

Characteristic of New Solid-Phase Extraction Sorbent: Activated Carbon Prepared from Rice Husks under Base Treated Condition

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ABSTRACT

A characterization of activated carbon (ACs) prepared from rice husks (RHs) under base treated condition as a new sorbent for solid-phase extraction (SPE) to extract 4-nonylphenol isomers (4-NPs) in water samples has been done. The ACs prepared from RHs usually exhibits low specific surface area due to its high ash content, but in case of its application for SPE, there are other factors need to be considered, such as the existence of functional groups inside the sorbent, that can enhance interaction of non-polar sorbent with analyte in the water matrices. In this case, silanol groups from ash content may affect the extraction efficiency for 4-NPs. The ACs made from RHs were chemically impregnated with ZnCl₂ and carbonized at 800°C. To investigate the role of silica, three types of ACs were prepared, i.e., untreated ACs (AC-Si, contain silica), base treated ACs (AC-B-Si, remain some silica inside), and ACs made by base treated RHs (AC-B, no silica), the surface area obtained from these treatments were 1352 m²/g, 1666 m²/g, and 1712m²/g respectively. ACs made by base treatment has the highest surface area (related to BET), which indicate that silica removal process promotes the formation of open pore system on ACs and enhances the surface area of ACs. However, extraction efficiency measured by GC-MS in SPE process showed the reversal trends (i.e., AC-Si= 32.08%, AC-B-Si= 82.63%, AC-B=51.78%), among them the AC-B-Si sorbent reveal the best performance in SPE process. It is indicated that although silica usually exhibits low specific surface area, but control presence of silica as a polar functional group has a positive influence in the interaction between non-polar sorbent and 4-NPs.

Keywords: activated carbon, base leaching, silica, SPE, 4-NPs

INTRODUCTION

Activated carbon (ACs) is an amorphous carbon, produced by carbonaceous materials or char who had been treated with special treatment to gain high surface area. The basic structural unit of ACs is closely approximated by the structure of pure graphite, but in the formation of layers, the carbon structure changes that cause the distance between layers is not the same.¹

ACs (classified as reversed phase sorbents) was certainly one of the first solid-phase materials used for extracting medium – to – low polarity organic compounds from water. But this sorbent was left because irreversible adsorption and low recoveries were obtained for some analytes, and were replaced with *n*-alkyl-silica until another carbonaceous sorbent, graphitized carbon black (GCB), introduced in 1980s. These disadvantages of activated carbon are due to inhomogeneous structures of the classical carbons, comparing GCB.² However, interest in this field are not reduced, nowadays many researchers developed a new

SPE sorbents based on carbonaceous sorbents as known as ACs from commercially and un-commercially (ACs made from agricultural waste) and also modified ACs, improve the properties of ACs to reduce the limitations of ACs itself.^{3, 4, 10}

Now we were focusing on study of ACs made from agricultural waste, rice husks (RHs). The utilization natural fibers as precursor of ACs, to reduce and empowering agricultural wastes is one of challenge in this study, but other big reason is about high concentration of silica inside RHs itself. The ACs prepared from RHs usually exhibits low specific surface area due to its high ash content (carbon-silica composite), but in case of its application for SPE, there are other factors need to be considered such as the existence of functional groups inside the sorbent that can enhance interaction of non-polar sorbent with analyte in the water matrices. In this case, silanol, hydroxyl functional group groups provide from ash content may affect the extraction efficiency of ACs. But on the other hand, the high concentration of silica inside pore decreases of the adsorption capacity of ACs due to pore blocking process.⁸

The disadvantage of silica inside ACs seems become more interesting, since most sorbents used for SPE are based on silica,⁸ and also the silanol groups provide hydroxyl functional group that can enhance the interaction between sorbent and analytes. If we can create a new method to produce ACs from rice husk with high surface area also contain hydroxyl functional hopefully we can reduce the limitation on low recoveries properties, and increases the extraction efficiency of ACs.

This study was prepared three kind of ACs made from RHs which chemically was impregnated with $ZnCl_2$ (RHs: $ZnCl_2 = 1:2$) and carbonized at $800^\circ C$ under un-oxidized environment ($N_{2(g)}$), i.e., untreated ACs (AC-Si, contain silica), base treated ACs remain some silica inside (AC-B-Si), and ACs made by base treated RHs with no silica (AC-B), and. The extraction efficiency of three kind of ACs will evaluate use nonylphenol (4-NPs) as target compound in GC-MS system.

EXPERIMENT

Materials used and sample preparation

Preparation of ACs

The raw material in this experiment was rice husk obtained from rice mill. It was washed thoroughly with distilled water to remove soil and clay and then dried in oven 24h at $105^\circ C$. Laboratory grade zinc chloride ($ZnCl_2$, purity 98%) by Merck acted as activating agent, and sodium hydroxide (NaOH) by Sigma-Aldrich, Hydrochloric acid (HCl, 37% (v/v)) supplied by Merck as basic and acid agent.

In this study we prepared three difference kind of ACs, i.e. untreated ACs (AC-Si, contain silica), ACs treated with base with no silica (AC-B); and base treated ACs remain some silica inside (AC-B-Si), to find out the best ACs used as SPE sorbent and make a clear understanding about the role of silica in case of the interaction of silica with analytes 4-nonylphenol (4-NPs, tech-grade supplied by Sigma-Aldrich). Three steps follows are processes to made activated ACs. The process of preparing ACs from RHs can be divided into three stages, which are illustrated as follows:

a. Base leaching

The dried RHs was refluxed with 1 M NaOH solution in a glass round-bottomed flask at 373K within a thermostat (1 grams of RHs need 3.5 mL of 1 M NaOH). After the basic solution was drained, the RHs was washed with warm distilled water until the filtrate was free from the base, and then dried at 373K for 24 h.⁵

b. Activation and carbonization process (chemical process)

RHs and ZnCl_2 (1:2) mixed together, and then oven dried at 105°C for 24 hours. A sample of the impregnated RHs placed in a crucible, then inserted into a tubular furnace on nonoxidizing environment with applied pure nitrogen gas at 230 mL/minutes, were used to maintain highly inert activation conditions and to minimize the effects of gases emitted from the sample. This carbonization process maintained at the desired temperature (800°C) for 2 hours.

c. Acid washing

After carbonization process, ACs that still contains ZnCl_2 and low concentration of ash were refluxed with 100 mL 3M HCl solution at 100°C for 1 h (1 gram of ACs need 20 mL 3 M HCl) (Park and Jang, 2003). After the acidic solution was drained, the ACs were washed with hot distilled water several times to until the pH of filtrate water reach to $\text{pH}=7$. The washed samples were dried at 105°C for 24 h, and then ground to form powder ACs.⁵

All the steps explained above is a procedure to make ACs (AC-B), and for other such as (AC-Si) is generally the same as the procedure described above, but without base leaching treatment on the starting precursor (RHs). Then, to make (AC-B-Si), we made some modifications based on procedure to produce (AC-B), the base leaching treatment was not applied on RHs (we changed), base leaching treatment was applied on carbon result from carbonization process.

All these processes provide us to analyze difference kind of ACs with difference concentration of silica inside. ACs (AC-Si) was made without do a base leaching treatment and this ACs use as a control, in a process to study about role and interaction of silica with analytes.

Analysis of physical properties of ACs

To make a clear understanding about ACs and its interaction with analyte, we have to know the physical properties of ACs, such as surface area and porosity, morphology, and also functional group on to ACs.

The samples were characterized by surface area and porosimetry analyzer, measured using the adsorption of nitrogen (Micrometric, model ASAP2010) in temperature (77.35K). The specific surface area of each ACs was calculated by the Brunauer-*Emmet-Teller* (BET) method in relative measure range (0.06 – 0.20). This study assumes that the cross-sectional area for the nitrogen molecule is 0.162 nm^2 . The single point total pore volume was determined from the amount of adsorbed nitrogen expressed as liquid state at a relative pressure of approximately (0.99). The average pore diameter was determined using the equation ($4V/A$), where A is the BET surface area and V is the single point total pore volume.

The morphology of precursor (RHs) and ACs was obtained with a scanning electron microscope (FEI, Nova Nano SEM 450), and also the composition of precursor (RHs) and ACs were measured using a FTIR spectrometer (Perkin Elmer, Spectrum 2000).

Analysis abundance of silica (ash content)

The ash content (ash %) of an ACs is the residues that remain when the carbonaceous portion is burned off. The ash content of ACs was determined by standard method (ASTM designation D 2866-94). Approximately 1-2 g of powdered ACs was placed into weighed ceramic crucible. ACs and crucible were dried for 24 h at 80°C and reweight to obtain the dry carbon weight. The samples were heated in the furnace at $650\pm 25^\circ\text{C}$ for 3h, the crucibles

were cooled in desiccators, and the remaining solid (ash) were weighted. The percent of ash was calculated by:

$$\% \text{ ash} = \frac{\text{remaining solid wt (g)}}{\text{dry carbon weight (g)}} \times 100\%$$

SPE procedures

SPE is very similar with the liquid chromatography column but the sorbent of SPE is not really require to made the sorbents should have a very specific surface area and pore size (narrow distribution). Stringent specifications are not necessary in SPE.⁸ We decided to make ACs from rice husk in range 340 mesh, and packed on to SPE cartridges. For the extraction process of 4-NPs, two kind of commercial SPE cartridge was used for comparison, Oasis^R HLB cartridges (3mL/100mg, surface area 809 m²/g) and GCB SupelcoTM ENVITM-carb (3mL/250mg). These commercial SPEs were compared with 3 kinds of ACs SPE cartridges from our preparation (3mL/200mg/≤340mesh) (AC-B, AC-B-Si, and AC-Si).

Before extraction Oasis^R HLB and GCB SupelcoTM ENVITM-carb were pre-conditioned with 5 mL MeOH and 5 mL DI water respectively on SPE manifold (VacMaster, IT Sorbent Technology, Cambridge, UK). The water sample 10 mL, pH7 (was spiked with 100 μL 4-NPs standard 100ppb) was passed through to those cartridges at flow rate 1 mL/ sec. when the extraction was completed, those cartridges were washed with 5 mL of a 5% solution of MeOH in water, and subsequently air-dried under a vacuum for at least 10 min. the 4-NPs residue were then eluted from those cartridges with 6 mL acetone and 6 mL dichloromethane (HLB and GCB respectively). The extracts were than completely evaporated to dryness with a gentle stream of nitrogen. The residue was re-dissolved in a solution (100 μL) of DCM, and subjected to injection port derivatization GC/MS analysis.

Similar to the above procedure (commercial one), the cartridge packed with ACs from rice husks (AC-Si, AC-B-Si, and AC-B) were pre-conditioned with 5 mL acetone and 10 mL DI water. Then 10 mL of a water sample, pH7 (was spiked with 100 μL 4-NPs standard 100ppb) was passed through to those cartridges at flow rate 1 mL/ sec. After the sample solution had passed through, the cartridge was washed with 10 mL DI water to remove co-adsorbed matrix materials from the cartridge. Then the sorbent (ACs) was dried by applying air-dried under a vacuum for 5 min. Subsequently the analytes retained on the SPE cartridge were eluted with 6 mL acetonitrile. The extracts were than completely evaporated to dryness with a gentle stream of nitrogen. The residue was re-dissolved in a solution (100 μL) of DCM, and subjected to injection port derivatization GC/MS analysis.

GC-MS analysis

The analyses were performed using a Varian CP-380 GC directly connected to a Varian Saturn 2000 ion-trap mass spectrometer. A ChromatoProbe (Varian) and temperature-programmed injector (linear: 3.4 mm i.d.) were used to introduce large-volume samples for injection-port derivatization. In a typical run, the sample solution (10 μL) was mixed with BSTFA (1 μL) in a micro-vial (volume: 20 μL), the vial was placed in a ChromatoProbe vial holder, and then positioned in the GC injection-port. The temperature was held at 80 °C for 2 min for the silylation reaction converts the hydroxyl groups of 4-NPs into their corresponding trimethylsilyl-derivatives (TMS-derivatization). Followed by solvent vaporization, after which, the temperature was rapidly increased to 250 °C to allow the introduction of TMS-

derivatives into analytical column. A DB-5MS capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness, J&W) was used. The following GC temperature program was employed: 70 $^{\circ}\text{C}$ for 2 min; a temperature ramp of 30 $^{\circ}\text{C}/\text{min}$ up to 120, continuously rise the ramp of 20 $^{\circ}\text{C}/\text{min}$ up to 300 $^{\circ}\text{C}$, and holding this temperature for 3 min. the temperature of the transfer line was set at 280 $^{\circ}\text{C}$. Full-scan EI spectra were acquired under the following condition: mass range 100-500 m/z , scan time 1s, solvent delay 10 min, ion trap temperature 200 $^{\circ}\text{C}$, emission current 20 μA (at 70 eV electron energy).

RESULT AND DISCUSSION

The high ash content on ACs seems to be a bad influence, since silica obstructs the pore formation and lead decreasing surface area of ACs.⁸ Otherwise, in term of SPE, this adverse effect give an extra challenge and increase the curiosity, accordingly silica inside ACs from RHs provide highly hydroxyl functional group (silanol), expected to increase the interaction between nonpolar sorbent (ACs) with target compound (4-NPs) in water sample.

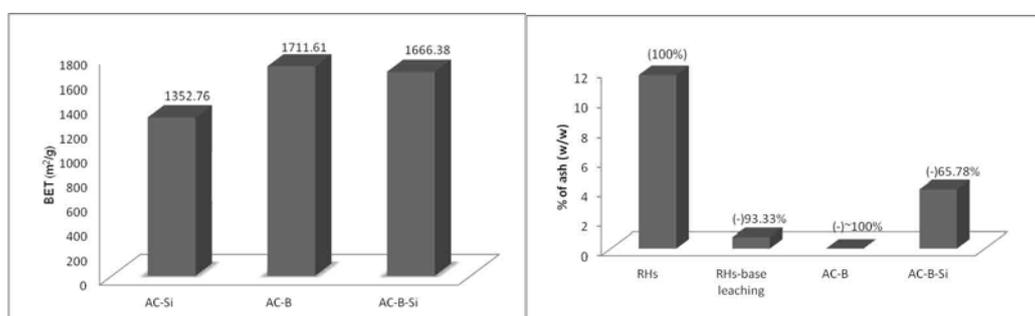


Figure 1. Effect of base leaching treatment on BET surface area of ACs

Figure 2. Presence of ash content

Physical properties of ACs from RHs

BET, surface area

Figure 1 shows the effect of base treatment on BET surface area. The minimum BET surface areas occur in the ACs without base leaching treatment (AC-Si). This result related with the high ash content inside AC-Si (Figure 2.) that block its open pore system (Figure 3). This result is similar with other study about ACs from RHs, reveal that ACs from rice husk (without any treatment) usually exhibits low specific surface area caused by its high ash contents.⁵ The blocking process of silica, prevent the ability of open pore system provide a path for a particle heading towards to inner pore system of the ACs. Seems likely, when the door was closed, automatically make the room inside (inner pore system) become non-activated.

ACs with base treatments (AC-B, AC-B-Si) relatively has high values of surface area (related to low concentration of silica). Figure 2. The low concentration of silica inside ACs decreases the potential of silica to accumulate in the surface (block the surface of ACs), see Figure 3.

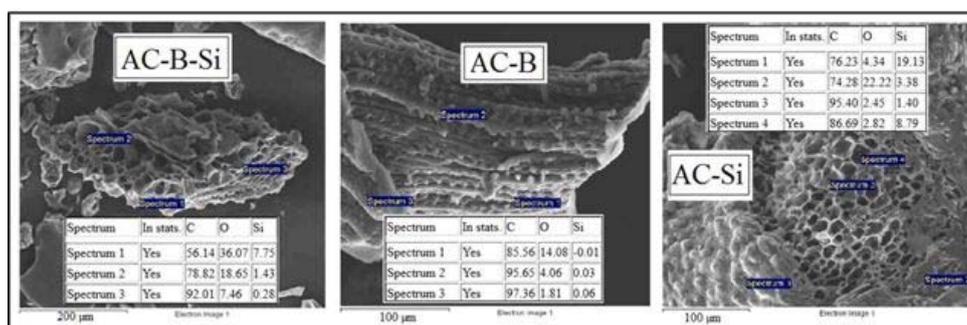


Figure 3. SEM imaging of ACs (the open pore system)

BET surface area of AC-B slightly higher than AC-B-Si. This diversity of BET values is caused by different concentration of silica inside ACs. See Figure 2. Inside AC-B-Si still contain 4 % ash (w/w), than AC-B almost no silica inside (un-detected). Aside from, low concentration of silica inside AC-B, the other reason why this type of ACs exhibit highest BET surface area comparing others, due to the pretreatment process on the precursor (base leaching treatment) that used to made AC-B. These base leaching processes in RHs not only remove the ash content inside but also attack mostly lignin (Figure 4).

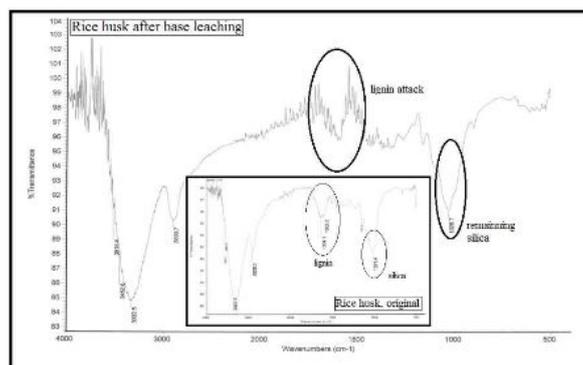


Figure 4. FTIR spectra of rice husk after base leaching

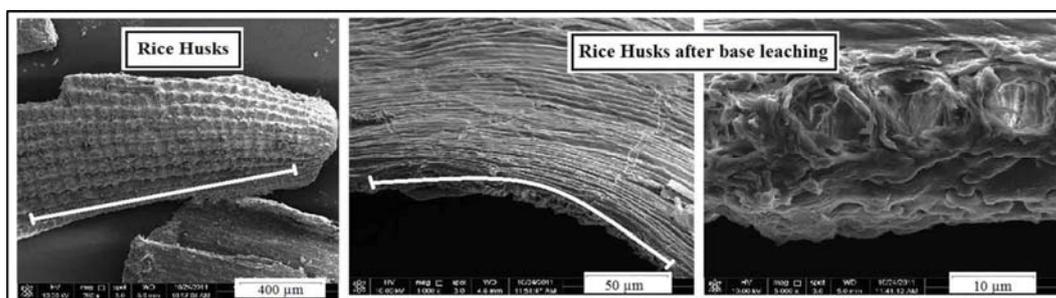


Figure 5. SEM imaging of RHs, and RHs after base leaching

The removing of lignin from RHs generate the structural changing, RHs which was originally rigid and hard transformed become more warped. Also, after base leaching process (remove the ash content and attack mostly lignin), it create holes in the surface of the

precursor and provide pathway to activating agent (ZnCl_2) easily entered to the inner of RHs, see Figure 5. This process will promote optimization of dehydration and carbonization process, due to increase the contact area between RHs and activating agent.⁵

Other information based on Figures 1 and 2, the ash content decreases significantly after the base leaching process, and create significantly increases the surface area AC-Si to AC-B-Si (AC-B-Si is produce by treated the AC-Si with base). This indicates that the disappearance of silica (open the blocking system of silica) simultaneously create more surface area and new pore structure, in the other hand, base leaching process generate ACs with higher surface with low remaining silica.

Comparing with AC-B (ACs produce by treated-RHs), the surface area of AC-B-Si is lower than AC-B. This result can be explained by consideration of uncompleted silica removal on base treatment toward ACs (AC-Si), because some silica inside inner system of the ACs (AC-Si) may not removed and still remain inside. While AC-B, the silica removal (in the starting material) with base treatment was improved by pyrolysis process, due to the ability of silica react with the ZnCl_2 in pyrolysis process.⁵

Pore structure analysis

Accordingly IUPAC classification, ACs prepared from rice husk in chemicals activation using ZnCl_2 have a pore structure character of mesoporous and microporous. Considering, the application of this ACs as SPE sorbent for 4-NPs (structure size 1.143 nm), the mesoporosity expected to be dominant. Hence, in this study we were producing ACs in quit high temperature (800°C). Carbonization process has several important levels that determine the character of the carbon that would be obtained. The ACs with high microstructure will be generated at a temperature of 500°C , with some pores are still covered by the tar. So as, to obtain greater porosity it is necessary to increase the temperature until 800°C . Therefore, in the production of ACs, the study was conducted at temperature 800°C with the aim to producing ACs with high mesoporosity.⁶

Table 1. Average pore size of three differences ACs

No.	Activated carbon	BET (m^2/g)	Average pore size (nm)
1.	AC-B	1711.61	2.57
2.	AC-B-Si	1666.38	2.52
3.	AC-Si	1352.76	2.56

Table 1 shows that three different kind of ACs prepared from RHs have similar average pore sizes (in range small mesopore). It is indicate that removing silica with base leaching treatment not really affected on the pore structure of ACs. This property (pore structure) is affected just by activating agent, impregnation ratio, and activation temperature. Since we use same method to produce AC-Si, AC-B, AC-B-Si (chemical activation with ZnCl_2 in ratio 2:1 weigh activating agent/weigh RHs, at 800°C), then, pore size of ACs are not so different each other.

Performance of ACs as SPE sorbent

Role of surface area

In term of ACs as sorbent, high surface area is the most important thing. But, in case of SPE, we need to consider another factor. Since there is some popular sorbent called GCB, that essentially non-specific and non-porous sorbent, also HLB with relatively low surface area (comparing ACs), but generate high extraction efficiency of 4-NPs, and it caused by the presence of functional group inside the sorbent. GCB has hydroquinone groups. HLB, has two types functional group inside, the hydrophobic functional groups are represented by (N-vinylpyrrolidone) and the lipophilic on is represented by divinylbenzene, see Table 2. More after, not only have functional group that can enhance the interaction between sorbent and analyte (Figure 6 and 7), but also these two sorbents have ability to promote easily releasing kinetic (GCB has include as non-porous sorbent, HLB with big number of average pore size, Table 2).

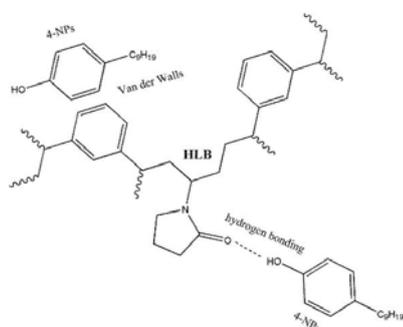


Figure 6. Interactions between 4-NPs and HLB

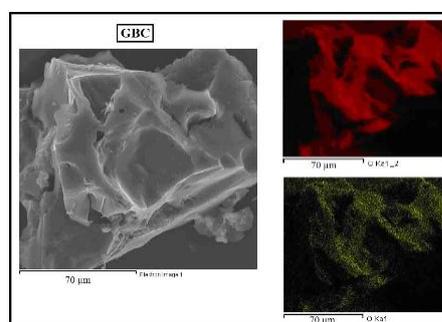


Figure 7. SEM-EDX mapping of hydroxyl functional group in the surface of GCB

Role of pore size

From Table 2 and 3, (make a comparison), we can conclude that surface area of sorbent does not become the major factor to increase the extraction efficiency of ACs, instead the pore size and the appearance of functional group seems become the most contributing factors.

Table 2. physical properties and extraction efficiency of commercial sorbents

No.	Sorbent	BET (m ² /g)	Average pore size (nm)	Extraction efficiency	SD	%RSD	Functional group
1.	HLB	809	8.10	88.43	0.98	1.11	Hydrophobic Lipophilic Balance
2.	GCB	85.74	3.39	91.63	1.97	2.12	Hydroxyl

The reason why this factor enhanced becomes one of major factor to increase the extraction efficiency of ACs is because the large pore size help releasing kinetic of analyte that already attached on sorbent. The host (minimization of pore size) will lead slower release kinetics.⁹ Based on Table 1, AC-B, and AC-Si, AC-B-Si has a quit similar average pre size.

But only AC–B–Si shows the high extraction efficiency of 4-NPs. These phenomena can explain if we are referring to the open pore system in each ACs. See Figure 8 to 10. From these SEM imaging, reveal that AC–B–Si have the base pore system comparing the other. AC–Si seems to be have a good open pore structure also, but, some part was blocked by the high concentration of silica (as explained above). Whereas about AC–B, it seems AC–B did not have a proper open pore system, it because AC–B produced by base treated RHs that also promote removing lignin. RHs which were originally rigid and hard transformed become more warped, see Figure 5, this properties lead high shrinkage effect occurs more in AC–B comparing other ACs. Also holes in the surface of the precursor that provide pathway to activating agent ($ZnCl_2$) easily entered to the inner of RHs, cause, no accumulation of $ZnCl_2$ on the surface, which usually acts as a large open pore-forming system in the surface of ACs.

Table 3. physical properties and extraction efficiency of ACs

No.	Activated carbon	BET (m^2/g)	Average pore size (nm)	Extraction efficiency	SD	%RSD	Silica
1.	AC–B	1711.61	2.57	51.78	0.71	1.37	No
2.	AC–B–Si	1666.38	2.52	82.64	2.16	2.61	Yes (low)
3.	AC–Si	1352.76	2.56	32.08	1.66	5.17	Yes (high)

Role of silica

In common SPE sorbent, we already familiar with the sorbent based on silica or silica bonded sorbent. But, in this study, ACs from rice husk look similar as “carbon bonded silica” regarding silica content inside the ACs sorbent. Silica used as a very successfully adsorbing agent, as it does not swell or strain, has good mechanical strength, can undergo heat treatment, and also the surface of silica provide silanol group. These all properties of silica used as good considerations, but, in many literatures said that silica inside ACs decrease the surface area. So, if we can arrange appropriate concentration of silica inside of ACs, we can combine the advantages of ACs (porous materials with high surface area) and silica (provide silanol), and generate new generation of ACs for SPE application.

Based on the understanding described above, also the data from Table 2, supported by Figure 9 and Figure 11. We can reveal the reason why AC–B–Si has a high extraction efficiency comparing the other ACs, is because AC–B–Si not only have good open pore system, but also 4% of silica inside this ACs (that provide hydroxyl functional group) are uniformly spread around the surface (same as GCB).

Silica on surface of ACs is increase the polarity of these sorbent, with the oxygen-containing functional group that plays an important role in the process of hydrophilic adsorption. In other hand, silanol can enhance the interaction between ACs and target that diluted in water matrices. With controled silica inside AC–B–Si, the interaction between 4-NPs and the sorbent is not only weak π -- π interaction, but also hydrogen bonding provided by silanol.

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CONCLUSION

A new SPE sorbent based on ACs from rice husk was successfully developed for enrichment and determination of 4-NPs in water samples. Based on this study “Evaluation of the Extraction Efficiency of Activated Carbon Prepared from Rice Husk as Solid Phase Extraction Sorbent to Determine Nonylphenol in Water Sample” we concluded that:

- ACs with proper concentration of silica reveal as the best sorbent for SPE
- Regarding easily releasing process on mesopore structure. The pore sizes of ACs give a large influence in extraction efficiency comparing the high number of surface area.

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