THE CONCENTRATION EFFECT OF Cd^{2+} ION AND Cr^{3+} CO-ION ON ADSORPTION PROCESS BY NATA DE COCO - CARBON COMPOSITE

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Abstract

Adsorption studies were done so far by using some local and natural materials. Mostly the surface behavior of Cd^{2+} ion and Cr^{3+} co-ion were investigated. In this paper, dynamics on the surface made of bacterial cellulose are investigated. The possibility to cross-link cellulose fiber with activated carbon granules and the different dynamics arising from different properties are expected. The batch adsorption was done with different concentration of Cd^{2+} as well as the presence of Cr^{3+} with various concentration. The amount of adsorption is seen indirectly, mainly by using Atomic Adsorption Spectroscopy. The possible interaction on surface can be interpreted from the FT-IR while the surface morphology of the composites is observed by SEM. The result indicates more dynamics on the surface in higher adsorbate concentration and also the presence of co-ion Cr^{3+} decreases the Cd^{2+} adsorption. The composite material shows more surface interaction with the inorganic metals while the cellulose surface is independent on the adsorbate concentration. Some further attempts to extract more details of the surface adsorption-desorption processes are taken into consideration.

Keywords: *adsorption, adsorbent, nata de coco, commercial charcoal.*

1. Introduction

Nata de coco is one of the favorit products which is produced from fermentation of coconut water by *Acetobacter xylinum*. Since the *nata* is made of cellulose fiber, by the aid of the bacteria when sources of nitrogen and oxygen are present, the material is called bacterial cellulose [5].

The formation of the nata starts by the formation of cellulose yarns to slowly become sheets. The *Acetobacter xylinum* bacteria can form cellulose microfibril around the surface of its body, like envellope and finally thick cellulose fiber is formed. At the end, the cellulose will be a white and transparent sheet with smooth and slippery surface, the so called *nata* [6]. The texture of cellulose is very potencial to be used as adsorbent. The porous structure is benefecial, as well as the hydroxyl groups (- OH) and the surface of the material enables many types of physical interaction to occur.

On the other hand, activated carbon can be exploited as adsorbent. Charcoal basically consists of carbon (87 - 97%) and other component like hydrogen, oxygen, sulfur and other component according to used raw material [3]. Activated carbon is an inorganic adsorbent and it has pore structure and can bind adsorbat molecules or small particles including solvent molecules. A composite made of cellulose and carbon can be considered beneficial since it is consist of inorganic and organic parts blended together. Hopefully the ability of the composite to adsorb small particles or molecules can be enhanced physically.

2. Materials and Methods

2.1 Materials

Acetobacter xylinum, aquades, then coconut water and sugar were both obtained from traditional market, while other chemicals such as $Cd(NO_3)_2.4H_2O$, $Cr(NO_3)_3.9H_2O$, glacial acetic acid, as well as commercial carbon and ammonium sulfate were supplied by E-Merck.

2.2 Preparation of Nata de Coco and Nata de Coco-Carbon Composite

One liter of filtered coconut water were boiled for more than one hour, then 4 gram of sugar and 75 gram ammonium sulfate were added. Addition of glacial acetic acid solution is done to the mixture is done to maintain the pH at approximately 4-5. The hot solution then was then distributed to the plastic trays. After cooling, 100 mL of *Acetobacter xylinum* starter solution was added. The solution was then settled for incubation for 14 days to form

the *nata de coco*. For the composite, the nata de coco mixture was incubated for 7 days before 2 gram of commercial carbon was added. More 7 days time was needed to form the nata de coco-carbon composite.

2.3 Preparation of Nata de Coco and Nata de Coco-Carbon Composite Powder

Formed nata were harvested and washed repeatedly with water. Then they were rinsed with boiling water to remove the remains of acetic acid and other organic components as well as the sour odour. The the nata was cut into cubes and blended finely. Finally the blended nata gels was dried at 90^{o}C to constant mass before they were shieved to 40 mesh size.

2.4 Measurement of Cd^{2+} and Cr^{3+} Adsorbed by Nata de coco and Nata-carbon composites.

1 gram adsorbent is mixed with 50 mL sample ($CdNO_3$ solution, 50 ppm) in erlenmeyer, then it is shaked at 100 rpm speed for 60 minute. The filtrat of the mixture contained the remaining ion after adsorption process. The ion concentration is then measured using AAS. The residue is then washed with water and the concentration of the leached ions was also measured. The wavelength of Cd(II) and Cr(III) are λ_{Cd} = 228,3 nm dan λ_{Cr} = 357,9 nm.

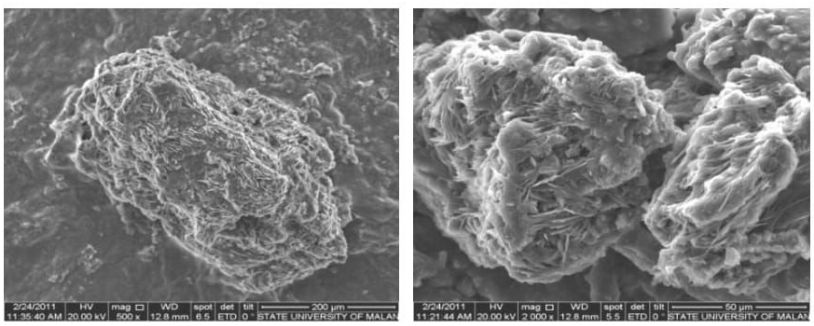
2.5 SEM Picture taking

A piece of nata and nata-carbon composite is coated with gold for about 5 nm thickness. Then the picture of the best magnification were taken.

3. Result and Discussion

In this experiment the addition of commercial charcoal for the composite was done on the 7th day to minimise the growth of contaminants. During the early fermentation process the cellulose fiber was not much and contamination to the media occurs easily. The carbon from the charcoal also adsorbs some component from the medium as well as the bacteria itself. After 7 days, the bacteria entered death phase and the amount of dead bacteria is bigger than the active ones.

The composite of nata-carbon actually undergo phase separation since they could not mix 100%. The different properties of organic cellulose and inorganic carbon made the composite depend on the crosslinking of the fiber and granules physically. When the composite is washed with water some of the carbon granules were loosened from the network. The nata had small interaction with carbon on the surface area. However the SEM pictures using 500x and 2000x magnification indicated the crosslinks between fine cellulose fiber with the carbon granules (figure 1). The surface of carbon granule was covered up by the cellulose from the biochemistry processes from *Acetobacter xylinum*.



(a) **(b)**

Figure 1. Scanning Electron Microscopy image of the cellulose-carbon composite surface (a) 500x and (b) 2000x

Characterization of the *nata de coco* as well as the composite was done. The water content of dried nata de coco and nata de coco-carbon composite were 4,871% 2,200%. Usually the smaller the water content the greater the abiluty to adsorb particles. The ash contentwere 1,697% and 1,784% for nata and composite respectively. Usually the greater the ash content the smaller the adsorption ability. The density of the nata and composites were 1,305 g/cm^3 and 1,390 g/cm^3. Density is used to express the level of adsorbent mass each volume. The Iodine adsorption

test informs the specific surface area of an adsorbent. For this test, nata and nata-carbon composite had the value of 11,051% and 10,053%. The greater the value the greater the specific surface of the adsorbent.

In this experiments, the concentration of Cd^{2+} ions was varied between 10, 25, and 50 ppm. The adsorbent was shaked at 100 rpm within 60 minute. After 60 minutes it was considered that the equillibrium of the adsorption system was reached. The result can be seen in Figure 2. When the concentration of the metal ion was increased, the percentage of the adsorbed particles on the surface increased as well. The nata de coco and the nata-carbon composite behaved similarly. When the amount of particles present in surface liquid determine the complexity on the surface. The adsorbate would move to the surface and be attached there for a certain time while at the same time the movement of the solvent molecules also hit the surface as well as the attached particles. When the amount of particles were increased, the speed of the moving molecules and the collision occured more frequently, more number of metal ions would be attached to the surface and desorbed back to the bulk liquid at higher speed. Moreover the possible interaction between the adsorbate and the metal particles as well as the solvent molecules would determine the complexity on the surface. The competition of the particles to be attached to the surface would depend on the concentration of the metal ions. However, at the highest concentration the adsorption decreased the amount of adsorbed ions. It indicated the equillibrium at the surface was reached and the desorption occured more compared to the adsorption. Moreover the RMTD mechanism plays important role, more displacement occured on the surface and the amount of desorption increased. Somehow the surface of the adsorbent could be saturated with adsorption and desorption competition and thedesprtion exeeded the adsorption.

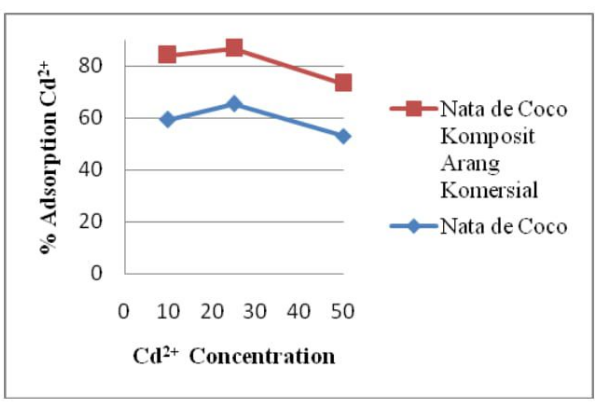


Figure 2. Curve of Ion Cd^{2+} Adsorption by Nata de Coco and Nata de Coco Carbon Composite with Ion Cd^{2+} Concentration Variation

In research, nata de coco adsorbent and nata de coco carbon composite adsorbent representing media pore. Existence of pore in the adsorbent can caused components of adsorbat trapped in it. Besides of this, existence of active situs in the form of group - OH from cellulose also can caused the happening of interaction with molecules of adsorbat. Interaction which possible happened is interaction of dipol-dipol between ion Cd^{2+} and cellulose, interaction of dipol-dipol induce between ion Cd^{2+} and carbon, and than interaction of dipol-dipol induce between carbon and cellulose.

While for research with existence of ion intruder were done by using ion Cr^{3+} concentration variation equal to 10, 25 and 50 ppm with ion concentration of Cd^{2+} remain to 25 ppm. Pursuant to obtained curve at Figure 3 and Figure 4, can be seen that with existence of addition ion intruder $Cr^{3+}$of resulting significant degradation of adsorption percentage. The same as previous clarification, that adsorption between adsorbat molecules happened caused pore trap and than existence of active situs in the form of group - OH which used interaction with adsorbat component. Existence of group - OH having the polar character who give adsorption opportunity for metal ion. Metal ion polarization of group - OH, so that will happened interaction of dipol-dipol.

Existence of addition ion intruder Cr^{3+} in adsorption ion Cd^{2+} process causing very tight emulation. Obtained Figure 3 indicated that degradation adsorption percentage of ion Cd^{2+} caused by addition of ion intruder Cr^{3+}, can be evaluated from ion radius size measure and from payload of each ion. Basically ion Cd^{2+} owning ion radius equal to 0,950 Å, while ion Cr^{3+} owning ion radius equal to 0,615 Å. That causing intruder ion having an effect in adsorption process. Ion radius Cr^{3+} smaller than ion Cd^{2+} so more easierly come into pore of adsorbent. Apart from ion radius,

existence of ion intruder can be evaluated from difference of payload between ion Cd^{2+} and ion Cr^{3+}. Payload of ion Cr^{3+} bigger than ion Cd^{2+}, that causing ion Cr^{3+} owning ability to induce adsorbent more strength, so that caused easierly to adsorption by adsorbent and more difficult to desorption.

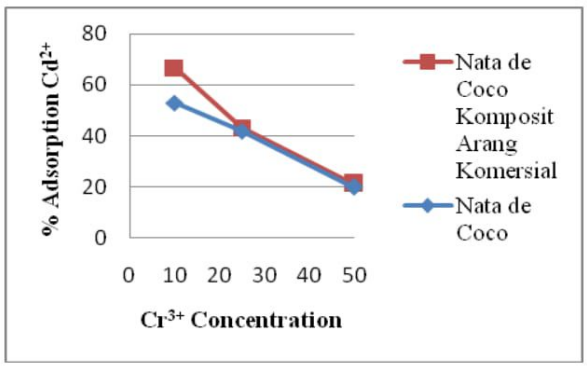


Figure 3. Curve of Ion Cd^{2+} Adsorption by Nata de Coco and Nata de Coco Carbon Composite with Ion Intruder Cr^{3+} Concentration Variation

Movement of adsorbat component during adsorption process taking place at random and make a move freely. Crush between adsorbat component in the adsorption system caused the happening competition between spesies adsobat to patch at the adsorbent surface. Such as Kimmich (2002), at the adsorption system will happened superdifusi at surface liquid. Existence of superdifusi will caused dynamics adsorption and desorption which quickly and random, so can caused adsorption of adsorbat whereas and can be thrown. After thrown, adsorbat can patch again at the adsorbent surface in the different situs (following pattern of Reorientation Mediated by Transational Diplacement). That caused the existence of competition between adsorbat component in the adsorption process.

For influence of ion intruder Cr^{3+} to adsoption percentage of ion Cr^{3+} can be seen at figure 4. In the curve show that degradation adsorption of ion Cr^{3+} happened, that inversely proportional with existing theory. If greater concentration will cause more interaction with adsorbent happened. So that progressively exeed in competition to patch of adsorbent surface. Research result showed that disagree with existing theory, maybe caused by active situs in the adsorbent surface have saturated. So event desorption of ion Cr^{3+} happened, and causing degradation adsorption percentage of ion Cr^{3+}.

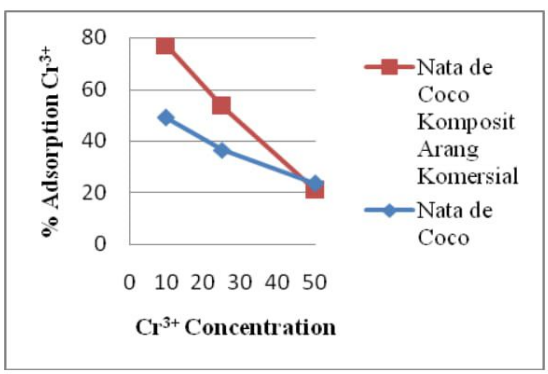


Figure 4. Curve of Ion Cr^{3+} Adsorption by Nata de Coco and Nata de Coco Carbon Composite with Ion Intruder Cr^{3+} Concentration Variation

Comparison of ability between nata de coco and nata de coco carbon composite only seen at result of research using ion Cd^{2+} concentration variation. Ability of nata de coco carbon composite adsorption bigger than

independentce nata de coco. This result as according to theory that charcoal owning high adsorption, so if enhanced and made composite will be able to improve percentage of ion metal adsorption.

Basically, composite consist of especial materials and reinforcement type to increase strength. Such as those which explained, that existence of addition commercial charcoal can improve adsorption ability of adsorbent.That caused commercial charcoal is adsorbent with high adsorption ability, caused by internal pore. Addition of charcoal at nata de coco can improve adsorption ability, caused of active situs in the form of group - OH and existence of pore. Composite which made can permeate and trap more ion Cd^{2+}.

Something else able to be made base that nata de coco carbon composite can have adsorption ability higher than nata de coco adsorbent is compiler component. Nata de coco have water content able to caused increase competition between adsorbat component. While at nata de coco composite, there are additional component commercial charcoal able to replace water. Characteristic of commercial charcoal reverse with water replaced. That caused ability of nata de coco carbon composite higher than nata de coco.

In research, nata de coco carbon composite have been used for the adsorption process also seen by using SEM (Scanning Electron Microscopy). Comparison of SEM result between nata de coco carbon commercial before and after adsorption process can be seen at Figure 5.

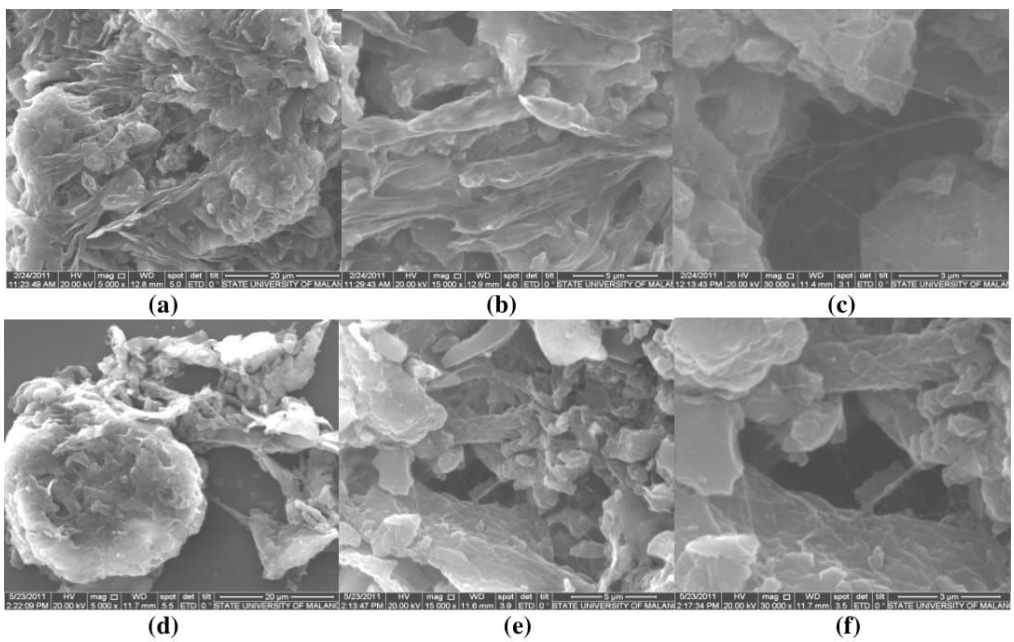


Figure 5. Result SEM of Nata de Coco Carbon Composite Before Adsorption, (a) 5000x (b) 15000x (c) 30000x . Result SEM of Nata de Coco Carbon Composite After Adsorption, (d) 5000x (e) 15000x (f) 30000x

Based Figure 5, nata de coco carbon composite adsorbent before and after used for the process of adsorption have same surface structure. Indicate that event of adsorption is physics adsorption, so not have an effect morphology of adsorbent.

4. Conclusion

Based on conducted research, the results obtained of (a) Increase the concentration of Cd^{2+} affect on the process of adsorption by the adsorbent, (b) Increase the concentration of ion intruders Cr^{3+} on adsorption by the adsorbent causing degradation of adsorption percentage ion Cd^{2+} and Cr^{3+}, (c) Ability of nata de coco carbon composite adsorption bigger than independence nata de coco.

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