husk-based carbon was activated using 40% H_3PO_4 for 2, 6, 10, 14, 15 and 16 hours. The activated carbon was then modified by contacting it into SLS in different concentration 10, 20, 30, 40, 50, 60 and 70 ppm for 5 hours. Finally, the SMAC was then applied to remove Pb ionic metal. Moreover, several characterisation techniques were performed including FTIR, SEM, UV-Vis and AAS.

Keywords: activated carbon, surfactant-modified active carbon, adsorption, rice husk

Introduction

Rice husk is an abundant by-product of rice milling, and so far it is only used as fuel in red rocks production, cooking and sometimes thrown away as waste which causes pollution to the environment. Moreover, rice husk has also been applied as adsorbent for handling waste water caused by hazardous heavy metals [1, 2] dye molecules in the form of carbon and activated carbon [3]. Before being used as an adsorbent, rice husk is burned into carbon to poduce rice husk-based carbon. To improve the ability of rice husk-based carbon as an adsorbent, carbon is treated with activating agents such as H_3PO_4, $ZnCl_2$, K_2CO_3 etc. [4]. These activating agents are to eliminate the impurities contained in the pores so as to the pores of rice husk-based carbon become opened which result in increasing the diameter of the pores, pore volume and surface area of adsorbent. One of the activating agents used on the activation of carbon is H_3PO_4. This acid is commonly applied for activation of rice husk-based carbon since it has high thermal stability and covalent character used to open the pores of the carbon [5].

In addition to activation of carbon using activating agents, the adsorption efficiency and capacity of carbon can be improved by modification of the surface using surfactant (called SMAC). After modifying with surfactants, the surface of the activated carbon changes from hydrophobic to hydrophilic which also affects on the wettability and adsorption efficiency.[6] Surfactants applied to modify carbon surface can be either anionics or cationics; however, effect of surfactant types on the performance of adsorption activity of carbon depends on the adsorbates, for example, sodium lauryl sulfate (SLS) attached onto a coconut-based activated carbon surface gave high performance on cationic metals adsorption [7] compared to cetyl trimethylammonium bromide (CTAB). Another research conducted by Hao showed that activated-carbon modified with anionic surfactant greatly affected the efficiency of Cu^{2+} or Pb^{2+} removal [8]. Moreover, Mahmoud [9] reported that activated carbon modified with sodium lauryl sulfate improved the absorption of Ce (IV) nearly twice greater than that of activated carbon, from aqueous solution; activated carbon used was cotton stalks-based carbon.

Rice husk-based carbon has been well-known as adsorbent, the modification of activated carbon from this biomass using surfactant has not yet been reported. Therefore, this present work aims to produce activated carbon from rice husk modified with surfactants sodium lauryl sulfate (SLS) and then applied for Pb ions removal. Several factors influencing the performance of adsorbent were optimized such as contact time between activating agent and carbon during activation process and the concentration of surfactant being adsorbed to produce SMAC.

Experimental Methods

Materials. The materials used were rice husk purchased from Semarang, Central Java Indonesia, H_3PO_4 40% (v/v), NaOH, H_2SO_4, $NaH_2PO_4.1H_2O$, chloroform, soft filter paper, and $Pb(NO_3)_2$ solution, sodium lauryl sulfate (SLS) powder, phenolphthalein, methylene blue, aquadest. All the reagents were of analytical grade purchased from Merck Index, Indonesia.

Rice Husk Carbonization. Rice husk-based carbon was conducted by washing the rice husk and then drying in the sun. Subsequently, the dried rice husk had been burned in the closed chamber for 5 hours at ~250 ^{0}C. The obtained carbon was then sifted using the top ending 100 mesh sieve.

Activation of Carbon. 20 gram rice husk-based carbon had been contacted with H_3PO_4 40% (v/v) for 2, 6, 10, 14, 15 and 16 hours at room temperature. 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 oven (Isotemp 630F,) at 105°C for 1 hour and then being smoothed using a mortar and sifted with 100 mesh sieve [10].

Determination of the Activated Carbon Adsorption Efficiency. 1 gram rice husk-based activated carbon had been contacted with 100 mL surfactant in different concentration 10, 20, 30, 40, 50, 60 and 70 ppm for 5 hours. After that, the mixtures were filtered and the obtained filtrates were treated using MBAS method [11] to extract the unadsorbed surfactant. The obtained surfactant in every sample was then analyzed using UV-Vis spectrophotometer (spectroscopy UV-Vis Shimadzu UV-1201).

Characterisation of Activated Carbon. In order to determine the character of activated carbon including pore size, pore volume, surface area, morphology and functional groups on activated carbon surface which are of important on the adsorption process, several techniques were used including SAA (Quantochromenove - AsiQwin 1200e), SEM-EDS (JEOL-JSM-6510LV) and FTIR (Prestige 21 Shimadzu).

The adsorption of Pb^{2+}. 1 gram surfactant-modified activated carbon was put in a glass beaker and then 25 mL $Pb(NO_3)_2$ 20 ppm solution as model pollutant was added. The contact time between SMAC and $Pb(NO_3)_2$ was 4 hours. The sample was then filtered. The obtained filtrate was analyzed using *atomic absorption spectrophotometer* (AAS Shimadzu AA-640IF) to determine the Pb^{2+} unabsorbed by SMAC.

Results and Discussion

The Activation of Rice Husk Based-Carbon. Table 1 showed that the optimum contact time between activating agent and carbon during activation process was 15 hours with adsorption efficiency and capacity of 51.80 % and of 1.04 mg/g respectively. At short contact time, the activating agent was unable to open the pores of the carbon optimally. On the other hand, when the contact time was longer (16 hours), the adsorption efficiency decreased since the pores of carbon maximally were opened by the activating agent so that when the contact time increased the activating agent would be dissolved in the water.

The Adsorption of SLS Surfactant onto Activated Carbon. Table 2 presented the adsorption of SLS at different concentration onto carbon activated using H_3PO_4 40% for 15 hour as shown in Table 1. The higher the concentration of SLS, the higher the adsorption efficiency of activated carbon. It can be seen that the activated carbon modified with SLS 60 ppm has the highest efficiency with the amount of 75.95%; however, when the concentration of SLS higher than 60 ppm, the efficiency of adsorption become lower which could be because the pores of activated carbon was saturated by the surfactants so that the rest of surfactant was not adsorbed by the pores

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[12]. As a result, the unadsorbed surfactants would be dissolved in water. On the other hand, when the concentration of SLS was very low (10 ppm), the adsorption efficiency was also low since not all of activated carbon pores adsorbed SLS.

Table 1 The adsorption of SLS onto carbon activated using H_3PO_4 40% in different contact time

Contact Time (hours)	Concentration of SLS (ppm)	Concentration of SLS Adsorbed(ppm)	Adsorption Capacity (mg/g)	Adsorption Efficiency (%)
2	20	1,22	0,12	6,10
6	20	10,14	1,01	50,68
10	20	7,96	0,80	39,78
14	20	4,90	0,50	24,51
15	20	10,36	1,04	51,80
16	20	0,68	0,07	3,40

Table 2 The adsorption of SLS onto rice husk-based carbon activated using H_3PO_4 40% for 15 hour

Concentration of SLS (ppm)	Concentration of SLS Adsorbed (ppm)	Adsorption Efficiency (%)
10	0,93	4,30 %
20	10,36	51,80 %
30	14,11	47,03 %
40	28,55	71,32 %
50	37,67	75,34 %
60	45,575	75,95 %
70	52,545	75,06 %

Characterization of Activated Carbon. The material characterization was applied including FTIR and SEM-EDS for carbon activated using H_3PO_4 40% for 15 hour. As a comparison, the untreated carbon was also characterized.

Fourier Transform Infrared. The FTIR spectra of untreated carbon and activated carbon can be seen in Fig. 1. The vibration modes at 3600, 2367 and 1654 cm^{-1} in both spectra are attributed to –OH [13], -PH [13] and C=O[14], respectively. The difference of the two samples was demonstrated by the presence of peak at 1079 cm^{-1} in untreated carbon and 1066 cm^{-1} in activated carbon assigned to C-O stretching in alcohol, phenol or ester [15] and P-O-P vibration, respectively. The later vibration mode confirmed that interaction between H_3PO_4 and carbon after activation process occurred.

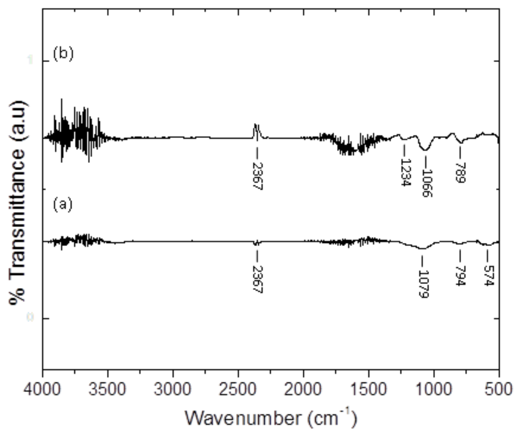


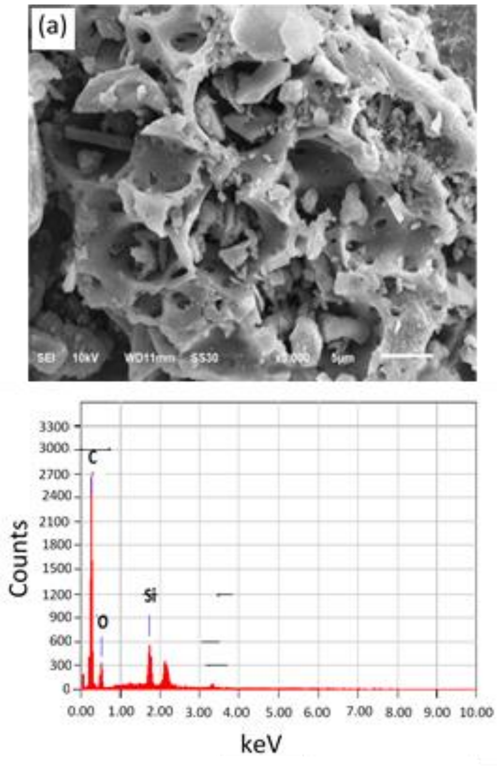
Figure 1 FTIR spectra of (a) carbon without activation and (b) carbon activated using H_3PO_4 40% with the contact time 15 hour

Scanning Electron Microscopy Electron Dispersive X-Ray (SEM-EDX). The SEM images of both untreated and activated carbons are shown in Fig. 2. It can be seen in Fig 2(a) that the morphology of untreated carbon showed brittle, irregular surface and hollow. Without activation using H_3PO_4 as activating agent, the carbon still contained impurities such as Si compounds that caused the irregular shape of the surface and less homogeneous. After activation using H_3PO_4 40 % with the contact time of 15 hour, the morphology of carbon changed (Fig. 2(c). The surface of this carbon was smoother and the pores were more pronounced and uncovered by the brittle components as observed in Fig. 2(a-above) which could be ashes. These changes indicated that the activation process using H_3PO_4 enabled removing impurities present in the carbon.

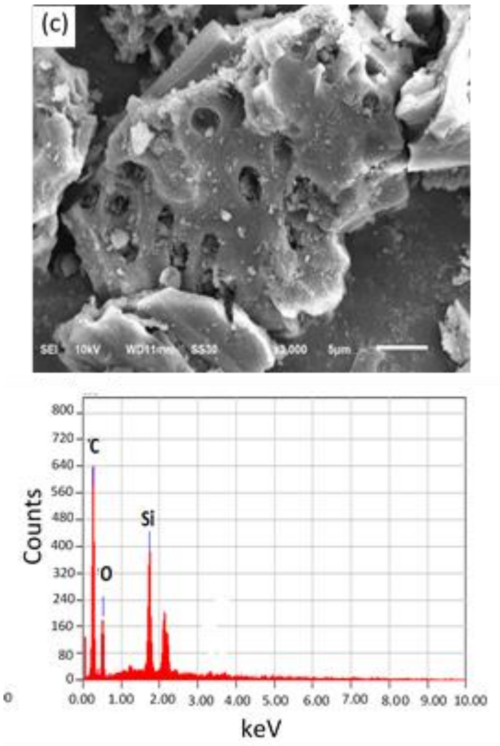
The EDS spectra presented in Fig. 2 (b, d) showed that untreated carbon and activated carbon consisted of similar components, namely, carbon, oxygen and silica. However, the percentage of these elements in every sample is different as presented in Table 3. The C and O elements contained in carbon without activation are 88.12% and 9.09%, respectively. Meanwhile, the percentage of elements containing in activated carbon are 80.34% and 14.19% for carbon and oxygen, respectively. In addition to the main constituent (carbon), there are also other elements contained in both samples in very low percentage, namely, Si and K which could be the impurities from rice husk.

Table 3. The composition of elements present in untreated carbon and activated carbon

Samples	Percentage (%) of Elements				
	C	O	Si	K	P
Carbon without activation	88,12	9,09	2,45	0,34	-
Carbon activated using H_3PO_4 for 15 hour	80,34	14,19	5,10	0,37	-



(b)



(d)

Figure 2 SEM images and spectra of carbon without activation (a, b) and (c, d) carbon activated using H_3PO_4 40% with the contact time 15 hour

Surface Area Analysis (SAA). Surface area analysis of carbon with and without activation presented in Table 4 shows the relationship between carbon adsorption ability on SLS and physical properties including surface area, radius and volume of pores. Carbon without activation had surface area and radius of pores smaller than that of the activated carbon. The surface area and radius of pores were 0.406 m^2g^{-1} and 15.294 Å, respectively for untrated carbon and 4.639 m^2g^{-1} and 305.642 Å, successively for activated carbon. The increase of both physical properties is due to the activation process using H_3PO_4 as this activating agent has a role to open the pores of the carbon so that the adsorption efficiency of activated carbon is higher than that of carbon without activation as described in Table 2.

Activated carbon modified with surfactant at concentration of 60 ppm had 0 m^2g^{-1} surface area adsorbing N_2. It may occur because the surface of activated carbon was fully covered by surfactant so that the pores were unable to adsorb N_2 gases. The basic principle of SAA

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is based on the amount of N_2 gas adsorbed on the surface of solids with certain surface area [16].

Table 4 Surface area analysis of carbon, activated carbon and surfactant-modified active carbon (SMAC)

Samples	Surface area adsorbing N_2 (m^2g^{-1})	Total volume of pores (ccg^{-1})	Radius of pres (Å)
Carbon without activation	0.41	0.01	15.29
Carbon activated using H_3PO_4 for 15 hour	4.64	0.60	305.64
Surfactant-modified active carbon (SMAC)	0	0.01	78.82

Application of SMAC for Lead (Pb) Removal in Artificial Lead Waste. SMAC fabricated by carbon activated using H_3PO_4 40% with the contact time of 15 hours and modified by adsorbing SLS 60 ppm for 4 hours was then applied to remove Pb in artificial lead waste. The result is presented in Table 5. It can be seen that the activated carbon had higher adsorption efficiency up to 99.95 % for 20 ppm lead adsorption than that of carbon without activation (99.89%) even though the increase was insignificant.

Table 5 Efficiency of Activated Carbon Adsorption Systems at High Temperature to Pb

Sample	Concentration of Pb before adsorption (ppm)	Concentration of Pb after adsorption (ppm)	Adsorption Efficiency (%)
Untreated carbon	20	0.022	99,89
Activated carbon	20	0.010	99.95

Conclusion

It can be concluded that surfactant modified activated carbon (SMAC) enabled to remove lead in artificial lead waste with the adsorption efficiency 99.95%. However, further experiment need to be conducted in order to investigate the effect of Pb concentration on the adsorption efficiency of SMAC.

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