UTILIZING SURFACE PROPERTIES OF SOME LOCAL MATERIALS FOR ADSORPTION AND SEPARATION CHEMISTRY PURPOSES: SURFACTANT'S ROLE

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Abstract

The dynamics on surfaces plays important role in various area of application. Chemical and physical properties of the surface of adsorbent, adsorbates, and also the condition for adsorption process are the factors to control dynamics, mainly when physical adsorption occurs. Therefore modifying the surface might result on separation and exclusion process, aiming some target compounds in a natural mixture.

Some surface of interest are cellulose from fine particle of rice husk and the activated carbon from it, wet bacterial cellulose from nata de coco and its dried fine pieces of it were tested for some adsorption of heavy metal ions under some circumstances. Parameters including the particle size, pH, concentration and the presence of co-ions were explored.

On the other hand, some types of surfactants are well known for their interesting properties that enhance the performance of surfaces in adsorption and desorption processes. The ability of surfactant to make micellar aggregats is also beneficial for separation purposes. Some previous adsorption systems are explored and compared in this paper. More analytical methods are AAS, FT-IR, SEM, Uv-Visible, GC-MS, are being emplyoyed to extract information about small particles adsorption. Cd(II) and Cr(III) as well as nitrate ions, mixtures of compunds in noni fruit (Morinda citrifolia) extract, with and without surfactant.

The result shows some interesting surface properties that might be taken into account for other application purposes. Different behavior of heavy metals as well as organic compounds in mixture make the result of further pursue is expected.

Keyword: adsorption, surface properties, surfactant

1. INTRODUCTION

Adsorption process has been an investigated thouroughly using modern instrumentation since the last three decades. Some fundamental and theoretical concepts, including those from the computational chemistry area, have expanded the possibilities of sophisticated applications. The macroscopic and microscopic studies, direct and indirect investigations enhace the understanding about the surface properties of the material. Porous materials offer great good properties owing to high surface area and the pore spaces.

Basically in the porous media the particle dynamics is affected by some factors. Interaction between surface wall and small adsorbate particles depend on the complexity due to the properties of surface, adsorbates themselves, as well as environment. After some NMR experiments it was known one of the possible mechanism is called *reorientation mediated by translational displacement, RMTD* [1-5]. Particles move dynamically approaching the surface, attached there for a certain retention time and desorbed back to the bulk liquid. Rotation and diffusion plays role before they return to the surface using different orientation. This processes can be seen in the figure 1.

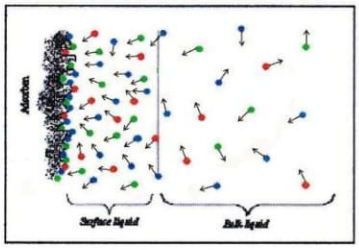

Figure 1. RMTD mechanism in the surface of adsorbent

Nuclear Magnetic Resonance relaxation and diffusion experiments are employed to map the molecular dynamics on the surface. With the insight from NMR experiments, more investigations are emphasized in the

factors affecting adsorption such as pH and temperature as well as surface modification. Other spectroscopy technique were used to see indirectly the effect of external factors to the ampount of particle adsorbed.

Adsorbent used in this paper is the bacterial cellulose called *nata de coco*. This microporous cellulose fiber is made by *Acetobacter xylinum* when sugar is present in the medium. The surface of the biomass has hydroxyl groups and also the strong hydrogen bonding with solvents and other adsorbate molecules. This biomass has also swelling capacity and this also be used to entrap particles. When the adsorption on the surface is considered "physical" then desorption of adsorbates can be easily obtained. Especially small and simple particles can be retained only for a certain time on the surface before being desorbed back to the bulk liquid as can be seen in the previous figure. This "strange kinetics" on the surface was analized in a thoughrough review of NMR tomography methods [1]. This physical property can be very useful in the future for separating and recovering the target components in the mixture.

The wet or dry porous media can change its surface structure according to the modification introduced to the active sites. The modification can be made using utilization of surface properties. Some trials to modify surface structure using surfactants were reported but not for this type of cellulose biomass [6]. In this paper the use of alkyl benzene sulphonate (ABS) surfactant will be tested. The use of *nata de coco* as well as other natas for this application will be important in the future.

Surfactant itself is usually organic compounds that are amphiphilic or containing both hydrophobic groups (the *tails*) and hydrophyic groups (the *heads*). Therefore, a surfactant molecule can be water insoluble and at the same time oil soluble. Surfactant molecules will migrate to the water surface, where the insoluble hydrophobic group may extend out of the bulk water phase, while the water soluble head group remains in the water phase. This alignment and aggregation of surfactant molecules at the surface acts to alter the surface properties of water or interface of materials. The surfactant formula of ABS surfactant can be seen below.

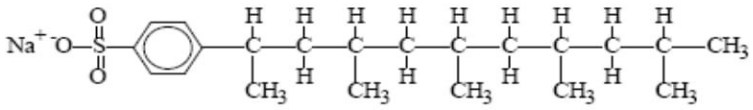

Figure 2. The molecular formula of alkylbenzene sulphonate.

On the other hand a benefecial fruit used in this experiments is noni fruit (*Morinda citrifolia*) which contains a number of phytochemicals. Scopoletin, octoanoic acid, vitamin C, terpenoids, alkaloids, anthraquinones (such as nordamnacanthal, morindone, rubiadin, and rubiadin -1-methyl ether, anthraquinone glycoside), β-sitosterol, carotene, vitamin A, flavone glycosides, linoleic acid, alizarin, rutin, and a putative proxeronine are some of the major and rare antioxidants present [5-9]. Using gas chromatography and mass spectrometry the profile of the mixture after treatment can be followed.

The purpose of this experiment is to see the profile of surface interaction between cellulose and different chemicals in the extract, as well as to see the possibility of surface modification changing the profile of the mixture components after adsorption process. In the long run the utilization of the surface properties can be forced to extraction of selected compounds if the mixture compounds. Moreover, more selective preparation and extraction methods will be conducted to obtain better separation effect for the components

2. MATERIAL AND METHODS

2.1 Chemicals, solvents and samples

The chemicals used for this research so far were obtained from E. Merck Germany. Solvents used were Chloroform, Methanol (p.a. grade). The ripe Noni fruit is obtained from the university garden in Malang. *Nata de coco* was made of coconut water and raw sugar from the local market. Acetic acid solution was made from Glacial Acetic Acid also from E. Merck, Germany. The starter bacteria (*Acetobacter xylinum*) was bought from Biology Department, The State University of Malang, Indonesia.

Some analytical instrumentation are used for this report were UV-Vis Shimadzu Pharmaspect 1700 Spectrophotometer, Prestige 20 FT-IR Spectrophotometer, and Shimadzu GC-MS 2010 Plus Spectrometer. Additional pictures were taken from Inspect-850 FEI Scanning Electron Microscope after the *nata* sample was coated with gold as thick as 5 nm.

2.2 Preparation of *nata de coco*

Nata de coco was prepared by boiling the coconut water and sugar for around two-threee hours. The raw materials and all equipment used should be sterilized. The acetic acid was poured into the mixture before the

starter bacteria. The final mixture was then settled in containers for some days (normally 15 days) to let the cellulose fibre to form.

After being harvested the *nata* was again boiled for some hours to stop the process of biomass formation as well as to kill the remaining bacteria and to clean the material from contaminant. The *nata* was then blended to be cut to small pieces and dried in an oven at about 90ºC to contant mass. Then the dry nata was sieved to 20-50 mesh in size.

2.3 Preparation of Morinda citrifolia extract

The ripe noni fruit was sliced with around 5 mm thickness and dried under the sun. 25.996 g of the dried fruit is then immersed in methanol-water (200 and 50 mL) for 1 hour. The solution was the evaporated around 10 hours at 60 ^{0}C to remain 38 mL of raw extract. This mixture was the acidified using H_2SO_4 until the pH 3 before the chloroform was added and equillibrated. The chloroform extract was taken, this contains terpenoids and phenolic compounds. The remained water-acid extract was the made into pH 10 using NH_4OH. Again a mixture of chloroform-methanol (3:1) was added, equillibrated and separated. The $CHCl_3$-MeOH extract contains alcaloids, and the water-base extract will have the quarterner alcaloids as well as the N-oxides of the noni fruit.

2.4 Preparation of the adsorption process

As much as 0.5 mL of each extract is diluted 40 times, 0.005 of LAS and ABS surfactant were added to some of them. Around 1 gram of dried nata was added before the mixture was shaked about 50 minutes at 100 rpm speed. The filtrate was ready for IR, uv-vis, and GCMS measurement. The IR spectra of residue were also taken.

2.5 Preparation of *nata* picture and IR-spectra

A amount of dried *nata* was coated with gold for scanning electron microscopy, since cellulose is a non-conducting material. The dried and sieved *nata* was ground with KBr to get the reflectant infrared spectrum of some functional groups present on the surface. The liquid extracts are also measeured to get the IR mixture profile before and after treatment.

2.6 Spectra and picture recording.

Some SEM pictures were taken from a small piece of *nata de coco*. Different magnification was explored to get the closest image possible this time. The FT-Infrared reflectant spectra were of fine ground dry *nata* in KBr were also recorded using KBr as the background. Some IR spectrum of liquid extracts were also taken using KBr windows.

GC chromatograms were taken for the three kinds of original extract, and the “remains” after adsorption. The results were compared to each other to see the profile of the surface adsorbent with and without surfactant.

3. RESULT AND DISCUSSION

From the SEM pictures the rough cellulose surface can be seen. In some different gelling time the formation of the fiber can also be clearly identified. In good preparation condition the pores of the biomass can also be noticed (figure 3). However, since the material is non-conductive, details of the pore structure cannot be obtained.

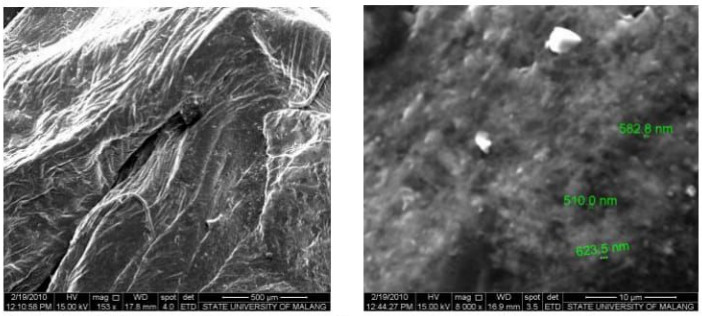

Figure 3. Nata surface as seen by scanning electron microscopy

The infrared spectrum of the dried nata indicates key indicators for cellulose in the sample (figure 4). The spectrum also describes some functional groups present in the surface. The domination of hydroxil groups bonded on the surface indicated by the very wide peak around 3300 cm^{-1}. Medium peak around 2900-3000 as well as in the finger print region around 1500 cm^{-1} came from the –C-H of the benzene rings of the cellulose. The spectrum before and after adsorption process are not much different. It means that the absorption process did not change the surface of the cellulose. Moreover we can take conclusion that the adsorption on the surface is mainly physical adsorption. The infrared spectra must be anlysed futher to extract the necessary information about the type of surface interaction occuring before the surface is dried again.

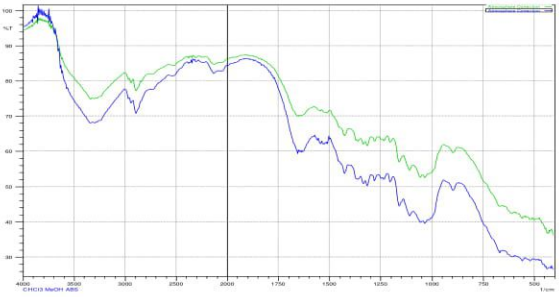

Figure 4 Infrared Spectra (reflectant) of nata cellulose before (green) and after (blue) adsorption process using ABS surfactant as surface modifier.

The Infrared spectra in Figure 5 are taken for getting the mixture profile of $CHCl_3$-MeOH extract, before and after nata adsorption. They indicate no major chemical changes occuring during adsorption, before and after adsorption, with and without surfactant. The pattern of the spectra appearance remains more or less the same. Therefore the absorption is mainly physical absorption which can be complicated but not much giving influence on the chemistry point of view.

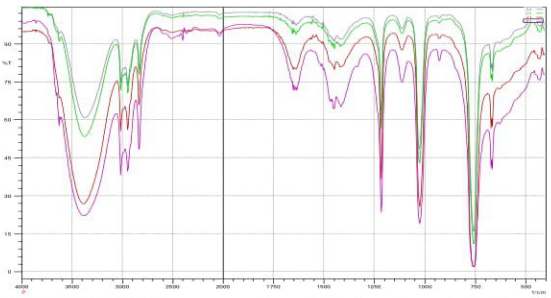

Figure 5 Infrared Spectrum of CHCl3-MeOH extract of noni fruit: the original extract (purple), the extract added by ABS surfactant (green), the extract after nata adsorption (pink), the extract after adsorption on nata modified by ABS surfactant (red)

The feature of surface modification must be carefully interpreted while the gas chromatograms of the mixture are compared as the infrared spectrum. In fact some components in the original $CHCl_3$-MeOH extract dissapear after ABS surfactant addition. Some of them are not recovered after adsorption. Those compounds have retention time between 9 and 11 minutes in this system, might be the non stable compounds in the mixture. Some more investigation is under consideration since when this is the case then one can use the simple GCMS measurement to follow a chemical reaction.

On the other hand, some peaks appear after nata adsorption, with and without ABS modification. Some strong peaks with retention time 3.033, 3.425, and 3.817 are recognized from the mass spectra as methyl ester of hexanoic acid, 1,2,3-propanetriol and ureum. While pentadecanoid acid, 9-hexadecenoic acid as well as 9-octadecenoic acid (z) appear in the retention time 16.308, 18.425 and 20.725 minute. There must be some reason why those peaks appear after nata adsorption. They might be the by product of degradation of some major components in the extract, or even some new products of the possible reactions between the components, the components and the surfactant molecules with or without the presence of polar surface of cellulose. Moreover, the peaks that appear after the nata adsorption are broad. The broad peaks indicate strong interaction between the components and the surface of the colum-pack as the stationary phase. Some possible interactions of the components and the sufactant aggregates might be the topics of next investigation.

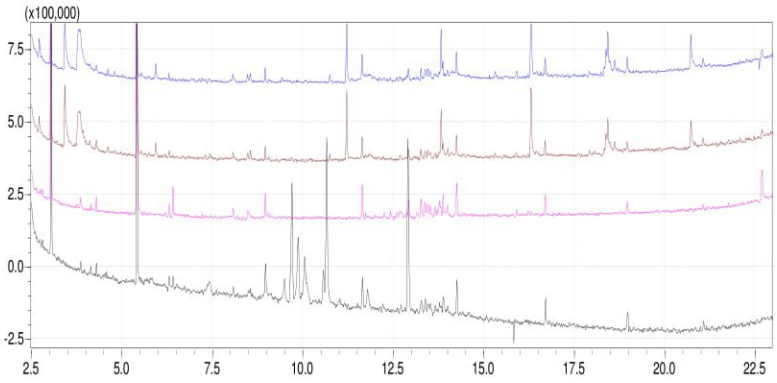

Figure 6 Chromatogram of $CHCl_3$-MeOH extract of noni fruit, the axtract plus ABS surfactant, the extract after nata adsorption, and the extract-ABS after nata adsorption (the first to fourth row)

The fact the surfactant reduces the surface tension must also be taken into account in adsorption process. This enable solvent and all solutes go more freely into the pore structure. This makes the adsorption of chemicals in the organic solvents can occur easier. Since the molecules have different shape and size, the real process would be very complex. The RMTD mechanism does not apply anymore in such system. One molecule can be adsorbed partly or in several part of its body to the surface area. Components of the phytochemical mixture can also be attachted to the surfactant aggragates or may be micelles. This certainly alters the properties in the surface. Some molecular tumblings and collision must occur and possible chemical reactions must be considered. This micelle will contribute to the aggregation of other phytochemicals as well as to the sequence of separation in the surface area.

CONCLUSION

Cellulose surface of the nata de coco adsorb phytochemical components and separate them according to the physical and chemical properties of the compounds. The mixture has profile adsorbtion as seen by uv-vis and infrared spectra as well as chromatograms. On of the presence of alkylbenzene sulphonate the profile mixture of $CHCl_3$-MeOH extract is altered. Some surface interaction is influenced and the ability of the surface to separate components.

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