pH Optimation and Effect of Composition in Cellulose-Carbon Composite to The Adsorption of Cd^{2+} Ion

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Abstract

Nata de coco is a biomass containing cellulose made by Acetobacter xylinum, which is now used as adsorbent. Its surface is rich of hydroxyl (-OH) groups which possesses high ability to interact with polar or semipolar adsorbate. On the othe hand activated carbon is also used widely for adsorbent. In this paper, composite with different compositions are being investigated as adsorbent of Cd^{2+} ions with various conditions. Batch adsorption is done with emphasis in the dynamics of different pH as well as concentration of metal ions. The amount of adsorbed particles is seen indirectly using some analytical instrumentation such as AAS to see the metal concentration after adsorption, SEM to see the morphology of the surface. The result shows the effect of carbon composition of the composite on the surface dynamics. More surface dynamics arises from higher ion concentration is not surprising from the study so far. The low pH indicates complexity on the surface since the property of hydroxyl groups is more pronounced. Some further investigation expects some more details about the surface dynamics.

Key words: adsorption, *nata de coco*, commercial carbon, composite

1. INTRODUCTION

In general, the concept of adsorption can be explained by the theory of adsorption from Langmuir and Freundlich. These isotherms are applied to plain surfaces in which a monolayer adsorption occurs. The isotherm cannot explain the adsorption in porous media where the non-localised adsorption domindates the whole process. The usual adsorption can be considered as localized adsorption and the adsorbed molecules will not move around the surface of the adsorbent (Bird, 1993:317). The dynamics of adsorbate molecules in porous surface will undergo different mechanism as suggested by Kimmich (2002) which is called Reorientation Mediated by Translational Displacement (RMTD). This process occurs in the surface liquid. The molecules will be adsorbed and desorbed back to the bulk liquid before coming back to the surface with different orientation. At the surface layer the molecules undergo superdiffusion.

From the literature it is known that the active functional group on cellulose, which is hydroxyl groups on the surface of *nata de coco* is the main reason for Cr^{3+} adsorption based on FT-IR spectrum [Afrizal, 2008]. The making *nata de coco* in rpinciple is a polymerization of glucose into polysaccharide compounds known as cellulose (Yuliani, et al., 2010). Utilization of thecellulose of *nata de coco* has several advantages, it has high purity, high degree of crystallinity (for the crystalline cellulose), high tensile strength (Krystinowicz, 2001), made of natural materials (renewable resources) that is very abundant in nature and is also biodegradable (Admin, 2008). The potential of *nata de coco* to be used as as adsorbent is due to its richness of hydroxyl group that can interact with hail and adsorbate components.

In addition to *nata de coco*, charcoal is a porous solid substance usualli used to adsorp contaminants of organic as well as inorganic compounds. Charcoal is made of carbon (87-97%) and other substances such as hydrogen, oxygen, sulfur (Jankowska et al., 1991:9). Commercial charcoal is used to be blended in the cellulose fiber to make a composite material. According to Bird (1993:317) the most efficient adsorbents are the highly porous solids such as charcoal. In Yano, et al (2007) silica is used in the manufacture of bacterial cellulose nanocomposite with because it has a high absorption.

Cellulose contained in *nata de coco* has a lower adsorption capacity than the commercial charcoal. Despite having a small adsorption power, the use of *nata de coco* as the adsorbent needs to be done in order to find effective and economical material from natural polysaccharides.

2. SAMPLE AND METHODS

2.1 Adsorbent and sample

2.1.1 Preparation adsorbent

Adsorbent used is *nata de coco* (NDC), commercial charcoal and *nata de coco* (NDC) composite commercial charcoal. *Nata de Coco* made by mixing 1 L of coconut water, 4 grams of ZA (*Zwavelzuur Ammonium*), 75 grams of sugar bring to a boil and checked at pH 4 (CH_3COOH was added to adjust pH). Solution in hot conditions in brass have been poured into sterilized. Closed newspaper, after the cold added 50 mL starter, pan tied up and brooded for 14-15 days. *Nata de Coco* commercial charcoal manufacture composite similar to the steps above, but the *nata de coco* is made only by curing for 7 days. Commercial charcoal is then added with the addition of 0,25 g of variation; 0,5 g; 0,75 g and 1 g. Then brooded for 7 days. Commercial charcoal are used have been neutralized by boiling with aquades then oven dried at 80-90°C.

Nata de Coco and *nata de coco* composite harvested and boiled for 2 hours until no smell sour. Then cut into pieces, mashed and dried with a glass plate at a temperature of 80°C oven. Nata sheet is cut into pieces and crushed to obtain powder and then sieved to 20-50 mesh size.

2.1.2 Preparation sample

Laboratory sample $Cd(NO_3)_2$ 25 ppm prepared from 1000 ppm mother liquor. Mother liquor is made by dissolving 2,772 g of salt $Cd(NO_3)_2.4H_2O$ with little aquades in a beaker. After all solids dissolved, incorporated in 1000 mL measuring flask and diluted to mark boundaries. Preparation of standard solution of 25 ppm is done by gradual dilution of making the solution 500 ppm, 100 ppm and 25 ppm.

2.2 Characterization

Characterization performed included water content, ash content, density, and absorption of iodine solution.

2.2.1 Determination of Moisture Adsorbent

A total of 0,5 gram of adsorbent is weighed and then put in oven 110°C for one hour. After that, put in a desiccator until constant weight is obtained.

2.2.2 Determination Levels of Ash

A total of 0.5 gram of adsorbent was weighed and put in a furnace at a temperature of 650°C for 3 hours then put in a desiccator and weighed until constant weight is obtained.

2.2.3 Determination of Density

The density of the adsorbent was determined using piknometer 25 mL, which is known empty weight. Piknometer is filled with 20 mL aquades and added a known weight of adsorbent and filled again with aquades. Further closed, weighed, and measured its density.

2.2.4 Determination of Power Absorption Iodine Solution

A total of 1 gram of adsorbent included in erlenmeyer, added 25 mL of 0.1 N iodine solution was shaken gently and stored in a dark place for 2 hours. After 2 hours the solution is filtered and added to 10 ml of 20% KI solution and 150 mL aquades then shaken until homogeneous. Titration is then performed with a solution of 0,1 N $Na_2S_2O_3$ until pale yellow, then add 2-3 drops of starch indicator and titrated back to the blue starch is lost. As the use of blank correction according to the above procedure without the addition of adsorbent.

2.3 Adsorption

Adsorption process is conducted to determine the optimization of the variation in commercial charcoal addition of *nata de coco* composite commercial charcoal and the effect of pH on the *nata de coco* and *nata de coco* composite commercial charcoal. Optimization of the addition of charcoal variation performed by mixing 50 ml of sample solution with 1 gram of charcoal powder composites by variation *nata de coco* addition of 0,25 g charcoal; 0,5 g; 0,75 g and 1 g. Solution was shaker for 60 minutes at 100 rpm, and then filtered. The initial sample solution (without adsorbent) and the filtrate was measured using AAS screening results.

Each sample was taken by 50 mL (pH 2, 4 and 6) was added 1 gram of adsorbent. The sample was shaken at 100 rpm, with a contact time of 60 minutes. The mixture is filtered, the filtrate obtained and initial samples was measured by AAS (λCd = 228.8 nm). The treatment is done for *nata de coco* and *nata de coco* composite commercial charcoal. The addition of charcoal used in the manufacture of commercial charcoal composite *nata de coco* in accordance with the results of the optimization that has a variation of adding charcoal adsorbed the highest percentage.

2.4 Theoretical analysis of data

Absorbance data Cd^{2+} standard solution of the sample solution prepared calibration curve. Calibration curve made with drain Cd^{2+} concentration on the absciss with absorbance on the ordinate. The concentration of Cd^{2+} adsorbed is obtained using the formula:

$$\%\ Adsorption = \frac{consentration\ before\ adsorption - concentration\ after\ adsorption}{consentration\ before\ adsorption}$$

3. RESULTS AND DISCUSSIONS

Morphological appearances *Accetobacter xylinum* bacteria is presented in Figure I.

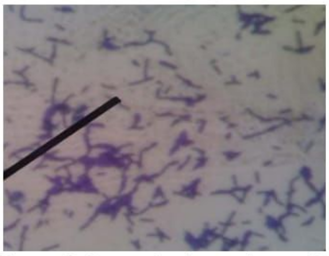
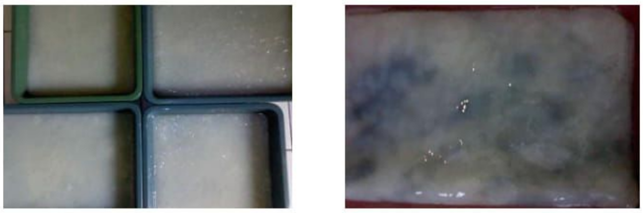


Figure I. Bacteria ***Accetobacter Xylinum***

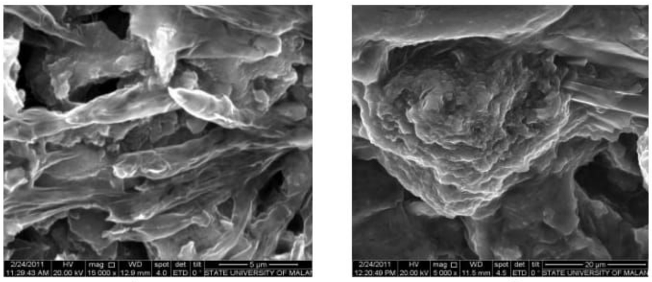
Physical characteristics of the resulting *nata de coco* is to have a chewy texture, dense and white-colored composite. *Nata de Coco* blackish due to the addition of charcoal that has been entered into the *nata de coco* layer. *Nata de coco* and *nata de coco* composite charcoal can be seen in Figure II.



A B

Figure II. *Nata de Coco* (A); *Nata de Coco* Charcoal Composite Commercial (B)

Charcoal was added to the *nata de coco* which was 7 days based on preliminary test results of SEM *nata de coco* composite commercial charcoal. Preliminary test include the addition of charcoal in situ in the addition of variations on days 0, 4, 5, 6, 7, 11 and 13 days. SEM results showed that the composite *nata de coco* surface structure of the composite with the addition of charcoal on day-7 has a surface structure that more clearly than the addition of charcoal on day 13. On the 7th day of cellulose forming many pores, whereas on day 13 nata looks bumpy surface. The results of SEM surface composite *nata de coco* can be seen in Figure III.



A B

Figure III. SEM Results The addition of *Nata de Coco* Charcoal Day-7 (A);
SEM Results The addition of Charcoal Day *Nata de Coco* -13 (B)

On day-7 *Accetobacter xylinum* are in growth phase (log), so the number of cells that grow more than the dead. The addition of charcoal on the day-to-13 occurs when bacteria almost had a death phase and the formation of cellulose does not take place optimally. Phase toward the deaths occurred due to the nutrients in the media was running out.

SEM results *nata de coco* composite charcoal after adsorption can be seen in Figure IV. Based on the results of SEM, there is no difference in morphology and structure of the *nata de coco* composite surface before and after adsorption process. The absence of significant differences in morphology, indicating that the Cd^{2+} ion adsorption on *nata de coco* composite commercial charcoal does not affect the surface features of nata. It proves that the interaction that occurs in cellulose is a weak interaction or included in the adsorption of physics.

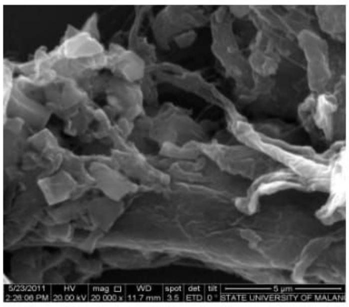


Figure IV. Surface Morphology After *Nata de Coco* Composite Commercial Charcoal Adsorption

Nata de coco charcoal formed composite having phase separation to form 2. Charcoal layer that interacts with the cellulose can be detached from the thick *nata de coco*. Figure occurrence of phase separation can be seen in Figure V.

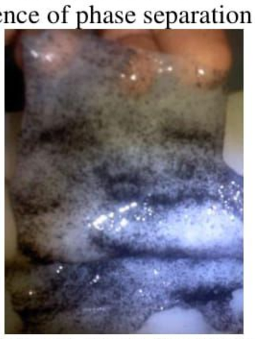


Figure V. Phase Separation

Charcoal an inorganic compound while *nata de coco* is an organic compound. Charcoal trapped and bound by the cellulose to form a thin layer of nata. The interaction carbon-cellulose is a weak and include dipole-dipole induksian. This interaction occurs because the polar -OH groups induce C in charcoal that is non-polar.

Characterization of adsorbents aiming to determine the quality of the adsorbent to be used in the adsorption process is based on the Indonesian Industrial Standard (1989) regarding the requirement of quality adsorbent. Adsorbent characterization data calculation results are presented in Table II.

Table II. Results Characterization of *Nata de Coco* and *Nata de Coco* Composite Adsorbent Commercial Charcoal

Characterization	Results
Nata de Coco Powder	
Water content	8,333 %
Ash content	3,27 %
Specific gravity	1,348 g/mL
The absorption of test solution of iodine (I_2)	9,389 %
Nata de Coco Composite Charcoal Commercial in Addition 0,25 g	
Water content	6,594 %
Ash content	2,5 %
Specific gravity	1,198 g/mL
The absorption of test solution of iodine (I_2)	15,981 %

Water content *nata de coco* is greater than the *nata de coco* composites. *Nata de coco* has a high water content because the *nata de coco* consists of 98-99% water (Pardosi, 2008). The water that would cover the artifacts in the adsorbent pores of the adsorbent thus affecting the adsorption process. The higher levels of water covering the pores of the adsorbent led to decreased adsorption power.

Characterization of ash content indicates the amount of mineral salts and inorganic materials contained in a adsorbent. According to SII is allowed a maximum ash content of 2,5%, while the ash content *nata de coco* 3,27% larger than the *nata de coco* composite 2,5%. Determination specific adsorbent surface area is determined by the absorption of test solution of iodine (I_2). Iodine absorption is proportional to the surface area of adsorbent. The larger the numbers, the ability of iodine to the higher adsorption of other substances. *Nata de coco* composite surface area is greater than the *nata de coco*, so that the adsorption of the composite is higher than the *nata de coco*.

The highest percentage of Cd^{2+} ions adsorp on the variation of the addition of charcoal in Table III are used as the basis for the analysis of the effectiveness of *nata de coco* commercial charcoal composites with variations in pH.

Table III. Percentage of Cd^{2+} Ions Adsorp by *Nata de Coco* Charcoal Composite Variations Additions Charcoal

Ndc **Composite Commercial Charcoal in Variation Addition**	**Actual Concentration Cd^{2+} ion Before (ppm)**	**Actual Concentration Cd^{2+} ion After (ppm)**	**Adsorption Concentration of Cd^{2+} Ion (ppm)**	**Adsorption Percentage of Cd^{2+} Ion**
0,25 g	22,706	2,026	20,68	91,08
0, 5 g	22,706	2,124	20,582	90,65
0,75 g	22,706	3,231	19,475	85,77
1 g	22,706	16,725	5,981	26,34

The amount of adsorbent is one of the parameters that can affect the adsorption capacity (Subbaiah et al. 2011). Percentage of adsorp Cd^{2+} ions was highest in the addition of 0,25 g of charcoal at 91,08%, so the *nata de coco* composite commercial charcoal with the addition of 0,25 g of charcoal used in the adsorption phase pH variation. The cause of the reduced Cd^{2+} ions are adsorp due to the influence of contaminants contained in the *nata de coco* composite manufacturing process. In the carbonation process of charcoal, not all active sites on the cellulose part carbonized charcoal has the power so that the adsorption is not optimal even though it has been activated charcoal and obtained commercially. Curve is the relationship between variations in the addition of charcoal and the percentage of Cd^{2+} ions adsorption are presented in Figure VI.

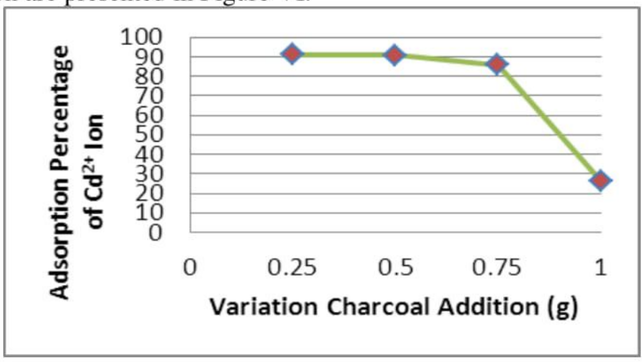


Figure VI. The Relationship Curve and Percentage Variation Charcoal Addition Cd^{2+} Ions Adsorption

According Fengel (2005) charcoal has a porosity of about 70%. Porous structure causes the phenomenon that occurs in charcoal is physical adsorption due to the adsorbate can be trapped in the pores. In bacterial cellulose Cd^{2+} ion will polarize the -OH group on cellulose resulting dipole-dipole interaction whose strength is very weak and that adsorption occurs is physical adsorption.

Percentage adsorption *nata de coco* pH variations are presented in Table IV, while the percentage of data *nata de coco* adsorption charcoal composites are presented in Table V.

Table IV. Percentage of Cd^{2+} Ions Adsorption by The *Nata de Coco* Powder pH Variation

pH	Actual Concentration Cd^{2+} ion Before (ppm)	Actual Concentration Cd^{2+} ion After (ppm)	Adsorption Concentration of Cd^{2+} Ion (ppm)	Adsorption Percentage of Cd^{2+} Ion
2	24,926	23,313	1,613	6,47
4	24,097	17,974	6,123	25,41
6	22,706	14,117	8,589	37,83

Table V. Percentage of Cd^{2+} Ions Adsorption by The NDC Commercial Charcoal Composites Powder pH Variation

pH	Actual Concentration Cd^{2+} ion Before (ppm)	Actual Concentration Cd^{2+} ion After (ppm)	Adsorption Concentration of Cd^{2+} Ion (ppm)	Adsorption Percentage of Cd^{2+} Ion
2	24,926	24,809	0,117	0,47
4	24,097	20,222	3,875	16,08
6	22,706	9,976	12,73	55,06

Relationship curve percentage adsorption ions Cd^{2+} (aq) to pH variations on the adsorbent *nata de coco* showed by Figure VII, while the commercial charcoal adsorbent composite *nata de coco* is shown in Figure VIII.

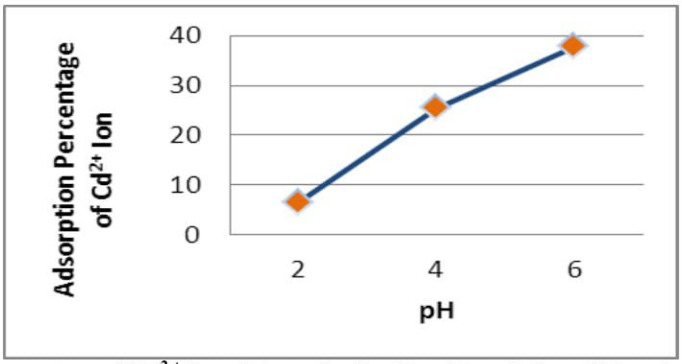


Figure VII. Percentage of Cd^{2+} Ions Adsorption by The pH variation of *Nata de Coco* Powder

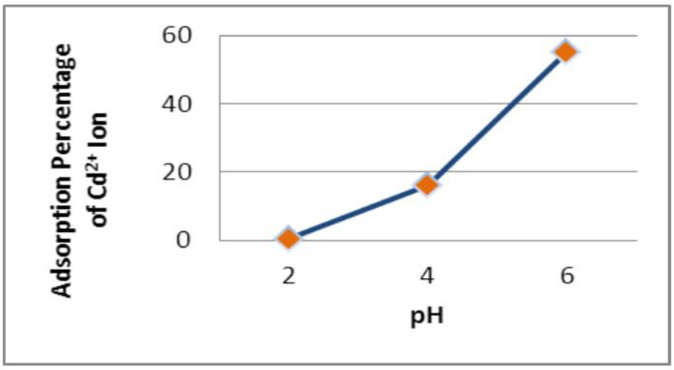


Figure VIII. Percentage of Cd^{2+} Ions Adsorption by The Powder *Nata de Coco* Commercial Charcoal Composites pH Variation

Based on Tables IV and V the maximum adsorption occurred at pH 6, the sample of Cd^{2+} ions that can be absorp by the *nata de coco* and *nata de coco* composite powder charcoal. At pH 6 the appropriate conditions to enhance the adsorption of Cd^{2+} ions. Adsorbate $Cd(NO_3)_2$ at pH near neutral form ions Cd^{2+} (Srivastava, et al, 2004), so that the positively charged Cd can interact with -OH groups as active sites on the *nata de coco* will form dipole-dipole with Cd^{2+} ions.

At pH 4 *nata de coco* composite charcoal having adsorp a smaller percentage than the *nata de coco* is influenced by fungal contaminant in the production of nata. Another factor, is in the process of carbonation is not all active sites on the cellulose part carbonized charcoal has the power so that less than optimal adsorption. Although there are still remaining active sites in the charcoal, at a low pH is predicted active site (-OH) will be hydrolyzed. This resulted in the C atom on the charcoal will be charged partial positive so that the possibility of NO_3^- ions will be more absorp than Cd^{2+} ions.

Percent adsorption at pH 2 the lowest because the content of H^+ ions as competitors are increasing in the sample solution, resulting in lower power Cd^{2+} ion adsorption. The more acidic pH of the adsorbate causes the partial positive charged C atoms and NO_3^- binding and hydrogen bond. The number of H^+ ions which increases will tend to bind with the active -OH groups, because the O atoms are negatively charged atoms will attract H atom. The occurrence of hydrogen bonding between -OH groups with H atoms derived from water and serve as the solvent is an inhibiting the formation of the interaction between Cd^{2+} ions with the active site of bacterial cellulose at low pH.

4. CONCLUSIONS

The addition of 0,25 g of charcoal on *nata de coco* charcoal composite commercial shows the percentage of adsorp Cd^{2+} ion that is 91,08% of the largest. Near-neutral pH conditions (pH 6) can enhance the ability of Cd^{2+} ion adsorption. *Nata de coco* charcoal composite commercial shows the percentage of adsorp Cd^{2+} ion is higher (55,06%) than the adsorbent *nata de coco* with a percentage of 37,83%.

5. ACKNOWLEDGEMENT

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