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A SIMPLE AND HIGH YIELD PROCEDURE FOR THE MODIFICATION OF RICE HUSK SILICA AND CAPPING WITHB-CYCLODEXTRIN: APPLICATION FOR BIOREMEDIATION IN FUTURE

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Abstract
In this paper, a simple immobilization of β-cyclodextrin (β-CD) on silica from rice husk ash is reported. Silica isolated from rice husk ash is chlorinated with 3-(chloropropyl)triethoxysilane (CPTES) for the attachment of chlorine group on the surface of silica via a simple sol-gel technique. Immobilization of β-CD with modified silica has been performed using the mixing process. The confirmation of β-CD binding onto the surface of modified silica has been done by FTIR, SEM, and EDX analysis. This immobilized preparation can be used for the immobilization of enzyme as well as in the adsorption of aromatic pollutants present in the wastewater in the future.

Keyword : Rice husk ash, Immobilization, Cyclodextrin, Silica modification.

1. Introduction

Rice husk ash (RHA) is a major waste product of the rice mill industry. The silica (SiO_2) content of the ash is more than 94% in RHA [1]**.** The silica surface consists of two types of functional groups, i.e. the siloxane (Si-O-Si) and the silanol (Si-OH) groups. It was found that the main modification pathway occur via a reaction of a particular molecule with the silanol group on the silica surface[2]. The organo-chloro functionalization of amorphous silica is an important starting point for the preparation of a wide variety of silica based materials.
Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six or more linked D-glucopyranose units. The most widely studied CDs are those composed of six, seven and eight of these units, denoted as α-, β- and γ-CD, respectively. The conical shape of these molecules results in well defined hydrophobic central cavities (with top and bottom diameters of 5.3 and 4.7 Å for α-CD, 6.5 and 6.0 Å for β-CD and 8.3 and 7.5 Å for γ-CD) that can accommodate the inclusion of various organic molecules with suitable geometry and function [3]. CDs themselves, however, are highly water soluble and must therefore be processed into solid forms before they can be implemented into usable separation technology. The conversion of CD into an insoluble material form is required to make possible their use in practical applications such as environmental remediation [4,5] and chiral chromatography [6]. In recent years, reseachers use different approach in producing CD-functionalized materials. A commonly approach used is the post modification process. For instance, silica can be first modified with an alkyl amine function (prepared by post-modification or sol gel), followed by reaction with a variety of organic molecules [7].
In this paper, silica was collected from raw material, rice husk ash; the addition of the Cl group was done by a simple procedure as described in the text. Capping of β-CD with the modified silica was performed very easily by the help of Cl group present in the surface of silica. A detailed characterization of these hybrid materials was carried out by FTIR, SEM/EDX analysis. This immobilized preparation can be used for the immobilization of enzyme as well as in the adsorption of aromatic pollutants present in the wastewater, in future.

2. Experimental

2.1 Materials and methods

Chemicals used were AR grade having high purity and were used as received. These include β-CD (Sigma), sodium hydroxide (Systerm, 99%), nitric acid (Systerm, 99%), 3-(chloropropyl)triethoxysilane (Sigma), acetone

(Systerm) and ethanol (System, 99.6%). The rice husk (RH) was collected from a rice mill from P. Pinang, Malaysia.

2.2 Modification of silica

The rice husk ash was chosen as the source of amorphous silica [8] as it is available in abundance. The silica was extracted from rice husk using a previously reported method [9]. The silica that have been extracted from rice husk was modified by 3-(chloropropyl) triethoxysilane (CPTES) using a previously reported method [10]. Briefly, the silica (obtained from RHA) was stirred in 350 mL of 1.0 M NaOH at room temperature for 1 h. A 6 mL solution of CPTES was added to the solution and was titrated slowly with 3.0 M nitric acid until the pH of the solution reached 3.0. The gel obtained was aged for 2 days and was separated by centrifuge at 4000 rpm for 8 min. The sample obtained was washed by copius amount of water followed by 10 mL of acetone and left to dry in the oven at 60 ^{o}C for 24 hours. Finally, it was ground using pestle and mortar to produce fine powder.

2.3 Capping of RHA-Cl with β-cyclodextrin

About 0.95 g of RHA-Cl and 0.4 g of NaOH was stirred in 60 mL DMF for 15 minutes. Separately, an amount of β-CD was stirred in 60 mL DMF. The two solution were mixed together in a 250 mL beaker and left under constant stirring for 8 hour at 80 ^{o}C. The gel form were repeatedly washed with copious amount of water. Final washing was done by 10 mL of 99% ethanol. The sample was then dried at room temperature. This sample was labeled as RHA- β-CD.

2.4 Instruments

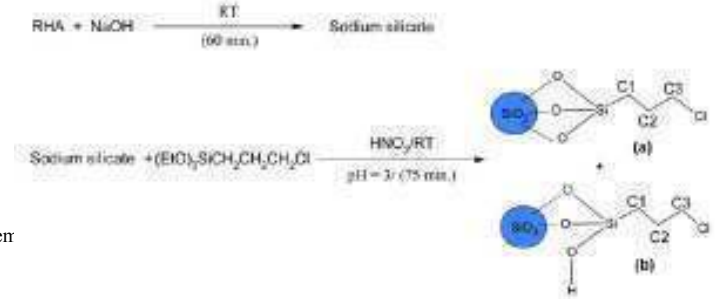
FT-IR spectra

The Fourier transform infrared (FT-IR) spectral studies were performed using KBr pelleting technique with Perkin Elmer System 2000 instrument in a range of 400-4000 cm^{-1}. FT-IR analysis was carried out to determine the variation of the functional groups present in the native compounds and in the prepared complex.

Scanning Electron Microscopy
Scanning Electron Microscopy (SEM) of the prepared sample was carried out using a Leica Cambridge S360 scanning microscope. All the studied surfaces were coated with gold to avoid charging under the electron beam.

Energy Dispersive X-ray analysis
The Energy Dispersive X-ray analysis (EDX) using (QBSD) Quadrant-Back Scattering Detector signal detector was coupled with SEM.

3. Results and Discussion



Schem [10].

3.1. SEM

The SEM images of modified silica (RHA-Cl) and RHA-β-CD composite are shown in Figure 1. The images of RHA-Cl exhibit highly porous structure and also have average size distribution between 5 to 20 μm. In the other hand, RHA-β-CD has the average size distribution between 2 to 10 μm and they exhibit a relatively dense surface with shallow surface cavities. Similar findings were also reported by some earlier workers [11].

3.2. EDX

EDX analysis showed the presence of silicon, carbon, oxygen and chlorine in RHA-Cl and RHA-β-CD. The average value obtains for carbon and chlorine in RHA-Cl was 24.95%, 4.38% while cyclodextrin modified silica (RHA-β-CD), 29.85% and 2.05%. Although the mentioned values did not show any stoichiometric relationship between modified silica and β-CD, it show the incorporation on the silica surface. The increased value of carbon and decreasing value of chlorine in RHA- β-CD confirmed the fact that chlorine group in RHAS-Cl have been replaced by β-CD.

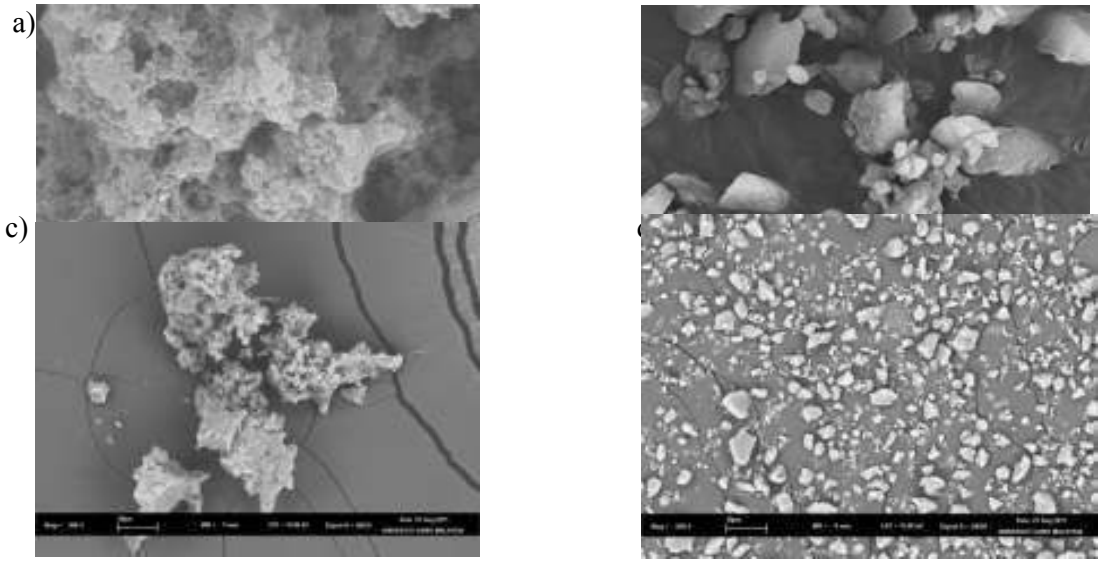


Figure 1. SEM images of (a) RHA-Cl at 5000 magnification and (b) RHA-BCD at 5000 magnification (c) RHA-Cl at 500 magnification (d) RHA-BCD at 500 magnification

3.3. FTIR spectra

To identify the functional groups on the RHA -β-CD, FT-IR analysis was carried out. Figure 2 shows the FT-IR spectra of RHA-Cl, RHA-β-CD and its differential spectra. Typically the Si-O-Si vibrations appear around 1081 cm^{-1} associated with condensed silica network in RHA Silica (RHA). This vibration was observed to shift to 1083 cm^{-1} in RHA-β-CD. This strong absorption band in the differential spectra at 1081 cm^{-1} indicate the presence of mixture $–(Si\text{-}O\text{-}Si)_n$- and –Si-O-Si-C- in RHA-Cl and RHA-β-CD. The broad band around 3473 cm^{-1} in RHA-β-CD is usually assigned to O-H vibration from Si-O-H and HO-H of adsorbed water. The C-H stretching vibration can be observed at 2967 cm^{-1} and 2958 cm^{-1} in RHA-β-CD and the differential spectra. The band around 1430 cm^{-1} and 1381 cm^{-1} were assigned to the C-H bending vibrations of the CH_2 group symemetrical and asymmetrical vibrations. The RHA-β-CD and the differential spectra show the appearance of absorption bands assigned to C-Cl bond at 667 cm^{-1}. Recently some workers published some articles related to the modification of silica, and similar finding was observed [10].

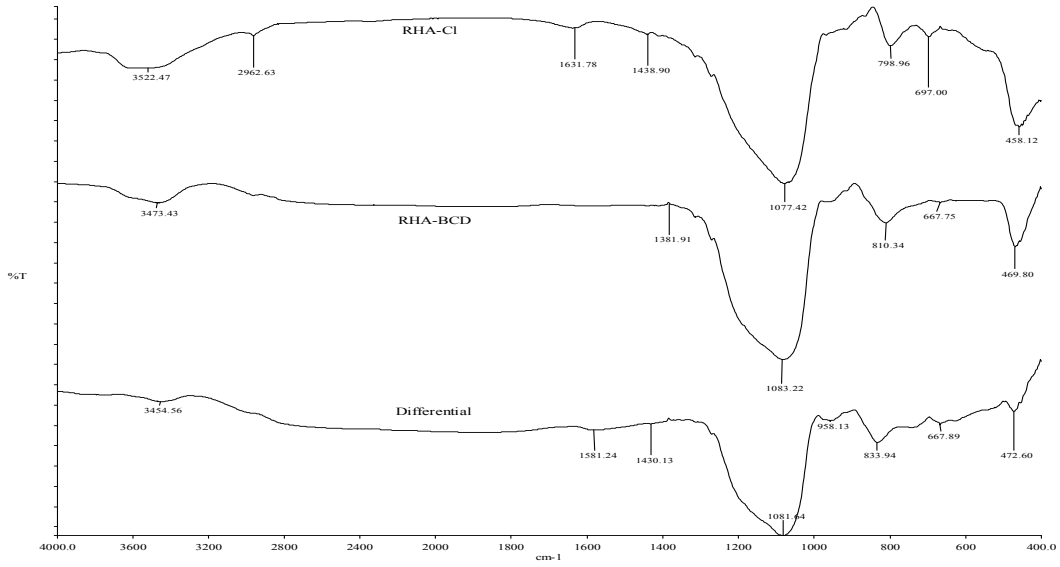


Figure 2. FT-IR spectra of RHAS-Cl, RHAS-BCD and their differential spectra

4. Conclusion

The present study demonstrates a procedure used to modified RHA Silica with β-CD, is a simple, low cost, environmental friendly and time saving method with the use of non-toxic chemicals. In this work, the modified rice husk silica which is an agricultural waste was modified with CPTES and was used to prepare silica immobilized with β-CD. Such preparation is suitable for the adsorption of aromatic pollutants from the wastewater but also in the field of enzyme immobilization. The high yield attachment of a glucose moiety on the surface of modified silica is a good clue for the glycosylated enzyme immobilization. To scale up this technology we are thinking to use this capped silica-β-CD up to the industrial level in the form of removal of aromatic pollutants in batch as well as continuous reactor.

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References

[1] S. Chandrasekhar, K. G. Satyanarayana, P. N. Pramada, P. Raghavan, T. N. Gupta. (2003). Review processing, properties and applications of reactive silica from rice husk. *J. Mater. Sci*. 38, 3159-3168.

[2] S. Dash, S. Mishra, S. Patel, B.K. Mishra. (2008). Organically modified silica: Synthesis and applications due to its surface interaction with organic molecules. *Adv. Colloid Interface Sci*. 140, 77–94.

[3] R. Huq, L. Mercier. (2001). Incorporation of cyclodextrin into mesostructured silica. *Chem. Mater*. 13, 4512-4519.

[4] G. Crini, H. N. Peindy, F.Gimbert, C. Robert. (2007). Removal of C.I. Basic Green 4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies. *Separation and Purification Tech*. 53, 97–110.

[5] T. N.T. Phan, M. Bacquet, M. Morcellet. (2002). The removal of organic pollutants from water using new silica supported β-cyclodextrin derivatives. *Reactive and Functional Polymers,* 52, 117–125.

[6] D. Lubda, K. Cabrera, K. Nakanishi, W. Lindner. (2003). Monolithic silica columns with chemically bonded β-cyclodextrin as a stationary phase for enantiomer separations of chiral pharmaceuticals. *Anal. Bioanal. Chem.* 377, 892–901.

[7] J. H. Clark, D. J. Macquarrie. (1998). Catalysis of liquid phase organic reactions using chemically modified mesoporous inorganic solids. *Chem. Commun.* 853-860.

[8] T. Radhika, S. Sugunan. (2006*).* Structural and catalytic investigation of vanadia supported on ceria promoted with high surface area rice husk silica. *J. Mol. Catal. A Chem*. 250, 169–176.

[9] F. Adam, J. H. Chua. (2004). The adsorption of palmytic acid on rice husk ash chemically modified with Al(III) ion using the sol–gel technique. *J. Colloid Interface Sci*. 280, 55–61.

[10] F. Adam, H. Osman, K. M. Hello. (2009). The immobilization of 3-(chloropropyl)triethoxysilane onto silica by a simple one-pot synthesis. *J. Colloid and Interface Sci*. 331, 143–147.

[11] D. D. Asouhidou, K. S. Triantafyllidis, N. K. Lazaridis, K. A. Matis. (2009). Adsorption of Remazol Red 3BS from aqueous solutions using APTES- and cyclodextrin-modified HMS-type mesoporous silicas. *J. Colloids Surfaces A Physicochem. Eng. Aspects*, 346, 83–90.

[12] F. Adam, S. Balakrishnan, P. L. Wong. (2006). Rice husk ash silica as a support material for ruthenium based heterogenous catalyst. *J. Phy. Sci*. 17 (2), 1–13